Tr. J. of Chemistry
20 (1996) , 222 – 227.

Extractive Spectrophotometry of Palladium(II) With 3,4,5- Trimethoxybenzaldehyde Thiosemicarbazone

A. M. A. KHADER, K. S. PRASAD
Department Chemistry, University, of Mangalore,
Mangalagangothri-574 199, INDIA

Received 25.9.1995

The extractive spectrophotometric determination of palladium(II) using 3,4, 5-trimethoxybenzaldehyde thiosemicarbazone (TBTSC) is discussed in this study. It forms an intense yellow-coloured chloroform-soluble complex with paladium(II) in an acidic medium. The molar absorptivity at 370nm is 8.35×10^4 1. mol^{-1} cm^{-1}. The complex system conformed to Beer's Law up to a concentration limit of 12 ppm. The Sandell's sensitivity was 8. 57 ng. cm^{-2}. The interference of various ions was studied, and palladium(II) in its alloy compositions was analysed.

Introduction

Thiosemicarbazones are a class of compounds which are widely employed as analytical reagents for a variety of metals in various quantitative methods of analysis. Several thiosemicarbazones have been reported in published studies as spectrophotometric reagents for palladium. 4- Ethylsulphonylbenzaldehyde thiosemicarbazone[1] showed interference by Pt(IV), Au(III), Ag(I), Hg(II) and Cu(II). The simultaneous determination of Pd(II) and Pt(IV) was carried out using furylacrolein thiosemicarbazone[2,3]. Grecu and Neamtu[4] used nicotinaldehyde thiosemicarbazone. Bhaskare and Surekha Devi[5] proposed furoin thiosemicarbazone in which Cu(II) and Ni(II) severely interfered. Quinoline-2-aldehyde thiosemicarbazone[6] and phenanthraquinone monothiosemicarbazone[7] showed severe interference by Au(III), Pb(II) and SCN^-, and the latter also showed interference by Cd. 2-Methyl-1,4-napthaquinone thiosemicarbazone[8] requires one hour for maximum colur development, and Ru(III), Rh(III), Ir(IV) and thiosulphate interfered. Ni(II) interfered in the case of 4-salicylamino-1-diacetylmonoxime-3-thiosemicarbazone[9] and Co(II), Ni(II) and Ag(I) interfered in the case of glyoxal bis-(4- phenyl thiosemicarbazone)[10]. 5,6-Dimethyl-2-nitroindane-1,3-dione dithiosemicarbazone[11] suffered from interference of Co(II) and Os(VIII). Severe interference by Pt-group metals and also base metals was reported for quinone monothiosemicarbazone[12]. In the case of p-anisaldehyde thiosemicarbazone[13] interference by platinum metals was suppressed by using suitable masking agents. Hg(II) and Cu(II) interfered in the case of nicotinaldehyde-4-Phenyl-3-thiosemicarbazone[14]. Metal complexes of thiosemicarbazone[15–16] have attracted special attention due to their antitubercular activity[17]. The antitumour activity of a number of thiosemicarbazone complexes has already been discussed[18–22].

In this study extraction and spectrophotometric determination of palladium (II) in microgram levels using 3,4,5-trimethoxybenzaldehyde thiosemicarbazone in chloroform is discussed.

Experimental

Reagents: A standard solution of palladium(II) was prepared by dissolving 1g of paladium(II) chloride in an excess of potassium chloride solution, and was standardised by the dimethylglyoxime method[23]. Palladium(II) solutions of varying concentration were prepared by suitable dilution of the stock solution. 3,4,5-trimethoxybenzaldehyde thiosemicarbazone (M. P. 210° C) was prepared by refluxing an equimolar mixture of thiosemicarbazide and 3,4,5-trimethoxybenzaldehyde in ethanol. The product was recrystallised from aqueous ethanol. The reagent was used as a 0.1% (w/v) solution in ethanol. A Beckmann DU-6 spectrophotometer (Beckmann Instruments Inc: IRVINE, CA 92713 U. S. A.) was used to measure absorbance with a pair of matched 10.0 mm cells.

Recommended Procedure for the determination of palladium(II) is as follows.

To an aliquot containing palladium(II) solution (75 ppm), 0.8 ml of conc. hydrochloric acid and 1 ml of 0.1% TBTSC in ethanol were added and diluted to 10 ml. The yellow coloured complex formed was extracted with 2x3 ml portions of chloroform by shaking for 2 minutes. The chloroform extract was dried over anhydrous sodium sulphate and transferred to 10 ml volumetric flask. A standard calibration curve was obtained by plotting absorbance vs. concentration.

Results and Discussion

Absorption Spectrum

The intense yellow chloroform-soluble complex of palladium(II) and TBTSC have maximum absorption at 370 nm (Figure 1), while the ligand and the Pd(II) solutions have no absorption capacity in this region.

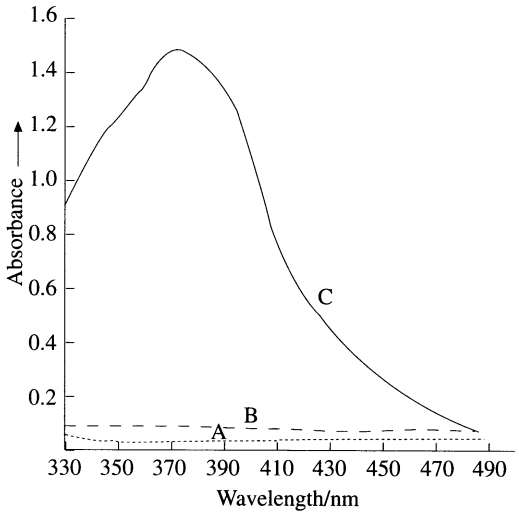

Figure 1. A-Absorption spectrum of $PdCl_2$ vs water blank. B-Absorption spectrum of 0.1% TBTSC solution vs solvent. C- Absorption spectrum of Pd(II)-TBTSC complex vs solvent

Extraction with chloroform was carried out at different pH levels, keeping the other conditions stable. The highest absorbance was observed when hydrochloric acid concentrations were maintained at 1.0 M and all other absorbance determinations were performed at this acidity. For instantaneous and maximum clour development, at least a 15-fold excess of reagent was found to be necessary. The absorbance of the coloured species remained unchanged for at least 48 hours.

Extraction into chloroform is dependent on the concentration of hydrochloric acid. Maximum extraction of coloured species was possible in the acid range of 0.8 to 1.2 M hydrochloric acid. From solutions having acid concentrations outside this range, the extraction of the coloured species into chloroform is incomplete (Figure 2).

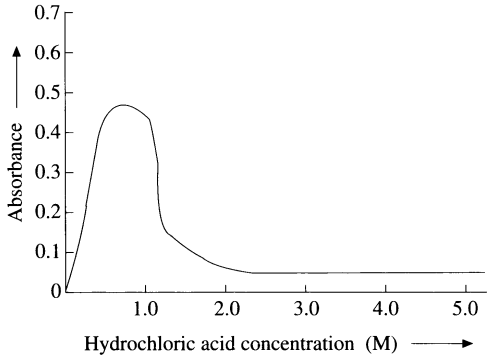

Figure 2. Effect of acid concentration on extraction Pd(II)-TBTSC system-λmax-370 nm

Beer's Law and Sensitivity

A calibration graph was constructed at 370 nm against a reagent blank under optimum conditions. Beer's law was obeyed for palladium concentrations up to 12 ppm. From the Ringbom's plot, the optimum concentration range for effective spectrophotometric determination of palladium (II) was found to be 0.7-9.0 ppm. The Sandell's sensitivity and the molar absorptivity were 8. 57 ng. cm^{-2} and 8.35 X10^4 1 mol^{-1} cm^{-1}. respectively. The precision and accuracy of the method for the determination of different quantities of Pd (II) are given in Table 1.

Table 1. Determination of Precision and Accuracy For Pd(II)- TBTSC system

Pd taken (ppm)	Pd found* (ppm)	Standard deviation	Relative Standard deviation	Standard analytical error
1.504	1.501	0.005	0.333	0.148
3.003	3.001	0.004	0.133	0.059
6.002	6.001	0.003	0.050	0.022
9.006	9.003	0.002	0.022	0.010

* Average value of five replicate determinations

Stoichiometry and nature of the complex

Job's method of continuous variations and the mole ratio methods were used to determine the stoichiometric ratio of palladium-TBTSC in the complex. The metal to ligand ratio (M:L) was confirmed to be 1:2. The complex species exists as $[Pd(TBTSC)_2](C1)_2$ with $C1^-$ as the counter ion.

The complex species is extracted into chloroform and the extracted species can be re-equilibrated with water. The presence of $C1^-$ ions in the aqueous phase has been detected to confirm the above formulations.

The cationic nature of the complex was ascertained by the adsorption of the coloured species from an aqueous solution on a cation exchange column of Amberlite IR-120. The adsorbed species can be eluted completely with 2 M hydrochloric acid. However, the complex was not adsorbed on an anion exchange column of Amberlite IRA-400, thus confirming the cationic nature of the complex.

Interference Study

The effect of diverse ions on the absorbance value of palladium (II) TBTSC complex was examined by adding different quantities of these ions to a solution containing 7.5 ppm of palladium (II). An error of ± 2 % in the absorbance values was considered to be tolerable. Platinum group metals, Cu(II), Ni(II), Co(II), Pb(II), Ag(I) and anions like F^-, I^-, $C_2O_4^{2-}$ do not interfere at varying concentration ranges. The results are presented in Table 2.

Table 2. Tolerance Limits of Diverse Ions in The Determination of Palladium (II)

(Palladium (II) taken = 7.5 ppm)

Ion added	Tolerance limit (ppm)	Ion added	Tolerance limit (ppm)
F^-	3000	$C1^-$	6400
Br^-	6300	I^-	100
NO_3^-	8000	SO_4^{2-}	9000
PO_4^{3-}	1800	$C_2O_4^{2-}$	500
SCN^-	300	Tartrate	2100
Citrate	500	EDTA	640
Acetate	1500	Ni(II)	150
DMG	100	Zn(II)	1680
Co(II)	100	Fe(III)	150
Cu(II)	100	Hg(II)	150
Cd(II)	2100	W(VI)	80
Ag(I)	100	Ti(IV)	72
Al(III)	1600	Pt(IV)	60
V(V)	120	Ir(III)	15
Zr(IV)	240	Ru(III)	38
Rh(III)	32	-	-

The tolerance limit shown by the present ligand is comparable to those reported earlier for other thiosemicarbazones. The salicylaldehyde thiosemicarbazone method involves extraction of the Pd(II) complex into cyclohexanol and reports higher tolerance for some of the platinum group cations; phenanthraquinone monothiosemicarbazone[7], involving extraction into chloroform shows interference from Cd(II) and reasonable tolerance for other ions.

But in those ligands like 1,3-cyclohexanedione bisthiosemicarbazone[13] where the absorbance measurements were made in aqueous solution, lower tolerances were reported.

Application of the method to some synthetic samples:

This method was used to determing the amount of palladium in some alloy compositions. Different amounts of metal salts including that of palladium were mixed together. The samples (0.3 g) were brought into solution by dissolving in aqua regia (15-25 ml), and the solution was evaporated to about 5 ml. Afer cooling to room temperature, it was diluted to 500 ml in a volumetric flask. The palladium content in these samples was determined by using the recommended procedure. The results are given in Table 3.

Table 3. Determination of Palladium in Synthetic Samples

Sample.	Certified Composition (%)	Amount of Palladium taken (ppm)	Amount of palladium found (ppm)	Average (ppm)
P-S-C dental Wires	Pd-44	10.00	10.04	
	Ag-41		10.01	
	Cu-15		10.07	10.04
			10.08	
			10.00	
Oakay alloy,	Pd-10.5		5.01	
	Ni-60	5.00	5.04	
	Pt-20		5.06	5.03
	V-9.5		5.02	
			5.00	

Conclusion

The proposed spectrophotometric method for Pd (II) shows instantaneous colour development, and the extraction can be completed within minutes. The reagent can be easily obtained in its pure form. This procedure is suitable for the determination of palladium in alloy compositions.

References

1. S. Komatsu, H. Nishmura and Z. Hiroaki, **Nippon Kagaku Zasshi., 79,** 895 (1958).
2. V. P. Karentseva, M. D. Lipanova and L. I. Mas'Ko., **Zh Anal. Khim., 27,** 1561 (1972).
3. V. P. Karentseva, M. D. Lipanova and I. S. Mustafin, **Zh. Anal. Khim., 26,** 1144 (1971).
4. I. Grecu and M. Neatmu, **Lucr. Conf. Nat Chim. Anal., 3rd 3,** 222 (1971).
5. C. K. Bhaskare and Surekha Devi, **Talanta, 25**, 544 (1978).
6. D. V. Khasnis and V. M. Shinde, **Talanta, 26,** 593 (1979).
7. D. V. Khasnis and V. M. Shinde, **J. Indian Chem. Soc., 59,** 93 (1982).
8. S. K. Singh, S. K. Sindhwani and R. P. Singh, **J. Chin. Chem. Soc., 29,** 201 (1982).
9. M. E. M. Khalifa, K. M. Ibrahim and A. A. El Asmy, **Indian J. Chem., 25A,** 501 (1986).
10. A. Asuero, A. M. Jimenez and A. Herradovm, **Analyst, 111,** 747 (1986).
11. Y. Lingayya, K. H. Reddy and D. V. Reddy, **Talanta, 34,** 789 (1987).
12. K. Shravah, P. P. Sinha and S. K. Sindhwani, **Analyst, 111,** 1229 (1986).
13. K. N. Thimmaiah, H. S. Gowda and Ahmed Maqbool, **Indian J. Chem., 22A,** 690 (1983).
14. J. S. Lee, K. Uesugi and W. H. Choi, **Anal. Proc. 32(7),** 279- 281 (1995).
15. D. R. Williams, **Chem. Rev., 72,** 203 (1972).
16. A. Furst and R. T. Haro, **Prog. Exp. Tumor. Res., 12,** 102 (1969).

17. G. Domagk, R. Behenisch, F. Mierzsch and H. Schmidt, **Naturwissenschaften., 33,** 315 (1946).
18. K. Kanoongo, R. Singh and J. P. Tandon., **Bull. Chem. Soc. Japan., 62,** 1385 (1989).
19. B. G. Patil, B. R: Havinale, J. M. Shallom and Chitnis M. P., **J. Inorg. Biochem., 36,** 107 (1989).
20. M. Moham, A. Agarwal and N. K. Jain, **J. Inorg. Biochem., 34,** 41 (1987).
21. M. Mohan, M. Kumar, A. Kumar, P. H. Madhuranath and N. K. Jain, **J. Inorg. Biochem., 32,** 239 (1988).
22. A. Diaz and P. Cao, **Rev. Cubana Quim., 3,** 37 (1987).
23. A. I. Vogel "A text book of Quantitative Analysis" 4th ed. Longmans, London (1978).