A Redox Titration of Vanadium(IV), Hypochlorite, Hypobromite and a Mixture of Vanadium(IV) and Vanadium(V)

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Vanadium(IV) in an alkaline solution can be rapidly and quantitatively oxidised to vanadium(V) in an inert atmosphere by the use of a hypochlorite or hypobromite solution. This forms the basis of the methods of the determination of vanadium(IV), hypochlorite and hypobromite to be described in the present paper.

To an alkaline solution of vanadium(IV) sulphate, a known excess of a standardised hypohalite solution is added. After destroying the excess with a known amount of arsenic(III) oxide solution, the excess of arsenic(III) is finally determined by titration with a hypohalite solution, using methyl red as the indicator. For determining the amount of hypohalite, its known volume is added to an excess of a vanadium(IV) solution in the presence of alkali; then the vanadium(V) so formed is titrated with iron(II) sulphate, using *N*-phenylanthranilic acid as the indicator. These methods have the advantage that the reactions are rapid at room temperature, and the excess of the oxidising solution in the determination of vanadium(IV) is easily and completely removed. However, all the titrations must be carried out in an atmosphere of purified nitrogen, since the auto-oxidation of vanadium(IV) is serious in an alkaline medium. A method for the determination of vanadium(IV) and vanadium(V) mixtures is also suggested.

Experimental and Results

Reagents.—All the chemicals used were products of the British Drug House (B. D. H.), Analar (A. R.) or of the E. Merck Company.

The Vanadium(IV) Sulphate Solution.—Prepare an approximately 0.05 M solution containing 0.05 M sulphuric acid and standardise against permanganate at about 80°C.

The Hypochlorite and Hypobromite Solutions.—Prepare approximately 0.05 M solutions as described by Erdey and Vigh[1] and standardise iodometrically.

The Arsenic(III) Oxide Solution.—Prepare a 0.25 M solution.

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1) L. Erdey and K. Vigh, *Talanta,* **10,** 439 (1963).

The Procedure for the Determination of Vanadium(IV) with Hypochlorite of Hypobromite.—Place 5 to 10 ml. of a vanadium(IV) sulphate solution in a titration vessel, bubble nitrogen in for about 10 min., and add 5 to 10 ml. of 4 M sodium hydroxide and 5 to 10 ml. of the previously-standardised hypochlorite or hypobromite solution. When the solution becomes almost colourless (after 2—3 min.), add 5 to 10 ml. of a 0.05 M arsenic(III) oxide solution. Add 10 ml. of 6 M hydrochloric acid and 1—2 drops of methyl red indicator, and titrate the excess of arsenic(III) with the hypochlorite or hypobromite solution. A few results are recorded in Table I.

TABLE I. DETERMINATION OF VANADIUM(IV) (V^{IV}—V^{V} change)

Amount of vanadium(IV), mmol. Taken	Found	% Error
0.5070	0.5039	−0.61
0.5070	0.5077	+0.14
0.5320	0.5350	+0.56
0.5750	0.5740	−0.17

The Procedure for the Determination of Hypochlorite or Hypobromite.—Place about 10 ml. of a vanadium(IV) sulphate solution in a titration vessel, bubble nitrogen in for about 10 min., and add about 5 ml. of 4 M sodium hydroxide and 2 to 5 ml. of the hypochlorite or hypobromite solution. After 2 to 3 min., add 30 ml. of 6 M sulphuric acid and titrate the vanadium(V) with iron(II) sulphate, using *N*-phenylanthranilic acid as the visual indicator. A few results are given in Table II.

TABLE II. DETERMINATION OF HYPOCHLORITE AND HYPOBROMITE

Oxidising agent		Found by procedure described mmol.	Found iodometrically mmol.	% Error
Hypochlorite	(i)	0.2522	0.2520	+0.08
	(ii)	0.2515	0.2520	−0.12
	(iii)	0.2044	0.2038	+0.24
Hypobromite	(i)	0.0566	0.0567	+0.17
	(ii)	0.1690	0.1688	+0.11
	(iii)	0.1917	0.1910	+0.37

The Procedure for the Determination of Vanadium(IV) and Vanadium(V) in a Mixture.—For the determination of vanadium(IV) in the mixture, follow the procedure described earlier. In another aliquot, acidify the mixture with 6 M sulphuric acid to make the overall acidity about 3 M, and then titrate the vanadium(V) with iron(II) sulphate. A few results are given in Table III.

Tables I to III show that, in the concentration ranges from 0.2780 to 0.5750 mmol. of vanadium(IV) and 0.0567 to 0.2522 mmol. of hypohalites, the accuracy of the present method is ±0.6% and ±0.4% respectively. The variation co-efficient is ±0.15%.

The Effects of Foreign Substances.—The determination of vanadium(IV) is subject to interference by even a small amount of ammonia, urea, sulphide, thiosulphate, tetrathionate and hydrogen peroxide, whereas in the determination of hypochlorite and hypobromite, cerium(IV), chromium(VI), vanadium(V), etc., which are reduced by iron(II), interfere.

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TABLE III. DETERMINATION OF MIXTURES OF VANADIUM(IV) AND VANADIUM(V)

Amount of vanadium(IV) mmol.		Amount of vanadium(V) mmol.		% Error	
Taken	Found	Taken	Found	V(IV)	V(V)
0.2780	0.2778 (i)	0.7190	0.7190	−0.07	0.00
0.2780	0.2778 (ii)	0.5752	0.5763	−0.07	+0.19
0.2875	0.2865 (iii)	0.2738	0.2738	−0.35	0.00
0.2875	0.2865 (iv)	0.1369	0.1369	−0.35	0.00
0.5750	0.5783 (v)	0.1369	0.1369	+0.57	0.00