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## ANALYTICAL APPLICATIONS OF THE PHOTOLYSIS OF IRON(III) OXALATE : POTENTIOMETRIC DETERMINATION OF VANADIUM(V) AND CHROMIUM(VI)

Y. ANJANEYULU\*, R. N. SARMA, L. N. MURTHY and (LATE) V. PANDURANGA RAO  
*Department of Chemistry, Nagarjuna University, Nagarjunanagar 522 510, India*

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A potentiometric method for the determination of vanadium(V) and chromium(VI) individually with oxalate using the photochemical reduction of iron(III) is described. The titrations can be best carried out in 0.5 to 3.0N acidity with respect to sulphuric acid with a minimum exposure time of 12-13 minutes. The concentration of iron(III) is found not critical as long as certain minimum is present. The molar stoichiometric ratio for the quantitative reduction of vanadium(V) and chromium(VI) with oxalate are found to be 1 : 1 and 1 : 3 respectively.

**Keywords :** Photochemical Reduction; Iron(III) Oxalate; Vanadium(V); Chromium (VI); Potentiometry

### INTRODUCTION

THOUGH oxalate cannot reduce vanadium(V) (West & Skoog 1955) or chromium(VI) (Bakore & Jain, 1969) in normal acidity, the reduction can be effected with oxalate by irradiating the reaction mixture in presence of iron(III). Visual titrimetric methods are reported by us elsewhere (Panduranga Rao *et al.*, 1981) for the determination of vanadium(V) and chromium(VI) with oxalate using photochemical reduction of iron(III) oxalate with ferroin as internal indicator. This paper presents the results of our investigations on the potentiometric determination of vanadium(V) and chromium(VI) individually with sodium oxalate in presence of iron(III) under exposure to light.

### MATERIALS AND METHODS

#### *Apparatus*

A sensitive Potentiometer set up consisting of a Toshniwal portable Potentiometer (model No. PL52) with a built-in galvanometer was used in all potentiometric titrations. A bright platinum rod immersed in the titration mixture and a saturated Calomel half cell were used as indicator and reference electrodes respectively. The two cells were connected by a saturated ammonium nitrate solution salt-bridge.

A Phillips high pressure mercury vapour lamp ('Repro' lamp), with a power consumption of 125W was used for irradiating the titration mixture. This light source

\*Author for correspondence.

was connected to the mains through a constant voltage (220 + 0.2 volts) transformer. The intensity of the light produced by this light source (measured by 'SURYAMAPI' light intensity meter supplied by Central Electronics Limited, India) at a distance of 100mm, was found to be 28 mw/cm<sup>2</sup>.

### *Reagents*

Standard solutions of vanadium(V) (0.1M), chromium(VI) (0.1N), sodium oxalate (0.1M) and iron(III) sulphate (0.5M) are prepared as described elsewhere (Vogel, 1962). These solutions are used after appropriate dilution. All other chemicals and acids used are of analytical grade.

### *Recommended Procedure*

To a measured volume (ranging in between 5–20ml) of 0.05N vanadium(V) or chromium(VI) taken in a clean 250ml pyrex beaker, 5ml of 0.05M iron(III) and 5ml of 10N sulphuric acid are added and the total volume is made up to 50ml with double distilled water. The above mixture is then titrated with 0.05M sodium oxalate, keeping the overall titration period for 15 minutes under exposure to light from Repro lamp. The variation of potentials of the system with each aliquot of sodium oxalate added is followed by a Potentiometer using a bright platinum rod as indicator electrode and saturated calomel electrode as reference electrodes.

## RESULTS AND DISCUSSION

When solutions of vanadium(V) or chromium(VI) are titrated individually with sodium oxalate in presence of iron(III) under the exposure of light from Repro lamp, it is observed that the iron(III) formed in the photochemical reduction of ferric oxalate is found to reduce vanadium(V) to vanadium(IV) or chromium(VI) to chromium(III). The change in the concentration of vanadium(V) or chromium(VI) with increasing concentration of oxalate can be followed potentiometrically. The optimum conditions for these potentiometric titrations are established by varying the concentrations of sulphuric acid, iron(III) and time of exposure. These experiments revealed that in both cases the titrations can be best carried out in between 0.5N to 3.0N acid medium with respect to sulphuric acid with a minimum exposure time of 12 to 13 minutes and the concentration of iron(III) is found not critical as long as certain minimum is present. A large number of potentiometric determinations of vanadium(V) and chromium(VI) are made following the recommended procedure and some typical results are presented in Table I. From Table I, it is evident that the quantitative reduction of vanadium(V) and chromium(VI) occurs when the molar stoichiometric ratios between oxalate and vanadate is 1 : 1 and oxalate and chromium(VI) is 3 : 1.

The potentiometric titration curves obtained at various acidities and various concentrations of iron(III) are shown in Figs. 1A and 1B for vanadium(V) and in Figs. 2A and 2B for chromium(VI). It can be seen from Figs. 1A and 2A that the potentials of the indicator electrode are not responding to the changes in concentrations of vanadium(V) and chromium(VI) when the acid concentration is above

TABLE I

*X ml of 0.05M sodium vanadate or 0.05N (0.0166M) dichromate + 5ml of 10N sulphuric acid + 5ml of 0.05M ferric alum solution + enough double distilled water to make the total volume to 50ml. Titrated with 0.05M sodium oxalate—keeping the reaction mixture under the light from 'Repro' lamp.*

Volume of oxidant taken (in ml)		Volume of oxalate consumed (in ml)		Volume of oxidant found (in ml)		Molar stoichiometric ratio Oxidant : Oxalate	
(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
1.00	1.00	1.02	1.02	1.02	1.02	1 : 1.0099	1 : 3.012
2.00	2.00	2.06	2.02	2.06	2.02	1 : 1.0019	1 : 3.012
5.00	5.00	5.05	5.02	5.05	5.02	1 : 1.002	1 : 3.012
10.00	10.00	10.12	10.04	10.12	10.04	1 : 1.002	1 : 3.012
15.00	15.00	15.20	15.04	15.20	15.04	1 : 1.0033	1 : 3.012

(A) = vanadate  
(B) = dichromate

Average molar stoichiometric ratio:  
vanadium(V) : oxalate = 1 : 1  
chromium(VI) : oxalate = 1 : 3

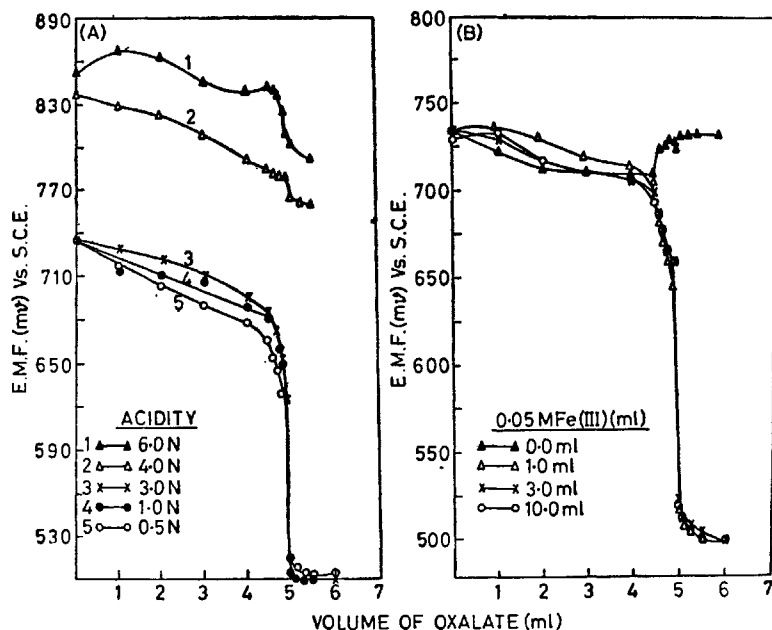


FIG. 1 (A)-(B)

3N. This may be attributed to the formation of an impervious film of platinum oxide at the surface of the platinum electrode as suggested by Smith and Brandt (Smith & Brandt, 1949). Figs. 1B and 2B curves indicate that in the absence of iron(III) the reduction of vanadium(V) or chromium(VI) do not take place even when

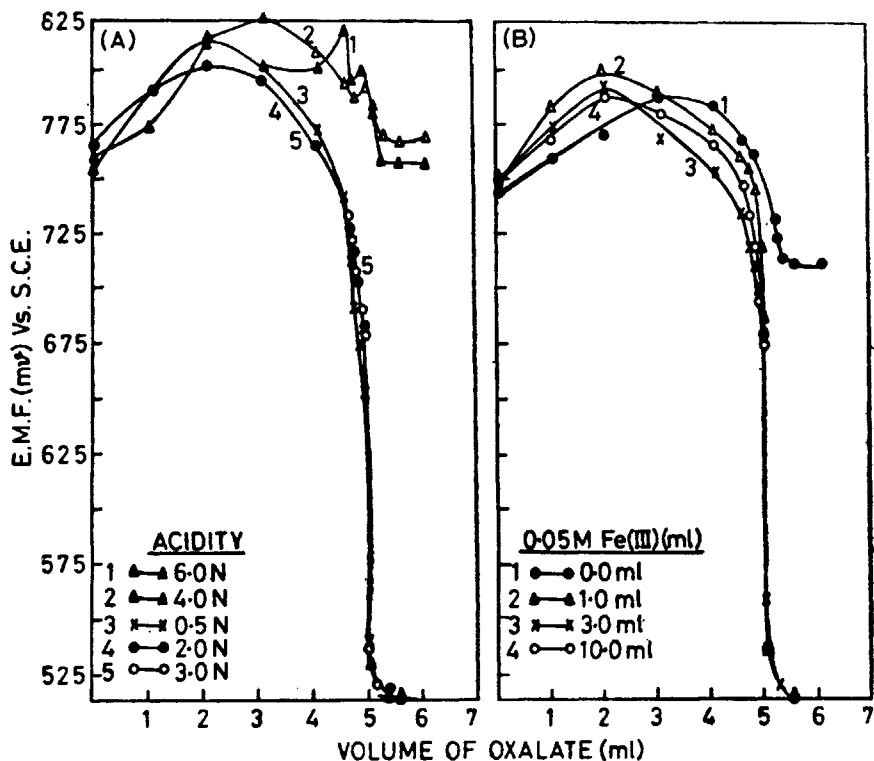


FIG. 2 (A)-(B)

large concentrations of oxalate are added. One interesting observation made in these titrations is that the potential increases initially from about 740 to 810mv and decreases gradually in the titration of chromium(VI) with oxalate while no such increase is seen in the case of vanadium(V). This may be due to the transitory formation of unusual oxidation states of chromium like Cr(IV) and Cr(V) which have a higher reduction potential than chromium(VI).

## REFERENCES

- Bakore, G. V., and Jain, C. L. (1969) *J. inorg nucl. Chem.*, 31, 805.  
 V. Panduranga Rao, Anjaneyulu, Y., and Sarma, R. N. (1981) (Communicated to *A. Z. anal. Chem.*).  
 Smith, G. F., and Brandt, W. W. (1949) *Anal. Chem.*, 21 948.  
 Vogel, A. I. (1962) *Text Book of Quantitative Inorganic Analysis*. ELBS, Longmans.  
 West, D. M., and Skoog, D. A. (1955). *Anal. Chim. Acta*, 12, 301