The Spectrophotometric Determination of Vanadium(IV) with Xylenol Orange

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Xylenol orange, in a slightly acidic medium, reacts with vanadyl ion to ~~give a~~ reddish violet complex, and it has widely been used as a metal indicator for vanadium in EDTA titration. Recently this laboratory needed a sensitive method for determining trace amounts of vanadium in uranium compounds. This paper describes the results of a spectrophotometric study of the vanadium-xylenol orange complex and of the application of this reagent to the determination of trace amounts of vanadium. The composition of the colored complex and methods for the elimination of some interfering substances are also discussed.

Experimental

Apparatus.—All absorbance measurements were made with a Hitachi Model EPU-2A spectrophotometer, using 1-cm. cells.

Reagents.—*Vanadyl Chloride Stock Solution.*—Pure vanadium pentoxide was treated with concentrated hydrochloric acid and redistilled ethyl alcohol[2]. The solution was standardized against a standard EDTA solution, using EBT as an indicator[3].

Xylenol Orange Solution.—The same as that used in a previous work[1].

Procedure.—Transfer a sample aliquot, containing 10 to 40 μg. of vanadium, to a 25 ml. Erlenmeyer flask. Add 1 ml. of 5% ascorbic acid and 2 ml. of a xylenol orange solution. Adjust the pH value to 2.8 ± 0.1 with an acetate buffer solution. Mix, and heat the solution on a boiling water bath for 2 to 3 min. Cool the solution, transfer it to a 25 ml. volumetric flask, and dilute it to the mark with small amounts of distilled water. Measure the absorbance of the solution at 562 mμ vs. a reagent blank.

Results and Discussion

Absorption Spectra.—The spectra of xylenol orange and its vanadium(IV) complex are shown in Fig. 1. The maximum absorption of the complex is found at 562 mμ.

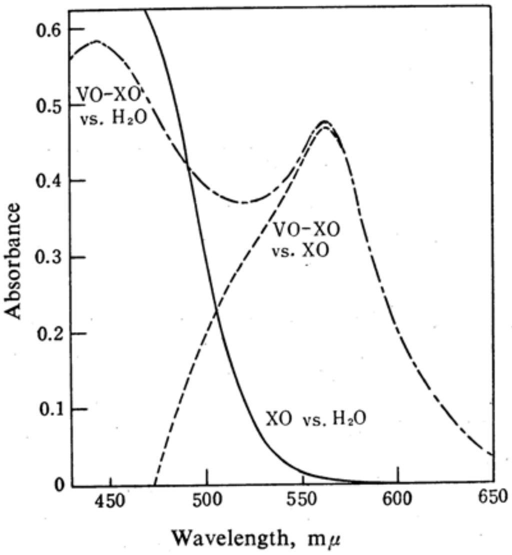

Fig. 1. Absorption spectra of xylenol orange and its vanadium complex.

V: 2×10^{-5} M XO: 9×10^{-5} M

Effect of the pH Value. — Figure 2 shows that the optimum pH value range for the color formation of the vanadium-xylenol orange complex is 2.8 ± 0.1.

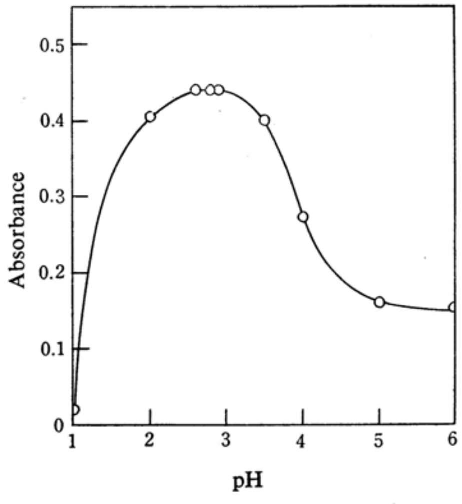

Fig. 2. Effect of pH on color development.

V: 24 μg.

Effect of the Addition of Xylenol Orange.—As is shown in Fig. 3, the absorbance gradually

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[1] K. Tonosaki and M. Otomo, This Bulletin, 35, 1683 (1962).

[2] T. Chitani, "Muki Kagaku (Inorganic Chemistry)" (In Japanese), Sangyo Tosho, Tokyo (1954), p. 497.

[3] K. Ueno, "KiretoTekitei (Chelatometric Titration)" (In Japanese), Nankodo, Tokyo (1960), p. 323.

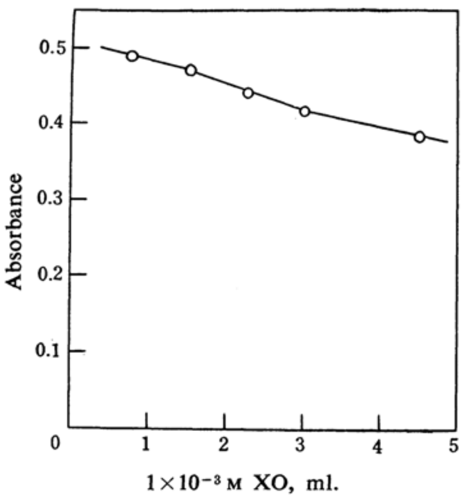

Fig. 3. Effect of addition of xylenol orange.
V: 24 μg.

decreases with the presence of increasing amounts of xylenol orange. However, the use of 1.5ml. of a 1×10^{-3} M xylenol orange solution is recommended for further experiments.

Effect of the Amount of Ascorbic Acid.—Ascorbic acid was used to prevent oxidation of the vanadyl ions to a vanadic state. It is suitable to add 0.2 to 1.5 ml. of a 5% ascorbic acid solution for less than 50 μg. of vanadium.

Effect of the Time of Standing.—Figure 4 shows the curves for the heated and the unheated solutions of the vanadium-xylenol orange complex. Curve I indicates that, for the unheated solution, it requires about 2 hr. for the complete color developement. However, the color formation is greatly accerelated by heating a mixture of vanadium and a xylenol orange solution on a boiling water bath for only 2 to 3 min. The color produced is stable for at least 24 hr.

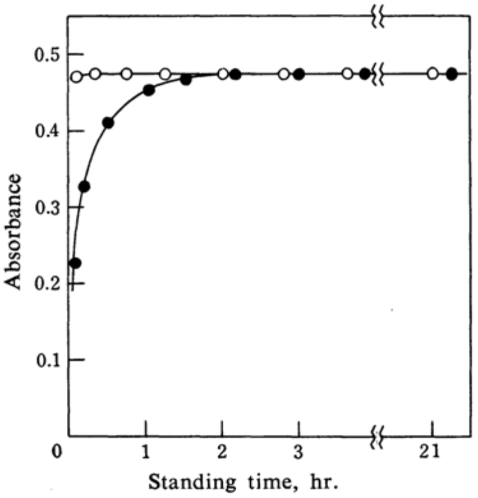

Fig. 4. Effect of time of standing.

V : 24 μg.
-●- : Unheated solution (I)
-○- : Solution heated on a water-bath (II)

Calibration Curve.—A linear concentration-absorbance relationship is obtained in the range between 10 to 40 μg. of vanadium (curve I in Fig. 5). The molar extinction coefficient of the vanadium xylenol orange complex is found to be 24000 at 562 mμ.

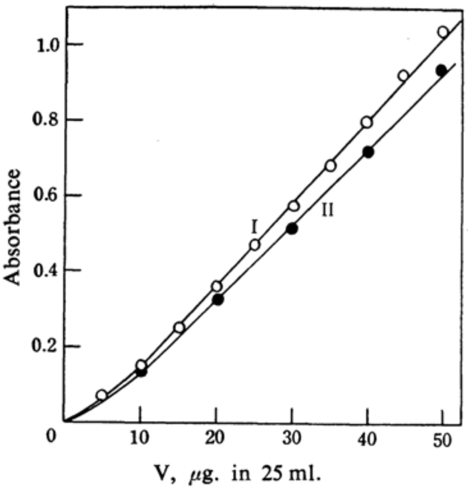

Fig. 5. Calibration curve.

I : In the absence of fluoride
II : In the presence of 50 μmol. of fluoride

Effect of Anions.—No interference is caused by chloride, nitrate, sulfate, thiosulfate, phosphate or tartrate under the conditions studied. As might be expected, such anion as oxalate, citrate, NTA (nitrilotriacetate) and EDTA (ethylenediaminetetraacetate), especially the last two, inhibit the color for mation of the vanadium-xylenol orange complex. A large amount of fluoride also decreases the absorbance moderately. If 1 ml. of a 0.4% fluoride solution is used for masking some interfering cations, the same amount of fluoride must be added in preparing the calibration curve (curve II in Fig. 5).

Effect of Cations.—The effect of foreign elements was studied by preparing solutions containing 0.5 μmol. of vanadium and the same amount of various cations. The results of these tests are presented in Table I. The cations, aluminum(III), bismuth(III), chromium(III), tin(II), thorium(IV), titanium(IV), yttrium(III) and zirconium(IV), form a colored complexes with xylenol orange to give a positive error in the determination of vanadium. Some of these cations, however, can be completely or partially masked by adding 1 ml. of a 0.4% fluoride solution (Table II). Interference from

TABLE I. EFFECT OF CATIONS ON DETERMINATION OF VANADIUM

Vanadium taken, 25 μg. (0.5 μmol.)

Cations added	Vanadium found μg.
Aluminum(III)	59.8
Barium(II)	24.9
Beryllium(II)	25.4
Bismuth(III)	52.2
Calcium(II)	25.0
Cadmium(II)	25.0
Cerium(III)	25.2
Cobalt(II)	25.1
Chromium(III)	29.8
Copper(II)	24.7
Iron(III)	25.2
Magnesium(II)	24.9
Manganese(II)	25.0
Nickel(II)	25.2
Lead(II)	25.0
Tin(II)	37.3
Strontium(II)	25.0
Thorium(IV)	72.3
Titanium(IV)	38.2
Thallium(III)	25.0
Uranium(VI)	25.4
Yttrium(III)	26.4
Zinc(II)	25.0
Zirconium(IV)	78.8

TABLE II. MASKING ETFECT OF FLUORIDE ON DETERMINATION OF VANADIUM

Vanadium taken, 25 μg. (0.5 μmol.)
Cations added, each 0.5 μmol.
0.4% solution of fluoride added, 1 ml.

Cation	Vanadium found μg.
Aluminum(III)	25.0
Beryllium(II)	25.0
Bismuth(III)	52.3
Chromium(III)	27.3
Tin(II)	27.6
Thorium(IV)	25.0
Titanium(IV)	24.7
Uranium(VI)	25.0
Yttrium(III)	24.8
Zirconium(IV)	25.3

bismuth can also be eliminated by adding thiosulfate. Interference from tin(II) can be avoided by oxidizing it to a stannic state and by adding fluoride before treatment by the recommended procedure*.

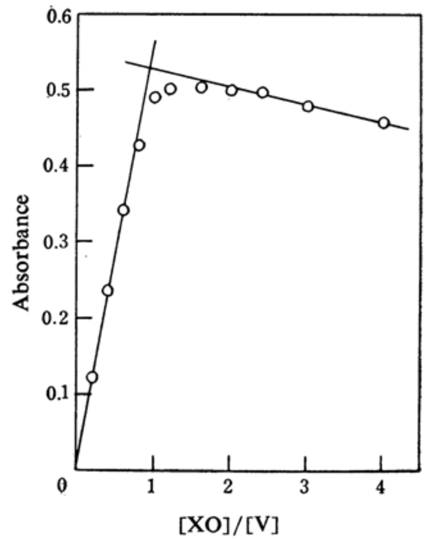

Fig. 6. Mole ratio method.
V: 24 μg.

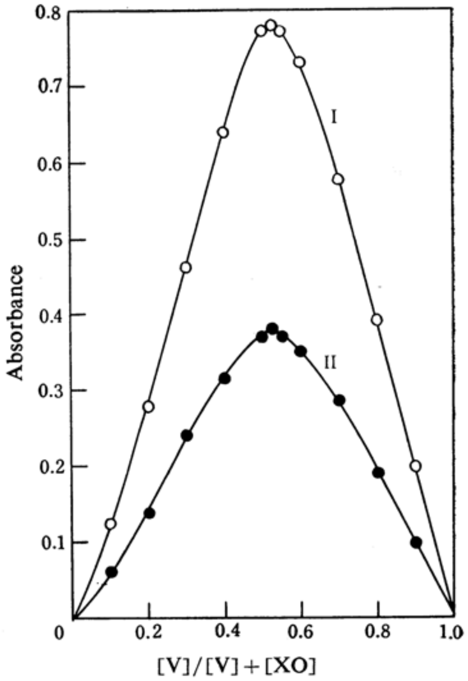

Fig. 7. Continuous variation method.
I: $[V]+[XO]=9.4\times10^{-5}$ M
II: $[V]+[XO]=4.7\times10^{-5}$ M

Complex Formation.—The mole ratio and the formation constant of the vanadium-xylenol orange complex was determined spectrophotometrically by the same method as that previously reported for the rare earth complex of xylenol orange[1] (Figs. 6 and 7). It is evident that vanadium(IV), like cerium(III) and other rare earths, forms a 1 : 1 complex with xylenol orange. The formation constant for the

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* As the tin(IV)-fluoride complex is very stable, it is not reduced by zinc or aluminum[4].

4) K. Sone and M. Tanaka "Teisei Bunsekikagaku" Transttd., Charlot, "L'Analyse Qualitative et lesRéaction en Solution" (In Japanese), Kyoritsu Shuppan, Tokyo (1958), p. 333.

complex at a pH value of 2.9 was calculated, from the curves shown in Fig. 7, as 2.8×10^6. It is expected that this dye will find many applications where a highly sensitive reaction for vanadium is desired.

Summary

The reddish-violet complex of vanadium with xylenol orange has been studied spectrophotometrically, and the conditions for using xylenol orange as a reagent for the determination of trace amounts of vanadium have been established. The complex shows a maximum absorption at 562 mμ, and the molar extinction coefficient of the complex is found to be 24000. It is a 1 : 1 complex and has a formation constant of 2.8×10^6 under the conditions studied. Such anions as oxalate, citrate and EDTA inhibit the color formation of the complex. Some of the interfering cations can, however, be completely or partially masked by adding a fluoride solution.

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