

spots were located by their fluorescence. For both *M. canis* and *M. gypsum*, a single spot was obtained with R_F values in the two solvents of 0.79-0.83 and 0.67-0.71 respectively. These findings would indicate that the fluorescent pigments of the two species of fungi are identical.

The fluorescence spectra of methanol extracts of *M. canis* and *M. gypsum* were studied with a model DU Beckman spectrophotometer modified by having the sample tube in the position of the usual light source. Excitation was provided by a General Electric 100-watt mercury lamp, type S-4. Fluorescence maxima for both species were found at 455-460 m μ , a value which differs considerably from that reported by Bereston and Crosswhite⁸.

The properties of the fluorescent pigment produced by *M. canis* and *M. gypsum* indicate that it is a pteridine. Efforts to identify it with a known pteridine have been unsuccessful.

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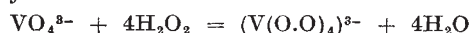
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Complexity of the Vanadium - Hydrogen Peroxide System

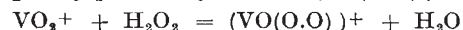
THE reaction of quinquevalent vanadium with hydrogen peroxide, which is a well-known spot test¹ and the basis of a colorimetric² and volumetric³ method for the estimation of vanadium, becomes rather complex on closer inspection. Depending upon concentrations and temperature of the reactants, this reaction can lead to four distinctly different forms.

(1) In alkaline solutions, concentrated in vanadium and hydrogen peroxide, the blue-violet tetraperoxy-orthovanadate ions^{4,5} are formed in the cold relatively slowly:



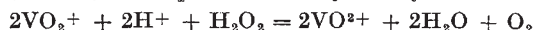
(2) An intermediate formed instantly in the above reaction is the yellow diperoxy-orthovanadate ion, $(\text{VO}_2(\text{O.O})_2)^{3-}$, which is stable in dilute, weakly alkaline to weakly acidic solutions of alkalinates⁶.

(3) In acidic solutions, the pale yellow pervanadyl ion⁶⁻⁸, VO_2^+ , instantly forms the deep red-brown monoperoxy-pervanadyl cation, $(\text{VO}(\text{O.O})^+)$:



forms (2) and (3) being related by the equilibrium: $(\text{VO}_2(\text{O.O})_2)^{3-} + 4\text{H}^+ = (\text{VO}(\text{O.O})^+) + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$

(4) In strongly acidic solutions, on the other hand, a reduction^{3,9} to the blue quadrivalent vanadyl ion, VO^{2+} , takes place relatively slowly:



the red-brown $(\text{VO}(\text{O.O})^+)$ ions being formed instantly as an intermediate. The reduction occurs quantitatively and within a few minutes in concentrated sulphuric acid, and more slowly in 72 per cent sulphuric acid, or 72 per cent perchloric acid. It can be seen from Fig. 1 that heating up to 81°C. does not interfere with the quantitiveness of reduction. In dilute acidic solutions, reduction occurs considerably more slowly and is no longer quantitative, solutions in nitric acid showing less readiness to undergo reduction than those in sulphuric or perchloric acids of corresponding strengths.

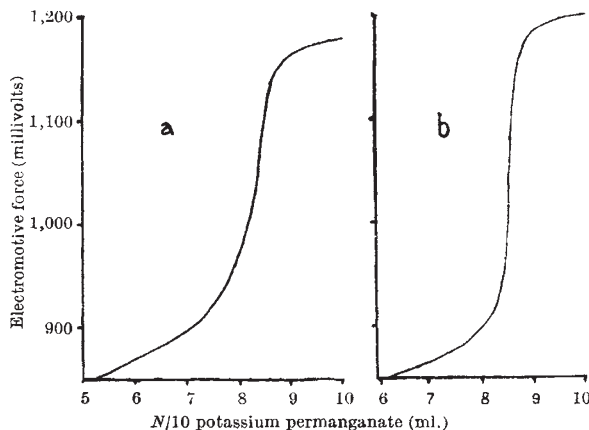


Fig. 1. Oxidation curves of VO_2^+ solutions with $N/10$ potassium permanganate after reduction with hydrogen peroxide (a) at 21°C and (b) at 81°C. 0-1000 gm. ammonium vanadate was dissolved in 30 ml. 72 per cent sulphuric acid (w/w) in each case

When reversing the order of mixing, that is, first dissolving the vanadium (V_2O_5 , or NH_4VO_3) in hydrogen peroxide (100 per cent by volume) and then acidifying the ensuing yellow solution of $(\text{VO}_2(\text{O.O})_2)^{3-}$ relatively slowly with concentrated sulphuric acid, a reduction to the blue VO^{2+} ion occurs quantitatively within a few minutes. We therefore recommend this procedure as basis of a selective method for the volumetric determination of vanadium.

It is evident from this review of the vanadium-hydrogen peroxide system that a colorimetric estimation of vanadium will require a low concentration of hydrogen peroxide, medium to low acidity (nitric acid in preference to sulphuric or perchloric acid), and a relatively low temperature. Similar considerations would apply to the spot test technique.

Detailed results of our investigation will be published elsewhere. We wish to acknowledge financial assistance from the British Cotton and Wool Dyers' Association and aid in apparatus from Imperial Chemical Industries, Ltd., Blackley.

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