Low-Level Mercury – Analytical Considerations

Sample Containers, Preservation & Holding Time

For low-level mercury analyses, there are two choices for sample containers, fluoropolymer (e.g. Teflon ™) or borosilicate glass. It is critical that the container caps seal tightly to avoid passive diffusion of mercury from the atmosphere. Each container should be double-bagged prior to shipment. We recommend that samples be shipped to the laboratory unpreserved and they no longer need to be iced during shipment. Under these conditions, samples must be preserved within 48 hours of sample collection. Method 1631 allows this period to be extended to 28 days if the sample is oxidized in the sample bottle. Bromine chloride or hydrochloric acid are appropriate preservatives.

Note: *Although high density polyethylene (HDPE) containers may be appropriate for higher level samples, method 1631 specifically prohibits their use for low level samples. Method development information indicated that passive diffusion from the atmosphere was too great to consider this type of container an acceptable option.*

Controlling Contamination: Focus on Sampling Procedures

Although laboratories are concerned with controlling sources of mercury contamination, experience has taught us that perhaps a bigger problem in obtaining reliable low-level mercury data is controlling contamination during sampling. The efforts necessary to control contamination increase significantly as detection limits and sample concentrations decrease.

Mercury tends to "stick" to surfaces so pumps and tubing used for composite sampling can be reservoirs of contamination. Equipment exhaust and dust can also be contributors. Even the sampling crew themselves can be a source of mercury contamination. In addition to worrying about contamination on hands and clothing, for very low level mercury sampling, your breath can contribute measurable amounts of mercury, particularly if you have amalgam dental fillings.

It might seem like collecting a reliable sample is an impossible dream, but it is possible to obtain a reliable sample for low level mercury by paying attention to hygiene. EPA method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (EPA 821-R-95-034) describes a "clean hands-dirty hands" procedure that has been shown to be effective. How rigorously you need to follow this procedure depends on the type of sample being collected, the sensitivity or detection limits desired, and the environment in which the sample is being collected.

The wastewater permits program is developing guidance for collecting samples for compliance. When this guidance is completed, it will be posted on the program's website.

Field Blank Requirements - Don't Skip Them!

Field blanks for mercury are defined as an aliquot of mercury-free reagent water that is placed in a sample container, shipped to the field and treated as a sample in all respects, including

contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures (definition from s. NR 106.145(9), Wis. Adm. Code).

A field blank is the best way to estimate how much mercury detected in a sample is "real" and how much is contamination. We encourage using a procedure for obtaining a field blank that exposes the blank to the same environmental conditions as the sample. One way to accomplish that uses "clean" procedures with the following basic steps (for a grab sample):

Before traveling to the collection site, fill the cleaned containers for the field blank and sample with reagent water. Double bag the bottles, with one bottle per double bag.
At the site, remove the field blank container from the double bags and discard the reagent water from the bottle. Remove the sample container from the double bags and pour the water from the sample bottle into the container for the field blank and return it to the double bags. Make sure that the container is labeled appropriately. Collect the sample and return the container to the double bags. Make sure that the sample is labeled appropriately.
Package for shipment. Avoid shipping highly contaminated samples with those for low level mercury. In general, at least one field blank is required for each day and sampling site. Field blank collection should be focused on effluent samples. NR 106.145(9), Wis. Adm. Code identifies the circumstances under which permittees may reduce the frequency for collecting field blanks.

At wastewater treatment plants, the permit may specify a 24-hour composite for the influent sample. The equipment and sample collection container should be cleaned before sampling and the tubing should be replaced regularly. Influent mercury concentrations typically exceed 50 ng/L so it's expected that most, if not all of the bias imparted by ambient contamination will be overwhelmed by the sample concentration. The logistical barriers of collecting a field blank through the composite sampler may be difficult to overcome. It may be necessary to devise other means to assess contamination in these samples.

Special Considerations

Because field blanks are so important in establishing the credibility of low level mercury data, we require them even for grab samples. The results must be reported with permit compliance samples.

For laboratories to maintain their capabilities for low level mercury analyses, they, too, must control contamination sources. Because mercury tends to stick to surfaces, it's easy to contaminate the instrument simply by analyzing samples. Higher concentration samples (100 ng/L and above) should not be analyzed with cleaner samples unless the samples are diluted or there are sufficient wash steps between samples to assure that there is no carry over of mercury from one sample to the next.

Clients should resist the temptation to request low level detection limits for samples that aren't that clean. Moreover, it's important that laboratories be notified about samples that are expected to contain higher levels of mercury so the samples can be handled appropriately to avoid contaminating the instrument.

Reporting Low-level Mercury Results

DNR identifies mercury as one of the substances that must be reported to the detection limit*. Results between the limit of detection (LOD) and limit of quantitation (LOQ) should be qualified

appropriately. Most compliance programs require that laboratories report their LOD and LOQ with the analytical results.

For wastewater permit compliance, the rules (NR 106.145) specify that reported results must be above the laboratory's quantitation limit unless the concentration is below 1.3 ng/L (the lowest water quality criterion in NR 105, Wis. Adm. Code). In other words, non-detects or qualified results for concentrations between LOD and LOQ are acceptable only if the concentration is below the water quality limit.

In addition to sample results, two types of blanks must be reported with results, field blanks and method blanks. Department staff evaluate blank results as part of their data quality assessment and compliance determinations.

Correcting Results for Blanks

Method blank concentrations may be subtracted from sample results *unless concentrations of mercury exceed the greater of the laboratory's LOD, 0.5 ng/L, or 5% of the sample result*. Remember that method blank concentrations must be reported whether or not sample results are corrected.

Field blank results must not be subtracted from sample results.

**__Note:__ The wastewater permits program requires that permittees report numerical values for all monitoring results greater than the limit of detection unless analyte-specific instructions in the WPDES permit specify otherwise. (NR 106.14(3)).*