

# SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM (V) WITH RUTIN (QUERCETIN 3-RUTINOSIDE)

BY BRAHM DEV AND B. D. JAIN

(Department of Chemistry, University of Delhi, Delhi-6)

Received February 4, 1963

(Communicated by Prof. T. R. Seshadri, F.R.S., F.A.Sc.)

SZARVAS and Jarabin have already reported the use of rutin for the spot test of vanadium.<sup>1</sup> The present investigation deals with the complex formation between vanadium (V) and rutin. It has been found that rutin can be employed for the spectrophotometric determination of vanadium (V). On the addition of an ethanolic solution of rutin to vanadium (V), the orange water-soluble complex which is obtained obeys Lambert-Beer's law at 435 m $\mu$  within the concentration range of 0.51-14.3 p.p.m. of vanadium and its colour intensity does not vary between pH 3.5 and 6.0.

## EXPERIMENTAL

An ethanolic solution ( $1 \cdot 10^{-3}$  mole/litre) of pure rutin<sup>2</sup> was employed. Standard vanadium (V) solution was obtained by dissolving Ammonium *meta*-Vanadate (A.R.). All other reagents employed were of A.R. quality.

Uvicam spectrophotometer, model S.P. 600, along with 1 cm. thick absorption cells was used for spectrophotometric measurements. Beckman pH Meter Model H 2 with a suitable glass electrode was used for pH measurement. Dilute HCl and dilute NaOH were used for pH adjustment.

### *Absorption Spectra*

Rutin showed the maximum absorption at 410 m $\mu$  while the vanadium-rutin complex showed a maximum at 425 m $\mu$ , when the reagent was employed as the reference solution. The absorption due to the reagent at this wavelength was quite appreciable. All subsequent spectrophotometric studies of the complex were however carried out at 435 m $\mu$  and the absorption due to the reagent at this wavelength was negligible. The absorption spectra of the complex at pH 1.5-8.0 in each case showed a maximum at about 425 m $\mu$ .

*Minimum Amount of Rutin Necessary for Determination of Vanadium*

The optical density at 435 m $\mu$  of a series of solutions containing rutin and vanadium in the molar ratios of 0.5:1 to 9:1 was determined and it was found that the optical density is maximum when the molar ratio of rutin to vanadium is 6. During subsequent estimations the molar ratio of the reagent to vanadium was maintained at 10. An excess of the reagent did not affect the optical density of the complex.

*Effect of pH on Vanadium-Rutin Complex*

It was found that at pH 3.5-6.0 the absorption by the complex remained constant (Fig. 1).

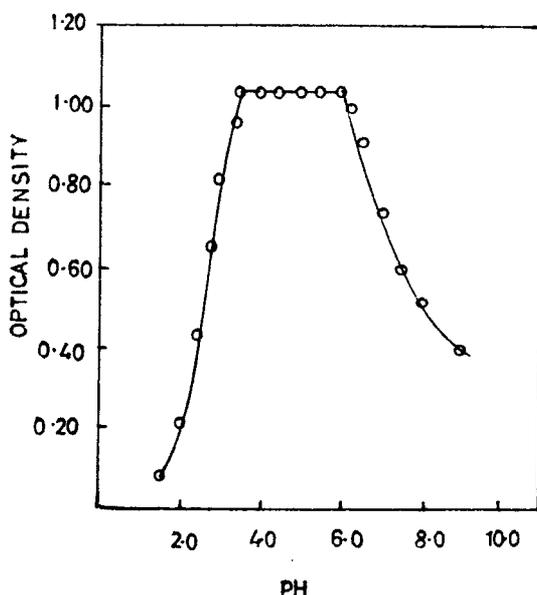


FIG. 1. Effect of pH on the development of colour.

*Stability of the Colour of the Complex*

The colour of the complex was stable for 6 hours, and it obeyed Lambert-Beer's law at 435 m $\mu$  for the concentration range of 0.51-14.30 p.p.m. of vanadium.

*Molar Composition of the Complex*

The molar composition of vanadium-rutin complex was determined by Job's method of continuous variations,<sup>3</sup> as modified by Vosburgh and

Cooper,<sup>4</sup> employing concentrations of (a)  $1 \cdot 10^{-3}$  M and (b)  $2 \cdot 10^{-3}$  M (Fig. 2) and it has been found that it contains the reagent and vanadium in the ratio of 2:1. The complex therefore has the molar composition  $VM_2$

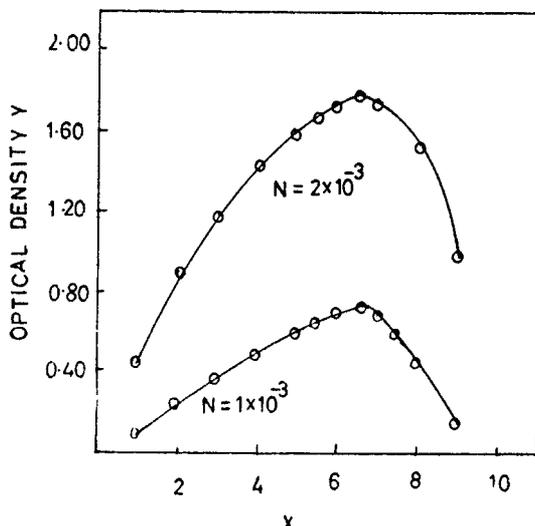


FIG. 2. X ml. of N-Molar Rutin added to  $(10 - X)$  ml. of N-Molar Vanadium (V).

where M is rutin molecule. The molar composition of the vanadium complex was also verified by the slope ratio method of Harvey and Manning.<sup>5</sup> For this purpose two series of solutions were prepared employing  $1 \cdot 10^{-3}$  M solutions of rutin and of vanadium. In one series, the vanadium concentration was varied, maintaining the concentration of the rutin constant and in a sufficient excess. In the other, rutin concentration was varied maintaining the vanadium concentration constant and in a sufficient excess. The optical densities of the solutions of both these series were determined at  $435 m\mu$  with alcohol as reference. The observed values are plotted as the curves P and Q of Fig. 3. In the curves P and Q, only the straight line portions AB and CD, respectively, were taken into account to find out the slopes:

$$\tan \theta_1 = \text{slope of the curve P (AB)} = 0.9$$

$$\tan \theta_2 = \text{slope of the curve Q (CD)} = 0.5$$

$$\text{Molar ratio of the complex} = 0.9/0.5 = 1.8 = 2.0 \text{ (approx.)}$$

Thus the slope ratio of the two curves indicates that the molar ratio of the rutin to vanadium in the complex is 2 and thus corroborates the results obtained by using Job's method.

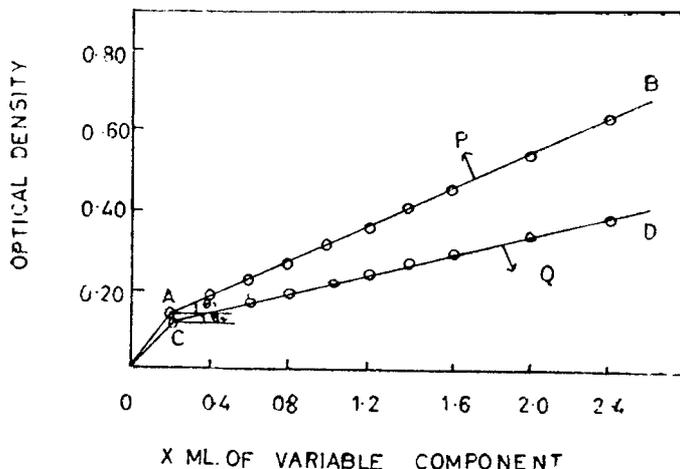


FIG. 3. Curve P: X ml. of  $1 \times 10^{-3}$  M Vanadium (V) Sol. added to 10 ml. of  $1 \times 10^{-3}$  M Rutin Sol. and Vol. made to 15 ml. with water. Curve Q: X ml. of  $1 \times 10^{-3}$  M. Rutin Sol. added to 10 ml. of  $1 \times 10^{-3}$  M Vanadium (V) Sol. and Vol. made to 15 ml. with water.

#### Stability Constant of the Complex

The stability constant of the complex was determined by the method based on Beer's law. Two solutions of vanadium-rutin complex were prepared so that the optical densities of both were either equal or nearly so, but contained different concentrations of metal ions and the chelating agent. In this way, pairs of such solutions were made. Since the dissociation constant is the same for members of a given pair, and the molar composition of the complex is 1:2 moles of reagent, concentrations of the complex and thus the value of K may be calculated from the relation:

$$K = \frac{(MKe)}{[C_{M_1} - (MKe)] [C_{Ke_1} - 2(MKe)]^2}$$

$$= \frac{(MKe)}{[C_{M_2} - (MKe)] [C_{Ke_2} - 2(MKe)]^2}$$

where  $C_M$ 's and  $C_{Ke}$ 's are the initial concentrations of vanadium and rutin respectively, and (MKe) denotes the concentration of the complex formed. The ionic strength of the solutions was maintained at a constant value by the addition of potassium nitrate (0.5 M) and the optical density measurements were made at  $435 \mu$ . The average value of  $\log K$  from several determinations was found to be 9.82 at  $17^\circ$ .

*Interference due to Foreign Ions*

It was found that phosphate, borate, oxalate, citrate, tartrate, aluminium, copper, beryllium, iron, tungsten, molybdenum, zirconium, uranium, ceric, titanium and thorium ions interfere even when present in minute quantities. The limits of interference due to other cations and anions for 1.275 p.p.m. of vanadium are given below:

Ion	Interferences	
	Taken as	p.p.m. tolerated
Acetate	Sodium acetate	200
Bromide	Potassium bromide	500
Chloride	Sodium chloride	2,000
Fluoride	Sodium fluoride	150
Iodide	Potassium iodide	400
Sulphate	Sodium sulphate	800
Sulphocyanide	Potassium sulphocyanide	200
Cerium (III)	Nitrate	800
Cobalt	Nitrate	900
Manganese	Chloride	1,000
Nickel	Nitrate	800
Lead	Nitrate	400
Lanthanum	Nitrate	1,000

## ACKNOWLEDGEMENT

The authors are grateful to Prof. T. R. Seshadri, F.R.S., Head of the Department, for his keen interest and helpful discussions.

## SUMMARY

Rutin has been used for the spectrophotometric determination of vanadium (V). Vanadium (V) forms with rutin an orange water-soluble complex, which obeys Lambert-Beer's law at 435 m $\mu$  within the concentration range of 0.51–14.3 p.p.m. of vanadium. The colour intensity of the complex does not vary between pH 3.5 and 6.0 and the molar composition of the complex shows that it contains vanadium and the rutin in the molar ratio

of 1:2. The stability constant of the vanadium-rutin complex has been determined by the method based on Beer's law. Limits of interference due to various cations and anions in this determination have been given.

#### REFERENCES

1. Szarvas, P. and Jarabin, Z. .. *Anal. Chim. Acta*, 1959, **20**, 330.
2. Brahm Dev and Jain, B. D. .. *J. Less-Common Metals*, 1962, **4**, 286.
3. Job, P. .. *Ann. Chim.*, 1928, **9**, 113.
4. Vosburgh, W. C. and Cooper, G. R. .. *J. Amer. Chem. Soc.*, 1941, **63**, 437.
5. Harvey, A. E. and Manning, D. L. .. *Ibid.*, 1950, **72**, 4488.