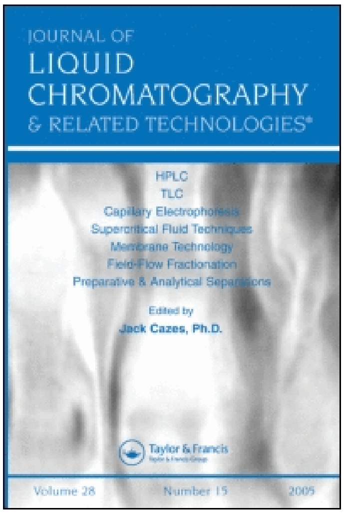

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Determination of Palladium Ion in River Water by Solvent Extraction with 5-Methyl-1,3,4-Thiodiazole-2-thiol Followed by Reversed Phase HPLC

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Abstract: A determination method for palladium (Pd) ion in river water has been developed by reversed phase HPLC. The Pd(II) ion was quantitatively extracted into benzene from an acidic solution as 5-methyl-1, 3, 4-thiodiazole-2-thiol (MTT) chelate. The extracted Pd-MTT chelate was then separated on a phenyl ethyl column with an eluent of methanol/water/0.01 mol/L MTT (90:10:0.5, v/v) and detected at 270 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 50 μg/mL (ppm). The detection limit of the Pd ion in 5 mL of water was estimated as 10 ppb by a signal to noise ratio of 3. Relative standard deviations of peak areas ($N = 6$) for 5, 0.5, and 0.05 ppm Pd standards were 1.5, 1.3, and 0.9%, respectively. The recoveries with a spiked river water sample for 5, 0.5, and 0.05 ppm Pd ion ($N = 6$) were $99.9 \pm 1.0\%$, $99.5 \pm 0.8\%$, and $94.0 \pm 1.1\%$. Effects of foreign ions on the determination of 0.2 ppm Pd were investigated with 57 metal ions. Almost none of the ions interfered except for Cu(II), Ag(I), Ni(II), Cd(II), Co(II), and Ti(IV) ions.

Keywords: 5-Methyl-1, 3,4-Thiodiazole-2-thiol (MTT), High performance liquid chromatography (HPLC), Palladium (Pd) ion, Photometric detection, River water, Solvent extraction

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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 according to the metal considerably. 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[6–10] combined with solvent extraction.

HPLC is a very popular and inexpensive apparatus, while the running cost is very low. In addition, operation of the HPLC is easy, and a more sensitive quantitative analysis is possible by combining precolumn derivatization HPLC with a simple solvent extraction.

We found that 5-methyl-1, 3,4-thiodiazole-2-thiol (MTT) reacted with the Pd(II) ion, and the Pd-MTT chelate was extracted into benzene from a weak acidic solution. The Pd chelate was stable in a reversed phase column when a certain amount of MTT was added into an eluent. The peak area of Pd-MTT chelate was proportional to the metal concentration. However, an analytical application of MTT was 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. 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-1580i inert pump (Japan Spectroscopic Co., Ltd, Tokyo, Japan), a Rheodyne 9725i injector (Cotati, CA) equipped with a 200 μL sample loop of polyether etherketone, a SPD-10AV*vp* photometric detector (Shimadzu Co., Kyoto, Japan), a Shimadzu Chromatopac C-R8A integrator, a Cosmosil 5 PE-MS (PE-MS: phenyl ethyl, monomeric type) stainless steel column (150 × 4.6 mm ID, Nacalai Tesque, Kyoto, Japan), and a Thermo Minder SX-10R thermostat water bath (Taitec Co., Koshigaya, Japan).

A Cosmosil 5 PE-MS stainless steel column (250 × 4.6 mm ID) was used for a screening test. An MS-E10R microsyringe (10 µL) with Ni-Ti alloy plunger was used for sample injection (Ito Co. Ltd., Fuji, Japan). Micropipettes were used for solutions of 2.5 mL or less. A Yamato SA-31 auto-shaker (Yamato Scientific Co., Ltd., Tokyo, Japan) was used for solvent extraction.

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 MTT ($C_3H_4N_2S_2 = 132.21$, CAS No. 29490–19-5) was obtained from Tokyo Kasei Kogyou Co. Ltd. (Tokyo, Japan). Further details are shown in Figure 1. A 0.01 mol/L (M) MTT solution was prepared as follows: MTT of 0.1322 g was dissolved in 20 mL of 2 M ammonia- 2 M ammonium chloride buffer solution (pH 9.0), and diluted to 100 mL with water. The 0.01 M MTT was preserved in a refrigerator (about 4°C). All metal standard solutions of 1000 µg/mL (ppm) for atomic absorption spectrometry were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). The Pd standard of 1000 ppm contained 1 M HNO_3. The other Pd solutions were prepared by dilution of the above solution (1000 ppm) with 1 M HNO_3. Methanol was distilled and filtered through a membrane filter (pore size, 0.45 µm). A hydrochloric acid-acetic acid solution of pH 2.0 was prepared with 1 M hydrochloric acid and 1 M acetic acid. Acetate buffer solutions (pH 3.0 to 6.0) were prepared with 2 M acetic acid and 2 M sodium acetate. Ammonia-ammonium chloride (NH_3-NH_4Cl) buffer solutions (pH 8.0–11.0) were prepared with 2 M ammonia and 2 M ammonium chloride solutions. River water was collected from the Tomuro River (a branch of 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.

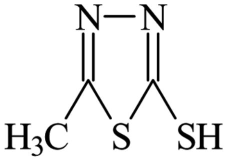

Figure 1. 5-methyl-1, 3,4-thiodiazole-2-thiol (MTT). $C_3H_4N_2S_2 = 132.21$, CAS No. 29490-19-5.

Recommended Extraction Procedure and HPLC Conditions

Transfer 4 mL of sample solution and 1 mL of 1 M HNO_3 into a 10 mL centrifuge tube with a glass stopper. For calibration curves, transfer a Pd standard solution (1 M HNO_3) and 1 M HNO_3 (total volume 1 mL) and 4 mL of water into a centrifuge tube. Add 2 mL of 2 M acetate buffer (pH 5.0). After mixing by hand, add 500 μL of 0.01 M MTT and 500 μL of benzene into the tube. Shake the contents for 20 min. After standing for 10 min, collect the organic layer. Determine the Pd concentration as Pd-MTT chelate in the extract under the following HPLC conditions.

Column: Cosmosil 5 PE-MS (150 × 4.6 mm ID, particle size 5 μm), column temp.: ambient (room temperature), eluent: methanol/water/0.01 M MTT (90:10:0.5, v/v), flow rate: 1.0 mL/min, injection volume of organic layer: 10 μL, detection wavelength: 270 nm.

Screening Test for 58 Metal Ions

To a 10 mL centrifuge tube, 10 μL of each metal solution of 1000 ppm, 5 mL of water, 2 mL of 2 M acetate buffer solution (pH 4.0), 500 μL of 0.01 M MTT, and 500 μL of 4-methyl-2-pentanone 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 PE-MS (250 × 4.6 mm ID, 40°C); eluent, methanol/water/0.01 M MTT (90:9:1, v/v); detection, 250 nm; injection volume of organic layer, 5 μL. A blank test was also conducted, and the chromatographic peaks were compared.

Chelate Composition of Pd-MTT Chelate

To a centrifuge tube, 4 mL of water, x μL of 4.70×10^{-4} M (50 ppm) Pd standard solution, (1000-x) μL of 1 M HNO_3, (5000-y) μL of water, y μL of 4.70×10^{-4} M MTT aqueous solution, 2 mL of 2 M acetate buffer solution (pH 5.0), and 500 μL of benzene were added. After shaking for 20 min, each organic layer was chromatographed and the four peak areas of Pd-MTT chelate were measured. Where, (x, y) were (0, 1000), (100, 900), (200, 800), (300, 700), (333, 667), (400, 600), (500, 500), (600, 400), (700, 300), (800, 200), (900, 100), and (1000, 0). These mole fractions of [Pd]/([Pd] + [MTT]) were 0, 0.1, 0.2, 0.3, 0.333, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively. Further experiments were carried out with 4.70×10^{-5} M (5 ppm) Pd standard and 4.70×10^{-5} M MTT 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 HNO_3, 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 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 the river water sample, 500 μL of Pd standard (50, 5, and 0.5 ppm), and 500 μL of 1 M HNO_3 were added. The Pd concentrations in these solutions (5, 0.5, and 0.05 ppm) were determined according to the recommended procedure, and the recovery percentages were calculated.

RESULTS AND DISCUSSION

HPLC Conditions

The screening test for the 58 metal ions indicated that only Pd ion was extracted into 4-methyl-2-pentanone at pH 4. Thus, the analytical column was changed to a shorter column (Cosmosil 5 PE-MS, 150 × 4.6 mm ID), and used at ambient temperature. Under these conditions (270 nm detection), the Pd ion produced four chromatographic peaks as shown in Figure 2. The retention times of the first peak (peak 1), peak 2, peak 3, and peak 4 were about 4.5, 5.6, 6.5, and 12.0 min, respectively. Because the four peaks did not appear in the blank chromatogram, all peaks were probably due to Pd ion.

Effect of detection wavelength on the peak areas of the four peaks is shown in Figure 3. The results of peaks 2 and 3 were similar to each other, and different from the results of peaks 1 and 4. Considering the base line noise and peak areas of peaks 1, 2, and 3, 270 nm was selected as the recommended detection wavelength. In order to elute the three peaks quantitatively, the addition of a small amount of MTT

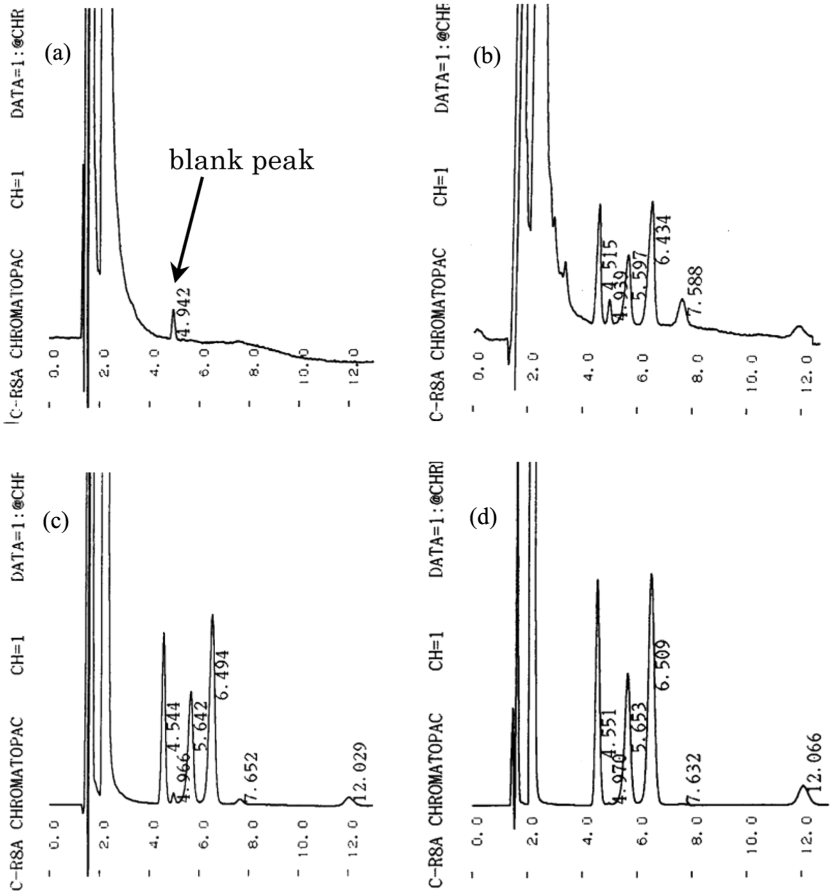

Figure 2. Chromatograms of blank and Pd-MTT chelates with Pd spiked river water samples. (a): blank, (b): 50 ppb Pd, (c): 0.5 ppm Pd, (d): 5 ppm Pd. Attenuation of integrator; a, 1; b, 1; c, 4; d, 7. Column: Cosmosil 5 PE-MS (150 × 4.6 mm ID), Detection: 270 nm, Eluent: methanol/water/0.01 M MTT (90:10:0.5, v/v).

in the eluent was required. Thus, a mixture of methanol/water/0.01 M MTT (90:10:0.5, v/v) was employed as the eluent.

Pd-MTT Chelate Composition

The composition of the Pd-MTT chelate was investigated by Job's method. The peak areas were plotted against the mole fraction of [Pd]/([Pd] + [MTT]) as shown in Figure 4. Peak 1 was considerably

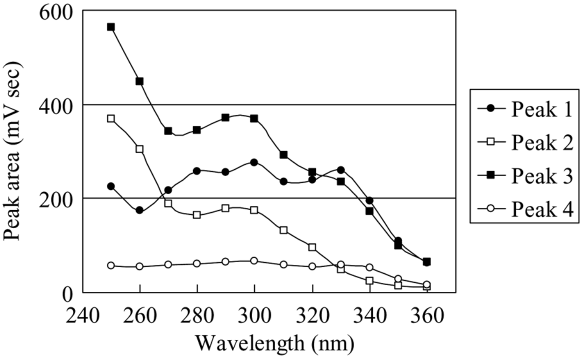

Figure 3. Effects of detection wavelength on peak areas of Pd chelate peaks.

smaller compared with Figure 2. For mole fractions of 0 to 0.3, clear green color organic layers (benzene) were obtained. However, the other organic layers also contained green precipitant probably due to Pd chelate. Figure 4 shows that the mole fraction of the maximum point for peaks 2 and 3 were 0.30. For peaks 1 and 4, the maximum points were 0.333 or 0.4. When 4.70×10^{-5} M (5 ppm) Pd standard and 4.70×10^{-5} M MTT solutions were used, the maximum point for peaks 2 and 3 were

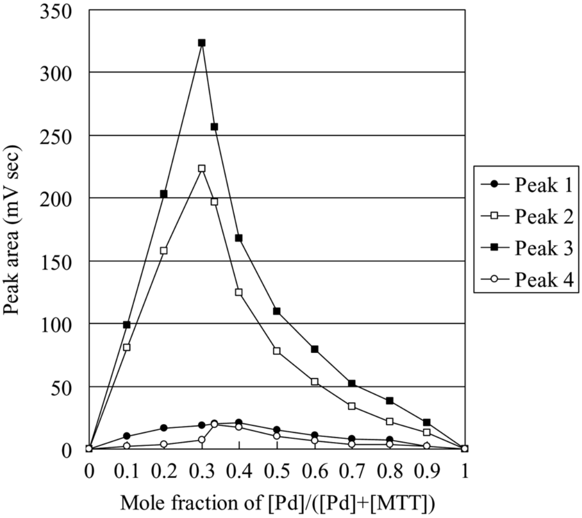

Figure 4. Determination of Pd-MTT chelate composition by Job's method. Experimental conditions are in the text.

0.30 and 0.333, respectively. For peaks 1 and 4, no clear maximum points were found.

If the mole ratio of Pd:MTT is 1:2, the mole fraction of the maximum point must be 0.333. The maximum points for peaks 2 and 3 were probably in the range of 0.3 to 0.333. The results suggested that the peaks 2 and 3 were the Pd-MTT chelates, and the mole ratio of Pd:MTT was probably 1:2. Because the retention times and absorption behaviors of peaks 2 and 3 were similar to each other, peaks 2 and 3 were probably produced by the geometrical isomers of cis- and trans-forms.

Extraction Conditions

Extraction solvents were also investigated with 4-methyl-2-pentanone, 1-octanol, 1-decanol, chloroform, and benzene. When 4-methl-2-pentanone was used, the resolution of peaks 2 and 3 was not satisfactory. When chloroform and benzene were used, higher peaks were obtained compared with 1-octanol and 1-decanol. Because chloroform is a chlorinated solvent, benzene was selected as the extraction solvent.

The effect of pH on the extraction of Pd-MTT chelate is shown in Figure 5. A large amount of MTT was used in the recommended extraction procedure compared with the experiment using Job's method. Figures 3 and 4 showed that the peak areas of peak 1 were significantly larger when enough MTT was added. These results suggested that peak 1 was also a Pd-MTT chelate. However, the formation constant of the chelate seemed lower than those of peaks 2 and 3.

Since three peaks showed constant peak areas with the acetate buffer solutions of pH 4, 5, and 6, a buffer solution of pH 5 was employed in the recommended procedure. Because the constant peak areas were obtained for peaks 1, 2, and 3 by shaking for 10–40 min, 20 min was selected. The extracted Pd chelate in the benzene solution was stable for at least 7 hours, because the peak areas of peaks 1, 2, and 3 did not change. Thus, immediate injection of the organic layer was not required.

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. Because peak 4 was small compared with the other peaks, the equation and correlation coefficients of the calibration curves were calculated with peaks 1, 2, and 3. Among the three peaks, peak 3 gave the best correlation coefficients (more than 0.999) and the widest linear range (10 ppb to

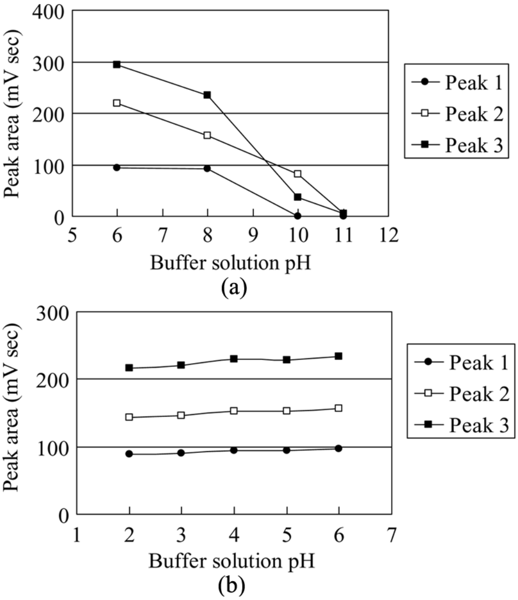

Figure 5. Effect of pH on extraction of Pd chelate. Detection wavelength; (a), 250 nm; b), 300 nm. Each peak area was plotted against the pH of the buffer solution. When the buffer solution of pH 5.0 was used, the pH of the aqueous phase was 4.80.

50 ppm). Organic layers obtained with 60, 80, and 100 ppm Pd standard all contained green precipitant. Thus, the organic layers were not injected into the column. More details are shown in Table 1.

Considering the above results, peak 3 was used for quantitative analysis. The repeatabilities of the peak areas of peak 3 are shown in Table 1. The relative standard deviations ($N = 6$) for 5, 0.5, and 0.05 ppm Pd were 1.5, 1.3, and 0.9%, respectively. The relative standard deviations of the peak areas for 5, 0.5, and 0.05 ppm Pd standards obtained on other days were less than 2%.

The detection limit of the Pd ion in 5 mL of solution was estimated as 10 ppb by a signal (peak 3) 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 2 shows that 45 metal ions did not interfere at 1000 times (200 ppm), or more, the concentration of the Pd ion. A Cu(II) ion of 0.04 ppm, 0.2 ppm Ag(I), and 0.2 ppm Ni(II)

Table 1. Calibration curves for Pd(II) ion and repeatabilities of peak areas

Concentration range	Equation of line	Correlation coefficient	Measuring point (ppm)
Calibration curves for Pd ion with peak 1			
10–50 ppm	$y = 23.506x + 633.07$	0.4478	0, 10, 20, 40, 50
1–10 ppm	$y = 82.746x + 0.1382$	0.9999	0, 1, 2, 4, 6, 8, 10
0.1–1 ppm	$y = 93.328x + 0.21$	0.9998	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1 ppm	$y = 79.229x - 0.0902$	0.9996	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10
Calibration curves for Pd ion with peak 2			
10–50 ppm	$y = 157.6x - 683.66$	0.9559	0, 10, 20, 40, 50
1–10 ppm	$y = 74.917x - 0.5342$	0.9998	0, 1, 2, 4, 6, 8, 10
0.1–1 ppm	$y = 84.254x + 0.0724$	0.9987	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1 ppm	$y = 72.708x - 0.1564$	0.9996	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10
Calibration curves for Pd ion with peak 3			
10–50 ppm	$y = 162.23x - 107.32$	0.9996	0, 10, 20, 40, 50
1–10 ppm	$y = 133.03x - 0.0264$	0.9999	0, 1, 2, 4, 6, 8, 10
0.1–1 ppm	$y = 147.01x + 0.6352$	0.9996	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
0.01–0.1 ppm	$y = 127.56x - 0.2792$	0.9999	0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10

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

Repeatabilities of peak areas (mV sec) for peak 3

5 ppm Pd		0.5 ppm Pd		0.05 ppm Pd	
No. of run	Peak area	No. of run	Peak area	No. of run	Peak area
1	694.540	1	64.965	1	6.157
2	680.835	2	65.997	2	6.161
3	668.762	3	65.154	3	6.104
4	671.986	4	65.278	4	6.109
5	666.417	5	65.071	5	6.012
6	671.790	6	63.409	6	6.093
Average	675.722	Average	64.979	Average	6.106
SD[a]	10.437	SD[a]	0.852	SD[a]	0.054
RSD[b] (%)	1.5	RSD[b] (%)	1.3	RSD[b] (%)	0.9

[a] Standard deviation.

[b] Relative standard deviation.

The relative standard deviations of peak areas for 5, 0.5, and 0.05 ppm Pd standards obtained on other days were less than 2%.

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

interfered with the determination of the 0.2 ppm Pd ion. More details are shown in Table 2. The Ag ion reacted with the chloride ion of NH_4Cl in 0.01 M MTT solution and formed a precipitant of AgCl. Although the Cu and Ni ions gave no chromatographic peaks in the screening test, the ions gave chromatographic peaks at 7.7 min under the recommended conditions. The peaks did not overlap with peak 3 of the Pd chelate. However, the peak areas of peak 3 showed interference from the Cu and Ni ions.

Recovery Tests of Pd Ion with River Water Sample

Typical chromatograms of Pd-MTT chelates with Pd spiked river water samples are shown in Figure 2. The results of recovery tests for 5, 0.5, and 0.05 ppm Pd ions are summarized in Table 3. The recoveries of 5, 0.5, and 0.05 ppm Pd ions were 99.0 ± 1.0%, 99.5 ± 0.8%, and 94.0 ± 1.1%, respectively. The correlation coefficients of calibration curves were more than 0.999. Recoveries obtained by the HPLC method on other days were 99.9 ± 1.3% for 5 ppm Pd, 99.1 ± 1.4% for 0.5 ppm Pd, and 94.1 ± 1.1% for 0.05 ppm Pd (N = 5). When calibration curves were prepared with 4 mL of river water and Pd standards, the recoveries of 0.05 ppm Pd were 100.5 ± 2.1% and 99.7 ± 1.7% (obtained on other days).

Table 3. 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	5.01	100.2	y = 131.88x – 5.0846	0.9999
2	0.00	5.00	5.03	100.6		
3	0.00	5.00	4.93	98.6		
4	0.00	5.00	4.97	99.4		
5	0.00	5.00	4.97	99.4		
6	0.00	5.00	5.07	101.4		
Av.			5.00	99.9		
SD			0.05	1.0		
RSD			1.0	1.0		
0.5 ppm						
1	0.000	0.500	0.501	100.2	y = 133.96x – 0.3084	0.9999
2	0.000	0.500	0.502	100.4		
3	0.000	0.500	0.498	99.6		
4	0.000	0.500	0.497	99.4		
5	0.000	0.500	0.495	99.0		
6	0.000	0.500	0.491	98.3		
Av.			0.497	99.5		
SD			0.004	0.8		
RSD			0.8	0.8		
0.05 ppm						
1	0.0000	0.0500	0.0478	95.6	y = 122.66x – 0.1346	0.9996
2	0.0000	0.0500	0.0470	94.0		
3	0.0000	0.0500	0.0464	92.8		
4	0.0000	0.0500	0.0464	92.8		
5	0.0000	0.0500	0.0469	93.9		
6	0.0000	0.0500	0.0474	94.8		
Av.			0.0470	94.0		
SD			0.0006	1.1		
RSD			1.2	1.2		

When calibration curves were prepared with 4 mL of river water and Pd standards, the recoveries of 0.05 ppm Pd were 100.5 ± 2.1%, and 99.7 ± 1.7% (obtained on other days).

CONCLUSION

The MTT was found to be a chelating reagent for ppm levels of Pd(II) ion. The presented method for the Pd ion did not require chlorinated solvents or acetonitrile for extraction and HPLC separation. The proposed extraction and HPLC procedure was simple and easy, and the HPLC apparatus used was the most popular HPLC apparatus equipped with a photometric detector. The HPLC method was applied to the determination of the ppm levels of Pd ion in spiked river water samples with precise results.

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