Spectrophotometric determination of trace amounts of palladium(II) using iodide and rhodamine 6G

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A sensitive and highly selective procedure for the spectrophotometric determination of palladium(II) is described. The method is based on the formation of ternary ion-association complex, Pd-I$^-$-rhodamine 6G, in a citrate buffered medium. The colour system absorbs maximally at 575 nm with molar absorptivity of 8.2×10^4 l mol^{-1} cm^{-1} and obeys Beer's law in the range 1-10 μg. The method has been applied successfully to the determination of palladium(II) in synthetic mixtures and in standard palladium activated charcoal.

Marczenko and Jarosz have reported methods for the estimation of Pd(II) in which Pd-SCN-methylene blue[1] or Pd-Br-rhodamine 6G[2] complexes were floated on benzene and then dissolved in acetone or dimethylformamide. Although the former is less sensitive ($\varepsilon = 1.7 \times 10^5$ l mol^{-1} cm^{-1}) than the latter ($\varepsilon = 3.0 \times 10^5$ l mol^{-1} cm^{-1}), it has better selectivity and flexibility in analytical conditions. However, these methods suffer from serious interference from siliver(I), platinum(IV), ruthenium(III), molybdenum(VI), tungsten(VI) and osmium(VIII). The present note describes a spectrophotometric method for the determination of Pd(II) based on the interation of anionic iodo complex of palladium(II) with rhodamine 6G. This method has been applied for the determination of palladium(II) in palladium-activated charcoal samples.

Experimental

Stock solution of palladium(II) (1000 μg/ml) was prepared by dissolving 1.662 g of PdCl$_2$ in 1 litre of distilled water containing 5 ml of conc. HCl. Working solutions (1 μg ml^{-1}) were prepared by suitably diluting this stock solution. Potassium iodide solution (5% w/v) was prepared by disolving 5 g of potassium iodide (E. Merck) in distilled water and diluting to 100 ml. Rhodamine 6G solution (0.005% w/v) was prepared by dissolving 0.0125 g of rhodamine 6G (BDH) in distilled water and diluting to 250 ml. Citrate buffer (0.4 M, pH 4) was prepared by dissolving 4.2 g of citric acid monohydrate and 5.9 g of trisodium citrate in 100 ml of water and adjusting the pH 4. Gelatin solution (1% m/v) was prepared by dissolving 1 g of gelatin in hot water. The solution was cooled and diluted to 10 ml.

A microcomputer based Shimadzu 160A double beam spectrophotometer with 1 cm cell was used. An ELICO LI-120 digital pH meter was used for pH adjustments.

General procedure

To an aliquot of the Pd(II) solution (up to 12 ml) containing up to 10 μg of Pd(II) in a 25 ml volumetric flask, were added 2.5 ml of citrate buffer, 3 ml of KI and 5 ml of rhodamine 6G followed by 1 ml of gelatin. The solution was mixed well and diluted to the mark with distilled water. The absorbance was measured at 575 nm against a reagent blank. A calibration graph for 1-10 μg of palladium(II) was prepared by the above procedure.

Analysis of palladium catalyst samples

Palladium activated charcoal (0.1 g) was dissolved in 20 ml of aqua regia. The solution was evaporated to dryness. Conc. HCl was added and evaporated repeatedly until all the nitric acid was removed. The solution was filtered and the filtrate was diluted to 100 ml with water. An aliquot of this solution was analysed for palladium(II) by the proposed method.

Results and discussion

The absorption spectra show that the interaction of iodo complex of palladium with rhodamine 6G proceeds with considerable bathochromic shift; the ternary complex has λ_{max} at 575 nm while that of the dye absorbs at 530 nm and (PdI$_4$)$^{2-}$ at 480 nm.

The effect of pH on the colour system was investigated in the pH range 2-7. Studies at higher acidities were not carried out as iodine is liberated below pH 2 and forms I$_3^-$ which interacts strongly with rhodamine 6G. The ternary ion-as-

Table 1—Effect of diverse ions on the determination of palladium(II)

[Palladium taken = 5 μg in 25 ml]

Ion	Tolerance limit
Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, Be^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+}, UO_2^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+}, La^{3+}, Tl^+, Zr^{4+}, Th^{4+}, Ce^{4+}, SCN^-, NO_3^-, MoO_4^{2-}, WO_4^{2-}, $Cr_2O_7^{2-}$, $B_4O_7^{2-}$, $C_2O_4^{2-}$, AsO_4^{3-} and VO_4^{3-}	200
Rh^{3+}	100
Ir^{4+}	20
Ru^{3+} and OsO_4	2
Cd^{2+} and Pt^{4+}	—

Table 2—Determination of palladium(II) in palladium activated charcoal

Sample	Pd(II) (μg)		Recovery (%)
	ICPAES	Present method	
Pd-activated charcoal (Loba Chemie, Bombay)	46.78	46.66	99.74
		46.50	99.40
		46.40	99.19

sociation complex was fully formed in the *p*H range 3-5. Citrate buffer (*p*H 4) was preferred to acetate or phthallate because it improved the selectivity of the method. The study shows that a maximum of 3 ml of 5% potassium iodide and 4 ml of 0.005% rhodamine 6G are required for complex formation and that further increase in their concentrations had no effect on the colour intensity. Under these optimum conditions it was found that a minimum of 10 min was necessary for complete formation of the binary complex $[PdI_4]^{2-}$. The order in which the reagents were added was not critical provided gelatin was added last. The colour system on stabilisation with gelatin remained stable for at least 24 h.

The colour system obeys Beer's law in the range 0-10 μg of palladium(II) in a final volume of 25 ml. The molar absorptivity was calculated to be 8.2×10^4 l mol^{-1} cm^{-1}. The coefficient of variation for ten determination of 2 μg of palladium(II) was 1.0%.

The ratio of palladium(II) : rhodamine 6G was established to be 1 : 2 by the molar ratio and Job's methods. The equilibrium shift method showed the ratio of palladium(II) : iodide to be 1 : 4.

Interference studies

The effect of various ions on the determination of 5 μg of palladium(II) in 25 ml was studied. An error of ± 3% in the absorbance was considered tolerable. The results are summarized in Table 1.

Analysis of synthetic samples

Synthetic samples of palladium(II) containing at least 1 mg of another metal ion [Fe(III), Mn(II), UO_2^{2+}, Cr^{3+}, Ni^{2+}, CO^{2+}, Al^{3+}, WO_4^{2-}, VO_4^{3-}, Zr^{4+}, Cu^{2+}, Fe^{3+}], 0.5 mg of Rh^{3+} or 0.1 mg of Ir^{4+}, either alone or in combination were tested. The results clearly demonstrate the potential of the method for the determination of palladium(II) in steels, alloys and minerals containing various noble and base metals.

Analysis of palladium activated charcoal

Table 2 shows the results of the determination of palladium(II) in palladium activated charcoal samples by the proposed method. The results obtained were compared with those obtained by ICP-AES. The results show good agreement between the two methods.

Acknowledgement

References

1 Marczenko Z & Jarosz M, *Analyst*, 106 (1981) 751.
2 Marczenko Z & Jarosz M, *Talanta*, 28 (1981) 561.