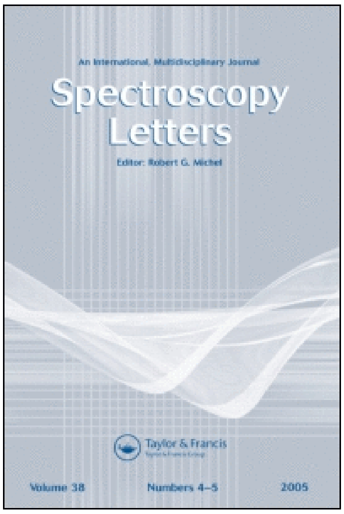

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Loss of Trace Elements From Natural Water During Storage 2. Behavior of $^{203}HgCl_2$, $CH_3{}^{203}HgCl$ and $^{65}ZnCl_2$ Added to Marine Water

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LOSS OF TRACE ELEMENTS FROM NATURAL WATER DURING STORAGE

2. BEHAVIOR OF $^{203}HgCl_2$, $CH_3{}^{203}HgCl$ AND $^{65}ZnCl_2$ ADDED TO MARINE WATER

Key Words: Trace Elements, Loss during Storage, $^{203}HgCl_2$, $CH_3{}^{203}HgCl$, $^{65}ZnCl_2$

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ABSTRACT

Dilute solutions (10-50 ppb) of mercury and zinc are prepared using artificial marine water and natural marine water, labelled with ^{203}Hg and ^{65}Zn.

^{203}Hg in inorganic form is lost considerably from both solutions caused by vaporization to the atomosphere and presumably by adsorption to the surface of containers. In natural marine water some biological activities participate for the behavior of both metals but it seems to be in smaller extent than that in pond water. ^{65}Zn remained constant with no loss under these experimental conditions.

When $CH_3{}^{203}HgCl$ is added to the solution instead of $^{203}HgCl_2$, ^{203}Hg is scarcely lost but a smaller amount is observed to be lost by vaporization from well-test tubes. In natural marine water, however, $CH_3{}^{203}HgCl$ is also lost in the similar manner as $^{203}HgCl_2$.

INTRODUCTION

As mentioned in the previous report$^{1)}$, very dilute solutions of mercury (Hg: 1-10 ppb), both artificial and natural, change rapidly during storage when stored without appropriate preservatives. The main factors of the loss of mercury from artificial solutions are found to be both the adsorption to the surface of containers and the vaporization to atomosphere. In natural water, some other factors including biological activities might participate, such as to make precipitaion with dead bodies of microbes. On the contrary, it was found that zinc is lost solely in natural water.

In this report, marine water is utilized and examined in the same way as the pond water in the previous report. In order to discriminate the effects of both salt concentration and pH, artificaial marine water is adopted as the control.

$^{203}HgCl_2$ and $CH_3{}^{203}HgCl$ are compared, because the form of mercury is one of the main interests in natural water as an environmental contaminant.

EXPERIMENTAL

The following radioisotopes are used, besides those already reported:$^{1)}$

$^{203}HgCl_2$ in 0.5 N HCl soln. Specific activity, 0.6 mc/mg

$CH_3{}^{203}HgCl$ in Na_2CO_3 soln. Specific activity, 2.42 mc/mg

Artificial marine water containing 30.5 ‰ NaCl, free from mercury contamination was obtained from CSK Standard Solution Service, Sagami Chemical Research Center, Japan. The date of preparation is June 2, 1969. The mercury content was found to be less than 0.01 ppb by long tube flameless atomic absorption method.$^{2)}$

Marine water is obtained from Tokyo bay, filtered with Millipore filter (HA 0.45 μ) to remove the floating materials, and kept in polyethylene containers about one month. The concentrations of Hg and Zn are less than 0.01 ppb and 10 ppb respectively,when the radioactive materials are added.

The experimental proceduree and the instruments used are the same as reported in the previous paper.$^{1)}$

RESULTS AND DISCUSSIONS

1 Behavior of inorganic ^{203}Hg and ^{65}Zn in artificial marine water.

The results are shown in Fig. 1 and 2. About 10 % of ^{203}Hg added to the level of 10 ppb is lost within 15 days, but ^{65}Zn remained 100 % upto 15 days. Compared with distilled water,$^{1)}$ disappearence from polyethylene containers is much slower (Fig.1), whereas the disappearence from well-test tubes by vaporization (Fig.2) is of the same measure. From these results, it may be concluded that in the solution of high salt solution and neutral pH (pH 7.6), the adsorption loss is less

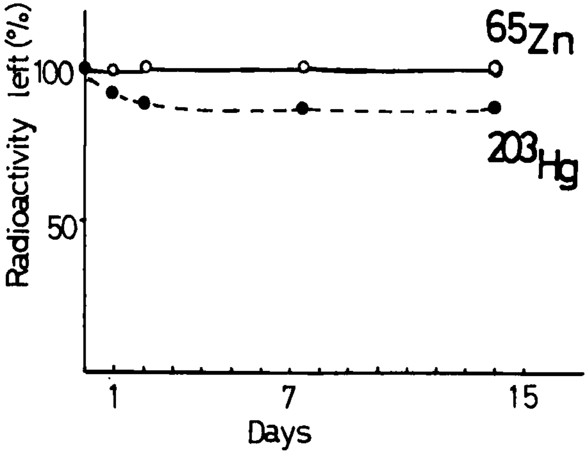

Figure 1 Behavior of ^{203}Hg and ^{65}Zn added in inorganic form to artificial marine water (in 100 ml polyethylene containers)

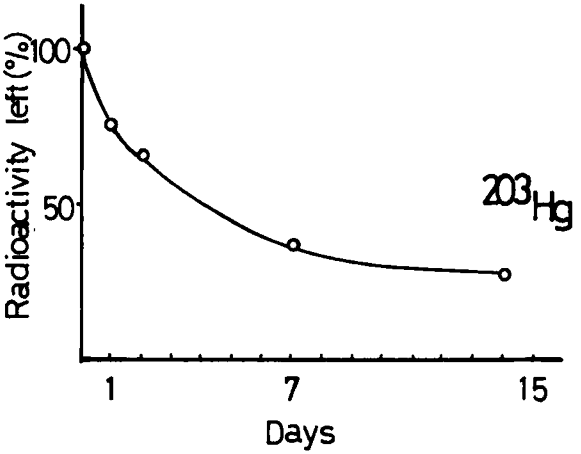

Figure 2 Vaporization of ^{203}Hg ($HgCl_2$) from artificial marine water in polyethylene well-test tubes

than that in distilled water but the vaporization loss is influenced by neither the concentration of the salt nor the pH.

2 Behavior of inorganic ^{203}Hg and ^{65}Zn in natural marine water.

The results are shown in Fig.3 and 4. Here, ^{65}Zn remained 100 % upto 15 days and ^{203}Hg is lost more rapidly than from the artificial marine water, in the polyethylene containers. The vaporization loss from the polyethylene well-test tubes is of the same extent as that from artificial marine water and resembles that from pond water, indicating that some common factors including biological activities and/or complex formation with inorganic and/or organic ligands existing in natural water may take part in the disappearence.

3 Recovery of ^{203}Hg from the containers.

After removing the solution at the end of the experiment, 100 ml polyethylene containers were dissected into two parts,

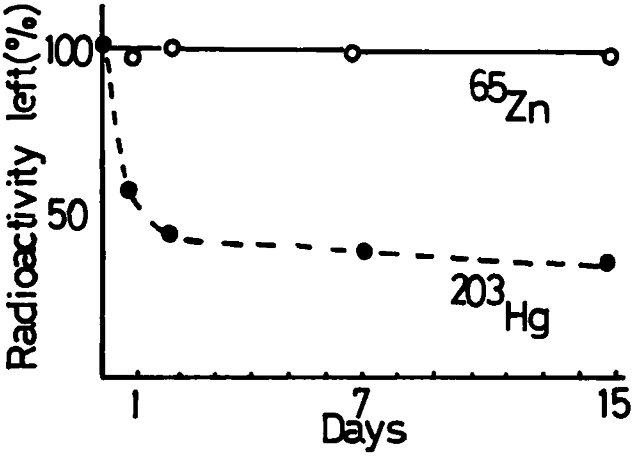

Figure 3 Behavior of ^{203}Hg and ^{65}Zn added in inorganic form to natural marine water (in 100 ml polyethylene containers)

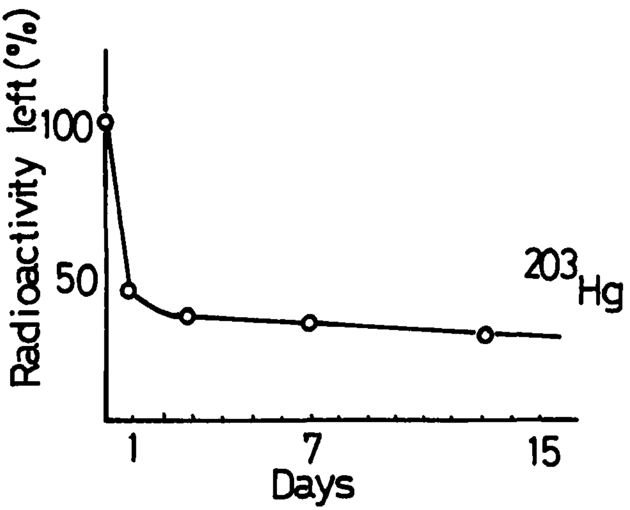

Figure 4 Vaporization of ^{203}Hg ($HgCl_2$) from natural marine water in polyethylene well-test tubes

the side wall and the bottom part. Both parts were again cut into small pieces and the radioactivity of them were measured in well-test tubes in order to estimate the depositted metals. The results are exhibited in Table 1 in the number of % of the initial radioactivity.

TABLE 1

Distribution of ^{203}Hg

(% of the initial radioactivity)

	Distilled Water*	Pond Water*	Marine Water**	Artificial Marine Water**
Container side wall	29	30	18	0.5
Bottom part	9	52	5	0.5
Solution	2	6	14	91
Vaporized amount (calculated)	60	12	63	8

* measured at 30th day
** measured at 14th day

Compared with the solution of low salt concentration, i.e. distilled water and pond water, in the solution of high salt concentration, the adsorbed amounts to the surface of containers are very much smaller, and for the difference between the artificial marine water and natural marine water, the latter is about 20 times larger. Another characteristic of natural marine water is the significance of the vaporized amount in the loss of ^{203}Hg, which is to be studied from the inorganic and biochemical point of view using more appropriate experimental systems.

4 The effect of the addition of 0.1 N HCl and 1 mM cysteine on the loss of ^{203}Hg from marine water.

In the former report[1)] as one of the most effective preservatives, the combination of 0.1 N HCl and 1 mM cysteine is proposed. It is examined in natural marine water(Table2), and this combined preservative is proved to be quite effective also for marine water.

5 Behavior of $^{203}HgCl_2$ and $CH_3{}^{203}HgCl$ in distilled water.

As one of organomercurial compounds, $CH_3{}^{203}HgCl$ is compared with $^{203}HgCl_2$. It has lower vapour pressure and more

TABLE 2

Preservative	Stored days 1	7	15
none	39	15	14
0.1 N HCl + 1 mM cysteine	99	95	99

(% of the initial radioactivity)

of biological importance according to its specific affinity to -SH groups, which is supposed to be one of the reasons of high concentration factor of Hg in the fish caught at Minamata area, the place known for the mercurial disease[3].

As shown in Fig.5 and 6, in distilled water, ^{203}Hg added as $HgCl_2$ disappeared rapidly in the similar manner as reported in the former report[1], by adsorption to the surface of containers and by vaporization to the atomosphere. However, $CH_3{}^{203}HgCl$ is scarcely lost within 15 days from the polyethylene containers and only a small amount(about 20 %) is lost from well-test tubes, which is supposed to be by vaporization to the vacant space above the solution in well-test tubes.

6 Behavior of $^{203}HgCl$ and $CH_3{}^{203}HgCl$ in natural marine water.

The results are shown in Fig.7 and 8. Compared with Fig.5 and 6, $CH_3{}^{203}HgCl$ does decrease in natural solution, although

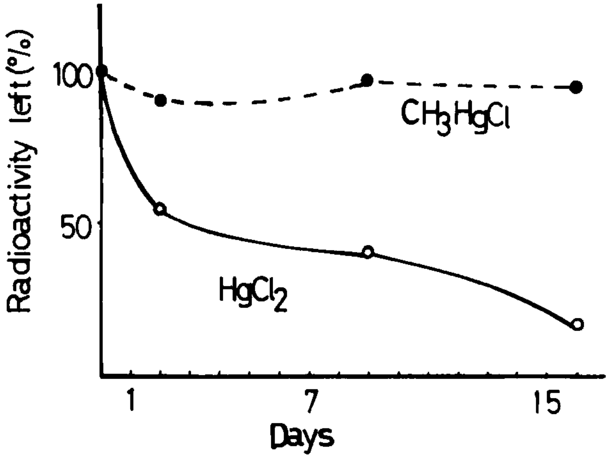

Figure 5 Behavior of $^{203}HgCl_2$ and $CH_3{}^{203}HgCl$ in distilled water(in 100 ml polyethylene containers)

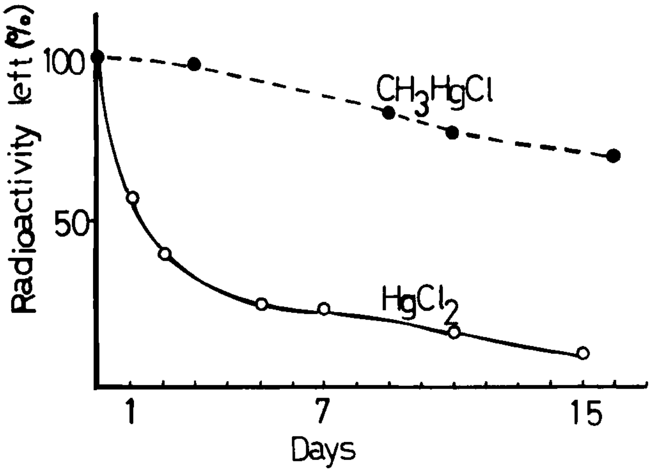

Figure 6 Vaporization of ^{203}Hg from distilled water in polyethylene well-test tubes

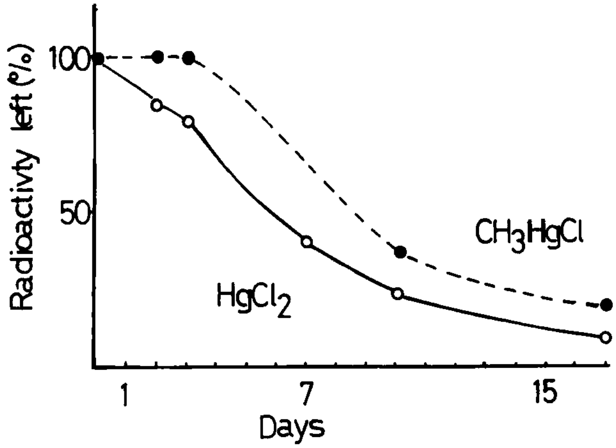

Figure 7 Behavior of $^{203}HgCl_2$ and $CH_3{}^{203}HgCl$ in natural marine water (in 100 ml polyethylene containers)

the rate of disappearence is slower than $^{203}HgCl_2$. Since the vaporized amount is similar to that from distilled water(Fig.6 and 8) the reasons of the loss from natural marine water, are supposed to be by adsorption to the surface of containers and

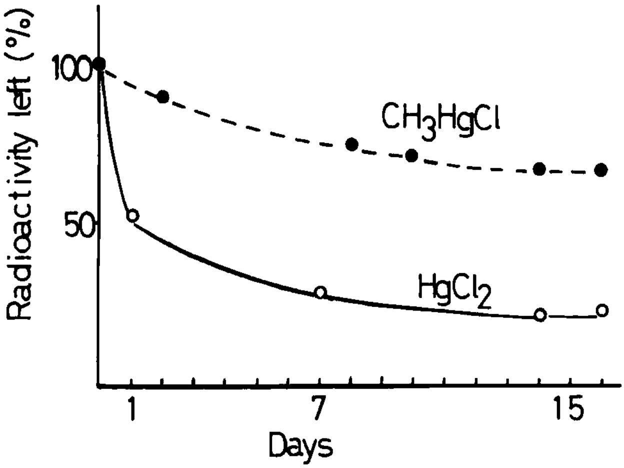

Figure 8 Vaporization of ^{203}Hg from natural marine water in polyethylene well-test tubes

by precipitation caused by biological activities and/or by complex formation with inorganic and/or organic ligands in natural marine water.

CONCLUSIONS

In marine water, ^{203}Hg added as inorganic form is lost from the solution while the sample water is kept in containers without any preservatives. The main cause of the loss is vaporization, but also both adsorption and precipitation seem to participate.

Addition of 0.1 N HCl with 1 mM cysteine is proved to be effective for sample reservation of marine water upto 15 days.

Organomercurial compound in the form of $CH_3{}^{203}HgCl$ is also lost in natural marine water, but not in distilled water within 15 days.

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