

Spectrophotometric determination of trace amounts of platinum (IV) with iodide and rhodamine 6G

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A sensitive and selective procedure for spectrophotometric determination of platinum (IV) with rhodamine 6G in presence of iodide has been described. The absorbance is measured at 575 nm and the molar absorptivity is found to be $1.26 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. The complex system obeys Beer's law in the range 0-12 μg of platinum (IV) present in 25 ml of final solution. The effect of pH and concentration of iodide and rhodamine 6G have been studied. The method has been applied successfully to the determination of platinum (IV) in the standard platinum carbon powder (platinum catalyst).

Platinum is a good catalyst and is widely used for hydrogenation reactions. Owing to its corrosion resistant nature and alloying ability, platinum and its alloys are used in dental and medicinal devices and in manufacture of jewellery.

Various reagents have been recommended for the determination of platinum, 4,4''-bis(dimethylamino)thiobenzophenone¹ is highly sensitive ($\epsilon = 2.98 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) but not selective. Among the few ion-association systems reported for platinum²⁻⁴, the interaction of $(\text{Pt}(\text{NH}_3)_6)^{4+}$ with eosine⁴ is of special significance because it is sensitive ($\epsilon = 8.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and reasonably selective as only Fe(III) and Rh(III) are reported to interfere seriously. Crystal violet⁵ or rhodamine 6G⁶ involve flotation with benzene followed by dissolution in acetone. Although the former is sensitive, but it suffers from serious interferences from Pd, Ir and Rh and must be carried out in subdued light. The latter is not easily reproducible as it involves the measurement of

colloidal solutions. Platinum determined with crystal violet⁷ and rhodamine B⁸ in presence of thiocyanate, though moderately sensitive requires a heating for 20 an 15 min and a standing time of 5 min and 1 h respectively. The platinum-iodide pyronine G⁹ ($\epsilon = 1.07 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) and palladium-iodide- rhodamine 6G¹⁰ $\epsilon = 8.2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ systems have been reported to have good selectivity. In continuation of our earlier work, as pyronine G is an impure commercial dye^{11,12}, we report herein a highly selective spectrophotometric method for the determination of platinum (IV). The method is based on the interaction of anionic iodocomplex of platinum (IV) with rhodamine 6G. This method has been applied for determination of platinum(IV) in platinum catalyst samples.

Experimental

A microcomputer based Shimadzu 160A double beam spectrophotometer was used. An ELICO-LI-120 digital pH meter was used for pH adjustment. All reagents used were of AR grade unless otherwise stated. All solutions were prepared using doubly distilled water.

Pure platinum wire (0.1 g) was dissolved in aqua regia. Concentrated hydrochloric acid was added and repeatedly evaporated until all the nitric acid was removed. The residue was dissolved in 2 ml of conc. HCl and diluted to 100 ml with doubly distilled water. The solution was suitably diluted to obtain a standard solution (5 ppm) of platinum(IV). Citrate buffer (0.4M) was prepared by dissolving citric acid monohydrate (10.02 g) and trisodium citrate (14.70 g) in doubly distilled water, adjusting the pH to 3 using either HCl or NaOH and diluting to 250 ml. Aqueous solutions of KI(5%), rhodamine 6G (0.01%) and gelatin (1%) were also prepared.

General procedure

To an aliquot of sample solution containing not more than 0.48 ppm of platinum (IV) in a 25 ml beaker was added 2.5 ml of citrate buffer. The pH was adjusted to 3 using HCl or NaOH under a pH

meter. The solution was transferred to a 25 ml volumetric flask and 2.5 ml of KI and 5 ml of rhodamine 6G were added followed by 1 ml of gelatin and diluted upto the mark with distilled water. The absorbance was measured at 575 nm using 10 mm quartz cells against a reagent blank. The concentration was established by reference to a calibration graph prepared for 0-0.48 ppm of platinum(IV) using standard platinum solutions, following the above procedure.

Analysis of platinum catalyst samples

Platinum activated carbon (0.1 g) was dissolved in 20 ml of aqua regia. The solution was evaporated nearly to dryness. Conc.HCl was added and repeatedly evaporated until all the nitric acid was removed. The solution was filtered and the filtrate was diluted to 100 ml. An aliquot of this solution was analysed for platinum (IV) by the proposed and ICP-AES methods.

Results and discussion

The formation of the coloured iodocomplex of platinum (IV) in 0.1-0.2 M HCl medium takes about 1 h for completion. It was observed, however, that platinum(IV) forms an anionic iodocomplex in weakly acidic media, which on interaction with Rhodamine 6G gives distinctively coloured product. The resulting ternary ion- associate precipitates on standing but can be stabilized by the addition of gelatin. The absorption spectra shows that the interaction of iodocomplex of platinum (IV) with rhodamine 6G proceeds with a considerable bathochromic shift. The ternary complex has a λ_{max} at 575 nm while the dye absorbs at 530 nm and $[PtI_6]^{2-}$ at 490 nm.

The effect of pH on the colour system was investigated and was found that the ternary complex was

fully formed in the pH range 2-4. Studies at higher acidities were not carried out as iodine was liberated which increases the blank value. Studies showed that at least 2 ml of 5% potassium iodide and 5 ml of 0.01% rhodamine 6G were required for constant and maximum absorbance of the complex. The colour developed instantaneously and remained stable for 24 h. the order of addition of reagent solutions was found not to be critical provided that the gelatin solution was added after the addition of other reagent solutions. The colour system obeys Beer's law in the range 0-12 μ g of platinum (IV) in a final volume of 25 ml. The molar absorptivity and coefficient of variation (for ten determinations) were calculated to be $1.26 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 1.1% respectively.

The ratio of platinum(IV) to rhodamine 6G was established to be 1:2 by mole ratio and continuous variation methods. These methods were unsuccessful when applied to the determination of the combining ratio of platinum(IV) to iodide as no colour development took place when they were present in molar proportions. However, the modified equilibrium shift method indicates a ratio of 1:6 for platinum(IV) to iodide. Hence, it is suggested that the ternary complex has the empirical composition $[PtI_6]^{2-} \cdot R_2^+$ where R^+ represents the rhodamine 6G cation.

The effect of various ions on the determination of platinum (IV) (5 μ g) was studied with different amounts of foreign ions (≤ 1 mg) by the recommended procedure. An error of $\pm 3\%$ in the absorbance was considered tolerable. 200 fold amounts of Na^+ , K^+ , Li^+ , Ca^{2+} , Be^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , UO_2^{2+} , Cr^{3+} , Fe^{3+} , Al^{3+} , La^{3+} , Tl^+ , Zr^{4+} , Th^{4+} , Se^{4+} , 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-} did not interfere in the determination of Pt(IV). Further, 200-fold amounts of Rh^{3+} , 20-fold amounts of Ir^{4+} , 10-fold amounts of Pd^{2+}

Table I— Determination of Pt(IV) in platinum catalyst

Sample	Pt(IV) added (μ g)	Pt(IV) (μ g)		Recovery (%)
		ICPAES method	Proposed* method	
Pt activated carbon (Aldrich)	-	35.0	35.3	100.9
	25	-	59.8	99.2
	50	-	84.6	99.2

*Average of three determinations

(complexing with ammonia before adjusting the pH and 2 fold amounts of Ru^{3+} and Os^{8+} also did not interfere in the determination of $5\mu\text{g}$ of platinum(IV). Table 1 shows the results of the determination of platinum(IV) in platinum activated carbon sample by the proposed method. The results show good agreement with those obtained by ICP-AES. The recovery of standard platinum(IV) added prior to the acid treatment of platinum activated carbon was also found to be good.

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