Successive Spectrophotometric Determination of Palladium and Platinum

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(Received April 17, 1976)

The absorbance of the water soluble red complex of palladium(II) and 4-(2-pyridylazo)resorcinol (PAR) was measured at 513 nm. Concd hydrochloric acid and tin(II) chloride were added to an aliquot of the red solution, and both the palladium complex and the excess of PAR were decolorized by the reduction of the azo radical of PAR. The absorbance of the platinum complex with tin(II) chloride was measured at 403 nm.

The photometric determination of many metals by using 4-(2-pyridylazo)resorcinol (PAR) has been described. It is known that palladium(II) reacts with PAR to form four kinds of stable 1 : 1 chelates. One of them is green at pH below 4 and the others are red at pH above 4.[1] We found that the water soluble red complex at pH 10.3—11 had an absorption maximum at about 520 nm in 0.01 M EDTA.[2] By the use of the EDTA–NaOH solution, not only a masking of many diverse ions but also a buffer action at 10.5 has been achieved, and 30 times of platinum(IV) was scarcely interfered in the determination of palladium.

The tin(II) chloride method is widely used for the spectrophotometric determination of micro amounts of platinum.[3] But in the presence of palladium it gives a positive error in the determination of platinum, so that the regions available to this method are limited.

It has been known that many azo compounds are easily reduced with tin(II) chloride in concentrated hydrochloric acid.[4,5] We found that PAR and its palladium complex were also reduced and almost completely decolorized. This reductive reaction was combined with the determination of platinum; the spectrophotometric determination of Pd–PAR complex was carried out at 513 nm and then the determination of platinum at 403 nm. By using this procedure the successive determination of palladium and platinum became possible.

Experimental

Apparatus. A Hitachi double beam spectrophotometer model 200-20 with 1 cm cuvettes, a Hitachi recorder model QPD53, and a Hitachi-Horiba pH meter model H-5 were used.

Reagents. A standard palladium stock solution was made by dissolving 500 mg of metal in aqua regia and evaporating to dryness on a water bath After evaporating to dryness three times with hydrochloric acids, the residue was dissolved with 0.1 M hydrochloric acid and made up to 500 ml with 0.1 M hydrochloric acid. This solution was standardized gravimetrically by the dimethylglyoxime method. The palladium test solution was prepared by diluting 5 ml of stock solution and 4.5 ml of 1 M hydrochloric acid and diluted to 500 ml with water. This test solution contained 9.86 μg of palladium per ml.

A standard platinum solution was made by dissolving 100 mg of pure platinum in a few ml of aqua regia and evaporating to dryness; then 5 ml of concd hydrochloric acid and 0.1 g of sodium chloride were added and the solution evaporated to dryness. The residue was dissolved in 20 ml of 6 M hydrochloric acid and the solution was diluted to exactly 1 l. This standard solution contained 100 μg of platinum per ml.

A 0.1% PAR solution was prepared by dissolving 0.25 g of PAR (free acid form, Dojin Pharmaceutical Laboratories, Kumamoto, Japan) to 2 ml of 1 M sodium hydroxide solution, and diluting to 250 ml with water. This solution was stored in a polyethylene bottle.

An EDTA buffer solution having a pH of 10.5 was prepared by adding 100 ml of 1 M sodium hydroxide to about 200 ml of EDTA aqueous solution in which was dissolved 18.6 g of EDTA (di-sodium salt) and diluting to 500 ml with water.

The tin(II) chloride solution was made by dissolving 115 g of $SnCl_2 \cdot 2H_2O$ in 170 ml of warm concd hydrochloric acid and diluting to 500 ml with water. A stick of pure tin was placed in the bottle to keep the solution in the reduced state.

All the other chemicals used were of reagent grade.

Recommended Procedure. To the sample solution containing 0—100 μg palladium and 0—300 μg platinum, 5 ml of 0.1 M EDTA buffer solution (pH 10.5) and 0.5 ml of 0.1% PAR solution were added (if needed, the pH ought to be adjusted to 10.3—10.5 by 0.1 M sodium hydroxide). Then the solution was warmed in a water bath at 80 °C for 10 min and was cooled. The solution was diluted to 50 ml with water to determine its absorbance at 513 nm. A blank was run through the whole procedure, using water.

To a 25 ml residual solution of determined palladium contents, 7 ml of concd hydrochloric acid was added and stirred, followed by the addition of 10 ml of tin(II) chloride solution. The solution was diluted to 50 ml with water to determine its absorbance at 403 nm.

The authentic absorbance of platinum was provided by substracting 0.001 for each 10 μg palladium from its observed absorbance. By these procedures palladium and platinum were successively determined.

Results and Discussion

Measurements of Absorption Spectra. Figure 1 shows the absorption spectra of PAR and Pd–PAR. In the previous paper[2] measurements were carried out at 520 nm. However, as it turned out that the absorption maximum of Pd–PAR complex was at 513 nm, in this study measurements were carried out at this wavelength at pH 10.3—10.5. Under these conditions the molar extinction coefficient was 2.6×10^4 and the sensitivity which gave the absorbance of 0.001 was 0.0041 μg-Pd^{2+}/cm^2. To the beaker containing 49.3 μg palladium, 5 ml of 0.1 M EDTA buffer solution and 0.5 ml of 0.1% PAR solution were added. The solution was heated at 80 °C for 10 min and cooled, then 7 ml of concd hydrochloric acid was added to it. In addition,

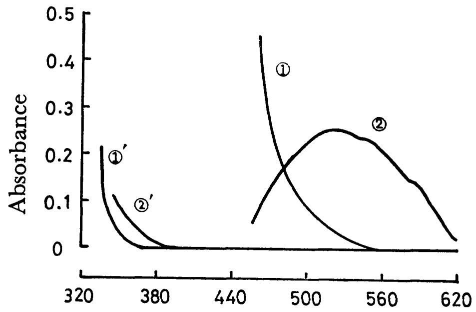

Fig. 1. Absorption curves of PAR, Pd–PAR and their decolorized.

①PAR (0.5 mg/50 ml), ② Pd–PAR (Pd: 49.3 μg/50 ml), ①′ and ②′ signify the solutions being reduced corresponding to ① and ②.

Table 1. Determination of palladium and platinum in synthetic mixtures

Absorbance of PAR complex$^{a)}$			Absorbance of tin(II) chloride complex			
Pd(II) added (μg)	Pt(IV) added (μg)	Absorbance at 513 nm	Pd taken (μg)	Pt taken (μg)	Absorbance at 403 nm	Correction value
0	100	0.002	0	50	0.040	
0	200	0.004	0	100	0.080	
0	300	0.003	0	150	0.120	
9.86	0	0.049	4.93	0	0.001	
29.6	0	0.147	14.8	0	0.001	
49.3	0	0.245	24.65	0	0.001	
9.86	100	0.050	4.93	50	0.041	0.040
9.86	200	0.049	4.93	100	0.082	0.081
9.86	300	0.049	4.93	150	0.122	0.121
29.6	100	0.147	14.8	50	0.041	0.038
29.6	200	0.148	14.8	100	0.084	0.081
29.6	300	0.146	14.8	150	0.123	0.120
49.3	100	0.244	24.65	50	0.045	0.040
49.3	200	0.244	24.65	100	0.085	0.080
49.3	300	0.245	24.65	150	0.125	0.120

a) Total volume 50 ml, PAR 0.5 mg/50 ml.

when one drop of tin(II) chloride was added, the solution of Pd–PAR complex changed from green to colorless. As the tin(II) chloride content increased, PAR and its palladium complex were reduced and almost completely decolorized. In Fig. 1, ① and ② are the absorption curves of PAR and Pd–PAR respectively, and ①′ and ②′ are the blanks of ① and ② respectively. ①′ and ②′ have no absorption at 403 nm, which is the wavelength for platinum. For determining the platinum contents, the sensitivity of this procedure was not different from Sandell's procedure.

The Successive Determination of Palladium and Platinum. The results shown in Table 1 were obtained from the analysis of some known synthetic mixtures containing 0—49.3 μg palladium and 0—300 μg platinum. In the case of no platinum, palladium gave an absorbance as if the absorbance of platinum were 0.001. In the presence of palladium, the absorbance of platinum increased 0.001 for each 10 μg palladium (5 μg palladium in determining platinum contents). By these corrections of the absorbance of platinum, a good linear relationship was found between the platinum content and its absorbance.

The Successive Determination of Other Metals and Platinum. As the photometric determination of many metals can be carried out by using PAR,[6] other metals and platinum can be determined in succession. In place of PAR the heterocyclic azo dyestuffs will be able to be used.

The authors wish to thank Dr. Eiichi Ibuki, Professor in the Kyoto College of Pharmacy, for his advice on this work. They also thank Dr. Hiromu Imai, Professor in Kansai University, and Dr. Takeshige Oyama, Professor in the Iron and Steel Technical College, for their ardent encouragement.

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