Approval of U.S. EPA Method 245.7 for Mercury: A Simple, Cost-Effective Method for Hg at National Water Quality Criteria

by David L. Pfeil

As part of the Methods Update Rule published March 12, 2007, in the *Federal Register*, U.S. EPA Method 245.7 was approved for the determination of mercury in wastewater. Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry provides better sensitivity and precision while requiring less sample preparation than the older cold vapor atomic absorption methods, such as 245.1 and 7470, etc. Laboratories that measure mercury in wastewater will find that Method 245.7 enables them to measure mercury to lower levels with less time and effort than previously.

Background

Method 245.7 was developed to satisfy the significantly lower detection limits required by recent amendments to the Clean Water Act (CWA). The method has a reporting limit of 5.0 ppt, satisfying the analytical requirements for most mercury water quality criteria. To put this in perspective, 12 ppt is the lowest water quality criterion for mercury outside the Great Lakes states. By comparison, Method 245.1 has a reporting limit of 0.2 ppb. With its lower reporting limits, Method 245.7 requires closer attention to controlling sources of contamination and therefore employs the “Clean Hands/ Dirty Hands” technique detailed in U.S. EPA Method 1669 for sample collection.

Simplified sample preparation

Samples should be filtered if necessary, stabilized with 5 mL/L of 12N HCl, and stored in Teflon™ (**DuPont**, Wilmington, DE) or borosilicate glass bottles. Prior to analysis, all samples and standards are treated with a bromide/bromate solution and allowed to stand for a minimum of 30 min to oxidize mercury to Hg^{+2}. Following the digestion step, all solutions should appear slightly yellow until reacted with hydroxylamine hydrochloride immediately before analysis.

This is clearly a much simpler and less time-consuming digestion than is used with the cold vapor atomic absorption spectrometry (CVAAS) methods that typically require digestion using HNO_3, H_2SO_4, and $KMnO_4$ followed by prereduction with hydroxylamine hydrochloride. Another simplification of Method 245.7 is that no sample heating step is specified. This eliminates both the time associated with those steps as well as the hardware necessary for water baths and/or digestion blocks. (Samples high in organic material may require a higher concentration of bromide/bromate solution, longer digestion periods, or mild heating to complete oxidation.)

Figure 1 *Hydra AF system.*

Analysis

As its title implies, Method 245.7 is for atomic fluorescence-based instruments. One such system, the Hydra AF (**Teledyne Leeman Labs**, Hudson, NH), is shown in *Figure 1*.

The Hydra AF was designed specifically to automate Method 245.7 analysis. As can be seen in the schematic diagram shown in *Figure 2*, a peristaltic pump mixes each sample or standard with stannous chloride solution (2% $SnCl_2$ in 10% HCl is recommended) to produce free mercury. Argon bubbles through the solution in a gas/liquid separator, transporting the free mercury to a high-sensitivity fluorescence cell for quantification.

The instrumentation is calibrated with solutions of known concentration using the required “calibration factor” algorithm (*Figure 3*). Method 245.7 requires an MDL of 1.8 ppt or less; the Hydra AF detection limits are typically better than 0.2 ppt. With an automated system such as this, only 2–3 min are required to run a sample.

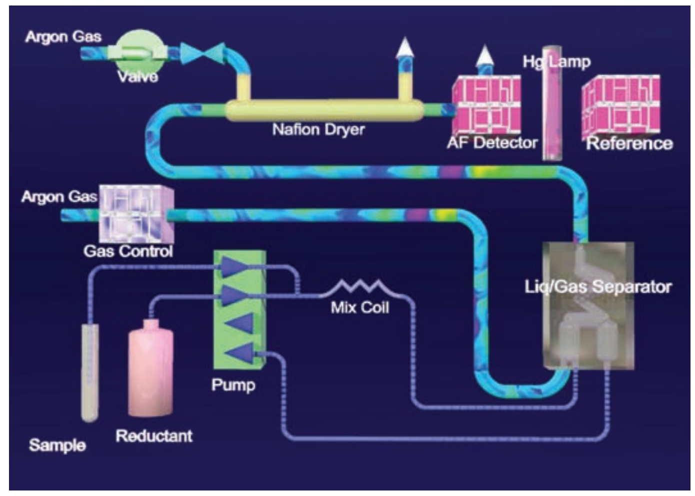

Figure 2 *Hydra AF schematic diagram.*

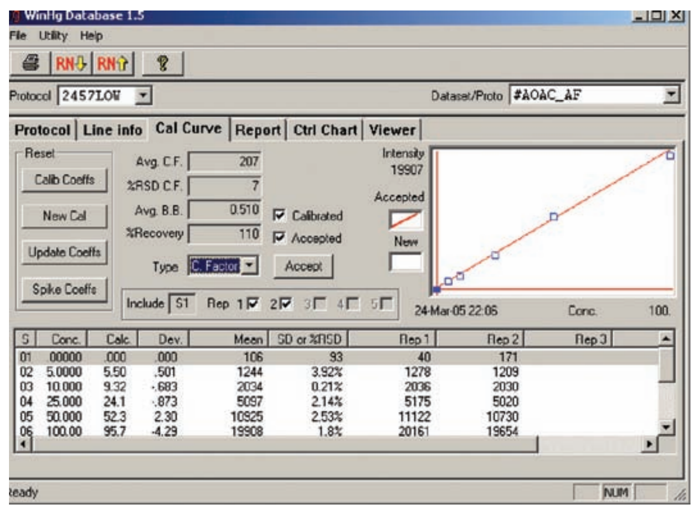

Figure 3 *Calibration curve for Method 245.7 with quality requirements satisfied (Section 10.1).*

Performance requirements

Method 245.7 is a “performance-based” method with required quality control checks, including significant attention to contamination control. Quality control starts with the calibration curve. Linearity, freedom from contamination, and low concentration accuracy must be demonstrated before analysis may proceed. (The %RSD of the calibration factors compares the slope of the curve at each standard. The slopes must be within 15%. The average bubbler blank [BB] is a measure of the method blank and must be below 5.0 ppt. Also, the %recovery is the accuracy of the low standard and must be 75–125% of the true value.) Throughout analysis, the continued validity of the calibration must be confirmed by method blank (≤5.0 ppt) and Ongoing Precision & Recovery Check (OPR @ 10 ppt). It is worth noting that although the high standard for Method 245.7 is one-half of the Method 245.1 report limit standard, one of the inherent strengths of atomic fluorescence is its linearity. Typically, the Hydra AF can be used for measurements up to 250 ppb. A variety of blanks are used to demonstrate that contamination is under control (typically less than 5.0 ppt). Because Method 245.7 is performance based and working concentrations are lower than many laboratories have experienced in the past, the company offers free technical support for method development to its customers.

Conclusion

Now that Method 245.7 has been approved for CWA monitoring by the U.S. EPA, individual states must consider providing this option to laboratories. Its sensitivity achieves the National Water Quality Criteria with less sample preparation than older cold vapor atomic absorption methods. Also, with Method 245.7, the time required for sample analysis is the same as older CVAAS methods. The end result is that Method 245.7 will allow laboratories to monitor mercury at the National Water Quality Criteria levels without any increase in cost or loss of productivity.

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