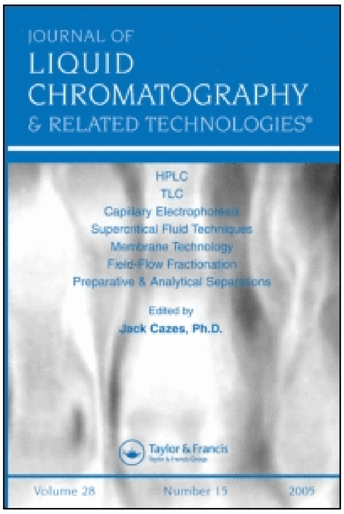

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Selective Determination of Mercury(II) Ion in Water by Solvent Extraction Followed by Reversed-Phase HPLC

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ABSTRACT

A selective determination method for mercury(II) ion in water by reversed-phase high performance liquid chromatography (HPLC) has been developed. A water sample of 5 mL was put into a 10-mL centrifuge tube with a stopper. Then, 1 mL of 2-mol/L (M) acetate buffer solution of pH 5.5 was added into the centrifuge tube. After mixing the contents, 1 mL of 0.5 M tetrabutylammonium bromide (TBA-Br) solution and 0.3 mL of 1-octanol were added. A mercury ion was extracted into an organic layer by shaking the contents for 10 min. The organic layer of 8 μL was injected into a C_{18} column with an eluent of methanol/water/0.5 M TBA-Br (65 : 31 : 4, v/v), and the effluent was monitored at 255 nm. The detected mercury compound was estimated as $[(TBA^+)_2 \cdot HgBr_4^{2-}]^0$.

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The correlation coefficient of the calibration curves (metal concentration vs. peak area), obtained with 5 mL of mercury standard, was more than 0.999 over the range of 10 ng/mL (ppb) to 10 μg/mL (ppm). The detection limit of Hg ion in a 5-mL solution was 0.8 ppb, which corresponded to three times the standard deviation of the blank peak area. Reproducibilities (RSD) of peak areas for 5-, 0.5-, and 0.05-ppm Hg ion were 1.8%, 0.6%, and 0.6%, respectively ($N = 5$). Recovery tests were carried out by the presented HPLC method with spiked river water samples. The recoveries for 5-, 0.5-, and 0.05-ppm Hg ion were 99.5%, 102.9%, and 99.8%, respectively. Effects of foreign ions on the method were investigated with 0.2-ppm Hg standard and 55 metal ions. Tolerance limits of Be(II) and Sc(III) were 20 ppm, and those of Bi(III) and Pd(II) were 40 ppm. The other metal ions of 100 ppm, or more, did not interfere with the determination of mercury(II) ion.

Key Words: Mercury(II) ion; High performance liquid chromatography; Ion pair extraction; Tetrabutylammonium bromide.

INTRODUCTION

Mercury (Hg) is well known as one of the most toxic metals. For mercury analysis, atomic absorption spectrometry combined with a reducing vaporization technique, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma-mass spectrometry are routinely used.

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] HPLC is not a very expensive apparatus, and the running cost is very low. In addition, operation of the HPLC is easy and specific skills are not required. Many metal ions have been determined as metal chelates with various chelating agents.

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. A more sensitive quantitative analysis (ng/mL level) is possible by combining pre-column derivatization HPLC with appropriate pre-concentration, such as solvent extraction.

We found that Hg(II) ion in acidic solution was extracted into some alcohols, such as 1-octanol or 1-decanol, in the presence of tetrabutylammonium bromide (TBA-Br). The extracted mercury compound gave no chromatographic peak with a methanol–water eluent and a C_{18} column. However, an eluent of methanol–water containing TBA-Br gave a sharp chromatographic peak. In addition, it was found that the peak area or height was proportional to the Hg(II) ion concentration under certain conditions.

In this paper, extraction and HPLC conditions were studied for selective and sensitive determination of Hg(II) ion in water. The detection limit, working range of calibration curve, reproducibility, and recovery were described. The composition of Hg compound extracted was also discussed.

EXPERIMENTAL

Instrumentation

The HPLC system consisted of a Jasco PU-1580i inert pump (Japan Spectroscopic Co., Ltd., Tokyo, Japan), Rheodyne 9725i injector (Cotati, CA), Jasco UVIDEC-100-VI photometric detector (Japan Spectroscopic Co., Ltd., Tokyo, Japan), Cosmosil 5 C_{18}-MS-II stainless steel column (250 × 4.6 mm ID, Nacalai Tesque, Kyoto, Japan), Chromatopac C-R8A data processor (Shimadzu Co., Kyoto, Japan), and a thermostat water bath. A micro syringe with an Ni–Ti alloy plunger was used for sample injection. A Yamato SA-31 auto-shaker (Yamato Scientific Co., Ltd., Tokyo, Japan) was used for solvent extraction. A pH meter model F-21 (Horiba, Ltd., Tokyo, Japan) was used to measure the pH of the aqueous layer. A micropipette was used for 1 mL or less volume of solution.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated. Milli-Q water was used for the aqueous-solution preparation. Hydrochloric acid was of super special grade for toxic metal analysis (Wako Pure Chemicals Industries Co., Osaka, Japan). Methanol was distilled and filtered through a membrane filter (pore size, 0.45 μm). A TBA-Br (Wako) solution of 0.5 mol/L (M) was also filtered through a membrane filter (pore size, 0.45 μm). The mercury standard solution of 1000 μg/mL (ppm) for AAS was obtained from Wako. The Hg solution was prepared with $HgCl_2$ and 0.02 M HCl. The other Hg solutions were obtained by dilution of the above solution (1000 ppm) with 0.1 M HCl. $HgSO_4$, HgI_2, $Hg(CH_3COO)_2$, and $HgBr_2$ were purchased from Wako. Other metal solutions of 1000 ppm used were purchased from Wako, and summarized in Table 1. For pH adjustment, 0.1 M HCl, 2 M acetic acid/1 M HCl (pH 1.5–3), 2 M acetic acid/2 M

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).

sodium acetate solution (pH 4–6), 2 M *tris*(hydroxymethyl)aminomethane/1 M HCl (pH 7 and 8), and 2 M NH_3/2 M NH_4Cl solutions (pH 9 and 10) were used. River water was collected from the Kakehashi River (Komatsu, Japan). Concentrated hydrochloric acid was added to the river water, immediately, to adjust the pH to 1. The solution was then filtered through a membrane filter (0.45 µm pore size) and used as the river water sample for HPLC analysis.

Recommended Extraction Procedure and HPLC Conditions

Transfer a sample solution, or an Hg standard solution (5.0 mL), into a 10 mL centrifuge tube with a stopper. Adjust the pH of the solution to about 5, if necessary. Add 1000 μL of 2 M acetic acid/2 M sodium acetate buffer solution (pH 5.5). After mixing, add 1000 μL of 0.5 M TBA-Br solution and 300 μL of 1-octanol. Shake the contents for 10 min. After standing at least for 5 min, determine the Hg compound extracted under the following HPLC conditions: column: Cosmosil 5 C_{18}-MS-II (250 × 4.6 mm ID, particle size 5 μm), column temperature: 40°C, eluent: methanol/water/0.5 M TBA-Br (65 : 31 : 4, v/v), flow rate: 1.0 mL/min, injection volume: 8 μL (organic layer), detection wavelength: 255 nm. Analysis time of HPLC (stop time): 12 min.

HPLC Conditions

Optimum detection wavelength was determined by the following experiment: according to the recommended extraction procedure, the Hg ion (1 ppm in a 5-mL solution) was extracted into 1-octanol. After phase separation, 5 μL of the organic layer was injected and analyzed under the recommended HPLC conditions, except for detection wavelength (240–330 nm). Each peak area was plotted against the wavelength.

Injection volume was investigated in the range of 3–20 μL. The peak area and peak height of Hg compound were measured and plotted against the injection volume.

Eluent composition was investigated with methanol/water/0.5 M TBA-Br mixture as an eluent, to obtain maximum peak height and reasonable retention time.

Extraction Conditions

For quantitative extraction of Hg ion into 1-octanol, effects of TBA-Br concentration, extraction pH, and shaking time were investigated. Into a centrifuge tube, 1000 μL of 50 ppm Hg standard and $(6 - x)$ mL of water were added. After mixing, 1000 μL of 2 M acetate buffer solution (pH 5.5) was added to the centrifuge tube, and the contents were stirred by hand. Finally, x mL of 0.5 M TBA-Br solution and 300 μL of 1-octanol were added, where x varied from 0 to 2. The total volume of each aqueous layer was 7 mL. The contents were then shaken for 10 min, and the 5 μL of the organic layer was chromatographed according to the recommended HPLC conditions. The peak area of the Hg compound peak was plotted against the volume of 0.5 M TBA-Br solution added.

Extraction pH (pH 0.7–9.5) was also investigated with various buffer solutions according to the recommended procedure, except for pH. After phase separation, the pH of the aqueous layer was measured by a pH meter, and the peak area was plotted against the measured pH. Shaking time for quantitative extraction of an Hg ion was examined over the range of 2–80 min.

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 200 μL of 5-ppm Hg standard were placed into a centrifuge tube, and diluted to 5 mL with Milli-Q water. Concentration of Hg ion 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 ion.

Recovery Tests with a River Water Sample

River water samples (pH 1) of 4.5 mL and 500 μL of Milli-Q water were taken into a centrifuge tube. To another centrifuge tube, 4.5 mL of a river water sample and 500 μL of an Hg standard were added. The concentrations of the Hg standard were 50, 5, and 0.5 ppm. Thus, the concentrations of added Hg ions in 5 mL solutions were 5, 0.5, and 0.05 ppm. The Hg concentrations in these solutions were determined according to the recommended procedure and HPLC conditions, and each recovery percentage was calculated by the results.

RESULTS AND DISCUSSION

HPLC Conditions

The detection wavelength (255 nm) was set for a maximum peak area of Hg compound as shown in Fig. 1. Because TBA-Br was required for the elution of an Hg compound, the effects of the TBA-Br concentration in eluent (methanol/water/0.5 M TBA-Br) on the peak height and retention time of the Hg compound were investigated. Considering the results shown in Fig. 2, 20 mM was employed, because the Hg compound gave maximum peak height and reasonable retention time. Thus, the mixture of methanol/water/0.5 M TBA-Br (65 : 31 : 4, v/v) was employed as the eluent for Hg determination,

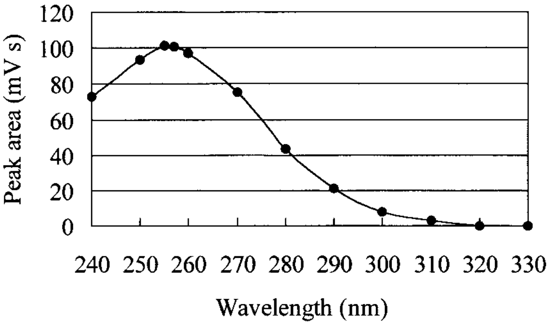

Figure 1. Peak area vs. detection wavelength.

and run at 1.0 mL/min. Injection volume was examined in the range of 3–20 μL. The linear range of peak area was 3–20 μL, while peak height was 3–10 μL. Thus, 8 μL was selected as optimum injection volume. The column temperature was set at 40°C considering the separation time (column pressure). A typical chromatogram obtained by the conditions was shown in Fig. 3a. Although, the retention time of the Hg peak was about 4.8 min, analysis time (stop time) was set at 12 min because of the base line disturbance near 10.5 min.

Extraction Conditions

TBA-Br was required for extraction of Hg ion. When tetramethylammonium chloride (TMA-Cl) was used instead of the TBA-Br, no chromatographic peak appeared in a chromatogram. As shown in Fig. 4, the

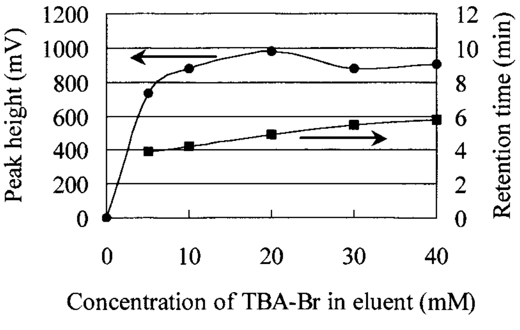

Figure 2. Effects of TBA-Br on peak height and retention time of Hg compound.

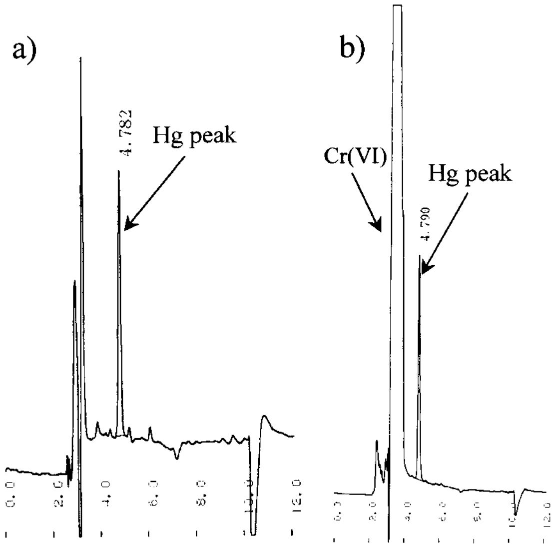

Figure 3. Typical chromatograms of (a) Hg compound and (b) effect of Cr(VI) ion. Concentration of metal ions in a 5-mL solution at the extraction step: (a) 0.05 ppm Hg, (b) 200 ppm Cr(VI), and 0.2 ppm Hg.

optimum amount of 0.5 M TBA-Br was determined as 1.0 mL, because the peak area of the Hg compound was maximum and constant in the range of 0.5 to 1.5 mL.

The effect of pH on the extraction of the Hg ion was shown in Fig. 5. Because, constant and maximum peak areas were obtained over the pH range of 1.8–8.5, pH 5.5 was employed. This pH is easily controlled by an

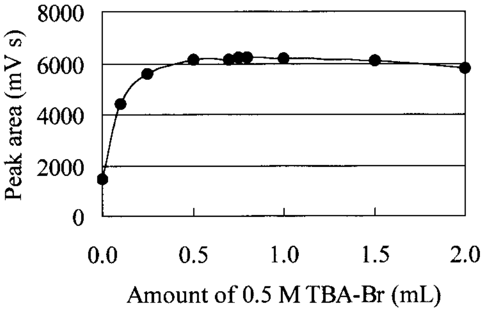

Figure 4. Effect of TBA-Br on extraction of Hg(II) ion.

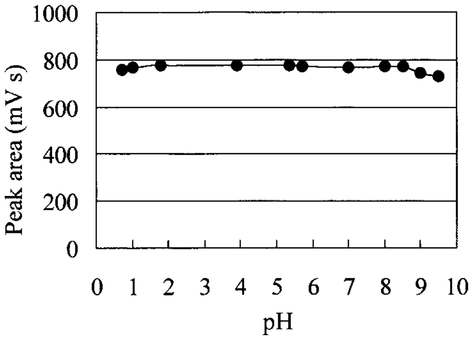

Figure 5. Effect of pH on extraction of Hg(II) ion.

acetate buffer solution (acetic acid/sodium acetate). If a large amount of foreign ion forms a precipitant of hydroxide, lower pH should be selected.

Because, the Hg ion was quantitatively extracted into 1-octanol by shaking for 5–80 min, 10 min was selected.

Stability of the Hg compound in 1-octanol (organic layer) was also examined. Extraction was carried out according to the recommended procedure, and the organic layer was put into a micro test tube with a stopper. After standing, the organic layer of 5 μL was chromatographed, and the peak area of the Hg compound peak was plotted against the standing time. The result indicated that the Hg compound extracted is stable for at least 8 hr, because constant peak area was obtained.

Composition of Extracted Hg Compound

Hg standard solutions used were prepared with $HgCl_2$ and 0.02 M HCl. It is well known that $HgCl_2$ is slightly soluble in water, while highly soluble in hydrochloric acid as $H_2[HgCl_4]$. At first, it was expected that the Hg ion was extracted as an ion pair of TBA_2HgCl_4. To estimate the composition of the Hg compound extracted, $HgSO_4$, HgI_2, $Hg(CH_3COO)_2$, and $HgBr_2$ were also tested as starting materials. Because $HgSO_4$ and HgI_2 were slightly soluble in water, solvent extractions were carried out with the aqueous solutions (1000 ppm Hg) of (1) $HgCl_2$, (2) $HgBr_2$, and (3) $Hg(CH_3COO)_2$. The peak area ratio obtained by the three solutions (1) : (2) : (3) was about 10 : 10 : 6. There was a precipitant of red color in the 1000 ppm solution of (3) Hg $(CH_3COO)_2$, and, thus, gave smaller peaks. It should be noted that the peaks of Hg compounds obtained by the three experiments gave exactly the same retention time. In addition, similar experiments carried out without acetate buffer solution also gave peaks of the same retention time. The agreement of the retention time indicated that the Hg compound extracted has the same composition, in spite of the different starting materials (salts).

When TBA-Br was absent in the eluent, no chromatographic peak appeared. Absence of TBA-Br at the extraction step also gave no peak. $HgBr_2$ is well known that the salt was soluble as $HgBr_4^{2-}$ in the presence of bromide anion.

All the results indicated that the extracted Hg compound was $[(TBA^+)_2 HgBr_4^{2-}]^0$, that is, at first the Hg ion (for example, $HgCl_4^{2-}$) was converted to $HgBr_4^{2-}$in the presence of TBA-Br at the extraction step, and then extracted as an ion pair of TBA_2HgBr_4. At least, the composition is consistent with our results.

Calibration Curves, Detection Limit, and Reproducibility

Calibration curves for Hg ions were prepared with Hg standards of varying concentrations by the recommended extraction procedure and HPLC conditions. Correlation coefficients of the calibration curves were more than 0.999 over the concentration range of 10 ppb–10 ppm, as shown in Table 2. The wide calibration range was compared with that of ICP-AES.

Reproducibilities [relative standard deviation ($N = 5$)] of Hg peak areas obtained with 5, 0.5, and 0.05 ppm Hg standard solutions were 0.9%, 1.8%, and 0.6%, respectively (Table 2). Reproducibilities obtained another day were 1.8%, 0.6%, and 1.1%, respectively.

The detection limit of the Hg ion in 5-mL solution was 0.8 ppb, which corresponded to three times the standard deviation of the blank peak area.

Effects of Foreign Ions

The effects of 55 foreign ions on the determination of 0.2-ppm Hg(II) ion (5 mL) were investigated. 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 0.2 ppm Hg ion. The tolerance limits of Be(II) and Sc(III) were 20 ppm (100-fold concentration of Hg ion), as shown in Table 3. Those of Bi(III), Pd(II), Ag(I), Sn(II), and V(V) were 40, 40, 100, 100, and 100 ppm, respectively. The other ions tested did not interfere with the determination of the Hg ion at a thousand times the concentration of the Hg ion. Some metal ions, such as Cr(VI), Pt(IV), and V(V) gave chromatographic peaks. The chromatogram obtained by 0.2 ppm Hg(II) and 200 ppm Cr(VI) was shown in Fig. 3b. As shown in Table 1 (salt), significant amounts of H^+,

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Table 2. Calibration curves for Hg ion and reproducibilities of peak areas.

Concentration range	Equation of line	Correlation coefficient	Measuring point (ppm)
Calibration curves for Hg ion			
1–10 ppm	$y = 511.94x + 10.136$	0.9999	0, 1, 2, 4, 6, 8, 10
0.1–1 ppm	$y = 522.53x - 1.1557$	0.9998	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1 ppm	$y = 490.96x - 0.2885$	0.9995	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10

5 ppm Hg		0.5 ppm Hg		0.05 ppm Hg	
No. of run	Peak area	No. of run	Peak area	No. of run	Peak area
Reproducibilities of peak areas (mV sec)					
1	2,529.203	1	268.359	1	24.306
2	2,526.687	2	276.998	2	24.663
3	2,556.798	3	273.922	3	24.607
4	2,579.847	4	281.147	4	24.370
5	2,566.949	5	279.453	5	24.389
Average	2,551.897	Average	275.976	Average	24.467
SD[a]	23.358	SD[a]	5.052	SD[a]	0.158
RSD[b] (%)	0.915	RSD[b]	1.831	RSD[b]	0.644

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

[a] Standard deviation.

[b] Relative standard deviation.

Table 3. Effects of foreign metal ions on determination of 0.2-ppm Hg ion.

Tolerance limit	Metal ions
200 ppm	Al(III), As(III), Au(III), Ba(II), Ca(II), Cd(II), Ce(III), Co(II), Cr(VI), 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), Mo(VI), Na(I), Nd(III), Ni(II), Pb(II), Pr(III), Pt(IV), Rh(III), Sb(III), Se(IV), Si(IV), Sm(III), Sr(II), Tb(III), Te(IV), Ti(IV), Tl(I), Tm(III), W(VI), Y(III), Yb(III), Zn(II), Zr(IV),
100 ppm	Ag(I), Sn(II), V(V)
40 ppm	Bi(III), Pd(II)
20 ppm	Be(II), Sc(III)

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 ion (0.2 ppm).

Cl^- NO_3^-, and SO_4^{2-}did not interfere with the determination of the Hg(II) ion. The effects of foreign ions described above, indicated that the presented HPLC method is highly selective for Hg(II) ion.

Recovery Tests with a River Water Sample

An Hg standard was added to the river water sample. Then, the Hg ion in the solution was analyzed by the proposed HPLC method. The recoveries obtained for 5, 0.5, and 0.05 ppm Hg ions were 99.5 ± 1.8%, 102.9 ± 1.9%, and 99.8 ± 1.9%, respectively (Table 4). As shown in Table 4, correlation coefficients of the calibration curves were more than 0.999. The high recovery indicated that the ions in typical river water did not interfere with the Hg determination.

CONCLUSION

In this paper, a highly selective HPLC method for Hg(II) ion has been shown. The presented method for mercury analysis requires a conventional HPLC apparatus equipped with a photometric detector, and does not use chlorinated solvents or acetonitrile for extraction or HPLC separation. This method is highly selective for Hg ions, and almost all metal ions examined gave no chromatographic peak. Thus, a shorter, or a narrower, column could be used for a rapid analysis or a lower running cost. The extraction procedure is simple and requires no specific skill. Though, this method is simple and easy, the calibration curves were linear over three orders of magnitude

Table 4. Recovery tests for Hg ion with a river water sample.

No. of run	Sample (ppm)	Added (ppm)	Found (ppm)	Recovery	Equation of calibration curve	Correlation coefficient
5 ppm Hg						
1	0.00	5.00	5.007	100.1	$y = 508.84x + 10.993$	0.9999
2	0.00	5.00	5.048	101.0		
3	0.00	5.00	4.843	96.9		
4	0.00	5.00	4.995	99.9		
Average			4.973	99.5		
SD[a]			0.090	1.79		
RSD[b]			1.803	1.80		
0.5 ppm Hg						
1	0.000	0.500	0.513	102.5	$y = 529.92x - 3.6716$	0.9999
2	0.000	0.500	0.508	101.6		
3	0.000	0.500	0.528	105.7		
4	0.000	0.500	0.509	101.8		
Average			0.514	102.9		
SD[a]			0.009	1.88		
RSD[b]			1.830	1.83		
0.05 ppm Hg						
1	0.0000	0.0500	0.0504	100.9	$y = 508.82x + 10.993$	0.9993
2	0.0000	0.0500	0.0490	98.0		
3	0.0000	0.0500	0.0510	102.0		
4	0.0000	0.0500	0.0492	98.5		
Average			0.0499	99.8		
SD[a]			0.0010	1.93		
RSD[b]			1.93	1.93		

[a] Standard deviation.

[b] Relative standard deviation.

(10 ppb–10 ppm), and the reproducibilites in the range were less than 2% as RSD. When a 5-mL sample solution was used for analysis, the detection limit of the Hg ion was 0.8 ppb.

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