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EPA Office of Water Method Update Rule Final – August 28, 2017

William Lipps
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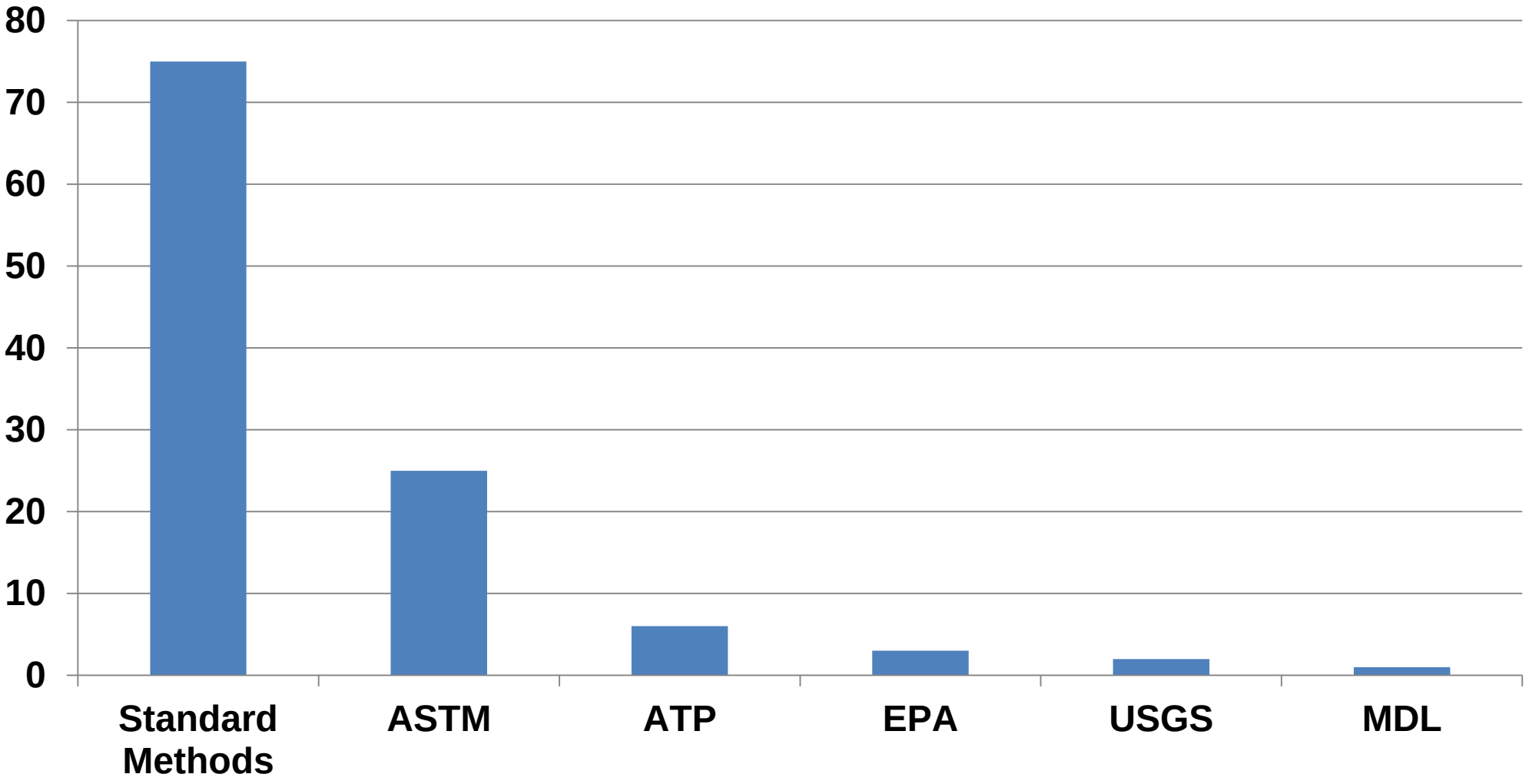
The update consists of minor changes, edits, revisions, and 7 new methods



The update includes no new EPA methods

- Revised or corrected EPA methods
- Revised or corrected Standard Methods
- Revised or corrected ASTM methods

- 6 new ATPs
- 2 new USGS methods
- Revised MDL procedure

The update included small revisions to Part 136.6

- **Vendor methods – use the EPA method QC criteria, not the vendors**
- **Notify the permitting authority that you will use a modified method.**

A Note on Revisions to EPA Methods

- **A revision does not include a technical change**
  - **Technical change requires re-validation**
- **Therefore, these revisions do not completely re-write methods!**
  - **Revisions consolidated memos and letters**
- **Method data from initial inter-lab studies (early 1980's)**

New CWA EPA methods requires validation and inter-lab studies

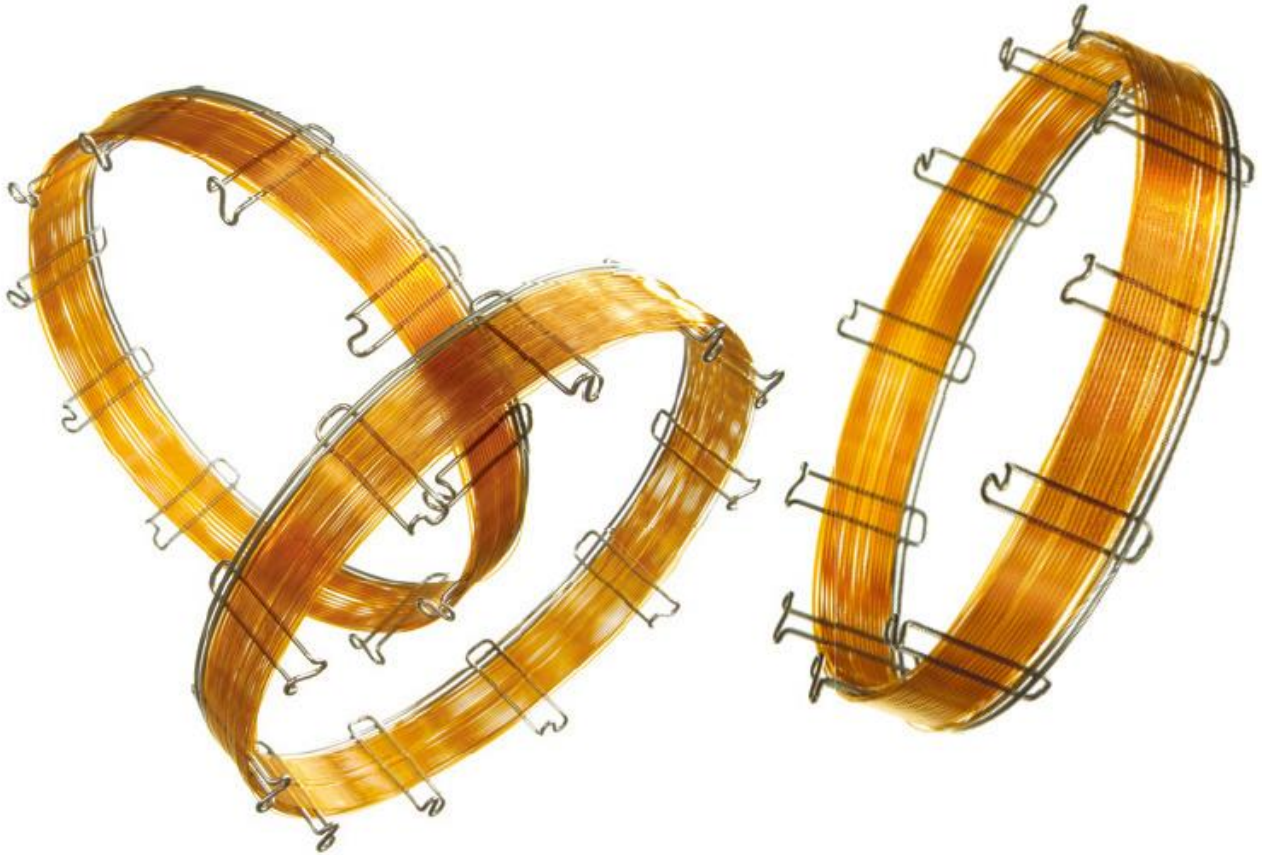
- **Methods at Part 136 require multiple laboratory validation (9 labs and 9 matrices)**
  - **Without an ILS EPA can only make minor changes**
  - **Or, rely on consensus standard organizations and ATPs**


History of 600 series methods
CUTTING EDGE
Priority pollutants
Packed Columns
P&T and LLE
Relative response factor
Multiple laboratory validated

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.**

New methods added capillary columns



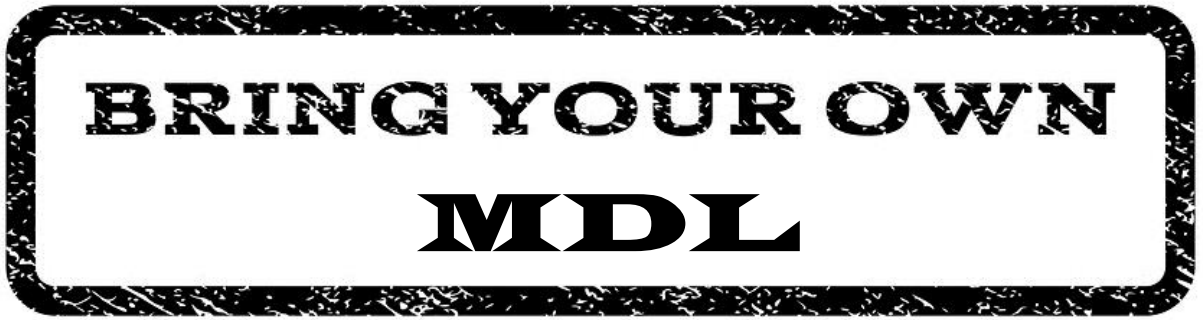
New methods added hydrogen as a carrier gas, or nitrogen as a purge gas

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

Attempt to “harmonize” methods across programs

All the EPA methods include new analytes

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



7 things you need to know about the revised method EPA 608

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

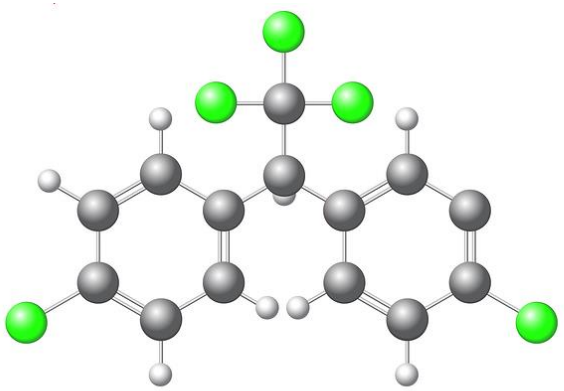
1. **New name – GC/HSD**
   - Halogen specific detector in addition to ECD
   - New detector data → EPA 1656

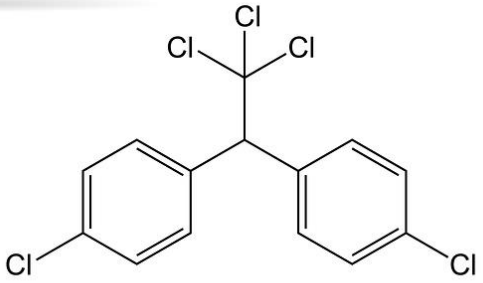
2. **Over 60 New analytes – Table 2**
   - Allows GCMS if sensitive enough
   - Toxaphene and PCB in Table 2

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

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**





9 things you need to know about the revised method EPA 624

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 $\leq 20\%$**

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**

11 things you need to know about the revised method EPA 625.1

EPA Method 625 is now Method 625.1

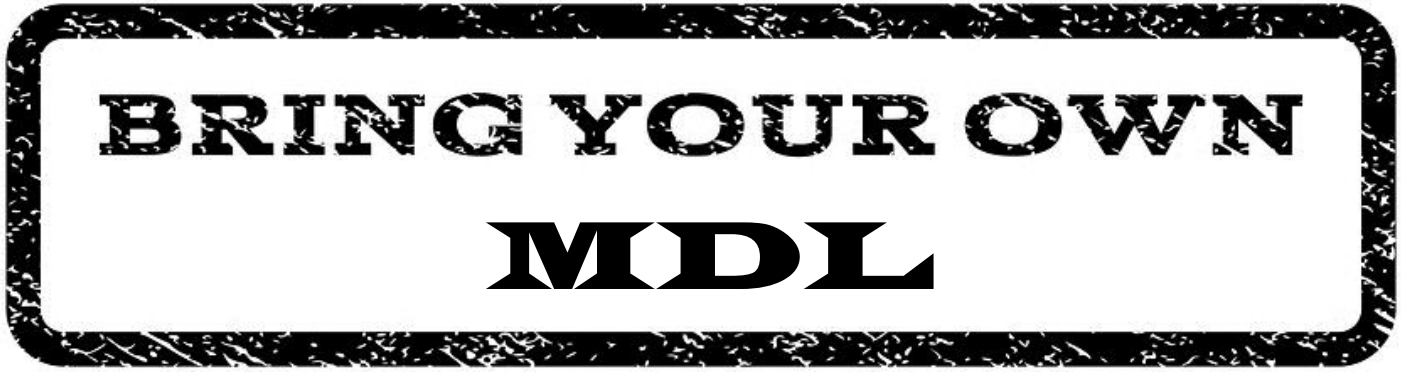
1. **Original priority pollutants include MDL and ML data**

   - Table 1 → 38 base neutral
   - Table 2 → 11 acid extractable

EPA Method 625.1

2. There are over 300 new analytes

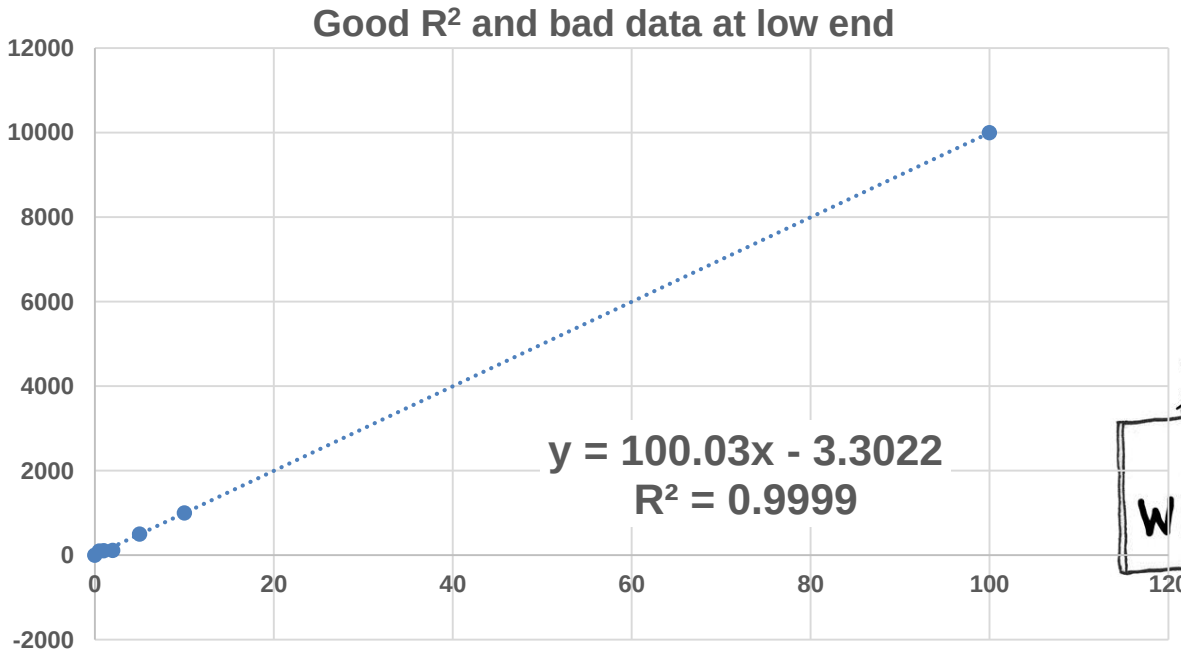
- **13 are priority pollutant pesticides and PCB's**
  - These have MDL and ML data
- **303 have no MDL or ML data**
  - YOU must establish your own



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



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

7. The CCV is a second Source Standard

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

9. 100 – 1000 ml sample size

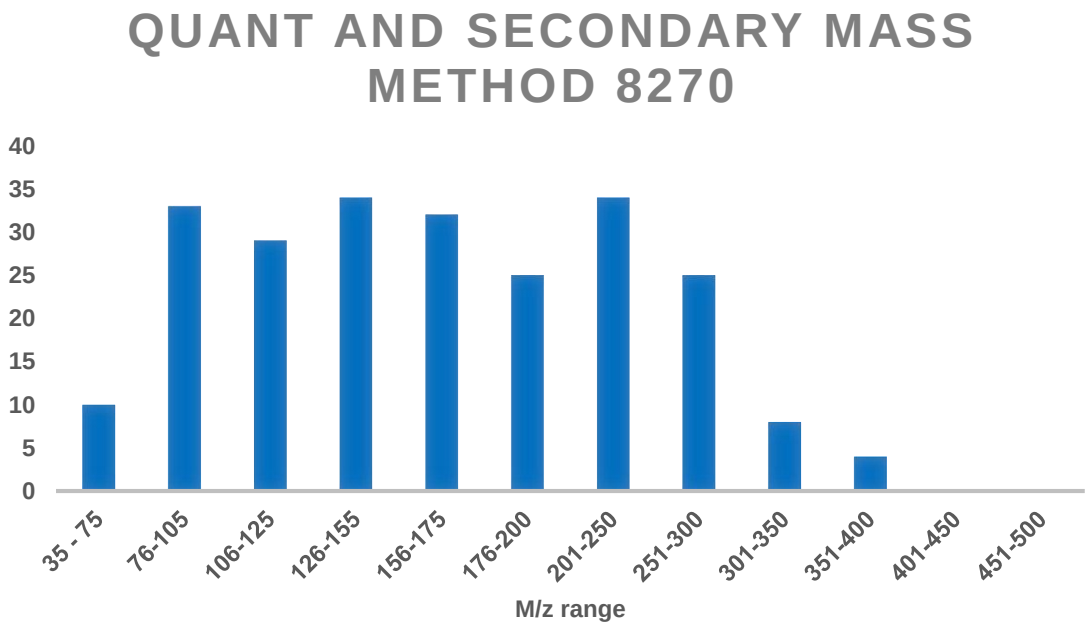
- Smaller sample volume = better for SPE
- Extract less means use less reagent
- New instruments can detect lower

10. One calibration Standard must be at ML

- 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)

11. DFTPP tune criteria more flexible, by footnote

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



Revision to the Part 136 Appendix B MDL

- **Originally Submitted by TNI**
- **MDL Calculation of spikes remains unchanged.**
- **Addresses background contamination, and multiple instrument MDLs**

Notice that the MDL is redefined

Current Definition	New Definition
99% Confidence that signal is greater than ZERO	99% Confidence that signal is greater than BLANK

Hypothetical Calculations of the MDL

	Spiked	Blank 1	Blank 2
	0.020	0	0
	0.015	0	0
	0.025	0.005	0.005
	0.018	0.020	0.005
	0.022	0	0
	0.016	0	0
	0.011	0	0
X	0.018	0.0036	0.0014
Sx	0.00467	0.0075	0.0024
MDL	0.014	0.022	0.009

One commenter's evaluation on change in their MDL

Compound (mg/L)	Old MDL	New MDL
SO_4	10	38
P	0.005	0.84
CN	0.005	0.014
TKN	0.5	1.59
B	0.010	0.036
Ag	0.003	0.006

For the new procedure, use ML and blanks from 7 previous batches to re-evaluate

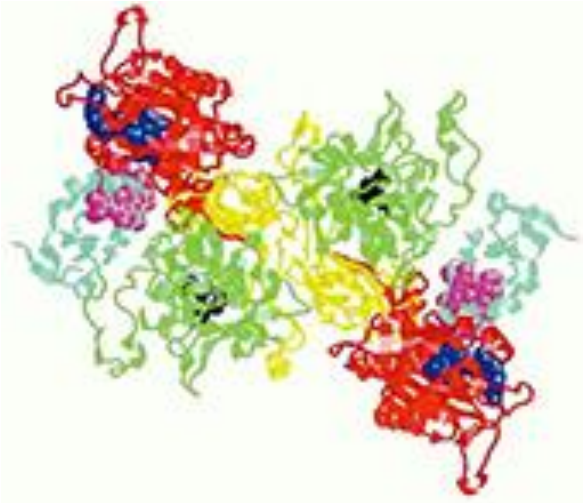
- Perform ML spikes with each batch to verify MDL
- Verify quarterly
- Recalculate MDL annually using existing data

ATP methods included in the 2017 MUR

- **NECi – Nitrate/Nitrite by Reductase**
- **Timberline – Ammonia by FIA GD-EC**
- **IDEXX – Colilert18**
- **NCASI (paper and pulp specific) – TN and TP**
- **HACH – sTKN**
- **HACH – Nitrate**

NECi Nitrate/Nitrite Method

- Reduces nitrate to nitrite using an enzyme
- Nitrite measured colorimetrically
  - Extensive Multiple laboratory study
  - All used Discrete Analyzers
    - Different manufacturers
  - Results equivalent to Cd reduction
  - Green method
- Originally approved as an ATP



USGS methods for nitrate/nitrite

- **Replaces cadmium with reductase**
  - **Low level and high level methods**
  - **First well validated Discrete Analyzer methods**

- **Same technique as NECi ATP**

Timberline Ammonia method

- **Flow Injection Gas diffusion with conductivity detection**
- **Green method**

- **Originally approved as an ATP**

IDEXX Colilert18 Method

- **Allows incubation at 44.5 ± 0.2 ºC**
- **Originally approved as an ATP**

NCASi TN (TKN) and TP Method

- Limited to paper and pulp (do not use)
- Alkaline persulfate digestion
- PO_4 and NO_3 measured by CFA

HACH TN (TKN) Test n Tube Method

- Alkaline persulfate digestion
- NO_3 measured colorimetrically
- Requires 2 tests
  - Total N
  - NO_3
  - TN – NO_3 = TKN
- Originally approved as an ATP

HACH NO_3 Test n Tube method

- NO_3 measured colorimetrically (345nm)
- Measures NO_3+NO_2 on preserved samples

- Originally approved as an ATP

And now for a summary of who done it

Most Method Development Activity Is Done By Volunteers

- **ATP**
  - **Manufacturers**
  - **Individual industry**
- **Consensus standards**
  - **Manufacturers**
  - **Industry**
  - **Commercial Labs**
  - **Municipal Labs**
  - **Universities**
  - **Government**

What methods may end up in the next MUR?

- **Total Nitrogen and Phosphorus**
  - **Alkaline persulfate and IC**
- **Total Nitrogen**
  - **High temperature combustion with chemiluminescence detection**
- **PCB's**
  - **GCMSMS?**
- **On-line analyzer methods**

Any Questions?

William Lipps

- **Environmental/Mining Marketing Manager**
- **ASTM D19 on Water Vice Chair**
- **Standard Methods Part 4000 Coordinator**

wclipps@shimadzu.com