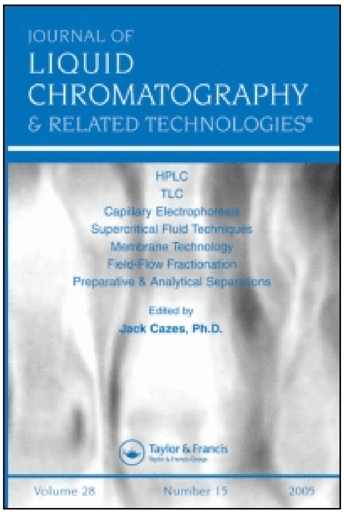

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Selective Determination of Palladium Ion in River Water by Solvent Extraction with 5-Chloro-2-Mercaptobenzothiazole Followed by Reversed-Phase HPLC

Susumu Ichinoki[a]; Saeko Otani[a]; Youichi Fujii[a]
[a] Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan

To cite this Article Ichinoki, Susumu , Otani, Saeko and Fujii, Youichi(2006) 'Selective Determination of Palladium Ion in River Water by Solvent Extraction with 5-Chloro-2-Mercaptobenzothiazole Followed by Reversed-Phase HPLC', Journal of Liquid Chromatography & Related Technologies, 29: 16, 2457 — 2469

To link to this Article: DOI: 10.1080/10826070600864932

URL: http://dx.doi.org/10.1080/10826070600864932

Journal of Liquid Chromatography & Related Technologies®, 29: 2457–2469, 2006

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070600864932

Selective Determination of Palladium Ion in River Water by Solvent Extraction with 5-Chloro-2-Mercaptobenzothiazole Followed by Reversed-Phase HPLC

Susumu Ichinoki, Saeko Otani, and Youichi Fujii
Faculty of Pharmaceutical Sciences, Hokuriku University,
Kanazawa, Japan

Abstract: A selective determination method for palladium (Pd) ion in river water by reversed-phase HPLC has been developed. The Pd ion was quantitatively extracted into 4-methyl-2-pentanone over the pH range of 0.5 to 4 as 5-chloro-2-mercaptobenzothiazole (CMBT) chelate. Job's method indicated that the Pd-CMBT chelate composition was $Pd(CMBT)_2$. The molar absorptivity of the Pd chelate was determined as 1.58×10^3 at 440 nm. The extracted Pd-CMBT chelate was then separated on a phenyl column with an eluent of methanol/2-propanol/1-hexanol/0.1 mol/L CMBT (40 : 50 : 9 : 1, v/v) and detected at 440 nm. The correlation coefficients of the calibration curves obtained with 5 mL Pd standards were more than 0.999 over the range of 10 ng/mL (ppb) to 10 μg/mL (ppm). The detection limit of the Pd ion in 5 mL water was estimated as 5 ppb by a signal to noise ratio of 3. Relative standard deviations of peak areas (N = 6) for 1 and 0.1 ppm Pd standards were 0.8 and 1.1%, respectively. The recoveries with a spiked river water sample for 5, 0.5, and 0.05 ppm Pd ion (N = 5) were 100 ± 1%, 98 ± 1%, and 98 ± 4%. Effects of foreign ions on the method were investigated with 57 metal ions. Almost none of the ions interfered except for Hg(II), Ag(I), and Cu(II).

Keywords: 5-Chloro-2-mercaptobenzothiazole, Palladium (Pd) ion, Solvent extraction, High performance liquid chromatography (HPLC), River water, Photometric detection

Address correspondence to Susumu Ichinoki, Faculty of Pharmaceutical Sciences, Hokuriku University, Ho 3, Kanazawa 920-1181, Japan. E-mail: s-ichinoki@hokuriku-u.ac.jp

INTRODUCTION

Though atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS) are routinely used for metal analysis, ICP-AES and ICP-MS require expensive instrumentation, and the detection sensitivity of AAS and ICP-AES varies considerably according to the metal. On the other hand, the application of high performance liquid chromatography (HPLC) for the separation and determination of metal ions has increased in recent years.[1–5] We also determined various metal ions by HPLC as metal chelates[6–9] combined with solvent extraction.

HPLC is a very popular and is not as expensive an apparatus; the running cost is very low. Additionally, operation of the HPLC is easy, and a more sensitive, quantitative analysis is possible by combining precolumn derivatization HPLC with a simple solvent extraction. Many metal ions have been determined as metal chelates with various chelating reagents. In the case of spectrophotometric detection, the sensitivity of the metal ion is influenced mainly by the molar absorptivity of the metal chelate.

We found that 5-chloro-2-mercaptobenzothiazole (CMBT) reacted with the Pd(II) ion, and the Pd-CMBT chelate was extracted into 4-methyl-2-pentanone from an acidic solution. The Pd chelate was stable in a reversed-phase column when a certain amount of CMBT was added into an eluent. The peak area of Pd-CMBT chelate was proportional to metal concentration. However, the analytical application of CMBT is not found.

In this paper, analytical conditions, such as extraction pH, shaking time, and eluent composition were studied for selective and sensitive determination of the Pd ion by reversed-phase HPLC. The molar absorptivity of Pd-CMBT chelate and mole ratio of Pd/CMBT were also determined. Effects of the foreign ions on the determination of the Pd ion were investigated with 57 metal ions. Pd ions in a spiked river water sample were determined by the HPLC method.

EXPERIMENTAL

Instrumentation

The HPLC system consisted of a Jasco PU-2080i inert pump (Japan Spectroscopic Co., Ltd, Tokyo, Japan), a Rheodyne 7125 injector (Cotati, CA) equipped with a 200 μL sample loop of polyether etherketone, a Jasco UVIDEC-100-VI photometric detector, a Cosmosil 5 Ph stainless steel column (250 × 3.0 mm I.D.), Nacalai Tesque, Kyoto, Japan), a Shimadzu Chromatopac C-R6A integrator (Shimadzu Co., Kyoto, Japan), and a thermostat water bath (Taitec Co., Koshigaya, Japan). A Cosmosil 5 C_{18}-AR-II column (250 × 4.6 mm I.D.) was used for a screening test. A Yamato

SA-31 auto-shaker (Yamato Scientific Co., Ltd., Tokyo, Japan) was used for solvent extraction. A Shimadzu UV-1200 spectrophotometer and a 1-cm quartz cell were used for the visible spectrum of Pd-CMBT chelate. Micropipettes were used for 1 mL or less volume of solutions (Figure 1).

Reagents

All reagents used were of analytical reagent grade unless otherwise stated. Milli-Q water was used for aqueous solution preparation and the extraction procedure. The chelating reagent CMBT (CAS No. 5331-91-9, $C_7H_4ClNS_2 = 201.70$) was obtained from Tokyo Kasei Kogyou Co. Ltd. (Tokyo, Japan). The CMBT was dissolved in 4-metyl-2-pentanone (methyl isobutyl ketone, MIBK) in a concentration of 0.1 mol/L (M). The 0.1 M CMBT was preserved in a refrigerator (about 4°C). Hydrochloric acid used was super special grade for metal analysis purchased from Wako Pure Chemical Industries (Osaka, Japan). All metal standard solutions of 1,000 μg/mL (ppm) for atomic absorption spectrometry was obtained from Wako, and summarized in Table 1. The other Pd solutions were prepared by dilution of the above solution (1,000 ppm) with 1 M HCl. Methanol was distilled and filtered through a membrane filter (pore size, 0.45 μm). A 2 M acetate buffer solution (pH 5.0) was prepared with 2 M acetic acid and 2 M sodium acetate. River water was collected from the Asano River (Kanazawa, Japan). The river water was 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 4 mL of sample solution and 1 mL of 1 M HCl into a 10 mL centrifuge tube with a stopper. For calibration curves, transfer a Pd standard solution (1 M HCl) and 1 M HCl (total volume 1 mL) and 4 mL of water into a centrifuge tube. Add 2 mL of 2 M acetate buffer (pH 4.0), if necessary. Finally, add 500 μL of 0.1 M CMBT/MIBK solutions into the tube. Shake the contents for 10 min. After standing for 10 min, collect the organic layer. Determine the Pd concentration as Pd-CMBT chelate in the extract under the following HPLC conditions.

Column: Cosmosil 5 Ph (250 × 3.0 mm I.D., particle size 5 μm), column temp.: 40°C, eluent: methanol/2-propanol/1-hexanol/0.1 M CMBT

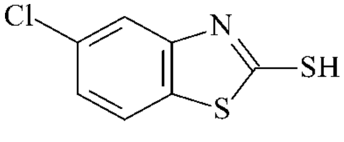

Figure 1. 5-Chloro-2-mercaptobenzothiazole (CMBT). CAS No. 5331-91-9, $C_7H_4ClNS_2 = 201.70$.

Table 1. Metal standard solutions used (1000 ppm)

Metal	Salt	Medium
Ag(I)	$AgNO_3$	0.1 M HNO_3
Al(III)	$Al(NO_3)_3$	0.5 M HNO_3
As(III)	As_2O_3	NaOH in water pH 5 with HCl
Au(III)	$HAuCl_4$	1 M HCl
Ba(II)	$BaCl_2$	1 M HCl
Be(II)[a]	$BeSO_4$	0.03 M HNO_3
Bi(III)	$Bi(NO_3)_3$	0.5 M HNO_3
Ca(II)	$CaCO_3$	0.1 M HNO_3
Cd(II)	$Cd(NO_3)_2$	0.1 M HNO_3
Ce(III)	$Ce(NO_3)_3$	1 M HNO_3
Co(II)	$Co(NO_3)_2$	0.1 M HNO_3
Cr(VI)	$K_2Cr_2O_7$	0.1 M HNO_3
Cs(I)	$CsNO_3$	0.5 M HNO_3
Cu(II)	$Cu(NO_3)_2$	0.1 M HNO_3
Dy(III)	$Dy(NO_3)_3$	1 M HNO_3
Er(III)	$Er(NO_3)_3$	1 M HNO_3
Eu(III)	$Eu(NO_3)_3$	1 M HNO_3
Fe(III)	$Fe(NO_3)_3$	0.1 M HNO_3
Ga(III)	$Ga(NO_3)_3$	1 M HNO_3
Gd(III)	$Gd(NO_3)_3$	1 M HNO_3
Ge(IV)	GeO_2	H_2O
Hg(II)	$HgCl_2$	0.02 M HCl
Ho(III)	$Ho(NO_3)_3$	1 M HNO_3
In(III)	In (metal)	0.5 M HNO_3
K(I)	KCl	H_2O
La(III)	$La(NO_3)_3$	1 M HNO_3
Lu(III)	$Lu(NO_3)_3$	1 M HNO_3
Mg(II)	$Mg(NO_3)_2$	0.1 M HNO_3
Mn(II)	$Mn(NO_3)_2$	0.1 M HNO_3
Mo(VI)	$(NH_4)_6Mo_7O_{24}$	H_2O
Na(I)	NaCl	H_2O
Nb(V)	NbF_5	1 M HF
Nd(III)	$Nd(NO_3)_3$	1 M HNO_3
Ni(II)	$Ni(NO_3)_2$	0.1 M HNO_3
Pb(II)	$Pb(NO_3)_2$	0.1 M HNO_3
Pd(II)	$PdCl_2$	1 M HCl
Pr(III)	$Pr(NO_3)_3$	1 M HNO_3
Pt(IV)	H_2PtCl_6	1 M HCl
Rh(III)	$Rh(NO_3)_3$	2 M HNO_3
Sb(III)	$SbCl_3$	3 M HCl
Sc(III)[a]	Sc (metal)	1 M HNO_3
Se(IV)	SeO_2	0.1 M HNO_3

(*continued*)

Table 1. Continued

Metal	Salt	Medium
Si(IV)	Na_2SiO_3	0.2 M Na_2CO_3
Sm(III)	$Sm(NO_3)_3$	1 M HNO_3
Sn(II)	$SnCl_2$	6 M HCl
Sr(II)	$Sr(NO_3)_2$	1 M HNO_3
Ta(V)	TaF_5	1 M HF
Tb(III)	$Tb(NO_3)_3$	1 M HNO_3
Te(IV)	$TeCl_4$	6 M HCl
Ti(IV)	$Ti(SO_4)_2$	1 M H_2SO_4
Tl(I)	$TlNO_3$	1 M HNO_3
Tm(III)	$Tm(NO_3)_3$	1 M HNO_3
V(V)	NH_4VO_3	0.45 M H_2SO_4
W(VI)	Na_2WO_4	H_2O
Y(III)	$Y(NO_3)_3$	1 M HNO_3
Yb(III)	$Yb(NO_3)_3$	1 M HNO_3
Zn(II)	$Zn(NO_3)_2$	0.1 M HNO_3
Zr(IV)	$ZrO(NO_3)_2$	1 M HNO_3

[a]Concentrations of the metal ions were 100 ppm.

(40 : 50 : 9 : 1, v/v), flow rate: 0.5 mL/min, injection volume of organic layer: 10 μL, detection wavelength: 440 nm.

Screening Test for 58 Metal Ions

To a 10 mL centrifuge tube, 25 μL of each metal solution of 1,000 ppm (Be, Sc: 100 ppm), 5 mL of water, 1 mL of 2 M acetate buffer solution (pH 5.0), and 0.1 M CMBT (1-hexanol solution) were added. After shaking for 20 min, the organic layer was separated and used for HPLC analysis. The HPLC conditions used were as follows: column, Cosmosil 5 C_{18}-AR-II (40°C); eluent, methanol/water/0.1 M CMBT (75 : 25 : 0.2, v/v); detection, 275 nm; injection volume of organic layer, 5 μL. A blank test was also conducted, and the chromatographic peaks were compared.

Chelate Composition of Pd-CMBT Chelate

To a centrifuge tube, 4 mL of water, x μL of 1,000 ppm (9.397×10^{-3} M) Pd standard solution, (1,000-x) μL of 1 M HCl, y μL of 1.175×10^{-3} M CMBT/MIBK solution, and (2,000-y) μL of MIBK were added. After shaking for 20 min, each organic layer was chromatographed and the peak area of Pd-CMBT chelate was measured. Where, (x, y) were (0, 2000), (25, 1800), (50, 1600), (75, 1400), (100, 1200), (125, 1000), (150, 800), (175, 600), (200, 400), (225, 200), and (250, 0). The mole ratios of [Pd]/([Pd] + [CMBT]) were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively.

Visible Absorption Spectrum of Pd-CMBT Chelate

To a 10 mL centrifuge tube, 2 mL of water, 1 mL of 50 ppm (4.70×10^{-4} M) Pd standard solution, 3 mL of 0.1 M CMBT/MIBK solution were added. Two sample solutions were prepared and the two organic layers were combined after shaking for 20 min. For the blank solution, 1 mL of 1 M HCl was added instead of 1 mL of Pd standard. The visible absorption spectrum of Pd-CMBT chelate was measured with the organic layers of standard and blank solutions.

Effects of Foreign Ions

The effects of foreign ions on the determination of the Pd ion were tested with 57 metal ions. Each foreign ion, 800 μL of 1 M HCl, and 200 μL of 5 ppm Pd standard were placed into a centrifuge tube, and diluted to 5 mL with water (Pd concentration: 0.2 ppm). The concentration of the Pd ion in the solution was determined by the recommended procedure. The recovery percentage was calculated from the peak area of the Pd chelate and that of the Pd standard (0.2 ppm) containing no foreign metal ions. 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 the Pd(II) ion.

Recovery Tests with a River Water Sample

Because no Pd ion in the river water sample was detected by the HPLC method, Pd ions were added to the river water. To a centrifuge tube, 4.0 mL of a river water sample, 500 μL of Pd standard (50, 5, and 0.5 ppm), and 500 μL of 1 M HCl were added. To each centrifuge tube 500 μL of 0.1 M CMBT was added. Because the pH of the solution was calculated as 0.7, acetate buffer solution was not added. After shaking for 10 min, Pd concentrations in these solutions (5, 0.5, and 0.05 ppm) were determined according to the recommended procedure, and the recovery percentage was calculated.

RESULTS AND DISCUSSION

Extraction Conditions

At first, 1-hexnanol was used as the extraction solvent. Thus, CMBT was dissolved in 1-hexanol in a concentration of 0.1 M. However, the CMBT/

1-hexanol solution became turbid in a week. Thus, MIBK was used instead of 1-hexanol. The volume of 0.1 M CMBT/MIBK solution was set at 0.5 mL, considering the concentration factor (about 10).

Extraction pH and shaking time were investigated according to the recommended procedure. The effect of pH on the extraction of Pd-CMBT chelate is shown in Figure 2. Since constant and maximum peak areas were obtained over the pH range of 0.5 to 3.9, pH 2.0 ± 1.5 was employed as the optimum pH. Because the Pd(II) ion was quantitatively extracted into MIBK by shaking for 5–60 min, 10 min was selected. The extracted Pd chelate in the MIBK solution was stable for at least 7 hours, because the peak area of the Pd chelate did not change. Thus, immediate injection of the organic layer was not required.

Separation Conditions and Injection Volume

Preliminary experiments indicated that 58 metal ions gave no metal chelate peak under the conditions used. However, the color of the organic layer was yellow to light brown for bismuth (Bi), copper (Cu), and Pd ions. This indicated that Bi, Cu, and Pd ions formed extractable chelate, but the chelate is unstable in the eluent, or retained strongly in the ODS stationary phase. Thus, various stationary phases and eluents were tested, and the detection wavelength was changed from 275 to 430 nm for detection of yellow color chelate. When a mixture of methanol/0.1 M CMBT (99 : 1, v/v) was used as eluent, only the Pd ion gave two chelate peaks with C_{18}, C_8, and phenyl stationary phases. Pd chelate sometimes gives two chromatographic peaks assigned to cis- and trans-isomers.[10] The difference between two retention times was the smallest with a phenyl column. Therefore, various eluents were tested to obtain a single Pd chelate peak with a Cosmosil 5 Ph column (250 × 3.0 mm I.D., 40°C). When a mixture of methanol/2-propanol/1-hexanol/0.1 M CMBT (40 : 50 : 9 : 1, v/v) was used as eluent, Pd chelate gave a single peak. Bi and Cu ions did not give

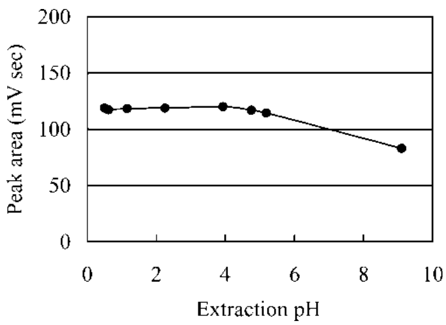

Figure 2. Effect of pH on extraction of Pd-CMBT chelate.

a chromatographic peak under the same conditions. Relative standard deviation of the Pd-chelate peak area (RSD, N = 9) in the presence of CMBT in eluent was better (RSD = 1.7%) than that of without CMBT (RSD = 3.4%).

The injection volume of the organic layer (MIBK) was also investigated in the range of 3–20 μL. Because peak area was proportional to injection volume in the range of 3–20 μL, 10 μL was selected as the optimum injection volume.

Pd-CMBT Chelate Composition

The composition of Pd-chelate was decided by Job's method. The peak areas were plotted against the mole fractions of [Pd]/([Pd] + [CMBT]) as shown in Figure 3. The maximum peak area was estimated at a mole fraction of 0.33 (that is [Pd]:[CMBT] = 1 : 2). The results indicated that CMBT ionized to H^+ and $CMBT^-$, then reacted with the Pd^{2+} ion to form $Pd(CMBT)_2$ chelate. Because CMBT is an asymmetric chelating reagent, the two Pd chelate peaks obtained with some reversed-phase columns are probably due to geometrical isomers of cis- and trans-forms.

Detection Wavelength and Molar Absorptivity of Pd-CMBT Chelate

The visible absorption spectrum was measured and is shown in Figure 4. For sensitive detection of Pd-CMBT chelate, maximum absorption wavelength 440 nm was selected.

The concentration of the Pd ion in the aqueous layer was 1.567×10^{-4} M. When the Pd ion was quantitatively extracted into an equal volume of

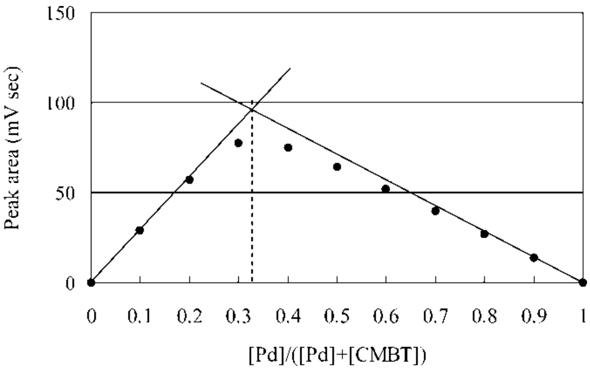

Figure 3. Determination of Pd-CMBT chelate composition by Job's method. Experimental conditions are in the text.

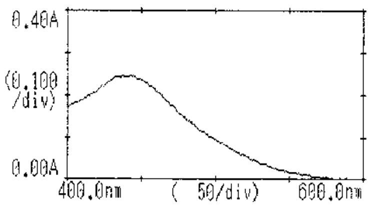

Figure 4. Visible spectrum (400–600 nm) of $Pd(CMBT)_2$ chelate.

the organic layer (MIBK), the concentration of $Pd(CMBT)_2$ chelates was also 1.567×10^{-4} M. Figure 4 shows that the absorbance at 440 nm is 0.248. Thus, the molar absorptivity of $Pd(CMBT)_2$ chelates was calculated as 1.58×10^3 from Lambert-Beer's Law ($0.248 = \varepsilon \times 1.567 \times 10^{-4}$ mol/L × 1 cm).

Calibration Curves, Repeatability, and Detection Limit

Calibration curves for the Pd(II) ion were prepared with Pd standards of varying concentrations by the recommended procedure. The correlation coefficients of the calibration curves obtained with 5 mL Pd standards were more than 0.999 over the range of 10 ppb to 10 ppm. Relative standard deviations (RSD) of peak areas ($N = 6$) for 1 and 0.1 ppm Pd standards were 0.8 and 1.1%, respectively. Although the correlation coefficients (CC) of the calibration curves and RSD varied day by day, the values of CC and RSD were more than 0.999 and less than 2%, respectively. More details are shown in Table 2.

The detection limit of the Pd ion in 5 mL water was estimated as 5 ppb by a signal to noise ratio of 3.

Effects of Foreign Ions

The effects of 57 foreign ions on the determination of the 0.2 ppm Pd(II) ion (5 mL) were investigated. Table 3 shows 46 metal ions did not interfere at 1000 times or more with the concentration of the Pd ion. A Hg(II) ion of 2 ppm, 4 ppm Ag(I), and 10 ppm Cu(II) interfered with the determination of the 0.2 ppm Pd ion. The Ag ion reacted with the chloride ion of HCl and formed precipitation of AgCl. More details are shown in Table 3.

Recovery Tests of Pd Ion with River Water Sample

Typical chromatograms of Pd-CMBT chelates are shown in Figure 5. The results of recovery tests for 5, 0.5, and 0.05 ppm Pd ions are summarized

Table 2. Calibration curves for Pd(II) ion and repeatability of peak areas

Concentration range	Equation of line	Correlation coefficient	Measuring point (ppm)
Calibration curves for Pd ion			
1–10 ppm	$y = 27.207x - 1.6624$[a]	0.9998	0, 1, 2, 4, 6, 8, 10
0.1–1 ppm	$y = 216.2x - 1.5175$[b]	0.9998	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1 ppm	$y = 383.84x + 0.2111$[c]	0.9997	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10
1 ppm Pd standard		0.1 ppm Pd standard	
Run no.	Peak area	Run no.	Peak area
Repeatability of peak area (mV sec)			
1	48.585	1	8.729
2	48.828	2	8.689
3	49.147	3	8.806
4	49.562	4	8.931
5	49.089	5	8.857
6	48.592	6	8.701
Average	48.967	Average	8.786
SD[d]	0.376	SD[d]	0.096
RSD[e] (%)	0.8	RSD[e]	1.1

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

Detector range (AUFS):

[a] 0.08.

[b] 0.01.

[c] 0.005.

[d] Standard deviation.

[e] Relative standard deviation.

in Table 4. The recoveries of 5, 0.5, and 0.05 ppm Pd ions were 100.0 ± 0.7%, 98.2 ± 1.0%, and 98.2 ± 4.0%, respectively. The correlation coefficients of calibration curves were more than 0.999. Recoveries obtained by HPLC on other days were 99.4 ± 0.2% (CC = 0.9999) for 5 ppm Pd, 98.2 ± 4.0% (CC = 0.9990) for 0.5 ppm Pd, and 99.6 ± 3.6% (CC = 0.9997) for 0.05 ppm Pd (N = 5). The high recoveries indicated that the ions in river water did not interfere with the HPLC determination of the Pd ion.

CONCLUSION

The proposed extraction and HPLC procedure is simple and easy, and the HPLC apparatus used is the most popular HPLC apparatus equipped with a

Table 3. Effects of foreign metal ions on determination of 0.2 ppm Pd(II) ion

Tolerance limit	Metal ion
200 ppm	Al(III), As(III), Ba(II), Be(II), Bi(III), Ca(II), Cd(II), Ce(III), Co(II), Cs(I), Dy(III), Er(III), Eu(III), Fe(III), Ga(III), Gd(III), Ho(III), In(III), La(III), Lu(III), Mg(II), Mn(II), Mo(VI), Na(I), Nb(V), Nd(III), Ni(II), Pb(II), Pr(III), Rh(III), Sb(III), Sc(III), Se(IV), Sm(III), Sr(II), Ta(V), Tb(III), Ti(IV), Tl(I), Tm(III), V(V), W(VI), Y(III), Yb(III), Zn(II), Zr(IV),
100 ppm	Ge(IV), K(I), Pt(IV), Si(IV), Sn(II)
40 ppm	Te(IV)
20 ppm	Au(III), Cr(VI)
4 ppm	Cu(II)
2 ppm	Ag(I)
1 ppm	Hg(II)

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 Pd(II) ion (0.2 ppm).

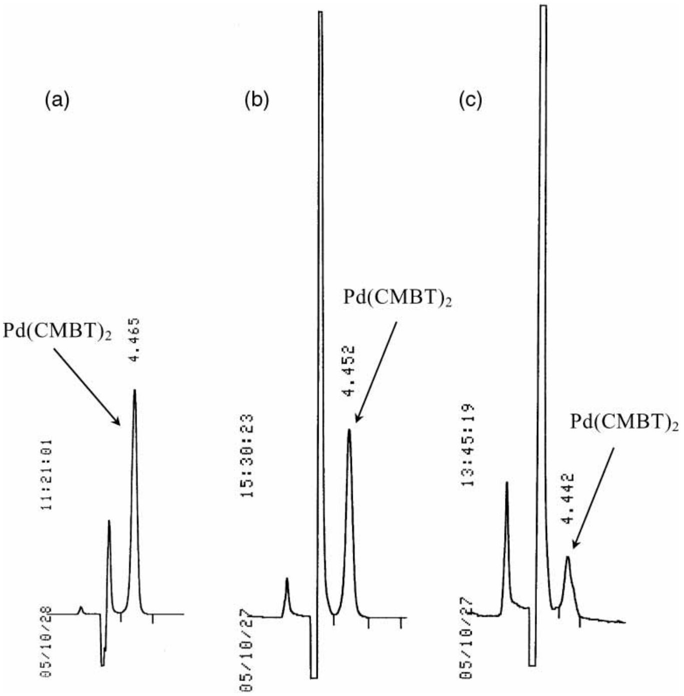

Figure 5. Chromatograms of Pd-CMBT chelates obtained with Pd spiked river water samples. (a) 5 ppm Pd spiked, (b) 0.5 ppm Pd spiked, (c) 0.05 ppm Pd spiked.

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

No. of run	Sample (ppm)	Added (ppm)	Found (ppm)	Recovery (%)	Equation of calibration curve	Correlation coefficient
5 ppm						
1	0.00	5.00	4.95	99.1	y = 27.207x − 1.6624	0.9998
2	0.00	5.00	5.01	100.1		
3	0.00	5.00	5.03	100.6		
4	0.00	5.00	4.98	99.7		
5	0.00	5.00	5.04	100.7		
Av.			5.00	100.0		
SD			0.03	0.7		
RSD			0.7	0.7		
0.5 ppm						
1	0.000	0.500	0.486	97.2	y = 216.2x − 1.5175	0.9998
2	0.000	0.500	0.497	99.5		
3	0.000	0.500	0.487	97.4		
4	0.000	0.500	0.490	98.0		
5	0.000	0.500	0.496	99.1		
Av.			0.491	98.2		
SD			0.005	1.0		
RSD			1.0	1.0		
0.05 ppm						
1	0.0000	0.0500	0.0475	95.0	y = 191.02x + 0.0094	0.9996
2	0.0000	0.0500	0.0476	95.1		
3	0.0000	0.0500	0.0522	104.5		
4	0.0000	0.0500	0.0483	96.5		
5	0.0000	0.0500	0.0500	99.9		
Av.			0.0491	98.2		
SD			0.0020	4.0		
RSD			4.1	4.1		

Detector response of the HPLC was 0.08 AUFS (5 ppm) and 0.01 AUFS (0.5 and 0.05 ppm).

Recoveries obtained by HPLC on other days were 99.4 ± 0.2% for 5 ppm Pd, 98.2 ± 4.0% for 0.5 ppm Pd, and 99.6 ± 3.6% for 0.05 ppm Pd (N = 5).

photometric detector. The extraction time and HPLC analysis time is 10 and 7 min, respectively. The presented method for the Pd ion does not require chlorinated solvents and acetonitrile for extraction and HPLC separation. The HPLC method was applied to the determination of the Pd ion in river water samples with precise results.

REFERENCES

1. Cassidy, R.M. The separation and determination of metal species by modern liquid chromatography. Trace Anal. **1981**, *1*, 122–192.
2. Nickless, G. Trace metal determination by chromatography. J. Chromatogr. **1985**, *313*, 129–159.
3. Timerbaev, A.R.; Petrukhin, O.M.; Zolotov, Y.A. Analytical application of liquid chromatography of metal chelates. Fresenius Z. Anal. Chem. **1987**, *327*, 87–101.
4. Robards, K.; Starr, P.; Patsalides, E. Metal determination and metal speciation by liquid chromatography. Analyst **1991**, *116*, 1247–1273.
5. Sarzanini, C. High performance liquid chromatography: trace metal determination and speciation. Adv. Chromatogr. **2001**, *41*, 249–310.
6. Ichinoki, S.; Yamazaki, M. Simultaneous determination of nickel, lead, zinc, and copper in citrus leaves and rice flour by liquid chromatography with hexamethylenedithiocarbamates extraction. Anal. Chem. **1985**, *57*, 2219–2222.
7. Ichinoki, S.; Okamoto, Y.; Ishikuma, H.; Fujii, Y. Selective determination of Mercury(II) ion by solvent extraction with *N*-(dithiocarboxy)sarcosine, diammonium salt followed by ligand exchange and reversed-phase high performance liquid chromatography with photometric detection. J. Liq. Chromatogr. & Rel. Technol. **2003**, *26*, 2797–2808.
8. Ichinoki, S.; Iwase, H.; Arakawa, F.; Hirano, K.; Fujii, Y. Selective determination of tin(II) ion in water by solvent extraction with salicylideneamino-2-thiophenol followed by reversed-phase high performance liquid chromatography with photometric detection. J. Liq. Chromatogr. & Rel. Technol. **2003**, *26*, 3129–3139.
9. Ichinoki, S.; Miyanaga, S.; Hattori, M.; Fujii, Y. Selective determination of iron in river water and standard bovine liver by solvent extraction with *N*-Benzoyl-*N*-phenylhydroxylamine followed by reversed-phase HPLC. J. Liq. Chromatogr. & Rel. Technol. **2005**, *28*, 1417–1429.
10. Ichinoki, S.; Yamazaki, M. Evaluation of benzoylacetone as a chelating agent for multielement analysis by reversed-phase HPLC with photometric detection. J. Chromatogr. Sci. **1990**, *28*, 258–262.

Received February 14, 2006
Accepted March 22, 2006
Manuscript 6828