



Mercury Preservation Techniques

Background

The analysis of environmental samples and the value of the observed data are dependent upon several factors:

- how representative the sample is,
- how stable the sample is, and
- how reliable the analytical procedures are.

Historically, interest has been focused on the stability of mercury compounds, especially in aqueous matrices. Factors that affect mercury stability include: the form of mercury, the container material, the matrix, and the preservation techniques.

The currently accepted method in the contract laboratory program (CLP) inorganic statement-of-work (SOW) for preservation of mercury samples requires a stabilization with 2% HNO₃ with an allowed holding time of 26 days prior to instrumental analysis. Researchers at the National Exposure Research Laboratory, Exposure Dose Research Branch in Las Vegas (EDRB-LV) have investigated the reliability of 2% HNO₃ as a preservative by studying the analytical data from synthetically prepared Performance Evaluation (PE) water samples. Aqueous quarterly blind (QB) samples that were spiked with inorganic forms of mercury showed significantly low mercury recoveries when analyzed using 2% HNO₃ preservative. Some researchers believe that mercury ions bind to the reactive sites on the surface of the high-density polyethylene (HDPE) water sample containers. Mercury ions are thought to be reduced at these sites. Then elemental mercury is lost on or through the walls of the plastic bottles. Mercury vapor may also be lost when the bottles are uncapped. Thus, mercury ions are lost to subsequent analyses and reenter the environment. Most low level (less than 100 ppb) mercury in synthetic environmental samples is lost within just a few days using 2% HNO₃ preservation.

The research challenge was to find a method for stabilizing aqueous mercury samples that would be simple to use in the field, effective at retaining the true mercury concentration, and could be used with all major inorganic analytical instruments without presenting an interference. Though several potential preservatives were tested, only one was found that would meet requirements.

The EDRBLV Solution

Researchers at the EDRB-LV found that a trace amount of gold chloride (AuCl₃) added to the HNO₃ solution preserved all forms of mercury. The gold acts as a strong oxidizing agent that converts or maintains mercury as mercuric ion which remains in solution. Optimization of this technique revealed that a 1 ppm solution of AuCl₃ in HNO₃ was sufficient and did not affect any other analytes or analytical techniques.

The price of gold is not a major factor in the overall cost of sampling and analysis because such low quantities of gold are needed. The cost for the AuCl₃ is only about 10% of the cost of the HNO₃ — or, about \$3 per 100 samples.

Inorganic samples preserved with AuCl₃ can be analyzed by anodic stripping voltammetry (ASV), cold vapor atomic absorption spectrometry (CVAAS), and even by inductively coupled plasma mass spectrometry (ICP-MS), without interferences from the gold in solution. Previously, ICP-MS was not used for mercury analysis because the mercury would deposit in the ICP-MS sample introduction system and be released during subsequent analyses (carryover). The gold stabilization method directly prevents deposition by keeping all mercury in solution. The ability to use ICP-MS for mercury analysis adds a valuable multi-element instrument to the suite of mercury detection systems.

There are additional benefits to using AuCl₃. Preservation with AuCl₃ doubles the solubility of silver in 2% HNO₃ and therefore helps stabilize silver. Silver is a relatively unstable element in water samples and this added preservation is a bonus.

Application

When water samples are taken for mercury analysis, field personnel should add HNO₃ with AuCl₃ to a final concentration of 2% HNO₃ and 1-ppm AuCl₃. The current procedure only calls for HNO₃. The samples can then be shipped to the analytical laboratory and analyzed without concern about mercury holding times. Early EDRB-LV experiments indicated that mercury concentrations in samples preserved with AuCl₃ and did not decrease even after two years of storage. Using the AuCl₃ preservative, NIST trace mercury in water standards (SRM 1641B) are stable for at least 10 years

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(the certificate value can still be met when analyzing 10-year-old 1641B). By extending the length of time samples can be held before analysis and by providing a simple method for ensuring sample integrity, the AuCl₃ spiking procedure could save time, money, and enhance data reliability. Costs to monitor and enforce mercury holding times would no longer be an issue when AuCl₃ preservation techniques are used.

Limitations

Experiments show that adding concentrations of several ppm AuCl₃ can precipitate Au and, therefore, may threaten to coprecipitate other analytes. But even at 2 ppm (twice the recommended concentration), coprecipitation was not observed in synthetic samples. If field personnel inadvertently add twice the amount of AuCl₃ needed, there would be no negative effect on the analytical results.

References

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