

Introduction

Frontier Geosciences, Inc. (FGS) has been one of the pioneers of developing and popularizing ultra-clean sampling techniques for environmental trace metals research and monitoring. In 1996, FGS co-authored the U.S. EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. This method was designed to support water quality monitoring programs authorized under the Clean Water Act, specifically created for measuring toxic metals at ultra-trace levels (low part per trillion to low part per billion range). Although primarily designed for ambient water research, these ultra-clean methodologies are now used extensively for monitoring waste-water treatment discharges and for mixing zone studies as well.



Preventing ambient water samples from being contaminated during sampling and analysis is imperative. It has been recently shown that many of the historical trace metal concentrations in ambient waters were erroneously high, because samples were contaminated during sampling and analysis. To prevent such errors, this method describes reliable sample collection with the necessary steps to preclude contamination in nearly all situations. Performing ultra-clean sampling techniques is one essential component of lowering detection limits for trace metals research and monitoring. Ultimately, detection limits

also depend on the sample matrix, dilution levels, detector sensitivity, and other laboratory operating conditions. Although clean-sampling technique is often described as a “method,” it is better viewed as a flexible “philosophy,” which requires biogeochemical and analytical understanding by the practitioner, as well as a good dose of common sense.

Method Summary

All sampling equipment and sample containers used for metals determination must be nonmetallic and free from any material that may contain metals. A sampling kit consisting of proper containers, bags, clean-room gloves, and instructions for the “clean hands/dirty hands” collection method

should be obtained from FGS. Bottles for the “clean hands/dirty hands” collection method will be double-bagged.

The use of locally obtained or untested containers is strongly discouraged as they may be the source of possible contamination. If time does not allow for shipping of approved containers, the client is advised to submit a bottle blank with the project.

For total and methyl mercury analysis, sample bottles may be either Teflon, which has been cleaned, tested, and double bagged in a laboratory clean-room, or borosilicate glass obtained from a supplier which certifies cleanliness for metals sampling (e.g., I-Chem, Series 200 or equivalent). For trace metals analysis, pre-cleaned Teflon or high density polyethylene (HDPE) should be used.

Samples are collected using rigorous ultra-clean protocols which are summarized as follows...

...Ideally, at least two persons wearing fresh clean-room gloves at all times are required on a sampling crew. The person designated “clean hands” is responsible for all operations involving direct contact with the sample bottle and transfer of the sample from the collection device to the bottle. The person designated “dirty hands” is responsible for the preparation of the sampler, operation of any machinery, and all other activities that do not involve direct contact with the sample.

...“Dirty hands” pulls a bagged bottle from the cooler and opens the outer, dirty bag, avoiding touching inside that bag.

...“Clean hands” reaches in, opens the inner bag (if present), and pulls out the sample bottle. “Clean hands” should not touch anything but the sample bottle, its cap, and the water being sampled.

...This bottle is opened. Under no circumstance should the bottle cap be placed on any surface while it is removed from the bottle.

...The cap is replaced and the bottle re-bagged in the opposite order from which it was removed.

...Clean-room gloves are changed between samples and whenever anything not known to be trace metal clean is touched.

For Aqueous sampling

...The bottle (including its cap) is rinsed three times with the sample water, and then filled almost completely.

Ultra-Clean Sampling for Waters, Soil/Sediments, and Tissues

Leaving a small headspace (e.g. 1% of bottle volume) is acceptable and provides space for subsequent acid preservation at the laboratory.

For Sediment sampling

...The bottle is then filled almost completely with sediment using a utensil known to be free from trace metal contamination. The sampler should ensure that the sampling site is representative of the immediate area.

For tissue sampling (fish, invertebrates, plants, etc.)

...In this case, a jar may or may not be necessary depending on the size of the sample. Larger samples can be put directly into the inner plastic bag while smaller samples can be placed into a jar. Tissue samples should only be handled by a person with clean gloves.

submerge the mouth of the bottle quickly and fully to minimize contamination from the surface micro-layer. Samples are collected by a surface-activated discrete sampler (e.g., Go-Flo), or by pumping the sample to the surface. Either a rigorously cleaned Teflon and silicone peri-staltic pumping system (low flow), or a cleaned submersible pumping system (high flow) can be used.

Any metals leaching from the pump or sampling hose are effectively diluted to undetectable levels by either pumping system.

QA/QC Procedures

To ensure accuracy, it is critical that the sampling team also employ quality assurance/quality control (QA/QC) procedures. At least one field blank should be processed per site, or one per every ten samples, to confirm that contamination has not occurred during collection or processing. Before using any sampling equipment on site, equipment blanks (bottle

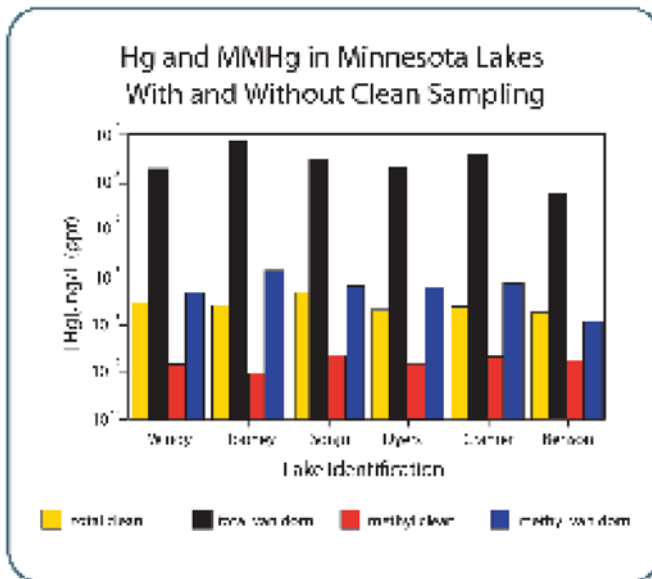
blanks and sampling equipment blanks) should be collected from each item that will be used in the field. To assess the precision of the field sampling and analysis, a field duplicate should also be collected at each site, or one field duplicate per every ten samples. In addition, extra samples should be collected to allow for necessary quality control analyses, such as matrix spike and matrix spike duplicate analyses.

Conclusion

The above description is a summary of ultra-clean sampling protocols. Please refer to Method 1669 for more details. The staff at FGS can also be contracted to conduct on-site training and seminars, or sample collection. FGS has an extensive collection of pre-cleaned, ultra-low level sampling equipment available. For more information on sample collection, contact Frontier Geosciences.

*Field preservation is required for the following analytes:

Total or Free Cyanide ~ 12mL 25% sodium hydroxide per 500 mL sample
Hexavalent Chromium ~ 12mL 25% sodium hydroxide per 500 mL sample
Fe(II) ~ 250µL concentrated hydrochloric acid per 250 mL sample



Samples should be sent overnight to the analytical laboratory unpreserved* to minimize contamination in the field. The samples will be preserved as required by the method after arrival at the laboratory. Sufficient ice should be added in the shipping container to maintain samples below 4 °C. Samples for total mercury and/or total metals analysis can be shipped at ambient temperature.



Samples may be collected from a boat or from land. Whenever possible, they should be collected facing upstream and upwind to minimize contamination due to the sampler, boat, or resuspended sediment. Surface samples are collected using a grab technique. The principle is to fill a sample bottle by rapid immersion of the collection bottle in water capping immediately to minimize exposure to airborne particulate matter. Care must be taken to