Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1572–1578

Spectrophotometric Determination of Rhodium(III) with Phenanthrenequinone Monosemicarbazone

H.C. RAI* and I. CHAKRABORTI

Department of Chemistry, L.S. College, Muzaffarpur-842 001, India

It was observed that rhodium(III) forms a brown complex with phenanthrenequionone monosemicarbazone (PQSC) on heating on a boiling water bath. The reaction has been studied for the spectrophotometric determination of the metal. Optimum conditions have been investigated and molar composition of the complex has been determined to be of the type $[Rh(PQSC)_3]$. Suitability of the determination in presence of diverse ions has been examined by the use of masking agents.

Key Words: Spectrophotometric determination, Rh(III), Phenanthrenequinone monosemicarbazone.

INTRODUCTION

Various chromogenic reagents for the determination of rhodium have been reported in literature[1-33]. Very few satisfactory methods are available for the spectrophtotometric determination of rhodimn. One of the most sensitive reagents reported for the purpose is tin(I) bromide[1, 2]. The sensitivity of the method is 0.0035 μg cm^{-2}. The composition of the complex is not known and the colour remains stable for 3 h. Although hydrobromic acid produces an increase in absorbance, the time required to achieve maximum absorbance also increases. Tin(II) chloride is also widely used but it is less sensitive. A red colour is developcd in 2 N HCl, which changes to yellow on dilution with water. The red form is less sensitive (sensitivity = 0.026 μg cm^{-1}) than yellow form (sensitivity = 0.0084 μg cm^{-1}). The compound is fairly stable but several metals, especially those of group VIII, interfere. 5-Amino-2-mercaptobenzimidazole is also a sensitive reagent. The method is free from the need of accurate control over working conditions. Excess of reagent is also without effect. However, platinum, iridium and iron interfere. The interferences due to copper and small amounts of iridium could be avoided by EDTA.

N,N′-bis(3-dimethylaminopropyl) dithiooxamide has been used as a reagent for the determination of rhodium. The determination is carried out in 7.5 N HCl medium. The interference due to cobalt and nickel was not observed but the platinum metals interfere seriously.

In case of thiosalicylamide[20] the reagent lacks sensitivity and ruthenium and osmium interfere in the determination. The chief disadvantage is its susceptibility to oxidation in presence of strong oxidising agents.

Recently, acenaphthenequionemonoxime[31] and tropolone[29] have been recommended for spectrophotometric determination of rhodium. The reagents are sensitive and are comparable with other well known reagents.

In the present method, phenanthrenequinone monosemicarbazone (PQSC) has been successfully used in the determination of rhodium(III). Although the method is not very sensitive but it is quite selective. Moreover, variations in factors such as excess of reagents, time of heating, amount of buffer etc. have no effect. Most of the associated metals either do not interfere or can be masked successfully. However, the interference due to some platinum metals could not be avoided.

EXPERIMENTAL

A standard solution of rhodium(III) was prepared by dissolving rhodium trichloride (Johnson Matthey) in 1 M hydrochloric acid. The solution was standardised gravimetrically by precipitating rhodium as the sulphide, followed by ignition to the oxide and then reduction to the metal in a current of hydrogen and cooling in carbon dioxide. Subsequent dilutions were made from this stock solution according to requirements.

Preliminary investigation

On mixing the solution of the metal salt with the reagent in ethanol in acidic medium or in presence of sodium acetate, no colour formation takes place. However, on heating the contents on a water bath, a brown precipitate appears. The precipitate was found to be partially soluble in alcohol and chloroform but soluble in dimethylformamide. The influence of variables has been investigated to find the optimum conditions for the determination.

RESULTS AND DISCUSSION

Absorption Spectra: The absorption spectra of the complex and the reagent at pH 8.0 are recorded in Fig. 1. The complex shows maximum absorption at 480 nm.

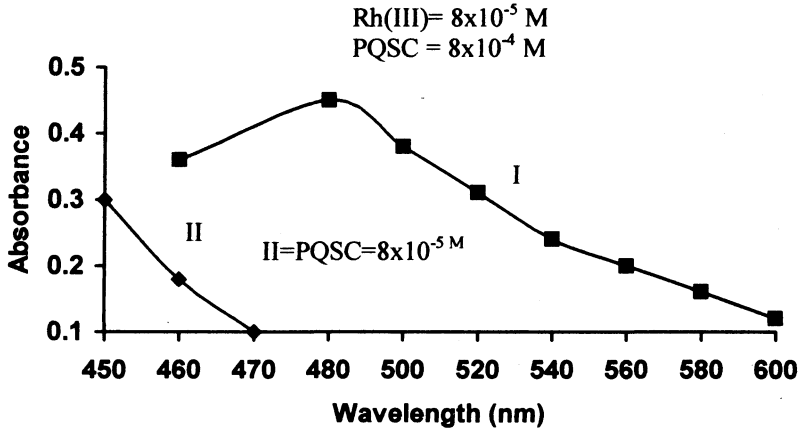


Fig. 1. Absorption spectra of PQSC and Rhodium(III) PQSC complex: I. Complex vs. Reagent blank; II. Reagent *vs.* DMF

Hence, the effect of other variables was studied at 480 nm against the cooresponding reagent blanks.

Rate of colour development and stability of the complex: A study of the rate of colour development was made as very little colour is developed at room temperature. The solutions were heated on a steam bath for different intervals of time and the absorbance was measured at 480 nm. The absorbance was found to become constant after heating for about 2 h. The results are incorporated in Table-1. In subsequent studies, the reaction mixtures were heated for 2 h. The complex was found to be quite stable and no change in absorbance was observed up to 48 h, after which measurements were discontinued.

TABLE-1
EFFECT OF HEATING TIME ON COMPLEX FORMATION

Time of heating (min)	Absorbance at 480 nm
0	0.003
10	0.105
30	0.285
50	0.338
70	0.385
90	0.412
110	0.444
120	0.444
150	0.444
180	0.442

Effect of DMF: The complex was found to be soluble in DMF. Increasing volumes of DMF were added and it was observed that complete dissolution of precipitate takes place in 70% DMF medium. Higher percentage of DMF had no effect on the absorbance. In subsequent work, the percentage of DMF was maintained at seventy.

Effect of pH: The effect of pH on the formation of the complex was investigated by preparing a series of solutions buffered at various pH values. 2.0 mL of 1×10^{-3} M rhodium(III) 4 mL 5×10^{-3} M reagent solution in ethanol and 4 mL of acetate buffer were added to stoppered bottles. The volume was raised to approximately 10 mL with water and the contents were heated on a water bath for 2 h, cooled to room temperature and made up to 25 mL with aqueous DMF so that the final solution contained 70% DMF. The apparent pH of the solution was taken to be the final pH of the system. The absorbances of these solutions are plotted in Fig. 2 which shows that there is no change in absorbance in the pH interval 7.2–8.8.

Effect of excess reagent: For this study, a set of solutions containing 2 mL of 1×10^{-3} M Rh(III) and varying amounts of ligand solution were taken. The pH was adjusted to 8.0 with acetate buffer and the volume in each case was made to approximately 10 mL. The contents were heated for 2 h on a boiling water bath, cooled to room temperature and dissolved in aqueous DMF. The absorbances

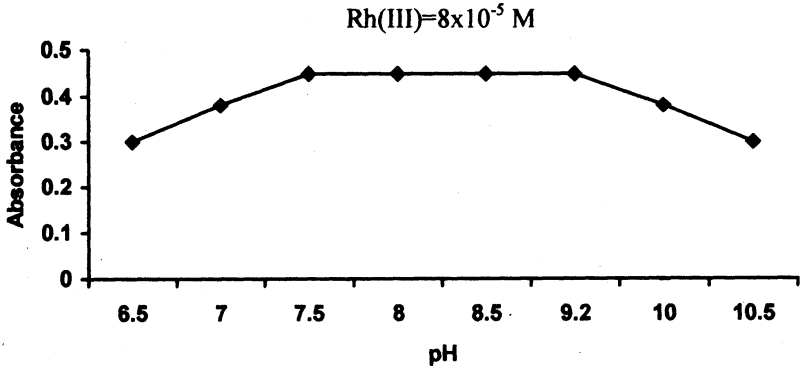


Fig. 2. Effect of pH on Rh(III) PQSC Complex

were measured at 480 nm against the corresponding reagent blanks and are plotted which shows that at least seven-fold molar excess of PQSC over rhodium is required for maximum absorbance. During the course of subsequent studies, therefore, ten-fold excess of PQSC was used.

Adherence to Beer's law and sensitivity of the reaction: Samples containing different amounts of rhodium and ten times excess of the reagent were taken. The solutions were buffered to pH 8.0, heated for 2 h and cooled to room temperature. The total volume was made to 25.0 mL with aqueous DMF and the absorbances were measured. The plot of absorbance against varying amounts of rhodium (not shown) indicates that the system adheres to Beer's law up to 16.46 ppm of rhodium. The sensitivity of the colour reaction, in terms of Sandell's definition, is 0.018 μg Rh/cm^2 for log I_0/I = 0.001. The molar extinction coefficient of the rhodium chelate comes out to be 5550. The optimum range for the determination of rhodium, as evaluated from Ringbohm plot (Fig. 3), is 3.98–1.72 ppm.

Recommended procedure for determination of rhodium(III): Aliquots containing 99–268 μg of rhodium are taken in a Pyrex stoppered bottle and 4 mL of (5×10^{-3} M) reagent solution in alcohol is added. The contents are buffered in the pH range 7.2–8.8 by the addition of 4.0 mL of acetate buffer; the volume is raised to approximately 10 mL with water and the contents are heated on a water bath for 2 h. After cooling to room temperature, the volume is made up to 25.0 mL with aqueous DMF so that the final solution is 7 : 3 (DMF : water). A blank containing all components except rhodium is prepared in a similar way and the absorbance of (Rh-PQSC) complex is measured against the blank at 480 nm. Knowing the absorbance, the amount of rhodium is deduced from the calibration curve.

Absorbance deviation: The precision of the procedure was checked by measuring the absorbances of eight samples, each containing a fixed amount of rhodium. In the determination of 205 μg of rhodium, the mean value of absorbance was found to be 0.444, with standard deviation of 0.0029.

Composition of the complex: The molar concentration of the complex was determined by Job's method of continuous variations[34, 35] and the mole ratio[36].

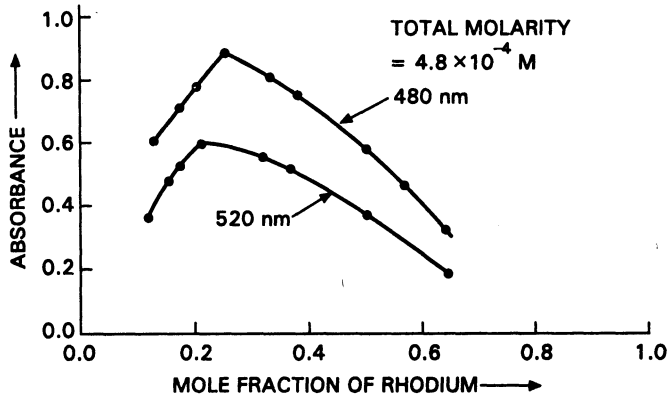


Fig. 3. Ringbom plot for Rh(III) PQSC complex

(i) Job's method: From a plot of absorbance against the mole fraction of rhodium (Fig. 4), it is concluded that the maximum absorbance is observed only when the metal : ligand ratio is 1 : 3.

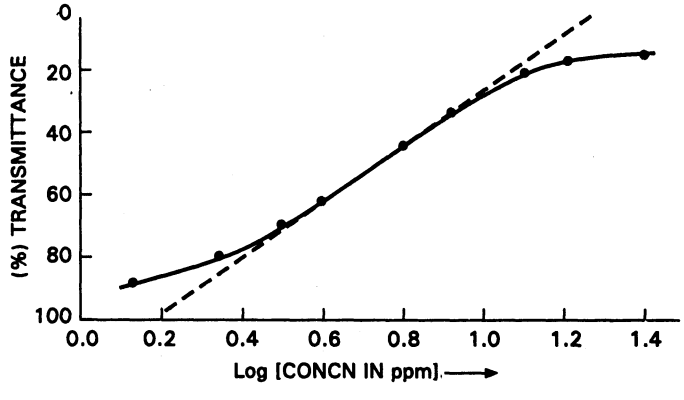
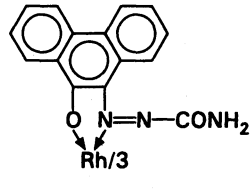


Fig. 4. Composition of Rh(III) PQSC complex by Job's method

(ii) Mole ratio method: A graph between absorbance against the mole ratios of PQSC shows that PQSC and rhodium combine in the ratio of 3 to 1, corroborating the results obtained by the method of continuous variations.

Based upon the coordination characteristics of semicarbazones and the molar composition of rhodium complex the following structure is tentatively assigned to the complex:



Stability constant of the complex: Stability constant of the metal complex was deduced by the standard method. The values E_M and E_S obtained from Fig. 4. are 0.444 and 0.375 respectively and that of K is calculated to be 1.05×10^{14}.

Effect of diverse ions: A series of synthetic samples containing known amounts of rhodium and diverse ions were prepared and analyzed by the recommended procedure. To make the procedure more useful, attempts have been made to mask the various interfering cations. Cobalt(II), nickel(II) and copper(II) react with PQSC at room temperature and interference due to these ions could be avoided by extracting them in chloroform. More of the ligand was added and the determination of rhodium was carried out in the usual way. Results of the study are incorporated in Table-2.

TABLE-2
DETERTNINATION OF RHODIUM IN PRESENCE OF DIVERSE IONS

Amount of rhodium taken = 8.23 ppm

Diverse ions	Amount tolerated (in ppm)	Diverse ions	Amount tolerated (in ppm)
Chloride	800	Cadmium(II)[1]	10
Bromide	400	Mercury(II)[2]	35
Iodide	500	Cobalt(II)	100
Nitrite	125	Nickel(II)	100
Nitrate	1000	Copper(II)	100
Sulphate	900	Silver(I)[3]	50
Phosphate	175	Uranium(VI)[2]	15
Fluoride	1000	Aluminium(III)	15
Oxalate	300	Thorium(IV)	20
Thiocyanate	400	Ruthenium(III)	2
Citrate	50	Palladium(II)	50
Tartrate	25	Lead(II)	40
Borate	100	Manganese(II)[2]	20
Sulphite	125	Vanadium(IV)	10
Zinc	50	Barium(II)	50

1. Masked with thiocyanate
2. Masked with fluoride
3. Precipitated and removed as chloride

ACKNOWLEDGEMENTS

The authors are thankful to Dr. Abhay Kumar, Head of the Chemistry Department and Dr. R.D. Pandey, the Principal, L.S. College, Muzaffarpur for providing library and laboratory facilities.

REFERENCES

1. F.E. Beamish, Analytical Chemistry of Platinum Metals, Pergamon Press, London (1966).
2. E.B. Sandell, Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc., New York (1959).
3. D.F. Boltz and M.G. Mellon, *Anal. Chem.*, **48**, 216R (1976).
4. F.E. Beamish and J.C. Van Loon, Recent Advances in the Analytical Chemistry of the Noble Metals, Pergamon Press, London (1982).
5. J.R. Stokeley and W.D. Jacons, *Anal. Chem.*, **35**, 149 (1963).
6. ———, *Talanta*, **10**, 43 (1963).
7. S.C. Srivastava, *Anal. Chem.*, **35**, 1165 (1963).
8. J.G. Sengupta, *Talanta*, 8, 785 (1981).
9. K.K. Saxena and A.K. Dey, *Indian J. Chem.*, **7**, 75 (1989).
10. L.N. Lomakina and I.P. Alimarin,Zh. Neorg.. Khim., 11, 2084 (1966).
11. L.N. Lomakina and I.P. Alimarin, *Vestnic Moscow Univ.*, **1**, 79 (1966).
12. A.T. Pilipenko and N.M. Maslei, *Ukrain Khim. Zhur.*, **33**,730 (1967).
13. S.K. Nath and R.P. Aggarwal, *Chim. Anal. (Paris)*, **47**, 257 (1965); **48**, 439 (1966).
14. O.W. Rollins and M.M. Oldham, *Anal. Chem.*, **43**, 146 (1971).
15. H. Hashitani, H. Yoshida and K. Motojima, *Bunseki Kagku*, **18**, 136 (1969).
16. S.C. Srivastava, V. C. Garg, and A.K. Dey, *Z. Anal. Chem.*, **248**, 305 (1990).
17. G.H. Ayrees and F.L. Johnson (Jr.), *Anal. Chim. Acta*, **23**, 448 (1960).
20. K. Sur and S.C. Shome, *Anal. Chim. Acta*, **48**, 145 (1969).
21. D.E. Ryan, *Analyst*, **75**, 757 (1950).
22. S.S. Berman, F.E. Beamish and W.A.E. McBryde, *Anal. Chim. Acta*, **15**, 363 (1956).
23. V.L. Wanger (Jr.) and J.H. Yoe, *Talanta*, **2**, 239 (1959).
24. A.I. Busev, U.M Ivanov and V.G. Gresi, *Zh. Anal. Khim.*, **23**, 15870 (1968).
25. S.C. Srivastava, K.N. Munsi and A.K. Dey, *J. Microchem.*, **14**, 37 (1989).
26. A.T. Pilipenko and P. F. Ol'khorich, *Ikrain Khim. Zhir.*, **34**, 397 (1968).
27. M. Otamo, *Bunseki Kagaku*, **17**, 125 (1968).
28. A.V. Rangekar and A.M. Khopkar, *Bull. Chem. Soc. (Japan)*, 39, 2169 (1966).
29. G.H. Rizvi, B.P. Gupta and R.P. Singh, *Microchim. Acta*, 459 (1972).
30. V. Radhushev and Prophorenko, *Zh. Anal. Khim.*, **27**, 2209 (1972).
31. S.K. Sindhwani and R.P. Singh, *J. Microchem.*, **18**, 686 (1973).
32. L.L. Kabanova and S.V. Ushova, *Zh. Anal.*, **29**, 2248 (1974).
33. K.K. Saxena and B.V. Agarwal, *Indian J. Chem.*, **14A**, 834 (1976).
34. P. Job, *Ann. Chim.*, **9**, 113 (1928).
35. H. Irving and T.B.J. Pierce, *J. Chem. Soc.*, 2565 (1959).
36. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).

(*Received*: 23 January 2003; *Accepted*: 28 April 2003) AJC-3066