Whether analyzing water in the lab or natural gas on-line, ppt sensitivity is key.

Given the regulatory importance of Hg in environmental chains and industrial processes (see box, “Mercury, Health, and Industry”), it is essential to provide accurate, reliable determinations for this toxic metal. Although there is considerable scientific interest in speciation of Hg, current regulatory requirements focus only on measuring total concentration of the element—still a no easy task since a 10-fold change in concentration can have a significant impact on the environment.

Hg is often present at low levels in complex environmental samples. The U.S. EPA has advanced water-quality criteria (WQC) for the protection of aquatic and marine organisms—12 parts per trillion (ppt) for freshwater ecosystems and 25 ppt for saltwater (1). Investigations to determine Hg in natural waters have established that total dissolved Hg (i.e., inorganic and organic species) concentrations are typically even lower than these WQC. For example, in ocean surface waters, the concentration can be lower than the method detection limit (MDL) of 0.05 ppt generally obtained in ultratrace analysis, and it can reach 2 ppt in the intermediate water layers of the ocean (2–4).

In freshwater systems, however, the concentration range can approach or surpass the WQC. For example, researchers found 0.5–100 ppt total dissolved Hg in contaminated California lakes (3), 0.6–1.1 ppt total dissolved Hg near the delta of the Lena River in Siberia where it flows into the Arctic Ocean far from human activities (5), and 0.5–6.4 ppt on the heavily industrialized Seine River in France (6).

Despite these major advances in knowledge about the range of concentrations in natural waters, the behavior of Hg in the environment is still poorly understood.

Traditional Methods

Hg is often present in complex matrices at low concentrations—the Hg levels of interest in current regulations are in the ppt range and lower, but conventional techniques such as atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) or mass spec-trometry (ICP-MS) cannot achieve these levels of sensitivity by direct measurement. Typically, these techniques are suitable for measurements in the parts per billion (ppb) range. Also, the most common sample-transfer mechanism is nebulization, which optimally transfers only 2% of the sample to the instrument; the remainder is waste. Matrix effects can also significantly reduce sensitivity and reliability.

U.S. EPA Method 245.1 (www.epa.gov/region9/lab/sops/sop515.html) uses an AAS detection approach to measure the Hg in water, so the levels of detection are higher and the response is nonlinear. The sample is digested with permanganate–persulfate solution. Digestion oxidizes all forms of Hg to Hg(II), which is then reduced with SnCl₂ to Hg(0). The elemental Hg is sparged from the sample and detected by atomic absorption.

Method 7474, similar to Method 245.1, was developed to measure Hg in sediment and tissue samples by AAS (www.epa.gov/epaoswer/hazwaste/test/pdfs/7474.pdf). In this method, a representative portion of sample is transferred to a closed fluorocarbon container in a microwave unit, where it is digested with nitric and hydrochloric acids. Digesting the sample under pressure facilitates the dissolution of organic compounds containing mercury. An aliquot of digested sample is then diluted and subjected to cold digestion with an acid–bromate–bromide mixture and analyzed in a similar fashion to that used for EPA 245.7. Method 245.1 offers Hg detection sensitivity in the sub-ppb range, while that of Method 7474 is from about 1 ppb to several parts per million (ppm). Analysis of the entire range cannot be accomplished at once, but different portions of the range can be analyzed, depending on the instrument gain settings.

A Time for Change

But as the regulatory requirements for Hg determination became more stringent, AAS methods became difficult to use and alternatives were needed. One aspect of the problem was solved with the development of vapor-generation (VG) techniques that effectively introduce 100% of samples into the instruments. In simple terms, the Hg in the samples is converted to the correct valency state and then reacted with SnCl₂ to generate Hg(0), which is separated from the liquid reagents in a gas–liquid separator and transferred to a suitable detector (Figure 1). The VG techniques also offer chemical pretreatment...
that yields 500-fold improvements in sensitivity. If VG is combined with very sensitive atomic fluorescence spectrometry (AFS), measurements of the total concentration of Hg can be made at levels that meet regulatory requirements.

As a result, one might imagine that it would be easy to achieve reliable analysis of Hg in simple matrices such as water. But even with these improvements, interlaboratory trials show wide variations in measurements—primarily through lack of attention to detail. The problem is that the measurement is just one simple step in the analytical process. Hg appears to have a mind of its own, and great care is required to ensure that the correct representative sample is taken, sample is transported to the measurement site and retained in its original form before analysis, and no interferences are in the sample matrix.

AFS-Based Methods

In the United States before 1998, all EPA methods for Hg were written around the use of AAS detection, often including an amalgamation step. European Committee for Standardization (CEN) methods also used similar techniques. However, the U.S. and Europe trod separate paths in developing standards, despite considerable coordination efforts by experts in both regions.

U.S. EPA Method 1631, Revision E (www.epa.gov/waterscience/methods/1631e.pdf), is used to determine Hg levels in samples ranging from seawater to sewage effluent by oxidation, purge and trap, and cold-vapor (CV) AFS. This method is used in the EPA’s data-gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation, and Liability Act, and the Safe Drinking Water Act. Method 1631 is “performance based”, so a laboratory can modify the method, provided all of the criteria are met.

A sample is collected directly into a clean, pretested, fluoropolymer bottle using sample-handling techniques designed for collection of Hg at trace levels. For dissolved Hg, the sample is filtered through a 0.45-µm capsule filter. The sample is preserved by adding either pretested HCl or BrCl solution, and before analysis, BrCl solution is added to a 100-mL sample aliquot to oxidize all Hg compounds to Hg(II). After oxidation, the sample is reduced with SnCl₂ to convert Hg(II) to volatile Hg(0). The Hg(0) is separated from solution by purging with nitrogen onto a gold-coated sand trap.

Method 1631 can determine Hg in the range of 0.5–100 ppt and may be extended to more sensitive levels by selecting a smaller sample size. The MDL and the minimum level of quantitation (ML) depend on the level of interferences rather than on any instrument limitations. The MDL for Hg is 0.2 ppt and the ML is 0.5 ppt when no interferences are present, but an MDL as low as 0.05 ppt can be achieved for low-Hg samples by using a larger sample volume, a lower BrCl level (0.2%), and extra care in sample handling.

Method 245.7 is similar to Method 1631 in that it determines Hg in water using CVAFS, but Method 245.7 uses liquid–gas separation and a dry tube for analyte isolation rather than a purge-and-gold trap (www.lib.utexas.edu/govdocs/EPA/245_7.pdf).

Trace-level measurement of Hg by this method is possible using CVAFS, a brominating digestion to minimize interference, and ultrapure argon as the carrier gas. Method 245.7 has been validated with MDLs in the range 0.3–1.8 ppt and revised to conform to EPA guidelines concerning format and quality-control procedures, but its application still awaits final approval.

In Europe, the CEN AFS method, EN 13506 (http://bonsline.techindex.co.uk), was formally introduced in 2002. Currently, there is a proposal to bring EN 13506 under the umbrella of the International Organization for Standardization (ISO), which should broaden its acceptance.

There is also argument about the usefulness of performance-based standards. EPA Method 1631 is one of the first generation of performance-based standards. In contrast with EN 13506, Method 1631 has two analytical stages, and as a direct consequence, it has to address more problem areas than its European counterpart. Because EN 13506 achieves the same detection levels as those required for Method 1631, there is some hope on the part of U.S. researchers that the European method will become acceptable in the United States.

In Perspective

Hg measurements are achievable, but they are not straightforward. Furthermore, analysis is a significant expense, but, unless the measurements of Hg are reliable, it is impossible to deal with its subsequent removal or treat the problems. To provide reliable data on Hg at ultratrace levels and to speculate the element require a sensitive approach with correct attention to detail.

References