2-Mercaptobenzothiazole Supported on Silica Gel for the Chromatographic Concentration of Cadmium, Copper, Lead, and Zinc in Natural Water Samples

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The preparation and characteristics of 2-mercaptobenzothiazole supported on silica gel (MBT–SG), and its application to the preconcentration and determination of cadmium, copper, lead, and zinc in natural water samples are described. The MBT–SG was prepared by impregnating silica gel with MBT in a dioxane–methyl acetate solvent mixture, drying, washing with deionized water, and finally drying. The chelating capacity of the material was 0.01 meq. Cu/g. Cadmium, copper, lead, and zinc were quantitatively retained on the MBT–SG at pH values of 4.8, 2.5, 4.8, and 6.5 for an aqueous solution, and at pH values of 4.8, 2.8, 4.8, and 6.5 for sea water. A column made of the material provided quantitative recovery of these metals from natural water samples at higher flow rates (2—5 l/h) than other chelating resins, *e. g.*, chelex 100. Cadmium was eluted with hydrochloric acid (1 : 99), copper and lead with acetone–hydrochloric acid mixture (9 : 1), and zinc with an acetate–hydrochloric acid buffer solution (pH 4.0). Then, the quantities of the four metals in their effluents were determined by atomic absorption spectrometry.

Because of their low concentration in natural water, including sea water, heavy metals often require preliminary concentration prior to the determination of their quantities. Recently, chelating resins have been conveniently used for this purpose by many investigators[1–3] in a manner originally described by Riley and Taylor.[1] Dingman *et al.*[4] prepared some new polyamine–polyurea resins and used them to concentrate several heavy metals from dilute solutions. They found that, among these resins, TEPA (tetraethylenepentamine polymerized with methylphenylene diisocyanate) is the most effective for this purpose when the resin is used in the column mode of operation with concentration factors as high as 1000. On the other hand, Mussarelli *et al.*[5–9] have used chitosan, a natural chelating polymer, to collect traces of transition metals from salt solutions and sea water using column chromatography. Since this natural polymer does not appreciably react with sodium and magnesium, it is useful for the separation of small amounts of transition metals from sodium and magnesium matrices. These methods are thought to be simpler and less time-consuming than solvent extraction[10] or the precipitation method. However, if a large volume of natural water must be treated, these resins cannot withstand the rapid flow of the sample water through the column.

Previously, Terada *et al.*[11] revealed the excellent ion-exchange properties of some inorganic exchangers supported on silica gel, *e.g.* KCFC–, NCFC–, and AMP–SiO_2, and applied them to the concentration of Cs-137 in natural water. Most inorganic exchangers appear to have been used preferentially for the concentration of alkali metals and some univalent metals such as silver and thallium *etc.*, but rarely for that of the transition metals.[12,13]

2-Mercaptobenzothiazole has been used as a precipitant for several metals, especially copper, gold, and lead to form sparingly soluble chelates in neutral solutions, and also as an extractant for solvent extraction of these metals. This reagent itself is insoluble in water, but soluble in ethanol, benzene, dioxane, and other organic solvents. This reagent will be used for the selective preconcentration of copper and some other transition metals in a large volume of natural water as previously described.[11]

The present paper describes a simple method for preparing such material, called 2-mercaptobenzothiazole–silica gel (MBT–SG), and its successful application to natural water concentration, especially for sea water, in the monitoring of the environmental pollution resulting from some heavy metals.

Experimental

Reagents. The 2-mercaptobenzothiazole, dioxane, methyl acetate, acetone, ethanol used were of analytical reagent grade.

A standard solution of metals was prepared as follows: copper metal was dissolved in nitric acid plus sulfuric acid, recrystallized lead nitrate was dissolved in nitric acid (1:100), zinc metal was dissolved in concd hydrochloric acid, nickel sulfate and cobalt sulfate were dissolved in deionized water, and chromium metal was dissolved in concd hydrochloric acid. Each stock solution was made up to contain the metal of interest at a concentration of 1000 ppm.

Silica gel of chromatographic grade (WAKOGEL C-100) was sieved in the range of 60—80 mesh and digested with a double volume of hydrochloric acid (1 : 1) for one day and then washed with deionized water until no chloride appeared in the washings. The cleaned silica gel was dried at 110 °C for one day.

Apparatus. A Perkin-Elmer 303-type atomic absorption spectrophotometer, Hitachi-Horiba M-5 type glass-electrode pH meter.

An Iwaki Model VS electric shaker.

A Toyo Type E-E SF200A fraction collector.

The chromatographic column was a glass tube of 9.8 and 20 mm inside diameters 140 mm in length with a coarse sintered-glass disc and a stop-cock at the bottom.

Preparation of 2-Mercaptobenzothiazole–Silica Gel (MBT-SG). About 70 g of silica gel (60—80 mesh) were put into a solution of 2-mercaptobenzothiazole in 100 ml of a dioxane–methyl acetate mixture (4 : 1 v/v) and stirred occasionally. After standing for about 20 h the supernatant was sucked out and the remaining silica gel impregnated with the reagent was then heated at about 80 °C at reduced pressure for about 20 h. The dried materials were washed repeatedly with deionized water to remove any nonadsorbed reagent until the washings appeared clear. Finally, the product was dried at about 80 °C under reduced pressure for about 20 h. The product was sieved (60—80 mesh) using a nylon sieve and stored in a darkened bottle.

Procedure for Batch Experiments. Into a 50-ml centrifuge tube, 10 ml of a metal solution (5 ppm), 5 ml of a buffer solution and 0.5 g of MBT–SG were mixed together. The contents were then agitated with an electric shaker for 30 min at room temperature. The supernatant was filtered through a millipore filter into a 20-ml measuring flask and adjusted to the desired volume. The metal concentration was measured with an atomic absorption spectrophotometer and then the percent retention was calculated.

Chelating Column Preparation. The chromatographic tube (20 mm in diameter) was filled with 10 g of dried MBT–SG, and a piece of glass wool was placed on the top of the column so that the bed was not disturbed during sample passage. In this case, the bed length became about 7 cm.

Procedure for Column Method. A given volume of an aqueous sample containing individual metal ions was adjusted to a suitable pH, then percolated through the column at a flow rate of 2—5 l/h under the suction of an aspirator. The lower level of the sample solution was maintained about 1 cm above the surface of the column bed during sample passage. After washing the column with about 20 ml of deionized water, an eluting solution of definite composition was passed through at a flow rate of about 1 ml/min. The effluent was collected in a measuring flask, diluted to the desired volume, and the metal concentration was determined with an atomic absorption spectrophotometer.

Results and Discussion

Characteristics of the Chelating Material. The amount of 2-mercaptobenzothiazole on the silica gel was determined as follows. One gram of the dried material was put onto the column tube. Then about 20 ml of ethanol was passed through to completely remove the reagent from the column. The effluent was collected in a 50-ml measuring flask and diluted to the desired volume with ethanol. Two milliliters of the solution were pipetted out and put into another 50-ml measuring flask and diluted to the desired volume with ethanol. The absorbance of the solution was measured at a wavelength of 327 nm using ethanol as a reference. The absorption spectra of the effluent and the ethanol solution of the reagent are shown in Fig. 1. Both absorption curves have identical absorption peaks at 239 and 327 nm. This fact suggests that the reagent was retained without any loss. The amount of reagent supported on the silica gel was found using the conventional working curve method to be about 11±1 mg per g of the material.

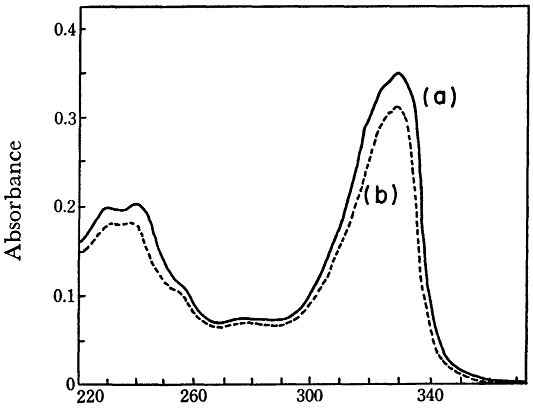

Fig. 1. Absorption spectra of 2-mercaptobenzothiazole.
(a) MBT dissolved in ethyl alcohol, (b) MBT in the effluent.

The chelating capacity for copper was measured by the batch method. Ten milliliters of the copper solution (50 ppm), 5 ml of a buffer solution (pH 4.0), and 0.5 g of MBT–SG were mixed together in a 50-ml centrifuge tube. The contents were then agitated for 30 min at room temperature. The copper concentration in the supernatant was measured with an atomic absorption spectrophotometer. The capacity was calculated to be about 0.01 meq. Cu(II)/g of MBT–SG. The chelating capacity of the material appeared to be large enough to collect copper from a large volume (*e. g.* 10 l) of sea water which is believed to contain as low as 1—20 μg copper per liter,[14] 10 g of the material has an operating capacity at least 32 times greater than the total amount of copper in 10 l of sea water (200 μg).

This solid chelating material also showed no change in its adsorbability after a storage period of about one month and was then dipped in a solution over the range from pH 1 to 10.

Recovery of Cadmium, Copper, Lead, and Zinc at Various pH Values. The recovery of each individual metal ion was examined by the batch method, using a 10 ml sample solution with a 5 ppm concentration of each metal and 0.5 g of MBT–SG, for a pure aqueous solution and for sea water of various pH values. The pH of the solution was adjusted using the following buffer solutions: sodium acetate plus hydrochloric acid for pH 1—5, potassium dihydrogen phosphate plus sodium hydroxide for pH 6—7, and boric acid plus potassium chloride and sodium hydroxide for pH 8—10. The results are illustrated in Fig. 2 along with those obtained using only silica gel. The pH value mentioned is that measured after equilibration. Copper was found to be retained quantitatively on the material at pH 2.5 for aqueous solutions and at pH 2.8 for sea water, but when untreated pure silica gel was put into an aqueous solution copper began to be adsorbed when the pH increased above 6. However, in the case of sea water only a recovery rate of 25% (the maximum value) was obtained at pH values of 7 or above. Cadmium and lead showed similar behavior on MBT–SG, and their quantitative retention values were obtained for pH 4.8—5.2 in both aqueous solutions and sea water. A remarkable difference in adsorbability was observed between MBT–SG and untreated silica gel. On the other hand, zinc ions showed similar adsorption rates for both MBT–SG and untreated silica gel and quantitative retention was obtained at pH 6.5 for both aqueous solutions and sea water. However, in column experiments, a reduction of about ten percent in the adsorption for zinc was observed when 5 l of an aqueous solution containing 2 ppb of zinc was passed through the untreated silica gel column at a flow rate of 4 l/h, although it was quantitative for the MBT–SG column.

From these results, the separation of copper from

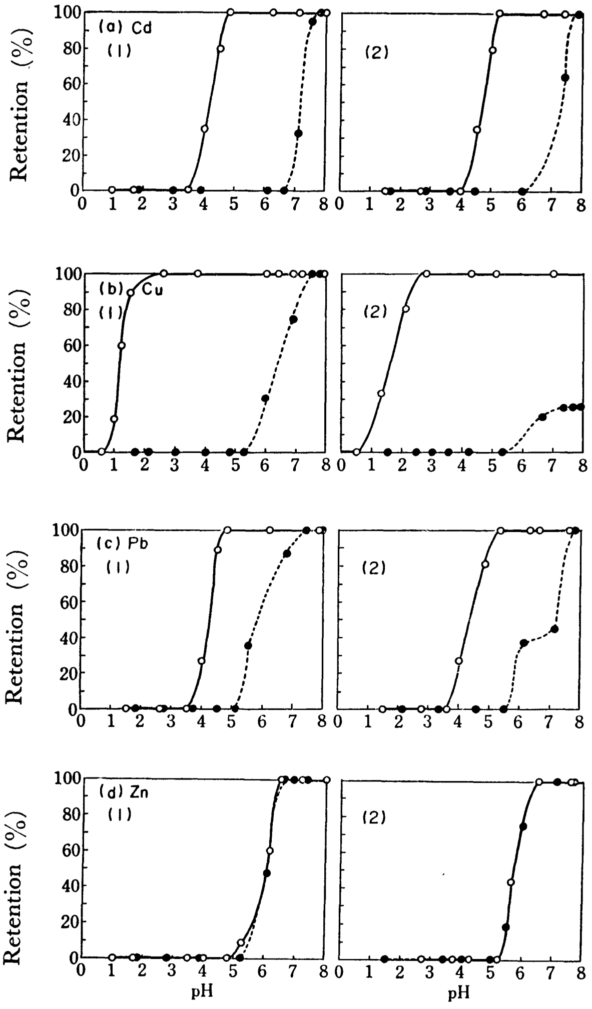

Fig. 2. Effect of pH on retention of (a) cadmium, (b) copper, (c) lead, and (d) zinc.
(1): Pure aqueous solution, (2): sea-water.
—○— MBT–SG, --●-- untreated silica gel.

lead and cadmium, and lead and cadmium from zinc will be possible with eluting solutions of different pH values with column operation.

Retention of Individual Ions on the Column. To examine quantitatively the retention of each metal ion on a column, several kinds of test solutions (an aqueous solution, a sodium chloride solution of ionic strength 0.63, and sea water) containing metals in various concentrations were passed through the column at different flow rates. In the experiment, copper(II) at pH 4.0, lead(II) at pH 5.0, and cadmium(II) and zinc(II) at pH 7.0 were individually fed onto a column (20 mm in dia. ×70 mm) of MBT–SG. After washing the column with about 20 ml of deionized water, cadmium was eluted with hydrochloric acid (1 : 99) and zinc with a buffer solution at pH 4.0 (sodium acetate–hydrochloric acid). Copper and lead adhered tightly to the column, and therefore, the following treatment was necessary to remove them quantitatively. Water held on the column had to be removed as much as possible by sucking under aspiration, then 20 ml of ethanol was run through to remove any untreated reagent, then copper and lead were eluted with 20 ml of a solvent mixture of acetone and hydrochloric acid (9 : 1 v/v). Each effluent was adjusted to be exactly 25 ml in a measuring flask and subjected to atomic absorption spectrometry for the determination of the quantities of the various metals.

TABLE 1. RECOVERY OF METAL IONS USING THE COLUMN METHOD

Ion	Vol. of sample (l)	Flow rate (l/h)	Concn of metal (ppb)	Recovery (%)
Cd(II)	1.0	2.3	100	100±2
	1.0	4.0	10	100±2
	5.0	4.2	1	100±2
	1.0	2.7	0.1	100±2
Cu(II)	1.0	3.7	100	100±2
	5.0	5.0	1	100±2
	5.0[a)]	5.0	1	100±2
Cb(II)	1.0	3.0	100	100±2
	5.0	2.5	1	100±2
	5.0[a)]	2.5	1	100±2
Zn(II)	1.0	3.0	100	100±2
	5.0	5.0	1	100±2
	5.0[b)]	4.1	5	100±2

Pure aqueous solution at adjusted pH 4.0 (Cu), 5.0 (Pb) and 7.0 (Cd and Zn).
a) NaCl solution, $\mu=0.63$. b) Sea water. MBT-SG: 10 g, column: 20 mm in dia. × 70 mm.

The separation data in Table 1 show that quantitative retention was obtained for cadmium in the 0.1—100 ppb range, and for copper, lead, and zinc below in the range from 1—100 ppb at flow rates from 2.3 to 5.0 l/h. Thus, preconcentration of each metal from 5 l of sample water was attainable within 1 h.

Elution of Each Metal. Zinc(II) was found to be eluted from the column with 20—25 ml of a buffer solution which contained 20 ml of 1 M sodium acetate and 16 ml of 1 M hydrochloric acid per liter (pH 4.0), while lead and copper were not released from the column at all; consequently, separation of lead and copper from zinc was achieved. However, part of the cadmium was released by passing this buffer solution through the column. Both cadmium and zinc were completely eluted with nitric acid (1 : 99) or hydrochloric acid (1 : 99), with the latter eluting solution being more favorable for the subsequent atomic absorption spectrometric determination of the cadmium content. However, in this case, 30—38% of the retained amount of lead was also released using 25 ml of either of the above acids while no copper appeared in the eluate.

Effect of Various Ions and Substances on the Adsorption of Cadmium, Copper, Lead, and Zinc. The various metal ions thought to react with MBT, cobalt(II), iron(III), and nickel(II) were examined for their effects on this separating procedure. One liter of a test solution containing cadmium, copper, lead, and zinc in concentrations of 5 ppm, as well as one of other ions in the concentration range of 0.1—10 ppm was prepared. This solution was passed through a column containing 7 g of MBT–SG at flow rate of 2—5 l/h. At the same time, the mutual separation of the four ions of interest was also

Table 2. Effect of various ions on the recovery of metal ions

Ion	Concn (ppm)	Recovery (%)[a)] Cd(II)	Cu(II)	Pb(II)	Zn(II)
Cd(II)	10	—	93	34	3
	1	—	≈100	≈100	≈100
Co(II)	10	≈100	59	52	≈100
	1	≈100	≈100	93	≈100
Cu(II)	5	33	—	32	≈100
	1	≈100	—	≈100	≈100
Fe(III)	1	27	53	3	3
	0.1	≈100	93	≈100	97
Ni(II)	10	≈100	39	2	≈100
	1	≈100	91	91	≈100
Pb(II)	10	37	48	—	10
	1	≈100	≈100	—	≈100
Zn(II)	10	39	19	34	—
	1	≈100	72	≈100	—

a) Metal: 0.05 ppm, MBT-SG: 7 g, column: 20 mm in dia. × 50 mm.

Table 3. Effect of various substances on the recovery of metal ions

Substance	Concn (mol/l)	Recovery(%) Cd(II)	Cu(II)	Pb(II)	Zn(II)
EDTA	10^{-5}	0	7	0	5
	10^{-6}	0	≈100	4	57
	10^{-7}	65	≈100	≈100	≈100
Citric acid	10^{-4}	89	53	46	6
	10^{-5}	≈100	≈100	100	92
Tartaric acid	10^{-4}	89	48	32	13
	10^{-5}	≈100	89	≈100	93
	10^{-6}	≈100	≈100	≈100	≈100

Metal: 0.05 ppm, MBT-SG: 7 g, column: 20 mm in dia. × 50 mm.

examined in varying concentrations. The results are given in Tables 2 and 3. At the 1 ppm level, iron(III) significantly reduced the recovery of the other four metal ions. Since iron(III) itself was found to be retained quantitatively on the both MBT–SG and on untreated silica gel at pH 7, it is not expected that iron competed with copper, cadmium, and lead on MBT. In fact, in the first solutions passed, which originally contained microgram amounts of each metal and 1 ppm of iron(III), no copper, cadmium, lead, and zinc at all were found. Therefore, iron appears to be adsorbed on the column as a hydroxide, retaining some of these metals with it and not liberating them on elution. Nickel(II) at the 1 ppm level produced a slight reduction in the recovery of copper and lead, and also zinc and cobalt at the same concentration produced the same effect for copper and lead, respectively. In general, 1 l of sea water contains about 0.3×10^{-3} meq. of heavy metal ions in all which is compatible with 0.03 g of MBT–SG. Therefore, the interference of heavy metal ions on the adsorption of these four metal ions from sea water may be practically neglected. On the other hand, some organic compounds, such as EDTA, citric acid, and tartaric acid, substantially hindered the adsorption of the metal ions. Particularly, EDTA considerably lowered adsorbability on MBT–SG of cadmium, lead, and zinc at a concentration of 10^{-6} mol EDTA/l. However, since in natural water, especially in sea water, these organic substances are never found in the concentrations shown in Table 3, the interference produced by these substances may be neglected.

Atomic Absorption Measurements for Copper and Lead. To determine the optimum conditions for atomic absorption measurements of copper and lead in an acetone–hydrochloric acid solvent mixture, the effects of acid and reagent concentrations and the mixing ratio of air and fuel were examined.

The effect of the hydrochloric acid concentration in acetone on the absorption of copper is shown in Fig. 3, from which it is seen that the smaller the absorbance, the higher the acid concentration. The solvent mixture used in the present experiments is considered to have no effect on the absorbance of copper. For lead, similar results were obtained. As shown in Fig. 4, the concentration of the MBT reagent in acetone had no significant effect on the absorption measurements under these conditions. Since the effluent became turbid when free MBT remained in it, excessive reagent was removed from the column by passing ethanol prior to the elution of the metal–MBT complexes with an acetone–hydrochloric acid solvent mixture. After several

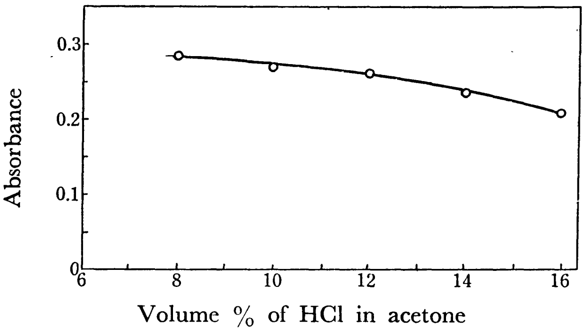

Fig. 3. Effect of concentration of hydrochloric acid in acetone on atomic absorption spectrometry for copper.

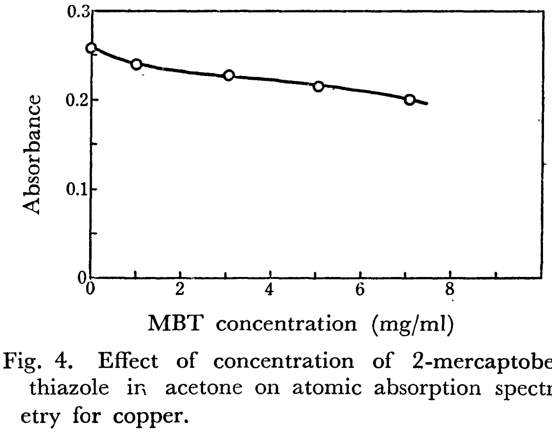

Fig. 4. Effect of concentration of 2-mercaptobenzothiazole in acetone on atomic absorption spectrometry for copper.

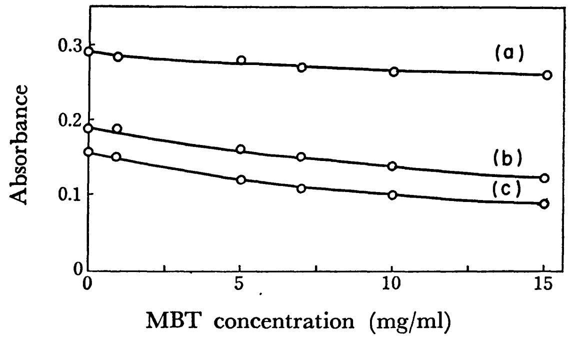

Fig. 5. Effect of mixing ratio of air and acetylene on atomic absorption spectrometry for copper in the presence of various concentration of MBT.
(a) Air : acetylene 4.7 : 2.7—5.0 : 3.0, (b) air : acetylene 9.0 : 7.0, (c) air : acetylene 9.0 : 9.0.

tests, it was found that the mixing ratio and the fuel flow rate had serious effects on the absorbance of copper and lead, and that maximum absorption was obtained at mixing ratios of air and acetylene of 4.7 : 2.7 to 5.0 : 3.0 for copper (Fig. 5) and 6.0 : 4.0 for lead.

Analytical Procedure Recommended. In general, the cadmium content of natural water is lower than the contents of the other three metals by a factor 10 to 100. Consequently, from these results, the copper, lead, and zinc contents should be determined in one sample after preconcentration using this method and the cadmium content should be measured in another smaller portion of the sample using flameless atomic absorption spectrometry.

Thus, the recommended procedure is as follows: two to five liters of the water sample adjusted to about pH 7, is passed through the MBT–SG column (20 mm in dia. ×70 mm) at a flow rate of 2—5 l/h. Even at a higher flow rate, if the sample solution is poured onto the column by aspiration, numerous minute air bubbles appear on all parts of the column which are of course, not filled with sample solution and rather quantitative retention of the metal ions can be maintained. This may result from closer contact between the sample solution film and the MBT–SG particles. Subsequently, the column is washed with about 20 ml of deionized water, and then 20 ml of an acetate–hydrochloric acid buffer solution (pH 4.0) is passed through at a flow rate of 1 ml/min. The effluent is diluted to the desired volume with deionized water in a 25-ml measuring flask and subjected to atomic absorption measurement for the zinc content. The absorbance is measured at a wavelength of 213.8 nm in a flame of air and acetylene (9 : 9). The column is washed again with 20 ml of deionized water and then with about 20 ml of ethanol, and finally 20 ml of a solvent mixture of acetone–hydrochloric acid in a volume ratio of 9 : 1 is passed through. The effluent is diluted to 25 ml with acetone and subjected to the atomic absorption measurement for copper and lead. The absorption is measured at wavelengths of 324.8 and 283.3 nm for copper and lead, respectively, in a flame of air and acetylene (5 : 3 for copper and 6 : 4 for lead).

Cadmium and zinc are detemined in another manner, as follows: two liters of the water sample adjusted to pH 7.0 is passed through the column. Then the column is washed with about 20 ml of deionized water, and 20 ml of hydrochloric acid (1 : 99) is passed at a flow rate of 1 ml/min. The effluent is diluted to 25 ml with deionized water and submitted to the atomic absorption measurement for cadmium and zinc. Cadmium is measured with flameless atomic absorption using a carbonrod atomizer at a wavelength of 228.8 nm and the absorption of zinc is measured as described above. From the remaining column material, copper can be eluted with an acetone–hydrochloric acid solvent mixture as indicated above.

Analysis of Tap, River and Sea Water. Using the recommended method, laboratory tap water, river water, and sea water were analyzed for cadmium, copper, lead, and zinc. The results are summerized in Table 4.

TABLE 4. CADMIUM, COPPER, LEAD AND ZINC CONTENTS OF VARIOUS WATER SAMPLES

Sample water	Cd(II) ppb	Cu(II) ppb	Pb(II) ppb	Zn(II) ppb
Pacific Ocean (10 m)	0.1_4[a]	0.2_2	3.1	3.0[a]
Pacific Ocean (7 m)	0.07[a]	20.9	3.4	$13._1$[a]
Tsukumo Bay (0 m)	—	0.2_7	—	2.9
Watarase River	—	55	6.7	74
Tap water (Marunouti)	0.03[a]	0.5[a]	—	8.3[a]

MBT–SG: 10 g, column: 20 mm in dia.×70 mm, flow rate: 5 l/h. a) MBT–SG: 7 g, column: 20 mm in dia. ×50 mm, flow rate: 2.3 l/h.

Two samples of Pacific Ocean water and a sample of Watarase River water were distributed to a number of laboratories in Japan for comparison of the analytical results and the results using the recommended method are in good agreement with those obtained by the other laboratories. The 7-m sample of Pacific Ocean water with remarkably high values for copper and zinc was collected with a pump equipped on a research vessel, the Hakuho Maru belonging to the University of Tokyo. This contamination may originated from the metal in the gun-metal parts of the pump used for the sampling.

Conclusion

2-Mercaptobenzothiazole–silica gel (MBT–SG) provides an easy means of preconcentrating cadmium, copper, lead, and zinc and of separating copper from cadmium, lead, and zinc, and lead and cadmium from zinc for subsequent atomic absorption measurements of the contents of each metal. The attractive features of this chelating material are the easiness of preparation, reproducibility, and fast adsorbability for several metal ions from water samples in spite of its relatively low chelating capacity. Because dissolution of the reagent from the column is too small to be measured, a large volume of sample water (5—10 l) can be treated with a relatively small column, and the preconcentrated metal ions can be eluted from the column with a small volume of eluant resulting in a high concentration factor.

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