LOSS OF TRACE AMOUNTS MERCURY FROM WATER SAMPLES DURING STORAGE

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SAMPLES DURING STORAGE

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Abstract

Several containers, preservatives, etc. have been suggested in relation to the preservation of liquid mercury samples. This memoir reports a comparison of sample containers and preservatives for synthetic and spiked water samples. Glass containers for preservation are better than polyethylene containers, and are best washed with *ca.* 3 N nitric acid.

The use of sulfuric acid coupled with strong oxidants such as potassium permanganate and potassium dichromate have been widely recommended for the preservation of mercury. The results of total mercury in fresh water using $H_2SO_4+KMnO_4$ showed no change during a storage time of about a month. On the other hand, sea water samples were acidified with 10 ml of 10 N sulfuric acid per liter, and this improved preservation efficiency greatly.

Permanganate is not desirable for routine analysis of water samples, because permanganate produces chlorine in high chloride samples, and this effect increases the value for blank. It is considered necessary to have a small amount of preservatives and little storage time. Analysis for mercury should be done as quickly as possible after sampling.

Introduction

Accurate determination of mercury in trace quantities has become increasingly important even in the p.p.b. level. However, storage of liquid samples has always been a problem because of the loss of mercury from the solution to container walls over extended periods of time. Several reports have shown through radioactive isotope studies [1, 2] that loss of mercury occurs by adsorption to container walls.

Benes and Rajman [3] studied the adsorption of mercury (II) on polyethylene and found that a 5-day old solution at pH 7 lost *ca.* 85% of the initial 6 p.p.b. mercury (II). They also showed that mercury loss was an exponential function of time.

Coyne and Collins [4] tested the loss of mercury from natural water stored in polyethylene jugs and was analyzed by the flameless atomic-absorption technique. They reported that *ca.* 80% of the initial 50 p.p.b. of mercury in unpreserved creek water was lost in 15 minutes.

Several factors which affect the stability of mercury solutions seem to have been reached. For example, it is agreed that low pH values, high ionic strengths and oxidizing environments help in keeping mercury in solution. Acids such as sulfuric acid [5, 6], nitric acid [4, 7-13], and hydrochloric acid [10, 13] have been widely used in the preservative

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agents.   Oxidants such as permanganate [2, 15] and dichromate [16-19] have been shown to prevent volatilization of mercury. Gold (III) [17, 19] and sodium chloride [20, 21] have also been used as preservatives.

The present study was undertaken to determine the loss of mercury in environmental water samples and in distilled water samples stored in various containers.   Possible ways of reducing the loss of mercury from environmental water samples are discussed.

Experimental

Apparatus

Shimadzu-MAF (II) Atomic Absorption Sectrophotometer, Rigaku Mercury SP and Nihon Instruments Mercury-automonitor with a Nihon-Denshikagaku Model U-100 strip chart recorder were used.

Absorption Cell : The cells were contructed from quartz glass, 165 mm and 100 mm in length.

Light Source : A hollow cathode lamp manufactured by Hamamatsu-TV Co. and mercury discharge lamp were used.

Shaker : Iwaki-KM (Model V-D) shaker was used.

Reagents

Stock Standard Mercury Solution : 10 ml of 10 N sulfuric acid was added to 1.3535 grams of mercuric chloride.   The resultant solution was then diluted to 1 liter with distilled water.   One milliliter equals 1 mg of mercury (1,000 mg/l).

Intermediate Standard Solution : Five milliliters of stock standard mercury solution and five milliliters of 10 N sulfuric acid were added in a 500 ml volumetric flask and made to volume with distilled water.   One milliliter equals 10 μg of mercury (10 mg/l).

Working Standard Solution : The 0.1 mg/l mercury standard solution was prepared by successively pipetting the intermediate standard solution into 500 ml volumetric flask and diluting to volume with distilled water.   Fresh working standard solution was prepared daily.

Certified reagent-grade chemicals were used for all analyses.   The sulfuric acid used was analytical special reagent grade for measurements of toxic metals.

10% Stannous Chloride Solution : A 10% stannous chloride solution was prepared using concentrated hydrochloric acid with distilled water as the diluent.

0.002% Dithizone-Chloroform Solution : 0.2% dithizone-chloroform solution [22] was diluted to 100 times with chloroform.

Sample Containers : One liter polyethylene and glass containers were used for all experiments.   Glass and polyethylene containers were treated with dilute acid in the following manner.   The containers were filled with 3N nitric acid and stored for about two weeks ; they were then rinsed with three portions of distilled water.

Sample Preparation : Most of the river water and sea water samples were not filtered prior to use.   Spiked water samples were prepared by first adding the appropriate preservative agents to a one liter portion of water and then adding the necessary volume of

standard mercuric chloride to achieve the final desired mercury concentration.

Procedure

Dilute mercury standards were prepared to cover the range 0.02-0.1 μg Hg (as $HgCl_2$). Samples were spiked with mercury (as $HgCl_2$). Several preservation studies and analyses were performed at room temperature. All solutions were stored in 1,000 ml containers throughout the study. During the storage periods of spiked water samples, several aliquots were taken and analyzed periodically with a new set of standards by the dithizone-extraction method or reduction-vaporization amalgam method. Figure 1, 2 show the procedure of mercury determination. From now on, soluble inorganic mercury is determined by procedure (II) [23]. For the determination of total mercury, procedure (I) [24] or Procedure (III) [23] are used.
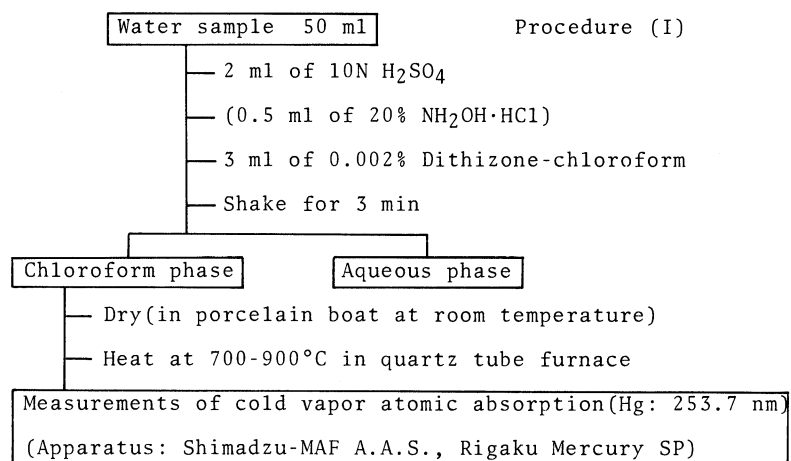
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      ┌──────────────────────┐
      │ Water sample   50 ml │          Procedure (I)
      └──────────────────────┘
          ├── 2 ml of 10N H2SO4
          ├── (0.5 ml of 20% NH2OH·HCl)
          ├── 3 ml of 0.002% Dithizone-chloroform
          ├── Shake for 3 min
   ┌───────────────────┐     ┌─────────────────┐
   │ Chloroform phase  │     │ Aqueous phase   │
   └───────────────────┘     └─────────────────┘
      ├── Dry(in porcelain boat at room temperature)
      ├── Heat at 700-900°C in quartz tube furnace
 ┌─────────────────────────────────────────────────────────┐
 │ Measurements of cold vapor atomic absorption(Hg: 253.7 nm)│
 │ (Apparatus: Shimadzu-MAF A.A.S., Rigaku Mercury SP)       │
 └─────────────────────────────────────────────────────────┘
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Fig. 1   Analytical procedure for the determination of mercury in water samples.

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 ┌──────────────────────┐              ┌──────────────────────┐
 │ Water sample 200 ml  │  Procedure   │ Water sample 200 ml  │  Procedure (III)
 │ (Reaction vessel)    │    (II)      │ (Reaction vessel)    │
 └──────────────────────┘              └──────────────────────┘
     ├── 2 ml of (1:1)H2SO4               ├──10 ml of 10N NaOH
     ├── 5 ml of 10% SnCl2                ├── 2 ml of 1,000 mg/1 Cu(II)
                                          ├── 5 ml of 10% SnCl2
          ├── Pass mercury free nitrogen at flow rate of 0.5 1/min
          │   for 10 min
          ├── Trap mercury on a porous gold
          ├── Heat at ca. 700°C for 40 s
          │   (Mercury free nitrogen at flow rate of 0.5 1/min)
 ┌──────────────────────────────────────────────────────────┐
 │ Measurements of cold vapor atomic absorption(Hg: 253.7 nm)│
 │ (Apparatus: Nihon Instruments Mercury-automonitor)        │
 └──────────────────────────────────────────────────────────┘
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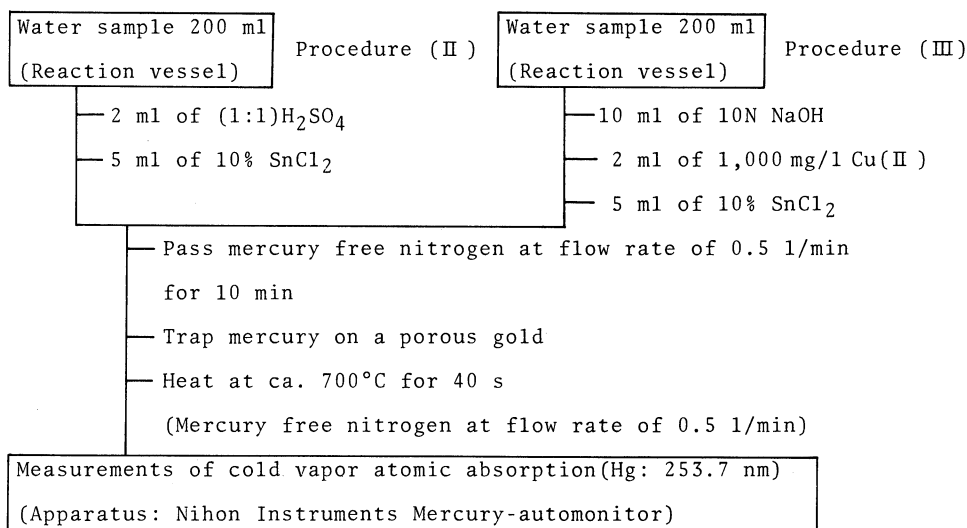
Fig. 2   Analytical procedure for the determination of mercury in water samples.

Results and Discussion

Several factors may affect the stability of mercury in solutions.   These include : (a) the level of mercury, (b) the type of container, (c) the method of cleaning, (d) the ionic strength and (e) the type of preservative agents (i.e., acid, oxidizing agents or complexing agents).

The natural water levels of mercury are in the range 0.001-n μg/l, and this range was covered in the present study.   Figure 3-9 are shown the loss of total mercury from spiked water samples.
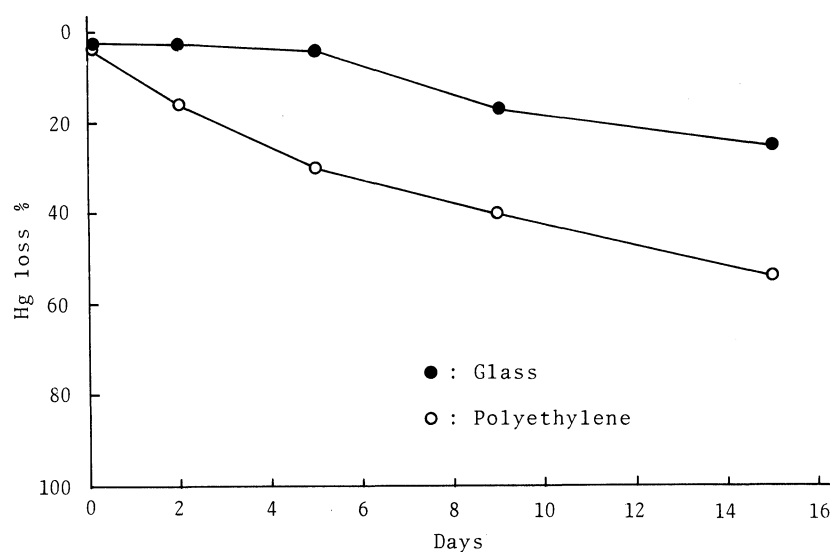
Fig. 3   Loss of mercury from 2 μg/l Hg (II) in distilled water stored in polyethylene and glass containers.
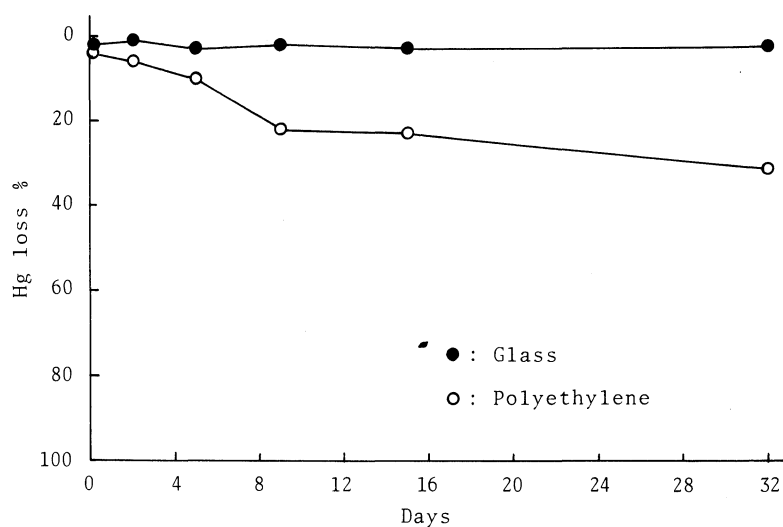
Fig. 4   Loss of mercury from 2 μg/l Hg (II) in distilled water acidified to 0.1 N with sulfuric acid stored in polyethylene and glass containers.

Water Solutions : We have monitored the loss of mercury from 2 μg/l of mercury (II) in unpreserved distilled water stored in polyethylene and glass containers. The results are shown in Figure 3. In polyethylene, loss of mercury in distilled water reached a value of about 50% of the initial concentration in 15 days. The glass container showed a slower rate of mercury loss in distilled water ; after 15 days of storage, it lost about 25% of the initial concentration. In all cases, there was expected rapid decrease of mercury concentration in the dilute solution, probably because of adsorption to the container walls *et al*. Figure 3 shows that this decrease is extremely rapid in polyethylene possibly because of an additional reduction mechanism.

Sulfuric Acid Solutions : When the distilled water samples were acidified to 0.1 N with
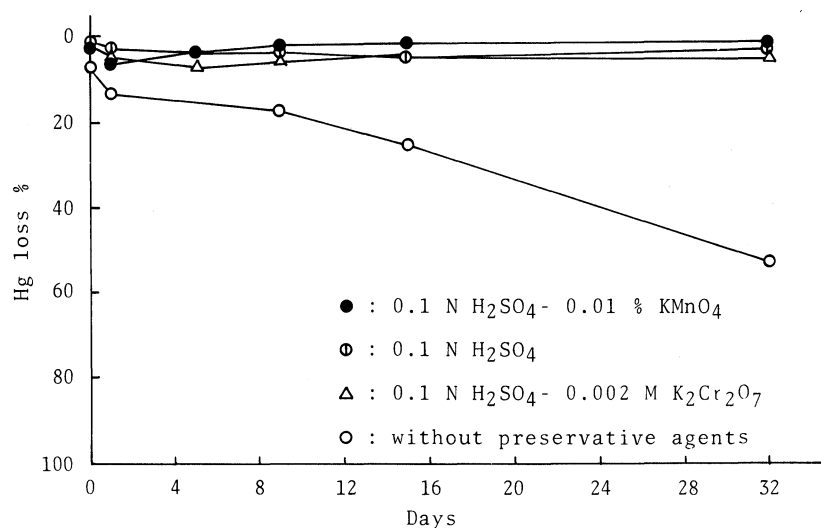
Fig. 5 Loss of mercury from 2 μg/l Hg (II) in distilled water stored glass containers after addition of preservative agents.
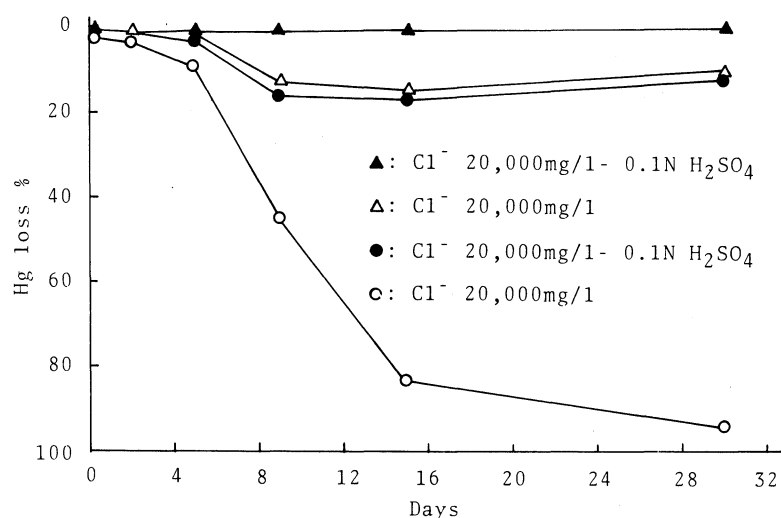
Fig. 6 Loss of mercury from 2 μg/l Hg (II) in standard solutions stored in polyethylene (●, ○) and glass (▲, △) containers after addition of preservative agents.

sulfuric acid, the results for mercury showed no change in glass containers, within the analytical error of the atomic absorption spectrophotometry method, during a storage time of about one month (Figure 4). However, Figure 4 shows that the decrease of mercury is somewhat greater in polyethylene. For this reason, glass containers were chosen for all further experiments on the long-term stability of spiked water samples with mercury.

Sulfuric Acid Solutions Containing KMnO$_4$ or K$_2$Cr$_2$O$_7$: Figure 5 shows that addition of sulfuric acid-potassium permanganate, sulfuric acid and sulfuric acid-dichromate to dilute mercury solutions improve the preservation of the solutions greatly. If the distilled water and standard mercury solution are added to the container before the preservatives, 7% of the mercury is lost immediately, 52% is lost by the 32th day. The use of acid coupled with strong oxidants such as potassium permanganate and potassium dichromate has been widely recommended. However, potassium permanganate produces chlorine in high chloride samples, and the additional potassium permanganate required to counter this effect increases the blank. In the determination of trace amounts of mercury, care is needed to prevent the contamination from chemicals and experimental environment.

Sulfuric Acid Solutions Containing NaCl : Figure 6 shows the loss of mercury in spiked distilled water stored in polyethylene containers. The preservation study was extended to 30 days. The results show that the sulfuric acid-chloride ion improves reasonably good preservation in a polyethylene container. Obviously, a glass container is better than a polyethylene container, including the sulfuric acid-chloride ion. Addition of sodium chloride to dilute mercury solutions acidified to 0.1 N with sulfuric acid improves the preservation of the solutions greatly.

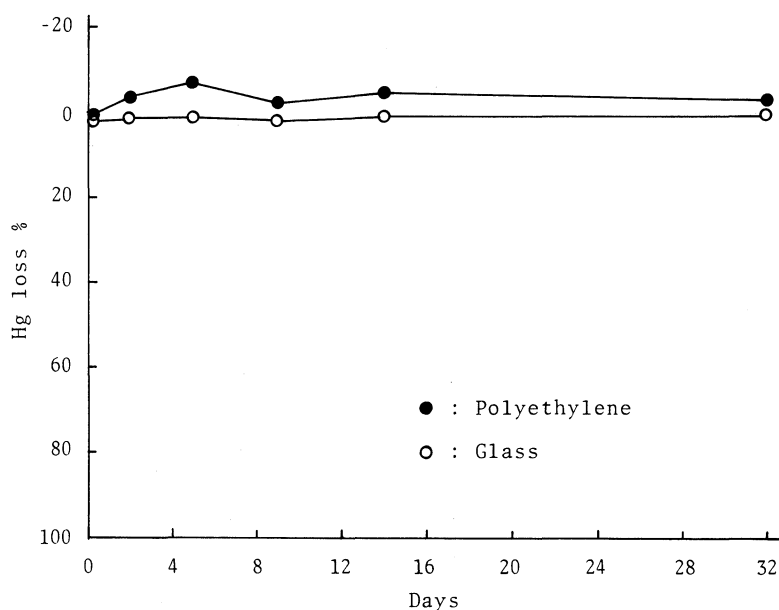*Containers for Preservation* : We have monitored the loss of mercury from 2 μg/l of

Fig. 7   Loss of mercury from 2 μg/l Hg (II) standard solutions preserved with 0.1 N
H$_2$SO$_4$ + 0.01% KMnO$_4$ in polyethylene and glass containers.

mercury (II) solutions preserved with 0.1 N sulfuric acid plus 0.01% potassium permanganate in polyethylene and glass containers. The results are shown in Figure 7. The present result shows that 0.1 N sulfuric acid plus 0.01% potassium permanganate is not suitable for polyethylene containers. The increase of mercury in polyethylene observed in this study could be a result of leaching of mercury from the container walls by the acid-permanganate solution. In a glass container, Figure 7 shows that 0.1 N sulfuric acid plus 0.01% potassium permanganate definitely improves preservation.

Environmental Water Samples Containing Hg (II) : We probed into the problem of loss of the mercury from spiked environmental samples. Figure 8 shows the loss of mercury
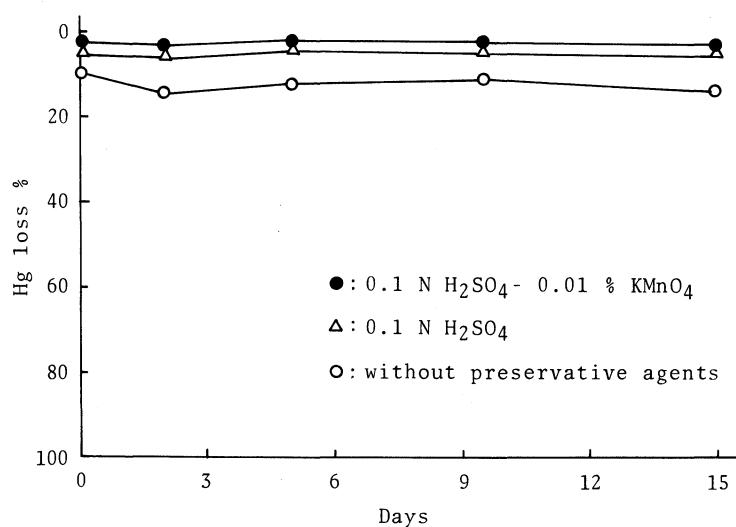

Fig. 8 Loss of mercury from 2 μg/l Hg (II) in river water stored in glass containers after addition of preservative agents.
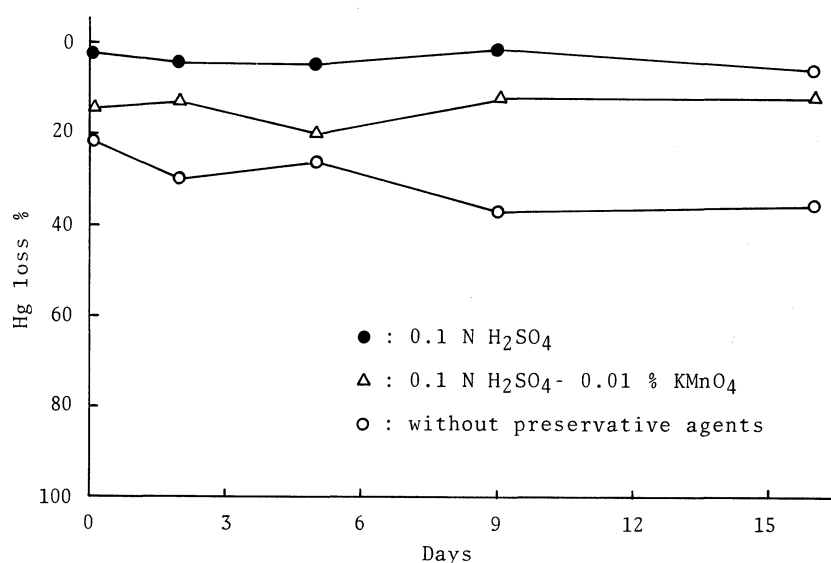

Fig. 9 Loss of mercury from 2 μg/l Hg (II) in sea water stored in glass containers after addition of preservative agents.
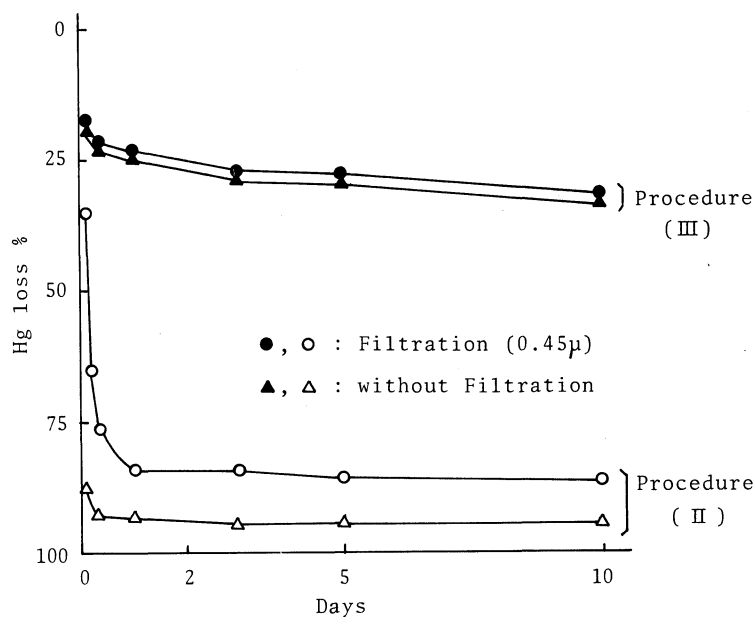
Fig. 10   Loss of mercury from 50 ng/l Hg (II) in river water stored in glass containers
after addition of 10 ml of (1 : 1) H_2SO_4 per liter.

in spiked river water. The results show that 0.1 N sulfuric acid plus 0.01% potassium permanganate is effective to any appreciable extent in preserving the mercury concentration in river water. When the river water sample and standard mercury solution are added to the container before addition of the preservative agents, 10% of initial mercury concentration is lost immediately, after 15 days of storage, it is about 15% of the initial concentration.

Let's have a look at sea water. Figure 9 shows the loss of mercury in spiked sea water. Permanganate is not desirable for monitoring sea water, because the permanganate is consumed for the reaction of the chloride ; the permanganate will be needed more abundantly. It is desirable to prevent the contamination from permanganate and operations.

Sea water samples acidified with sulfuric acid stored for 15 days in glass container showed a significantly higher stability. In the case of sea water, addition of sulfuric acid is best for mercury preservation.

Figure 10 shows the loss of mercury from 50 ng/l mercury (II) in acidified river water with sulfuric acid. In spite of filtration or without filtration, the mercury concentration drops sharply during the first day by procedure (II). In the case of acidified samples, about 20% of the added mercury was lost before the first analysis could be made by procedure (III) and the loss continued with time ; within one to ten days slightly all the added mercury was lost. The difference of the mercury loss by procedure (II) and procedure (III) is the sum of adsorbed inorganic-mercury on a suspended matter and soluble organic- mercury. In analysis of trace amounts mercury, the level of mercury and suspended matter have a great effect on the efficiency of preservation.

Conclusions

The following sums up the results of the experiment.

This report would seem to be characterized by attempting to document the actual rate of loss of mercury from synthetic and spiked natural water samples.   The results indicate that, at the mercury level of 0.05-2 μg/l, which is an environmentally significant level.

In terms of preservation, the present investigation indicates that the use of acid-potassium permanganate and acid-potassium dichromate that have been suggested by several authors is an effective preservative agents for standard mercury solutions and natural water.   However, acid-potassium permanganate is not desirable for routine monitoring of water samples which contains trace amounts mercury, because the permanganate produces chlorine in high chloride samples.   And then this effect increases the value for blank.   On the other hand, potassium permanganate used for trace amounts of mercury analysis is needed to prevent the contamination from chemicals and experimental environment.

Addition of sodium chloride to dilute mercury solutions acidified to 0.1 N with sulfuric acid improves the preservation of the solutions greatly.

In regard to container, glass is better than polyethylene for preservation and is best washed with *ca*. 3 N nitric acid and stored for about two weeks.

Even in slightly acidified water samples, the storage time should not exceed ten days, and analysis for mercury should be done as quickly as possible after sampling.

In the future, ideally, all experiments should be performed in a clean laboratory or a clean bench carefully protected from mercury.

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