

Satisfying Certification Requirements of U.S. EPA Method 1631

by David L. Pfeil and Denise Stalvey

Many laboratories have been hesitant to get involved with U.S. EPA Method 1631 for the determination of mercury in ambient waters. They envision working in ultrasterile environments and spending a great deal of time and money in the process. Typically, laboratories working with Method 1631 have had similar startup problems that they have overcome with proper planning and without undue expense. This paper details one laboratory's experience (Oxford Laboratory, Wilmington, NC) in its quest for state certification for U.S. EPA Method 1631.

Recent legislation

In 1987, the Clean Water Act (CWA) demanded the implementation of quality-based strategies to ensure that desired water quality standards were achieved and maintained. Mercury is one of the pollutants identified and regulated by the Act. The same year, the U.S. EPA and Environment Canada created the Great Lakes Initiative (GLI), which attacked mercury pollution at its source, calling for the virtual elimination of mercury through incentives and options for cost-effective pollution reduction. In subsequent legislation, the National Toxics Rule established maximum concentrations for mercury and other pollutants.

The analytical problem

The current water quality criteria (WQC) for mercury require lower detection limits than earlier

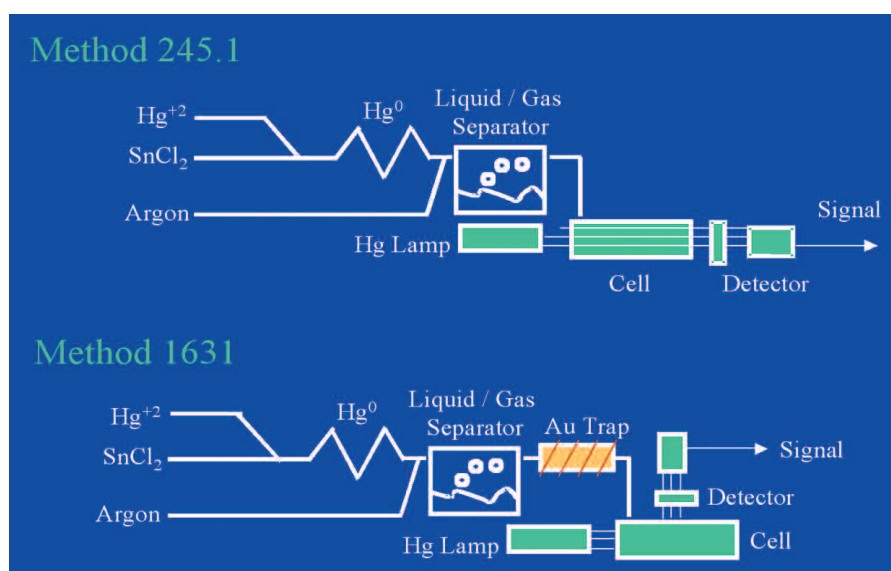


Figure 1 Method schematics.

methodologies (i.e., U.S. EPA Method 245.1) were capable of delivering. The new WQC has concentration objectives for mercury as low as 1.3 ng/L for wildlife; the reporting limit for U.S. EPA Method 245.1 was 200 ng/L.

Methodology

The U.S. EPA promulgated Method 1631 based on work done by Nicholas Bloom and associates at Frontier Geoscience (Seattle, WA). In this method, mercury is released from solution by reaction with stannous chloride and is then preconcentrated prior to quantitation. U.S. EPA Method 1631 has a method detection limit requirement of less than 0.2 ng/L, 1/1000th that of the previous method.

Method 1631 differs from 245.1 in two important aspects. While both methods are cold vapor techniques, only Method 1631 preconcentrates the atomic mercury vapor on a gold trap. Thus, the mercury from a large volume of water can be adsorbed on the gold surface. Heating the gold trap releases the accumulated mercury, which is carried via an argon stream to a spectrometer and appears as a sharp peak of only a few seconds' duration. Method 1631 also differs from 245.1 because it uses atomic fluorescence instead of atomic absorption. In fluorescence, the light source and detector are placed at right angles to each other so that only light that has been absorbed and reemitted by the analyte reaches the detector (see Figure 1). The fluorescence technique is generally considered more sensitive, has better lin-

earity, and has a more stable baseline than atomic absorption. The end result is that, while cold vapor atomic absorption instruments produce detection limits of about 1 ppt, instruments designed for Method 1631 typically produce detection limits on the order of 0.05 ppt.

Getting started

When a laboratory is considering whether or not to provide mercury analysis services employing U.S. EPA Method 1631, it normally begins by dissecting the method and guidance documents available from the U.S. EPA. These documents begin with the following:

- Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, August 2002
- Guidance for Implementation and Use of EPA Method 1631 for the Determination of Low-Level Mercury (40 CFR part 136)
- Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, July 1996
- Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities, Draft 1996.

Laboratory considerations

With most laboratories, the review of the method literature creates some concern regarding how facilities should be modified to reduce contamination. Oxford Laboratory purchased two separate laminar flow enclosures, one for sample preparation and the other for analysis. These enclosures were placed in a newly constructed room with freshly painted (sulfur-doped) walls and floor. The mercury laboratory was placed at a slight distance from the rest of the laboratory. A single, normally closed door with sticky footpad

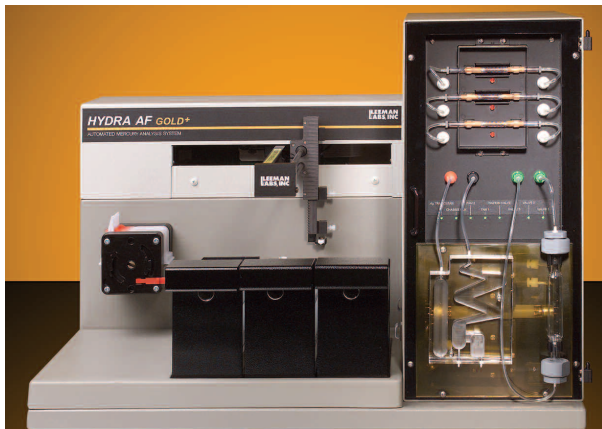


Figure 2 Hydra AF Goldplus.

provided access to the laboratory. A deionized water supply and argon were plumbed into the laboratory.

Instrumental considerations

Next, the laboratory wanted to choose a commercially available analyzer capable of meeting the analytical demands of U.S. EPA Method 1631. It ultimately selected the Hydra AF Goldplus system (Teledyne Leeman Labs, Hudson, NH) (Figure 2). The fully automated, continuous-flow system is compatible with both Methods 1631 and 245.7 (a cold vapor method for the determination of mercury using fluorescence without preconcentration). It prescreens samples using Method 245.7 to prevent contamination of gold traps. The system's operating software provides the calibration factor algorithm required by the U.S. EPA and automatically calculates the acceptance criteria of linearity, system blank, reporting level precision and recovery, continuing with the analysis of samples only when all criteria have been satisfied.

Initial demonstration of laboratory capability

With the laboratory completed and the instrument in place, it was time to start working with the method. Section 9 of U.S. EPA Method 1631 deals with quality control requirements.

Based on the experiences of several laboratories trying to qualify for the method, achieving the system blank, calibration factor precision, and low standard recovery have been the most troublesome areas.

The method specifies that to demonstrate the ability to generate acceptable accuracy and precision, the laboratory must obtain:

- A bubbler blank of ≤ 0.25 ppt for batch systems or a system blank of ≤ 0.5 ppt for flow injection systems (the average signal for these blanks is subtracted from signals for subsequent standards and samples)
- A calibration factor precision of $\leq 15\%$ RSD (the calibration factor is calculated for each standard by dividing its blank subtracted intensity by the standard concentration)
- A recovery of 75–125% at the reporting limit (typically 0.5 ppt)
- Initial precision and recovery (IPR) of 79–121% (typically 5.0 ppt)
- Ongoing precision and recovery (OPR) of 77–123% (typically 5.0 ppt)
- Method detection limit (MDL) of 0.2 ppt
- Matrix spike recovery of 71–125%
- Matrix spike duplicate relative percent difference of $\leq 24\%$ RSD.

To satisfy the initial demonstration of ability requirements for the State of North Carolina, an analytical sequence consisting of the following is required:

- Three system blanks
- At least five nonzero standards
- An IPR standard
- A QCS standard (a standard prepared from a different stock solution than the calibration standards)

- Seven replicates at low concentration (~1 ppt)
- A method blank
- Four replicates of the OPR standard
- A sample
- A sample with Hg spike
- A duplicate of the sample with Hg spike
- A method blank.

At Oxford Laboratory, the system blank initially ran about 0.55 ppt and was out of specification. The question to be resolved was whether the reagents, environment, technique, or instrumentation caused the problem. Based on previous experience, the most common cause of system blank failures is reagent contamination; thus the investigation began there.

Laboratory reagents

The following reagents were used in the sample preparation and analysis.

- H₂O: Deionized water system provided by Eagle Water (Durham, NC) with a D8911 Ultra-pure filter (Barnstead International, Dubuque, IA) added
- HCl: Subboiled, distilled HCl from O2SI (Charleston, SC), part number 060100-03-1L used for 1% HCl and BrCl solution
- HCl: Omnitrace grade (EM Science, Gibbstown, NJ) used for 2% rinse
- SnCl₂: J. T. Baker (Phillipsburg, NJ)
- Hydroxylamine hydrochloride: J. T. Baker
- BrCl solution: O2SI.

Of the above solutions, the HCl and the hydroxylamine hydrochloride can be purified with the addition of 1 mL/L of stannous chloride solution and bubbling. (The common technical term for the bubbling is sparging.) The stannous chloride can be purified simply by sparging. Each stock solution was bubbled with argon at about 5 LPM for a minimum of 30 min through a Teflon™ (DuPont,

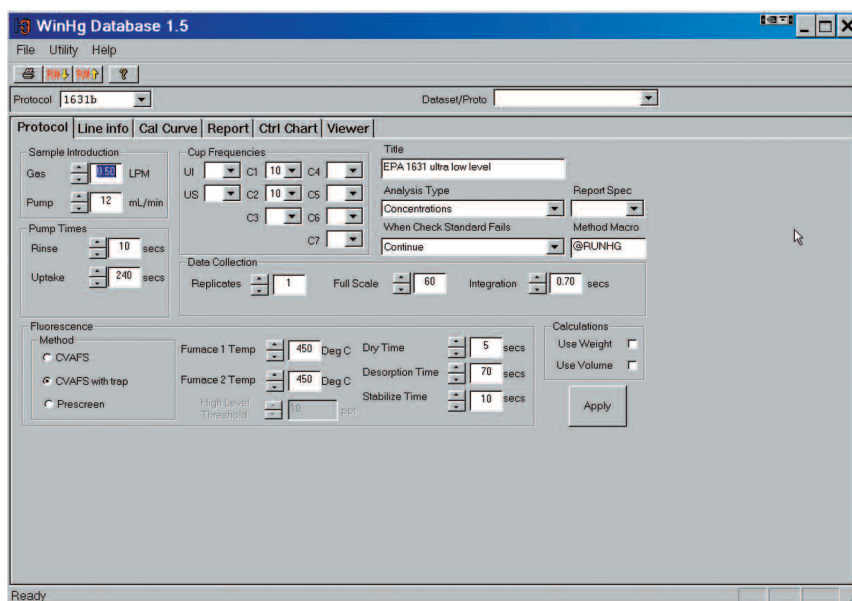


Figure 3 Instrument conditions for optimum performance.

Wilmington, DE) tube extension. This extension is a simple piece of Teflon tubing attached to the argon supply line; it alone comes in contact with the solutions to be cleaned.

With a continuous-flow system, new reagents are constantly pumped into the gas/liquid separator, and reagent contamination cannot be separated from the system blank signal. It is therefore critical in continuous-flow systems to establish a baseline with the purest reagents. The approach used was to begin with only prepurified (bubbled) reagents. The continuous-flow systems employ three reagent streams: the sample, the reductant, and the rinse stream. Baseline readings under 0.3 ppt were achieved by prepurifying the stannous chloride and rinse solution (2% HCl). The prepurified rinse solution was used for the sample as well. After an acceptable baseline reading using only prepurified reagents was demonstrated, the contamination level was determined for the laboratory's various deionized water sources and then the bromine monochloride.

Water supply

Surprisingly, the deionized water that

was plumbed into the laboratory contained about 1.5 ng/L of mercury, more than twice that of the local tap water. The deionized water sampled directly after a D8911 point-of-use purifier reduced the mercury content to less than 0.2 ng/L.

Bromine monochloride solution

Five milliliters of the bromine monochloride solution is normally added to 1.0 L of sample or standard. The first time the BrCl solution was prepared and added to the blank, the apparent mercury concentration exceeded 1.0 ng/L, presumably because of contaminated glassware. There is no convenient way to purify this solution once it is contaminated and thus it was discarded. The BrCl solution was remade immediately and it was determined that it contributed <0.1 ng/L mercury to the blank. Because this concentration is less than the method detection limit, the mercury contribution for this reagent was calculated by analyzing blanks with one, two, and four times the normal BrCl added, and a slope was estimated.

Oxford Laboratory stabilized calibration standards with 1% HCl. An ex-

Table 1 Results of certification sequence

| Sequence | State certification | | Conc. (ppt) | Initial demonstration of capability |
|----------|---------------------------|-----------|-------------|-------------------------------------|
| | Sequence content | Intensity | | |
| 1 | Blank | 13,438 | | |
| 2 | Blank | 17,029 | | |
| 3 | Blank | 14,439 | | 0.47 ppt; pass |
| 4 | 1 | 50,822 | | 113% Rec* pass |
| 5 | 5 | 172,712 | | |
| 6 | 10 | 331,330 | | |
| 7 | 15 | 425,569 | | |
| 8 | 30 | 973,459 | | RSDCF** 9%; pass |
| 9 | Blank | | 0.254 | <0.5 ppt; pass |
| 10 | IPR | | 4.82 | 96.4% Rec.; pass |
| 11 | QCS (10) | | 8.51 | 85.1% |
| 12 | 1 | | 1.17 | |
| 13 | 1 | | 1.15 | |
| 14 | 1 | | 1.05 | |
| 15 | 1 | | 1.02 | |
| 16 | 1 | | 0.977 | |
| 17 | 1 | | 1.03 | |
| 18 | 1 | | 1.06 | MDL 0.2 ppt; pass |
| 19 | Blank | | -0.01 | <0.5 ppt; pass |
| 20 | OPR | | 5.35 | Rec. 107% pass |
| 21 | OPR | | 5.25 | Rec. 105% pass |
| 22 | OPR | | 5.43 | Rec. 109% pass |
| 23 | OPR | | 5.39 | Rec. 108% pass |
| 24 | Sample (1.0 ng/L) | | 1.11 | |
| 25 | Sample spike (+12.5) | | 13.7 | Rec. 100.7% pass |
| 26 | Sample spike dup. (+12.5) | | 14.0 | Rec. 103.1% pass RPD 2.17% pass |
| 27 | Blank | | 0.17 | <0.5 ppt; pass |
| 28 | OPR | | 4.90 | Rec. 98% pass |

*rec = recovery.

**RSDCF = relative standard deviation of the calculated calibration factors.

amination of 1% HCl shipped in fluorinated linear polyethylene (FLPE) (Nalge Nunc International, Rochester, NY) and Teflon containers revealed 0.55 ng/L mercury for the FLPE containers and about 0.1 ng/L for the Teflon containers. U.S. EPA

Method 1631 specifies that containers be borosilicate glass or Teflon only. (This solution is available from Teledyne Leeman Labs in precleaned glass containers.) The time required to qualify the laboratory reagents was about 5 hr. Oxford Laboratory

has continued to improve its reagent cleanup procedures and today routinely achieves system blanks under 0.25 ppt.

Optimized instrument conditions

Obtaining the best sensitivity for a continuous-flow system requires the use of as much volume (sample and standard) as possible. The Hydra sample cup capacity is about 45 mL (for the container used with Method 1631), and an uptake time of 240 sec with a pump speed of 12 mL/min aspirated most of the cup contents. Figure 3 shows the instrument conditions used for optimum performance.

Meeting state certification requirements

After reagent qualification and instrument optimization, the state-required certification sequence was started. The curve was acceptable, with calibration factor precision of 9%, average system blank of 0.473 ng/L, and recovery of 113% for the low standard (1.0 ng/L).

Method blanks within the run

averaged 0.11 ng/L. Seven 1.0-ng/L samples yielded a method detection limit of 0.2 ng/L. Initial and ongoing precision and recovery checks (IPR and OPR) at 5.0 ng/L Hg run throughout the sequence resulted in a standard deviation of 0.077 ng/L and a recovery of 107%.

For the matrix spike and spike duplicate test, two aliquots of the 1.0-ng/L standard were spiked with 12.5 ng/L Hg each and run after the sample (1.0-ng/L standard). These solutions produced an average recovery of 102% and a relative percent difference (RPD) of 2.17%. Table 1 shows the details of the sequence run.

Method 1631 Certification in North Carolina

The management at Oxford Laboratory reviewed the sequence results and submitted them to the state, which certified the laboratory the same day. At present a minimum of six laboratories are certified for U.S. Method 1631 in North Carolina, and five of these use the Hydra AF system.

Conclusion

Based on the certification experience at Oxford and similar laboratories already involved with Method 1631, a few practical suggestions can be offered. First, it is important to clean all reagents that can be cleaned and then test each reagent before use. Because contamination can slip in from glassware, glassware used for Method 1631 should be kept separate. Only glass or Teflon containers should be used. Glass containers are inexpensive and will keep reagents sufficiently clean for extended periods.

Finally, it is important not to give up. Although it can be frustrating to search for the sources of contamination, once it is done, it is not likely the problem will recur.

Mr. Pfeil is ICP & Hg Product Manager, Teledyne Leeman Labs, Inc., 6 Wentworth Dr., Hudson, NH 03051, U.S.A.; tel.: 603-886-8400; fax: 603-886-9141; e-mail: dpfeil@leemanlabs.com. Ms. Stalvey is Metals Manager, Oxford Laboratory, Wilmington, NC, U.S.A.