Introduction to the 2017 Method Update Rule

Thursday April 26, 2018
1:00 – 3:00 pm

Today's webcast is the result of collaboration between the WEF Laboratory Practices Committee and the Association of Public Health Laboratories

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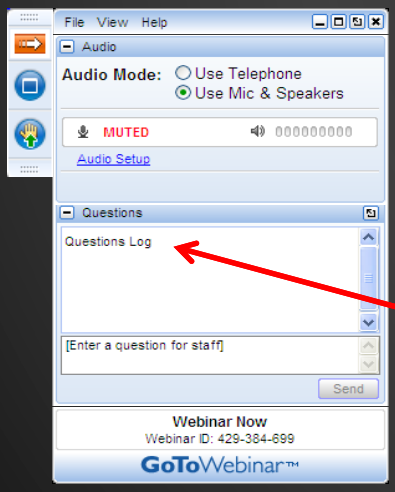
APHL ASSOCIATION OF PUBLIC HEALTH LABORATORIES

How to Participate Today



- **Audio Modes**
  - Listen using Mic & Speakers
  - Or, select "Use Telephone" and dial the conference (please remember long distance phone charges apply).
- **Submit your questions using the Questions pane.**
- **A recording will be available for replay shortly after this webcast.**

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Today's Moderator

Robert Smith

Applications Engineer – Wastewater

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Today's Speakers

- Jerry Parr
  - Overview of the 2017 Method Update Rule
- Yildiz Chambers-Velarde
  - Microbiology
- William Lipps
  - Organics
- Catherine Thompson
  - Implementing the new Method Detection Limit Procedure – One Lab's Perspective

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Our Next Speaker

Jerry L. Parr

Principal

Catalyst Information Resources

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Overview of the 2017 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!**

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2017 Methods Update Rule

- Finalized on December 2016
- Withdrawn March 2017
- Finalized August 28, 2017
- Effective September 27, 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**
  - 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 WETT errata sheet
- The 300.1 errata sheet
- Response to Comments document

300.1 errata not published as of April 2018

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Response to Comments Document

- 961 pages
- 650 pages on 600 series methods
  - Most comments rejected because EPA lacks interlaboratory data
- 130 pages on MDL

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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

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Tables 1 A and 1H. Microbiology

Table 1 A

- Updated versions
  - SM 9221 B, C, E, F -06
  - SM 9222 B, C, G-06
  - SM 9223-04
  - SM 9230 B, C-07
  - Colilert 18
- 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

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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.

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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 "$3.7x10^8$ CFU/mL."

Updated methods in Docket

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WET Errata

- 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.”
- Errata sheet **NOT** available in Docket, but was posted on the OST website in April

https://www.epa.gov/cwa-methods

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 CaCO3, mg/L	Electrometric endpoint or phenolphthalein endpoint		2310 B-11	D1067-11	I-1020-85[2]
2. Alkalinity, as CaCO3, 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]

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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

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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-NH_3 B-H-11
- 4500-NO^{2-} B-11
- 4500-NO^{3-} 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 SiO^{2-}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

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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

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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*.

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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

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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

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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.

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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

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Table 1F: Pharmaceuticals

- 624 changed to 624.1

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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

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Holding Times and Sample Preservation

- *E. Coli* and *Enterococcus*
  - Preservation changed from 0.0008% $Na_2S_2O_3$ to 0.008% $Na_2S_2O_3$
  - 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.

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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

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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

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Changes to Appendix A

New Methods

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

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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

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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

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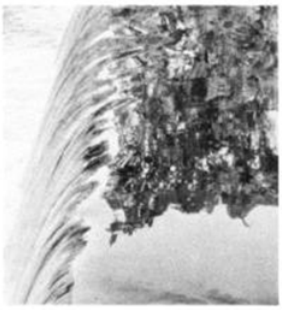
The development of trace analysis methodology brought with it a series of questions about method performance at low concentration levels of analyte (*1*, *2*, *3*). Under Section 304(h) of the Clean Water Act, as amended in 1977, (*4*) the Environmental Monitoring and



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

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 2013
- 2017 **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 but may create enormous hardships on the QC side
- MDL is a incredible improvement!
- MDL is completely consistent with the new TNI standard!

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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.
- The new MDL procedure is also referenced in the 2016 TNI laboratory standard and could be implemented now.

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Since Rule Promulgation

- EPA Publishes FAQ on OST website
  - https://www.epa.gov/cwa-methods/methods-update-rule-2017
- Drinking Water office publishes confusing memo on MDL
- Some states beginning to implement
- Consortium Proposes Data Collection Effort

Data Collection Effort

- Methods 608.3, 624.1, and 625.1
- Calibration IDC, LCS, MS, etc
- **We need labs to help!**

https://www.surveymonkey.com/r/JQ3GL65

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Our Next Speaker

Yildiz Chambers-Velarde

Senior Microbiologist

GENERAL DYNAMICS
Information Technology

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Microbiology

Tables IA and IH

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Table IA Changes

- Colilert-18® was approved for the analyses of fecal coliforms in wastewater
- SM 9230 D - 2007 was added as an approved method for enterococci MPN, multiple tube/multiple well
- Standard Methods 9222 (B, D, G) – 1997 were replaced with 9222 (B, D, G) – 2006
- Footnotes
  - Two new footnotes added
  - EPA methods citations updated

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Table IH Changes

- SM 9230 D - 2007 was added as an approved method for enterococci MPN, multiple tube/multiple well
- Standard Methods 9222 (B, D, G) – 1997 were replaced with 9222 (B, D, G) – 2006
- Footnotes
  - New footnote added
  - EPA Methods citations updated

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Recent Inquiries: Colilert-18®

- Is Colilert-18® approved for analyses of sewage sludge for fecal coliforms?
- Why didn't EPA approve Colilert-18® for analyses of ambient waters for fecal coliforms?
- Was it an oversight that SM 9223 B was not included for the analysis of wastewater for fecal coliforms?
- Can a dry incubator be used for fecal coliform analyses using Colilert-18®?

Recent Inquiries: Verifications

- *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.*
  - Are sampling sites considered individual grab sample locations or does this refer to something more like a facility or project area?
  - Does this mean at least 10 typical verifications monthly, with the 5 typical/5 atypical per site?

Recent Inquiries: MF

- Can *E. coli* be determined by 9222 G following 9222 D in ambient waters? In wastewater? Table IH lists 9222 B followed by 9222 G
- If a difference is observed between MF and MPN results for chlorinated effluents, which method results should be reported?

Changes in the Upcoming MUR

- Table IA – For *E. coli* the following MF two step methods will be added
  - EPA Method 1103.1
  - SM 9222 B/9222 G
  - D5392-93
- Table IA – Colilert-18® will be listed for Parameter 2 and removed from Parameter 1
- Table IH – The KwikCount method will be added for *E. coli*
- Verification requirements for total coliforms will be revised to be similar to fecal coliforms

Our Next Speaker

William Lipps

Senior Environmental
Marketing Manager

SHIMADZU

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Organics

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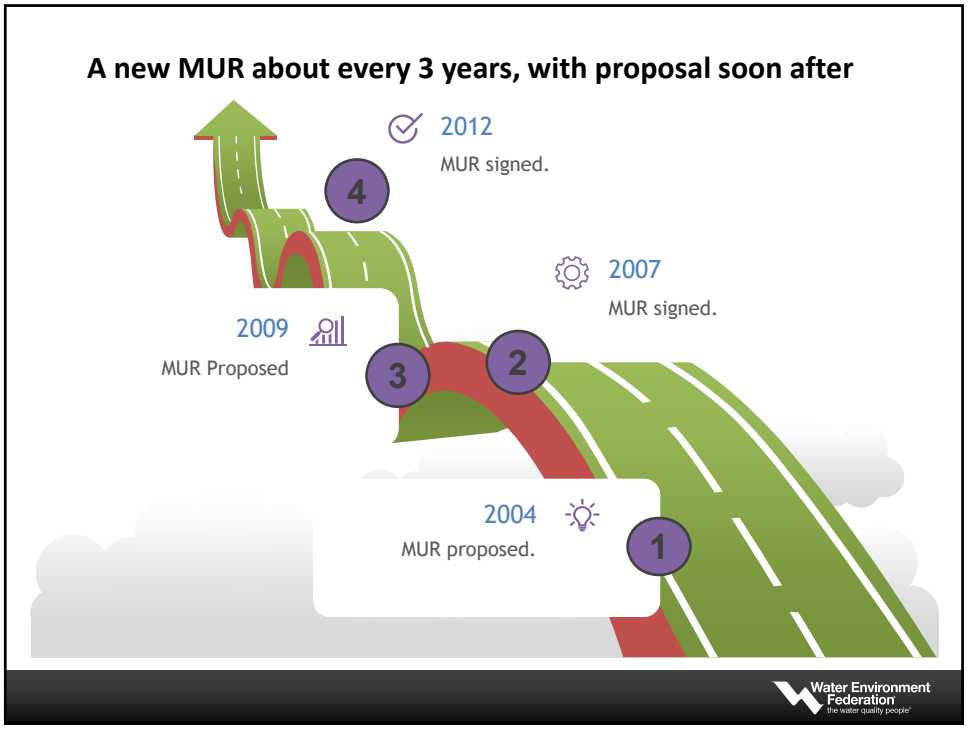
A new MUR about every 3 years, with proposal soon after
2012
MUR signed.
4
2007
MUR signed.
2009
MUR Proposed
3
2
2004
MUR proposed.
1
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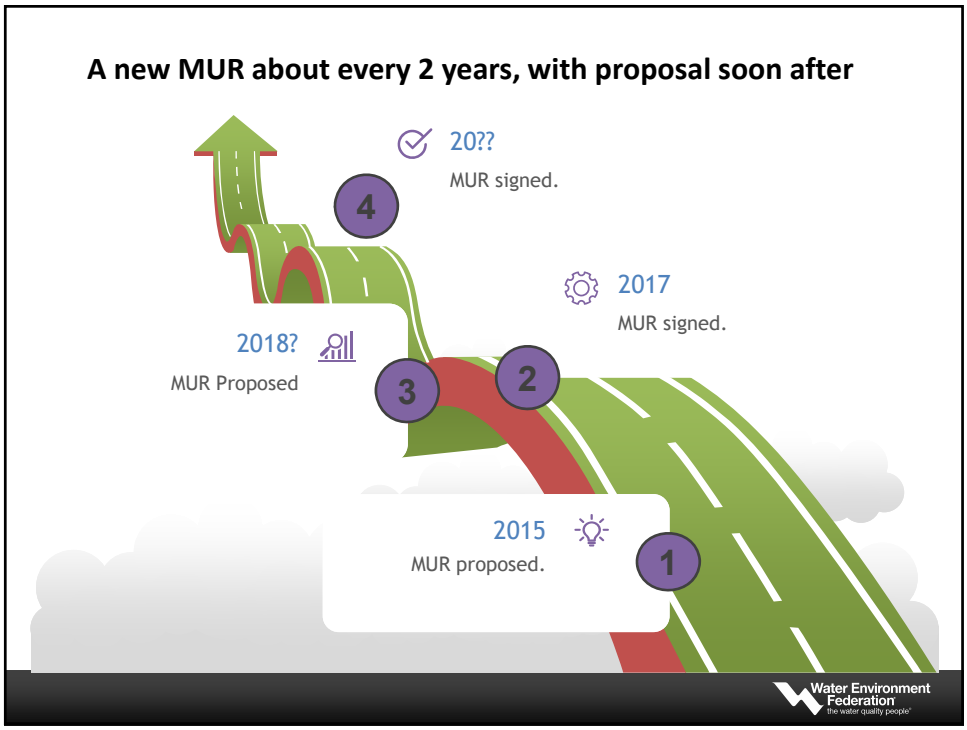
A new MUR about every 2 years, with proposal soon after
20??
MUR signed.
4
2017
MUR signed.
2018?
MUR Proposed
3
2
2015
MUR proposed.
1
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EPA's goal is more frequent, smaller updates

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A Note on Revisions to EPA Methods

- A revision does not include a technical change
- Therefore, these revisions do not completely re-write methods!
- Method data from initial inter-lab studies (early 1980's)

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New CWA EPA methods requires validation and inter-lab studies

- Methods at Part 136 require multiple laboratory validation (9 labs and 9 matrices)
  - **Without an ILS EPA can only make minor changes**
  - **Or, rely on consensus standard organizations and ATPs**

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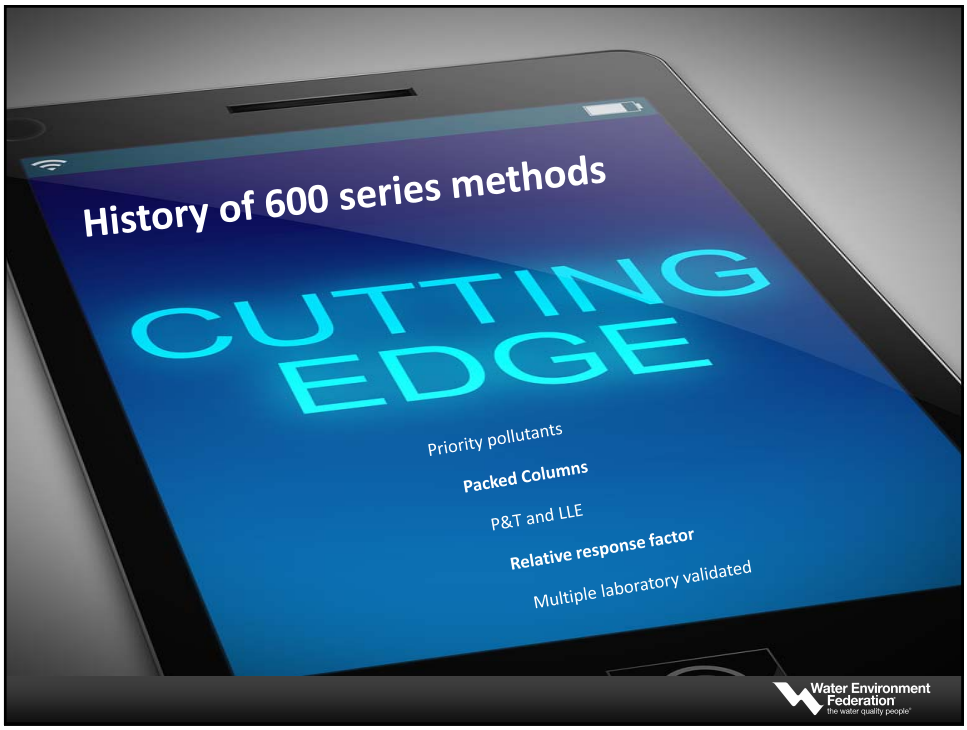

Methods 608.3, 624.1, and 625.1 incorporated what everybody is already doing

- Took the "Bill Telliard" letters and parts of 136.6 and added them to the text of the methods.

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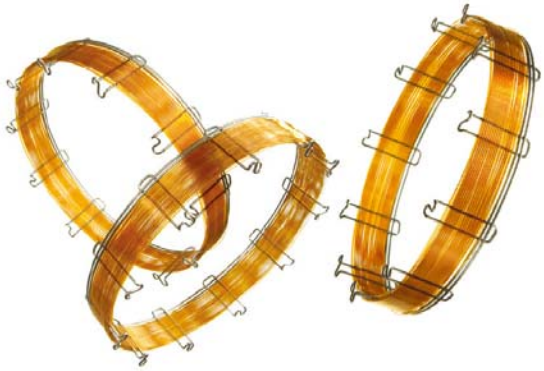
New methods added capillary columns



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New methods added hydrogen as a carrier gas, or nitrogen as a purge gas

- No specific tune criteria
- Must meet method QC acceptance criteria

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Attempt to "harmonize" methods across programs

- Above freezing to 6 °C
- Surrogates
- Internal Standards
- KD and Nvap (pesticides and semivolatiles)
- Criteria for Blanks
- Corrective actions

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All the EPA methods include new analytes

- No QC Data for new analytes, make your own
- 60 – 140 % Recovery
- **RPD ≤ 30%**
- **No MDL or ML data**

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EPA revised Method 608 (now 608.3) and adds a detector

1. New name – GC/HSD
   - **Halogen specific detector in addition to ECD**
   - **New detector data → EPA 1656**

2. Over 60 New analytes – Table 2
   - **Allows GCMS if sensitive enough**
   - **Toxaphene and PCB in Table 2**

3. Includes SPE
   - **< 1000 ml sample OK**

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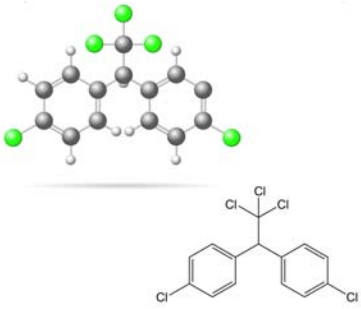
EPA Revised Method 608

4. Requires surrogates
5. GC Resolution criteria added
6. Endrin DDT breakdown criteria added
7. Lowest calibration standard at or below ML



EPA revised Method 624 (now 624.1)

1. Over 100 New analytes – Table 2
2. Table 1 = original priority pollutants

EPA Revised Method 624

3. Allows SIM
4. Table 2 analyte list contains
   - •analytes that may not purge well
   - •May require heat
   - •Alcohols (methanol)
5. Calibration RSD lowered to $\leq 20\%$

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EPA Revised Method 624

6. Requires MS/MSD
7. Must meet the ML for Table 1 analytes
8. **You can modify:**
   - **Purge volumes**
   - **Purge times**
   - **Purge flow rate and gas**
   - **Purge temperature**
   - **Trap sorbent and desorb time**
   - **Water management**
9. **Discharger decides what sample to spike**

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EPA Method 625 is now Method 625.1

1. Original priority pollutants include MDL and ML data
   - Table 1 → 38 base neutral
   - Table 2 → 11 acid extractable

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EPA Method 625.1

2. There are over 300 new analytes

- **13 are priority pollutant pesticides and PCB's**
  - These have MDL and ML data
- **303 have no MDL or ML data**
  - YOU must establish your own

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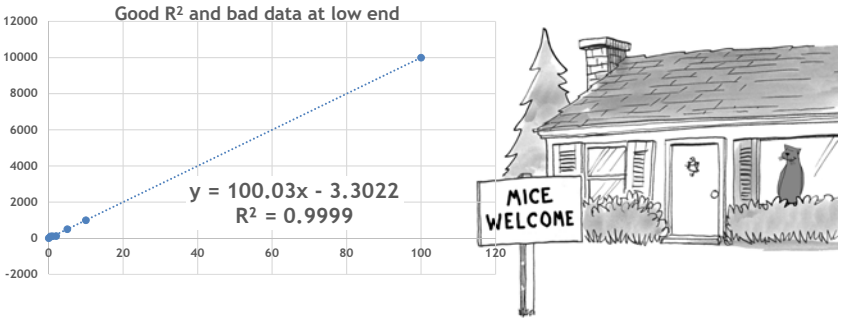
EPA Method 625.1

3. EI and CI ionization allowed; Table 4 for priority pollutants
   - Includes quant and secondary ions
   - Retention times (elution order)

4. No Quant ion, secondary ion, or retention time data for the 303 new analytes in Table 3

5. You can use RSE ≤ 35% instead of correlation coefficient



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EPA Method 625.1

6. Table 8 provides 38 surrogates or internal standards

- No quant ions or secondary ions
- No retention times
- Internal Standard response 50 – 200%

- Method Study 30 → no correlation of SS with analytes found

8. Solid Phase Extraction is allowed

- Individual lab or Vendor MUST validate Table 1 and Table 2
  - Spiked MS/MSD complete list, 4 IDC, 1 PT
  - Up to 9 matrices, depending
  - MDL (lab must do)
  - Must fortify with surrogates
  - Must meet 625 criteria for Table 1&2, or 60 – 140% for Table 3

https://www.epa.gov/cwa-methods/alternate-test-procedures

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9. 100 – 1000 ml sample size

- Smaller sample volume = better for SPE
- Extract less means use less reagent
- New instruments can detect lower

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10. One calibration Standard must be at ML (or MRL)

- Or as specified in a permit
- Or your own as long as lower than Table 1 or Table 2 ML
- Table 3 has no ML (develop your own)

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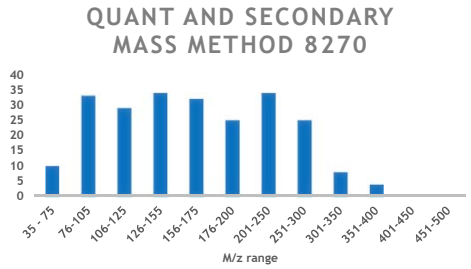
11.DFTPP tune criteria more flexible, by footnote

- Adds TOF criteria as Table 9B
- TOF criteria wider
- 442 can be base peak



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Data Collection Effort

- Methods 608.3, 624.1, and 625.1
- Calibration IDC, LCS, MS, etc
- **We need labs to help!**

https://www.surveymonkey.com/r/JQ3GL65

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Any Questions?

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Our Next Speaker

Catherine Thompson

Quality Assurance Officer

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Implementing the new Method Detection Limit Procedure

One Lab's Perspective

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Presentation Summary

- What is the same
- What is different
- Which methods are excluded
- Determination of the Initial MDL
- Ongoing Data Collection
- Ongoing (Annual) Verification

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Basics Unchanged

- Intent is still to determine the lowest result that reliably indicates the analyte is in the sample
- Calculation is still the Student's *t* times the standard deviation of the results
- Procedure still requires that all steps of the sample preparation and analytical process are performed

Definitions Compared

- 1984: The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is **greater than zero** and is determined from analysis of a sample in a given matrix containing the analyte.
- 2016: The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is **distinguishable from the method blank results**.

Significance of Change

Previous MDL

- Assumed blank results are centered around zero. When blank results are not centered around zero, the MDL will be biased low and false positives will result

New MDL

- Accounts for blank contamination by requiring calculation of an MDL_b (using the Mean and SD of the blanks) that is compared to the spike MDL (the MDL_S)

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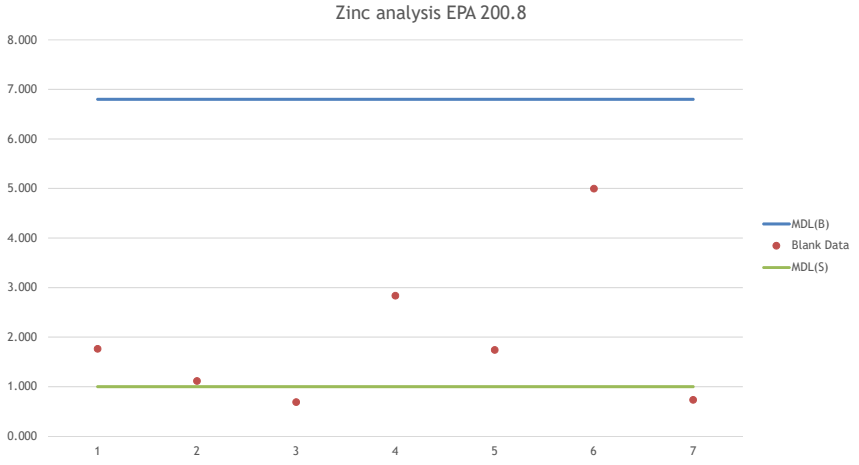
New MDL(b) Calculated Above Blank Levels



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Increased Variance

- New MDL includes data from low-level spikes and blanks analyzed over multiple days and can include multiple instruments, and multiple analysts
  - Initial MDL must include blanks and spikes prepared and analyzed over a minimum of three batches
  - Ongoing MDL data collection requires a minimum of two quarterly spikes and all routine method blanks

Other Differences

- No 10X rule. New procedure includes an addendum for determining the MDL for a specific matrix.
- Suggested spiking level is 2-10 times the estimated MDL but, for analytes with poor recovery, spiking in excess of 10 times is acceptable.
- Ongoing data used to recalculate a new MDL which is compared to the previous MDL. MDL is only required to be updated if comparison criteria is not method; otherwise previous MDL may be used.

Exceptions – Procedure is not applicable to the following:

- Methods that don't produce a continuous distribution such as whole effluent toxicity, presence/absence methods, and colony counting microbiological methods
- BOD, color, pH, specific conductance, and many titration methods and methods where low-level spikes can't be prepared
- *CAVEAT: An MDL_B may still apply (i.e. TSS)*

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Determination of the Initial MDL

1. Estimate an initial MDL
2. Analyze the initial MDL_s spikes and MDL_b blanks
3. Evaluate the data
4. Calculate the initial MDL_s and the MDL_b
5. Select the greater of the MDL_s or MDL_b as the initial MDL

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1. Estimate an Initial MDL

- The mean determined concentration plus three times the standard deviation of a set of method blanks.
- The concentration value that corresponds to an instrument signal-to-noise ratio in the range of 3 to 5.
- The concentration equivalent to three times the standard deviation of replicate instrumental measurements of spiked blanks.
- That region of the calibration where there is a significant change in sensitivity, i.e., a break in the slope of the calibration.
- Instrumental limitations.
- *Previously determined MDL.*

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2. Analyze the Initial MDL_s Spikes and MDL_b Blanks

- Prepare and analyze a minimum of seven spikes and seven blanks
  - Prepared in at least three batches on three separate dates
  - Analyzed on three separate dates (preparation and analysis may be same day)
  - May use existing data if within 24 months and in at least three batches (must use most recent data)

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2. Analyze - Multiple Instruments

- If multiple instruments will share the same MDL, analyses must include all instruments
  - Prepare and analyze at least two spiked samples and two method blanks on different dates for each instrument
  - Preparation and analysis may be same day and spike and blank may be analyzed together
  - The same prepared extract may be analyzed on multiple instruments as long as a there are a minimum of seven preparations in at least three separate batches

3. Evaluate the Spike Data

Results for each individual analyte must meet method qualitative identification criteria

And

Must provide a numerical result greater than zero

Or

Repeat the spiked samples at a higher concentration

3. Evaluate the data

- Do not remove statistical outliers for the initial MDL
- Documented gross failures (e.g., instrument malfunctions, mislabeled samples, cracked vials) may be excluded
- Use only data associated with acceptable calibrations and batch QC

4. Calculate the MDL_s

$$MDL_s = t(n-1,\ \ 1-\alpha=0.99)Ss$$

Where:

- MDL_s = the method detection limit based on spiked samples
- t(n-1, 1-α = 0.99) = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.
- Ss = sample standard deviation of the replicate spiked sample analyses.
- *NOTE: If more than 7 replicates are analyzed, obtain the correct student's t for that number of replicates*

4. Calculate the MDL_b

- If none of the method blanks give numerical results for an individual analyte, the MDL_b does not apply.
  - A numerical result includes both positive and negative results (and zero), including results below the current MDL
  - A numerical result does not include results of "ND" (not detected) commonly observed when a peak is not present in chromatographic analysis.

4. Calculate the MDL_b

- If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL_b equal to the highest method blank result.
- If all of the method blanks for an individual analyte give numerical results, then calculate the MDL_b using
- $MDL_b = \bar{x} + t(n-1,1-\alpha=0.99)Sb$ where $\bar{x}$ = mean of the method blank results (use zero in place of the mean if the mean is negative) and Sb is the SD of the blanks

5. Select the MDL

- Select the greater of the MDL_b or the MDL_s as the initial MDL.

NOTE: MDL is calculated using all calculations specified in the method and the result is expressed in the method-specified reporting units.

Ongoing Quarterly Data Collection

- In any quarter when samples are analyzed, prepare and analyze a minimum of two spiked samples, on each instrument, in two separate batches, at the same concentration as the initial MDL spike.
- If more than 5% of the spiked samples do not provide positive numerical results that meet the qualitative identification criteria, the spike level must be increased and an initial MDL re-determined.

Ongoing Quarterly Data Collection

- The method blank population should include all of the routine method blanks analyzed with each batch during the course of sample analysis
- Include all data with acceptable calibrations and batch QC, unless there are documented gross failures or the batch is rejected and the associated samples reanalyzed

Ongoing Quarterly Data Collection

- Ensure that there are at least seven spikes and seven blanks for the annual verification. If there is only one instrument, data may be drawn from the last two years
- If the method is altered in such a way that the sensitivity is changed, the initial MDL must be re-determined, and ongoing data collection started again

Ongoing Quarterly Data Collection

- A new instrument may be added by analyzing a minimum of two spikes and two blanks on the new instrument
  - If the method blanks results are below the existing MDL_b, the MDL_b is validated.
  - Combine the spike results with the existing results and recalculate the MDL_s (change the student's *t*) and compare to existing MDL_s
  - If the recalculated MDL_s is within 0.5 to 2.0 times the existing MDL, the existing MDL is validated; otherwise calculate a new MDL

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Ongoing (Annual) Verification

- At least once every 13 months, re-calculate the MDL_s and the MDL_b from the ongoing data collected and any data from the previous 24 months, including the initial MDL data, that was spiked at the same level
- For tests that are performed frequently, option allowed to use only the last six months of method blank data or the fifty most recent, whichever is greater

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Ongoing (Annual) Verification

- To calculate the MDL_b, use the criteria for the initial MDL_b.
  - If **no** numerical results, MDL_b does not apply
  - If **some** give results, set to highest result
  - If **all** give results, use equation

OPTION: If more than 100 method blanks are available, MDL_b may be set to the level that is no less than the 99th percentile of the method blank results

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Ongoing (Annual) Verification

For 164 results, the 99th percentile = n * 0.99								
164 x 0.99 = 162.36 rounded to 162								
A1	0.02							
…	…							
A160	1.5							
A161	1.7							
A162	**1.9**							
A163	5							
A164	10		=PERCENTILE(A1:A164,0.99)					
Using the 162nd result, the MDL_b is 1.9								

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Ongoing (Annual) Verification

- The verified MDL is the greater of the MDL_s or MDL_b
- If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged
- Otherwise, adjust the MDL to the new verification MDL

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Questions?

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