
Updates and Current Activities: Clean Water Act Methods Program

Richard Reding, Ph.D.
Office of Science and Technology (OST)
Florida Society of Environmental Analysts
October 2008



Office of Water

CWA Analytical Methods Activities

- The March 2007 Final Rule – Follow-up
- Method Development and Application Projects
- Detection & Quantitation Advisory Committee

**Follow-up to March 12, 2007
Methods Update Rule (MUR)
72 FR 11199**

Revised Table II, Part 136.3 – Cyanide Sampling

Procedures to preserve samples/mitigate interferences

- Footnotes 5 and 6 describe several options depending on interferences present
- One size does NOT fit all
- Footnote 6 allows analysts flexibility to develop other procedures for specific sample types/interferences
- Cyanide may still be held 14 days if treated correctly

Revised Table II, Part 136.3 – Cyanide Sampling

- Footnote 6 describes **recommended** procedures to remove or suppress cyanide interferences, such as:
 - Sulfur
 - Sulfide
 - Sulfite
 - Thiocyanate
 - Aldehydes
 - Carbonates
 - Chlorine and Hypochlorite

Revised Table II, Part 136.3 – Cyanide Sampling

- Is the word “recommended” in cyanide footnote 6 of value?
- Yes, cyanide mitigations may not work in all case so we allow the flexibility to develop other mitigations for specific sample types/interferences “...Any procedure for removal or suppression of an interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide...”
- Must I obtain an EPA waiver or ATP to do this? No.
- **Must I obtain an EPA waiver (136.3(e)) or an ATP to change other procedures in Table II?**
 - ATP – no
 - Waiver – yes, but generally requires less work than a typical ATP

Current Topics for Cyanide – ASTM Efforts

- D19 subcommittee's ongoing effort to better understand and explain how to measure cyanide in a variety of matrices
- Field mitigation/preservation challenges from multiple interferences and order in which interferences must be mitigated
- Prefer lab vs. field mitigation - holding time problem
- Plan to develop a practice to address cyanide sampling
- EPA will evaluate for webposting and potential rulemaking
- Meanwhile footnote 6 allows use of other procedures (including ASTM procedures) to mitigate interferences

Addition of Metals to Approved CWA Methods

- Method 200.7 (ICP-AES), Rev. 4.4

200.7 may be used to determine all analytes listed in the method, although some of these metals are not in Table IB. You must meet all general QC criteria (IDC, etc.) in 200.7.

- Method 200.8 (ICP-MS) Rev. 5.4

Boron, calcium, iron, magnesium, potassium, sodium, silica, tin, titanium and gold may be added, if all general QC criteria (IDC, etc.) in the method are met and the method provides the necessary sensitivity.

- Although no comparative data must be provided to EPA, as with any modification data must be available for audits

- Use collision cell technology with ICP-MS?

- CWA applications yes; SDWA not yet, but stay tuned.

Method Flexibility for Wastewater – 136.6

- New 40 CFR 136.6 (March 12, 2007)
 - Builds on the flexibility specified in section 9.2 of EPA's 1600-series chemical methods.
 - May modify methods to overcome matrix problems, automate methods, or otherwise improve the efficiency or accuracy of a compliance analysis without unnecessary delay.
 - Modifications are acceptable for compliance use, if the modification is documented to work, i.e., using your sample method performance should be comparable to that of the unmodified method.

Method Flexibility for Wastewater – 136.6

➤ What modifications are not within the allowable flexibility described in 136.6?

- Changes to the determinative step (e.g., the detector), changes to the quality control, changes that significantly alter the chemistry of the method, some (**not all**) changes to methods that measure a method-defined parameter, such as oil or grease, are not allowed within the flexibility described in 136.6.
- **Does not apply to SDWA, biological, or microbiological** pollutants, i.e. only to CWA methods for chemicals and some physical parameters.

Method Flexibility for Wastewater – 136.6

➤ A determinative technique is the detector

- For example, colorimetric detection of cyanide in EPA 335.2, and GC/MS detection of organics in EPA 625

➤ What is a method-defined parameter?

- A measurement intrinsically linked to a method-specific step
 - E.g., measures a property, such as COD, oil & grease, and turbidity, rather than the concentration of a chemical
 - Any procedure preceded by digestion (e.g., total metals) or a distillation that acts as a digestion (e.g., cyanide) is a method-defining step in the method and not within 136.6 scope

Withdrawal of MCAWW Methods

- March 12, 2007, withdrew 109 *Methods for Chemical Analysis of Water and Wastes* (MCAWW), or replaced with newer versions of the same numbered method.
- **Does this mean we also withdrew approval of any Alternate Test Procedure (ATP) program method associated with a withdrawn MCAWW method? No.**
 - We did not propose to do so. There are approved methods that use the same measurement technologies against which the ATP method may be linked.

Method Flexibility and the ATP Program

- Has 136.6 changed the CWA ATP program?
 - Yes, you must clearly explain why your method modification is outside the scope of 136.6. We will not review applications that omit this explanation, or methods that fall within the scope of 136.6.
- Do modified Part 136 methods with an ATP approval letter carry more weight than methods that no longer have a letter because the modification is within 36.6?
 - No, these methods may be used in the same situations as an older method that has an EPA letter

Specifying QC or Other Lab Procedures

- 40 CFR 122.41(e) describes “Conditions Applicable to all Permits...”
 - Proper O&M includes laboratory controls and QA
 - Some Part 136 methods are published in compendiums that include instructions for sample prep, quality control or other important steps separate from the specific analysis instructions
- Are these steps necessary?
 - If cited or logically part of the method, yes.
 - Not all generic instructions may be germane to your analysis – work these issues appropriately

Method Development and Application Projects

Current Activities

- Contaminants of Emerging Concern (**CECs**)
 - Method development and occurrence or other studies
 - Updating and revising several CEC GC or LC methods
- Preparing to validate qPCR method(s) for beaches
- Completing tests in wastewaters of a modified drinking water method for cryptosporidium
- Report on false positive and negative rates for fecal coliforms in biosolids
- Test of an enterococci and E. coli method in stormwaters

Monitoring Water Quality at Beaches

- Pathogens vs. Indicator Organisms
- Not practical to look for all pathogens (too many)
- We currently use bacterial indicators of fecal contamination
- In recreational waters, these are enterococci and *Escherichia coli* (*E. coli*)
- EPA epi studies positively correlated these indicators with human fecal contamination in beach waters

Recreational Water Quality Criteria

- Developing new criteria for recreational waters
- Culture methods not amenable to same-day monitoring
 - New criteria may include new monitoring methods, such as rapid genetic methods based on quantitative polymerase chain reaction (qPCR) tests
- Have a qPCR method for enterococci; developing others for *E. coli*, and *Bacteroides* (a human specific bacterium)
 - Writing a lab protocol to validate qPCR methods to measure pathogen DNA
- Plan to single-lab validate, peer review and publish some of these methods next year

CEC Interest and Ongoing Research

- Modern methods find more trace contaminants
- Reports of intersex fish have generated interest
- Researchers are studying CECs from viewpoints, such as pollution prevention, assessment of effects, treatment
 - Matrices and geographical locations
 - Identify and measure specific CECs
 - Fate and transport from sewer to water
 - Potential treatment or control technologies
 - Assess water quality and other impacts
- Partnering with other organizations and agencies

Ongoing Studies of CECs in the Environment

- Occurrence in Fish Tissue
 - Sampling for 37 PPCPs in fish tissue from effluent-dominated streams at five sites
- Health Services Industry collecting information on use and disposal activities
 - Focus on dental mercury amalgam discharges, and fate of unused pharmaceuticals at hospitals and LTC facilities.

Chemical Method Development Activities

- We have developed analytical methods to identify and measure CECs in wastewaters and biosolids
- Field testing these methods by characterizing occurrence in POTW influent/effluent
 - Pharmaceuticals – EPA Method 1694
 - Steroids & hormones – EPA Method 1698
 - Pesticides – EPA Method 1699
 - Flame retardants – EPA Method 1614
 - Nonylphenols – ASTM D 7065–06

PPCPs



EPA PPCP web site: <http://www.epa.gov/ppcp/>

Office of Water

Status of EPA Methods 1694, 1698, and 1699

- Single lab validated, and peer reviewed
 - Posted to both EPA's Waterscience Methods web site and EPA's PPCP web site in January, 2008:
 - <http://www.epa.gov/waterscience/methods/method/other.html>
 - <http://www.epa.gov/ppcp>
 - Not promulgated, but available for monitoring

- Current work
 - Field test on POTW influent and effluent
 - Add addt'l analytes to Method 1694
 - Use field and other tests to revise methods where warranted

Method 1694: PPCPs by LC/MS/MS

- Typical Analytes (of 74 total)
 - Acetaminophen (Tylenol)
 - Albuterol
 - Caffeine
 - Carbamazepine
 - Codeine
 - Ibuprofen (Advil)
 - Penicillins (3), e.g., Penicillin G
 - Sulfa drugs (9), e.g., sulfamethazine
 - Tetracyclines (12), e.g., oxytetracycline

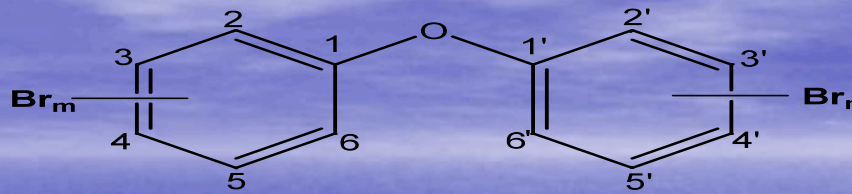
Method 1699: Pesticides by GC/HRMS

➤ Typical Analytes (of 60 total)

- γ -BHC (Lindane)
- p,p'-DDT
- α -(cis-)chlordane
- Quintozene
- Chlorpyrifos
- Diazinon
- Malathion
- Atrazine
- Cypermethrin



PBDEs - Chemical Structure



- Number of Bromines defines congener grouping
 - Mono- through deca-
- Positions of Bromines vary within a congener grouping
 - Substitution at the 2, 2' and the 2,2',6, 6' positions cause the congeners to be nonplanar
 - Congeners with substitution at the other positions are more planar

D7065-06 ASTM Method for NP and APEs

- Nonylphenol (NP) and alkylphenol ethoxylates (APEs) are surfactants
- Developed by EPA Region 5 laboratory; interlab validation with ASTM International in 2006
- ASTM published D7065-06 in 2007 Vol. 11.02
 - Not promulgated but available for monitoring
- Revising to lower detection to meet marine water criteria

MDL and ML: Status of a Federal Advisory Detection and Quantitation Committee

FACDQ

- Federal Advisory Committee for Detection and Quantitation (FACDQ) in Clean Water Act Programs
 - Established May 2005
- Participants drawn from
 - States
 - Regulated industry
 - Publicly owned treatment works
 - Testing laboratories
 - Environmental Community

Charge to the Advisory Committee

- Provide group advice and consensus recommendations to the EPA Administrator
- Final report December 2007 at www.epa.gov/waterscience/methods/det
- Although no consensus, committee provided detailed and useful recommendation for calculating limits, and for use of these limits in CWA programs

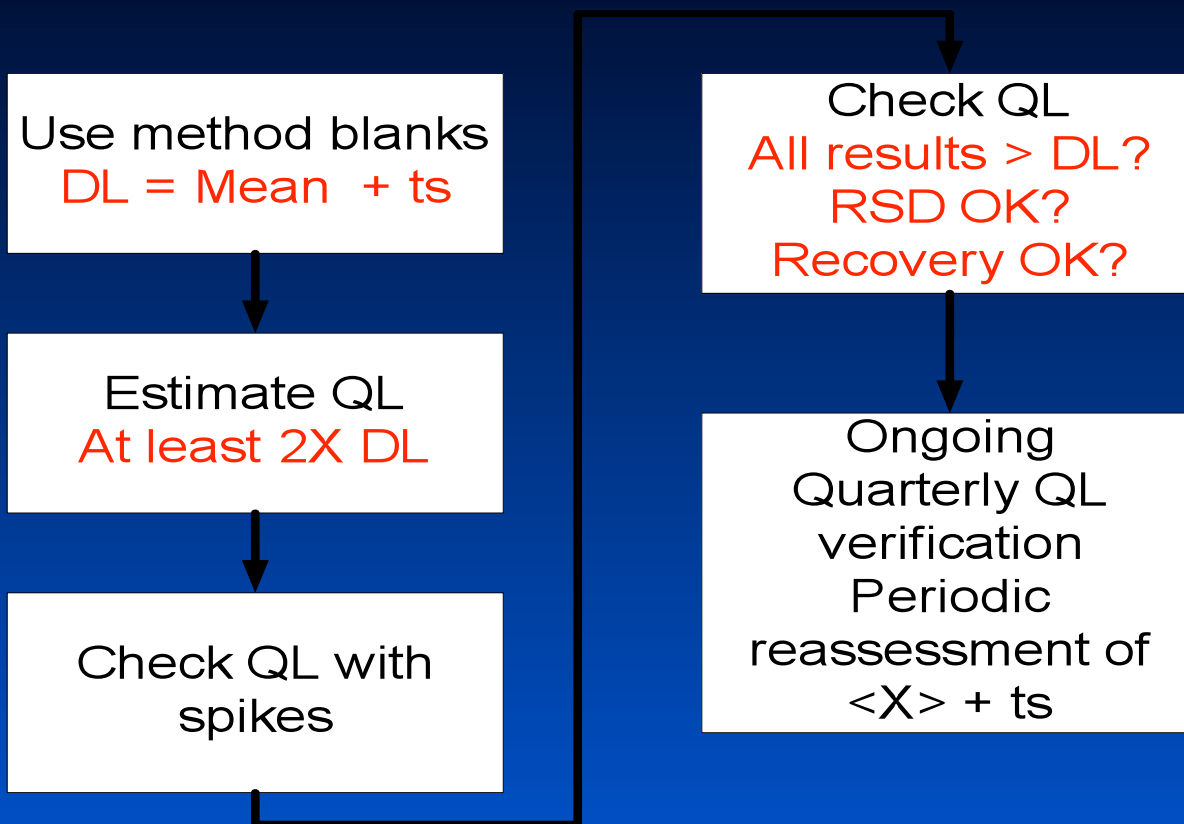
A Procedure Should

- Incorporate temporal variability
- Reflect routine performance
- Address matrices
- Evaluate the entire test method
- Address blank bias
- Address intermittent blank contamination
- Produce an explicit estimate of bias and precision
- Control false positive and negative rates

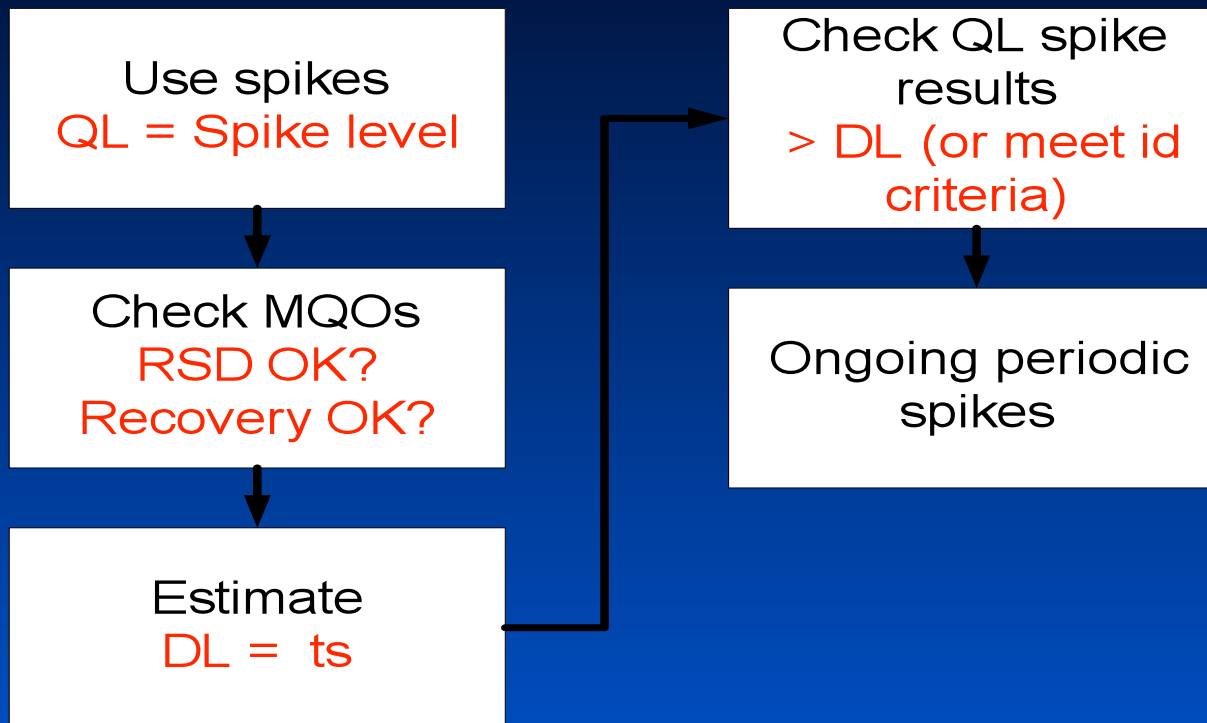
Other Desirable Characteristics

- Be clearly written
- Spiking instructions and interpretation not too complex for a typical analyst to perform in the laboratory
- Not too difficult to calculate a DL and QL from the lab spiking results – software a plus

Methods with numerical blank results



Methods with no or infrequent numerical blank results



Status and Next Steps

- Have collaborated with EPA programs to
 - Expand the scope of the FACDQ DL-QL procedure
 - As written allows for simple routine verification of ability to meet existing benchmark limit
 - Now also describes how a method developer may establish best performance in setting benchmark limits
 - Design the study plan for the next Lab Pilot of this procedure
- Preparing this study plan for a formal peer review
 - Pilot will evaluate the DL-QL procedure in a several labs with metals and organic chemical analytical methods
- Conduct the Lab Pilot in 2009
- Evaluate and peer review lab pilot results
- Conduct rulemaking – proposal, public comment, final rule

CWA Methods Team

- **CWA Methods Team - Lead Areas**

- Meghan Hessenauer – Health Services Study
- Brian Englert – Organic Methods
- Lemuel Walker – Method Flexibility
- Robin Oshiro – Microbiology
- Marion Kelly – Quality Assurance
- **Team Email - [OSTCWAMETHODS @ EPA.GOV](mailto:OSTCWAMETHODS@EPA.GOV)**



- epa.gov/waterscience/methods/

- Fact Sheets, FAQs, Rule Text, EPA Methods