

Amperometric Determination of Vanadium (V) as Copper Orthovanadate

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With 1 Figure

Summary

A rapid amperometric method for the determination of vanadium (V) has been described which involves titration of vanadium (V) as sodium orthovanadate against copper sulphate solution at $E_{de} = -0.20$ V (vs S.C.E.). The accuracy and reproducibility of the method is excellent particularly at higher temperature i.e. at 60°C. The method permits the determination of vanadium (V) down to 0.2 mM with an accuracy 1.0%.

There is hardly any reference in the literature regarding the determination of vanadium (V) by amperometric method, although a number of gravimetric methods¹⁾ and a potentiometric method²⁾ of determination of vanadium (V) are available. The authors during the course of studies on the formation of copper polyvanadates³⁾ at different pH levels by electrometric techniques observed that copper reacts stoichiometrically with sodium orthovanadate to produce a yellowish green precipitate of copper orthovanadate. Hence it was considered of an importance to study the possibility of developing this reaction as a precise and rapid method for the micro determination of vanadium (V).

Experimental

AnalaR (B.D.H.) reagents; Copper sulphate, vanadium pentaoxide, potassium nitrate, gelatine were used. Vanadium contents in V_2O_5 was checked by precipitating it as cupferrate from a solution of sodium orthovanadate.

¹⁾ P. E. BROWNING and H. E. PALMER, *Amer. J. Sci.* **30**, 220 (1910); L. MOSER and O. BRANDE, *Montash* **51**, 169 (1929).

²⁾ R. S. SAXENA and O. P. SHARMA, *Talanta* **11**, 863 (1964).

³⁾ Unpublished Investigations.

Amperometric titrations

A manual polarograph with scalamp galvanometer was used for amperometric work. A dropping mercury electrode with $m^{2/3}t^{1/6} = 2.752 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ was used in conjunction with a saturated calomel electrode connected through a low resistance salt bridge. Solution of sodium orthovanadate ($3 \text{ Na}_2\text{O} \cdot \text{V}_2\text{O}_5$) was prepared by dissolving vanadium pentoxide in requisite amount of boiling NaOH and a series of solutions containing various concentrations of vanadium (V) were thus prepared by its further dilutions. 20 mls of this solution containing 0.1 M KNO_3 as supporting electrolyte and 0.005% gelatine as maxima suppressor was taken in the cell each time and titrated against a standard solution of copper sulphate at an applied potential of $E_{\text{de}} = -0.20 \text{ V}$ (vs S.C.E.). Amperometric titration were carried out⁴) at various temperatures and it was established during the course of studies that at 60°C temperature and in the presence of 25% ethanol the accuracy and the reproducibility of the method becomes excellent: The results were found almost quantitative in these experimental conditions for the presence of even every small amount of vanadium (V). The corrected current values were plotted against volume of the titrant added and the amount of the standard solution consumed were evaluated from the equivalence points located graphically.

Discussion

Fig. 1 curves (a) and (b) represents amperometric titrations between sodium orthovanadate and copper sulphate at 60°C. It is observed during the course of titrations that the diffusion current is almost constant till the

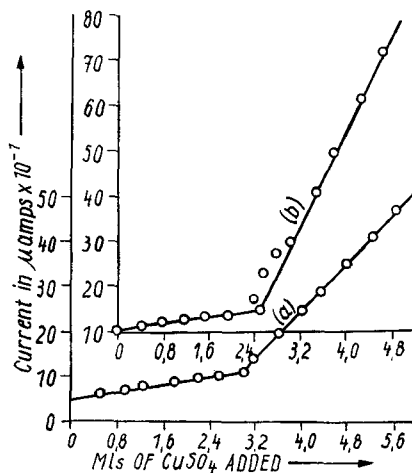
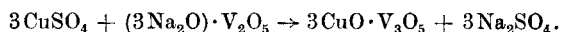


Fig. 1. Curve (a): 0.02 M Cu^{2+} added to 20 ml of 0.001 M V^{5+} , curve (b): 0.04 M Cu^{2+} added to 20 ml of 0.0016 M V^{5+}

⁴) C. M. GUPTA, Bull. chem. Soc. Japan **38**, 1401 (1965).

stoichiometric end point is reached and beyond it increases linearly with the addition of copper (VI); i.e. as a result of formation of copper orthovanadate at a stage where the molecular ratio of the reacting species V_2O_5 : Cu is 1:3 corresponding to the formation and precipitation of $3CuO \cdot V_2O_5$ at pH range of 8.0—9.5 and the reaction equilibria can be reforepresented as follows:



It is evident from the table, which illustrate the results and accuracy of the method, that the amperometric titrations of $CuSO_4$ with solution containing sodium orthovanadate in the presence of 0.1 M KNO_3 and 0.005% gelatine at 60°C provides precise results and can be suitable employed for the quantitative determination of vanadium (V).

The present investigation thus provides the amperometric method which is much more convenient than the other methods currently available in the literature. It is simple as it does not need costly chemicals or complicated procedure or equipments. The accuracy and reproducibility of the results is excellent and hence it can safely be recommended for the quantitative determination of even low concentration of vanadium (V) (10^{-4} to 10^{-5} M); of course in pure solutions. The cations which gives precipitate with orthovanadate and the anions such as molybdate end tungstates etc. should be avoided as their presence can cause interference.

Table 1

Amperometric determination of vanadium (V) as copper orthovanadate ($3CuO \cdot V_2O_5$) at $E_{de} = -0.20$ V (Vs. S.C.E.)

| Concentrations | | Calculated end points | Observed end points |
|-----------------------|----------|-----------------------|---------------------|
| $3Na_2O \cdot V_2O_5$ | $CuSO_4$ | | |
| M/800 | M/50 | 3.75 | 3.72 |
| M/1000 | M/50 | 3.00 | 3.00 |
| M/2000 | M/100 | 3.00 | 3.00 |
| M/2500 | M/100 | 2.40 | 2.40 |
| M/3500 | M/125 | 2.14 | 2.08 |
| M/5000 | M/250 | 3.00 | 2.88 |

Table 2

Amounts of vanadium (V)

| Present in mg/litre | Found in mg/litre | Error |
|---------------------|-------------------|-------|
| 29.11 | 28.72 | 1.0% |
| 40.76 | 40.76 | 0.00% |
| 50.95 | 50.95 | 0.00% |
| 101.90 | 101.90 | 0.00% |

The same reaction with reverse system when studied by potentiometric method by using a platinum electrode in a solution of CuSO_4 and titrating it against sodium orthovanadate, also gave excellent results showing the formation and precipitation of copper orthovanadate ($3 \text{CuO} \cdot \text{V}_2\text{O}_5$).

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