

Determining Mercury in Ambient Waters:

More sensitive methods and instrumentation are now available

Mercury has long been known to be a potent toxin but recently concern has increased significantly about chronic "low level" exposure to the metal. As early as 1830 the neurological effects of chronic inorganic mercury poisoning were recognized in the form of "Mad Hatter's" disease. By the late 1950s researchers had identified mercury 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 that mercury exposure is not merely an occupational hazard, nor is it limited to isolated cases of industrial abuse, but rather mercury is found everywhere in our environment and chronic exposure can have devastating consequences. Consider for example the impact of bioaccumulation of mercury. Bioaccumulation factors, the ratio of concentration in tissue (e.g. fish) to the concentration in the medium (e.g. a lake) can exceed 100,000:1. As a result of bioaccumulation, the mercury 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).

Recognizing how pervasive mercury pollution has become, many environmental agencies around the world have published advisories that 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 mercury exposure. For example, in the United States alone more than 2000 lakes and streams have fish advisories established.

Analytical Techniques

In recent years, mercury determinations have been performed using either cold vapor atomic absorption (CVAA) or cold vapor atomic fluorescence (CVAF) techniques. Recently, two EPA methods employing the more sensitive atomic fluorescence approach were developed to meet the increasing need for accurate, low-level Hg determinations. These new EPA methods are 1631 ("Sampling Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry") and 245.7 (Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry). The later is a faster, simpler technique but somewhat less sensitive than 1631.

In both methods, samples are preserved with hydrochloric acid after collection and digested for a minimum of 30 minutes with 0.1N potassium bromate/bromide. Following the digestion step, there should be residual oxidizer remaining (confirmed by yellow color or reaction to starch iodide test paper) that is reduced with hydroxylamine solution (1.2% w/v $\text{NH}_2\text{OH}\cdot\text{HCl}$) prior to analysis. In both techniques the digested sample is combined with stannous chloride to convert ionic mercury (Hg^{+2}) to volatile mercury (Hg^0). Argon is then bubbled through the sample

carrying the volatile mercury downstream to the detector in Method 245.7 or to gold traps in Method 1631. Figure 1 shows a schematic representation of the analytical instrumentation used. Method 1631 achieves lower detection limits (typically less than 0.05 ppt) by first pre-concentrating the mercury present in the sample onto gold coated glass beads while at the same time separating the mercury from interferences in the gaseous stream. Mercury and gold metal form a stable amalgam and mercury in the gas stream collects on the gold surfaces.

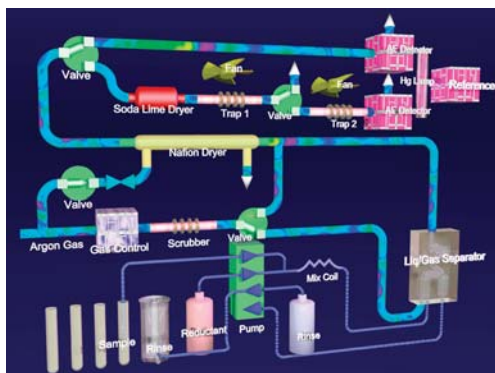


Figure 1: Schematic representation of Hydra AF Gold plus

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 transient analytical signal. Figure 2 shows the typical analytical signal for a 1 ppt Hg solution.

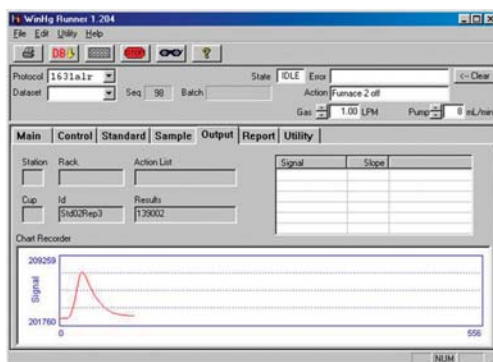


Figure 2: The Signal for a 1ppt Solution Using Purge & Trap Technique

Apparatus for Method 1631 and 245.7

The Hydra AF Gold plus is an instrument designed to satisfy the requirements of both Methods 1631 and 245.7. 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 Hg^0 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 that then flows to the high sensitivity 1631 mode atomic fluorescence detector.

An advantage to this dual detector approach is that the user can elect to prescreen samples for high mercury content using the lower sensitivity method 245.7 detection system and process only the low concentration (i.e. <0.1ppb) samples by Method 1631. With its built in autosampler, the Hydra AF Gold plus is designed to satisfy both Methods 245.7 and 1631 and to provide the added capability of prescreening samples automatically.

Comparison of methods 245.7 and 1631 and Conclusions

The simple fluorescence technique of Method 245.7 can typically achieve better detection limits than conventional CVAA when care is taken to keep the reagents and analysis environment mercury free. It carries the added advantage that the linear range can extend from low ppt to high ppb levels. Determining mercury in ambient waters at the new water quality criterion of 1.3 ppt, however, may be challenging using the simple fluorescence technique and is best approached using method 1631 with its gold amalgam pre-concentration of mercury prior to the measurement step. Those ambient waters whose mercury content is above the quality criterion could be analyzed using 245.7.

While Method 1631 has better detection limits (typically <0.05ug/L) than the simple fluorescence method and is generally less susceptible to interferences, sample cycle times are longer. For example method 1631 requires 5-10 minutes per sample depending on the volume of sample used. By contrast, automated systems for Method 245.7 require only 2-3 minutes per sample. In method 1631, samples with high mercury content can risk contaminating the instrumentation if some form of over range protection is not inherent to the system.

In conclusion, automated instruments are now commercially available to run both of these new EPA methods. Some of these systems will not only perform the analysis, but will also provide limited protection against contamination from very high concentration samples.

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Reprinted from October 2003



POLLUTION EQUIPMENT NEWS
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