

# Measuring Mercury in Ambient Waters by Cold Vapor Atomic Fluorescence: When Is Purge and Trap Preconcentration Really Necessary?

Numerous studies have raised concerns about the physiological impact of exposure to low-level mercury; this is especially true when present as methylmercury, the most commonly found organic form of mercury.

Inorganic mercury, when introduced into the environment through natural or anthropogenic sources readily migrates into lakes, rivers and streams where bacteria and other micro-organisms convert it to methylmercury. This form of mercury is particularly insidious because it bioaccumulates in aquatic species such that waters low in mercury can produce fish containing dangerously high levels of the substance. In fact, the bioaccumulation factor, or the ratio of concentration in tissue (fish) to the concentration in the medium (water), can exceed 100,000:1. As a result of bioaccumulation, methylmercury levels in fish can often exceed 'safe or acceptable' levels (usually one part per million or less) even though the water the fish inhabited was relatively clean. Similarly for humans, methylmercury (consumed primarily from contaminated fish) is readily assimilated and efficiently stored in the body so it becomes a growing problem over a lifetime of exposure. Factors such as these make methylmercury especially dangerous for "at risk" groups such as pregnant women and young children.

Recognizing how pervasive mercury pollution has become, and in an attempt to minimize its harmful effects, 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. For example, in the United States alone more than 2000 lakes and streams have fish advisories established.

## The Water Quality Criteria for Mercury

As Europe pursues the establishment of a water quality criteria for mercury, it may be worth studying the path Canada and the United States have taken. As a result of the Great Lakes Initiative (a combined effort between Canada and the United States to 'help restore, maintain, and protect' the ecosystem of the Great Lakes Basin) a new water quality criteria for mercury in ambient waters was established. This included a 1.3 ppt limit for Hg in ambient waters to ensure the protection of wildlife. Monitoring progress toward achieving the new water quality criteria for mercury required much more sensitive analytical methods than were previously available; as a result, two new methods employing cold vapor atomic fluorescence (CVAF) were promulgated by the USEPA. Method 1631E "Sampling Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" is a low-level mercury test method which uses a gold amalgamation trap to preconcentrate mercury. This method is similar to the European Standard EN 12338. Method 245.7 "Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry" is a faster, simpler technique but somewhat less sensitive than 1631E and is similar to EN 13506. Hereafter, this approach will be referred to as "simple fluorescence". Along with the lower concentrations of mercury in samples comes a greater risk of contamination so a new sample handling method was also developed, Method 1669: "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels".

## Sample Collection and Handling

The key feature of EPA Method 1669 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 a wind suit (pants and jacket of synthetic fiber). 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" team member touches only the pre-cleaned sampling equipment, the sample bottle and the inner bag. The "dirty hands" team 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 are then shipped overnight to the lab where they are preserved upon receipt.

## Sample Preservation and Digestion

Samples are preserved with hydrochloric acid. Prior to analysis they are digested for a minimum of 30 minutes with 0.1N potassium bromate/bromide solution. When done correctly, there should be residual oxidizer remaining (confirmed by yellow color or reaction to starch iodide test paper) that is then reduced with hydroxylamine solution (1.2% w/v  $\text{NH}_2\text{OH HCl}$ ). This digestion has been shown to produce blanks lower in mercury than the permanganate digestion often used with the cold vapor atomic absorption technique.

## Fluorescence Methods

In both the simple fluorescence and purge and trap fluorescence techniques the digested sample is mixed with a reducing agent such as stannous chloride to produce volatile mercury. The  $\text{Hg}^0$  is then transported into the gas phase by an argon purge and carried downstream to either preconcentrate on a gold amalgamation trap or straight on to the fluorescence detector for measurement.

The simple fluorescence technique typically achieves detection limits of about 0.1 ppt, or about 10x better than the currently popular cold vapor atomic absorption technique. Another advantage of simple CVAF is that the dynamic range is typically much wider than that of CVA; and extends from sub ppt to high ppb levels. Even so, determining mercury in ambient waters at "water quality criterion" levels (e.g. 1.3 ppt for the US) can be challenging without purge and trap preconcentration.

In the purge and trap CVAF approach, mercury from the sample is preconcentrated as a stable amalgam on a gold trapping surface. After mercury from the sample is trapped, the amalgam is heated to about 500°C and the released mercury proceeds to the fluorescence detector where it appears as a sharp transient signal. This approach to mercury analysis typically achieves detection limits well below 0.05 ppt.

While the purge and trap preconcentration approach has better detection limits and is generally less susceptible to interferences than the simple fluorescence approach, analysis times are longer. Commercially available automated instrumentation for Method 1631E require three (or more) minutes per sample depending on the design of the instrument and the volume of sample used. By contrast, without preconcentration, automated systems typically process samples in under two minutes.

## Instrumentation for Cold Vapor Atomic Fluorescence

One example of an instrument designed for cold vapor atomic fluorescence is the Leeman Labs Hydra II AF gold. This instrument is unique in that, not only is it designed to satisfy the requirements of both the simple fluorescence as well as purge and trap fluorescence techniques, but it also

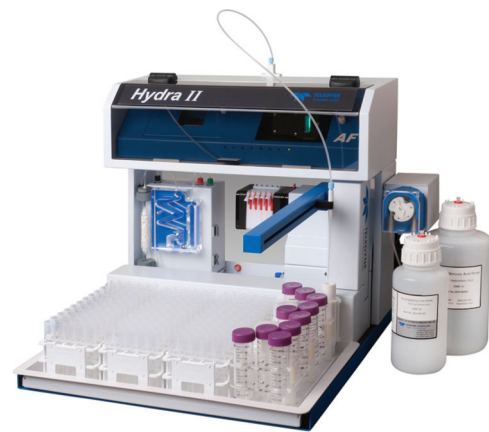


Figure 1a: The Hydra II AF gold

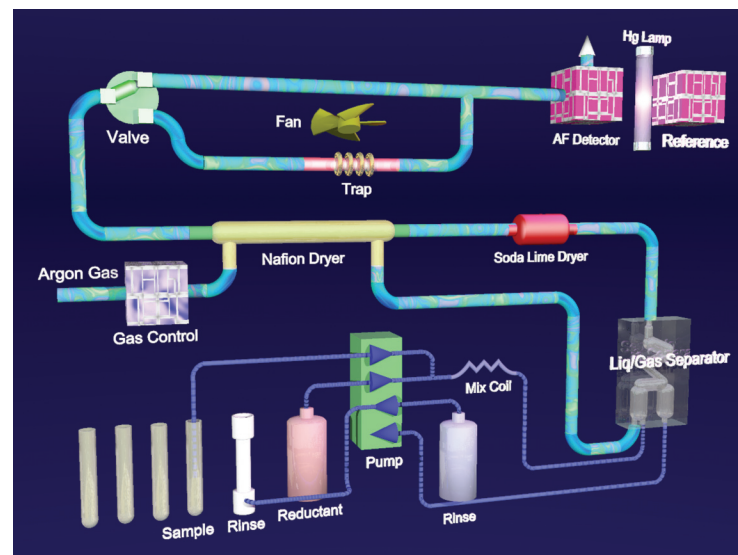


Figure 1b: Principle of operation

## AUTHOR DETAILS

Mr. David Pfeil  
Hg Product Manager  
Teledyne Leeman Labs  
6 Wentworth Drive  
Hudson, NH 03051 USA  
Tel: 603-886-8400  
Fax: 603-886-9141  
Email: dpfeil@teledyne.com  
Web: www.TeledyneLeemanLabs.com

provides a high concentration protection system to safeguard the instrument from samples with unexpectedly high concentrations of Hg. A photograph of the instrument and schematic diagram showing the principle of operation of the Hydra II<sub>AF</sub> gold are shown in Figure 1a and 1b. With this system a peristaltic pump is used to mix sample with reductant thereby converting Hg<sup>+2</sup> to Hg<sup>0</sup>. The Hg<sup>0</sup> is then removed from the liquid phase in its liquid/gas separator and carried through a 2-stage dryer to remove all traces of moisture. At this point an automated diverter valve is used to control whether the analysis is performed via simple fluorescence or by purge and trap fluorescence.

One consideration which can be especially important for today's high capacity commercial testing labs is the potential for instrument contamination from samples with unexpectedly high concentrations of Hg. Although ambient water samples should all be relatively low in mercury, today's commercial testing labs don't always get accurate information about the samples that their customers ship to them. A sample with a high concentration of mercury can wreck havoc on some instruments and lead to long and expensive decontamination procedures. This can be especially challenging for purge and trap instruments because all the volatile mercury from a sample collects on the gold trap prior to the instrument "knowing" how much mercury is in the sample. The Hydra II<sub>AF</sub> gold is unique in that it provides a high concentration protection system for both the simple fluorescence technique as well as the purge and trap technique. When the simple fluorescence approach is being used, high concentration protection is accomplished by the instrument continually monitoring the rate of change in signal for each new sample and then automatically taking the appropriate corrective action before system contamination can occur. When the purge and trap approach is being used, high concentration protection is accomplished by using the simple fluorescence system to perform a brief prescreen of each sample and then allowing further analysis only for those samples which are deemed safe (e.g. samples with concentrations below a user selectable set point).

The Hydra II<sub>AF</sub> gold achieves instrument detection limits well below 0.05 ng/L in purge and trap mode (preconcentrating sample for approximately 1 minute). For perspective, a 1 ng/L solution preconcentrated for 1 minute produced the signal shown in Figure 2. Figure 3 displays a graph of On-going Precision and Recovery (OPR) determinations made every twenty minutes over an eight-hour period. The OPR specified for Method 1631E is a 5 ng/L standard run before and after each batch (1-20) of 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.

**So, when is Purge and Trap Preconcentration Necessary ?**

The determination of mercury in ambient water is often highly regulated regardless of locale and the method to be employed may be defined by the agencies responsible. Purge and trap preconcentration requirements also are typically defined by these regulators. With that said, in our experience, purge and trap preconcentration is exceptionally helpful when trying to produce high quality measurements at or below about 5 ppt. This is at least partially substantiated by the observation that in the United States, analyses for mercury with a reporting level of 5 ng/L or more are permitted without preconcentration while preconcentration is required for reporting levels below 5 ng/L.

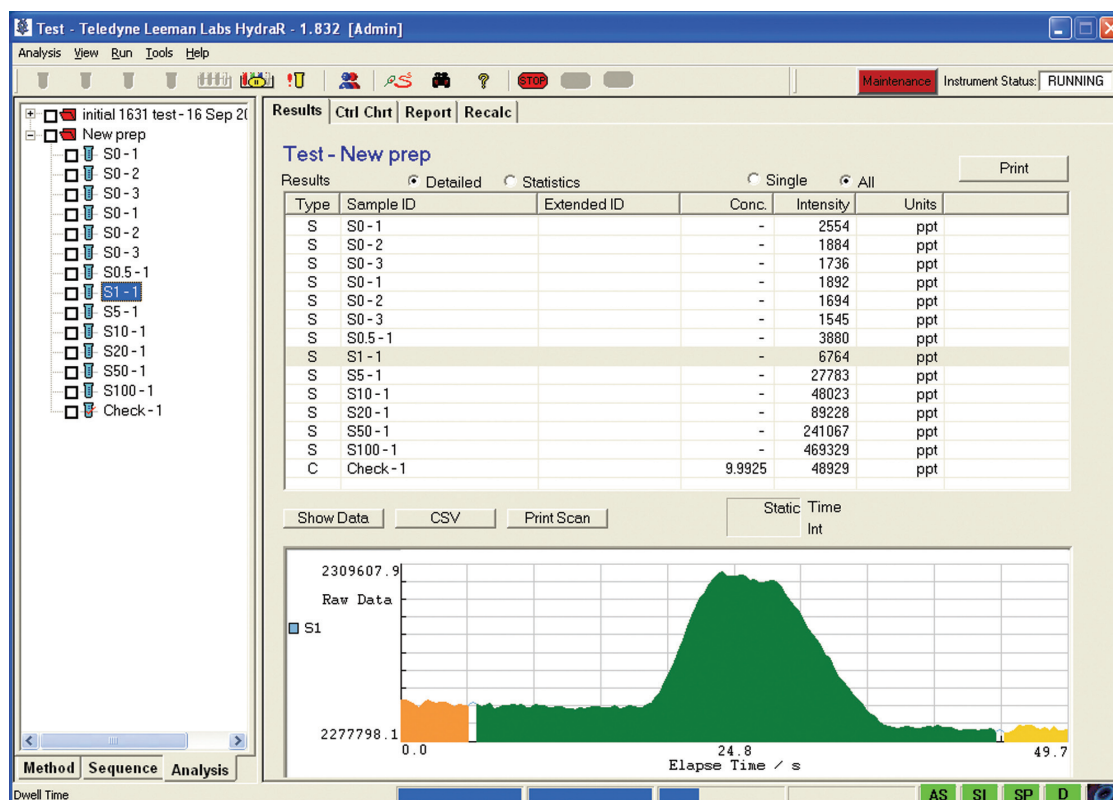


Figure 2: Hydra II<sub>AF</sub>Gold signal for a 1 ppt solution collected for one minute.

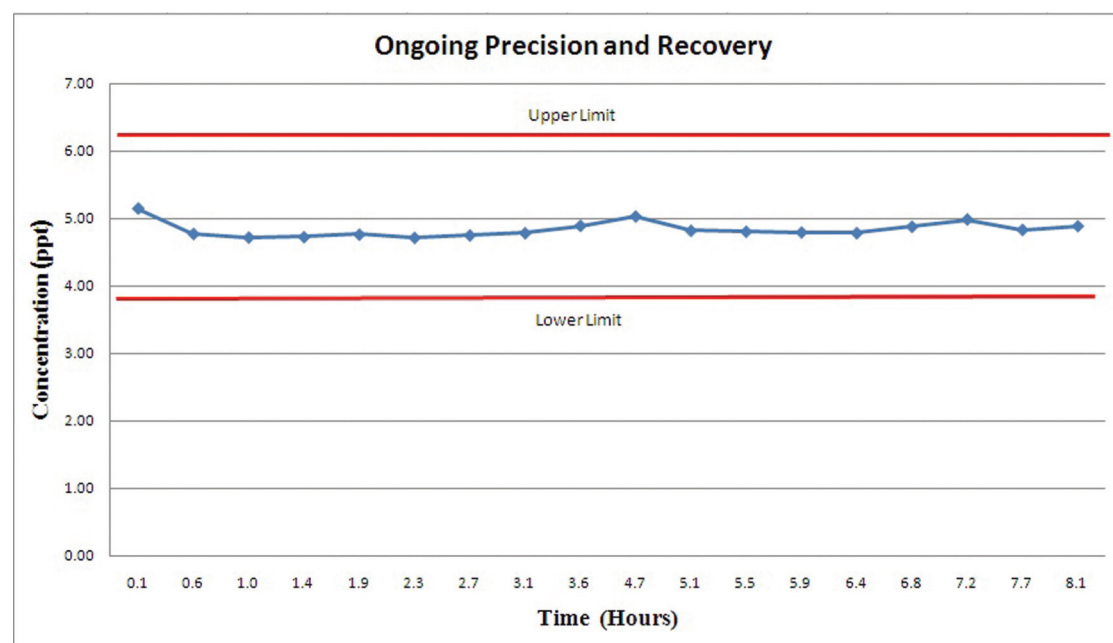


Figure 3: This graph shows the stability of a 5 ppt on-going precision and recovery standard collected over an 8-hour day.