Rapid spectrophotometric determination of platinum (IV) using piperonal thiosemicarbazone

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A simple, rapid, selective and sensitive spectrophotometric method for the determination of platinum has been proposed based on the colour reaction between platinum(IV) and piperonal thiosemicarbazone (PATS) in 0.008 - 0. 032 M sulphuric acid medium. The greenish yellow complex has an absorption maximum at 360 nm. Beer's law is obeyed upto 6.5 ppm of Pt and the optimum concentration range is 1 - 5.1 ppm of Pt. The molar absorptivity and Sandell's sensitivity are 3. 239×10^4 l mol^{-1} cm^{-1} and 0.006 μg cm^{-2}. respectively. The optimum conditions for complete colour development have been investigated by studying parameters like effect of medium, acidity, reagent concentration, time period and effect of diverse ions. The method is used for the determination of platinum in hydrogenation catalysts and platinum complexes.

Thiosemicarbazones are important organic analytical reagents and act as good chelating agents, forming stable complexes with various metal ions. Survey of the literature reveals that only a limited number of thiosemicarbazones, namely, 3-(5-chloro-2-furyl)- acrolein thiosemicarbazone[1], phthalimide dithiosemicarbazone[2], 1,3-cyclohexane dione-bisthiosemicarbazone monohydrochloride[3], phenanthren-equinonemono thiosemicarbazone[4], acenaphthenequin-onemono thiosemicarbazone[5]. anisaldehyde-4-phenyl-3-thiosemicarbazone[6] and 2-hydroxy-1-acetonaphthone thiosemicarbazone[7] are reported for the spectrophotometric determination of platinum. Most of these methods involve either heating[1,2,5,7] or extraction[4,6] of the reaction mixtures. In this note, the application of piperonal thiosemicarbazone as a selective spectrophotometric reagent in the determination of platinum (IV) has been reported. The method, besides being sensitive, is simple and rapid as it does not require heating or extraction.

Experimental

A Shimadzu UV-Visible spectrophotometer (UV-160A) with 10mm fused silica cells was used. All chemicals used were of either AR or chemically pure grade. The stock solution of platinum(IV) was prepared from chloroplatinic acid in distilled water and standardised gravimetrically by formic acid method[8]. The experimental solutions were prepared by diluting the stock solution to an appropriate concentration. Piperonal thiosemicarbazone (PATS) was synthesised by refluxing equimolar amounts of piperonal and thiosemicarbazide in methanol for three hours.The crude sample obtained on cooling was recrystallised twice from aqueous dioxan and characerised by elemental analysis. [Found (calcd), % are C = 48.40 (48.43), H = 4.22 (4.04), N = 18.74 (18.83), O = 14.42 (14.35), S = 14.38(14.35)]. A freshly prepared 0.05% solution of PATS in acetone was used.

To an aliquot of the sample solution containing 25-127 μg of Pt(IV) in a 25 ml standard flask, 2 ml of 0.2 M sulphuric acid and 3 ml of 0.05% solution of PATS in acetone were added. After the addition of 10 ml of ethanol, the solution was finally made upto 25ml with distilled water and shaken well. The reaction mixture was allowed to stand for 10 minutes to attain maximum colour intensity. The absorbance was then measured at 360 nm against the reagent blank. The platinum content in the aliquot was computed from the standard calibration curve.

Results and discussion

The greenish yellow complex of Pt(IV) with PATS shows maximum absorbance at 360 nm. At the same wave length, the reagent shows negligibly small absorbance. All subsequent studies were, therefore, made at 360 nm.

The reagent forms a sparingly soluble greenish yellow complex with Pt(IV) in aqueous medium and the complex was found to be completely soluble in 40% ethanol. Preliminary investigations of pH studies using different buffers showed that the complex had a maximum absorbance in acid medium. Therefore, attempts were made to find out suitable acid among HCl, H_2SO_4, HNO_3 and CH_3COOH. These studies revealed that the absorbance of the complex was maximum in sulphuric acid medium. Inorder to find out the optimum concentration of sulphuric acid needed for complete colour development, absorbance measurements were carried out at different

concentrations of sulphuric acid. The constant maximum absorbance was shown in a concentration range of 0.008 - 0.016 M H_2SO_4.

The effect of PATS concentration was studied by measuring the absorbance at 360 nm, of solution containing a constant amount of Pt(IV) and varying amounts of PATS. It was observed that 10 moles of PATS per mole of Pt was required for maximum colour development. However, the excess amounts of the reagent did not show any substancial change in absorbance.

The stoichiometry of Pt(IV) - PATS complex was studied by Job's method of continuous variation[9] and also by the mole ratio method[10]. Both the methods indicated the formation of a 1:2 complex between Pt(IV) and PATS. The reagent can act as a bidentate ligand by forming bonds with the metal ion through sulphur and hydrazino nitrogen, resulting in the formation of a five membered chelate.

The order of the addition of the reagent does not have any effect on the absorbance of the complex. The colour reaction between Pt(IV) and PATS requires 10 min waiting period for maximum colour development at lab temperature. Therefore, in all determinations the reaction mixture was allowed to stand for 10 min before measuring its absorbance. The colour of the solution remains stable for about 70 min.

The experimental investigations revealed that the method obeys Beer's law upto 6.5 ppm of Pt. The optimum concentration range for effective determination of platinum, calculated by Ringbom's plot methods 1-5.1 ppm. The molar absorptivity and Sandell's sensitvity of the method are 3.24×10^4 l mol^{-1} cm^{-1} and 0.006 µg cm^{-2}, respectively.

The absorbance measurements were carried out with a series of solutions having different concentrations of Pt in the optimum range following the above procedure. The results show that the standard deviation and coefficient of variation of the method do not exceed 0.023 and 0.88%, respectively. From these results, it is reasonable to infer that the method is precise and accurate.

Effect of diverse ions

The presence of various diverse ions were examined for their possible interference in the determination of 2.5 ppm Pt. An error of ±2% in the absorbance value was considered as tolerance limit. No interference was observed for the following anions at the amounts shown in ppm: nitrate (2000), sulphate

Table 1—Determination of platinum(IV) in real samples (n=3)

Sample	Platinum	
	Present. (%)	Found (%)
Pt - Al_2O_3 hydrogenation catalyst	5.00	4.98
Pt - charcoal activated catalyst	10.00	9.89
$Pt(C_2H_2N_4S_2)_2^*$	39.86	40.28
$Pt(C_6H_6N_2O)_2Cl_2^#$	38.24	38.16
$Pt(C_{16}H_{15}N_4O_2S)_2Cl_4^{@}$	19.65	19.50
$Pt(C_{13}H_{11}N_4O_2S)_2Cl_4^{\$}$	21.13	21.32

* Platinum complex with 4-amino-3,5-dimercapto-1,2,4-triazole
$^#$ Platinum complex with nicotinamide
$^@$ Platinum complex with 1-(o-methoxy phenyl)-4-benzamido thiosemicarbazone
$^\$$ Platinum complex with 1-($\propto$-furyl)-4-benzamido thiosemicarbazone

(3000), phosphate (600), fluoride (300), chloride (2000), bromide (500), thiocyanate (15), tartarate (1500), acetate (1600), borate (150) and oxalate (50). But the presence of iodide, thiosulphate, citrate, EDTA, thiourea and ascorbic acid cause severe interference. It is also found that the following metal ions do not interfere at the amounts shown in ppm: Mg(II) (150), Ca(II) (150), Zn(II) (2000), Cd(II) (500), Ba(II) (1500), Al(III) (200), Tl(I) (80), Ce(III) (20), U(VI) (100), Ti(IV) (30), Sn(II) (50), Sn(IV) (80), Pb(II) (2000), Bi(III) (50), Cr(III) (20), Mo(VI) (20), Mn(II) (250), Fe(III) (5), Co(II) (300), Ni(II) (400) Ru(III) (8), Rh(III) (8) and Ir(III) (6). However, the presence of Cu(II), Hg(II), Au(III) and Pd(II) cause severe interference.

In order to extend the utility of the present method, it was employed for the determination of platinum content in real samples of hydrogenation catalyst (from MERCK) and a few platinum complexes. A known weight of the catalyst was digested with aqua regia and heated to near dryness. The residue was shaken with very dilute nitric acid, filtered and made up to a known volume. Platinum complexes with 4-amino-3,5-dimercapto-1,2,4-triazole[12], nicotinamide[13], 1-(o-methoxyphenyl)-4-benzamido thiosemicarbazone[14] and 1-($\propto$-furyl)-4-benzamido

benzamido thiosemicarbazone[1a] were prepared by the reported procedures. A known weight of the complex was decomposed carefully with aqua-regia and evaporated to near dryness. The residue was extracted with very dilute nitric acid and made up to a known volume. Aliquots of the sample solutions were analysed by the recommended procedure. The results are given in Table 1. These results show that the method is reasonably accurate and can be employed for the analysis of platinum catalysts and platinum complexes. The proposed method offers advantages of simplicity, rapidity, reasonable selectivity and sensitivity without the need for heating or any extraction.

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