

Vanadium(V) with N-*m*-Tolyl-*m*-nitrobenzohydroxamic Acid

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N-*m*-Tolyl-*m*-nitrobenzohydroxamic acid forms a violet complex with vanadium(V) in 5.5-8.5M HCl. The chloroform extract of the 1:2 complex (metal:ligand) exhibits λ_{\max} at 540 nm. The system obeys Beer's law over the range 0.5-16.0 ppm of vanadium(V). The sensitivity of the reaction is 0.013 $\mu\text{g cm}^{-2}$. A procedure for the determination of vanadium in high-speed steel and steel has been developed.

N-PHENYLBENZOHYDROXAMIC acid and its derivatives have been extensively used for the spectrophotometric determination of vanadium(V)¹⁻⁵. Use of N-*m*-tolyl-*m*-nitrobenzohydroxamic acid as a spectrophotometric reagent for vanadium(V) is reported in this note.

The reagent N-*m*-tolyl-*m*-nitrobenzohydroxamic acid was prepared by the method described by Agarwal and Tandon⁶.

A standard solution of vanadium(V) was prepared by dissolving ammonium vanadate (AR) in doubly distilled water and determining the vanadium content by standard methods⁷.

Procedure — An aliquot containing 12.5-400 μg of vanadium(V) was made up to 15 ml and the acidity was maintained between 6.0 and 8.0M with respect to HCl. Chloroform solution (6 ml, 0.1%) of N-*m*-tolyl-*m*-nitrobenzohydroxamic acid was added and the contents shaken for 5 min when a violet colour developed. The phases were allowed to separate for two min and the chloroform layer collected in a beaker containing 1.0-1.5 g of anhydrous sodium sulphate. The aqueous phase was washed twice with 5 ml portions of chloroform to remove any violet colour left. The washings were transferred to the beaker and volume made up to 25 ml in a volumetric flask by the addition of chloroform. The absorbance was measured at 540 nm (Hilger Uvispek spectrophotometer) against the reagent blank prepared under identical conditions.

The colour intensity of the complex remains unchanged in the range 5.5-8.5M of HCl. Below and above this range the absorbance decreases. For complete development of colour, 8.0 ppm of vanadium(V) requires 5 ml (0.1%, w/v) of the reagent. The absorbance values remain constant for 5 days in the temperature range 20-40°. The system follows Beer's law over the range 0.5-16.0 ppm of vanadium(V) and the optimum concentration range as evaluated by Ringbom's method⁸ is 1.0-14.0 ppm. The percentage of relative error per 1% absolute photometric error⁹ is 2.72. The Sandell

ivity is 4210.

Various organic solvents such as benzene, carbon tetrachloride, chloroform, ethyl acetate, etc., can extract the violet complex from the aqueous phase. However chloroform is found to be most suitable as it gives a sharp peak at 540 nm whereas other solvents give a shoulder in this region.

Mole-ratio method¹¹ and Job's method of continuous variation¹² indicate the formation of a 1:2 complex (metal:reagent). The instability constant is of the order of 10^{-9} . The dissociation constant of the complex was also evaluated from a study of the absorbance of the complementary mixtures of non-equimolar solutions of V(V) and the reagent. The calculated¹³ value is of the order of 10^{-9} .

Effect of diverse ions — There was no interference from the following ions (50 mg each: NO_3^- , SO_4^{2-} , NO_2^- , F^- , Br^- , I^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , PO_4^{3-} , AsO_4^{3-} , $\text{C}_6\text{H}_4\text{O}_4^-$, citrate, tartrate, Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Al^{3+} , As^{3+} , Au^{2+} , Pd^{2+} , Pt^{4+} , rare earths, Se^{4+} , Te^{6+} , Ce^{3+} , Ce^{4+} , Fe^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , UO_2^{2+} , Cu^{2+} , Zr^{4+} , Bi^{3+} , Sn^{2+} and Th^{4+} .

The interference from Ti^{4+} , Mo^{6+} and W^{6+} can be eliminated by adding tartrate or oxalate (10 ml, 0.1M).

Analysis of steel — To test the reliability of the method, two samples of (i) high-speed steel (No. 64b, Bureau of Analysed Samples Ltd) and (ii) steel (No. 132, National Bureau of Standards, USA) were analysed for vanadium content.

The sample (containing approximately 1.0 mg of vanadium) was dissolved in 10 ml dilute H_2SO_4 (1:4) and a few drops of nitric acid were added to oxidize iron and tungsten. It was then filtered through a sintered glass crucible, washed with hot water and made up to 100 ml. To a 25 ml aliquot, 0.1N potassium permanganate was added dropwise until a faint pink colour was observed. Vanadium (V) content was determined by the recommended procedure in the presence of tartaric acid. High-speed steel [Found: V, 1.97; V present, 1.99%]. Steel [Found: V, 1.65; V present 1.60-1.68%].

References

1. PRIYADARSHINI, U. & TANDON, S. G., *Analyt. Chem.*, **33** (1961), 435.
2. RYAN, D. E., *Analyst*, **85** (1960), 569.
3. MAJUMDAR, A. K. & DAS, G., *Analyt. chim. Acta*, **36** (1966), 454; **31** (1964), 147.
4. MAJUMDAR, A. K. & DAS, G., *J. Indian chem. Soc.*, **42** (1965), 189.
5. GUPTA, V. K. & TANDON, S. G., *Analyt. chim. Acta*, **66** (1973), 39.
6. AGRAWAL, Y. K. & TANDON, S. G., *J. Chem. Engng Data*, **16** (1971), 371.
7. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1962.
8. RINGBOM, A. Z. *analyt. Chem.*, **115** (1938), 332.
9. AYRES, G. H., *Analyt. Chem.*, **21** (1949), 652.
10. SANDELL, E. B., *Colorimetric determination of traces of metals* (Interscience, New York), 1959, 84.
11. YOE, J. H. & JONES, A. L., *Ind. Engng Chem. Anal. Edn.*, **16** (1944), 111.
12. JOB, P., *C.R. Acad. Sci.*, **180** (1925), 928; *Ann. Chim. (Paris)*, **9** (1928), 113.
13. MAJUMDAR, A. K. & SEN, B., *Analyt. chim. Acta*, **8** (1953), 369.