

Short Communication

Pakistan J. Sci. Ind. Res, Vol. 31, No. 5, May 1988

RAPID SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM (II)†

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(Received January 5, 1988; revised June 4, 1988)

INTRODUCTION

Recently, several thiosemicarbazones, containing aldehydes or ketones have been studied as photometric reagents for the determination of metal ions [1-3]. Singh *et al.* [4], have reviewed several thiosemicarbazones which are used in photometric determination of transition metal ions including Pt (II). However, most of these reagents have limited usefulness due to longer extraction time, narrow range of pH, stability of complex with time etc.

In this short communication, we have proposed salicylaldehyde thiosemicarbazone (SATSC) as a photometric reagent for the estimation of Pt (II). This method is based on the instantaneous formation of an yellow precipitate of Pt (II) - SATSC in the wider range of pH.

SATSC was prepared by adopting the procedure of Sah and Daniels [5] (m.p. 235°). Stock solutions of SATSC (0.1 M) in 96% ethanol and Pt (II) Cl₂ (0.05 M) in 0.1M HCl were prepared. The latter was standardised according to standard procedure [6]. Walpole buffer solutions of pH values from 1.0 - 6.0 were prepared by mixing 0.1M HCl and 0.1M sodium acetate. The absorbance was measured with a spectrophotometer (Bausch and Lomb - USA, digital, model spectronic 21). Elico (India) digital pH meter (model LI-120) was used for pH measurements.

The yellow coloured Platinum (II) SATSC complex solution exhibits an absorption maxima at 388 nm and the reagent has an absorption maxima at 352 nm. All the present studies were made at 388 nm, where the reagent showed negligible absorption. The absorbance does not shift with the changing concentration of Platinum (II).

A set of experiments was carried out in order to study the influence of pH on the extraction of Pt (II) - SATSC complex. The absorbance of organic phase was found to be maximum in the pH range of 1.5 - 4.5. All the present studies were made around pH 3.5. Above the pH 4.5 the extraction was not quantitative. The order of addition of reagent was not critical and also the absorbance values

were not affected in the temperature range of 10-60°. At higher temperatures the absorbance value decreased gradually.

A 2.5 fold molar excess of the reagent over Platinum (II) was necessary for the maximum colour development and about 50 fold molar excess of reagent had no influence on the absorbance value. A constant absorbance value was observed upto 3 hours and thereafter the absorbance decreased slowly.

A simple graphical test was adopted for confirming single or multiple species formation. As per Colemann's analysis [12], a series of sets of wavelengths were selected from the absorption spectra and the absorbance values obtained for each set of wavelengths at varying Pt (II) concentration were plotted. Linear plots passing through the origin confirm single species formation.

The combining ratio of Pt (II) with SATSC was investigated by Job's method [7] and further verified by mole ratio method [8] as 1:1. The isolated solid complex was subjected to various physico-chemical studies [9] and indicated the empirical formula of the complex was [Pt (II) (SATSC) Cl₂].

The system obeyed Beer's law in the range 5-80 µg of Platinum (II) in 10 ml of the solution. The optimum concentration range evaluated by Ringbom's method was 8 - 73 µg/10 ml. The molar absorptivity of the complex at 388 nm was 6.5 x 10³ lit. mol⁻¹ cm⁻¹, the corresponding Sandell's sensitivity of the method was 0.019 µg/cm². The precision of the present method was evaluated by determining the same amount (50 µg/10 ml) of Pt (II) solution in 10 different samples and the mean absorbance has been found to be 0.615 with a standard deviation of 0.092. The important characteristic usually associated with the "fitting of best curve" is Pearson-product moment correlation coefficient, *r*. From the test of linearity observation (correlation coefficient, *r* = 0.9991) implies best linear association between the measured signal and true concentration observed in the proposed spectrophotometric method.

Procedure

An aliquot containing 5-80 µg of Platinum (II), 3 ml of buffer (pH = 3.5 ± 0.1) and add 1 ml of 0.01M reagent were

† Presented in the 12th Annual Symposium in Chemistry held at IIT, Madras, 1986.

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taken. The mixture shaken for 1 minute. To this 10 ml of *n*-butanol was added and the mixture was shaken vigorously (2 min). The two phases were allowed to separate, the organic phase separated, dried over sodium sulphate and the absorbance measured at 388 nm against reagent blank.

For studying the effect of diverse ions, 50 μg Platinum (II) was taken with varying amounts of foreign ions and the analysis was carried out by the procedure mentioned earlier. No interference was observed (error $\pm 2\%$ in absorbance) in the presence of 100 fold excess of each of Mn (II), Ca (II) and Ba(II); 50 fold each of Cd(II), Zn(II), thiocyanate and bromide; 4 fold each of Hg(II), Cu(II), Ni(II), Co(II), Fe(III), Ru(III), Rh(III) and Ir(III); 20 fold each of Al(III) and W(VI).

Of the various cations tested, Pd(II) interfere seriously; however, it can be eliminated upto 150 μg by masking with ammonia before the addition of buffer.

In order to test the usefulness of the proposed method, Platinum was determined in the synthetic samples in simulating compositions of Pt-W (4% W) Pt-Ir (10-40% Ir) and Pt-Ni (40-55% Ni) alloys and Al-Pt catalyst, cited in literature [10-11]. The result indicated in Table 1 showed

Table - 1. Analysis of synthetic samples.

Sl. No.	Mixture	Pt taken μg	Metal ion added μg				Pt found ⁺ μg
			Ir	W	Ni	Al	
1	Pt-Ir alloy	10.0	3.0	—	—	—	10.00
		15.0	1.5	—	—	—	15.04
2	Pt-W alloy	10.0	—	0.50	—	—	10.01
		15.0	—	0.75	—	—	15.03
		20.0	—	0.90	—	—	20.03
3	Pt-Ni alloy	10.0	—	—	7.8	—	9.85
		20.0	—	—	15.6	—	19.85
		30.0	—	—	21.5	—	30.00
4	Pt-Al catalyst	15.0	—	—	—	40.0	15.00
		35.0	—	—	—	92.5	34.88

+ Average of five determinations

the usefulness of the proposed method for the estimation of Pt (II) in alloys and catalyst.

The present reagent for the estimation of Platinum (II) reveals the following advantages: Simplicity, good sensitivity, high stability, insensitivity to temperature, rapidity of extraction (i.e., minimum shaking time) and wide working range of pH. Further the order of addition of reactant was not critical and about 50 molar excess of reagent had no adverse effect. The entire procedure needs only 15 minutes for extraction and assay.

Key words: Spectrophotometry, Platinum (II), Extraction.

REFERENCES

1. J.M Cano and F. Pino, *Talanta.*, **19**, 1959 (1972).
2. A.G. Asvero and J.M. Cano, *Analyst.*, **103**, 140 (1978).
3. J.M. Cano and F. Pino, *Anal. Chim. Acta.*, **75**, 335 (1975).
4. R.B. Singh, B.S. Grag and R.P. Singh, *Talanta.*, **25**, 619 (1978).
5. P.T. Sah and T.C. Daniels, *Rec. Trav. Chim.*, **69**, 1545 (1950).
6. F.E. Beamish and J.C. Van Loon, *Analysis of Noble Metals* (Academic Press, New York, 1977).
7. P. Job, *Ann. Chem.*, **9**, 113 (1928).
8. J.H. Yoe and A.L. Jones, *Ind. Engng. Chem. Anal. Ed.*, **16**, 111 (1944).
9. R. Palaniappan and Agnes Paul, *Indian J. Chem.*, **26A**, 1071 (1987).
10. V.M. Ivanov, G.N. Gorbunova, G.V. Kudryavtsev, G.V. Lisichkin and T.I. Shurupova, *Zh. Anal. Khim.*, **39**, 504 (1984).
11. S. Jaya, T.P. Rao and T.V. Ramakrishna, *Analyst.*, **109**, 1405 (1984).
12. J.S. Colemann, L.P. Varga and S.H. Mastin, *Inorg. Chem.*, **9**, 1015 (1970).