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Reductimetric determination of vanadium(V) with iron (II) in buffer medium and in presence of oxalate

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ABSTRACT

An accurate, convenient and inexpensive reductimetric titration method has been developed for the determination of vanadium(V) with iron(II). In this method vanadium(V) is titrated against iron(II) solution in a buffer medium of pH 3.5 – 4.5 [made of sodium acetate and hydrochloric acid] and in presence of 0.04M (or above) sodium oxalate. The end-point can be detected potentiometrically or visually using some oxazine dyes (Galloycyanine, Gollamine blue, Celestin blue, and Meladola's blue) as redox indicators. Vanadium(V) in the range of 8-25mg. and 4-13mg. can be determined by the potentiometric (accuracy + 0.4%) and visual end-point methods (accuracy + 0.6%) respectively. The conditional redox potentials of the oxidant [V(V)/V(IV)] and reductant [Fe(III)/Fe(II)] systems have been measured and based on the potentials data, the conditions needed in the titration has been explained. Based on the SIMUL hyperquade Computer programming, the nature of the species expected to be formed between Fe(III) and oxalate under the optimum conditions has been proposed. The interference of due to other ions has been studied.

Key Words: Vanadium(V), Iron(II), Buffer Medium Oxalate, Potentiometric and Visual methods, Oxazine dyes.

INTRODUCTION

A survey of literature reveals that a large number of methods have been reported for the determination of vanadium(V). These methods commonly utilize the reductants like iron(II) [1-4] [in dilute sulphuric acid or in a high concentration of orthophosphoric acid], iodide [1,2], sulphur dioxide [1-3], zinc or cadmium amalgam[2], chromium(II) [1,2] tin(II) [1,2],

titanium(III) [1,2], uranium(IV) [2], tungsten(V) [5], molybdenum(V) [2], copper(I) [2], mercury salts [1,2], ascorbic acid [1,2], hydrazine sulphate [2] etc.

However, no method is entirely satisfactory. For instance, the preparation and preservation of the conventional reductants (such as Cr(II), Sn(II), Ti(III), Cu(I) against atmospheric oxidation is a difficult task and need special storage apparatus. The methods developed employing the metal amalgam reductants (Zn & Cd) are tedious and time consuming. Some of the remaining methods are indirect in nature and must be carried out at elevated temperatures. In the method developed using iron(II) as a reductant in sulphuric and high phosphoric acid medium, number of metal ions interfere and high concentration of phosphoric acid makes the medium more viscous and the method expensive. Further, only a few redox indicators have been recommended in these methods.

We have now developed a convenient redoximetric titration method for the determination of vanadium(V) with iron(II) in buffer medium (pH 3.5 – 4.5) and in presence of oxalate. The new methods proposed obviate most of the disadvantages associated with the earlier methods. The end-point in these methods can be detected either potentiometrically or visually employing an oxazine dye as a redox indicator.

MATERIALS AND METHODS

Preparation of Solutions:

Vanadium(V) Solution: A 0.05M solution of vanadium(V) has been prepared from AR grade ammonium metavanadate (by boiling the solution with sodium carbonate) and the solution standardised³.

A 0.025M solution of vanadium(V) has also been prepared from the 0.05M solution by suitable dilution to be utilized in the visual methods.

Iron(II) Solution: A 0.05M solution of iron(II) has been prepared from AR grade ammonium iron(II) sulphate pentahydrate in 0.02N sulphuric acid medium and standardized⁶. From the solution a 0.025M solution has also been prepared by suitable dilution to be utilized in the visual end-point methods.

Hydrochloric Acid Solution: A 1N solution of hydrochloric acid is prepared from an AR grade acid.

Sodium Acetate Solution: A 1M solution of sodium acetate has been prepared from an AR grade sample.

Buffer Solutions: Buffer solutions of desired pH have been obtained by mixing suitable volumes of sodium acetate and hydrochloric acid solutions in a total volume of 50ml.⁷

Sodium Oxalate Solution: A 0.02M solution is prepared from an anhydrous AR grade sample.

Indicator solutions: 0.1% (W/V) aqueous solutions of the dyes Meldole's Blue (MLB), Gallamine Blue (GAB), Gallocyanine(GC), Celestin Blue (CLB) have been prepared.

Apparatus: A digital potentiometer has been utilized for potential measurements. A bright platinum electrode (0.2mm diameter) and a saturated calomel electrode have been used as indicator and reference electrodes respectively. The salt bridge consists of a 'U' tube with porous end glass plates and filled with a saturated KCl solution.

Recommended procedure:

To an aliquot (3 - 10ml) of vanadium(V) solution (0.05M) taken in a titration cell, 10ml of sodium acetate (1M) and about 10ml of sodium oxalate (0.2M) are added and the solution diluted to 50ml (pH of the solution 3.5 – 4.5). Purified nitrogen gas is passed for 3-4 minutes (to expel any dissolved oxygen). The contents are then titrated against iron(II) solution (0.05M) potentiometrically with the aid of a magnetic stirrer. The potential break at the end point is found to be 150-200mv for the addition of 0.05M iron(II) solution.

The procedure for the visual end-point method is the same excepting that a 0.025M solutions of vanadium(V) and a 0.025M solution of iron(II) made use of and the end point is detected employing an oxazine dye mentioned earlier as a redox indicator. The colour transitions of the indicators are sharp and reversible at the end point and these are from bluish violet to colourless with all the four indicators employed. No indicator correction need be applied in the titrations.

RESULTS AND DISCUSSION

Some of the typed results obtained by the recommended procedures have been shown in Table 1. The accuracy of the potentiometric method is + 0.4% while that of the visual end point method is found to be + 0.6%. The precision involved in both the methods have been assessed by computing the pooled standard deviation and 95% confidence limits as elucidated by skoog and west.⁸ These are included in the same Table.

Table-1:- Reductimetric Determination of Vanadium(V) with Iron (II)

Vanadium (V) Found*		Pooled standard deviation Sg, mg	1.96 x Sg √n mg	95% confidence limits x + 1.96 x Sg √n
Ref. Method ³ mg	Author's method x, mg			
A. Potentiometric Method				
7.65	7.62			7.58 to 7.66
11.48	11.44			11.40 to 11.48
15.30	15.36	0.05	0.04	15.32 to 15.40
19.13	19.20			19.16 to 19.24
20.40	20.32			20.28 to 20.26
25.50	25.58			25.54 to 25.62
B. Visual Method [Oxazine Dye as An Indicator]				
3.82	3.84			3.80 to 3.88
6.37	6.35			6.31 to 6.39
8.92	8.95	0.05	0.04	8.91 to 8.99
12.74	12.77			12.73 to 12.87

* Average of six determinations.

In both potentiometric and visual end-point methods vanadium(V) is rapidly and qualitatively reduced to vanadium(IV) by iron(II). At the end point all the four indicators employed have

been reduced to their corresponding colourless lenco-bases, as elucidated earlier⁹ in a two electron reduction step.

With a view to explain the conditions needed in the titration, the authors have determined the formal redox potentials of the oxidant system [V(V)/V(IV) Couple] and that of the reductant system [Fe(III)/Fe(II) couple] under the optimum conditions of the titration (i.e. in a pH medium of about 3.5 – 4.5 and in presence of about 0.04 M sodium oxalate) adopting the procedure of Conant and Fieser¹⁰. [Such type of observed potentials may be termed as conditional potentials]. The conditional potential of oxidant system [V(V)/V(IV) couple] has been found to be 570 mV+ 10mV; while that of the reductant system [Fe(III)/Fe(II) couple] is observed to be 110mV+ mV. From these potentials data it may be seen that there is a potential difference of about 460mV between the two systems facilitating the reduction of vanadium(V) by iron(II) under the experimental conditions.

Rao and Co-workers¹¹ are the earliest to report that iron(II) functions as a powerful reductant in a buffer oxalate medium. Later Murthy and Co-workers¹² initiated systematic investigations on the use of the reagent in analytical Chemistry. No doubt that iron(III) [rather than iron(II)] forms a strong complex with oxalate in the pH range 4-5, causing the decrease in the redox potential of iron system, thus enhancing the reducing ability of iron(II). The authors made an attempt to predict the nature of the complex expected to be formed between iron(III) and oxalate in the useful pH range of 4-5 through a computer programming known as SIMUL. Such an investigation revealed that tris-oxalate ferrate(III) are the predominant species formed in the region.

CONCLUSION

Among cations molybdenum(VI), uranium(VI), arsenic(V), tellurium(IV) & (VI), selenium(IV) & (VI) tungsten(VI) etc. do not interfere. Anions like chloride, nitrate, sulphate, acetate, perchlorate etc. do not interfere. But, nitrite ion interferes at all concentration.

REFERENCES

- [1] I.M. Kollhoff, R. Belchor, V.A. Stenger, and G. Matsugama, Volumetric Analysis-III, Titration methods: Oxidation-Reduction Reactions: Interscience publishers, Inc., Newyork, **1957**.
- [2] A. Berka, J. Vulterin, and J. Zyka, "Newer Redox Titrations" pergamon press, London, **1965**.
- [3] G.G. Rao, L.S.A. Dikshitulu, *Talanta*, **1963**, **10**, 295, 1023
- [4] K.V. Raju, G.D. Sudhakar, T.B. Patrudu, *Asian J. Chem*, **2007**, **19(1)**, 683.
- [5] A.R. Tourky, I.M. Issa and A.M. Doess, *Anal. Chem. Acta*, **1975**, **16**, 81.
- [6] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Ed. Longmans, London, **1961**, P.319.
- [7] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Theory and Practice, Longmans, London, 2nd Edn., **1951**, P.869.
- [8] D.A. Gkoog and D.M. West, "Analytical Chemistry" 3rd Ed., Holt Reinhart and Winston, **1978**, P.66.

- [9] K.V. Raju and G. Bangar Raju, *Analyst*, **1993**, **118**, P.101.
[10] J.B. Canont, and L.F. Fieser, *J. Am. Chem. Soc*, **1924**, **46**, 1858.
[11] G.G. Rao, N.V. Rao, *Talanta*, **1960**, **1**, 169.
[12] N.K. Murthy, Y.P. Rao and V.S. Narayana, *J. Ind. Chem. Soc.*, **1978**, **55**, 686.