

# Automated determination of mercury by cold vapor atomic fluorescence with gold amalgamation

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In the last 40 years, mercury pollution has caused numerous deaths and thousands of hospitalizations globally. The first significant occurrence was in Minimata, Japan, where hundreds of people were poisoned eating fish contaminated with mercury. Other episodes appeared in Japan (Nigata), Iraq, Pakistan, Guatemala, and Brazil.

Recently, mercury has appeared at high levels unexpectedly in some otherwise pristine locations. Researchers around the world are studying how mercury is transported and transformed within and between a variety of ecosystems. Studies continue in such diverse locations as the Arctic Circle and the Amazon jungle. In the United States, major projects are under way in the Everglades, the San Francisco basin, the Great Lakes, the Nevada desert, the Gulf of Mexico, and Alaska (to name a few).<sup>1</sup> As interest in mercury has increased, so has the demand for sample testing. Furthermore, to understand the mercury sources, its metabolism, and fate, a wider range of

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sample matrices need to be tested at lower limits of detection. Increasingly, atomic fluorescence, sometimes in conjunction with preconcentration using gold amalgamation, has provided the improved detection limits necessary to monitor ambient levels in the environment.

The ability to determine mercury at lower concentrations has shed light on other challenges in the analytical process. Contamination from both the sample collection and analysis process may inadvertently elevate the measured mercury concentrations. In particular, low-level mercury contamination has been found in sample collection equipment, sample containers, protective gloves, reagents, and the laboratory environment. U.S. EPA Method 1631<sup>2</sup> recommends using Method 1669<sup>3</sup> for detailed instruction on sample collection. While an in-depth discussion of Method 1669 is beyond the scope of this paper, a few points must be mentioned. One key concept of Method 1669 is "clean hands/dirty hands." The "dirty hands" sampler handles the outer protective bags, pumps, coolers, logbooks, and other pieces of

equipment that do not come in direct contact with the sample. The "clean hands" sampler handles the inner protective bags, sample containers, and ends of pump tubing.

A video for the U.S. EPA Office of Water (Washington, DC) demonstrates this process (DynCorp, Inc., Alexandria, VA), copies of which may be obtained from the U.S. EPA by e-mailing Maria Gomez-Taylor at [gomez-taylor.maria@epamail.epa.gov](mailto:gomez-taylor.maria@epamail.epa.gov).

Currently, sample bottles must be made of borosilicate glass or fluoropolymer since mercury may adsorb to, leach from, or permeate through other materials. Another limitation of more sensitive techniques such as 1631 is that the maximum as well as the minimum measurable concentrations have decreased, making prescreening samples more important. Method 1631, which is the most sensitive of the promulgated U.S. EPA methods for total mercury, is a labor-intensive manual method that requires the analyst to manually exchange gold amalgam traps, add samples and reagents, control the analysis process, and calculate results. This paper examines an automated approach to 1631 methodology with built-in prescreening capability.

### Apparatus for Method 1631

Method 1631 shows the general schematic of the apparatus needed for mercury determination using gold amalgamation. The suggested equipment appears in *Figure 1*.

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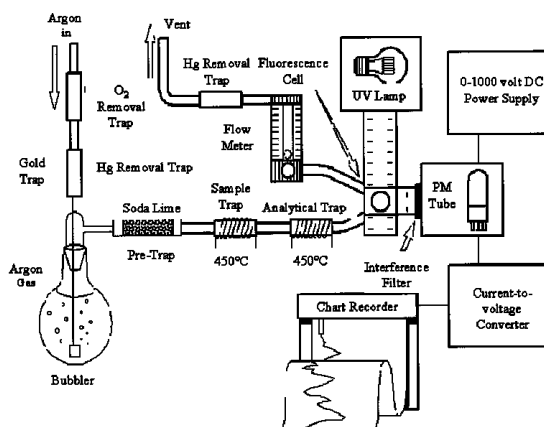


Figure 1 Apparatus for Method 1631.

In Method 1631, the analyst adds a properly digested sample and reductant (stannous chloride) to the bubbler chamber. The mercury in solution (as mercuric ions) reacts with the stannous chloride to form elemental mercury ( $\text{Hg}^0$ ). Mercury-free argon passes into the bubbler chamber through a gold trap or amalgamator. The argon stream purges the dissolved elemental mercury from the solution and carries it through the soda lime trap, where acid vapors and moisture are removed, to the first gold trap. The gold trap adsorbs the mercury present in the argon stream. After all the mercury originally in the sample collects on the first gold trap, the trap is heated to 450 °C, releasing all the adsorbed mercury. The argon stream carries this mercury to the second gold trap where it is re-adsorbed, while many of the potential matrix interferences are purged from the system. After an appropriate delay, the second gold trap is heated and the argon stream carries the re-released mercury to the fluorescence cell. A high-sensitivity fluorescence detector monitors the peak as the mercury passes through the cell, and a chart recorder captures the peak. The analyst uses the baseline-subtracted area under the peak for standards of known concentration to generate a calibration curve.

### *Automating Method 1631*

The method apparatus includes manual sample and reductant additions, manual control of the amalgamators, and manual calculation of results. Replacement of the bubbler with a continuous flow gas/liquid phase separator fed by a peristaltic pump automates sample and reductant introduction. An autosampler attached to the sample line provides automated sample exchange. The Hydra AF Goldplus (Leeman Labs, Hudson, NH) (Figure 2) is equipped with these automated features.

In addition to sample introduction, the analyzer automates all aspects of the analysis cycle, and concentration calculations, and provides overrange sam-

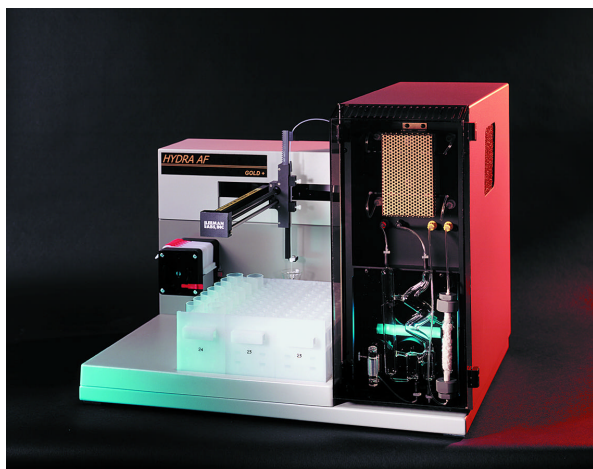
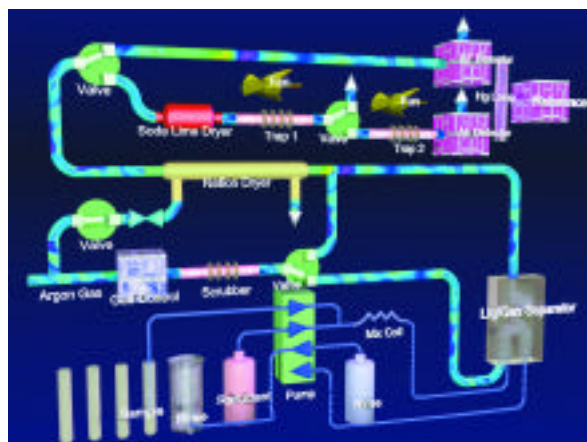


Figure 2 Hydra AF Goldplus mercury analyzer.



**Figure 3** Schematic of the Hydra AF Goldplus mercury analyzer.

ple protection. An external computer handles control of gas flows, the autosampler, peristaltic pump, and all other instrument systems. *Figure 3* shows the instrument's schematic design. The schematic includes a counter-flow Nafion™ dryer (**Perma Pure, Inc.**, Toms River, NJ) for improved moisture removal. The inclusion of this dryer and a second detector in the analyzer makes the system compatible with the less-sensitive Method 245.7<sup>4</sup> as well as Method 1631.

Interestingly, Method 245.7 can be employed to prescreen for high-mercury-content samples automatically. (For 245.7 mode, the valves are in the state, as shown in *Figure 3*). Sample and reductant enter the gas/liquid phase separator with clean argon. The argon stream carries the free mercury through the dryer, and valve 1 at the top left of the schematic 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 Goldplus monitors the rate of signal increase and immediately terminates a sample whose concentration may 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.

In the 1631 mode, valve 1 directs the sample vapor to the gold traps for a specified period of time that corresponds to the volume set by the analyst. The longer the valve remains in this position, the more mercury is collected on the first trap. It is worth noting that while mercury collects on trap 1, the argon stream exits the system through valve 2, bypassing the fluorescence cell. After the desired uptake period, valve 1 returns to its 245.7 mode position; the sample sipper returns to the rinse cup; sample is rinsed from the phase separator; and valve 3 is opened, bypassing the phase separator and providing a clean argon stream directly to the gold traps. At this

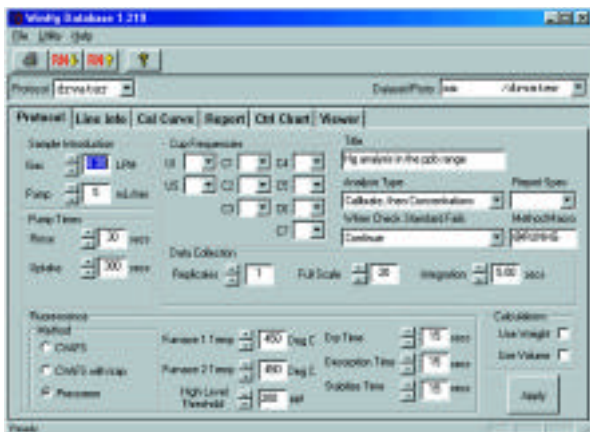


Figure 4 Hydra AF Goldplus protocols.

point, valves 1 and 2 are repositioned to provide argon flow through both traps and the 1631 mode fluorescence cell. Trap 1 heats to 450 °C (suggested) and the mercury migrates to trap 2. After heating is complete, the trap 1 fan activates, followed by trap 2 heating to 450 °C and signal measurement. Upon completion of the measurement, fan 2 activates to cool the second gold trap, and the instrument is reset to run the next sample.

Control for the system employs a **Microsoft** (Redmond, WA) Windows™-based graphical user interface compatible with 95, 98, 2000, and NT operating systems. *Figure 4* shows the protocol window, which contains all of the controls, temperatures, and timing for an analysis cycle. In the lower left of the figure are radio buttons (shown in prescreen mode) for the method selection. Described above is the prescreen mode employing simple atomic fluorescence (Method 245.7) to qualify samples prior to formal analysis by purge and trap gold amalgamation. As mentioned earlier, the instrument is capable of operating in either 245.7 or 1631 mode alone.

The uptake time defines how long the sample will be collected on the first trap. The high-level threshold is the maximum concentration that a sample may contain and still be analyzed by the purge-and-trap technique without dilution. Typically, the threshold value is near the highest standard in the 1631 mode calibration curve. The software provides independent fields for each furnace temperature control. The dry time is the period that dry argon passes over trap 1 after the sample is collected before heating begins. The desorption time is the length of the heating cycles. The stabilize time is the interval between traps 1 and 2 heating.

### Performance

The Hydra AF Goldplus typically achieves instrument detection limits below 0.05 ng/L using a 5-min uptake time (approx. 40 mL). *Figure 5* shows the signal produced by a 1-ng/L solution with a 5-min uptake. *Table 1* provides the cycle times for the various modes of analysis.

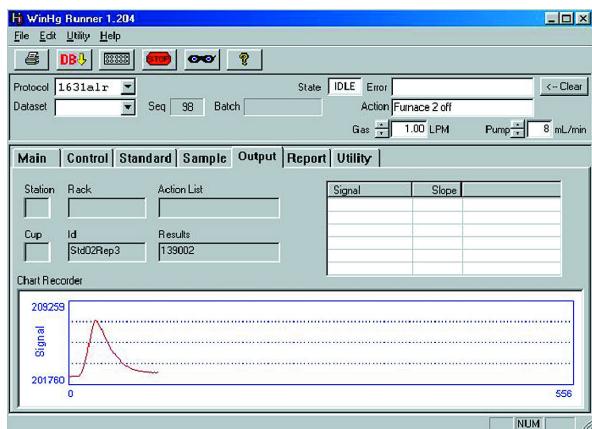


Figure 5 Signal for a 1-pt solution using the purge-and-trap technique.

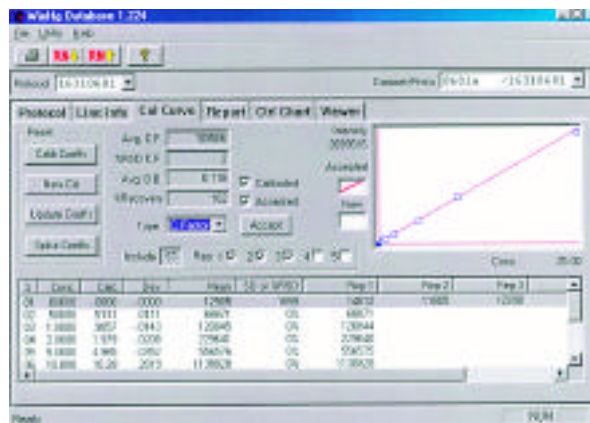


Figure 7 Initial calibration.

Table 1

Analysis mode	Hydra AF Gold plus analysis cycle times	
	Uptake volume (mL)	Time (min)
245.7	—	2–3
1631	8	4–5
1631	40	8–9

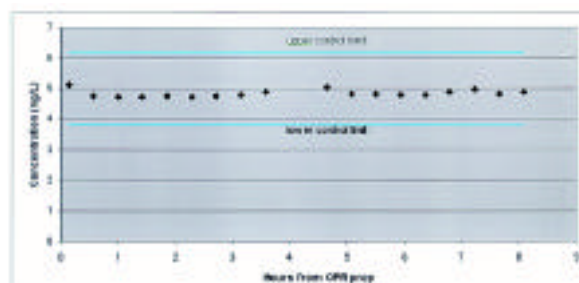


Figure 6 Instrument reproducibility for the OPR standard.

Figure 6 is a chart of repetitive ongoing precision and recovery (OPR) determinations taken over an 8-hr period. The OPR specified for Method 1631 is a 5-ng/L standard run periodically to ensure that the instrument calibration is stable. Acceptance limits for the OPR are  $\pm 23\%$ . All measurements taken throughout the sequence are well within the method requirements.

### Calibration requirements for 1631

The 1631 method provides operational objectives to help ensure the accuracy of the results. One of the criteria is that the blank (bubbler or calibration blank) must contain no more than 0.25 ng/L Hg. Figure 7 shows that the calibration blank readings were

Table 2

Matrix	Matrix spike data		
	Original sample concentration (ng/L)	Matrix spike recovery (%)	MS/MSD difference (%)
Effluent A	2.03	110.6	1.2
Surface pond #1	0.72	80.0	8.0
Surface pond #2	2.66	58.0	3.9
Manufacturing industrial effluent	2.09	80.9	2.9
Steel processing effluent	14.4	57.3	6.9
Effluent B	12.8	88.5	0.2
Effluent C	5.28	121.1	6.1
SPLP leachate*	3.43	71.7	8.4
Groundwater A**	<0.5	111.0	1.1
Groundwater B**	<0.5	93.2	16.6
Groundwater C**	<0.5	84.6	5.7
Galvanizing plant effluent**	<0.5	89.3	0.8

\*Synthetic precipitation leaching procedure.<sup>5</sup>

\*\*Matrix spike at 2.5 ng/L.

well below the limit. The average calibration blank concentration was 0.118 ng/L.

In Method 1631, “calibration factors” determine the slope of the calibration curve. A calibration factor for 0.5 ng/L ( $CF_m = (68871 - 12905)/0.5 = 111932$ ) is calculated by subtracting the average blank peak area from the area of a standard and then dividing by the concentration of that standard. The %RSD of all the calibration factors must be less than 15%, and the percent recovery for 0.5 ng/L standard ( $\%R = [(68871 - 12905)/109506](100/0.5) = 102\%$ ) of the low (0.5 ng/L) standard must be 75–125%. Figure 7 shows that the Hydra AF Goldplus easily meets both calibration factor and 102% recovery on the low standard. Unlike a linear least-squares regression, the calibration factor approach gives each point equal weight and often provides more accurate results at the low end of the calibration range. The WinHg software (Leeman

**Labs**) provided with the Hydra AF Gold*plus* calculates average blank concentration, calibration factors, and recoveries automatically.

### *Matrix spikes*

Method 1631 increases the matrix spiking frequency relative to previous mercury analysis methods. Few matrix interferences were observed during method development, validation, and early production use. As this method is applied to a wider range of matrices with multiple instrument vendors, laboratories, and analysts, the influence of sample matrix is expected to increase. Thus, matrix spiking in each matrix type is recommended to document method performance in the matrix of interest. *Table 2* shows some recent matrix spike/matrix spike duplicate data from 5-ng/L spikes. Reproducibility is good, though suppression of mercury recovery is evident in two matrices.

### *Conclusions*

The Hydra AF Gold*plus* has the stability and sensitivity needed to meet or exceed Method 1631 requirements. It automates many of the manual operations in the purge-and-trap technique (Method 1631). This automation relieves much of the burden previously placed on the analyst to introduce samples, control the analytical process, and calculate results. The prescreen mode protects the sensitive gold amalgamation traps from samples with high mercury content, reducing the likelihood of time-consuming cleanup.

### **References**

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5. Method 1312. Synthetic precipitation leaching procedure. Washington, DC: U.S. EPA, Office of Solid Waste, Nov 1994.

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