Proposed changes to Clean Water Act Methods 608, 624, and 625

A great improvement in methodology, but issues with consistency, QC and reporting

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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

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

Proposed Changes to Appendix A

New Methods

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

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Summary

- Expanded to include additional analytes
  - Table 1 = “Analytes of Interest”
  - Table 2 = Expanded Analytes (Table 3 for 625.1)
- Added Reporting Limits (Minimum Level or ML)
- Much more flexibility in the procedure
- More QC and more requirements for reporting
- Some inconsistencies
- Some interesting new concepts
- Some interest new identification techniques

Analytes of Interest

- Those required to be determined by a regulatory/control authority or in a permit, or by a client.
- If a list of analytes is not specified, the analytes in Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes.
- MDLs and MLs provided for most analytes

Expanded Analytes

- Very long lists
  - 67 pesticides
  - 105 volatiles
  - 315 semivolatiles
- Very little performance data
- Includes some that are likely not measurable
  - Methanol
  - Phthalic anhydride
- Includes analytes of little or no regulatory concern that may not be measurable

May lead some data users to requests tests that are not practicable

Minimum Level

- EPA Concept that has existed for >20 years
- ML = MDL x 3.18
  - 3.18 =10/3.14 = Curries L_Q
- Round to the nearest 1, 2 or 5 x 10^n
  - So ML Values would be 1, 2, 5, 10, 20, 50, etc
- MLs published in the method = MDL x 3
- If MDL is wrong, 3 x MDL is also wrong

Inconsistencies

- Storage and replacement of standards
- Standard traceability
  - 608.3 = to a national standard, when available.
  - 624.1/625.1 = to NIST or other national standard
- Second Source standard
- Closing CCV
  - 608.3 = Yes
  - 624.1/625.1 = No
- Batch definitions
  - 608.3/625.1 = 20 samples
  - 624.1 = 12 hours

Storage of Standards

- 608.3
  - Store neat standards or single analyte standards in the dark at -20 to -10 °C.
  - Store multi-analyte standards at 4°C or per manufacturer's recommendations.
  - Place a mark on the vial at the level of the solution so that solvent evaporation loss can be detected.
- 624.1
  - Store standard solutions at -10 to -20°C, protected from light, in fluoropolymer-sealed glass containers with minimal headspace.
- 625.1
  - Store at <6 °C and protect from light.
  - Check frequently for degradation or evaporation, especially just prior to preparing calibration standards from them.

Replacement of Standards

- **608.3**
  - Stock standard solutions must be replaced after 12 months or sooner if comparison with quality control check standards indicates a change in concentration.
  - Analyze all standard solutions within 48 hours of preparation. Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions prepared by the laboratory or mixed with purchased solutions after one year, or sooner
- **624.1**
  - Replace after one month, or sooner if the concentration changes by more than 10 percent.
- **625.1**
  - Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions after one year, or sooner if comparison with QC check samples indicates a problem.

Second Source Standard

- 608.3
  - different manufacturer or different certified lot
  - verify the accuracy of the initial calibration
  - concentrations must be within 20% difference of the true value
- 624.1
  - Not listed in Reagents
  - Not used to check ICAL
  - = LCS
  - Criteria = Table 7
  - May run 2 consecutive LCS
- 625.1
  - Not listed in Reagents
  - Not used to check ICAL
  - = CCV
  - Criteria = Table 6
  - May run 2 consecutive

Calibration Curves

- 608.3
  - At least three levels (5 recommended, 6 for quadratic)
  - Low point must be below published ML
- External Standard
  - If the RSD is less than 20%, linearity can be assumed
  - If curve, must be inversely weighted to concentration
  - Must have R^2 of 0.99 or RSE of 20%
- Internal Standard
  - If the RSD is less than 15%, linearity can be assumed
  - If curve, must be inversely weighted to concentration
  - Must have R^2 of 0.99 or RSE of 15%
- 624.1/625.1
  - At least five levels (6 for quadratic)
  - Average RF may be used if RSD < 35%
  - If curve, must be inversely weighted to concentration
  - Must have R^2 of 0.92 or RSE of 35%
  - Low point must be below published ML
  - ML can be rounded, but may not be above published level; i.e., ML of 4.8 cannot be rounded to 5

Correlation Coefficients for Evaluation of Analytical Calibration Curves

Anal. Chem. 1981 (C.L. Grant)

- One practice which should be discouraged is the use of the correlation coefficient as a means off evaluating goodness of fit of linear models.
- Thorough statistical analysis of analytical calibration data should be used to provide optimal evaluation of results. The correlation coefficient is not an effective statistic for this purpose.

Calibration Verification

- 608.3
  - Verified at the beginning and end of each 24-hour shift
  - Criteria published in Table 4, e.g.
    - Aldrin =75-125
    - Dieldrin = 48-125
  - Table 4 criteria includes all sample processing steps

608 was once per day and 15%

- 624.1
  - = LCS
  - Criteria in Table 7, e.g.
    - Bromoform = 70-130
    - Bromomethane = 15-185

This is the same as 624

- 625.1
  - 20% difference changed to Table 6 (Q?)
  - Values can be as high as 13-200%

Quality Control

- Old Methods
  - DOC per analyst
    - Precision and accuracy
    - One time
  - Blank
  - 10% MS
  - 10% QC Check
  - Statements of accuracy
- New Methods
  - DOC per **laboratory**
    - Precision, accuracy and **MDL**
    - Initial and annually (should)
  - Blank
  - 5% MS; 5% MSD
  - LCS per batch
  - Surrogates
  - Internal standard areas (50-200%)
  - Statements of accuracy
  - PT Samples (recommended)

IDC/DOC

- 4 replicate QC Check samples
  - Concentration at or below mid-point
  - Compare results to QC criteria (Tables 4, 6, or 7)
  - For analytes with no criteria, use 136.6
    - Criteria from an “equivalent” method
    - Default criteria (e.g., 60-140%)
- MDL Study
  - As described in Appendix B
  - MDLs must be equal to or lower than those in the method, OR
  - 1/3 the regulatory level

MS/MSD

- Spike at least 5% of samples from each **site**
- Data user to identify samples and analytes
- If direction cannot be obtained, the laboratory must spike at least one sample in duplicate per batch.
- Spiked sample results should be reported only to the data user whose sample was spiked.
- **If recovery falls outside the designated range, the result for the analyte in the sample is suspect and may not be reported or used for permitting or regulatory compliance.**

Statements of Accuracy for Wastewater

- Calculate the average recovery and sd from MS/MSD (for each discharge?)
- Calculate interval X ± 2sd
- Update on a regular basis
- What would this be used for?

This was in the 1984 versions of these methods

QC Limits for MS/MSD

- Calculate new limits after 20 MS/MSD
- Update every two years
- 80% of limits better than QC Table
- QC Table are the maximum limits

LCS

- One LCS per batch of 20 or less
- Use criteria in QC Table (Table 4, 6 or 7)
- Repeat the test for those analytes that failed to meet the criteria. If these analytes now pass, system performance is acceptable and analysis of samples may proceed. If this occurs, repeat the test using a fresh LCS, or perform and document system repair.
- Update criteria using same procedure as MS/MSD

Blanks

- One blank per batch
- Re-extract if blank result is:
  - Greater than MDL, or
  - Greater than 1/3 compliance limit, or
  - Greater than 1/10 sample concentration
- If re-testing of blanks results in repeated failures, the laboratory should document the failures and report the problem and failures with the data.

NELAP: the concentration is at or above the reporting limit, AND greater than 1/10 of the amount measured in the sample

Surrogates

- Must be spiked in every sample
- Laboratory develops limits; 60-140% can be used as interim limits
- Any failure, re-analyze sample if available
- Surrogate recoveries from the blank and LCS may be used as pass/fail criteria by the laboratory or as required by a regulatory authority, or may be used to diagnose problems with the analytical system.

Blank Subtraction

- **When subtracting two measurements**, the uncertainty in the final measurement is equal to the sum of the uncertainties in the original measurements:
- $(A \pm s) - (B \pm s) = (A - B) \pm (sA + sB)$
- Dieldrin: MDL = 6; ML = 18; s = 42%
- C = (18 -6) ± *(7.5+2.5) = 2 - 22*

http://physicsed.buffalostate.edu/pubs/MeasurementAnalysis/MA1_9ed.pdf

Specific Method Issues

608.3 Second Column Confirmation

- If values from two columns are in agreement within a factor of 2, analyte is present
- If not within factor of 2
  - If interferent is detected on second column, report result and advise data user of interference
  - If no interferent is detected, report ND at the lower concentration

Interesting concept. Do you agree?

624.2 Mass Spectrometer

- Scan rate changed to 7 scans/second
- Mass range = 35-260 with suggestion to go to 25-260 for:
  - Acrolein (m/z 56, 55, 58)
  - Acrylonitrile (m/z 53, 52, 51)
  - Choloromethane (m/z 50, 52)
  - Vinyl chloride (m/z 62, 64)
- Interferences below m/z 35
  - Methanol (m/z 29, 31, 32)
  - Nitrogen (m/z 28)
  - Oxygen (m/z 32)
  - Argon (m/z 40)

624.1 GC resolution

- Valley between 1,2-dibromoethane and chlorobenzene must not exceed 25
- 1,2-dibromoethane is not listed as an analyte
- The two compounds have very different spectra
  - 1,2-dibromoethane 107 (109, 188)
  - chlorobenzene 112 (77, 114)

GC/MS Identification

- Retention time: ±30 seconds changed to 0.06 RRT
- Relative intensities changed from ±20% to 50% to 200%
- New: “m/z’s present in the acquired mass spectrum for the sample that are not present in the reference mass spectrum must be accounted for by contaminant or background m/z’s.”
- Isomers must have peak resolution of 50% compared to 25% in Method 624/625 (and methods 524/525)

QC Failures

If continued re-testing results in repeated failures, the laboratory should document the failures (e.g., as qualifiers on results) and either avoid reporting results for analytes that failed or report the problem and failures with the data. Failure to report does not relieve a discharger or permittee of reporting timely results. Results for regulatory compliance must be accompanied by QC results that meet all acceptance criteria.

624 allowed QC check to override MS failure; no criteria for blanks

Reporting

- Report quantitative data to ML to 3 significant figures
- Report the lower of two results from 608.3
- Report results less than ML as < ML, “or as required by the regulatory authority or permit”
- Allows for blank subtraction if requested or required
- Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results.

Reporting Caveat (1.7.1)

- EPA has promulgated this method at 40 CFR Part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in Section 15.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

600s: Summary of Technical

- Updated technology to current practice
- Much more flexibility
- Additional analytes
- Some inconsistencies between the methods

Summary: QC and Reporting

- New concepts may be troublesome
  - Making data user select samples to be spiked
  - Establishing accuracy/precision per site/discharge
  - Reporting rules for 608.3
  - Revised identification criteria for 624.1 and 625.1
  - Blank subtraction
- Daily calibration checks are problematic
  - Not consistent with current industry practice
  - Will greatly increase error
- QC section is problematic
  - Not consistent with current industry practice
  - Cannot realistically be done
  - Will increase laboratory fraud
  - The caveats help, but not enough

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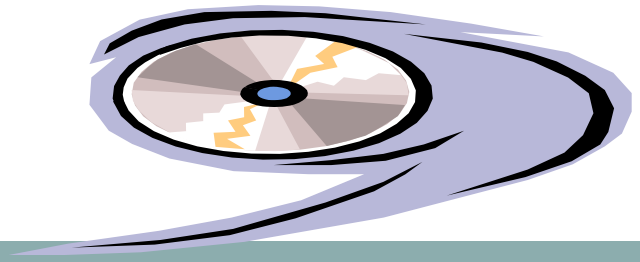
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