
Status of EPA Method 1631 for the Determination of Low-Level Mercury

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Background

- ◆ **EPA Method 1631: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry***
 - Applicable to determination of Hg at Water Quality Criteria (WQC) levels
 - Supports implementation of National Toxics Rule and Great Lakes Water Quality Initiative
 - Interlaboratory validation study completed prior to proposal
 - Joint effort with the Electric Power Research Institute (EPRI)
 - Twelve participating laboratories / One referee laboratory
 - Validated in reagent water, freshwater, effluent, marine water



Background (cont.)

- ◆ EPA developed Method 1631 for determining mercury levels in the low ng/L range (approximately 400 times more sensitive than other approved methods)
 - Method 1631, Revision A was proposed on May 26, 1998 (63 FR 28868)
 - 30 comment packages received during comment period
 - NODA was published on March 5, 1999 (64 FR 10596)
 - Method 1631, Revision B was promulgated on June 8, 1999 (64 FR 30417)



Settlement Agreement

- ◆ Petition for judicial review filed with U.S. Court for the District of Columbia
 - **Settlement Agreement** between Petitioners and EPA signed October 19, 2000
 - Provisions of the Settlement Agreement include:
 - **Guidance** on matrix interferences by March 1, 2001
 - **Notice of Final Rulemaking** (Method 1631, Revision C) by June 15, 2001 modifying test method sections 12.4.2 and 9.4.3.3 to clarify use and reporting of field blanks



Settlement Agreement (cont.)

- Provisions of the Settlement Agreement (cont.)
 - **Proposal** of additional clean techniques and quality control requirements by September 30, 2001
 - **Final Action** on the proposal by September 30, 2002
 - **Reassessment** of Method Detection Limit and Minimum Level (MDL/ML) procedures
 - ✕ Proposal by February 28, 2003
 - ✕ Final Action by September 30, 2004



Purpose of Guidance Document

- ◆ *Guidance for Implementation and Use of EPA Method 1631 for the Determination of Low-Level Mercury (40 CFR part 136), EPA 821-R-01-023, March 2001*
 - To develop consistent national policy on the implementation and use of Method 1631
 - Fulfills provision in the Settlement Agreement on matrix interferences
 - Provides assistance to analytical and regulatory communities
 - Responds to requests for information on specific details of the method



Topics Covered by Guidance

◆ Use of **Clean Techniques** to preclude contamination

- Explains method requirements
- Recommends additional clean techniques
- Information on requirements and recommendations from:
 - Method 1631
 - Sampling Guidance (EPA Method 1669)
 - Trace Metals Sampling Video
 - Clean Spaces Guidance
 - Trace Metal Cleanrooms



Topics Covered by Guidance (cont.)

◆ Matrix Interferences

- Known matrix interferences
- How to determine that an interference exists
- How to overcome an interference
- How to demonstrate that failure of the QC acceptance criteria is due to a matrix interference
- Available regulatory relief if MDL and ML are not achievable



Topics Covered by Guidance (cont.)

- ◆ Information needed to demonstrate that regulatory relief may be appropriate
 - MDL, IPR, and blank data to demonstrate laboratory performance
 - Field, equipment, and reagent blank data to demonstrate sampling and analysis systems are free from contamination
 - MS/MSD data to demonstrate recovery and precision are not within QC acceptance criteria
 - Confirmation of out-of-specification MS/MSD by second laboratory
 - Steps taken to attempt to mitigate interference

Topics Covered by Guidance (cont.)

- ◆ Known interferences: iodide, gold, high organic content
- ◆ Suggestions to mitigate a matrix interference:
 - Dilution - diluted sample concentration must be at or above ML
 - Iodide - for iodide concentrations greater than 3 mg/L, pre-reduce sample with SnCl_2
 - Gold - cannot be overcome; gold interference due to sampling or laboratory contamination can be controlled
 - High organics - oxidize sample with additional BrCl , UV photo-oxidation, heat



Topics Covered by Guidance (cont.)

◆ Flexibility in EPA Method 1631

- Method 1631 is “performance-based”
 - Changes that do not compromise method performance are allowed
 - Changes to improve performance or reduce measurement cost are allowed
- Examples of allowable changes:
 - Automation of dual-amalgamation system
 - Single-trap amalgamation
 - Changes in bubbler design
 - Use of CVAAS if less sensitivity is acceptable



Topics Covered by Guidance (cont.)

◆ Frequently Asked Questions

- General Questions
- Sampling Techniques and Requirements
- Blanks (Reporting and Use)
- Quality Control Requirements
- Miscellaneous



Frequently Asked Questions

◆ General Questions

- When should I use Method 1631 ?
- Is Method 1631 required ?
- What are allowed method modifications ?
- Is Method 1631 for total, total recoverable, or dissolved mercury measurements ?



Frequently Asked Questions (cont.)

◆ Sampling

- Allowed sampling containers
- Composite versus grab sampling
- Sample preservation in the field versus the laboratory
- Sample filtration
- Recommendations of proper sampling



Frequently Asked Questions (cont.)

◆ Blanks

- Definition of Bubbler Blank, Field Blank, Equipment Blank, Reagent Blank, and Method Blank
- Frequency of blanks
- Allowance for blank subtraction
- Reporting requirements



Frequently Asked Questions (cont.)

◆ Quality Control Requirements (Blanks)

Test	Minimum Frequency	Criteria
Bubbler Blanks	1 after each OPR At least 3 per batch	Each bubbler blank ≤ 50 pg Mean of 3 bubbler blanks < 25 pg Standard deviation of 3 < 10 pg
Reagent Blanks	Each new batch of reagents, and in triplicate each month	≤ 25 pg
Field Blanks	10% from same site at same time	< 0.5 ng/L or $\leq 1/5$ Hg in associated sample (whichever is greater)
Bottle Blanks	1 per cleaning batch	< 0.5 ng/L or $\leq 1/5$ Hg in associated sample (whichever is greater)
Sampler Check Blank	1 following each cleaning	< 0.5 ng/L or $\leq 1/5$ Hg in associated sample (whichever is greater)

Frequently Asked Questions (cont.)

◆ Quality Control Requirements (cont.)

Test	Spike Amount	Minimum Frequency	Criteria
Method Detection Limit (MDL)	Follow 40 CFR 136, Appendix B	Initial demonstration	0.2 ng/L or 1/3 the regulatory compliance limit (whichever is greater)
Initial Precision and Recovery (IPR)	5 ng/L	Initial demonstration 4 replicates	Average percent recovery = 79 - 121 Relative standard deviation $\leq 21\%$
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Compliance limit or 1-5x background, (whichever is greater)	10% from a given sampling site or discharge	Percent recovery = 71 – 125 Relative Percent Difference ≤ 24
Ongoing Precision and Recovery (OPR)	5 ng/L	Prior to and after analysis of each analytical batch	Percent recovery = 77 - 123
Quality Control Sample (QCS)	Within calibration range	1 per batch	No specification; follow specification provided by supplier

Frequently Asked Questions (cont.)

◆ Quality Control Requirements

- The type, frequency and criteria of the QC samples presented are the minimum required by Method 1631
- Laboratories may wish to increase the level of QC to further support measurements of mercury in various matrices
 - Increased analysis of reagent blanks
 - Addition of method blank analyses
 - Increased frequency of matrix spikes
 - Additional field blanks and equipment blanks



Other Topics Covered by Guidance

◆ Sources of Information

- Regulatory background
- Supporting data
- Support documents
- Sources for documents

◆ Where to get additional help

◆ Appendix A - Standard Operating Procedures for Sample Collection



Final Rulemaking on Field Blanks (Method 1631, Revision C)

- ◆ Section 12.4.2 - Report results for Hg in samples, reagent blanks, and field blanks separately. In addition, if blank correction is requested or required by a regulatory authority or in a permit, subtract the concentration of Hg in the reagent blank or the field blank from the concentration of Hg in the test sample to obtain the net Hg concentration in the test sample.



Final Rulemaking on Field Blanks (Method 1631, Revision C) (cont.)

- ◆ Section 9.4.3.3 - If sufficient multiple field blanks (a minimum of three) are collected, and the average concentration (of the multiple field blanks) plus two standard deviations is equal to or greater than the regulatory compliance limit or equal to or greater than one-half of the level in the associated sample, results for the associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.



Proposed Rulemaking on Clean Techniques and Quality Control Provisions

◆ Additional requirements to minimize contamination

- Use of a clean room or clean bench
- Minimization of exposure of apparatus to contamination
- Use of only fluoropolymer or borosilicate glass for sample collection
- Analysis of bubbler blank
- Processing samples away from sources of airborne contamination



Proposed Rulemaking on Clean Techniques and Quality Control Provisions (cont.)

- ◆ Additional requirements to minimize contamination (cont.)
 - Analysis of bottle blanks
 - Intake of outside air to the class-100 clean room/area
 - Field filtration and preservation in accordance with Method 1669
 - Bottle storage in clean polyethylene bags until analysis
 - Use of “Clean Hands / Dirty Hands” sample collection techniques



Status of Method 245.7 for Determination of Mercury

- ◆ Method 245.7: *Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry*
 - Does not use dual-trap system
 - EPA currently is evaluating the test method through an interlaboratory validation study
 - Appears suitable for Hg levels as low as 1 - 3 ng/L
 - EPA may propose this method at 40 CFR part 136



For Additional Information

◆ Contact:

- EPA's Analytical Methods Staff
 - Phone: 202-260-7120
- EPA's Sample Control Center
 - Phone: 703-461-2100
 - E-mail: SCC@DynCorp.com
- OST's website
 - www.epa.gov/ost/methods, or
 - www.epa.gov/ost/guide

