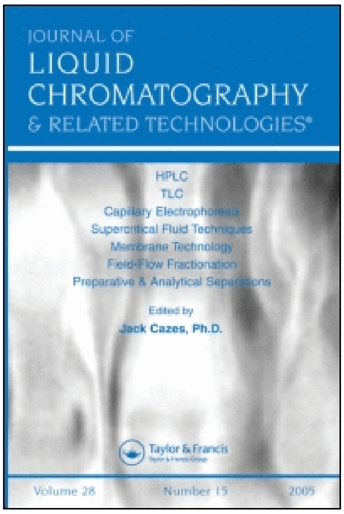

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Selective and Sensitive Determination of Mercury(II) Ions in River and Sea Water by an Automatic HPLC System Combined with On-line Column Enrichment

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Selective and Sensitive Determination of Mercury(II) Ions in River and Sea Water by an Automatic HPLC System Combined with On-line Column Enrichment

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Abstract: A selective and sensitive determination method for mercury (Hg) ions in river and sea water by reversed-phase high performance liquid chromatography (HPLC) has been developed. A one milliliter water sample containing Hg(II) ions was put into a 4 mL sample tube. To the sample tube, 2 mL of 0.5 mol/L (M) tetrabutylammonium bromide (TBA-Br) solution was added to form a neutral Hg compound. The Hg compound subsequently became pre-concentrated in a mini-column packed with 5 μm ODS. By switching the valve, the Hg compound was separated in an ODS analytical column, and detected with a photometric detector (255 nm). These processes occur automatically, except for the addition of water samples and 0.5 M TBA-Br. The correlation coefficient of the calibration curves (metal concentration *vs.* peak area) obtained with 1 mL of mercury standard was more than 0.9995 over the range of 1 ng/mL (ppb) to 10 μg/mL (ppm). The detection limit of Hg ions in 1 mL solution was 0.5 ppb, which corresponded to 3 times the standard deviation ($N = 8$) of the blank peak area. Effects of foreign ions on the method were investigated with 0.1-ppm Hg standard and 55 metal ions. Forty two metal ions of 200 ppm did not interfere with the determination of Hg(II) ions. Tolerance limits of Pd(II) and Ag(I) were 5 and 10 ppm, respectively. Recovery tests were carried out by the presented HPLC method with spiked river and sea water samples. The recoveries with a spiked river water sample for 400-, 40-, and 4-ppb Hg ion ($N = 5$) were 100.1 ± 0.2%, 100.1 ± 1.3%, and 97.9 ± 2.3%, respectively. Those with a sea

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water sample for 400-, 40-, and 4-ppb Hg ion ($N = 5$) were 100.9 ± 1.0%, 99.9 ± 1.8%, and 99.1 ± 9.4%, respectively.

Keywords: Mercury(II) ions, River water, Sea water, HPLC, On-line column enrichment

INTRODUCTION

Atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are routinely used for metal analysis. Inductively coupled plasma-mass spectrometry (ICP-MS) is sometimes used for more sensitive analysis. However, ICP-AES and ICP-MS require expensive apparatuses, and the detection sensitivity of AAS and ICP-AES differ considerably according to the metal. On the other hand, the application of high performance liquid chromatography (HPLC) in the separation and determination of metal ions has increased in recent years.[1–5] The HPLC apparatus is not too expensive and the running cost is very low.

The authors have reported metal determination methods by reversed-phase HPLC with photometric detection using dithiocarbamate,[6,7] β-diketones,[8,9] *N*-(dithiocarboxy)sarcosine, diammoniumsalt,[10], and salicylideneamino-2-thiophenol[11] as pre-column chelating agents.

Mercury (Hg) is well known as one of the most toxic metals. In a previous paper,[12] the authors reported a selective HPLC determination method for Hg(II) ions in a 5 mL solution as ion pairs with TBA-Br combined with solvent extraction. The lower determination limit was 10 ng/mL (ppb) and separation time was 12 min.

For continuous monitoring of Hg concentration in river and sea water, an automatic HPLC system is desirable with regard to reproducible calibration curves, wide working range, and running cost. In this work, a scaling down of sample size (5 to 1 mL), improvement of lower determination limit (10 to 1 ppb), and reduction of separation time (12 to 8 min) were accomplished as well as automation of the HPLC system combined with online column enrichment.

In this paper, pretreatment procedure for water samples, and HPLC conditions for pre-concentration and separation were studied for selective and sensitive determination of Hg(II) ions in river and sea water. The effect of 55 foreign ions on the determination of Hg ions was also examined. The detection limit, working range of calibration curve, reproducibility, and recoveries are described.

EXPERIMENTAL

Instrumentation

The HPLC system consisted of a Shimadzu (Kyoto, Japan) LC-6A pump (as pump B), Shimadzu LC-10A*i* pump (titanium alloy, as pump B), Shimadzu

SCL-10A system controller, Shimadzu SIL-10A auto injector, Shimadzu SPD-10AV *VP* photometric detector, Shimadzu PCV-12AH six-port valve, Develosil ODS-UG-5 column (enrichment column, 10 × 4.0 mm I.D., stainless steel, Nomura Chemical, Seto, Japan), Cosmosil 5 C_{18}-MS column (analytical column, 150 × 4.6 mm I.D., stainless steel, Nacalai Tesque, Kyoto, Japan), Shimadzu C-R4A data processor, and constant temperature water bath (40°C) as shown in Figure 1.

A pH meter model F-21 (Horiba, Tokyo, Japan) was used to measure the pH of aqueous solution. A micropipette was used for 1 mL or less volume of solution.

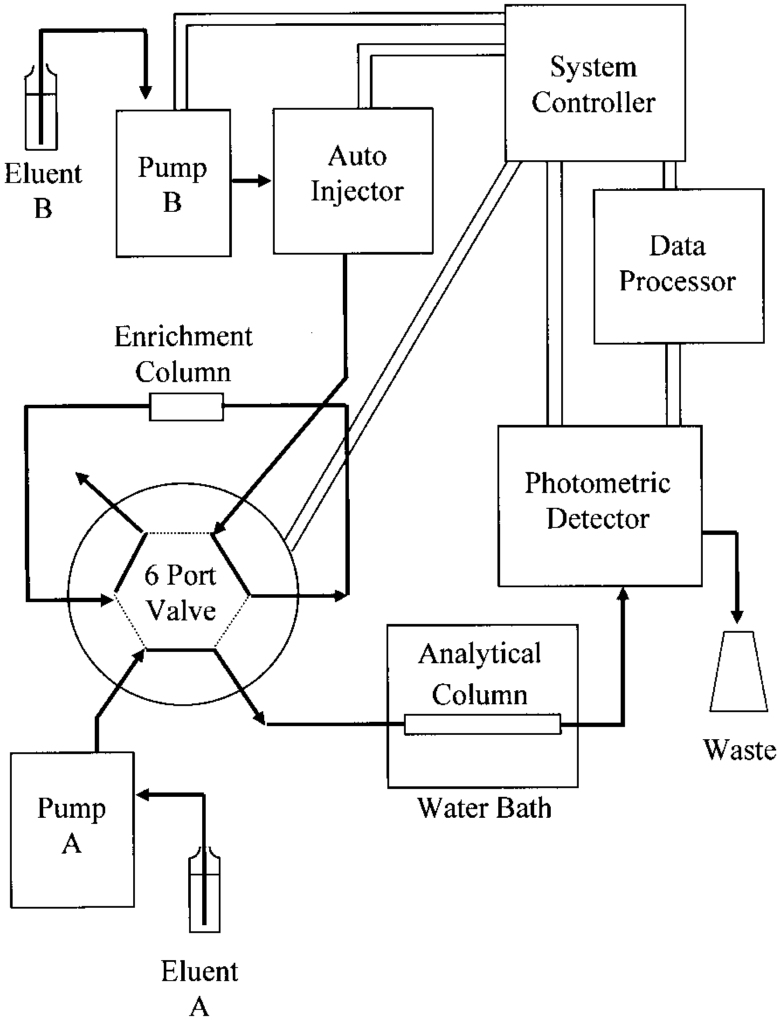


Figure 1. HPLC system for automatic determination of Hg(II) ion.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated. Milli-Q water was used for aqueous solution preparation. Hydrochloric acid was of super special grade for toxic metal analysis (Wako Pure Chemicals Industries, Osaka, Japan). Methanol was distilled and filtered through a membrane filter (pore size, 0.45 μm). Tetrabutylammonium bromide (TBA-Br, MW = 322.37, Wako) of 161 g, was dissolved in Milli-Q water in a concentration of 0.5 mol/L (M). The solution was also filtered through a membrane filter (pore size, 0.45 μm). All metal solutions of 1000 or 100 μg/mL (ppm) for AAS were purchased from Wako, and summarized in Table 1. A 1000 ppm Hg standard solution was prepared with $HgCl_2$ and 0.02 M HCl. The other Hg solutions were obtained by dilution of the above solution (1000 pm) with 0.1 M HCl. The mixture of 2 M HCl/water/0.5 M TBA-Br (1:79:20) was used as a cleaning solution for the auto-injector. River water and sea water was collected from the Kakehashi River (Komatsu, Japan) and the Sea of Japan (Kanazawa, Japan), respectively. Concentrated hydrochloric acid was added to the river and sea water immediately to adjust the pH to 1. The solutions were then filtered through a membrane filter (0.45 μm pore size) and used as the river and sea water samples for HPLC analysis.

Recommended Pretreatment Procedure and HPLC Conditions

Transfer a sample solution or an Hg standard solution of 1.0 mL into a 4 mL sample tube with a stopper. Adjust the pH of the solution to 1, if necessary. Add 2.0 mL of 0.5 M TBA-Br solution and stop the tube. Shake the contents for 10 seconds by hand and leave standing for at least for 15 min. Then, determine the Hg compound under the following HPLC conditions and a time program shown in Table 2.

Enrichment and analytical columns were described above. Eluent B (for enrichment): water/0.5 M TBA-Br (80:20, v/v), eluent A (for analysis): methanol/water/0.5 M TBA-Br (63:17:20, v/v), flow rate: 1.0 mL/min. Degass eluent A with an ultrasonicator and an aspirator before use. Injection volume: 1000 μL, detection wavelength: 255 nm, analysis time of HPLC (stop time): 8 min, column temperature: 40°C.

Rinse injection port 10 times with a cleaning solution and inject 1000 μL of a blank solution (0.1 M HCl:0.5 M TBA-Br = 1:2, v/v) twice, to reduce memory effect of Hg compound after injection of sample solution.

Effects of Foreign Ions

The effects of foreign ions on the determination of Hg ions were tested with 55 metal ions. Each foreign metal ion and 500 μL of 0.2 ppm Hg standard (pH 1) were placed into a sample tube, and diluted to 1000 μL with 0.1 M HCl. Concentration of Hg ions in the solution was determined by the recommended procedure and HPLC conditions. The recovery percentage was calculated from the peak area and that of the Hg standard containing no foreign metal ions.

Recovery Tests with River and Sea Water Samples

A river or sea water sample (pH 1) of 800 μL and 200 μL of 0.1 M HCl was prepared in a sample tube. To another sample tube, 800 μL of a river or sea water sample and 200 μL of Hg standard were added. The concentrations of the Hg standard were 2000, 200, and 20 ppb. Thus, the concentrations of added Hg ion in the 1-mL solutions were 400, 40, and 4 ppb. The Hg concentrations in these solutions were determined according to the proposed HPLC method, and each recovery percentage was calculated from the results.

RESULTS AND DISCUSSION

HPLC Separation Conditions

While a 250 mm length ODS column was used in the previous work,[12] a shorter analytical column (150 mm) was used to reduce analysis time and to obtain a higher peak of the Hg compound. Because TBA-Br was required for the quantitative elution of the Hg compound, the composition of eluent A (for separation) was investigated with a methanol/water/0.5 M TBA-Br mixture. The concentration of TBA-Br in the eluent affected the retention time of the Hg compound peak, in spite of the same methanol content. The higher the concentration of TBA-Br, the longer the retention time of the Hg compound peak. The results suggested that TBA-Br served as an ion pair reagent as discussed in a previous paper.[12] The preliminary experiments of calibration curves indicated that 16% or more (16–20%) content of 0.5 M TBA-Br was required to obtain a linear calibration curve for 1 to 10 ppb of Hg(II) ion. Contents of methanol and water were decided because of the reasonable retention time of the Hg compound peak (about 5 min). Thus, the mixture of methanol/water/0.5 M TBA-Br (63:17:20, v/v) was selected as eluent A. Because eluent B is used for enrichment of the Hg compound, methanol is not required. On the other hand, TBA-Br was also required in eluent B for quantitative retention of the Hg compound in an enrichment column. Thus, the mixture of water/0.5 M TBA-Br (80:20, v/v) was selected as eluent B. The concentration of the TBA-Br is the same as in eluent A.

The detection wavelength (255 nm) and analytical column temperature (40°C) were the same as in the previous paper.[12]

Table 1. Metal standard solutions used

Metal	Salt	Medium	Metal	Salt	Medium
Ag(I)	$AgNO_3$	0.1 M HNO_3	Mn(II)	$Mn(NO_3)_2$	0.1 M HNO_3
Al(III)	$Al(NO_3)_3$	0.5 M HNO_3	Mo(VI)	$(NH_4)_6Mo_7O_{24}$	H_2O
As(III)	As_2O_3	NaOH in water pH 5 with HCl	Na(I)	NaCl	H_2O
Au(III)	$HAuCl_4$	1 M HCl	Nd(III)	$Nd(NO_3)_3$	1 M HNO_3
Ba(II)	$BaCl_2$	1 M HCl	Ni(II)	$Ni(NO_3)_2$	0.1 M HNO_3
Be(II)[a]	$BaSO_4$	0.03 M HNO_3	Pb(II)	$Pb(NO_3)_2$	0.1 M HNO_3
Bi(III)	$Bi(NO_3)_3$	0.5 M HNO_3	Pd(II)	$PdCl_2$	1 M HCl
Ca(II)	$CaCO_3$	0.1 M HNO_3	Pr(III)	$Pr(NO_3)_3$	1 M HNO_3
Ce(III)	$Ce(NO_3)_3$	1 M HNO_3	Pt(IV)	H_2PtCl_6	1 M HCl
Cd(II)	$Cd(NO_3)_2$	0.1 M HNO_3	Rh(III)	$Rh(NO_3)_3$	2 M HNO_3
Co(II)	$Co(NO_3)_2$	0.1 M HNO_3	Sb(III)	$SbCl_3$	3 M HCl
Cr(VI)	$K_2Cr_2O_7$	0.1 M HNO_3	Sc(III)[a]	Sc (metal)	1 M HNO_3
Cs(I)	$CsNO_3$	0.5 M HNO_3	Se(IV)	SeO_2	0.1 M HNO_3
Cu(II)	$Cu(NO_3)_2$	0.1 M HNO_3	Si(IV)	Na_2SiO_3	0.2 M Na_2CO_3

Dy(III)	$Dy(NO_3)_3$	1 M HNO_3	Sm(III)	$Sm(NO_3)_3$	1 M HNO_3
Er(III)	$Er(NO_3)_3$	1 M HNO_3	Sn(II)	$SnCl_2$	6 M HCl
Eu(III)	$Eu(NO_3)_3$	1 M HNO_3	Sr(II)	$Sr(NO_3)_2$	1 M HNO_3
Fe(III)	$Fe(NO_3)_3$	0.1 M HNO_3	Tb(III)	$Tb(NO_3)_3$	1 M HNO_3
Ga(III)	$Ga(NO_3)_3$	1 M HNO_3	Te(IV)	$TeCl_4$	6 M HCl
Gd(III)	$Gd(NO_3)_3$	1 M HNO_3	Ti(IV)	$Ti(SO_4)_2$	1 M H_2SO_4
Ge(IV)	GeO_2	H_2O	Tl(I)	$TlNO_3$	1 M HNO_3
Hg(II)	$HgCl_2$	0.02 M HCl	Tm(III)	$Tm(NO_3)_3$	1 M HNO_3
Ho(III)	$Ho(NO_3)_3$	1 M HNO_3	V(V)	NH_4VO_3	0.45 M H_2SO_4
In(III)	In (metal)	0.5 M HNO_3	W(VI)	Na_2WO_4	H_2O
K(I)	KCl	H_2O	Y(III)	$Y(NO_3)_3$	1 M HNO_3
La(III)	$La(NO_3)_3$	1 M HNO_3	Yb(III)	$Yb(NO_3)_3$	1 M HNO_3
Lu(III)	$Lu(NO_3)_3$	1 M HNO_3	Zn(II)	$Zn(NO_3)_2$	0.1 M HNO_3
Mg(II)	$Mg(NO_3)_2$	0.1 M HNO_3	Zr(IV)	$ZrO(NO_3)_2$	1 M HNO_3

[a] Concentrations of the metal ions were 1000 ppm, except for Be and Sc (100 ppm).

Table 2. Time program for automatic pre-concentration and HPLC analysis

Time (min)	Command	Value	Action
6.9	ZERO A		Adjust absorbance to zero
7.0	RV. A	1	Change valve for elution position
7.0	START		Start data processor
11.0	RV. A	0	Change valve for concentration position
13.8	S. PRET		Start sample injection procedure
16.0	STOP		Stop time program (Analysis is repeated.)

Enrichment Conditions

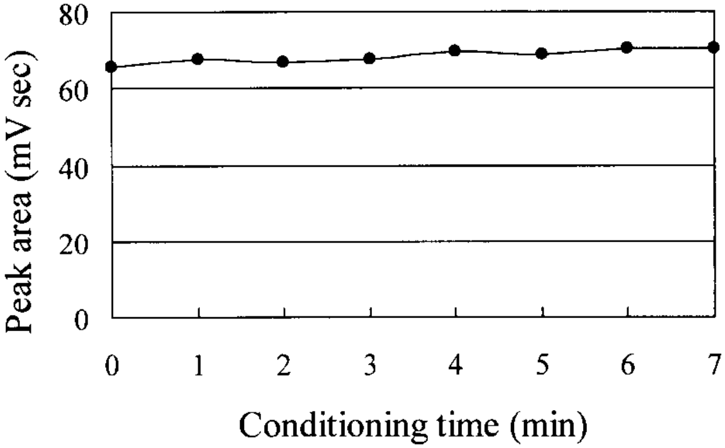
Before injection of a pretreated sample solution, the six-way valve should be switched to the concentration position, and the eluent B should be made to flow to the enrichment column for several minutes, otherwise, a part of the Hg compound was eluted from the enrichment column due to the high methanol content in the eluent A. This conditioning time should be optimized.

After injection of the sample solution, eluent A was made to flow for several minutes because the pH of the injected solution is 1.2; the solution is liable to damage the ODS analytical column. Thus, the rinse time was also investigated.

The results of the conditioning and rinse times were shown in Figure 2. Because the sample solution contained no organic solvent, the loss of Hg compound was negligible for the conditioning times examined. From the results of Figure 2, conditioning time and rinse time were set at 5 and 7 min, respectively.

Sample Pretreatment

When solvent extraction was used for pre-concentration of Hg(II) ions, optimum volume of 0.5 M TBA-Br was in the range of 0.5 to 1.5 mL for a 5 mL sample solution, and 1 mL was employed in the previous paper.[12] From this result, it seems that the optimum volume of 0.5 M TBA-Br for a 1 mL sample solution was 0.1 to 0.3 mL. However, the correlation coefficient of the calibration curve for 1 to 10 ppb Hg(II) ion was lower than 0.99 under this condition. Thus, effects of the TBA-Br concentration on the linearity of the calibration curve for 1–10 ppb Hg ion were investigated with various volumes of 0.5 M TBA-Br (0, 0.1, 0.2, 0.5, 1, and 2 mL). Because the addition of 1 mL and 2 mL of 0.5 M TBA-Br gave linear calibration curves for 1–10 ppb Hg ion, 2 mL was selected for a 1 mL sample solution. Standing time between the addition of TBA-Br and injection did not affect the peak area of neutral Hg compound for at least 15 to 95 min.



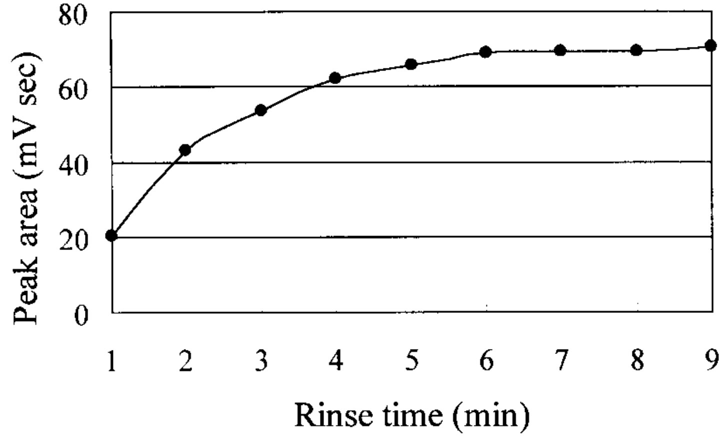


Figure 2. Effects of conditioning time and rinse time on peak areas of Hg compound. Concentration of Hg(II) in a 1 mL solution was 40 ppb.

When 2 mL of 0.5 M TBA-Br was added to 1 mL of the sample solution of pH 1, the pH of the resulting solution was 1.2. Buffer solution was not required because the peak area of neutral Hg compound was constant over the pH range of 1.0 to 8.5, and linear calibration curves were obtained at pH 1.2, as mentioned below.

Calibration Curve, Reproducibility, and Detection Limit

Calibration curves for Hg(II) ions were prepared with an Hg standard of varying concentrations by the recommended procedure and HPLC conditions.

Correlation coefficients of the calibration curves were more than 0.9995 over the concentration range of 1 ppb to 10 ppm, as shown in Table 3. The wide calibration range was compared with that of ICP-AES.

Relative standard deviations ($N = 6$ or 5) of Hg peak areas obtained with 5 ppm, 500 ppb, 50 ppb, and 5 ppb Hg standard solutions were 1.0, 1.1, 0.8, and 1.9%, respectively (Table 3).

The detection limit of Hg ions in a 1 mL solution was 0.5 ppb, which corresponded to 3 times the standard deviation ($N = 8$) of the blank peak areas. The chromatograms obtained by 0.2 ppm and 6 ppb Hg (II) standards are shown in Figure 3.

Effects of Foreign Ions

The effects of 55 foreign ions on the determination of 0.1 ppm Hg(II) ions (1 mL) were investigated. The tolerance limit value of the foreign ion

Table 3. (a) Calibration curves for Hg ion and (b) reproducibilities of peak areas (mV/sec)

Concentration range	Equation of line	Correlation coefficient	Measuring point (ppb)
(a)			
1–10 ppm[a]	$y = 9.1751x + 0.9884$	0.9996	0, 1, 2, 4, 6, 8, 10 (ppm)
100–1000 ppb[b]	$y = 0.5022x + 0.1917$	0.9999	0, 100, 200, 400, 600, 800, 1000
10–100 ppb[c]	$y = 0.5055x + 0.1496$	0.9998	0, 10, 20, 40, 60, 80, 100
1–10 ppb[d]	$y = 1.0894x + 1.8052$	0.9997	0, 1, 2, 4, 6, 8, 10

(b)	Peak area			
No. of run	5 ppm	500 ppb	50 ppb	5 ppb
1	61.220	65.035	26.736	7.526
2	62.690	66.695	27.362	7.528
3	62.590	66.448	27.171	7.585
4	62.397	65.565	27.342	7.225
5	62.666	65.001	27.043	7.494
6	63.138	66.216	27.156	($N = 5$)
Average	62.450	65.827	27.135	7.472
SD[e]	0.650	0.731	0.230	0.142
RSD[f] (%)	1.0%	1.1%	0.8%	1.9%

y: peak area (mV sec), x: concentration of Hg ion (ppm or ppb).

Detector range (AUFS): [a]2, [b]0.5, [c]0.05, [d]0.02.

[e] Standard deviation.

[f] Relative standard deviation.

Detector range was changed with concentration of Hg (II) ion.

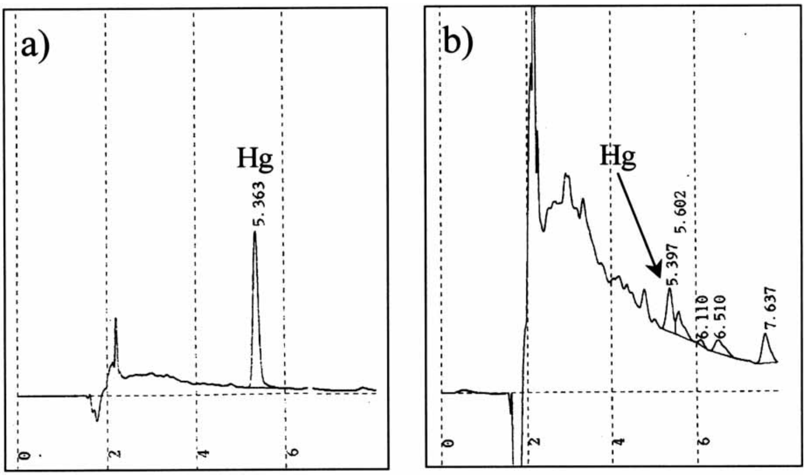


Figure 3. Typical chromatograms obtained from 1 mL of 0.2 ppm Hg (a) and 6 ppb Hg (b) standard solutions.

concentration was taken as the value that caused an error of less than 10% in the recovery of Hg ions. The tolerance limits of Pd(II) and Ag(I) were 5 ppm and 10 ppm, respectively (50 and 100 fold concentration of Hg ions). When Pd(II) and Ag(I) ions were added to the Hg standard (0.1 M HCl), yellow and white precipitations were formed, respectively. The tolerance limits of Bi(III), Pt(IV), and Mo(VI) were 20 ppm. More details are shown in Table 4. Forty two ions, including Na(I), did not interfere with the determination of Hg ion at two thousand times the concentration of Hg ions. Some metal ions such as Cr(VI), Pt(IV), and Mo(VI) gave chromatographic peaks. As shown in Table 1 (Salt), significant amounts of hydrogen, chloride,

Table 4. Effects of foreign metal ions and NaCl on determination of 0.1 ppm Hg ion

Tolerance limit	Metal ion or salt
200 ppm	Al(III), As(III), Ba(II), Ca(II), Ce(III), Co(II), Cs(I), Cu(II), Dy(III), Er(III), Eu(III), Fe(III), Ga(III), Gd(III), Ge(IV), Ho(III), In(III), K(I), La(III), Lu(III), Mg(II), Mn(II), Nd(III), Ni(II), Pb(II), Pr(III), Rh(III), Se(IV), Sm(III), Sn(II), Sr(II), Tb(III), Te(IV), Ti(IV), Tl(I), Tm(III), V(V), Y(III), Yb(III), Zn(II), Zr(IV)
100 ppm	Au(III), Cd(II), Cr(VI), Sb(III), Si(IV), W(VI)
50 ppm	Be(II), Sc(III)
20 ppm	Bi(III), Pt(IV), Mo(VI)
10 ppm	Ag(I)
5 ppm	Pd(II)
3.5 w/v%	NaCl

Note: The tolerance limit value of the foreign ion concentration was taken as the value that caused an error of less than 10% in the recovery of Hg(II) ion (0.1 ppm).

Table 5. Recovery tests of Hg ion with river and sea water samples

No. of experiment	Added (ppb)	Found (ppb)	Recovery[a] ± SD[b] (%)	Equation of calibration curve (y = mV sec, x = ppb)	Correlation coefficient
River water (Result 1)					
R-400-1	400	400.6 ± 0.8	100.1 ± 0.2	$y = 0.1267x - 0.9186$	0.9998
R-40-1	40.0	40.04 ± 0.52	100.1 ± 1.3	$y = 0.486x + 0.2896$	0.9999
R-4-1	4.00	3.916 ± 0.093	97.9 ± 2.3	$y = 1.1618x + 1.3952$	0.9996
River water (Result 2)					
R-400-2	400	399.3 ± 3.4	99.8 ± 0.8	$y = 0.1255x - 0.2528$	0.9999
R-40-2	40.0	40.01 ± 0.31	100.1 ± 1.3	$y = 0.5104x - 0.7146$	0.9999
R-4-2	4.00	4.098 ± 0.123	102.4 ± 3.1	$y = 1.0846x + 1.3206$	0.9999
Sea water (Result 1)					
S-400-1	400	403.6 ± 3.8	100.9 ± 1.0	$y = 0.5022x + 0.1917$	0.9999
S-40-1	40.0	39.97 ± 0.73	99.9 ± 1.8	$y = 0.5055x + 0.1496$	0.9998
S-4-1	4.00	3.965 ± 0.376	99.1 ± 9.4	$y = 1.0894x + 1.8052$	0.9997
Sea water (Result 2)					
S-400-2	400	400.9 ± 2.5	100.2 ± 0.6	$y = 0.1239x - 0.0989$	0.9999
S-40-2	40.0	40.53 ± 0.58	101.3 ± 1.4	$y = 0.4841x - 0.0805$	0.9997
S-4-2	4.00	4.157 ± 0.358	103.9 ± 9.0	$y = 0.4841x - 0.0805$	0.9996

The different slopes of the calibration curves were caused by difference of the detector ranges.

[a] Recovery (%) = (Found/Added) × 100.

[b] Standard deviation ($N = 5$).

nitrate, and sulfate ions did not interfere with the determination of Hg(II) ions. The tolerance limits of NaCl (3.5 w/v %) indicated that this method could be applied to sea water samples, because the NaCl concentration in sea water is about 3.2 to 3.5 w/v %.

The effects of foreign ions described above indicated that the presented HPLC method is selective for Hg(II) ions, except for some metal ions.

Recovery Tests with River and Sea Water Samples

Hg concentrations in the collected river and sea water samples were lower than detection limits (0.5 ppb) of the presented HPLC method. Therefore, Hg standards were added to the river and sea water samples, and the Hg ions in the solutions were analyzed. Table 5 shows the results of the recovery tests. When Hg standards were added to the river water sample, the recoveries obtained for 400-, 40-, and 4-ppb Hg ions were 100.1 $\pm$ 0.2, 100.1 $\pm$ 1.3, and 97.9 $\pm$ 2.3%, respectively. With the sea water sample, the recoveries obtained for 400, 40, and 4 ppb Hg ions were 100.9 $\pm$ 1.0, 99.9 $\pm$ 1.8, and 99.1 $\pm$ 9.4%, respectively. The standard deviations of the recoveries were less than 2.5%, except for the 4-ppb spiked sea water sample. Table 5 shows that the two results obtained on other days showed good agreement with each other. As shown in Table 5, correlation coefficients of the calibration curves were more than 0.9995. The high recovery indicated that the ions in typical river and sea water did not interfere with the Hg determination.

CONCLUSION

In this paper, a highly selective automatic HPLC method for ppb levels of Hg(II) ions has been shown. In this method, pre-concentration of the Hg ion is carried out automatically by the column enrichment technique. This method requires only methanol as an organic solvent. This method is highly selective for Hg ions, and almost all metal ions examined gave no chromatographic peak. The use of a narrower column with lower flow rate may enable continuous maintenance free operation for 24 hr.

The calibration curves for Hg ions were linear over four orders of magnitude (1 ppb–10 ppm), and high recoveries were obtained with the spiked river and sea water samples.

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