

Overview of EPA Method 1631, Revision E

By

Roy W. Byrd

Division of Water Resources

Water Science Section

Metals Group

April 16, 2014

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

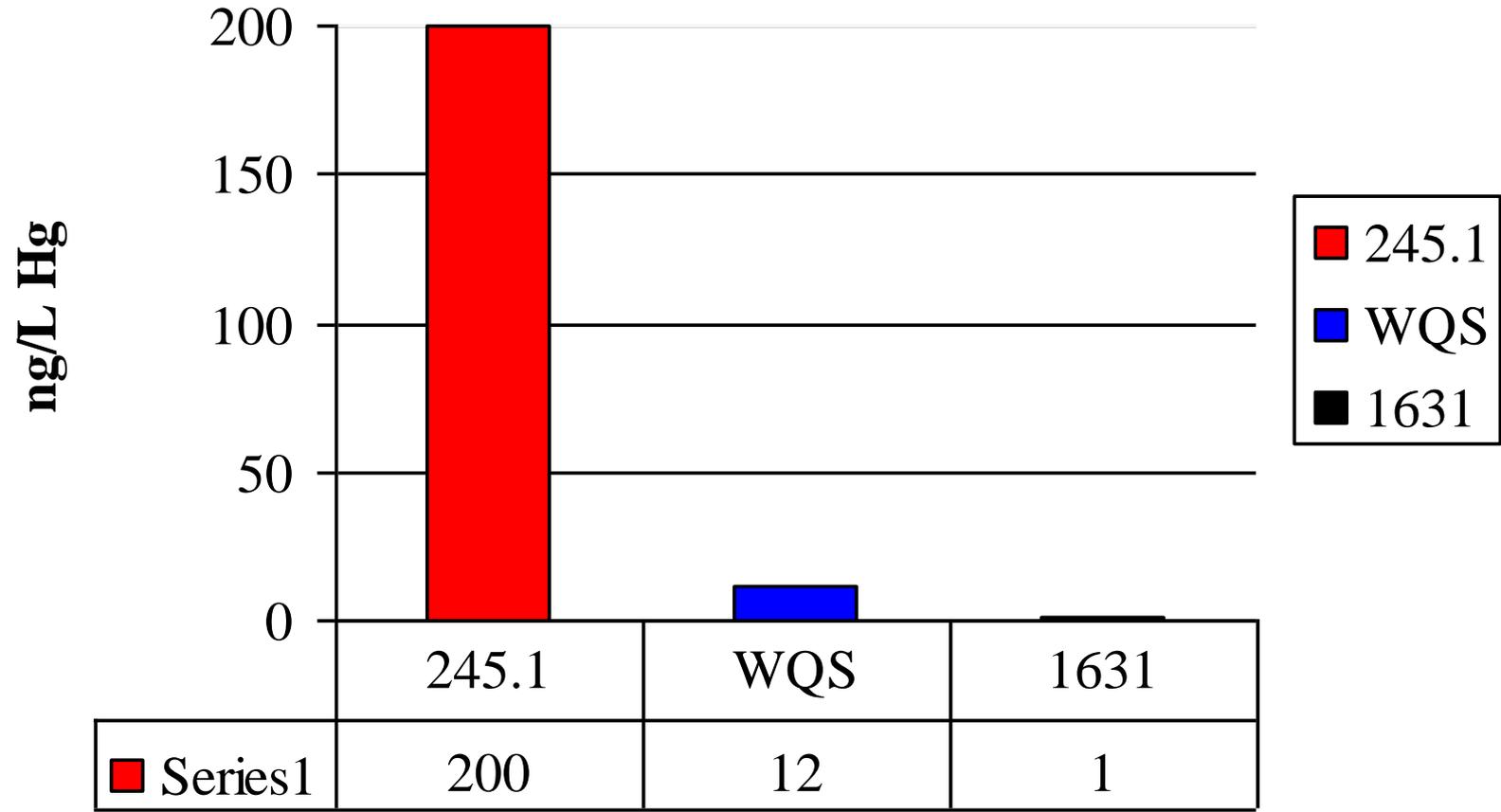
Background (cont.)

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)
- Method 1631, Revision B was promulgated on June 8, 1999 (64 FR 30417)
- Method 1631, Revision C was promulgated on June 18, 2001
- Method 1631, Revision E was promulgated on October 29, 2002

Comparison of Methods With WQS*

*Water Quality Standards



EPA 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

Additional Information

“Method 1631: Guidelines Establishing Test Procedures for the Analysis of Pollutants; Measurement of Mercury in Water” on the WEB at <http://www.epa.gov/ost/methods/1631.html>

Clean Techniques Review

General requirements

- .Clean sampling and storage procedures
- .Clean sample handling procedures in field and lab
- .Use of clean bench or a clean room
- .Comprehensive QA/QC program
- .Analysis of blanks, blanks, and more blanks
- .Level of cleanliness needed may vary, depending on target concentration and sampling location

Why Bother?

Town of Falmouth, Maine conducted a study in 1998*

Historical Methods (Method 245.1) = < 220 ppt

Method 1631 = 62.9 ppt

Method 1631 with Method 1669 = 15.3 ppt

*Courtesy of Judy Schofield of DynCorp, Science and Engineering Group

Blanks in Revision E

- **Bottle Blank** – The bottle blank is used to demonstrate that the bottle is free from contamination prior to use. Reagent water known to be free of mercury at the MDL of this Method is added to a bottle, acidified to pH <2 with BrCl or HCl, and allowed to stand for a minimum of 24 hours. The time that the bottle is allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water is analyzed.
- **Bubbler Blank** – For this Method, the bubbler blank is specific to the bubbler system and is used to determine that the analytical system is free from contamination. After analysis of a standard, blank, or sample, the solution in the bubbler is purged and analyzed. A minimum of three bubbler blanks is required for system calibration..
- **Equipment Blank** – Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility.
- **Field Blank** – Reagent water that has been transported to the sampling site and exposed to the same equipment and operations as a sample at the sampling site. The field blank is used to demonstrate that the sample has not been contaminated by the sampling and sample transport systems.

Blanks in Revision E (continued)

- **Method Blank** - Method blanks are used to determine the concentration of mercury in the analytical system during sample preparation and analysis, and consist of a volume of reagent water that is carried through the entire sample preparation and analysis. Method blanks are prepared by placing reagent water in a sample bottle and analyzing the water using reagents and procedures identical to those used to prepare and analyze the corresponding samples. A minimum of three method blanks is required with each analytical batch.
- **Reagent Blank**-Reagent blanks are used to determine the concentration of mercury in the reagents (BrCl, NH₂OH-HCl, and SnCl₂) that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of reagents is prepared.
- **System Blank**— For this Method, the system blank is specific for the flow-injection system and is used to determine contamination in the analytical system and in the reagents used to prepare the calibration standards. A minimum of three system blanks is required during system calibration.

Quality Control Requirements (Blanks)

Test	Minimum Frequency	Criteria
Bubbler Blanks	3 must be analyzed during calibration and each batch	Mean of 3 bubbler blanks < 25 pg (0.25 ng/L) Standard deviation of 3 < 10 pg (0.10 ng/L) none ≥ 50 pg Section 9.4.1
System Blank (flow injection)	3 must be analyzed during calibration and each batch	Mean of 3 bubbler blanks < 0.50 ng/L Standard deviation of 3 < 0.10 ng/L none ≥ 0.50 ng/l Section 9.4.2
Reagent Blanks	Each new batch of reagents	< 20pg (0.20 ng/L) Section 9.4.3.1
Method blank	3 must be analyzed per batch	< 0.50 ng/L Section 9.4.4.2
Field Blanks	collected from the same site at same time as the sample or samples	< ML or # 1/5 Hg in associated sample (whichever is greater) *** See Section 9.4.5 on using data if field blank is contaminated.
Equipment Blanks	1 following each cleaning	Level specified for field blanks. Section 9.4.5
Bottle Blanks	“At 5% of the bottles from a given lot should be tested,”	Level specified for field blanks. Section 9.4.5

Quality Control Requirements (cont.)

Tests	Requirements	Minimum Frequency	Acceptance 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) Section 9.2.1
Initial Precision and Recovery (IPR)	5 ng/L	Initial demonstration 4 replicates	Average percent recovery = 79 - 121 Relative standard deviation \geq 21% Section 9.2.2
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Compliance limit or 1-5x background or 1-5 x ML, (whichever is greater)	10% from a given sampling site or discharge	Percent recovery limit 71 – 125% Relative Percent Difference \geq 24% Section 9.3
Ongoing Precision and Recovery (OPR)	5 ng/L	Prior to and after analysis of each analytical batch	Percent recovery limit 77 – 123% Section 9.3.4
Quality Control Sample (QCS)	Within calibration range	1 per batch	No specification; follow specification provided by supplier

Rule on Field Blanks

EPA Method 1631, Revision E - September 2002

“12.5.2 Report results for Hg in samples, method blanks and field blanks separately. In addition to reporting results for the samples and blank(s) separately, the concentration of Hg in the method blanks or field blanks associated with the sample may be subtracted from the results for that sample, or must be subtracted if requested or required by a regulatory authority or in a permit.”

Interferences

“4.4.1.... At the time of promulgation of this Method, gold and iodide were known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent.”

Table 3⁽¹⁾ Precision and Recovery for Reagent Water, Fresh Water, Marine Water, and Effluent Water Using Method 1631

Matrix	*Mean Recovery %	*Precision (% RSD)
Reagent Water	98.0	5.6
Fresh Water (Filtered)	90.4	8.3
Marine Water (Filtered)	92.3	4.7
Marine Water (Unfiltered)	88.9	5.0
Secondary Effluent (Filtered)	90.7	3.0
Secondary Effluent (Unfiltered)	92.8	4.5
⁽¹⁾ Table 3, EPA Method 1631 Revision E		