Die vorliegende Arbeit wurde im Anorganisch-Chemischen Institut der Technischen Universität Berlin durchgeführt. Wir danken dem Direktor des Instituts, Herrn Prof. Dr. G. JANDER, für Unterstützung und Diskussion und der Deutschen Forschungsgemeinschaft sowie dem Bundesatomministerium für die Bereitstellung von Mitteln und Apparaten. — Die Arbeiten werden fortgesetzt.

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Colorimetric Titration of Vanadium with Alkaline Ferricyanide

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(Received January 27, 1959)

The volumetric procedures for the quantitative determination of vanadium are numerous, more convenient and less influenced by interfering elements than the gravimetric methods. FURMAN[2] treated vanadic acid with ferrous sulphate using diphenylamine indicator, while WILLARD and YOUNG[7] preferred diphenylbenzidine owing to its negligible indicator correction. In the electrometric titration, vanadate is treated with titanous chloride or chromous chloride[3]. Quantitative conversion of V^V to V^{IV} with Mo^V[5] in acid medium, and with iodine[4] in neutral, alkaline or acid medium, has also been utilised in the determination of vanadium.

Titration of vanadyl salt solution with a standard oxidant like permanganate at a slightly elevated temperature is perhaps the most common and convenient method of vanadium estimation[6]. Oxidation of V^{IV} with potassium ferricyanide has also been carried out using an electrometric end point[1].

In the following investigation vanadium has been estimated by oxidising the blue vanadyl salt to the pentavalent state by alkaline potassium ferricyanide. When the vanadyl solution is gradually added to the yellow solution of potassium ferricyanide, the intensity of the yellow colour decreases, until at the end point the solution becomes colourless. This gradual disappearance of the yellow colour has been utilised for the colorimetric determination of vanadium.

Experimental

Vanadyl sulphate was obtained by the reduction of vanadium pentoxide (B.D.H. reagent) by H_2S. Weighed quantity of vanadium pentoxide was mixed with nearly equal amount of sodium carbonate and this was extracted with acidulated (H_2SO_4) water. H_2S was passed through this solution till it had a uniform blue colour indicating the complete reduction of pentavalent vanadium to the tetravalent state. Excess of H_2S was then boiled off and the vanadyl sulphate solution thus obtained was standardised against a standard permanganate solution.

Table 1. *Change of Transmittance of Ferricyanide Solution with the Addition of Vanadyl Sulphate Solution*

0.0258 g of ferricyanide, 1 ml of $25^0/_0$ NaOH solution and 7 ml of water

Amount of vanadyl sulphate soln. (0.0196 M) ml	Density scale reading
0	0.200
0.24	0.215
0.53	0.233
1.08	0.283
1.54	0.338
1.73	0.373
1.80	0.411
1.92	0.421
1.96	0.429
2.00 Equi. point	0.437
2.04	0.433
2.09	0.429

Potassium ferricyanide solution was prepared from recrystallised samples and was made up to the volume with NaOH solution.

The colorimetric titration was carried out with the aid of a Hilger Spekker Absorptiometer (model H 760) using a blue filter having maximum transmission in the range of 450—500 mμ. Aliquots of alkaline ferricyanide solution were taken in the 20 ml pyrex glass cell and the density scale reading was adjusted at a minimum. As vanadyl sulphate solution was introduced in the cell through a caliberated micro-burette, the transmittance gradually increased and became maximum at the equivalence point (Table 1). Varying amounts of ferricyanide solution of known strength were thus titrated with vanadyl sulphate solution. A few of the typical readings are returned in Table 2.

Table 2. *Colorimetric Titration of Alcaline Ferricyanide with Vanadyl Sulphate*

Blue filter — maximum transmission 450—500 mμ

Alkali concentration %	Amount of ferricyanide taken g	Volume of vanadyl sulphate soln. ml	Amount of vanadium		Difference g
			Calculated g	found g	
0.5	0.0200	1.58	0.003100	0.003160	+ 0.00006
2.0	0.0258	2.00	0.003999	0.003999	nil.
2.5	0.0129	0.96	0.0019995	0.0019995	nil.
4.0	0.0500	1.36	0.007750	0.007630	—0.00012
7.0	0.0129	1.01	0.0019995	0.0020195	+ 0.00002
8.0	0.0450	2.92	0.006980	0.006950	—0.00003

Discussion

The reaction between alkaline ferricyanide and vanadyl ion is quantitative and proceeds as follows:

$$2\,Fe(CN)_6^{3-} + V_2O_2^{4+} + 12\,OH^- \rightarrow 2\,VO_4^{3-} + 2\,Fe(CN)_6^{4-} + 6\,H_2O.$$

This indicates that 2 molecules of ferricyanide are equivalent to one of vanadyl salt. The calculated titre values based on this assumption tallied favourably with the experimental observations (cf. Table 2). It is seen that as small as 0.5 mg per milliliter of vanadium and 1—2 mg per milliliter of ferricyanide may be titrated with a maximum error of 2.5%. Column 1 in Table 2 also shows that a variation of the alkali concentration over a wide range does not affect the accuracy of the results adversely.

Out of the two ways of titrations i.e., that of ferricyanide with vanadium and vice versa, the former was smooth and quantitative. The reverse process in which ferricyanide was added to V^{4+}, the results were not trustworthy owing to the instability of the tetravalent vanadium in presence of alkali.

Summary

The gradual disappearance of the yellow colour of ferricyanide with the addition of vanadyl ions in alkaline medium has been made the basis of the quantitative determination of both vanadium and ferricyanide. The colorimetric titrations were carried out with the aid of a Hilger Spekker Absorptiometer with a blue filter having maximum transmission in the range of 450—500 mμ. It is shown that the accuracy of the results compares favourably with those obtained by other standard procedures.

Acknowledgement. Sincere thanks of the author are due to Prof. S. S. JOSHI, D. Sc. (London) and Dr. G. S. DESHMUKH, D. Sc. for facilities and kind interest in the work.

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