Mercury Collection and Analysis in Ambient and Effluent Waters using EPA Method 1631

A Historical Perspective

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Mercury

- Toxic priority pollutant across EPA programs including air, water, hazardous waste and pollution prevention
- Persistent, ubiquitous, and harmful to human health and the environment at relatively low levels
- Bioaccumulative chemical of concern. Thirty-nine states have issued fish consumption advisories due to mercury contamination

Regulation Under the Clean Water Act

- 1987 amendments to CWA mandated increased emphasis on water quality-based permitting
  - States must adopt specific numeric criteria for all toxic pollutants expected to interfere with designated uses of a water body
  - States must implement water quality-based control strategies to ensure water quality is attained
  - Water quality controls reflect *water quality standards* designated by each state
    - Designated use(s) of water body or segment
    - WQC necessary to protect designated use(s)
    - Anti-degradation policy

Regulation Under the Clean Water Act (cont.)

- Translating from Dissolved WQC to a Total Recoverable WQC
  - EPA recommends that the WQS be defined in terms of dissolved concentrations
  - NPDES regulations require effluent discharges to be defined in terms of total recoverable metals concentrations
- Guidance on the translation of dissolved WQC to total recoverable WQC is found in *The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion* (February 16, 1996 draft)

EPA Response to CWA Amendments

- *Great Lakes Water Quality Agreement* (1987)
  - Joint EPA and Environment Canada agreement
  - Calls for virtual elimination of mercury while providing incentives and options for cost-effective implementation that consider mercury sources
- National Toxics Rule (40 CFR 131.36)
  - Established numeric WQC for toxic pollutants
  - Brought non-compliant States into compliance with 1987 amendments to CWA Section 303(c)(2)(B)
- Final Water Quality Guidance for the Great Lakes System (1995)
  - 60 FR 15366
  - Responds to CWA Section 118(c)(2)(C)

Mercury - Water Quality Criteria

Criterion	NTR (ng/L)	Great Lakes (ng/L)
Freshwater Acute	2400	1440
Freshwater Chronic	12	770
Marine Acute	2100	-
Marine Chronic	25	-
Human Health	140	1.8
Wildlife	-	1.3

Contamination Concerns

- Some mercury reported in water samples may be due to contamination rather than actual sample concentrations
- Methods approved by EPA before 1999 did not address trace-level contamination issues and do not incorporate clean techniques or guidelines
- Use of clean sample handling techniques for determination of mercury at WQC levels is recommended to preclude false positives arising from sample collection, handling, or analysis

Development of Trace Level Methods

- EPA's Analytical Methods Staff (AMS) was charged with developing guidance for sampling and analyzing trace metals
- Initial goal was development of methods for 13 metals listed in the National Toxics Rule at 40 CFR 131
- Goal revised to address criteria listed in Great Lakes Guidance
- AMS objective is to detect pollutants at one-tenth of the lowest WQC, which is based on the use of dissolved metals
- Development of Method 1631 for mercury initiated in 1996

Development of Trace Level Methods (cont.)

- Guidance on Establishing Trace Metals Clean Rooms in Existing Facilities
- Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring
- Method 1669: Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels
- Video: Sampling Ambient and Effluent Waters for Trace Metals

Method 1631

Method 1631: *Mercury in Water by Oxidation, Purge and Trap, and CVAFS*

EPA developed Method 1631 to determine mercury reliably at ambient water quality criteria levels.

		Lowest WQC
▫ Method Range:	0.5 - 100 ng/L	human health = 1.8 ng/L
▫ MDL:	0.2 ng/L	wildlife = 1.3 ng/L

Interlaboratory Study Results

Method 1631 Interlaboratory Study results supported draft method performance criteria

QC Element	Study Results	Draft Method
MDL	0.09 ng/L (pooled)	0.2 ng/L
Calibration Linearity	12 (RSD)	15 (RSD)
IPR: precision	17 (RSD)	21 (RSD)
recovery	86 - 113 %	79 - 121 %
OPR: recovery	76 - 123 %	77 - 123 %

Notice of Data Availability (NODA)

- Published on March 5, 1999 (64 FR 10596)
- Included
  - Results of Method 1631 Application to Effluent Matrices
  - Data Summary - Application of Method 1631 to Industrial and Municipal Effluents
  - Evaluating Field Techniques for Collecting Effluent Samples and Supporting Quality Control Data
  - Method 1631 Effluent MDL Study

Summary of Public Comments

Comments received on Method proposal (30 comment packages) and NODA (6 comment packages)

- Support approval of methods for trace levels or mercury
- Support integrity of Method 1631
- Concern for cost and practicality
  - Requirement for clean techniques
  - Method equipment and performance
- Concern for regulatory implications
  - Applicability to effluent
  - Permits generally written at lowest detection limit

Concern for Cost and Practicality

- Clean techniques in EPA Method 1669 are recommended as essential elements to be incorporated when using Method 1631
- Laboratories required to meet method QC
- Clean space/clean room costs: $5,000 - $100,000
- Instrument costs: $20,000 - $ 25,000
- Cost per sample analysis: $75 - $150

Additional Methods - Development and Validation

EPA has initiated a validation study to support approval of draft Method 245.7: *Determination of Ultra-Trace Level Total Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry*

Matrices: freshwater, marine water, and municipal and industrial effluent

Range: 1.0 - 100 ng/L

MDL: 0.3 - 3.3 ng/L

Comparison - Mercury Methods

	Method 1631	Method 245.7
Digestion	BrCl / $Sn^{2}Cl$ / $NH^{2}OH{\cdot}HCl$	BrCl / $Sn^{2}Cl$ / $NH^{2}OH{\cdot}HCl$
Separation	Purge Gold Trap	Liquid Gas Separator Dryer Tube
Detection	CVAFS	CVAFS
MDL	0.2 ng/L (validated in 12 labs)	0.3 – 3.3 ng/L (observed in 3 labs)
Range	0.5 – 100 ng/L (validated in 12 labs)	1 – 100 ng/L (interlaboratory study underway)
Time	15 - 30 minutes	10 - 15 minutes

Development of Trace Level Methods (cont.)

- **Method 1630:** Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
- **Method 1631:** Mercury in Water by Oxidation, Purge and Trap, and CVAFS
- **Method 1631 Appendix A:** Digestion Procedures for the Determination of Total Mercury in Tissues, Sludge, Sediments, and Soils
- **Method 1632:** Inorganic Arsenic in Water by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry
- **Method 1632A:** Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry
- **Method 1637:** Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption Spectrometry
- **Method 1638:** Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry
- **Method 1639:** Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry
- **Method 1640:** Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry

Method 1669

- EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels
  - Incorporates clean techniques from USGS and other experts
  - Provides procedures necessary to produce reliable results at the lowest water quality criteria published by EPA
  - Designed to support collection of ambient water samples
  - Performance-based

Ongoing Method Development Efforts

- Metal Species
- Oxidation States
  - Toxicity and bioavailability can vary with the oxidation state of the metal
  - Quantification of the metal in a particular oxidation state in an environmental sample may necessitate the use of different sample handling procedures, holding times, and analytical methods
- Organo-metallic species
  - Bioaccumulation of methyl mercury in organisms is 10^6-10^8
  - Sample preparation and analytical procedures may differ from those used for inorganic metal forms