

Extractive Spectrophotometric Determination of Vanadium as Vanadium(III)-Thenoyltrifluoroacetone Complex

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Using 2-thenoyltrifluoroacetone (HTTA) as a reagent, analytical studies have been carried out on vanadium but most of the vanadium extractions reported are based on vanadium(V) or vanadium(IV). The vanadium(III)-TTA complex has not been studied for its analytical applications. The proposed method makes use of the extraction of V^{III} -TTA complex into benzene for the determination of vanadium. The studies involving optimisation of conditions, stoichiometry of the complex, interference of foreign ions and applicability to synthetic and natural samples have been carried out and the results of such studies are reported here.

Results and Discussion

On studying the absorption spectrum of vanadium(III)-TTA complex in benzene, it was observed that the complex shows an absorption band at 400 nm, where the absorbance of the reagent blank is very small and hence all absorbance measurements were carried out at 400 nm. Besides benzene, the complex gets extracted into other solvents, such as carbon tetrachloride, carbon disulphide, ethyl acetate, chloroform, dichloromethane, n-butanol, n-hexane, isoamyl alcohol, amyl acetate and isobutyl methyl ketone. The quantity extracted, decreases in the above order of the solvents. The effect of different parameters affecting the extraction of the complex was studied. On the basis of such studies the optimum conditions found for maximum extraction of V^{III} -TTA complex are : 1.0–2.0 g of sodium dithionite, 1 ml of TTA solution (2–4%), initial pH 2.0–5.0, 2 min of waiting time after thenoyltrifluoroacetone addition, 1–2 min of equili-

bration time and two extractions each with 10 ml of benzene.

The complex is stable for more than 48 h. Single extraction remove more than 94% of vanadium. However, second extraction is recommended for quantitative recovery of vanadium from aqueous phase. Beer's law is obeyed upto $10 \mu\text{g V ml}^{-1}$ with Sandell sensitivity of $0.006 \mu\text{g V cm}^{-2}$. The limit of determination is $0.5 \mu\text{g V ml}^{-1}$.

Effect of diverse ions : The effect of various anions and complexing agents on the extraction of V^{III} -TTA complex was studied. 500 mg each of sodium chloride, sodium sulphate, sodium acetate and 100 mg of potassium iodide are tolerated. Nitrate, oxalate, tritrate, fluoride and EDTA interfere. However, limited amounts of some complexing agents can be tolerated, such as 300 mg of ascorbic acid, 100 mg of thiourea, 50 mg phosphate, 40 mg of citrate and 1 ml of thioglycolic acid (added after reduction) in the extraction of the complex.

Interference studies of different cations were carried out in the determination of $100 \mu\text{g}$ of vanadium by the proposed method. Of the 26 metal ions tested, only Fe^{II} , Fe^{III} , Mo^{VI} and U^{VI} are found to give coloured extracts under the proposed conditions of vanadium extraction. However, the extraction of these elements can be prevented by making use of suitable masking agents. The extraction of Fe^{II} and Fe^{III} can be checked by adjusting the pH to 2.0–2.5 and adding 0.2–0.3 g of ascorbic acid. The interference of Mo^{VI} and U^{VI} is avoided by chloride and citrate respectively. Cr^{VI} is not

extracted but its presence causes a considerable decrease in vanadium extraction, thus its tolerance limit is restricted to 0.1 mg. Hydrolysable metal ions, such as Th^{IV} , Zr^{IV} , Bi^{III} , Sb^{III} , As^{III} and Sn^{II} form emulsion in higher concentrations but can be tolerated upto 1.0 mg. The presence of Ba^{II} , Al^{III} , Pb^{II} and Ni^{II} lowers the extraction of vanadium, however, the decrease in vanadium extraction in presence of these ions can be compensated by adding 2–3 times the TTA concentration as required in the procedure. The tolerance limits for different metal ions in 10 ml of solution are : 10 mg each of Be^{II} , Mg^{II} , Zn^{II} , Cd^{II} and Mn^{II} ; 5 mg each of Fe^{II} , Fe^{III} , Cu^{II} , Ca^{II} , Sr^{II} and Co^{II} ; 2 mg each of Ba^{II} , Hg^{II} , Al^{III} , Ni^{II} and Pb^{II} ; 1 mg each of Ti^{IV} , Zr^{IV} , Th^{IV} , Sn^{II} , U^{VI} , Mo^{VI} , W^{VI} and Re^{VII} ; 0.5 mg each of As^{III} , Sb^{III} and Bi^{III} . Applicability of the method has been tested by the analysis of some synthetic samples and a steel sample with satisfactory results.

Experimental

Procedure : To the solution (~5 ml) containing 100 μg of vanadium sodium dithionite (1.0 g) was added. The solution was allowed to stand for 1 min followed by the addition of TTA solution (1.0 ml, 2% in acetone) and enough distilled water so as to make total volume of the aqueous phase to 10 ml. After 2 min the complex was extracted with benzene (2 \times 10 ml) each time shaking for

a min. The combined extract was treated with anhydrous sodium sulphate (0.5 g) for removing traces of water, and the volume was made upto 25 ml with benzene. The absorbance of the yellowish brown complex was measured at 400 nm against the reagent blank. Vanadium content was computed from the standard calibration curve.

A Shimadzu UV-140-02 spectrophotometer was used for absorbance measurement.

Analysis of carbon steel : The steel sample (0.1 g) was treated with HCl (1 : 1; 5 ml) and heated till the volume was reduced to 2–3 ml. Then after adding water (5 ml), evaporation was repeated. After cooling, the volume of the solution was made upto 25 ml with distilled water. Aliquots of this solution were used for analysis.

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References

- 1 A K DE and S RAHMAN, *Anal Chem*, 1963, **35**, 1095, A IKEIATA and T SHIMIZU, *Bull Chem Soc*, 1965, **38**, 1385, A DOADRIO, F LORENZO and C MOLINA, *An Quim*, 1972, **68**, 357, N A KRASNANSKAY and V M PFSHOKYA, *Zh Anal Khim*, 1972, **27**, 1620, K HIZOSHI and A HIDEO, *Nippon Kagaku Kaishi*, 1972, **1**, 90