Determination of Trace Amounts of Palladium(II) in Water by Metal-Furnace Atomic Absorption Spectrometry after Preconcentration on Chitin

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Palladium(II) reacts with halogenide ions, such as chloride ion and bromide ion, to form anionic complexes. The acetyl amino groups of chitin are protonated in an acidic medium, acting as an anion exchanger. The property of chitin was applied to the preconcentration and microdetermination of palladium(II). The palladium(II) chloro complex was quantitatively adsorbed onto chitin over the pH range of 2.5–4.0. The chitin which adsorbed the palladium(II) was separated from the sample solution by a membrane filter, and dispersed in pure water. The resulting suspension was introduced directly into a tungsten metal-furnace atomizer. An ashing temperature of 1000°C and an atomizing temperature of 2300°C were selected. The detection limit for palladium(II) was 0.06 µg/100 cm³ ($S/N \geq 3$). The proposed method was applied to the determination of trace amounts of palladium(II) in water samples.

Keywords Palladium(II), protonated chitin, preconcentration, tungsten metal furnace atomic absorption spectrometry

Palladium is a noble metal which can be widely used as a catalyst for the oxidation of phenolic materials^{1–3} and electrical contact points. In the field of analytical science, palladium is used as a matrix modifier for the determination of several metals, such as molybdenum and thallium, by graphite-furnace atomic absorption spectrometry (AAS).^{4–6} In this way, palladium is widely used in various fields. Therefore, a quantitative understanding of palladium has become important. For that purpose, numerous AAS methods following preconcentration techniques, such as coprecipitation⁷, solvent extraction^{8–10} and adsorption–elution^{11–17}, have been developed. The adsorption–elution method is one of the effective preconcentration techniques. Activated carbon (AC)¹¹, chelating resin^{12,13}, ion-exchange resin^{14,15} and porous polymer^{16,17} were used as the adsorbent. This method can require a pertinent choice of the eluent and elution procedure. Thus, a direct injection method, in which the metal adsorbed-adsorbent/water suspension is introduced onto the furnace in electrothermal AAS, would be much more useful because of no need for an elution procedure.

One of the present authors has reported a method in which metal ions, such as beryllium¹⁸, indium¹⁹ and gold²⁰ adsorbed AC/water suspension, are injected directly into the graphite furnace or tungsten metal furnace. These methods are very simple and make it possible to determine ultratrace levels of the metal ions.

Chitin has recently been used for the preconcentration of anionic complexes of metal ions by using its property as an anion-exchanger in an acidic medium. This property of chitin was applied to the determination of some metal ions by AAS after preconcentrated onto chitin as their maleonitriledithiolate²¹ and 1-nitroso-3,6-disulfo-2-naphtholate[nitroso R(NR)]^{22,23} anionic complexes. Hoshi *et al.* have reported the spectrophotometric determination of iron(III) after being preconcentrated as its 8-hydroxyquinoline-5-sulfonate anionic complex.²⁴ Hase *et al.* synthesized the dithiocarbamate-chitin, and used it for the preconcentration of some metal ions.²⁵

The present authors reported a method for the determination of trace amounts of gold(III) by tungsten metal-furnace AAS with the direct injection of a chitin/water suspension adsorbing gold(III) chloro anionic complex.²⁶ This method is simple and useful because a chelating reagent, such as NR, and an elution procedure are unnecessary. Palladium(II) reacts with the chloride ion to form a stable anionic complex similar to gold(III). In this study, the method was extended to the determination of trace amounts of palladium(II) in water samples.

Experimental

Apparatus

A Seiko Instrument, Inc. SAS-7500 atomic absorption

spectrophotometer equipped with a flameless atomizer (PS-200; a tungsten metal furnace) was used for all of the experimental work. A hollow-cathode lamp of palladium was operated at 10 mA, and a deuterium lamp was used for background correction. All measurements were made in the peak-height mode.

An Iwaki glass TM-152 MIXER was used for dispersing the chitin/water suspension. The suspension was manually introduced into the tungsten metal furnace by an Eppendorf micropipet. A Horiba M-8L pH meter was used for pH adjustments of the sample solution.

Reagents

A standard palladium(II) solution was prepared by the dilution of 1000 µg/cm³ atomic absorption standard (Wako Pure Chemicals Co., Ltd.) with 0.1 mol dm⁻³ hydrochloric acid, as required. The standard solution was obtained by dissolving palladium(II) chloride in 1 mol dm⁻³ hydrochloric acid. Palladium(II) has been used to form a palladium chloro anionic complex in standard solution, and its complex is very stable. A palladium(II) bromide solution was prepared by dissolving palladium(II) bromide (Nacalai Tesque Inc.) in hydrobromic acid, and was further diluted with water, as required. In this solution, palladium(II) has been used to form a palladium bromo anionic complex; its complex is very stable.

Chitin powder (Nacalai Tesque Inc.), prepared to a grain size of less than 300 mesh, was washed successively with 1 mol dm⁻³ hydrochloric acid and water, then dried at 70°C for 24 h in a dry oven. Highly purified water was obtained using an Organo Puric-S system. All other reagents were of analytical and extra-pure reagent grade.

Adsorption experiments

The experiments were carried out by a batch method. To a 100 cm³ of sample solution containing palladium(II), 100 mg of chitin was added after adjusting its pH to the optimum range with diluted ammonia water and nitric acid. The solution was stirred for 30 min with a magnetic stirrer, and separated with a membrane filter. The adsorption amounts of palladium(II) onto chitin were determined in order to measure the concentration of the resulting filtrate.

Analytical procedure

The pH of sample solution (100–500 cm³), containing less than 2.0 µg of palladium(II), was adjusted to 3.0 with hydrochloric acid and diluted ammonia water. A 50 mg of chitin was added to the solution. The mixture was stirred for 15 min with a magnetic stirrer so as to adsorb palladium(II) onto the chitin. The palladium(II) which was quantitatively adsorbed onto the chitin was separated from the sample solution through a membrane filter (pore size, 8.0 µm; Millipore Co., Ltd.). The palladium(II) adsorbed onto the chitin was then carefully transferred into a stoppered test tube with 5.0 cm³ of water, and dispersed using an ultrasonic agitator. After

Table 1 Instrumental operating conditions

Wavelength/nm	244.79
Slit width/nm	0.20
Lamp current/mA	10
Flow rate of purge gas/dm ³ min ⁻¹	Ar: 3.0 H ₂ : 1.0
Injection volume/mm ³	10
Drying	130°C/30 s
Ashing	1000°C/10 s
Atomizing	2300°C/4 s

shaking for 15 s, a 10 mm³ aliquot of the palladium(II)-adsorbed chitin/water suspension was injected directly into the tungsten metal furnace with a micro pipette (Eppendorf Co., Ltd.) within 10 s. The absorbance (peak height) was measured under the instrumental conditions listed in Table 1.

Results and Discussion

Adsorption of palladium(II)

Palladium(II) reacts with halogenide ions, such as chloride ion and bromide ion, to form anionic complexes. Thus, the effect of the pH on the adsorption of palladium(II) chloro complex and palladium(II) bromo complex onto chitin from an aqueous solution were investigated. The results are shown in Fig. 1. The palladium(II) chloro complex and palladium(II) bromo complex were quantitatively adsorbed onto chitin in the pH range from 2.5 to 4.0, respectively. The adsorption rate decreased along with a decrease in the pH at a lower pH range. These results were the same as that described for gold(III) halogenide anionic complexes.²⁶ The adsorption rate also decreased along with an increase in the pH at a higher pH range because of incomplete adsorption of their anionic complexes, since chitin does not act as an anion exchanger in the neutral to basic pH region. Further, the adsorption isotherms of the palladium(II) chloro complex and palladium(II) bromo complex onto chitin from an aqueous solution at the optimum pH range were investigated.

The Freundlich equation is generally applicable for the monolayer adsorption of a single species from the liquid to the solid phase.²⁷ The equation can be expressed as

$$q = kC^{1/n}$$

and

$$\log q = \log k + 1/n \log C,$$

where q is the adsorption amount (mg g⁻¹), C is the residual amount (mg g⁻¹) and k and $1/n$ are arbitrary parameters.

These isotherms obeyed the Freundlich equation; the results are shown in Fig. 2. In Fig. 2, the plots of $\log C$

Fig. 1 Effect of pH on the adsorption of palladium(II). (●), palladium(II) chloro complex; (○), palladium(II) bromo complex; palladium(II) $10 \mu\text{g}/100 \text{ cm}^3$; chitin, 100 mg; adsorption time, 30 min.

Fig. 2 Freundlich plots of palladium(II) adsorption on chitin. (●), palladium(II) chloro complex; (○), palladium(II) bromo complex; chitin, 100 mg; pH, 3.0; volume of sample solution, 100 cm^3 ; temperature, room temp.

vs. $\log q$ describe a straight line, respectively. The Freundlich equation parameters obtained from Fig. 2 are summarized in Table 2. In general, the value of $1/n$ is usually less than 1 for a substance which is readily adsorbed, while the value is greater than 2 for a substance which is not readily adsorbed. The values for the palladium(II) chloro complex and the palladium(II) bromo complex were less than 1, respectively. Consequently, both the palladium(II) chloro complex and palladium(II) bromo complex can be classified as a

Table 2 Freundlich's equation parameter

Metal species	$k/\text{mg g}^{-1}$	$1/n$
Palladium(II) chloro complex	44.1	0.34
Palladium(II) bromo complex	15.8	0.26

substance which is readily adsorbed onto chitin. Moreover, the adsorption ability is also higher when the value of k is larger. As shown in Table 2, the k value for palladium(II) chloro complex is 3-times larger than that for the palladium(II) bromo complex. Therefore, the use of the palladium(II) chloro complex is more effective for the preconcentration of trace amounts of palladium(II).

In the following part, palladium(II) means palladium(II) chloro complex.

Analytical conditions

The effects of the ashing and atomizing temperatures on the absorbances of palladium for the palladium(II)-adsorbed chitin/water suspension were investigated by varying the temperature from 400 to 1600°C and 2000 to 2800°C, respectively. The other conditions were kept constant, as shown in Table 1. The relationship between the absorbance and the ashing temperature is shown in Fig. 3. In the case of the suspension, the maximum absorbance of palladium was obtained in the range from 400 to 1200°C. When the temperature at the ashing stage was below 400°C, background absorption appeared due to smoke evolution from the chitin, although it did not interfere with the absorbance measurement. When the temperature at the ashing stage was above 1200°C, the absorbances for both the palladium(II) standard solution and the suspension obtained with the proposed method decreased, due to a

Fig. 3 Effect of ashing temperature on the absorbance of palladium. (●), palladium(II) adsorbed chitin/water suspension; (○), palladium(II) aqueous standard solution; injection volume, 10 mm^3 .

possible loss of palladium by partial volatilization during the ashing stage.

The effect of the atomizing temperature on the sensitivity was similarly studied. In the case of the suspension, the maximum absorbance of palladium was obtained in the range from 2000 to 2500°C.

It was observed that the chitin acts as a sensitizer for palladium during the atomization step; that is, the absorbance of the suspension increases in comparison with that of the palladium(II) standard solution.

Considering these results, we selected an ashing temperature of 1000°C and an atomizing temperature of 2300°C for palladium analyses by metal-furnace AAS.

Effect of the pH and the amounts of chitin

The effects of the pH on the adsorption of palladium(II) onto chitin was examined using the proposed analytical procedure. Palladium(II) was quantitatively adsorbed onto chitin in the pH range from 2.5 to 4.0, as mentioned before. Moreover, the effect of the amounts of chitin on the adsorption of palladium(II) was investigated. The quantitative adsorption of palladium(II) was obtained at more than 40 mg of chitin. However, more than 100 mg of the chitin was employed for the analytical procedure, the chitin was not well dispersed into water, and it was difficult to exactly take a definite amount of the chitin suspension. Accordingly, 50 mg of chitin was used for the determination of palladium(II) in this work.

Effects of the adsorption time and dispersion time

Palladium(II) was quantitatively adsorbed onto chitin by stirring for more than 10 min with a magnetic stirrer. Therefore, an adsorption time of 15 min is employed for the analytical procedure.

Palladium(II)-adsorbed chitin was dispersed homogeneously in 5.0 cm³ of water using an ultrasonic agitator. Then, a 10 mm³ aliquot of the suspension was injected directly into the tungsten metal furnace. Although the absorbance signal decreased rapidly in the case of standing for over 20 s after dispersion, a constant absorbance was obtained within 10 s.

Calibration graph and detection limit

After the analytical procedure was applied to a 100 cm³ sample solution containing 1.0 µg of palladium(II), the same procedure was applied again to the filtrate. No palladium(II) was found in the filtrate, which means that the recoveries of palladium(II) was about 100%. The calibration curves obtained with the proposed analytical procedure for a 100 cm³ of sample solution was linear up to 2.0 µg palladium(II). The influence of the sample size was investigated by varying the volume of a sample solution containing 1.0 µg of palladium(II). A nearly quantitative recovery was obtained with the proposed analytical procedure in the 100–500 cm³ range. Thus, use for a 500 cm³ sample solution can give a concentration factor of 100. The detection limit ($S/N \geq 3$) for palladium(II) was 0.06 µg/500 cm³. The relative

Table 3 Effects of diverse ions on the recovery of palladium(II)

Diverse ion	Amounts added/mg	Recovery, %
Co(II)	0.05	98
Ni(II)	0.05	97
Cu(II)	0.1	98
Zn(II)	0.1	100
Pb(II)	0.1	92
Fe(III)	1.0	98
Al(III)	0.1	100
Mg(II)	0.1	100
K(I)	1.0	100
Na(I)	1.0	98
Ca(II)	1.0	97
Cl ⁻	10	100
CH ₃ COO ⁻	10	100
PO ₄ ²⁻	10	98
NO ₃ ⁻	10	100
SO ₄ ²⁻	10	97

Palladium(II), 1.0 µg/100 cm³; chitin, 50 mg; pH, 3.0; adsorption time, 15 min.

standard deviations of ten measurements was 4.0–5.0% at 0.1 µg/500 cm³.

Effect of diverse ions

The effects of diverse ions on the determination of palladium(II) were investigated. The recoveries of palladium(II) by the proposed analytical procedure were measured in 100 cm³ solutions containing 1.0 µg of palladium(II) and matrix ions. The experimental results are shown in Table 3. These results show that a number of common cations, such as calcium(II), potassium(I), sodium(I) and iron(III), did not interfere with the determination of palladium(II). Similarly, various anions, such as Cl⁻, CH₃COO⁻, NO₃⁻ and SO₄²⁻, did not interfere. Therefore, the proposed analytical procedure can be applied to the determination of palladium(II) in water samples.

Determination of palladium(II) in water samples

The palladium(II) contents in river water and plating wastewater were measured by the proposed analytical procedure after suspended matter was removed using a membrane filter (pore size, 0.45 µm; Millipore Co., Ltd.). Table 4 shows the results of analyses of the original sample solution and of sample solutions to which known amounts of palladium(II) were spiked. The recoveries of the spiked palladium(II) were over 99%.

In conclusion, the proposed method, in which the palladium(II) chloro anionic complex is quantitatively adsorbed onto chitin powder, is effective for the preconcentration of trace amounts of palladium(II). The proposed method is rapid and simple, and applicable to the determination of trace amounts of palladium(II) in water samples.

Table 4 Determination of palladium(II) in water samples

Sample	Palladium(II)		
	Added/ μg	Found/ μg	Recovery, %
River water ^a	—	N.D.	—
(Kimitsu, Chiba-pref.)	0.10	0.100	100
	0.20	0.202	102
Plating factory wastewater ^b	—	0.171	—
	0.10	0.269	99
	0.20	0.372	100

N.D. $\leq 0.06 \mu\text{g}$ palladium(II)/100 – 500 cm^3 ; chitin, 50 mg; adsorption time, 15 min.

a. Sample volume, 500 cm^3 .

b. Sample volume, 100 cm^3 .

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