

Effectiveness of the Preservation Protocol within EPA Method 200.8 for Soluble and Particulate Lead Recovery in Drinking Water

Regional Applied Research Effort - Addressing Drinking Water Challenges through Science and Innovation

Background

The U.S. Environmental Protection Agency (EPA) is responsible for establishing national regulations under the Safe Drinking Water Act (SDWA). Regulations protect public health by establishing Maximum Contaminant Levels (MCLs) or other enforceable thresholds for contaminants including microorganisms, disinfection byproducts, inorganic/organic chemicals, and radionuclides. Water quality monitoring by drinking water utilities is necessary to demonstrate regulatory compliance with these enforceable limits.

The Lead and Copper Rule (LCR) is unique when compared with other regulations because compliance sampling for lead (and copper) occurs at household taps rather than at the entry point to the distribution system. This is because premise plumbing materials can be primary sources of lead and copper contamination. Furthermore, the LCR established an action level (AL) rather than an MCL for lead (and copper). If more than 10% of the water samples exceed an AL of 0.015 mg/L for lead, then the drinking water utility is required to implement certain treatment techniques to control lead corrosion.

EPA Method 200.8

EPA Method 200.8 (Figure 1) is an accepted method for the determination of total lead and other trace elements in water (and wastes) by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Among other instructions, the method provides a protocol for standard acid preservation of water samples to pH < 2 because this step can affect lead quantification. If the sample turbidity is > 1 NTU, more rigorous subsequent acid digestion is also required. Adding acid preservative to water samples aims to prevent metal precipitation and reduce metal adsorption onto the walls of sampling bottles, thereby rendering all the metal soluble and thus quantifiable by ICP-MS.

Review of the literature indicates that the extent of lead contamination, the form of the lead (dissolved versus particulate), the preservation pH, the type of sampling container, and the type of water sample are important factors affecting acid preservation of water samples for lead quantification.

Project Purpose

The purpose of this project was to investigate the effectiveness of the sample preservation protocol outlined in Method 200.8 in recovering lead from water samples. Lead recoveries were studied in various water samples spiked with lead by evaluating lead sorption and desorption from sample bottles using ICP-MS. Specific concerns with the acidification protocol, bottle types and occurrence of particulates in water were investigated in two phases. Phase One of the study (Figure 2, left) focused on the recovery of 50 µg/L dissolved lead within different water sources, bottle types and preservation pHs. The lead recovery in glass and high-density polyethylene (HDPE) bottles was examined in DI water,

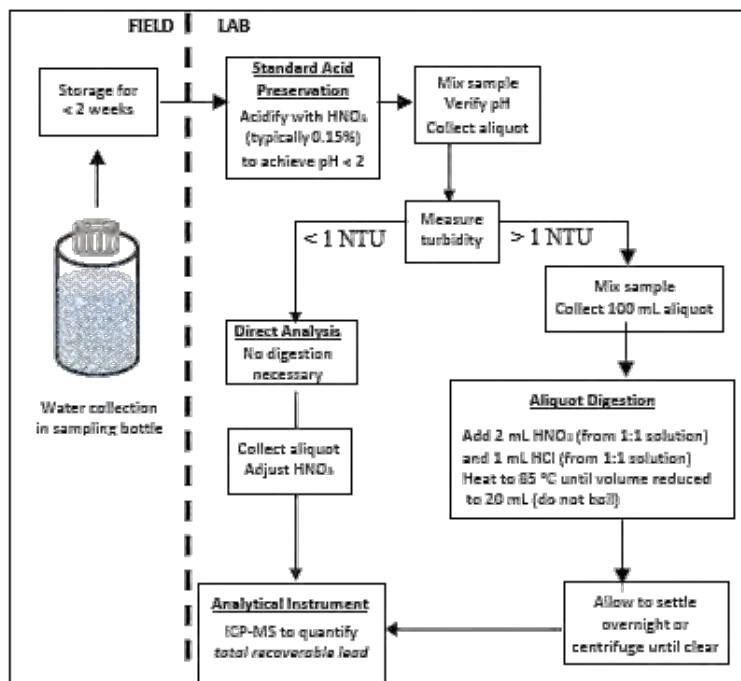


Figure 1. EPA Method 200.8 (ICP-MS) specifies procedures to quantify total recoverable lead (and other trace metals) in drinking water samples.

ground water, surface water and DI water containing 100 mg/L calcium (Ca). Similarly, lead recovery was compared between altered sample preservations at pH 2, 4, 5, 6 and 7. Phase Two examined the recovery of particulate lead from water samples using direct and total recoverable analyses. Specifically, the recovery of lead phosphate, basic lead carbonate and lead (IV) oxide was evaluated.

Phase One Results & Conclusions

Unpreserved glass bottles showed a significant decrease in lead concentration prior to acidification in all water sources. Within these glass bottles, DI water showed the greatest decrease (Figure 2, right), followed by ground water, surface water and then DI water spiked with Ca. After acidification to a pH < 2, lead recovery increased and showed no significant difference to the immediately preserved bottle in the DI (Figure 2, right), surface, ground and DI spiked with Ca trials.

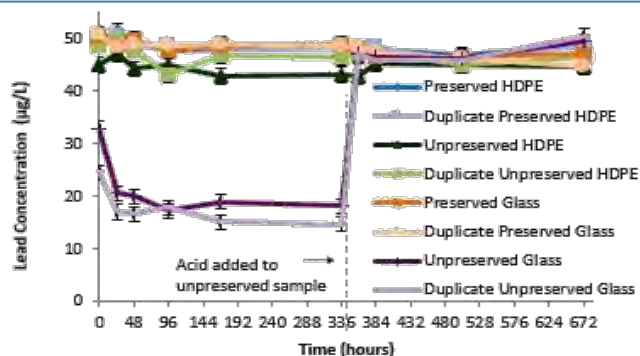


Figure 2. LEFT: Duplicate 2 mL aliquots from each sample bottle (HDPE versus glass) were collected for lead analysis at specified time intervals in Phase One. RIGHT: Representative results of lead concentration in DI water contained in glass and HDPE bottles in Phase 1.

In the trials investigating the relationship between lead recovery and preservation pH in DI water samples, as pH increased, lead recovery decreased. As also seen within the other water source trials, the lowest lead recovery occurred in glass bottles preserved to pH 7 in this trial. It was also determined that pH 4 was not an optimal preservation pH because it did not always yield as high of a lead recovery as pH < 2. In some cases, there was a significant difference between preservation to pH 4 and to a pH < 2. This difference was seen in DI, surface and ground water samples collected in glass bottle; however, this difference was not seen in the bottles containing DI water spiked with 100 mg/L Ca. It is believed that calcium competed with lead to occupy sorption sites on the bottle's surface, thereby forcing lead to remain in solution at both preservation pHs.

Overall, samples preserved to pH < 2 recovered greater than 90% of the initial spiked dissolved lead concentration of 50 µg/L, independent of sample container type and delays in acidification.

Phase Two Results & Conclusions

Recovery of lead particulates was more problematic than recovery of dissolved lead. A "well mixed" acid preserved sample was not always attainable due to particulate inhomogeneity even if samples were vigorously agitated prior to aliquoting. A concentration of 2% HNO₃ and 1% HCl provided complete solubilization of the three investigated lead compounds. This technique would require the addition of large amounts of reasonably expensive high purity acids (i.e., 20 mL nitric and 10 mL hydrochloric acid) to the 1L water samples mandated in the LCR. An alternative pre-filtration procedure offers advantages over the digestion procedure, specifically given the lower cost associated with the acid requirements. However, recovery of lead was not complete at 88.6% on average after the pre-filtration procedure.

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