

Spectrophotometric and Analogue Derivative Spectrophotometric Determination of Rhodium(III) with 2-(5-Bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)phenol

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A sensitive spectrophotometric method for the determination of rhodium(III) has been established by reacting rhodium(III) with 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)phenol (5-Br-PAPS). 5-Br-PAPS reacts with rhodium(III) to form a water-soluble 1 : 2 (metal : ligand) complex on heating at 95 °C. The rhodium(III) - 5-Br-PAPS complex has two absorption maxima at 557 and 600 nm in the pH range 4.0–9.2. The molar absorptivity is $1.09 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 600 nm. The favourable selectivity of the method is obtained by the addition of EDTA as a masking agent after formation of the rhodium(III) - 5-Br-PAPS complex. The sensitivity of the method can be increased about ten times by employing analogue derivative spectrophotometry.

Keywords: Rhodium(III) determination; spectrophotometry; analogue derivative spectrophotometry; 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)phenol

Several spectrophotometric methods for the determination of rhodium(III) have been published, including methods involving *p*-nitrosodimethylaniline,¹ 1-(2-pyridylazo)-2-naphthol,² 5-(2-pyridylazo)-*p*-cresol,³ rhodamine 6G⁴ and diphenylcarbazine.⁵ However, either the sensitivity or the selectivity of the above methods is insufficient.

2-(5-Bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)phenol (5-Br-PAPS) was first synthesised by Makino *et al.*⁶ It is a water-soluble pyridylazo compound and has the same chelating system as 4-(2-pyridylazo)resorcinol (PAR), but is more sensitive than PAR for the determination of most metals, having molar absorptivities in the region of $1 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ for several transition metal complexes. 5-Br-PAPS has been used for the spectrophotometric determination of zinc(II),^{6–8} vanadium(V),⁹ chromium(III),¹⁰ uranium(VI),⁸ cobalt(II),⁸ nickel(II)⁸ and ruthenium(III).¹¹ This reagent was also used as a pre-column reagent¹² for the high-performance liquid chromatographic determination of these metal complexes. 5-Br-PAPS reacts with rhodium(III) to form a stable blue complex on heating at 95 °C. The rhodium(III) - 5-Br-PAPS complex, once formed, is not decomposed by the addition of EDTA, whereas most other metal complexes are readily decomposed by EDTA. The selectivity of the colour development is increased by the addition of EDTA after formation of the rhodium(III) - 5-Br-PAPS complex.

In this paper, a sensitive and fairly selective spectrophotometric method is described for the determination of rhodium(III) with 5-Br-PAPS. The method can be made even more sensitive by the use of an analogue derivative spectrophotometric technique.

Experimental

Apparatus

Spectrophotometric measurements were made with a Hitachi 100–10 spectrophotometer and a Hitachi 200–20 recording spectrophotometer. To obtain the derivative spectrum, a modified Hitachi 200–0576 derivative unit composed of two analogue differentiation circuits (each having six different time constants^{13,14}) was connected in series between a Hitachi 200–20 recording spectrophotometer's output and a Hitachi 200 recorder's input.

Reagents

All reagents were of analytical-reagent grade, and all solutions were prepared with distilled, de-ionised water.

The 5-Br-PAPS solution ($5 \times 10^{-3} \text{ mol l}^{-1}$) was prepared by

the dissolution of 0.120 g of 5-Br-PAPS (Dojindo, Japan) in 50 ml of water.

The rhodium(III) solution ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolution of 0.140 g of rhodium(III) nitrate (Mitsunaga Kagaku, Japan) in 100 ml of 1 M hydrochloric acid. The rhodium(III) content in the solution was determined by chelatometry.¹⁵ Working solutions were prepared by dilution of this solution.

Procedures

Zero-order spectrophotometry

Pipette suitable aliquots of aqueous samples containing up to 8 μg of rhodium(III) into a 10-ml test-tube. Add 1 ml of ethylene glycol, 1 ml of $5 \times 10^{-3} \text{ mol l}^{-1}$ 5-Br-PAPS solution and 0.5 ml of 2 mol l^{-1} sodium acetate solution (pH 4.9). Dilute with water to 7 ml and then heat the solution at 95 °C in a water-bath for 30 min. After cooling, transfer the solution into a 10-ml calibrated flask and dilute to the mark with water. Measure the absorbance of the resultant solution against a reagent blank at 600 nm in a glass cell of 10-mm path length.

Second-derivative spectrophotometry

Record the second-derivative spectrum from 700 to 500 nm against a reagent blank by using a combination of both first- and second-order differentiation circuits of No. 6, which give maximum amplification factors, and a scan speed of 120 nm min^{-1} . Measure the vertical distance from a peak to a trough in the second-derivative spectrum.

Results and Discussion

Absorption Spectra

The absorption spectrum of the rhodium(III) - 5-Br-PAPS complex at pH 4.9 is shown in Fig. 1, together with its second-derivative spectrum. The absorption spectrum has two peaks at 600 and 577 nm. It is thought that the splitting of the absorption spectrum results from the charged quinoidal form based on the resonance structures of the rhodium(III) - 5-Br-PAPS complex. In the second-derivative spectrum the signal from the detector is amplified and the sensitivity of the method increases markedly.

Effect of pH and Solvent

The pH dependence of the rhodium(III) - 5-Br-PAPS complex formation was investigated by heating at 95 °C for 30 min. The maximum absorbance of the complex is obtained in the pH

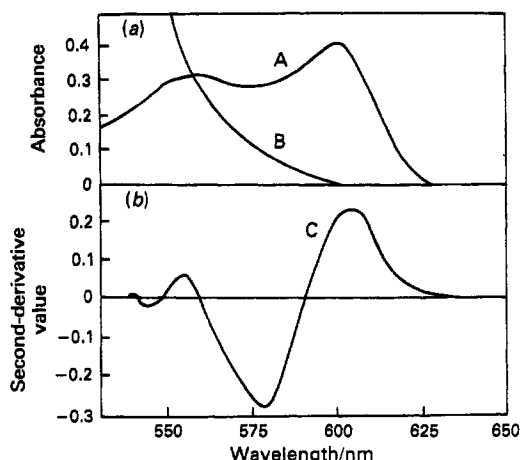


Fig. 1. Absorption spectrum and second-derivative spectrum of rhodium(III) - 5-Br-PAPS complex. (a) Absorption spectrum: Rh^{III} , $0.4 \mu\text{g ml}^{-1}$; 5-Br-PAPS, $5 \times 10^{-4} \text{ mol l}^{-1}$; ethylene glycol, 10% V/V; pH, 4.9. (b) Second-derivative spectrum: Rh^{III} , $0.04 \mu\text{g ml}^{-1}$; other conditions as in (a). A and C, Rh^{III} - 5-Br-PAPS complex; and B, reagent blank

range 8.1–9.2. At higher pH there is a tendency for the interference of foreign metal ions to increase. Therefore, a lower pH of 4.9 was chosen for routine work.

The formation of a platinum(II) complex with a heterocyclic azo compound is promoted in water-soluble organic media, which not only play the role of diluent, but also participate in the complex formation¹⁶ and prevent hydrolysis of the platinum(II).⁷ On the basis of this fact, several water-soluble organic solvents such as ethylene glycol, dioxane, dimethylformamide and glycerin were added in aqueous solution to promote the formation of the rhodium(III) - 5-Br-PAPS complex. Consequently, for an ethylene glycol content of 10% V/V the absorbance of the rhodium(III) - 5-Br-PAPS complex increases by about 26% over that obtained in aqueous solution.

Effect of Reagent Concentration and Heating Time

The concentration of 5-Br-PAPS does not significantly alter the absorbance of the rhodium(III) - 5-Br-PAPS complex, provided that it is present at more than $4 \times 10^{-4} \text{ mol l}^{-1}$. The minimum concentration required was selected, i.e., $5 \times 10^{-4} \text{ mol l}^{-1}$, because 5-Br-PAPS is an expensive reagent.

The reaction between rhodium(III) and 5-Br-PAPS at room temperature is very slow. The formation of the rhodium(III) - 5-Br-PAPS complex is accelerated by heating. The effect of the heating time at 95°C on the formation of the complex was studied. The absorbance of the complex abruptly increased with heating for 20 min, but there was only a slight increase after 20 min, and the maximum absorbance was obtained after 90 min. A heating time of 30 min was adopted as 90% of the maximum absorbance is obtained after this time. The rhodium(III) - 5-Br-PAPS complex, once formed, is stable and gives a constant absorbance for 2 h.

Composition of the Rhodium(III) - 5-Br-PAPS Complex

The composition of the rhodium(III) - 5-Br-PAPS complex was determined by the method of continuous variation. The results are shown in Fig. 2. The method indicates that the ratio of the metal to 5-Br-PAPS is 1:2.

Calibration Graph

Zero-order spectrophotometry

A straight line calibration graph passing through the origin was obtained for rhodium(III) concentrations of 0.04 – $0.8 \mu\text{g ml}^{-1}$. The equation for the graph was $\text{Rh}(\mu\text{g ml}^{-1}) = 0.914A$, where A is the absorbance. The sensitivity for an

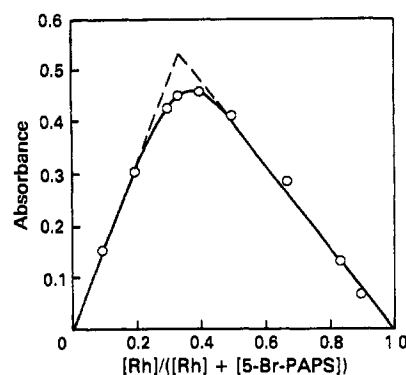


Fig. 2. Continuous variation graph for rhodium(III) - 5-Br-PAPS complex. $[\text{Rh}^{\text{III}}] + [5\text{-Br-PAPS}] = 2.5 \times 10^{-5} \text{ mol l}^{-1}$. Other conditions as in Fig. 1(a)

Table 1. Influence of foreign ions on the determination of $4 \mu\text{g}$ of Rh^{III} . A 1-ml volume of $5 \times 10^{-2} \text{ M}$ EDTA solution was added after the formation of the Rh^{III} - 5-Br-PAPS complex

Metal ion	Tolerance limit/ μg
$\text{Ca}^{\text{II}}, \text{Mg}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}$	2000
$\text{Pb}^{\text{II}}, \text{Zn}^{\text{II}}$	500
In^{III}	200
$\text{Al}^{\text{III}}, \text{Mn}^{\text{II}}, \text{Th}^{\text{IV}}$	100
Cu^{II}	50
$\text{Fe}^{\text{III}}, \text{Ni}^{\text{II}}, \text{Zr}^{\text{IV}}$	10
$\text{Bi}^{\text{III}}, \text{Co}^{\text{II}}, \text{Cr}^{\text{III}}, \text{Pd}^{\text{II}}, \text{Pt}^{\text{II}}, \text{Ti}^{\text{IV}}, \text{V}^{\text{V}}$	<10

absorbance of 0.001 and the molar absorptivity calculated from the above equation were 0.95 ng cm^{-2} and $1.09 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively.

Second-derivative spectrophotometry

The calibration graph, prepared by plotting the second-derivative value versus the rhodium(III) concentration, was a straight line passing through the origin when the peak to trough values were plotted. The equation for the graph, measured by employing a combination of circuit No. 6 and a scan speed of 120 nm min^{-1} , is $\text{Rh}(\text{ng ml}^{-1}) = 73D$ for the peak to trough measurements, where D is the second-derivative value represented by the conversion of the value into absorbance. It can be seen from this equation that rhodium(III) can be easily determined down to the 5 ng ml^{-1} level by the proposed method.

Effect of Foreign Ions

A number of metal ions were examined to establish their interference in the determination of rhodium(III). Lactic acid was added before the addition of 5-Br-PAPS and EDTA was added after the formation of the rhodium(III) - 5-Br-PAPS complex as masking agents in the proposed procedure, then the mixture was again heated at 95°C for 5 min. The selectivity of the method is improved because many metal complexes are decomposed by the addition of EDTA. The effect of foreign ions on the determination of rhodium(III) is summarised in Table 1. It can be seen that bismuth(III), cobalt(II), chromium(III), palladium(II), platinum(II), titanium(IV) and vanadium(V) interfere seriously. The determination of rhodium(III) is feasible in the presence of other common metal ions below the tolerance limit.

Conclusions

5-Br-PAPS is one of the most sensitive reagents for the spectrophotometric determination of rhodium(III), that is, the molar absorptivity of the rhodium(III) - 5-Br-PAPS

complex is $1.09 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 600 nm. The selectivity of the method is improved by the addition of EDTA after the formation of the rhodium(III) - 5-Br-PAPS complex. The sensitivity of the method can be increased about ten times by employing analogue derivative spectrophotometry, and the determination of rhodium(III) at the p.p.b. level is then feasible.

References

1. Wilson, R. B., and Jacobs, W. D., *Anal. Chem.*, 1961, **33**, 1654.
2. Busev, A. I., Ivanov, V. M., Gorbunova, N. N., and Cresl, V. G., *Tr. Kom. Anal. Khim., Akad. Nauk. SSSR*, 1969, **17**, 360.
3. Goroshko, G. G., Dedkov, Yu. M., and Ermakov, A. N., *Zh. Anal. Khim.*, 1978, **33**, 1114.
4. Kalinowski, K., and Marzenko, Z., *Mikrochim. Acta*, 1985, **1**, 167.
5. Sarmah, K., and Das, H. K., *J. Indian Chem. Soc.*, 1985, **62**, 631.
6. Makino, T., Saito, M., Horiguchi, D., and Kina, K., *Clin. Chim. Acta*, 1982, **120**, 127.
7. Homsher, R., and Zak, B., *Clin. Chem.*, 1985, **31**, 1310.
8. Oshita, K., Wada, H., and Nakagawa, G., *Anal. Chim. Acta*, 1983, **149**, 269.
9. Shijo, Y., and Sakai, K., *Bunseki Kagaku*, 1984, **33**, E435.
10. Shijo, Y., and Sakai, K., *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1455.
11. Shijo, Y., Nakaji, K., and Shimizu, T., *Nippon Kagaku Kaishi*, 1987, **31**.
12. Shijo, Y., and Sakai, K., *J. Chromatogr.*, 1985, **333**, 133.
13. Ishii, H., and Koh, H., *Nippon Kagaku Kaishi*, 1980, 203.
14. Ishii, H., Odashima, T., and Imamura, T., *Analyst*, 1982, **107**, 885.
15. Yoshino, Y., Hatazawa, S., Saito, M., and Ouchi, A., *Chem. Lett.*, 1980, 1085.
16. Demina, V. M., Isaev, I. D., Éike, M. Yu., and Fedorov, V. A., *Koord. Khim.*, 1980, **6**, 44.
17. Blandmaer, M., Burgess, I., and Hamshire, S., *Transition Met. Chem.*, 1979, **4**, 291.

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