

# When U.S. EPA Method 245.7 (Determination of Hg by Atomic Fluorescence) Is Approved, Will You Be Ready?

by David Pfeil

Before the new millennium, the U.S. EPA proposed two new fluorescence-based methods for the determination of mercury in ambient waters: Method 1631<sup>1</sup> and Method 245.7.<sup>2</sup> These methods were developed to achieve the significantly lower detection levels required by the Clean Water Act and the National Toxics Rule. Some laboratories may find Method 245.7 to be an attractive alternative to Method 1631 because it has a shorter cycle time for analysis, less stringent contamination control requirements, and can provide a wider dynamic range. The obvious downside is that it does not provide for the ultralow measurement levels achievable with Method 1631. *Table 1* provides a brief comparison of some aspects of the two methods.

Now that it appears Method 245.7 will soon be approved by the U.S. EPA, analysts may ask themselves, "Is Method 245.7 right for me?" To help answer that question, this paper describes Method 245.7, its requirements, and the results obtained with a commercially available cold vapor atomic fluorescence (CVAF) mercury analyzer.

## Sample handling

Method 245.7 employs much of the same sample handling protocol as Method 1631. For example, it employs the "clean hands, dirty hands" approach to sample collection detailed in Method 1669.<sup>3</sup> It requires that sample containers be made of borosilicate glass or Teflon™ (DuPont, Wilmington, DE). After collection, samples must be preserved with 5 mL/L of 12 N HCl. Bromine monochloride (BrCl) is then used to oxidize the mercury in the samples to the mercuric (Hg<sup>+2</sup>) species. The oxidation step requires a minimum of 30 min and typically does not require sample heating. By comparison, in Method 1631, the oxidation step requires a minimum of 12 hr. Finally, each sample receives a small amount of hydroxylamine hydrochloride to react with the excess bromine, changing the solution from yellow to colorless prior to analysis.

**Table 1 Comparison of Methods 1631 and 245.7**

	Method 1631	Method 245.7
Preservative	BrCl or HCl (5 mL/L)	HCl (5 mL/L)
Oxidant	BrCl	BrCl
Oxidation time	>12 hr	>30 min
Prereduction with NH <sub>2</sub> OH	Yes	Yes
Gold amalgamation	Yes	No
Analysis cycle time	10 min	3 min
Required MDL	0.2	1.8
Required ML	0.5	5.0
IPR/OPR concentration	5 ppt	10 ppt

## Analysis

During analysis, sample and stannous chloride are mixed together to reduce mercury to Hg<sup>0</sup> while argon is bubbled through the sample to carry the mercury into the gas phase. In Method 245.7, the argon carrier gas sweeps the mercury vapor directly to a fluorescence cell for quantitation.

## Instrumentation

The Hydra AF (Teledyne Leeman Labs, Hudson, NH) was used for the remainder of this work. The Hydra AF is a fully automated CVAF specifically designed to meet the hardware and QC requirements of Method 245.7. The system provides a built-in autosampler, very wide dynamic range, and sophisticated high-concentration protection system. The instrument and its schematic diagram are shown in *Figures 1* and *2*, respectively.

## Instrument conditions and calibration

Section 10.1.1.2 of Method 245.7 dictates the use of calibration standards of 5, 10, 25, 50, and 100 ng/L (ppt) as well as a calibration blank. For operation in the low ng/L concentration range, the Hydra AF was run using an argon flow rate of 0.3 L/min, peristaltic pump speed of 10 mL/min, rinse time of 60 sec, uptake time of 20 sec, and integration time of 45 sec. Although Method 245.7 is a

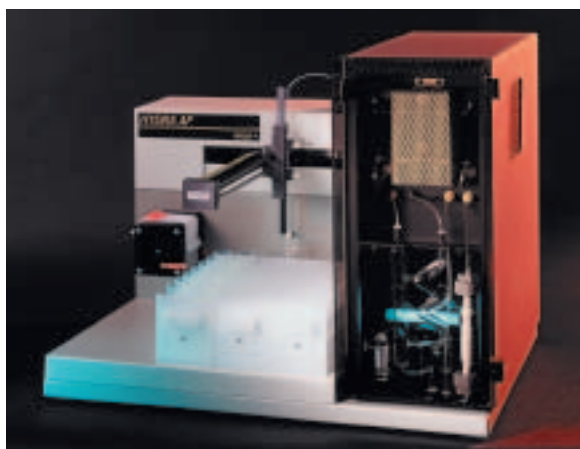


Figure 1 Hydra AF mercury analyzer.

performance-based method and therefore allows some flexibility in hardware configurations, all QC requirements of the method must be met. One of those requirements involves the use of a weighted linear calibration algorithm called the calibration factor (CF), which is the slope of the line from the blank to each nonzero standard (i.e., change in signal divided by change in concentration). During analysis, the sample signal divided by the average calibration factor yields the concentration for the sample. This algorithm forces the calibration through zero (concentration) and fits the low end of the calibration curve particularly well, much more so than can be attained using a standard linear fit. Figure 3 shows a calibration curve generated with the Hydra AF. There are several QC requirements that the calibration must satisfy before it can be used for analysis. First, the relative standard deviation (RSD) of the CFs must be less than 15%, demonstrating that the curve is sufficiently linear. Next, the recovery of the lowest standard (5 ng/L) must be in the range of 75–125%. Finally, at least two calibration blanks must return apparent concentrations less than the minimum level (ML) of 5 ng/L. Figure 3 shows the calculated values for each of the QC requirements: %RSD CF, %Recovery, and systems blank (labeled “Avg. B.B.” in the figure).

### Quality control and initial demonstration of performance (Section 9)

Section 9 of Method 245.7 outlines quality control and includes an initial demonstration of performance specification, which must be met before reporting analytical results using the method. These criteria are addressed in detail in the next several sections of this paper.

#### Detection limit

Method 245.7 requires a detection limit that is less than or equal to the method detection limit (MDL) or less than one-third the regulatory compliance limit, whichever is greater. The MDL requirement is <1.8 ng/L. Table 2 shows seven replicates of a 1.0-ng/L standard that were used to determine the MDL for the system. The standard deviation of the replicates is 0.22 ng/L, yield-

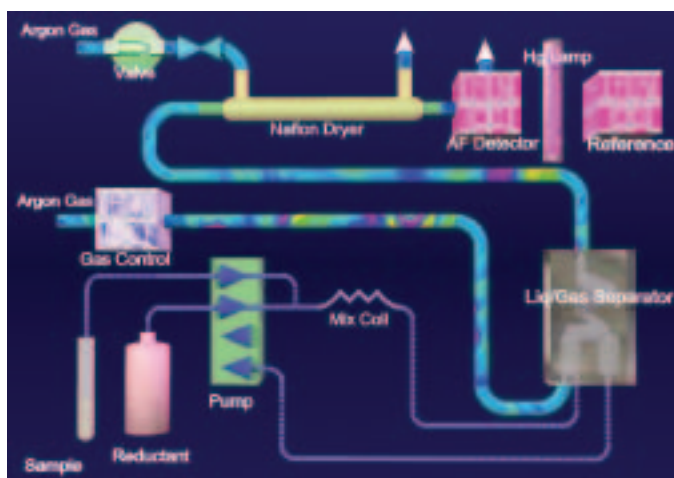


Figure 2 Flow diagram for Hydra AF.

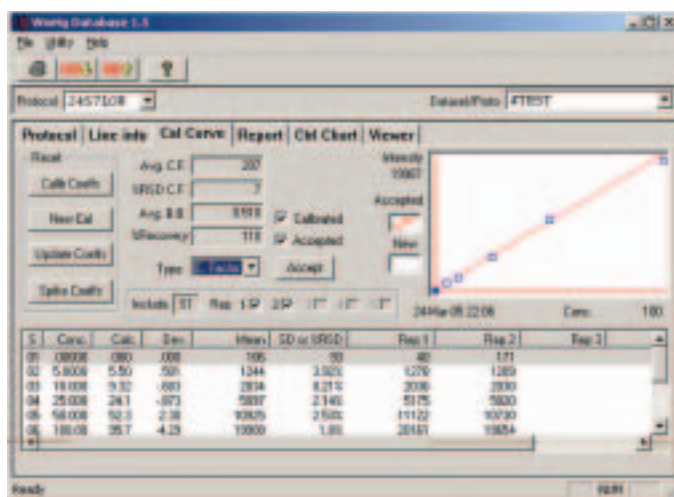


Figure 3 Calibration curve for Method 245.7 with quality requirements satisfied (Section 10.1.1).

ing a 3σ detection limit of 0.66 ng/L.

#### Initial demonstration of freedom from contamination

Immediately after calibration, a blank solution was analyzed; it returned a mercury concentration of 0.458 ng/L, an order of magnitude below the required ML level of 5.0 ng/L.

**Table 2 Method detection limit**

Concentration (ng/L)
0.883
1.48
0.936
1.12
1.03
1.4
1.14
RSD = 0.22 ng/L
MDL = 0.66 ng/L

#### Initial precision and recovery (IPR)

Section 9.1.1.3 of Method 245.7 requires four replicates of the IPR solution, a standard containing 10 ng/L of mercury.

For these four replicates, the average percent recovery must be within 78–108%, and standard deviation of the percent recoveries must be less than 16%. The results of this study are shown in *Table 3*.

### Blanks

Method 245.7, like Method 1631, requires the analysis of several types of blanks to demonstrate freedom from

contamination. These include reagent blanks, field blanks, equipment blanks, and bottle blanks. Reagent blanks are required in triplicate each time new reagents are prepared and once for each set of 20 samples. Six replicates of reagent blank returned the concentrations shown in *Table 4*. The method requires the reagent blank mercury concentration to be less than the ML of 5.0 ng/L.

Because no field samples were collected, no field or equipment blanks were analyzed in this study. Bottles used for this work were pretested and certified clean (bottles were supplied by ESS [Environmental Sampling Supply, Oakland, CA]).

### Ongoing precision and recovery (OPR)

Method 245.7 requires the analysis of an OPR solution (10 ng/L standard) before each batch of samples and at the end of each batch or 12-hr shift. A batch can contain up to 20 samples. *Figure 4* shows a graph of OPR analyses repeated approx. every 30 min for a 10-hr period along with acceptance limits for the OPR.

### Matrix spike (MS) and matrix spike duplicate (MSD)

The method requires a sample spike and a spike duplicate for every 10 samples to verify method performance on a given matrix. Duplicates of a sample containing 27.1 ng/L Hg were spiked with 15 ng/L Hg. The results obtained were 43.7 and 42.6 ng/L, corresponding to 110 and 103% recovery, respectively. The relative percent difference (RPD) between the two spike results was 2.55%. Accept-

	Concentration (ng/L)	Recovery (%)
1	9.58	95.8
2	9.38	93.8
3	9.22	92.2
4	9.42	94.2
Avg.	9.40	94.0
SD	0.15	1.48

Reagent blank Hg conc. (ng/L)
0.231
0.018
0.070
0.472
0.157
0.238

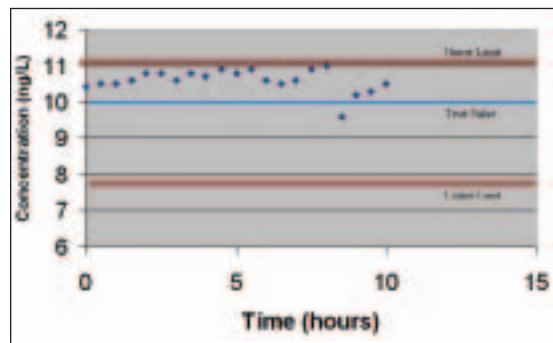


Figure 4 Ongoing precision and recovery.

Sample	Diluted conc. (ng/L)	Corrected conc. (mg/L)	True conc. (mg/L)	Recovery (%)
1641d	80.5	1.69	1.59	106.8
ERA	58.1	4.06	4.0	101.6

able spike recoveries fall between 63 and 111%, and acceptable %RPDs are 18% or less.

## Certified Reference Materials (CRMs)

Two reference materials demonstrated the accuracy of the method: 1641d, a certified water sample from NIST, and a methylmercury sample (lot no. 66061) obtained from **Environmental Resource Associates (ERA, Arvada, CO)**. Both materials had mercury concentrations in the mg/L range and required significant dilution. *Table 5* shows excellent correlation between the measured and true values.

## Analysis at elevated concentrations

One of the concerns with Method 245.7 and Method 1631 is the analysis of samples that have elevated concentrations of mercury. As with the CRMs mentioned earlier in this report, such samples may require significant dilution; however, the Hydra AF has computer-controlled peristaltic pump speed and gas flow; thus, calibration for higher concentrations is possible. This is demonstrated in *Figure 5*, in which the Hydra AF is used to establish a calibration from blank through concentrations normally used in Method 245.1 (Hg in ppb by cold vapor AA). The curve demonstrates excellent precision (typically 1% RSD or better) and linearity well into the ppb range. As with the low-level calibration offered earlier, the algorithm employed was U.S. EPA's CF. Note that even at these elevated concentrations, the %RSD of the CFs is 1% and the recovery for the low standard was 100%. It is important to note that, because of carryover, samples with mercury concentrations well into the ppb range should not be analyzed at the same time as samples in the low ppt range.

## Conclusion

Once approved, Method 245.7 should enable the analyst to determine mercury from the low levels mandated by the

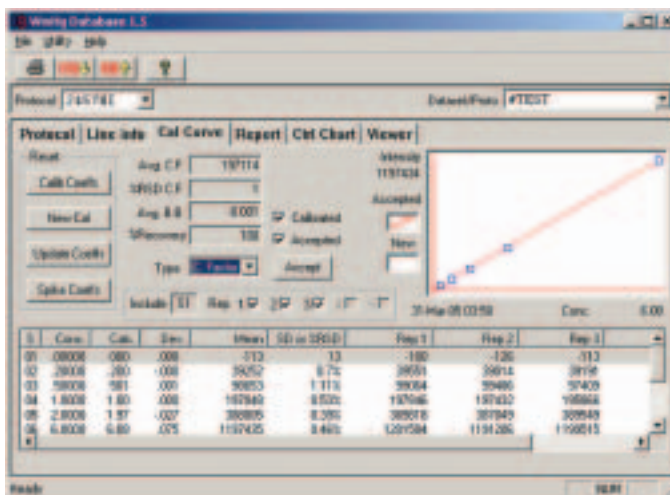


Figure 5 Calibration at Method 245.1 concentrations.

National Toxics Rule into the range for samples from contaminated sites, all with the same instrument and sample handling procedure. The Hydra AF has proven itself to be a capable instrument through which to implement Method 245.7.

For the analyst interested in performing both Methods 245.7 and 1631, the Hydra AF gold plus meets all of the hardware and QC requirements of both methods. The instrument is supplied with two fluorescence detectors and an automated valve for method selection. Earlier publications have described this spectrometer's performance when employing Method 1631.<sup>4,5</sup>

## References

1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Aug 2002.
2. Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry (draft), Dec 2003.
3. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, July 1996. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
4. Pfeil DL, Bruce ML. Automated determination of mercury by cold vapor atomic fluorescence with gold amalgamation. *Am Lab* 2001; 33(18):26-33.
5. Bruce M, O'Meara P, Irwin S, Smith J, Strait R. Mercury Falling: New requirements for low-level mercury monitoring necessitate changes in sample collection and analysis procedures and protocol. *Wat Env Tech*, Nov 2001.

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