Determining Mercury in Ambient Waters: How low do we need to go and how do we get there?

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The toxic effects of mercury have been known for many years, but more and more nowadays, the dangers of 'low level' exposure to it are also causing concern. The Great Lakes Initiative in North America led to the development of two new methods for mercury analysis—USEPA Methods 1631 and 245.7. However, both systems had faults, so Method 1669 was developed, combining the best qualities of each.

An instrument has been developed which both meets the requirements of Methods 1631 and 245.7 and prescreens samples automatically.

Sue Fakes

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Introduction

Mercury has long been known to be a potent toxin but recently concern has increased significantly about 'low level' exposure to the metal, particularly as methylmercury, the predominant organic form of the element. As early as 1830 the neurological effects of chronic inorganic mercury poisoning were recognised as 'Mad Hatter's disease'. By the late 1950s researchers had identified methylmercury poisoning as the cause of the strange neurological disorders observed in some of the inhabitants of Minimata and Nigata, Japan. These incidences came primarily from the consumption of fish contaminated with mercury that had been dumped in local waters. It is important to note, however, that mercury exposure is not merely an occupational hazard, nor is mercury pollution limited to isolated cases of industrial abuse, but rather mercury is found everywhere in our environment.

Recognising how pervasive mercury pollution has become, many environmental agencies around the world have published advisories which limit the recommended consumption of certain types of fish, or fish caught in specified bodies of water in order to reduce the risk of chronic methylmercury exposure. For example, in the United States alone more than 2000 lakes and streams have fish advisories established.

Mercury and the Environment

There are numerous natural and man-made sources of mercury. Of the man-made sources coal-fired power plants, mining, chlor-alkali plants, and waste incinerators are the major contributors. Sources such as coal-fired power plants emit tons of mercury into the atmosphere annually. Once in the atmosphere, mercury can travel with the wind for thousands of miles before being deposited, usually with rainfall. Commonly found bacteria are known to methylate these mercury deposits and aquatic ecosystems play an important role in concentrating the resultant methylmercury. In fact, the bioaccumulation factor or the ratio of concentration in (fish) tissue to the concentration in the medium can exceed 100,000:1. As a result of bioaccumulation, the methylmercury levels in fish may exceed what has been established as 'safe or acceptable', usually one part per million (or less) even though the water the fish inhabited was relatively clean (perhaps as low as one part per trillion mercury).

The Great Lakes Initiative

The Great Lakes Initiative, a combined effort between the United States and Canada, was created to 'help restore, maintain, and protect' the ecosystem of the Great Lakes Basin. It established new water quality criteria for mercury in ambient waters including a 1.3 ppt limit for wildlife. The GLI also includes guidance documentation with provisions designed to achieve the water quality requirement for mercury. Monitoring the progress toward the quality criteria for mercury required much more sensitive analytical methods. Two new methods employing atomic fluorescence have been developed to meet this demand. USEPA Method 1631 ('Sampling Mercury in Water by Oxidation, Purge and Trap, and Cold Vapour Atomic Fluorescence Spectrometry') is a low-level-mercury test method that was approved by the U.S. Environmental Protection Agency (EPA) in 1999. USEPA Method 245.7 (Mercury in Water by Cold Vapour Atomic Fluorescence Spectrometry) is a faster, simpler technique but somewhat less sensitive than 1631. Along with the lower concentration of mercury in samples comes a greater risk of sample contamination so in conjunction with the two analytical methods a new sample handling method was developed (Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels).

Sample Handling

The key feature of USEPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels is the concept of a 'Clean Hands/Dirty Hands' team. In this approach at least two people are required for sample collection. All members are outfitted in shoulder length gloves and wind suit (pants and jacket of synthetic fibre). Sample bottles that have been cleaned previously and stored inside two zip closure bags are used to collect the samples. The team member designated as dirty hands opens the outer bag. Next, the clean hands team member opens the inner bag, removes the bottle, collects the sample, caps the bottle, returns it to the inner zip bag and seals the bag. (The clean hands member touches only the pre-cleaned sampling equipment, the sample bottle and the inner bag.) The dirty hands member seals the outer bag, labels the sample and stores it for transport to the analysis lab. Before collecting the next sample, both members replace their gloves with clean ones. Samples should be shipped overnight to the analysis lab and preserved on receipt.

Analytical Techniques

In Method 1631 and 245.7 samples are preserved with hydrochloric acid. Prior to analysis samples are digested for a minimum of 30 minutes with 0.1N potassium bromate/bromide solution. There should be residual oxidiser remaining (confirmed by yellow colour or reaction to starch iodide test paper) that is then reduced with hydroxylamine solution (1.2% w/v NH_2OH◊HCl). In both techniques the digested sample is combined with stannous chloride reducing agent to convert ionic mercury (Hg^{+2}) to volatile mercury (Hg^0). Mercury-free argon bubbled through the sample carries the volatile mercury downstream to the detector in Method 245.7 or to gold traps in Method 1631.

Method 1631 achieves lower detection limits (typically less than 0.05 ppt) by pre-concentrating the mercury present in the sample onto glass beads coated with a very thin layer of gold while at the same time separating the mercury from potential interferences that may be present in the gaseous stream. Mercury and gold metal form a stable amalgam and mercury in the gas stream collects on the gold surfaces.

After sufficient mercury is trapped the amalgam is heated to about 450 °C and the released mercury proceeds to the detector where it appears as a sharp analytical signal. Shown below in Figure 1 is a typical analytical signal collected for a 1 ppt Hg solution.

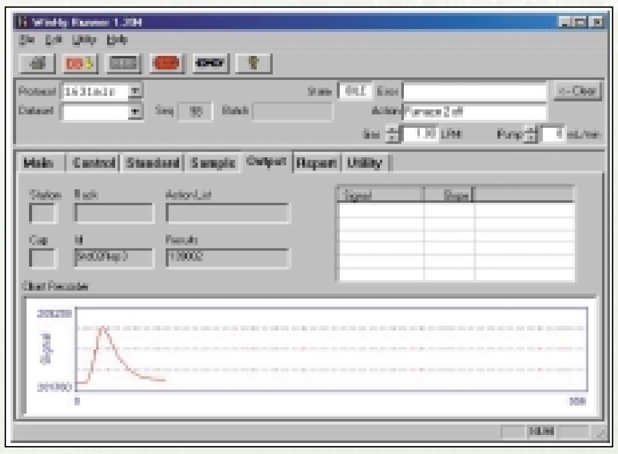

Figure 1: The Signal for a 1ppt Solution Using Purge & Trap Technique

Apparatus for Method 1631 and 245.7

The Leeman Labs Hydra AF Gold plus is an instrument designed to satisfy the requirements of both Methods 1631 and 245.7. A simplified schematic of the Hydra AF Gold plus appears below in Figure 2.

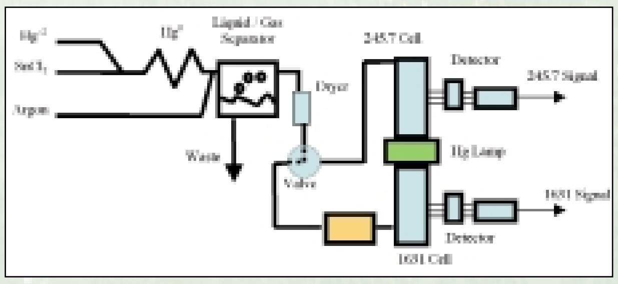

Figure 2: Schematic of the Hydra AF Goldplus

During analysis a peristaltic pump mixes each sample with reducing agent to convert Hg^{+2} to Hg^{0}. In the liquid/gas separator an argon stream passes through the mixture and carries the Hg0 through a dryer to remove moisture.

A valve diverts the gas stream into the 245.7 cell for simple fluorescence or onto the gold trap where the mercury accumulates until the trap is heated. In 1631 mode heating the gold trap releases all the accumulated mercury as a single peak.

Performance

The Hydra AF Gold plus typically achieves instrument detection limits well below 0.05ng/l using a 5 minute uptake time (approximately 25 ml). For perspective, 25 mls of a 1 ng/l solution produced the signal shown earlier in Figure 1.

Figure 3 contains a chart of repetitive OPR (on-going precision & recovery) determinations taken every fifteen minutes over a four-hour period. The OPR specified for Method 1631 is a 5 ng/l standard run before and after each batch (1-20 samples) to ensure that the instrument calibration is stable. Accepted limits for the OPR are +/- 23%. All measurements taken throughout the sequence are well within the method requirements.

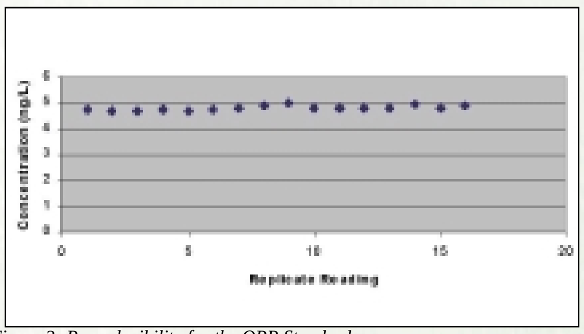

Figure 3: Reproducibility for the OPR Standard

Comparing 245.7 and 1631 Methods

The simple fluorescence technique of Method 245.7 can typically achieve better detection limits than the currently popular cold vapour atomic absorption method when care is taken to keep the reagents and analysis environment mercury free. Another advantage is that the linear range can extend from low ppt to high ppb. Determining mercury in ambient waters at the new water quality criterion of 1.3 ppt, however, may be challenging unless the instrumentation surpasses the required method detection limit of 0.5 ppt. Those ambient waters whose mercury content is above the quality criterion could be analysed using 245.7.

While Method 1631 has better detection limits than the simple fluorescence method and is generally less susceptible to interferences, sample cycle times are longer and samples with high mercury content risk contaminating the analysis instrumentation. Commercially available automated instrumentation for Method 1631 requires five to ten minutes per sample depending on the volume of sample used. By contrast, automated systems for Method 245.7 need only two to three minutes per sample.

Prescreening Samples

Because the volatile mercury is trapped in Method 1631 the detector cannot be used as part of an early warning process to prevent contamination from samples with unexpectedly high mercury concentration. It is, however, possible to prescreen samples for high mercury content using Method 245.7 instrumentation and process only the low concentration (<100 ng/l) samples by Method 1631. The Hydra AF Gold plus is an analyser that not only satisfies both Method 245.7 and 1631 but also can prescreen samples automatically as well.

With the Hydra AF Gold plus sample and reductant enter the gas/liquid phase separator with clean argon. The argon stream carries the free mercury through the Nafion dryer and the method switching valve (shown in Figure 1) directs the stream through the 245.7 detector, bypassing the gold traps. In this mode, high concentration samples start to produce a fluorescence signal shortly after reaching the phase separator. The Hydra AF Gold plus monitors the rate of signal increase and will immediately terminate a sample whose concentration could contaminate the system. Only after the sample has proven to be sufficiently low in mercury content is the valve repositioned to direct the sample stream onto the gold traps. Selection of the prescreen mode is accomplished on the Protocol screen (See Figure 4) by clicking on the prescreen radio button.

Which Method to Choose

The determination of mercury in ambient water often is highly regulated and the method to be employed may be defined by the agencies responsible. Sometimes alternative test procedures are permitted but the burden of proving such procedures acceptable will almost certainly fall on the analyst. If Method 1631 detection limits are required,

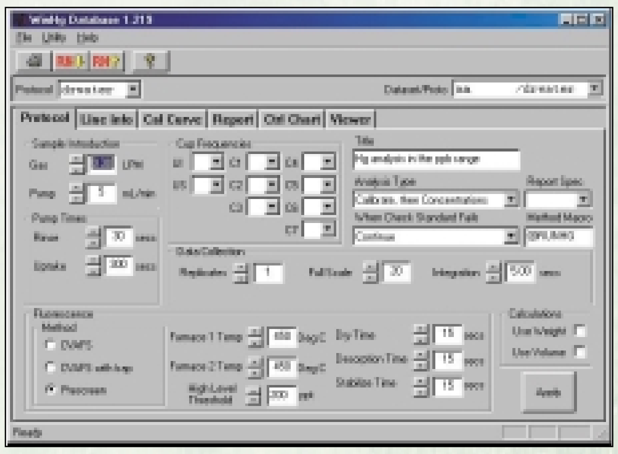

Figure 4: Hydra AF Goldplus Protocols

prescreening samples for high mercury content by an alternate, less sensitive technique may prevent serious down-time while the analytical system is decontaminated.

References

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3) ‘Method 245.7: Mercury in Water by Cold Vapour Atomic Fluorescence Spectrometry (Draft)’, United States Environmental Protection Agency, Office of Water, January 2001

4) ‘Method 1669: Sampling Ambient Water for Trace Metals at EPA Quality Criteria Levels’, United States Environmental Protection Agency, Office of Water, July 1996