

Rapid Spectrophotometric Determination of Platinum(IV) with Thioridazine Hydrochloride

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Thioridazine hydrochloride is proposed as a new reagent for the spectrophotometric determination of platinum(IV). The reagent forms 1:1 complex in phosphoric acid medium containing copper catalyst. The complex exhibits maximum absorption at 650 nm with a molar absorptivity of $3.41 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Beer's law is obeyed over the concentration range 0.2-7.0 ppm of platinum (IV). The efficacy of the reagent is shown by the determination of platinum in platinum alloys.

Most of the existing spectrophotometric methods for the determination of platinum involve either heating the solution or allowing it to stand for a long time for maximum colour development. In this note we report our results on the complexation reaction between platinum(IV) and 2-methylmercapto-10-[2-(1-methyl-2-piperidyl)ethyl]phenothiazine hydrochloride or thioridazine hydrochloride (TH) with a view to developing a method for the rapid spectrophotometric determination of microamounts of platinum. The proposed method offers the advantages of simplicity, rapidity, reasonable selectivity and sensitivity without the need for heating or extraction.

The stock solution of Pt(IV) was prepared from platinum wire (99.99% pure) in 1 M hydrochloric acid¹, and diluted to give a standard solution containing 25 μg of Pt(IV)/ml. Copper(II) solution (0.1 M) was prepared from copper(II) sulphate (AR). The reagent solution (0.2% wt/vol) was prepared in doubly distilled water and stored in the refrigerator. Solutions of diverse ions of suitable concentrations were prepared using AR grade reagents.

Standard procedure

To a Pt(IV) solution containing 2.5 to 175 μg of Pt(IV)/ml were added 10 M phosphoric acid (5 ml), 0.10 M copper (II) sulphate solution (1 ml) and 0.2% TH solution (5 ml) and the solution was diluted to 25 ml with doubly distilled water. The solution was mixed well and its absorbance measured after 5 min at 650 nm against a reagent blank. The platinum (IV) concentration of the sample solution was deduced from the standard calibration graph.

Thioridazine hydrochloride (TH) reacts with platinum(IV) in hydrochloric, sulphuric or phosphoric acid medium at room temperature ($28 \pm 1^\circ\text{C}$) forming a green complex in the presence of copper (II) catalyst. However, the complex in hydrochloric or sulphuric acid medium is less stable and many foreign ions interfere. In phosphoric acid medium the maximum complex formation takes place in 5 min, after mixing the reagents. The absorbance remains unchanged for a period of 48 min. The effective phosphoric acid concentration is found to be 1.6-4 M. Below and above this specified range, the absorbance is less. Hence 2 M phosphoric acid medium is chosen for all measurements.

This reagent (TH) forms a complex with platinum (IV) only in the presence of copper (II) catalyst concentration in the range of 800-1800 ppm. Below 800 ppm of copper (II), the time required for the maximum complex formation increases. Beyond 1800 ppm the absorbance is slightly increased, hence a concentration of 1000 ppm of copper(II) is chosen for subsequent work.

The complex exhibits maximum absorbance in the wavelength region 640-664 nm, in which region the reagent and platinum (IV) do not absorb at all. A 48-fold molar excess of TH is required for the reaction to go to completion. There is no appreciable change in the absorbance or colour of the complex if the order of mixing the reactants is varied. The absorbance remains constant in the temperature range $6-45^\circ\text{C}$.

Beer's law is valid over the platinum concentration range of 0.2-7 ppm. The optimum concentration range for the effective spectrophotometric determination of platinum evaluated by Ringbom's method is 1.0-6.1 ppm. According to Sandell's expression the sensitivity of the reaction is 7 ng cm^{-2} and the molar absorptivity is $3.41 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The standard deviation calculated from five determinations in a solution containing 3 ppm of Pt(IV) is 0.03 and the relative error is less than 2%.

The Job's continuous variation, mol ratio and slope ratio methods indicate the formation of 1:1 metal-ligand complex having an apparent stability constant ($\log K$) equal to 5.21 ± 0.1 at 28°C . That the complex is positively charged is revealed by the discharge of its colour when a solution of the complex is passed through Amberlite IR-12(H^+) or Dowex-50-W-X8.

In order to assess the possible analytical applications of Pt-TH complex the effect of some foreign ions which often accompany platinum was studied by adding different amounts of the diverse

Table 1—Determination of Platinum in Synthetic Alloys

Alloy	Amount of Pt taken (ppm)	Metal ion added (ppm)			Amount of Pt found*	Standard deviation
		Ni	Rh	Ir		
Pt-Ni	2.0	1.4	—	—	2.02	0.016
	6.0	4.2	—	—	5.98	0.032
Pt-Rh	1.5	—	0.16	—	1.46	0.016
	4.5	—	1.13	—	4.56	0.021
Pt-Ir	2.0	—	—	0.5	2.01	0.007
	6.0	—	—	4.0	6.03	0.025

* Average of five determinations

ions. The following amounts (ppm) of foreign ions were found to give an error of less than 2% in the determination of 4 ppm of Pt(IV): Fe(III), 530; Fe(II), 60; Co(II), 320; Ni(II), 300; Zn(II), 2500; Cd(II), 1000; Al(III), 60; Cr(III), 200; Ti(IV), 600; Te(IV), 70; Ag(I),

0.8; Ir(III), 40; Rh(III), 35; Os(VIII), 10; Pd(II), 0.8; Ru(III), 0.2; Au(III), 0.5; chloride, 30000; bromide, 1500; fluoride, 1000; iodide 0.3; nitrate, 8000; sulphate, 6000; acetate, 800; oxalate, 150; citrate, 2000; tartrate, 2000; EDTA, 1600; and dimethylglyoxime, 120. The tolerance limit of Pd(II) and Ru(III) could be raised to 2.5 and 1.0 ppm by using dimethylglyoxime and EDTA, respectively, as masking agents.

Synthetic mixtures containing the metal ions corresponding to the compositions of platinum alloys were prepared. The platinum content was determined following the standard procedure. The results in Table 1 show that nickel, iridium and rhodium in the alloys of platinum do not interfere in the determination of platinum.

References

- 1 Sanke Gowda H, Thimme Gowda A & Made Gowda N M, *Analyt Chem*, **56** (1984) 358.