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NOTES

Analytical Properties of 2-Hydroxy-1-Acetonaphthone Thiosemicarbazone: Spectrophotometric Determination of Platinum

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Analytical properties of a new compound, 2-hydroxy-1-acetonaphthone thiosemicarbazone (2-HANT) is reported. Platinum (IV) forms a 2 : 3 (M : L) complex with 2-HANT at pH 5.5 on heating and has maximum absorbance at 346 nm. The molar absorptivity and Sandell's sensitivity of the method are 6475 1 mol^{-1} cm^{-1} and 0.0301 μg cm^{-2} respectively.

Thiosemicarbazide derivative of hydroxyacetophenones have been extensively employed as analytical spectrophotometric reagents[1–5]. However, no attempts are made so far to explore the analytical potentialities of the thiosemicarbazone derived from hydroxyacetonaphthones. Hence, in this note we report the analytical properties of 2-hydroxyacetonaphthone thiosemicarbazone (2-HANT) and its use for the spectrophotometric determination of platinum. Survey of the literature[5] reveals that only a limited number of thiosemicarbazones *viz.*, acenaphthoquinone thiosemicarbazone[6], *p*-anisaldehyde-4-phenyl thiosemicarbazone[7], 1,3-cyclohexanedione dithiosemicarbazone hydrochloride[8], furylacrolein thiosemicarbazone[9,10], phenanthroquinone monothiosemicarbazone[11], phthalimide dithiosemicarbazone[12], salicylaldehyde thiosemicarbazone[13] are reported for the spectrophotometric determination of platinum. Platinum reacts with most of the reported thiosemicarbazones only on heating. Further, each method has its own disadvantages like extraction, slow colour development, interference from associated ions, and rigid experimental conditions etc. The present method based on 2-HANT is free from all these drawbacks and is simple, rapid, selective and reasonably sensitive.

2-HANT prepared by the literature method[4]. A 5 × 10^2 M reagent solution in DMF was used for the studies. Standard platinum(IV) solution was prepared by

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*Address for correspondence: 17/84–A, T.V. Street, Nellore–524 001, India dissolving 1 gm of platinum(IV) chloride in 1 ml of conc. HCl and diluting to 100 ml with distilled water. It was standardized by the usual method[14].

To an aliquot containing 0.08–13.65 ppm of platinum(IV), 12.5 ml of buffer solution (pH 2.5), 3 ml of DMF and 1 ml of 2-HANT (5×10^2 M) solutions were added. The contents were diluted to 25 ml with distilled water. The reaction mixture was heated on a boiling water bath for 30 min, cooled to room temperature (30 ± 5°C) and the absorbance of the solution is measured at 346 nm against a reagent blank prepared under identical conditions.

Platinum(IV) forms pale green coloured complex with 2-HANT in 12% aqueous DMF medium. The reaction is slow at room temperature and requires heating. Maximum colour development was observed on heating the solution on a boiling waterbath for about 30 min. The complex is stable for 6 hrs. and exhibits maximum absorption at 346 nm, where the absorption by the reagent is negligible. The optimum pH range for maximum colour development was 5.0–6.0. Hence, pH 5.5 was chosen for further studies. A five-fold excess of the reagent is sufficient for getting full colour development. The order of addition of the constituents of the reaction mixture has no effect on the absorbance.

The system obeys Beer's law in the range 0.08–13.65 ppm of platinum(IV). The optimum concentration range evaluated from Ringbom's plot is 2.34–13.45 ppm. The molar absorptivity and Sandell's sensitivity of the method are 6475 $1\ mol^{-1}\ cm^{-1}$ and 0.0301 $\mu g\ cm^{-2}$ respectively. The standard deviation of ten determinations each containing 7.8 ppm of platinum is 0.0043.

Vosburgh and Cooper's method indicates the presence of one complex species in solution. Job's and mole ratio plots show the presence of 2 : 3 (M : L) species. The stability constant of the complex is 4.51×10^4.

The interference of diverse ions was studied using 5.85 ppm of platinum(IV) by following the recommended procedure. An error of ±2% in absorbance reading was found to be tolerable. Of the various cations and anions tested individually in the determination of platinum(IV) no interference was observed in the presence of 250, 190, 150, 60, 40, 25, 15, 5 and 2-fold excess of iodide, tartrate, sulphate, citrate, bromide; phosphate, nitrate; oxalate, tetraborate, chloride, fluoride, perchlorate, thiocyanate, bromate, thiourea, EDTA, Cd(II), U(VI), Zn(II), Th(IV), Mo(VI), W(VI), Al(III), Mn(II) and ascorbic acid respectively. Ni(II), V(IV), V(V), Cr(VI), Ce(IV), Pd(II) and Ru(III) are tolerated only up to equal amounts However, the tolerance limit for Ni(II), V(IV or V) and Pd(II) could be increased up to 5-fold excess by using EDTA as masking agent. Interference due to Cu(II), Co(II), Au(III) and Ag(I) could be removed by using thiourea, ascorbic acid and chloride as masking agents respectively.

In order to assess the analytical applicability of the proposed method, it was applied to the determination of platinum in a simulated solutions of alloy/catalyst. The results are presented in the Table 2, which show that the proposed method is selective and reasonably sensitive for the determination of platinum(IV).

TABLE 1
CHARACTERISTICS OF METAL ION-2-HANT COMPLEXES

Cation	pH	λ_{max} nm	Molar absorptivity lit mol^{-1} cm^{-1}	M : L	Beer's law range	Optimum conc. Range (ppm) Ringbom plot	Stability constant
Cobalt(II)	7.0–7.5	306	28700	1 : 1	0.12–2.95	0.08–2.90	2.27×10^5
Palladium(II)	4.5–6.5	310	13850	1 : 1	0.21–7.42	1.27–7.40	5.53×10^4
Copper(II)	6.5–7.5	346	10100	1 : 1	0.26–5.76	0.77–4.48	4.77×10^4
Silver(I)	6.5–7.0	306	9375	2 : 2	0.44–5.44	1.32–5.52	5.10×10^{19}
Iron(III)	3.0	300	7025	1 : 1	0.47–4.71	0.71–4.30	4.95×10^4
Platinum(IV)	5.0–6.0	346	6475	2 : 3	0.08–13.65	2.34–13.45	4.51×10^4
Nickel(II)	8.0	356	5275	1 : 2	0.70–4.10	1.76–3.52	2.86×10^8
Vanadium(IV)	4.5	300	5000	1 : 1	—	—	—
Vanadium(V)	5.0	360	3375	1 : 1	0.41–4.07	0.61–3.57	2.14×10^4

TABLE 2
DETERMINATION OF PLATINUM IN A SIMULATED ALLOY/CATALYST SOLUTIONS

Alloy/Catalyst	Amount of (ppm)			Error (%)
	Platinum taken	Metal ion added	Platinum found*	
Pt-W alloy	5.30	W 0.24	5.33	0.57
(Pt 95.2%	7.08	W 0.38	7.16	1.13
W 4.8%)	10.62	W 0.48	10.58	0.38
Binary catalyst	2.80	Al 7.50	2.79	0.36
Pt–Al	5.60	Al 15.00	5.57	0.54
catalyst (Pt 27.3% Al 72.7%)	8.40	Al 22.00	8.46	0.71

*Average of three determinations.

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REFERENCES

1. G.V.R. Murthy and T.S. Reddy, *Curr. Sci. (India)*, **58**, 1024 (1989).
2. ________, *Chem. Acta Turc.*, **17**, 189 (1989).
3. ________, *J. Indian Council of Chemists*, **4**, 69 (1988).
4. ________, *Talanta* (in press).

5. R.B. Singh and H. Ishii, *Crit. Rev. Anal., Chem.*, **22,** 381 (1991).
6. S.K. Singh, R.K. Sharma and S.K. Sindhwani, *Bull. Chem. Soc. (Jpn.)*, **59,** 1223 (1986).
7. K.M.M.S. Prakash, L.D. Prabhakar and D.V. Reddy, *Anal. Lett.*, **20,** 959 (1987).
8. K.H. Reddy, K.M.M.S. Prakash, K.G. Reddy and D.V. Reddy, *J. Indian Inst. Sci.*, **65,** 119 (1984).
9. V.P. Kerentseva, M.D. Lipanova and I.S. Mustafin, *Zh. Anal. Chem.*, **26,** 1144 (1971).
10. V.P. Kerentseva, M.D. Lipanova and L.I. Masko, *Zh. Anal. Chem.*, **27,** 1561 (1972).
11. A. Wasey, B.K. Puri, M.C. Mehra, M. Satake and M. Katyal, *Curr. Sci. (India)*, **53,** 745 (1984).
12. A. Guzman, D.P. Bendito and F. Pino, *An. Quin.*, **70,** 828 (1974).
13. R. Palaniappan and V. Revathy, *Pak. J. Sci. Ind. Res.*, **31,** 378, (1988).
14. A.K. Dey, Separation of Heavy Metals, Pergamon Press, Oxford (1961).

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