

## A Rapid Method for Spectrophotometric Determination of Microgram Amounts of Platinum(IV)<sup>†</sup>

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Propionylpromazine phosphate (PPP) forms an yellowish-brown 1:1 complex ( $\log k = 5.25 \pm 0.1$ ) with platinum(IV) at room temperature ( $27 \pm 1^\circ\text{C}$ ) in orthophosphoric acid medium containing copper(II) as catalyst. The complex exhibits absorption maximum at 512-516 nm. The sensitivity of the reaction is  $0.032 \mu\text{g}/\text{cm}^2$  and the molar absorptivity is  $5.95 \times 10^3 \text{ litre mol}^{-1} \text{ cm}^{-1}$ . Beer's law is valid over the concentration range 0.4-6.8 ppm. The reagent has been used successfully for the spectrophotometric determination of platinum in the synthetic mixtures corresponding to platinum-rhodium alloys used in thermo couples and platinum-ruthenium and platinum-iridium alloys used in jewellery.

Propionylpromazine phosphate (PPP) was proposed as a metal-ion indicator for palladium(II)<sup>1</sup> and as a spectrophotometric reagent for palladium(II) and osmium(VIII)<sup>2</sup>. An oxidimetric method for the determination of the compound was also proposed with cerium(IV)<sup>3</sup>. The results reported in this note clearly indicate that PPP can be recommended as a sensitive reagent for the rapid spectrophotometric determination of platinum(IV).

Standard Pt(IV) solution was prepared by dissolving a known weight of platinum wire (99.99% pure) in hot aqua regia, the resultant solution evaporated almost to dryness, a small amount of hydrochloric acid added to the residue and the solution was again evaporated to dryness. This process was repeated three or four times and after the final evaporation, hydrochloric acid (5 ml) was added and the solution made up to 500 ml with doubly distilled water. The stock solution was further diluted to give a solution containing  $20 \mu\text{g Pt}/\text{ml}$ .

A 0.5% aqueous solution of PPP (Bayer, Leverkusen, W. Germany) was prepared and stored in a refrigerator.

Solutions of orthophosphoric acid, copper(II) sulphate and diverse ions of suitable concentrations were prepared using analytical grade reagents.

### Procedure

To an aliquot of the stock solution containing 10-170  $\mu\text{g}$  of Pt(IV) were added 10 M orthophosphoric

acid (5 ml), 0.05 M copper(II) sulphate (2 ml) and 0.5% PPP (4 ml) and the volume made up to 25 ml with doubly distilled water. The solution was mixed well, kept for 15 min and its absorbance measured at 515 nm against a reagent blank prepared in the same way. The amount of platinum was then deduced from the standard calibration curve.

PPP forms an yellowish-brown complex with Pt(IV) at room temperature ( $27 \pm 1^\circ\text{C}$ ) in orthophosphoric acid containing Cu(II) as catalyst. The rate of reaction and stability of the colour depend on the strength of the acid medium. The Pt-PPP complex exhibits maximum absorption at 512-516 nm. in which region absorption due to Pt(IV) is negligible. Maximum absorbance is achieved in orthophosphoric acid concentration range of 1.0 to 3.0 M; below 1.0 M orthophosphoric acid the development of the colour is slow above 3.0 M the reagent is slowly oxidised.

Constant absorbance is obtained 15 min after adding the reagent to Pt(IV) solution, and remains constant for 40 min in the temperature 10-40°C. A 44-fold molar excess of the reagent is necessary for the full development of the colour intensity. The optimum amount of the reagent is 4 ml of a 0.5% PPP solution in a final volume of 25 ml.

Beer's law is valid over the concentration range 0.4-6.8 ppm and the optimum concentration range, evaluated by Ringbom's method<sup>4,5</sup> is 1.0 to 6.2 ppm. The Sandell's sensitivity is  $0.032 \mu\text{g}/\text{cm}^2$  and the molar absorptivity is  $5.95 \times 10^3 \text{ litre mol}^{-1} \text{ cm}^{-1}$ . Sample solution containing 100  $\mu\text{g}$  of Pt(IV), prepared by the standard procedure, gave a mean absorbance of 0.122 with a standard deviation of 0.012 and a relative error of  $\pm 0.8\%$ .

Job's method of continuous variation<sup>6,7</sup>, mole ratio method<sup>8</sup> and the slope ratio method<sup>9</sup> indicate the formation of 1:1 complex between the metal and the reagent. The apparent stability constant of the complex was calculated by the method of Foley and Anderson<sup>10</sup> as modified by Mukherji and Dey<sup>11</sup> and by mole ratio method<sup>8</sup>. The values obtained by two methods are  $5.20 \pm 0.1$  and  $5.30 \pm 0.1$  respectively in 2.0 M orthophosphoric acid at  $27 \pm 1^\circ\text{C}$ .

The yellowish-brown coloured Pt(IV)-PPP complex is cationic, since the cation exchanger Amberlite IR-120(H) completely retains the colour.

The following amounts ( $\mu\text{g}/\text{ml}$ ) of foreign ions are found to cause an error  $< 2\%$  in the determination of 4  $\mu\text{g}$  of Pt(IV) per ml: Re(VII), 20; Rh(III), 10; Ir(III), 15; Ru(III), 2.4; Os(VIII), 2; Cu(II), 125; Ni(II), 24; Co(II), 112; Fe(III), 2;  $\text{F}^-$ , 800;  $\text{Cl}^-$ , 8000;  $\text{Br}^-$ , 2500;  $\text{NO}_3^-$ ,

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Table 1—Determination of Platinum(IV) in Synthetic Platinum Alloys Used in Thermocouple and Jewellery

Pt(IV) taken (ppm)	Rh(III)/Ru(III)/Ir(III) added (ppm)	Pt(IV) found* (ppm)
1.2	0.18 <sup>a</sup>	1.21
	0.06 <sup>b</sup>	1.20
	0.12 <sup>c</sup>	1.19
3.6	0.54 <sup>a</sup>	3.62
	0.18 <sup>b</sup>	3.60
5.6	0.36 <sup>c</sup>	3.58
	0.84 <sup>a</sup>	5.65
	0.28 <sup>b</sup>	5.60
	0.56 <sup>c</sup>	5.55

a = Rhodium(III); b = Ruthenium(III); and c = Iridium(III).

\*Five determinations for each.

5500;  $\text{SO}_4^{2-}$ , 4400;  $\text{PO}_4^{3-}$ , 2100;  $\text{CH}_3\text{COO}^-$ , 3200;  $\text{C}_2\text{O}_4^{2-}$ , 250; Citrate, 4000; tartrate, 4200 and EDTA, 200.

The proposed method was applied to the determination of platinum in synthetic mixtures corresponding to Pt-Rh alloys used in thermocouples

and Pt-Ru and Pt-Ir alloys used in jewellery. The results of these investigations are presented in Table 1.

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