Environmental Sampling for Low-Level Trace Metals per EPA Method 1669

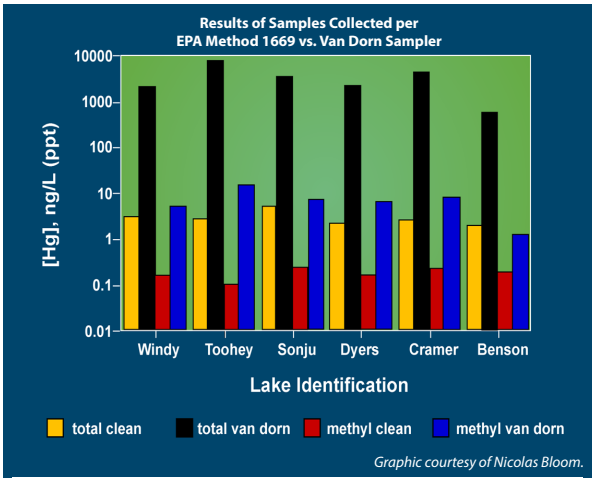
In an effort to achieve the ambient level detection limits for various metals required by the Clean Water Act, the US Environmental Protection Agency (EPA) developed a number of "performance-based" analytical methods specifically for the measurement of metals and metal species at ultra-trace levels, from low parts-per-billion to sub parts-per-trillion concentrations.

These analytical methods include EPA Method 1630 for the determination of methylmercury, EPA Method 1631 for the determination of low-level mercury, EPA Method 1632 for the determination of various arsenic species, EPA Method 1638 for the determination of trace metals by ICP-MS, and EPA Method 1640 for the determination of trace metals in seawater by ICP-MS.

However, during the development of these analytical methods the EPA found that one of the greatest difficulties in obtaining reliably accurate data for metals at such low concentrations was not necessarily due to any technical limitations of the methods, but rather due to contamination occurring from improper collection, handling, and transporting of the samples.

Therefore, "clean" sampling and handling techniques were developed to avoid the inadvertent contamination of samples prior to analysis, as described in EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Samples to be analyzed by any of the above 1600-series methods should be collected according to these procedures in order to ensure the accuracy of any reported results.

Below is a graph that shows total mercury and methylmercury results for samples collected from six lakes in the Great Lakes Area using two different sampling techniques. The results reported when samples were collected using a conventional Van Dorn sampling apparatus were orders of magnitude greater than those reported when samples were collected using the techniques described in EPA Method 1669.



This method entails specific sample collection procedures in order to minimize and monitor for contamination. This includes the exclusive use of ultra-clean and pre-tested sample collection containers and other field-sampling equipment.

In order to demonstrate compliance with the method, it can also be necessary to collect extensive field quality control samples, such as:

- trip blanks
- field blanks
- equipment blanks
- field duplicates

The table below outlines the recommended containers, field preservation, temperature ranges, and holding times for preservation and analysis, per analytical method.

EPA Method 1669 also requires that a two-member team participate in the collection of samples. "Clean Hands" is responsible for all procedures involving direct contact with the sample and the sample container. "Dirty Hands" is responsible for preparing the sample containers for collection, operating any machinery, and all other activities that could lead to contamination of the sample.

"Dirty Hands"

- does not disturb sample source
- does not touch primary container bags
- does not touch sample containers
- does not touch "clean equipment"
- handles all "non-clean" materials
- opens/closes shipping containers
- opens/closes secondary container bags
- operates pump/metallic equipment

"Clean Hands"

- does not touch "non-clean" materials
- does not touch secondary container bags
- does not touch shipping containers
- handles all "clean" materials
- assembles sample tubing & filters
- directly contacts sample source
- opens/closes primary container bags
- directly holds sample container

All samples are collected and shipped to the laboratory for analysis in the specified containers, which are also individually double-bagged to prevent potential cross-contamination. Since field preservation and filtration presents yet another opportunity for sample contamination, it is strongly preferred when feasible to rush ship samples from the field to an ultra-clean laboratory where conditions are more controlled.

General Container & Preservation Recommendations for Aqueous Samples

Analyses	Container	Field Preserve	Temperature	Holding Time
Trace Metals ICP-MS	125-250 mL HDPE	no	ambient	Preserve - 14 days Analysis - 180 days
Trace Metals EPA 1640 (seawater)	125 mL-2 L HDPE	no	ambient	Preserve - 14 days Analysis - 180 days
Total Mercury EPA 1631	125-250 mL FLPE or glass	no	ambient	Preserve - 28 days Analysis - 90 days
Methylmercury EPA 1630	250 mL FLPE or glass	preferably	0-4 °C	Preserve - 48 hrs. HCl ▲ Analysis - 180 days
Arsenic Species EPA 1632	125-250 mL HDPE	yes	0-4 °C	Preserve - immediately HCl Analysis - 28 days
Arsenic Species★ IC-ICP-MS	125 mL HDPE 6mL vacutainer	yes	0-4 °C	Preserve - immediately EDTA Analysis - 28 days
Cr(VI) ★ IC-ICP-MS	125 mL HDPE	yes	0-4 °C	Preserve - immediately $NH_4OH/(NH_4)_2SO_4$ Analysis - 28 days (14 days for DW)
Selenium Species★ IC-ICP-MS	125 mL HDPE	no	0-4 °C	1 year (cryofrozen at lab)

Samples that will be filtered in the laboratory *must not* be field preserved, *must* be kept cold, and *must* be rush shipped. There are matrix specific recommendations for the filtration and preservations of many sample types; therefore, it is always recommended to confirm sampling plan with a Brooks Applied Labs staff member prior to sample collection.
★ *Field filtration is strongly recommended to avoid co-precipitation of metals.* ▲ *Saline waters preserve with* H_2SO_4.

While EPA Method 1669 contains a significant amount of detail regarding the precise manner in which samples should be collected in a number of different situations and using various equipment, it is crucial to recognize that this method is also "performance-based" like other 1600-series methods.

Preventing sample contamination requires more of a philosophy than a strict procedure, and the method can be altered to accommodate specific data quality objectives or field conditions so long as the quality control program is sufficient to demonstrate the cleanliness of the technique.

Sampling Services & Training

Due to our extensive experience performing EPA Method 1669, Brooks Applied Labs is frequently contracted to provide sampling services for specific projects that demand exceptional quality. We also frequently lead instructional courses at conferences and under contract to clients in how to properly perform this ultra-clean technique.

Our full-day instruction courses include a half-day in the classroom with lectures covering the circumstances under which low-level detection limits are be required, the EPA analytical methods that must be used, proper handling and preservation of samples, necessary sampling supplies, considerations that should be made prior to and during sampling activities in order to avoid contamination, various sampling and field-filtration techniques, and field quality control sample collection requirements.

The second half of the day, participants engage in hands-on field exercises where they are given the opportunity to practice several surface water sampling protocols using various sample collection methods and following the "Clean Hands/Dirty Hands" techniques.

Certified Clean Sampling Equipment

At Brooks Applied Labs, we routinely provide our clients with sample collection equipment that is cleaned, tested, and certified to be free of trace metals, ensuring that sampling can be performed in compliance with EPA Method 1669, that the requisite field quality control samples are collected, and that potential sources of contamination are identified or eliminated. All sampling equipment is double-bagged and typically shipped in sealed coolers directly to field locations.

BROOKS APPLIED LABS CERTIFIED

- FLPE and HDPE bottles
- FLPE and HDPE jars
- FLPE and HDPE carboys
- reagent water for collecting blanks
- fluoropolymer and silicon tubing
- in-line and syringe filters
- gloves
- preservatives

To learn more about this innovative method and how it can benefit your projects or about our sampling services and instructional courses, contact us today. Please visit our website at **www.brooksapplied.com**, email us at **info@brooksapplied.com** or call **206-632-6206**.