

Mercury Falling

New requirements for low-level mercury monitoring necessitate changes in sample collection and analysis procedures and protocol

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Many municipal and industrial facilities that use and discharge water are experiencing changes in their mercury-monitoring requirements.

Method 1631 ("Sampling Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry") is a low-level-mercury test method that was approved by the U.S. Environmental Protection Agency (EPA) in 1999, and is being written into many new National Pollutant Discharge Elimination System (NPDES) permits. This means that some facilities must test for mercury for the first time, while other facilities that had been monitoring mercury previously must test at levels 400 times lower than before.

Method 1631 is so much more sensitive than the conventional mercury test, Method 245.1 ("Manual Cold Vapor Technique"), that new units of measure commonly are used. Rather than measuring mercury in parts per billion ($\mu\text{g/L}$), Method 1631 measures it in parts per trillion — nanograms per liter (ng/L). One nanogram is 1/1000 of 1 μg . One part per trillion is approximately equal to one pinhead-sized drop of mercury in an Olympic-sized swimming pool.

Along with these changes come many questions.

- What are the chemical and regulatory drivers behind the requirements to test for lower levels of mercury in water?
- What relevance does historical site data have in low-level testing?
- What special procedures should be followed during sampling?
- Are there new sample shipping and receiving constraints?
- What does your laboratory need to do to meet the sensitivity and accuracy requirements and avoid contamination?

Answering these questions is important, because neglecting the special requirements of low-level mercury testing may lead to inaccurate results that are biased

high and noncompliant with a facility's permit. Almost all of the common mistakes lead to high-biased results.

Drivers

The primary chemistry driver for the new low-level-mercury requirements is bioaccumulation in the food chain. Mercury in water is absorbed by microscopic life forms, which, in turn, are eaten by small fish and other aquatic animals. Larger fish and animals eat the smaller fish and animals, and mercury accumulates in the fatty tissues, becoming more concentrated as it moves up the food chain. Eventually, mercury can accumulate in top-of-the-chain predators, including bears, eagles, ospreys, and humans at concentrations high enough for reproductive and nervous-system disorders and other chronic mercury-exposure symptoms to surface.

According to EPA, 41 states have issued fish-consumption advisories due to mercury contamination. The phrase "mad as a hatter," made famous in *Alice in Wonderland*, referred to the once-common occupational hazard faced by hat makers. Mercury commonly used in the hat-making process accumulated in the hatters, eventually disturbing their neurological systems and mental faculties.

Table 1. Water Quality Targets for Mercury

Criterion	NTR (ng/L)	Great Lakes (ng/L)
Freshwater acute	2400	1440
Freshwater chronic	12	770
Marine acute	2100	N/A
Marine chronic	25	N/A
Human health	140	1.8
Wildlife	1.3	

NTR = National Toxics Rule.

Great Lakes = Great Lakes Water Quality Agreement.

ng/L = nanograms per liter.

N/A = not applicable.

Because of its pervasiveness and bioaccumulative nature, mercury is identified as a toxic priority pollutant in several EPA programs for air, water, hazardous waste, and pollution prevention, including the Clean Water Act (CWA). The 1987 CWA amendments mandated that states must adopt specific numeric criteria for all toxic pollutants expected to interfere with designated uses of a waterbody, and implement water quality-based control strategies to ensure water quality is maintained.

EPA's response to the CWA amendments resulted in the following regulations:

- the Great Lakes Water Quality Agreement, an effort between EPA and Canada that calls for the virtual elimination of mercury while providing incentives and options for cost-effective implementations that consider mercury sources;
- the National Toxics Rule, which establishes numeric water quality criteria for toxic pollutants and brings noncompliant states into compliance with the 1987 CWA amendments; and
- the Final Water Quality Guidance for the Great Lakes System, which responds to Sec. 118 (c)(2)(C) of the Clean Water Act.

The National Toxics Rule and the Great Lakes Water Quality Agreement generated the water quality criteria in Table 1 (p. 34). However, during the generation of these data, some low-level contamination concerns were identified.

First, some mercury concentrations identified in water samples may have been due to sample collection and laboratory contamination, rather than actual sample concentrations. Secondly, approved EPA methods before 1999 did not address the trace-level contamination issue or incorporate clean techniques or guidelines. Using clean-sample-handling techniques to determine mercury at water quality criteria levels is recommended to preclude false positives arising from sample collection, handling, or analysis.

Historical Site Data

Currently, Method 1631 is the only low-level-mercury test method to receive federal regulatory approval. If approved by EPA, Method 245.7 ("Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry"), presently in draft form, will offer a less-sensitive and slightly less-expensive alternative to Method 1631.

If a particular outfall or sampling point consistently has

produced measurable results ($>0.2 \mu\text{g/L}$ or 200 ng/L) with Method 245.1, there probably is no analytical need to switch to the more sensitive and more expensive Method 1631. If, however, a regulator requires that Method 1631 be used, it is necessary to provide the previous mercury test results from the effluent to the analytical laboratory, so it can protect its clean area and screen the sample to determine the correct dilution.

If false positives are suspected with cold-vapor atomic absorption (Method 245.1), a large dilution followed by Method 1631 analysis may be one way to work around this sample difficulty and still produce a reporting limit of $0.2 \mu\text{g/L}$. In some instances, simply changing to Method 1631 will resolve the problem, even without a dilution.

Communicating the permit or local regulatory limit to the laboratory also is useful background information.

Sample Collection

Sampling involves information and processes from both Method 1631 and Method 1669 ("Sampling Ambient Water for Trace Metals"). Special collection techniques, equipment requirements, and cleaning procedures are recommended to reduce the chance of contamination. These methods also describe additional quality control samples that may provide useful data to assist in interpreting actual sample data.

Method 1669 requires that either fluoropolymer or borosilicate glass bottles be used for sample collection. Common plastic bottles are unacceptable because of mercury's tendency to diffuse through, adhere to, or leach from plastics. Severn Trent Laboratories (STL), a North Canton, Ohio, analytical laboratory, uses inexpensive, disposable 40-mL borosilicate vials with Teflon-lined caps. Each lot is tested to ensure that the vials meet Method 1631's cleanliness requirements of less than 0.5 ng/L of mercury.

STL uses 40-mL vials because they can be used for sample collection and preparation, and then directly loaded into the instrument autosampler. Because the bottles are not reused, there is no chance of carryover contamination. Lastly, the small vials tend to be less prone to breakage during shipping. The vials are slipped into a foam cube, double bagged, and placed in a bubble-pack bag for shipping from laboratory to client and for return shipment from client to laboratory. Packing one sample per double

bag prevents cross contamination between samples from different locations or timeframes.

Clean hands–dirty hands sample collection as described in Method 1669 is recommended for low-level sampling. A designated "dirty-hands" person handles all machinery, the sample

Table 2. Mercury Contamination Sources

Reagents	Equipment	Environment	Analyst
reagent water	sample bottle	laboratory air	gloves
hydrochloric acid	hoses and tubes	particulates	laboratory coat
potassium bromide	gas-supply line	bench top	dental work
potassium bromate	autosampler vial	ventilation hood	
stannous chloride	gas–liquid separator		
hydroxylamine hydrochloric acid	pipet tips		
argon			

cooler, and the outer sample bag. A “clean-hands” person opens the inner bag, removes the sample vials, fills the vials with the sample, replaces the vials in the inner bag, and seals it. The dirty-hands person seals the outer bag, applies a client label, and returns it to the cooler. A videotape demonstrating these techniques is available from EPA’s Office of Water or STL.

Method 1669 also describes manual surface sampling, grab sampling, depth sampling, continuous-flow sampling, and in-line sample filtration. As a final note on sampling, EPA’s Office of Water recommends against collecting samples during precipitation events if there is a possibility that rain or snow may get into the sampling container.

Quality Control Provisions

Methods 1669 and 1631 include numerous quality-control provisions. Single-use glass bottles must be pretested by lot, and reusable containers must be tested by cleaning batch to document that they meet method cleanliness requirements. Sampling equipment that comes in contact with the sample also should be tested and documented as clean. Field blanks use pretested reagent water to demonstrate that the sampling equipment and the sample collection techniques used in the field do not contaminate the sample. Many laboratories (including STL) can supply water for such uses. One field duplicate and one matrix spike duplicate pair are recommended for every 10 samples. The laboratory also can provide and analyze a trip blank if a client is concerned about contamination during transport.

Sample Shipping

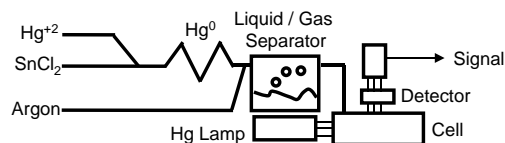
Affixing a client label on the outer bag of the bottle kit is necessary to ensure that the laboratory’s sample-receiving department can log in the sample properly without having to open the double bags. Facility labels on each sample bottle are not recommended. If a facility strongly desires to label each bottle, it should be done in a manner designed to ensure the cleanliness of the sample bottles and inner bag.

About 150 mL are needed for each sample to facilitate screening, dilutions, and reruns. Matrix spike samples need about 300 mL. Only bottles from the same sample should be packed in the same foam cube and bag to prevent cross contamination.

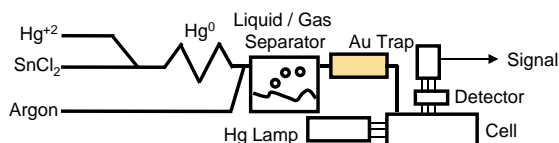
Method 1631 allows for field preservation with high-purity concentrated hydrochloric acid. However, STL recommends that samples be shipped to the laboratory on the day of collection, and that the laboratory preserve the samples with bromine monochloride within 48 hours of sample collection. Field preservation increases the opportunity for accidental contamination. STL is performing an EPA-funded holding-time study to demonstrate that unpreserved samples intended for total mercury analysis are stable for longer than 48 hours. Lengthening the unpreserved holding time should ease

Mercury Analyzers

Method 245.7 : Leeman Labs, Hydra AF



Method 1631 : Leeman Labs, Hydra AF Gold



As implemented on Leeman Labs Inc. (Hudson, N.H.) Hydra mercury systems.

some of the shipping constraints and facilitate more efficient sample handling both in the field and at the laboratory.

Sample Receipt and Preparation

When a sample cooler arrives at the laboratory, the sample-receiving department unpacks it and compares the client label on the outer bag with the chain of custody. The double bags are inspected for integrity (seals and tears), but not opened. After login, the samples are forwarded to the laboratory’s metals group for preservation. Inside the mercury clean area, the sample bags are opened, and laboratory labels are applied to each vial. A small amount of sample is removed from each vial for screening, and a bromine monochloride–hydrochloric acid solution is added to preserve the sample and start the oxidation process. Screening at large dilutions is done to protect the mercury analyzer from high-concentration samples and determine the proper dilution (if any) needed for final analysis.

Analytical Process

Method 245.7, which currently is undergoing the EPA approval process, is simpler and less sensitive than Method 1631, and has a reporting limit of 5 ng/L.

Method 245.7 starts with the oxidizer–preservation step using bromine monochloride as described above. After an overnight (or longer) oxidation step, hydroxylamine hydrochloride is added to remove excess oxidizer shortly before loading the sample into the mercury system autosampler. The automated instrument mixes stannous chloride with the sample to convert all mercury to the elemental form, which then is purged from the water with argon. The cold (room-temperature) mercury vapor is swept through an atomic fluorescence detector that produces a signal proportional to the amount of mercury.

The primary difference between Method 1631 (which fully approved by EPA and is being written into many new permits) and Method 245.7 is that Method 1631 requires the addition of one or two gold traps between the purge device and the atomic fluorescence spectrometer. The gold traps collect mercury from 40 to 100 mL of sample. Once the sample is completely purged of mercury, the trap is heated to release the mercury. This more concentrated mercury "slug" is swept into the atomic fluorescence spectrometer. The trapping step increases sensitivity by a factor of about 10 relative to Method 245.7.

The figure (above) illustrates the analysis segments of the two methods. For Method 245.7, the mercury-containing sample is pumped in from the autosampler and mixed with stannous chloride to convert it to elemental mercury. The mercury then is purged from the water in the gas-liquid separator and swept into the atomic fluorescence detector. Method 1631 is similar, except that a gold trap has been added between the gas-liquid separator and the detector. This trap accumulates the mercury from a large volume of sample, improving the sensitivity of the method.

To calibrate for Method 1631, several quality control specifications must be met. The relative standard deviation of the calibration factors must be less than 15%. The accuracy of the low standard must be between 75% and 125% of the true value. The calibration blank concentration must be less than the reporting limit of 0.5 ng/L. The next revision of Method 1631 likely will reduce the calibration-blank criteria to less than 0.25 ng/L.

Method detection limits were calculated using the standard process described in 40 *CFR* 136. STL's current method detection limits for Method 245.7 and Method 1631 are 0.9 and 0.06 ng/L, respectively. Both of these method detection limits meet the method requirements of 1.8 ng/L for Method 245.7 and 0.2 ng/L for Method 1631.

Ideally, method and calibration blanks should be completely free of mercury. However, many parts of the process contribute to measured mercury background

in the laboratory (see Table 2, p. 36). Careful control of reagents, environment, analyst, and equipment are necessary to meet the blank requirements of Method 1631 and produce accurate data at the reporting limit.

To maintain the cleanliness of the low-level-mercury area, access is limited to analysts who need to work there. Most metal fixtures either have been eliminated or coated to reduce metal exposure. There are designated spaces for various parts of the process: incoming samples, sample preservation, sample storage, low-level-sample preparation, calibration-standard preparation, and the mercury-analysis instrument.

By carefully designing the area and the process, it is possible to produce clean spaces without the expense of a full-blown clean room. For example, STL has installed a filtered-air autosampler that is important for maintaining sample cleanliness while samples wait for analysis.

Both methods 1631 and 245.7 are performance-based. Many labs (including STL) have implemented performance-based modifications for instrument automation, sample volume, reagent concentration, and composition. STL has discussed with EPA the most important challenges of implementing the manual Method 1631 on an automated system.

Although the sampling and analytical processes can seem cumbersome, they are necessary. Low-level-mercury testing is being driven by regulations based on documented bioaccumulation concerns. To improve the reliability of low-level-mercury results, it is important to pay close attention to many seemingly small details that can be very significant to the overall accuracy of the monitoring process.

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