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The Chromatographic Concentration of Mercury in Sea Water with 2-Mercaptobenzothiazole Supported on Silica Gel

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A solid chelating material, 2-mercaptobenzothiazole supported on silica gel (MBT-SG), was prepared and used for the preconcentration of inorganic and organic mercury compounds from a sea-water sample. The chelating capacity of the material was 12 μeq. Hg/g. The mercury(II) ion, the methylmercury ion, and the ethylmercury ion were quantitatively retained on the MBT-SG at pH values of 1.0, 5.0, and 4.0 respectively from an aqueous solution, and at pH values of 4.0, 4.5, and 5.0 respectively from a sea-water. A column packed with the material provided a quantitative recovery of these ions from a sea-water sample at a high flow rate (1—3 l h^{-1}). Mercury was eluted by the use of a acetone–hydrochloric acid mixture (25: 1) or a 1% thiourea solution in 0.1 mol dm^{-3} hydrochloric acid. The latter effluent was submitted atomic-absorption spectrometry after reductive vaporization for the determination of mercury.

The analytical data on mercury in sea water which have been obtained up to the present time vary widely, from 2 to 2800 ng l^{-1}.[1–6] Such a wide variation in the values may be attributed to the following factors; i) contamination from an acid added to the sample for preservation;[7,8] ii) a change in chemical species, accompanied by an acidification of the sample,[9–11] iii) contamination from the container material,[12] iv) loss by vaporization and adsorption from the water sample[13,14] and contamination from air-borne particulate in the laboratory.[15–19] Therefore, it is preferable that mercury be concentrated as early as possible after sample collection in order to minimize the loss and contamination during storage.[20,21]

Previously, a simple method for the preconcentration and determination of several metals in natural waters was reported by Terada *et al.*[22] By their method, copper, zinc, lead, and cadmium in sea water could be rapidly concentrated on a column of a newly prepared chelating material, 2-mercaptobenzothiazole supported on silica gel (MBT-SG). This material was also found to be useful for the rapid concentration of inorganic and organic mercury compounds from sea water. A simple method for the rapid concentration, followed by the atomic-absorption spectrometric determination, of mercury in sea water using the MBT-SG column will be described in the present paper.

Experimental

Reagents. 2-Mercaptobenzothiazole-silica gel (MBT-SG) was prepared in the same way as was described in a previous paper.[22] Before use, the silica gel was washed with hydrochloric acid (1+1), nitric acid (1+2), and deionized water, succesively.

Standard Solution of Mercury (II) Nitrate. A 0.5 g of distilled mercury was dissolved in 30 ml of nitric acid and then diluted to 250 ml with deionized water.

Chloromethylmercury and Chloroethylmercury Labelled with ^{203}*Hg.*[23] About 0.3 g of dimethylmercury or diethylmercury was dissolved in about 2 ml of cold ethanol (Solution A). About 0.3 g of mercury (II) chloride was dissolved in about 2 ml of cold ethanol and spiked with ^{203}Hg (Solution B). To Solution A, Solution B was added, then, after a few seconds, the product separated as a white crystalline precipitate was filtered through a filter paper, Toyo No. 5C, washed with cold ethanol, and then dried by means of an air current at the pump. Finally, the labelled chloromethylmercury or chloroethylmercury was crystallized from a hot ethanol solution. The specific activities of these compounds were 1.3×10^8 cpm g^{-1} and 2.7×10^8 cpm g^{-1} respectively. The radioactive tracer ^{203}Hg was purchased from the Radiochemical Centre, Amersham (England). The radioactive purity of this tracer was checked by means of a Ge (Li) detector coupled with a 1024 multichannel analyzer.

Standard Solution of Chloromethylmercury. 40.2 mg of labelled chloromethylmercury was dissolved in water, and then 8 ml of hydrochloric acid was added. The solution was diluted to 100 ml with deionized water. This solution was diluted to the desired concentration with deionized water before every use.

Standard Solution of Chloroethylmercury. 50.3 mg of labelled chloroethylmercury was dissolved in a small volume of ethanol (1 ml), and the then mixture was diluted with deionized water. Eight milliliters of hydrochloric acid were then added to this solution, and the solution was diluted to 100 ml with deionized water. This solution was diluted to the desired concentration before every use.

1% Thiourea Solution in 0.1 mol dm^{-3} *Hydrochloric Acid.*

10% Tin (II) Chloride Solution in 1 mol dm^{-3} *Hydrochloric Acid.* The solution was bubbled by the air pump for 10 min at a flow rate of 0.5 l min^{-1}.

10 mol dm^{-3} *Sodium Hydroxide Solution.*

Apparatus. The apparatus used included two Hitachi-Horiba pH meters, M-5 and M-7; a Kobe Kogyo Co., Model STL-200 (44.5×50.8 mm NaI (Tl) crystal), well-type scintillation counter; a Hitachi 170-50 atomic-absorption spectrometer with a 18-cm-long quartz-absorption cell (this apparatus was connected to a Hitachi recorder).

The chromatographic column was a glass tube 12 mm in diameter and 140 mm in length, with a coarse sintered-glass disc and a stop-cock at the bottom.

A Toyo E-E SF200A fraction collector was also used.

Procedure for Batch Experiments. Two milliliters of the mercury test solution, (50 ppm, containing ^{203}Hg for mercury (II), 37.4 ppm and 46.5 ppm as mercury for chloromethylmercury and chloroethylmercury respectively), 10 ml of a buffer solution, and 0.5 g of MBT-SG were put into a 50-ml centrifuge tube and mixed. The mixture was then agitated mechanically at 340 strokes min^{-1} for 5 min at room temperature. The supernatant was filtered through a dry sheet of Toyo No. 5C filter paper. Each 3 ml of the filtrate was submitted to gamma-ray counting, afetr which the retention recovery was calculated.

Procedure for Column Method. The chromatographic tube (12 mm in diameter) was filled with 5 g of dried MBT-SG, and then a piece of filter paper was placed on the top of the column. In this case, the bed length became about 7 cm. A given volume of sea water containing individual mercury species was adjusted to a suitable pH, and then percolated through the column at a flow rate of 1—3 l h^{-1}. After washing the column with about 10 ml of deionized water, the mercury was eluted by the use of a 1% thiourea solution in 0.1 mol dm^{-3} hydrochloric acid or a solvent mixture of acetone and hydrochloric acid (25: 1) at the flow rate of about 1 ml min^{-1}. Then the effluent was made up to 25 ml, and a 3-ml aliquot of the solution was pipetted into a test tube for the measurement of its radioactivity by means of a gamma-ray scintillation counter.

Recommended Analytical Procedure. The following procedure is recommended: after the sample is collected, a 1- to 2-l portion is immediately adjusted to *ca.* pH 5.5 with hydrochloric acid and then pessed through the MBT-SG column (2 g of the material), which had been washed with 25 ml of the thiourea eluting solution and 25 ml of mercury-free sea water successively, at the flow rate of 1 to 2 l h^{-1} under gentle suction. Mercury-free sea water is prepared by passing sea water through the MBT-SG column. Subsequently, about 25 ml of the 1% thiourea eluting solution is passed through the column at the flow rate of about 1 ml min^{-1}. Then, the column is washed with about 10 ml of deionized water. The effluent and the washing are collected in a 100-ml Erlenmyer flask, and an additional 10 ml of deionized water is added to the flask. In a 50-ml beaker, about 6 ml of 10 mol dm^{-3} sodium hydroxide solution is placed, and then 5 ml of a 10% tin (II) chloride solution in hydrochloric acid is added under vigorous stirring, after which the solution is poured into the above Erlenmyer flask containing the column effluent. The flask is immediatly closed with a silicon rubber stopper provided with inlet- and outlet-tubes, the former being connected to a small air pump, and the latter, to a glass tube containing magnesium perchlorate. Then, the content is submitted to the determination of mercury by means of atomic-absorption spectrometry. The front of the magnesium perchlorate tube has been connected to a quartz atomic absorption cell 18 cm in length. After the flask has been shaken for 1.5 min, the air is bubbled through the solution at the flow rate of 0.5 l min^{-1} using an air pump. The absorbance is measured at 254 nm.

The reagent blank test has to be carried out throughout the whole procedure except for passing the sample water down the column.

Results and Discussion

Characteristics of the Chelating Material. The chelating capacity of MBT-SG for mercury, as measured by the column method, was found to be about 12 μmol per g of MBT-SG. This is comparable with that obtained for copper(II) (10 μmol per g of MBT-SG) and appears to be enough to collect mercury from a large amount of sea water, because 1 l of sea water is estimated to contain as little as about 0.3 μmol of heavy metal ions in all. This is compatible with 0.03 g of MBT-SG.

This solid chelating material also showed no loss of the mercury once retained on it even after a storage period of about one year. Therefore, this material can be submitted to atomic-absorption spectrometry or radioactivation analysis for mercury after carrying back it to laboratory without any loss and contamination of the element. An ordinary disposable syringe tube (5 ml) may be conveniently used as a column tube on board ship.

Recovery of Mercury(II), Methylmercury, and Ethylmercury ions at Various pH *Values.* The recovery of each individual mercury species was examined for a simple aqueous solution and for sea water of various pH values by the batch-experiment technique, as has been described previously. The pH of the solution was adjusted by sodium acetate plus hydrochloric acid for pH 1—5, and potassium dihydrogen phosphate plus sodium hydroxide for pH 6—8.

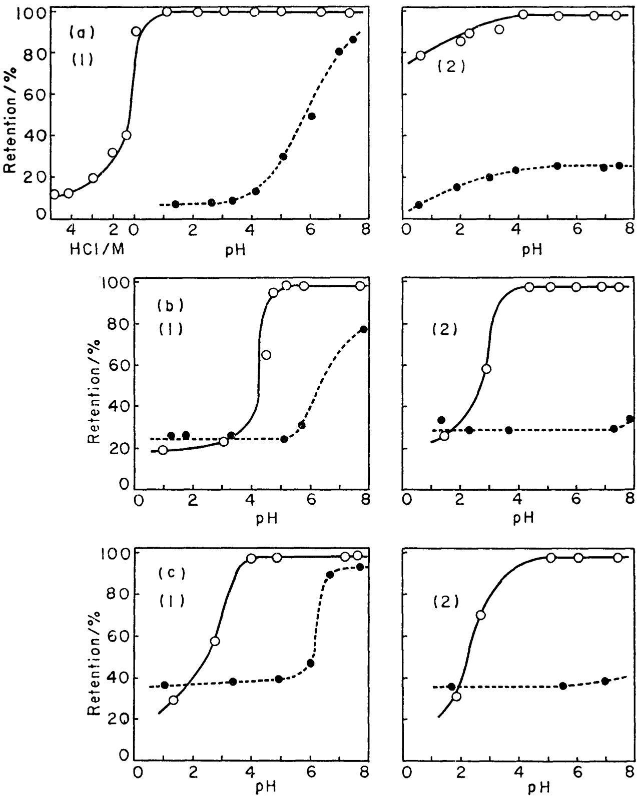

Fig. 1. Effect of pH on retention of (a) mercury(II), (b) methylmercury(I), and (c) ethylmercury(I).
(1): Aqueous solution, (2): sea water;
—○— MBT-SG; ---●--- untreated silica gel.

The results are shown in Fig. 1, along with those obtained by using untreated silica gel. The pH value mentioned is that measured after the equilibration. The mercury(II) ion was found to be retained completely on the chelating material at pH 1 for the aqueous solution and at pH 4 for sea water, but when untreated silica gel was put into an aqueous solution, the mercury(II) ion began to be adsorbed at pH 4. In the case of sea water, however, a recovery of 30% was only obtained at pH values of 6 or above.

The complete retention of the methylmercury ion from an aqueous solution and sea water were achieved at pH 4.5 and 4 respectively with MBT-SG, and a remarkable difference in adsorbability between the two adsorbents was observed. In the aqueous solution, the ethylmercury ion behaved quite similarly to the methylmercury ion, but in sea water a quantitative retention of ethylmercury on MBT-SG was obtained at pH 5.

Consequently, the pH value of 5 to 5.5 was chosen as the operating pH for the column experiments.

Retention of Individual Ions on the Column. One-liter portion of sea water containing a metal ion in various concentration were passed through the column at different flow rates. Each mercury species retained on the column was eluted with 20 ml of a mixture of acetone and hydrochloric acid (25: 1). The effluent was made up to 25 ml, and then a 3 ml portion of the aliquot was pipetted into a test tube for gamma-ray counting. Table 1 shows that the quantitative recovery of the mercury(II) ion in the concentration range of 0.032—20 ppb was attained from 1 l of sea water.

Table 1. Recovery of mercury(II), methylmercury(I), and ethylmercury(I) by the column method[a)]

Ion	Concentration ppb	Flow rate $l\ h^{-1}$	Recovery %
Hg(II)	20	1—2	100
	1	2—3	100
	0.032	1—3	100
$CH_3Hg(I)$	200	1—2	100
$C_2H_5Hg(I)$	200	1—2	100

a) MBT-SG: 5 g; column: $\phi 12 \times 70$ mm.

In the cases of methylmercury and ethylmercury ions, their quantitative retention was also observed from 1 l of sea water of a very low concentration (below 0.2 ppm), and they were easily released from the column with the same mixed solution of acetone and hydrochloric acid. Thus, the preconcentration of the inorganic and organic mercury from 1 l of a sample solution is easily attainable within only 20 to 30 min.

Effect of Various Ions and Organic Substances on the Adsorption of Mercury. Since various metal ions are well-known to react with MBT, copper(II), lead(II), zinc(II), cadmium(II), nickel(II), cobalt(II), and iron(III) were examined for their effects on this preconcentration procedure of mercury. One liter of sea water, containing the mercury(II) ion in a concentration of 1 ppb, both methylmercury and ethylmercury ions in a concentration of 0.2 ppm, and one of the above-mentioned ions in a concentration of 1 ppm, was passed through a column containing 5 g of MBT-SG (70 mm long) at the flow rate of $2\ l\ h^{-1}$. As shown in Table 2, none of these metal ions at the 1 ppm level had any effect on the adsorption of any mercury species. Sea water generally contains only 50 ppb of heavy metal ions in all; therefore, the effects of these metal ions on the adsorption of mercury from sea water may, for practical purposes, be disregarded.

Table 2. Effect of diverse ions on the recovery of mercury compounds by the column method

Ion	Concn. ppm	Recovery/% Hg(II)	 $CH_3Hg(I)$	 $C_2H_5Hg(I)$
Cu(II)	1	100	100	100
Pb(II)	1	100	100	100
Zn(II)	1	100	100	100
Cd(II)	1	100	100	100
Ni(II)	1	100	100	100
Co(II)	1	100	100	100
Fe(III)	0.1	100	100	100

Table 3. Effect of various substances on the recovery of mercury(II) by the column method[a)]

Substance	Concentration mol dm^{-3}	Recovery %
Cysteine	10^{-4}	83
Cystine	10^{-4}	80
EDTA	10^{-4}	100
Citric acid	10^{-4}	98
Tartaric acid	10^{-4}	99
SCN^-	10^{-4}	96

a) MBT-SG: 3 g; column: $\phi 12 \times 50$ mm.

Some organic compounds were also examined for their effects. In this case, a solution containing mercury in a concentration of 20 ppb and the organic compounds in a concentration of about 100 times that of mercury was passed through the column. The results are shown in Table 3. Several organic ligands such as EDTA, citric acid, and tartaric acid, did not interfere, and thiocyanate slightly reduced the adsorbability of mercury on MBT-SG. On the other hand, cysteine and cystine appreciably reduced the recovery of mercury. Apparently, this is due to the higher affinity of these ligands to mercury. For methylmercury and ethylmercury ions, similar experiments were not done because each specific activity of their labelled compounds became too low to perform the test of a reasonably low concentration of mercury. However, comparable recoveries of them with the mercury(II) ion can be expected from the results shown in Fig. 1 and Table 2.

Since, in sea water, these organic substances are never found beyond the concentration shown in the Table, the interference of these substances may also be negligible. In fact, in the present recovery experiment, the quantitative retention of each of the three kinds of mercury ions was achieved from a sea-water sample which had been collected at Tsukumo Bay, Noto Peninsula, and assumed to be more polluted by domestic activity than open sea water.

Elution of Mercury. Mercury was retained intimately on the column, therefore, elution with a single mineral acid, such as hydrochloric acid or nitric acid, gave a poor recovery of mercury. Various kinds of solvents and their mixtures were tested for adoption as the eluent by the batch method; the results are shown in Table 4. Among the various kinds of solutions tested, a solvent mixture of acetone and hydrochloric acid (in a mixing ratio of 9: 1 or 25: 1)[22)] and a 1% thiourea solution in 0.1 mol dm^{-3} hydrochloric acid[21)] were found to be most adequate for the elution of

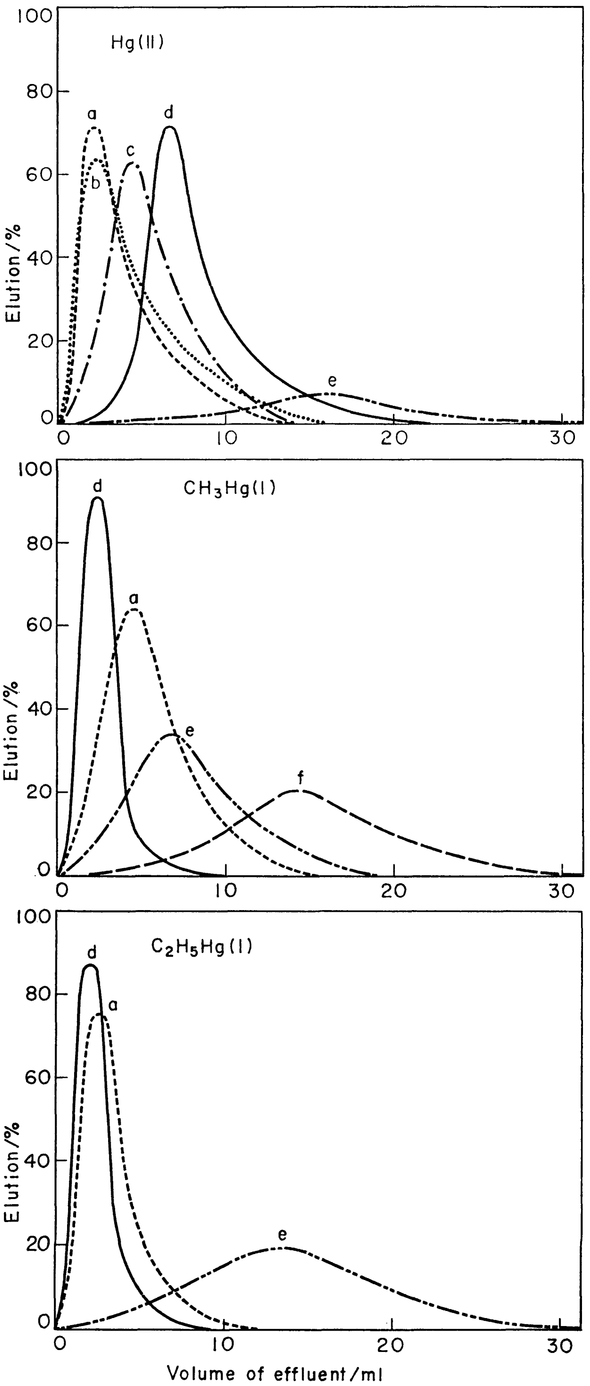

Fig. 2. Elution of mercury(II), methylmercury(I), and ethylmercury(I) retained on MBT-SG.
(a) Ethanol, (b) 1% thiourea in HCl (0.1 mol dm^{-3}), (c) acetone–HCl (9: 1), (d) acetone–HCl (25: 1), (e) HCl (1 mol dm^{-3}), (f) HCl (0.1 mol dm^{-3}).

mercury from the column.

The elution curves with various eluting solutions are shown in Fig. 2, from which about 20 ml of the solvent mixture of acetone and hydrochloric acid, and 20 ml of the 1% thiourea solution in hydrochloric acid seem to be suitable for obtaining quantitative recovery of mercury from the column. The former solvent mixture, however, released not only mercury, but also the chelating reagent from the column to some extent, and became difficult to submit the eluate to the subsequent atomic-absorption spectrometry of mercury because of the interference of the coexisting reagent, which was likely to give a higher value of mercury. On the other hand, the latter solvent could not dissolve the chelating reagent, and no interference occured in the atomic-absorption spectrometry of mercury in the effluent.

Table 4. Release of mercury(II) retained on MBT-SG
(Batch Experiment)

Substance	Released/%
HCl (1 mol dm^{-3})	5.4
HCl (6 mol dm^{-3})	12.4
HCl (10 mol dm^{-3})	7.9
HCl (1 mol dm^{-3})+NaCl	23.2
HNO_3 (1 mol dm^{-3})	8.8
HNO_3 (6 mol dm^{-3})	49.6
H_2SO_4 (3 mol dm^{-3})	15.0
Ascorbic acid	6.8
Ethanol	50.7
Acetone–HCl (9: 1)	76.4
Acetone–HCl (25: 1)	75.0
1% thiourea in HCl (0.1 mol dm^{-3})	76.0

Shaking time: 5 min.

Blanks were usually obtained when MBT and thiourea were employed. However, if the column was washed with the thiourea eluting solution by passing it through the column prior to the passage of the sample, a rather higher blank attributable to the MBT reagent was completely eliminated, and the overall blank value reached that caused by thiourea (about 2 ng of mercury).

Reductive Vaporization of Mercury. According to Umezaki *et al.*,[24] both inorganic and organic mercury compounds can be reduced to metal by the use of the tin(II) ion in a 1 mol dm^{-3} sodium hydroxide solution containing a trace amount of the copper(II) ion; also, the mercury can be driven off by the aeration of this solution. In the present study, this treatment was directly applied to the effluent containing a radioactive tracer of mercury, and the mercury thus evolved was introduced into 10 ml of the 1% potassium permanganate solution. After diluting this solution to 25 ml, a 3 ml portion was taken out and its gamma activity was counted. About 93% of the mercury in the effluent vaporized and was absorbed in the permanganate solution. Therefore, the result obtained by this procedure has to be corrected by this factor. On the other hand, when the initial effluent was made up to 1 mol dm^{-3} in a hydrochloric acid solution containing tin(II) chloride, mercury was not vaporized at all.

Table 5. Analysis of sea water

Method	Preconcentration factor	Mercury content ng/l
Direct analysis after MnO_4^- oxidation[a)]	—	280±40
The present method[b)]	8	280±20

a) Sample: 50 ml. b) Sample: 200 ml.

Analysis of Sea Water for Mercury. The present method was applied to a sea-water sample collected from a very shallow beach near Kanazawa Harbour. The sea water was filtered through cleaned absorbent cotton and analyzed after preconcentration by a factor of eight. The results are given in Table 5, along with those obtained by direct analysis without preconcentration after the permanganate oxidation of the sample. The mercury content is rather high for coastal water, but the two sets of results show a good agreement.

Conclusion

2-Mercaptobenzothiazole-silica gel(MBT-SG) provides an easy means for the preconcentration of mercury(II), methylmercury(I), and ethylmercury(I) prior to the ordinary cold-vapor atomic-absorption spectrometry. The great advantages of this chelating material, in spite of its relatively low chelating capacity, are the ease of preparation and the fast adsorptions of mercury compounds from the water sample. Moreover, mercury retained on MBT-SG can be preserved without any loss or any contamination for one year. The loss of the reagent from the column during the passage of a large volume of sample solution is inappreciably small, so 2—5 l of sea water can be treated with a relatively small column. The mercury ion preconcentrated in this way can be eluted from the column with a small volume of an eluent with a high concentration factor. Furthermore, as mercury compounds in sample water rapidly react with MBT on the column, the time necessary for the preconcentration is considerably shorter than in the other method. By the present method, mercury in concentration range of 2—50 ng can be determined.

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