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Spectrophotometric Determination of Platinum(IV) with Phenanthrenequinonemonosemicarbazone

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When phenanthrenequinonemonosemicarbazone (PQSC) reacts with platinum(IV) a brown precipitate is formed in heating. The precipitate is partially soluble in ethanol and chloroform and soluble in dimethylformamide. Because of the intensity and stability of the colour formed with platinum(IV) this system has been studied in detail with a view to utilize this reaction for the spectrophotometric determination of the metal.

Key Words: Spectrophotometric determination, Pt(IV), Phenanthrenequinonemonosemicarbazone.

INTRODUCTION

p-Nitrosodimethylaniline and potassium iodide have been employed for the spectrophotometric determination of platinum. *p*-Nitrosodimethylaniline forms an orange-red colour with platinum(IV) and is highly sensitive. The colour is stable for more than 24 h. In order to obtain maximum colour development, it is necessary to use a large excess of reagent. Time of heating, pH changes and amount of buffer are critical factors. Potassium iodide is a useful reagent for the determination of platinum but it is least selective oxidising impurity as well as palladium, gold, iron, copper and bismuth must be absent. Moderate concentration of sodium chloride interferes.

o-Phenylenediamine is highly sensitive. The optimum range for the determination is 4–12 ppm and the colour is stable for 1 h. The associated base metals and other platinum metals interfere.

Extensive studies have been made for the estimation of platinum metals[1–3]. Investigations on the use of phenanthrenequinonemonosemicarbazone (PQSC) as a spectrophotometric reagent for the determination of platinum(IV) have been carried out. Optimum conditions for the determination and molar compositions have been established and determination of platinum has also been attempted in presence of diverse ions.

EXPERIMENTAL

Reaction of Platinum(IV) with PQSC

Preliminary investigations showed that Pt(V) reacts with PQSC on heating and on cooling a precipitate is formed. The precipitate was found to be insoluble in ethanol or chloroform, but readily dissolved in dimethylformamide.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of Pt-PQSC in 60% DMF is recorded in Fig. 1. The spectral curve of the complex shows maximum absorption at 460 nm. Hence this wavelength was used during the course of subsequent work.

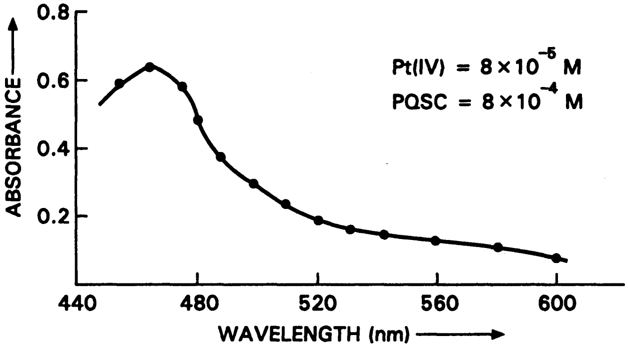

Fig. 1

Rate of complex formation

The complex of platinum(IV) with PQSC is formed on heating the mixture on a water bath. The colour gradually increases on prolonged heating, the platinum complex is completely precipitated after 1.5 h. After cooling to room temperature, the precipitates were dissolved in 60% DMF and the volume was made to 25 mL. The absorbance readings after heating for various intervals of time are given in Table-1.

TABLE-1
EFFECT OF HEATING

Time in minutes	Absorbance at 460 nm
0	0.000
10	0.075
30	0.172
50	0.325
60	0.436
75	0.615
90	0.690
100	0.690

The absorbance in the above table shows that maximum colour development is achieved after heating for 1.5 h. During the course of subsequent work, the mixtures were heated for about 1.5 h to ensure maximum colour development.

Effect of pH

To study the dependence of formation of chelates on pH, a series of solutions containing constant amount of metal and excess of the reagent were buffered at different pH values. After heating to 1.5 h they were cooled to room temperature and the volume was made to 25 mL, maintaining 60% DMF medium. The absorbances were measured at 460 nm against the reagent blanks prepared under identical conditions. The results, plotted in Fig. 2, show constancy in absorbance in the pH range 7.0–9.0. Subsequent work has been carried out at pH 8.0.

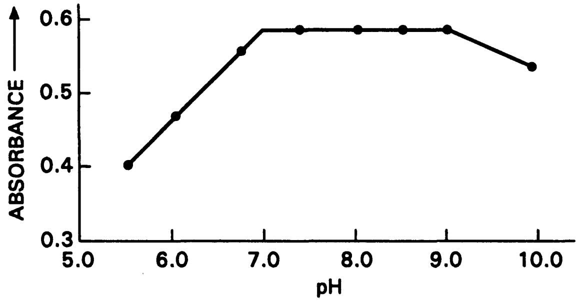

Fig. 2

Effect of excess reagent

Increasing amounts of the reagent in ethanol were added to a fixed amount of metal ion (2 mL of 1 × 10^{-3} M). The pH of the solution was kept constant at 8.0 in each case. The solutions were heated for 1.5 h, cooled to room temperature and diluted to 25 mL in 60% DMF. The absorbances, measured at 460 nm, are plotted in Fig. 3 from which it is seen that seven times molar excess of the reagent is sufficient to give maximum colour development. However, in subsequent studies, tenfold molar excess of the reagent was added.

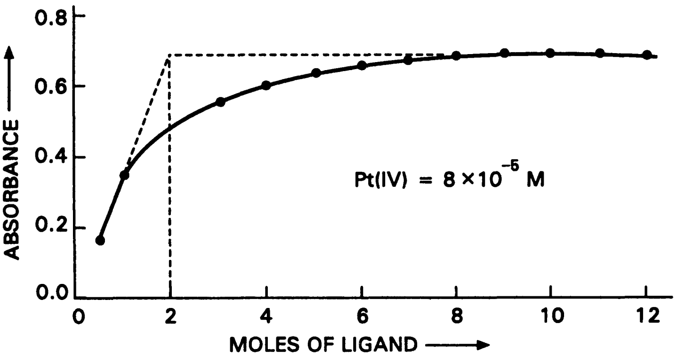

Fig. 3

Effect of time on absorbance

The absorbance was measured after different intervals of time and was found to remain constant for 48 h, after which measurements were discontinued.

Validity of Beer's law and sensitivity of the reaction

The validity of Beer's law was investigated by taking samples containing varying amount of Pt(IV) and an excess of the reagent at pH 8.0. The absorbance plotted in Fig. 3 shows that the system adheres to Beer's law up to 21.45 ppm of platinum. The optimum range of concentration for the determination of platinum as deduced from Ringbom plot (Fig. 4) is 3.47–19.95 ppm. The sensitivity of the reaction, according to Sandell's definition, is 0.022 μg Pt/cm^2 for log (I_0/I) = 0.001. The molar extinction coefficient of the chelate comes out to be 8625.

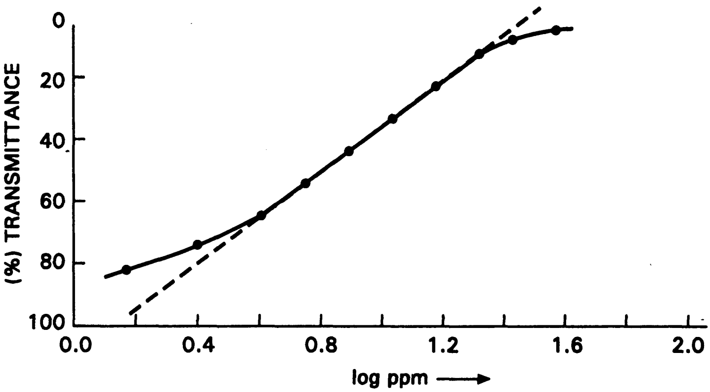

Fig. 4

Recommended procedure

To a suitable aliquot of solution containing 86.7 – 498.7 μg of platinum(IV) 4 mL of 5 × 10^{-3} M reagent solution in ethanol and 4 mL of acetate buffer of pH 0.8 are added. The solution is diluted to approximately 10 mL with water and heated for 1.5 h on a boiling water bath, cooled to room temperature and dissolved in DMF so that the final solution is 60–70% with respect to DMF. The absorbance is measured at 460 nm against the corresponding reagent blank and the amount of platinum is deduced from the calibration curve.

Precision of the method

From measurements of solution containing a fixed amount (16.6 ppm) of platinum and ten times molar excess of PQSC, absorbance deviations were calculated. The mean absorbance was 0.69 with standard deviation of 0.0039 and relative average deviation of ± 0.435%

Composition of the complex

(i) By Job's method

For this purpose equimolar solutions of the reactants were used, the 4.8×10^{-4} M in all cases. The results, plotted in Fig. 5, show a maximum at 0.33 mole fraction of platinum, which indicates the formation of a 1 : 2 (M : L) complex.

(ii) By mole ratio method

The results obtained during the study of the effect of excess of reagent have been employed for this purpose. In Fig. 3 a break in the curve is obtained at the point where reagent and metal are in the ratio of 2 : 1, which gives the molar composition of the complex corrobarating the results obtained by the method of continuous variations.

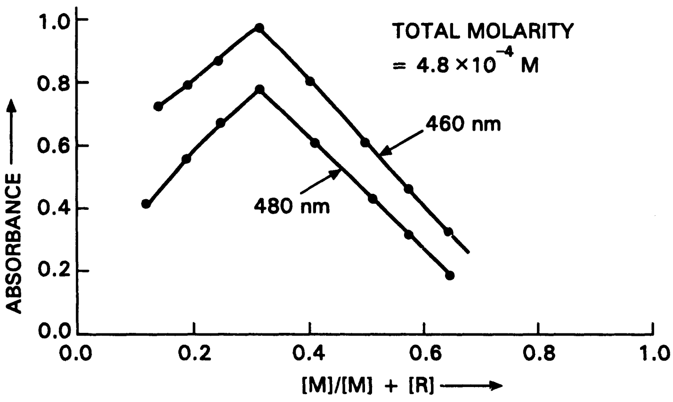

Fig. 5

Formation constant of the complex

Stability constant of the complex has been deduced by the standard method. The values of E_m and E_s obtained from the effect of excess of reagent, Fig. 4, are 0.69 and 0.50 respectively. The value of *a* is 0.2754 and k comes out to be 1.35×10^9.

Effect of diverse ions

The effect of diverse ions on the determination of 15.6 ppm of platinum was studied at pH 8.0 Co(II), Ni(II), Cu(II), Pd(II), Zn(II) and Pb(II) were removed by extraction with chloroform at room temperature. Solvent was precipitated with chloride. Masking agents have been used in some other cases. Results of this study are incorporated in Table-2. However, ruthenium(III), rhodium(III) and iridium(III) interfere seriously.

TABLE-2
DETERMINATION OF PLATINUM(IV) IN PRESENCE OF FOREIGN IONS

Platinum taken = 15.6 ppm

Foreign ions	Amount tolerated (in ppm)	Foreign ions	Amount tolerated (in ppm)
Chloride	1000	Calcium	200
Bromide	1000	Silver(I)	50
Iodide	500	Lead(II)	100
Nitrite	300	Cobalt(II)	300
Nitrate	1000	Vanadium(IV)	30
Sulphite	250	Palladium(II)	100
Phosphate	650	Antimony(III)	50
Fluoride	2000	Strontium(II)	500
Perchlorate	1000	Molybdenum(VI)	50
Oxalate	200	Uranium(II)	100
Thiocyanate	400	Nickel(II)	300
Citrate	400	Cadmium(II)	150
Tartrate	700	Mercury(II)	10
Borate	200	Zinc(II)	100
Thiosulphate	30	Copper(II)	350
Aluminium(III)	200	Osmium(VIII)	50
Magnesium(II)	100	Thorium(IV)[1]	20
Beryllium(II)	250	Zirconium(IV)[1]	20

[1] masked with fluoride.

Conclusion

Phenanthrenequinonemonoxime has been used over the pH range 2.9–4.0 with poor sensitivity, but high selectivity. PQSC is more sensitive over the pH range 7.0–9.0. As compared to tin(II) chlorides and *o*-phenylenediamine, PQSC is less sensitive but it is more selective.

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