Quantification of Trace Mercury in Water: Solving the Problem of Adsorption, Sample Preservation, and Cross-Contamination

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Adsorption, sample preservation, and cross-contamination are the major impediments to the accurate and sensitive analysis of low-level mercury samples. Common measures to deal with this issue are to use Teflon, quartz, or borosilicate glass bottles for sampling, standard solution and sample preservation with oxidative chemicals, to prepare standard solutions daily and to use dedicated glassware. This paper demonstrates that these measures are neither efficient nor effective. Two common laboratory sample containers (borosilicate volumetric glass flasks and polypropylene tubes) are investigated for the preparation and preservation of water samples and standard solutions of 0.2–1 µg L\(^{-1}\) with 2% HNO\(_3\). Mercury adsorption rates of 6–22% are observed within 30 min and after 48 days, the adsorption is greater than 98%. In stark contrast, no adsorption is found during a testing period of 560 days when the solutions are subject to potassium permanganate-persulfate digestion. New glass flasks and polypropylene bottles are free of mercury contamination but reused flasks are a major source of mercury cross-contamination. To minimize adsorption and cross-contamination, standard solutions are treated by potassium permanganate-persulfate or BrCl digestion, and each individual sample and standard solution should be stored and prepared in single-use polypropylene bottle, without transference.

1. Introduction

Mercury pollution is one of the world’s major environmental threats and its toxicity and damage to human health, in particular to young children, has been clearly established.\(^1\) Global mercury emissions have surged since the 1950s and currently human activities result in mercury emissions of 2000 metric tons per year.\(^2\) Bioaccumulation of mercury in fish is well recognized and hazards associated with eating fish have become public health concerns.\(^3\) A typical example of the impact of mercury pollution on humans is Minamata disease discovered in Japan in 1956 (2265 victims were officially recognized and 1784 of whom died). High concentrations of mercury in North American freshwater fish have prompted health authorities in Canada and most U.S. States to warn against eating too much fish.\(^4\) A full understanding of mercury toxicity and damage to the environment and living organisms is dependent on the accurate and sensitive analysis of mercury and its speciation.\(^5\)

The common laboratory practice for the preservation of sample and calibration standard solutions for trace metal analysis is to use volumetric glass flasks and/or high-density polyethylene (HDPE) plastic bottles and 2% v/v HNO\(_3\). For most elements, standards and samples at µg L\(^{-1}\) and mg L\(^{-1}\) with 2% v/v HNO\(_3\) are stable for months. However, mercury
Table 1. Instability of mercury samples and solutions reported in the literature (1972–2013).

| Sample type       | Container | Hg Conc. [µg L⁻¹] | Preservation | Mercury loss rate | Year [Ref.] |
|-------------------|-----------|-------------------|--------------|-------------------|-------------|
| Distilled water   | PE        | 50                | pH 1, HCl    | 100% in 10 days   | 1972[6h]    |
| Creek water       | PE        | 50                | pH 1, HCl    | 80% in 10 days    | 1972[6h]    |
| Distilled water   | PE        | 25                | 2% HNO₃      | 75% in 150 h      | 1973[6f]    |
| Distilled water   | Glass     | 1                 | 1% HNO₃      | 70% in 10 days    | 1974[6f]    |
| Distilled water   | PE        | 1                 | 5% HNO₃      | 75% in 15 days    | 1979[6f]    |
| Distilled water   | PE        | 1                 | 1% HNO₃      | 75% in 15 days    | 1983[6f]    |
| Distilled water   | PE        | 30                | 0.5 µ L HNO₃ | 100% in 50 days   | 1988[6f]    |
| Distilled water   | PE        | 4                 | 1% HNO₃      | 87% in 12 days    | 1990[6f]    |
| Potable water     | Glass     | 1                 | 2% HCl       | 40% in 10 days    | 1996[6f]    |
| Lake water        | Teflon    | 0.01–0.4          | 2% HNO₃      | 50% in 10 days    | 2005[6f]    |
| Distilled water   | PP        | 1                 | 10% HNO₃     | 94% in 7 days     | 2005[6f]    |
| River Water       | Teflon    | 0.003–0.013       | 1% HCl       | 70% in 7 days     | 2013[6f]    |

*PE, PP, and HDPE denote polyethylene, polypropylene, and high-density polyethylene.*

Standards and samples are an exception. Significant losses of mercury from µg L⁻¹ solutions have been observed regardless of container materials (typical examples are summarized in Table 1).[6f] The proposed mechanisms for this instability of mercury standard and sample solutions have included adsorption on the container’s interior wall, mercury volatilization/permeation and conversion of mercury species.[6d,7] Parker and Bloom reported that acidification of environmental waters with 2% HNO₃ may cause coagulation of natural organic matter (NOM) on to which mercury may be adsorbed.[6d] The adsorbed Hg²⁺ can be reduced to Hg²⁺ and/or Hg⁰ (elemental mercury) in the presence of a reducing agent occurring either naturally (i.e., micro-organisms, humic acids)[8] or as impurities in solution[9] or by photoreduction.[10] Hg⁰ could then disproportionate spontaneously producing Hg²⁺ and elemental mercury.[9,11] Consequently, elemental mercury is lost by permeation and diffusion through the wall of plastic bottles[6d,e,9,12] and volatilization and diffusion through the threads of the bottle cap.[13]

The mechanism for the loss of mercury from solution has long been a subject of debate.[6d,7] For instance, the adsorption mechanism is unable to explain why similar rates of adsorption have been observed for containers of different materials (Table 1). Feldman[6e] observed 70% losses of mercury from 1 µg L⁻¹ in 1% HNO₃ in 250 mL glass flasks in 10 days while Heiden and Aikens[6b] reported 75% losses for similar solutions in 500 mL PE containers in 15 days. We also observed similar rates of mercury losses from µg L⁻¹ solutions preserved in 50 mL volumetric glass flasks and PP centrifuge tubes. Creswell et al. observed positive biases of total mercury analysis from 2% HNO₃ and that water samples be preserved with HNO₃, HCl, BrCl, KBrO₃, or KBr in HDPE, glass or fluoropolymer bottles on collection or within 48 h of collection.[15] Nevertheless, substantial losses of mercury in quartz and glass containers were still observed within 30 min from preparation.[15] In addition, handling and manipulation of strong acids or oxidative, hazardous chemicals in field sampling pose safety and environmental risks.[15c-f]

To reduce the risks of mercury contamination, the U.S. EPA standard methods require that at least 5% of the bottles from a given lot should be tested by filling with reagent water acidified to pH < 2, standing for a minimum of 24 h and then analyzing for contamination (24 h acid filling test).[15c,f] However, we often observed mercury contamination for glass flasks after sample digestion even though the flasks had been identified as not contaminated by the 24 h acid filling test prior to sample digestion. Parker and Bloom found that new glass flasks were free of mercury contamination.[6e] However, the use of new volumetric glass flasks for each sample and standard solution is a very costly imposition for routine analysis and testing.

The accurate determination of mercury concentrations at low levels has long been a challenge[5d,e,7a,14,16] and the problem is illustrated by an inter-laboratory proficiency study of trace mercury analysis in water (Figure 1), which demonstrates the wide variability of determinations. It is generally recognized that the instability of mercury solutions and mercury cross-contamination are the two major causes for the large errors in trace mercury quantification. This study is aimed at investigating the stability of mercury solutions and samples preserved in glass flasks and PP centrifuge tubes and the elimination of mercury cross-contamination to improve the accuracy of trace mercury quantification.

2. Results and Discussion

As discussed previously, considerable losses of mercury from µg L⁻¹ solutions (2% HNO₃) were observed within 30 min...
from preparation. Indeed, we observed 6–22% losses of mercury from standard solutions of 0.2–1 µg L$^{-1}$ in 2% HNO$_3$ from 50 mL volumetric glass flasks within 30 min from preparation. The solutions lost 36–43% of mercury from 50 mL PP centrifuge tubes in one day and the losses increased with standing time of the solution, reaching 98% by 48 days (Figure 2).

Overall, no significant differences were observed in the stability of standard mercury solutions (0.2–1 µg L$^{-1}$ in 2% HNO$_3$) stored in glass flasks and PP tubes while the adsorption rates observed here were similar to the results reported in the literature (Table 1). Interestingly, mercury solutions were quite stable in the 50 mL PP tubes during the test period of 560 days following KMnO$_4$–K$_2$S$_2$O$_8$ digestion (Figure 2). The treated solutions were tightly capped and placed on the laboratory bench. This observation indicates that the container material (glass or PP), light radiation and seasonal variations in ambient room temperature had no influence on the stability of mercury solutions after the KMnO$_4$–K$_2$S$_2$O$_8$ digestion.

The KMnO$_4$–K$_2$S$_2$O$_8$ digestion is designed to oxidize all Hg species to inorganic Hg$^{2+}$ and therefore should have no effect on the Hg$^{2+}$ in the standard mercury solutions, which are prepared by simply diluting the stock solution (20 mg L$^{-1}$ in 4% HNO$_3$) with 2% HNO$_3$. In this context, the long-term stability of mercury solutions after the KMnO$_4$–K$_2$S$_2$O$_8$ digestion was because the digestion deactivates the interior surface of containers, thus preventing adsorption of mercury. To verify this hypothesis, the glass flasks and PP tubes were treated with the KMnO$_4$–K$_2$S$_2$O$_8$ digestion to “deactivate” the interior surface of the flasks and tubes and then mercury solutions were added for the stability test. The solutions prepared with 2% HNO$_3$ in the “deactivated” glass flasks and PP tubes lost greater than 65% of mercury after 48 days whilst the solutions prepared with the “digestion solution” were stable both in “un-deactivated” and “deactivated” containers (Figure 3). Thus the KMnO$_4$–K$_2$S$_2$O$_8$ digestion can be seen to play no role in deactivating container surfaces.

The oxidative chemicals (K$_2$Cr$_2$O$_7$, KBrO$_3$, KMnO$_4$, or BrCl) are designed to maintain mercury in the form of Hg$^{2+}$ in an oxidizing environment. Clearly, mercury in the solutions prepared with “digestion solution” was not in an oxidizing environment because the oxidative chemicals KMnO$_4$ and K$_2$S$_2$O$_8$ are completely reduced by the presence of the excess reducing agent, hydroxylamine hydrochloride (see Section 4, Experimental Section). The digestion solutions consisted of K$^+$, SO$_4^{2-}$, Mn$^{2+}$, Cl$^-$, NH$_4^+$, and HONH$_3$Cl and are of high ionic strength and it is possible that the presence of these ions
prevents the adsorption of mercury. Indeed, inorganic ions such as Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4^{2-}\), HCO\(_3^-\), Na\(^+\), and K\(^+\) could occupy the active sites of the container’s interior surface, thus reducing the rate of mercury adsorption.\(^{[7a]}\)

To examine the effect of ionic strength on mercury stability, we added NaCl and NaNO\(_3\) to the solutions (Figure 4). The stability of mercury increased with increasing ionic strength (i.e., salt concentration). Mercury was more stable in NaCl solutions than in NaNO\(_3\) solutions and mercury solutions prepared with NaCl and NaNO\(_3\) were more stable in glass containers than in PP plastic containers. The increased stability of mercury with increased NaCl concentration has been observed previously.\(^{[17]}\)

Considering the stabilizing effect of NaCl and NaNO\(_3\), we also investigated the desorption of mercury from the interior surface of 50 mL glass volumetric flasks and 50 mL PP tubes by NaCl and NaNO\(_3\). The samples of 25 mL 2% HNO\(_3\) solution containing 0.05 µg Hg (i.e., 2 µg L\(^{-1}\)) in 50 mL glass flasks and PP tubes were placed on laboratory bench. After 28 days, 25 mL 6% NaCl or 6% NaNO\(_3\) was added and then equilibrated for 7 days prior to CVAFS measurement. We found that 94 ± 2% and 74 ± 3% of mercury was recovered from glass by NaCl and NaNO\(_3\), respectively and much lower recoveries (54 ± 1% and 53 ± 1%) from the PP tubes. Therefore, the addition of salts (i.e., increasing ionic strength) is able to desorb mercury from glass and plastic PP containers. In this context, it would be interesting to see whether the KMnO\(_4\)–K\(_2\)S\(_2\)O\(_8\) digestion is able to quantitatively recover mercury from the interior surface of sample containers, in particular from PP containers.

Table 2 shows mercury recovery of 88–110% from de-ionized, tap and creek water samples. These samples were stored in glass flasks and PP tubes without preservatives, placed on the laboratory bench for 21 days and then digested in the original flasks and tubes by the KMnO\(_4\)–K\(_2\)S\(_2\)O\(_8\). The results indicate that the KMnO\(_4\)–K\(_2\)S\(_2\)O\(_8\) digestion quantitatively recovered mercury adsorbed on the interior surface of both glass flasks and PP tubes, because at least 60% of the mercury would have been adsorbed from such unpreserved samples in accordance with previous results (Figure 2). We also observed that mercury was quantitatively recovered in unpreserved environmental water samples in glass bottles within 28 days from sampling when the BrCl digestion was performed in the original sampling glass bottles (Figure 5). The above results demonstrate that sample preservation with acid or oxidative chemicals is not necessary in field sampling if the KMnO\(_4\)–K\(_2\)S\(_2\)O\(_8\) digestion is performed in the original sampling bottles (glass and PP) prior to total mercury analysis.

Table 2. Quantification of trace mercury in water samples preserved with 2% HNO\(_3\) in volumetric borosilicate glass flasks and PP tubes for 21 days by CVAFS.

| Sample type | Mercury concentration [µg L\(^{-1}\)] |
|-------------|--------------------------------------|
|             | Borosilicate glass flasks | Polypropylene (PP) tubes |
| De-ionized water | 0.994 ± 0.081 (99.4%) | 0.997 ± 0.095 (99.7%) |
| Tap water | 1.084 ± 0.128 (108%) | 0.887 ± 0.022 (88.7%) |
| Creek water | 1.102 ± 0.110 (110%) | 0.882 ± 0.015 (88.2%) |

The samples (25 mL containing 0.05 µg Hg) were prepared with de-ionized, tap and creek water, preserved with 2% HNO\(_3\) in 50 mL volumetric borosilicate glass flasks and 50 mL PP tubes and placed on laboratory bench. After 21 days, the samples were digested by KMnO\(_4\)–K\(_2\)S\(_2\)O\(_8\) digestion in the same flasks and tubes and then made up to the mark (50 mL). The results are the average of three separate preparations with standard deviation and percentage recovery.

Figure 4. Stability of 1 µg L\(^{-1}\) mercury solutions preserved with different concentrations of NaCl and NaNO\(_3\) in 50 mL volumetric glass and PP (polypropylene) flasks. A) NaNO\(_3\)-Glass, B) NaNO\(_3\)-PP, C) NaCl-Glass, D) NaCl-PP. Salt concentration: ● = 0.1%, ▲ = 0.3%, ○ = 1%, △ = 3%.
The above results confirm that adsorption of mercury ions on the interior wall of container is the dominant cause for the loss of mercury from standard solutions and samples. Yu and Yan provided a well-summarized report on the factors affecting the stability of mercury solutions and samples, including concentration of mercury species, sample composition, container material, storage temperature, pH of sample solution and light. In general, the relative adsorption rate decreases with increasing concentration of mercury in the solution. Toribara et al. observed that the more dilute Hg(II) solutions would be less stable and lose mercury more readily. The stock mercury solution employed in this study was 20 mg L$^{-1}$ preserved in HDPE bottle with 4% HNO$_3$. The supplier provided a one-year guarantee of the stability from the date of receipt. Different batches of this mercury stock solution were tightly capped and stored in laboratory cupboards without any other particular protection. We tested the stability of these stock solutions by instant CVAAS measurement after appropriate dilutions and found that the concentration was within an error of 5% over a period of 5 years from date of receipt. Clearly, the long-term stability of these mercury stock solutions in the HDPE bottles did not support the loss mechanism of mercury via diffusion through the wall of sample containers and the threads of sample bottle’s cap. The long-term stability of these 20 mg L$^{-1}$ solutions was most likely that the amount of mercury adsorbed was insignificant relative to the total amount of mercury from such high concentrations.

Mercury contamination has long been a critical issue in trace mercury analyses and chemicals used for preservation and digestion are the major sources of mercury contamination. In particular, used glass bottles and flasks incur high risks of mercury contamination. The U.S. EPA recommends contamination checks by filling the bottles with dilute acid (pH < 2), standing for at least 24 h and analyzing the solution while the APHA standard method recommends use of dedicated glassware whenever possible.

Table 3 shows the results for blank testing of used and new volumetric glass flasks. The dedicated flasks used for mercury solutions/samples preparation and storage were cleaned by a typical acid cleaning procedure (see Section 4). Prior to use, these flasks were filled with 2% HNO$_3$, placed on a bench for 72 h and then analyzed directly by CVAAS. No mercury contamination was identified (Entry 2, Table 3). However, significantly elevated mercury concentrations were detected in these dedicated flasks following the KMnO$_4$–K$_2$S$_2$O$_8$ digestion (Entry 3, Table 3). Initially, we considered that it was possibly due to contamination of the chemicals used and/or digestion procedure. By contrast, we found that the blank values for new glass flasks by the same digestion procedure were negligible (Entry 4, Table 3). Therefore, the high blank values from the used flasks-KMnO$_4$–K$_2$S$_2$O$_8$ digestion samples were not from the chemicals used.

3. Conclusion and Recommendation

Findings of this work are:

1) The typical cleaning procedure using 40% HNO$_3$ soaking overnight is not able to completely remove trace amount of mercury from the interior surface of glass flasks;
2) Glass flasks and bottles for sample preparation and storage incur high risks of mercury cross-contamination;
3) There are no significant differences in the rates of mercury adsorption from µg L⁻¹ solutions in 2% HNO₃ between volumetric glass flask and polypropylene tubes;
4) The KMnO₄–K₂S₂O₈ and BrCl digestion quantitatively desorbs mercury from the interior surface of bottles back into solution;
5) Mercury samples and standard solutions are extremely stable both in glass flasks and PP tubes after the KMnO₄–K₂S₂O₈ or BrCl digestion;
6) There are no differences in the stability of mercury standards treated by the KMnO₄–K₂S₂O₈ digestion and prepared by a simple dilution using the KMnO₄–K₂S₂O₈ digestion blank solutions.

The following recommendations are made to eliminate mercury adsorption and cross-contamination:

1) Use new PP bottles for field sampling and storage for trace total mercury analysis and do not add additional “preservative” chemicals;
2) Digest, make up and preserve/store the sample in the original sampling bottles;
3) Use new PP bottles for standard solutions and prepare the standards as per samples;
4) Calibrate the instrument using as-prepared standard solutions until finished (prepare new after 3 months).

4. Experimental Section

Chemicals and Apparatus: High-purity water used throughout the study was prepared from Millipore Milli-Q deionized-water system (Billerica, MA, USA). Ultrapure concentrated nitric acid (HNO₃, 69% w/w), analytical grade sulfuric acid (H₂SO₄), hydrochloric acid (HCl), stannous chloride (SnCl₂), hydroxylamine hydrochloride (HONH₃Cl), potassium permanganate (KMnO₄), and potassium persulfate (K₂S₂O₈) were obtained from BDH Chemicals, Poole, England. Stock solutions of 20 mg L⁻¹ (4% HNO₃, Alpha Resources, U.S.A.) and 100 µg mL⁻¹ (4% HNO₃, National Institute of Metrology, China) were used for preparation of sample solutions of 0.1–1 µg L⁻¹ by dilution with 2% HNO₃.

Cleaning Procedure for Glass Flasks and Bottles: Glass flasks or PP centrifuge tubes by dilution from stock mercury solutions. After preparation, the solutions and samples in glass flasks and PP tubes were “de-activated” by the KMnO₄–K₂S₂O₈ digestion and the de-activated flasks and tubes were used for storing mercury solutions. After preparation, the solutions and samples in glass flasks and PP tubes were capped and placed on the open laboratory bench (i.e., full exposure to ambient light and temperature).

Mercury solutions of 1 µg L⁻¹ were prepared in 50 mL volumetric glass flasks or 50 mL PP centrifuge tubes by dilution from stock mercury solutions with 2% HNO₃ or the digestion blank solution (see Section 4, KMnO₄–K₂S₂O₈ Digestion). For comparing stability of mercury solutions, the glass flasks and PP tubes were “de-activated” by the KMnO₄–K₂S₂O₈ digestion and the de-activated flasks and tubes were used for storing mercury solutions. After preparation, the solutions and samples in glass flasks and PP tubes were capped and placed on the open laboratory bench.

KMnO₄–K₂S₂O₈ Digestion: Mix the sample thoroughly to achieve homogeneity and transfer 25 mL aliquot of the sample into a 50 mL volumetric borosilicate glass flask or 50 mL polypropylene centrifuge tube, add 1 mL of concentrated HNO₃ and 10 mL of 0.25 mol L⁻¹ H₂SO₄. Mix the solution after each addition, then add 7.5 mL of 5% w/v KMnO₄ solution and 2.5 mL of 5% w/v K₂S₂O₈ solution to the flask and mix thoroughly. Place the flask in the water bath for 1 h at 95 °C.

Analysis with CVAAS or with CVAFS: Mercury was determined by cold vapor atomic absorption spectrometer using tin(II) chloride as reductant at a wavelength of 253.7 nm or cold vapor atomic fluorescence spectrometer using sodium borohydride as reductant. Loss and recovery of mercury from solutions were calculated by

\[
\text{Loss rate} = \frac{C_0 - C}{C_0} \times 100\%\quad (1)
\]

\[
\text{Recovery rate} = \frac{C}{C_0} \times 100\%\quad (2)
\]

where \(C_0\) is initial concentration of mercury and \(C\) is the concentration of mercury after sample processing.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

adsorption, cross-contamination, mercury solution, stability, water samples

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