

Simultaneous Laser Thermal Lens Spectrometric Determination of Trace Platinum and Palladium in an Aqueous Solution

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A selective and sensitive method for determination of platinum and palladium(II) in an aqueous solution simultaneously by laser thermal lens spectrometry, based on the complex reaction of 2-(3,5-dichloropyridylazo)-5-dimethylaminoamline (3,5-diCl-PADMA) with platinum and palladium, has been developed. It is shown that the palladium complex can be formed at room temperature, while the platinum complex can be only formed after being heated in a boiling water bath. By using this difference of reaction temperature and the characteristic of the complexes mentioned above, the method for simultaneous determination of platinum and palladium was established in an aqueous solution without a pre-separation. The results show that the dynamic linear ranges of determination for platinum and palladium are 0.005—0.04 $\mu\text{g/mL}$ and 0.005—0.25 $\mu\text{g/mL}$ respectively, and that the detection limits are both 0.002 $\mu\text{g/mL}$. The method has been applied to the determination of platinum and palladium simultaneously in alloy and catalyst samples with satisfactory results.

Keywords laser thermal lens spectrometry, simultaneous determination, platinum, palladium, 2-(3,5-dichloropyridylazo)-5-dimethylaminoamline

Introduction

It is an important research topic to determine directly the components of a complex system without a prior separation. By utilizing the differences of reaction condition of the metal ions with chromogenic reagent (temperature or acidity) or the different characteristics of the complexes, some spectrophotometric methods have been developed for the determination of multi-element in a complex system simultaneously.¹⁻³ These methods are simple and selec-

tive. However, the sensitivities of the spectrophotometric methods are still unsatisfactory.¹

Thermal lens spectrometry (TLS) is a high sensitive spectrometry based on the photo-thermal effect. When a laser pump beam having a Gaussian radial intensity profile (TEM₀₀ mode) is passed through an absorbing sample, nonradiation relaxation of the excited molecules leads to heating of the solvent in the path of the pump beam. The greater amount of heat deposited in the center of the beam generates a temperature gradient of refractive index which changes the divergence of the beam, the thermal lens effect.^{4,5} Another probe beam is directed through the sample coaxially to the pump beam and the intensity of the beam is monitored with a pinhole/photodiode combination. The change in peak intensity is a sensitive indicator of the sample concentration. The TLS has been developed into a high sensitive, quantitative method for the determination of trace-level metal ions in chemical, environmental and food samples over normal spectrophotometric analysis.^{5,6} However, up to now there are few reports on TLS applications in simultaneous determination of multi-element, especially for precious metals.⁷

In this study, a new chromogenic reagent, 2-(3,5-dichloropyridylazo)-5-dimethylaminoamline (3,5-diCl-PA-DMA), was synthesized and investigated. It was shown that platinum(IV) and palladium(II) can react with 3,5-diCl-PADMA to form stable complexes in strong acidic medium, which exhibit absorption maximum at 634 nm and 623 nm, respectively. However, the reaction temperature is different to form the complexes of platinum and palladium. The palladium complex can be formed at

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room temperature, while the platinum complex can be only formed after being heated in a boiling water bath for 80 min. Based on the temperature difference of complex reaction of 3,5-diCl-PADMA with platinum and palladium, a novel method for simultaneous determination of platinum and palladium in an aqueous solution by laser thermal lens spectrometry was proposed without a pre-separation. The method has been successfully applied to the determination of platinum and palladium simultaneously in alloy and catalyst samples.

Experimental

Apparatus

The instrument of laser thermal lens spectrometry used in this experiment has been described in detail elsewhere.⁸ A single mode He-Ne laser ($\lambda_{632.8\text{ nm}}$) acts as both exciting and probing beam. After being modulated and focused, the laser beam irradiates on the determined solution. The TLS signals produced in the determined solution were detected and processed by a photoelectric device and an M1052 lock-in amplifier.

Spectrophotometric measurements were made using a Shimadzu Model UV-260 spectrophotometer. Elemental analyses were done with a PE Model PE-2400 analyzer.

Synthesis of 3,5-diCl-PADMA

4.2 g (0.02 mol/L) of diazotate of 3,5-dichloro-2-amino-pyridine was dissolved in 50 mL of aqueous ethanol solution (1:1, V:V), and cooled to 0 °C. To this diazotized solution 4.3 g (0.02 mol/L) of *N,N*-dimethyl-1,3-phenylenediamine dihydrochloride in 50 mL of aqueous ethanol solution (1:1, V:V) was added dropwise with vigorous stirring. Then, 8 mL of hydrochloric acid (1:1, V:V) was added dropwise, and stirring was continued for an additional 4 h. The solution was adjusted to pH 4–5 with 50% sodium acetate solution. A precipitation of red crystals was obtained, filtered and washed with water. The crude reagent was then purified by recrystallization twice from ethanol-water. The yield was about 30%. M.p. 197.4–198.3 °C. Anal. calcd for $\text{C}_{13}\text{H}_{13}\text{N}_5\text{Cl}_2$: C 50.34, H 4.23, N 22.59; found C 50.57, H 4.18, N 21.79.

Reagents

Standard platinum solution 0.2000 g of pure

platinum (99.99%) was dissolved in 20 mL of aqua regia and the solution was evaporated to 2–3 mL. 0.1 g of sodium chloride was added, and the solution was heated until it was nearly dry. Then, 5 mL of hydrochloric acid was added and the mixture was evaporated almost to dryness, repeating three times. The residues were dissolved in 20 mL of hydrochloric acid (6 mol/L), transferred and diluted to 200 mL in a volumetric flask with hydrochloric acid (1.5 mol/L). The solution contains 1.000 mg/mL platinum, and a working solution (1.0 $\mu\text{g/mL}$) was prepared by dilution with 0.5 mol/L hydrochloric acid.

Standard palladium solution 0.1000 g of pure palladium (99.99%) was dissolved in 50 mL of aqua regia. 1 mL of 20% sodium chloride was added, and the solution was heated until it was nearly dry. Then, 2 mL of hydrochloric acid was added and the mixture was evaporated almost to dryness, repeating three times. The residues were dissolved in hydrochloric acid (1 mol/L), transferred and diluted to 100 mL in a volumetric flask with hydrochloric acid (1 mol/L). The solution contains 1.000 mg/mL of palladium, and a working solution (1.0 $\mu\text{g/mL}$) was prepared by dilution with distilled water.

3,5-diCl-PADMA solution A 3,5-diCl-PADMA solution (1.0×10^{-3} mol/L) was prepared by dissolving 0.0618 g of 3,5-diCl-PADMA in ethyl alcohol and diluting it to 200 mL in a volumetric flask.

Sulphuric acid solution A sulphuric acid solution (6 mol/L) was prepared by diluting the appropriate mass of concentrated sulphuric acid to 250 mL in a volumetric flask.

All chemicals used were of analytical-reagent grade, and the solutions were all prepared with redistilled water.

General procedure

Two aliquots of sample solution containing platinum and palladium were respectively added to two 10 mL color comparison tubes (tubes A and B). Then, to tube A was added 0.4 mL of H_2SO_4 solution (6 mol/L), 0.4 mL of 3,5-diCl-PADMA solution (1.0×10^{-3} mol/L) and 6 mL of acetone, and the mixture solution was diluted to the mark with water and mixed well. After 25 min, the TLS signal intensity of the palladium S_{Pd} was determined. Subsequently, to tube B was added 0.4 mL of H_2SO_4 solution (6 mol/L) and 0.4 mL of 3,5-diCl-PADMA solution (1.0×10^{-3} mol/L), and diluted to the mark with water and mixed well. The solution of tube B was heated

in a boiling water bath for 80 min, taken out, cooled to room temperature. 6 mL of acetone was then added and diluted to the mark with water and mixed well. The TLS signal intensity of the platinum and the palladium S_T was determined. The platinum S_{Pt} was calculated, $S_{Pt} = S_T - S_{Pd}$.

Results and discussion

Solvent and absorption spectra

It is known that the intensity of the TLS signal depends on the thermo-physical characteristics of the solvent medium. In order to enhance the TLS signal intensity, the TLS measurement should be done in an aqueous organic solvent.^{9,10} The selected solvent should have a high signal enhancement rate, and the absorption maximum of the complex in the selected solvent can match the wavelength of the laser well. The common used solvents of ethanol and acetone can all meet the requirements mentioned above. However, it was found that the solvent of water-acetone (3:5, V:V) can make the maximum absorbance of the platinum and palladium complexes increased by about 40% and 10% compared with aqueous medium, respectively. While the solvent of water-ethanol (3:5, V:V) can only provide a 26% increase for platinum, but no increase for palladium. Therefore, the solvent of water-acetone (3:5, V:V) was selected as the solvent for the TLS measurement.

The absorption spectra of 3,5-diCl-PADMA and the complexes of platinum and palladium in water and water-acetone mixture (3:5, V:V) were measured respectively and shown in Fig. 1. It can be seen that the absorption spectra are different with the addition of acetone. In the absence of acetone, the complexes of platinum and palladium exhibit absorption maximum at 631 and 620 nm, respectively. Addition of acetone results in a modest red shift from 631 to 634 nm for platinum and 620 to 623 nm for palladium, meanwhile the absorbances increase by about 40% and 10% at their maximum absorption peak, and 168% and 18% at their another absorption peak near 580 nm, respectively. However, the absorbance of the reagent itself at the absorption wavelength of the complexes decreases. This may be due to the promotion effect of acetone, a proton acceptor, on the deprotonation of the protonized reagent and its metal complexes in strong acidic medium. The deprotonation of the reagent, here

means the deprotonation of the nitrogen atom of the pyridyl ring, makes the complex reaction more complete and so the absorbances of the complexes increase. The deprotonation of the metal complexes, here means the transfer of the complexes from species MLH_2^{2+} (λ_{max} near 630 nm) to species MLH^+ (λ_{max} near 580 nm), causes the absorptions near 580 nm increasing much more than that near 630 nm. In addition, the inhibition effect of the organic solvent on the hydrolytic polymerization of the metal ions and the depolymerization effect of it on the chelating reagent may also be the reasons for absorbance increasing of the complexes. The He-Ne laser (λ 632.8 nm) was selected for TLS measurement.

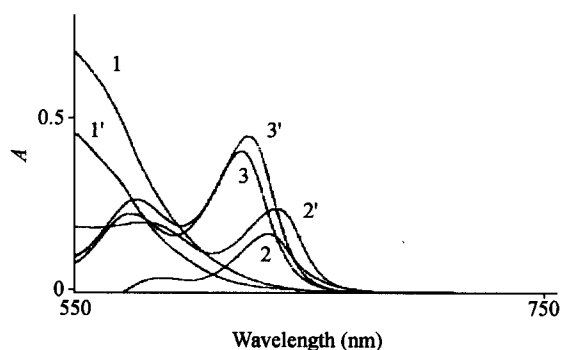


Fig. 1 Absorption spectra of 3,5-diCl-PADMA vs. water blank (1, 1') and platinum (2, 2') and palladium (3, 3') complexes vs. reagent blank. Reagents and conditions: 3,5-diCl-PADMA, 4×10^{-5} mol/L; Pt(IV), $0.5 \mu\text{g/mL}$; Pd(II), $0.65 \mu\text{g/mL}$; curves 1, 2, 3: water; curves 1', 2', 3': water-acetone mixture (3:5, V:V).

Effect of acid medium and its concentration

It was found that the complex reaction of 3,5-diCl-PADMA with platinum and palladium could be performed in the medium of sulphuric acid, hydrochloric acid or perchloric acid. The absorbances were same in 0.04—0.48 mol/L H_2SO_4 and 0.01—0.06 mol/L HCl for platinum complex, and in 0.02—1.6 mol/L H_2SO_4 , 0.02—1.3 mol/L HCl and 1.6—4.8 mol/L HClO_4 for palladium complex. Subsequent determinations were therefore carried out in 0.24 mol/L H_2SO_4 .

Effect of the reagent concentration

The TLS signals of a series of solutions containing $1.0 \mu\text{g/mL}$ platinum or palladium and various amounts of 3,5-diCl-PADMA (1.0×10^{-3} mol/L) were measured.

It was found that 0.35 mL and 0.06 mL of 3, 5-diCl-PADMA (1.0×10^{-3} mol/L) sufficed for complex 1.0 $\mu\text{g/mL}$ platinum and palladium, respectively. Therefore, 0.4 mL of 3, 5-diCl-PADMA (1.0×10^{-3} mol/L) was used in subsequent work.

Color development, stability and effect of temperature

The reaction temperature and time for 3, 5-diCl-PADMA with platinum and palladium are quite different. The palladium complex can be formed completely after being reacted for 20 min at room temperature or 1 min at 90–100 °C, and then remain stable even if being heated in boiling water bath for 2 h. However, the platinum complex was not formed at room temperature at all, but only formed completely after being heated in a boiling water bath for 80 min. It was just the different temperature required for the complex formation mentioned above that allows the simultaneous determination of platinum and palladium directly in an aqueous solution without a pre-separation. For a sample containing both platinum and palladium, 25 min of reaction time at room temperature was selected to determine palladium, and 80 min of heating in boiling water bath was selected to determine the total of platinum and palladium.

Calibration graph

The calibration graphs were obtained by the general procedure. They show good linearity over the two ranges of 0.005–0.060 $\mu\text{g/mL}$ and 0.05–0.40 $\mu\text{g/mL}$ for platinum, and 0.005–0.060 $\mu\text{g/mL}$ and 0.05–0.25 $\mu\text{g/mL}$ for palladium. The linear regression equations of platinum were $S_{\text{Pt}} = 61.8 C + 0.02$ ($r = 0.9988$, 0.005–0.060 $\mu\text{g/mL}$) and $S_{\text{Pt}} = 30.3 C - 0.023$ ($r = 0.9995$, 0.05–0.40 $\mu\text{g/mL}$), and the linear regression equations of palladium were $S_{\text{Pd}} = 36.3 C - 0.025$ ($r = 0.9988$, 0.005–0.060 $\mu\text{g/mL}$) and $S_{\text{Pd}} = 17.8 C - 0.024$ ($r = 0.9990$, 0.05–0.25 $\mu\text{g/mL}$) (where, C is the concentration of metal ions in $\mu\text{g/mL}$). The limit of detection, which was calculated according to the 3δ -criterion, of both platinum and palladium was 0.002 $\mu\text{g/mL}$.

Effect of foreign ions

The influence of the diverse ions on the simultaneous

determination of 0.1 $\mu\text{g/mL}$ platinum and palladium was investigated by applying the recommended method to solutions containing fixed amounts of platinum and palladium in the presence of increasing quantities of the interfering ion. The results are given in Table 1. The tolerance limit was taken as the amount that caused an error of $\pm 5\%$. It was shown that relatively large amount of coexisting ions, including all other noble metal ions, does not interfere in the simultaneous determination of platinum and palladium. The tolerance limit of copper(II) can be increased to 70 by addition of 2.5 mL of H_2SO_4 (6 mol/L) after the complex reaction has been completed.

Table 1 Interferences of foreign ions on the determination of Pt(IV) and Pd(II)^a

Foreign ion	Tolerance limit, [Ion]/[Pt(IV)] or [Pd(II)] ($\mu\text{g}/\mu\text{g}$)
Fe(III)	500
Ni(II)	800
Co(II)	200
Cu(II)	20
Ag(I), Au(III)	70
Ir(III)	30
Rh(III), Ru(III), Os(III)	6
NaCl	> 1500
KI, EDTA	50

^a[Pt(IV)] and [Pd(II)] were both 0.1 $\mu\text{g/mL}$.

Recovery test

The standard recovery test was done for some synthetic samples containing varies amounts of Pt(IV) and Pd(II) according to the general procedure. The results are presented in Table 2. As shown in Table 2, the recovery ratios for both Pt(IV) and Pd(II) were ranged from 96% to 105%.

Table 2 Recovery test of Pt(IV) and Pd(II) in synthetic samples

Added (μg)		Found (μg)		Recovery (%)	
Pt	Pd	Pt	Pd	Pt	Pd
0.40	0.20	0.39	0.21	97	105
0.30	0.30	0.31	0.30	103	100
0.20	0.40	0.21	0.39	104	97
0.10	0.50	0.10	0.48	100	96

Analysis of samples

The method has been applied to the simultaneous-determination of platinum and palladium in alloy and catalyst samples. The procedure was as follows: An accurately weighed sample was dissolved in 20 mL of aqua regia and the mixture was evaporated on a sand-bath until nearly dry. 2 mL of concentrated hydrochloric acid was added and the solution was heated almost to dryness, repeating 2–3 times until no NO₂ fumes appear. The residue was dissolved in 10 mL of 6 mol/L hydrochloric acid, filtered and diluted to 100 mL in a volumetric flask with water and mixed well. The sample solution was then determined by the recommended general procedure, and the obtained results are shown in Table 3. The accuracy

and precision of the method are satisfactory.

Conclusions

By using the temperature difference of the complex forming reaction, the simultaneous determination of platinum and palladium by high sensitive thermal lens spectrometry can be done directly in an aqueous solution without pre-separation. The sensitivity of the method is over that of normal spectrophotometry. In our opinion, work in this direction will conduce to expanding the areas of application of TLS. And also the method proposed here is a practical candidate for simultaneous determination of platinum and palladium in practical analysis.

Table 3 Determination results of Pt(IV) and Pd(II) in samples ($n = 8$)

Sample	Certified ($\mu\text{g/g}$)		Found ($\mu\text{g/g}$)		RSD (%)		Recovery (%)	
	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
Catalyst ^a	151	302	148	304	1.26	1.56	98.0	101
Alloy-88 ^b	482	482	479	478	0.97	1.47	99.4	99.2

^a The results certified are obtained by the spectrophotometric method. ^b Certified by authorized Chinese Analysis Centers.

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