



Global Best Practices for High Quality Analysis of Waters for Trace Metals & Mercury

This EnviroMail highlights important practices for the collection of water samples for analysis of trace metals and mercury which can greatly improve the quality of test results, preventing false positives and false negatives, while also improving the efficiency of field sampling events.

Ultra-Clean Sample Bottles for Trace Metals

One of the most crucial aspects of trace metals analysis is the quality of the sample container. All plastics will leach trace amounts of common metals when exposed to nitric acid preservative, and for many metallic elements, the quality of the sample container is the most limiting factor where trace-level detection limits (DLs) are needed.

ALS recently conducted a global study of sample containers to identify the best and cleanest bottles used by any of our trace metals labs around the world, evaluating over forty sample containers sourced from seven countries. We conducted ultra-trace metals testing down to 1/10th of the ALS Canada trace metals DLs, with testing done at two ALS labs that offer some of the lowest commercially available metals DLs in the world – in Vancouver and Lulea, Sweden. Testing protocols included short and long-term leaching studies with acidified samples as well as suitability testing for use with pre-charged concentrated nitric acid, which is a common practice for metals testing in some regions. Our studies confirmed that pre-charging any plastic containers with concentrated nitric acid tends to liberate higher concentrations of many common elements from the container walls (e.g., chromium), which can limit the levels to which reliable DLs can be provided.

By using sample containers selected specifically for their suitability and cleanliness for trace metals, in conjunction with rigorous bottle proofing protocols, ALS can offer lower DLs with confidence that false positives will not occur due to contamination from sample bottles.



Figure 1: Illustrative picture

Our container selection and proofing protocols are designed to ensure that prerinsing with sample is never required or even recommended for any tests we offer.

Preservation of Metals with Nitric Acid

Sample preservation is used with many tests to ensure test analytes are stabilized, so measured sample concentrations represent the sample condition at time of collection. For trace metals, preservation with nitric acid reduces sample pH to < 2 to ensure solubility of metals prior to analysis, preventing sorption to container walls or precipitation as metal oxides or hydroxides.

Traditionally, preservation for metals has been conducted in the field, but recently there has been recognition that lab preservation of metals samples is preferable for numerous reasons. In fact, the US EPA has recommended lab preservation as the best practice for sampling of metals in water for at least 35 years (Method 200.2, 1989). Among other benefits, lab preservation avoids restrictions with Transportation of Dangerous Goods (TDG), and avoids contamination risks and hazards that can occur when handling concentrated acids in the field.

Lab Preservation – Best Practice for Trace

Lab preservation is recommended as the best practice for trace metals analysis of waters to maximize data quality and to improve sampling logistics. Requirements for lab preservation of metals are that samples must be preserved with nitric acid in their original sampling container, with no sub-sampling or analysis permitted until completion of a 16-hour equilibration period, to ensure full solubilization of metals prior to analysis. Because of the 16-hour equilibration requirement, lab preservation is unsuitable for same-day analysis requirements. Hold times are the same as for field preservation (6 months from time of sampling), as long as preservation occurs within 14 days of sampling.

Lab preservation is suitable for total metals and for fieldfiltered dissolved metals. In all cases, field filtration is required to provide defensible test results for dissolved metals (refer to section on field filtration for more details).

Lab preservation offers data quality improvements over other preservation options for several reasons:

- Lower and more reliable detection limits can be offered - especially for chromium - versus containers pre-charged with nitric acid, due to leaching of metals over time from plastics by concentrated acid. Low-level chromium DLs are useful to screen for aquatic life risks due to hexavalent chromium.
- Contamination risks are minimized by reducing physical handling in the field, and by collecting samples quickly with minimal exposure to dust (e.g., at windy mine sites).
- Eliminates potential cross-contamination of nutrient samples with nitrate from nitric acid.
- Addition of acid preservatives in the lab utilizes highgrade nitric acid, tested daily before use for purity control, and added to samples in a clean, controlled, dustfree environment.

Where the absolute lowest possible DLs are required, ALS recommends lab preservation with specially prepared acidcleaned bottles (ACBs), which we provide for specific specialty test codes for ultra-trace level metals.

Related EnviroMail

EnviroMail 03 / Europe: Proper Water Sampling Practise Prior to Metals Determination

Field Preservation for Metals: Applications and Precautions

ALS also offers two field preservation options for metals in special circumstances.

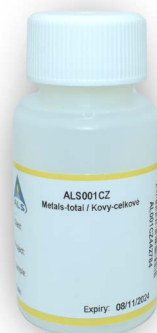
The use of pre-charged sample containers for metals in water is an effective and easy-to-use approach, although the DLs of some metals (chromium) are limited.

Field preservation can also be achieved using small vials of 18% wt/wt nitric acid which are added to samples in the field. This is a good option where same-day analysis is required (to avoid the 16-hour equilibration time for lab preservation), but requires additional precautions to reduce contamination risks for metals or nitrate during sampling.

Mercury Sampling with Pre-Charged Glass Vials

Best practice for collection of water samples for testing of mercury is quite different from other metals. Because dissolved mercury can readily sorb to plastics (especially at low or trace levels). Unlike other metals, dissolved mercury is stabilized much more effectively with hydrochloric acid than with nitric acid, because mercury tends to form the stable anion $[HgCl_4]^{2-}$ in the presence of HCl, which helps to prevent sorption to container walls.

Lab preservation is also possible for mercury, but the equilibration period at the lab after preservation is longer than for other metals, at 24 hours versus 16 hours, which often adds an additional day to turnaround times. Water samples for routine-level mercury testing are normally sampled in 40 mL glass vials with tightly-sealed leakproof PTFE-lined septa caps, which virtually eliminates leaks. ALS recommends pre-charged mercury vials for routine-level testing because this practice expedites turnaround times with no significant disadvantages.



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