The Spectrophotometric Determination of Titanium with Hydrogen Peroxide and Xylenol Orange[1]

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(Received June 18, 1963)

The yellow complex of titanium-hydrogen peroxide has been widely used for the spectrophotometric determination of titanium.[2-4] By treatment of the complex with EDTA, Sweeter and Bricker[5] found a new complex, the absorption spectrum of which differed from that of titanium-hydrogen peroxide. Recently Musya and Ogawa[6] applied the above reaction to the spectrophotometric determination of titanium and clarified the composition of the

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[1] This work was presented at the Tohoku Branch Meeting of the Chemical Society of Japan, Hirosaki, October, 1962.

[2] A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 695 (1945).

[3] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., Inc., New York (1949), p. 423.

[4] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York (1950), p. 572.

[5] P. B. Sweeter and C. E. Bricker, *Anal. Chem.*, **26**, 196 (1954).

[6] S. Musya and K. Ogawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1686 (1957).

new complex. No workers, however, have yet applied such a reaction to the spectrophotometric determination of metals with xylenol orange in the presence of a "third reactant."

The present author has dealt with a number of metal chelates of xylenol orange and has found that, upon the addition of the third reactants, most of these chelates do not produce any new complex which is useful for the spectrophotometric determination of the corresponding metals. When, however, titanium(IV) salt is treated with xylenol orange in the presence of hydrogen peroxide, a new, red complex with an absorption maximum at about 535 mμ is formed. This study was undertaken to determine the conditions under which up to 70 μg. of titanium could be determined spectrophotometrically and to ascertain the composition of the new chelate by means of appropriate spectrophotometric techniques.

Experimental

Reagents and Apparatus.—The solutions of titanium and xylenol orange and the spectrophotometer used were the same as those reported on previously.[7]

A solution of hydrogen peroxide was used after standardizing it as usual against a standard solution of potassium permanganate. Perchloric acid was used for all acidity adjustments because of its low complexing action.

All experiments were carried out at 25±0.5°C.

Standard Procedure for the Determination of Titanium.—To a 25 ml. volumetric flask containing up to 70 μg. of titanium, 0.2 to 5 ml. of a 0.3% solution of hydrogen peroxide, 3.5 to 6 ml. of a 1×10^{-3} M solution of xylenol orange, and 2 to 3 ml. of a 0.5 N solution of perchloric acid were added. The solution was diluted to the mark with water, mixed, and allowed to stand for about 15 min. The absorbance of the solution was then measured at 532 mμ against a solution containing the same amounts of hydrogen peroxide, xylenol orange and perchloric acid.

Results and Discussion

Absorption Spectra.—The absorption spectrum of the titanium-hydrogen peroxide-xylenol orange complex is greatly affected in its shape by the concentration of perchloric acid and also by the amount of hydrogen peroxide and xylenol orange. Under the conditions described above, however, a reproducible spectrum with an absorption maximum at about 532 mμ* was obtained. The spectra thus obtained are shown in Fig. 1.

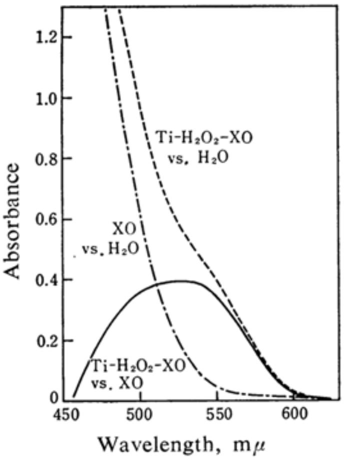

Fig. 1. Absorption spectra.
Ti : 32.4 μg., H_2O_2 : 0.3% soln. 1ml., XO : 1.65×10^{-4} M, $HClO_4$: 0.05 M

The Effect of Acidity.—A choice of perchloric acid concentration is quite significant, for the absorption maximum and also the stability of the color are greatly affected by the concentration of perchloric acid. A series of solutions containing 23.2 μg. of titanium, 3.3 ml. of a 1×10^{-3} M solution of xylenol orange, and varying amounts of perchloric acid were prepared. The results obtained will be summarized in the following three sections.

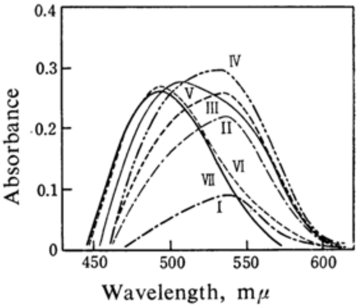

Fig. 2. Effect of acidity on the spectra of the Ti-H_2O_2-XO complex.
Ti : 23.2 μg., H_2O_2 : 0.3% soln. 5ml., XO : 1.32×10^{-4} M, $HClO_4$ concn. : I ; 0.174 M, II ; 0.116 M, III ; 0.078 M. IV ; 0.06~0.04 M, V ; 0.029 M, pH : VI ; 4.0, VII ; 4.5~5.0

The Relationship between Acid Concentration and Absorption Spectra.—Figure 2 shows the effect on the absortion spectra of the concentration of perchloric acid added to the solution containing titanium, hydrogen peroxide and xylenol orange. From the inspection of the curves, it is found that, depending on the concentration of perchloric acid two different absorbing species can subsequently be formed; one of them, which is formed in the considerably high acidic region, has an absorption

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[7] M. Otomo, This Bulletin, to be published.

* The absorption maximum shifts subsequently to 535 mμ with the increasing amount of titanium.

maximum at 535 mμ, while the other, which is formed in the slightly acidic region, has an absorption maximum at 495 mμ. In the practical spectrophotometric determination of titanium, the former complex was used; thereby not only could the hydrolysis of titanium be prevented, but also the interference of other cations could be conveniently reduced.

Maximum Color Development.—The reaction is not as rapid as the speed (about 15 min.) required for maximum color development. Figure 3 shows that the maximum absorbance is obtained over the perchloric acid concentration range 0.04 to 0.06 N.

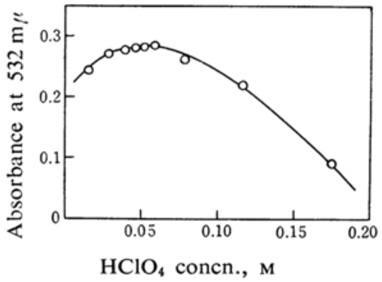

Fig. 3. Effect of acidity.
Ti: 23.2 μg, H_2O_2: 0.3% soln. 5ml.,
XO: 1.32×10^{-4} M

The Relationship between Acid Concentration and Color Stabiliy.—The stability of the color increases with the perchloric acid concentration. In solutions at low concentrations of perchloric acid, the absorbance of the colored solution decreases slowly with time, probably because of the hydrolysis of titanium. In solutions at high acidities, the color is stable for a long period, but the color development is not complete. When, however, the perchloric acid concentration was kept at 0.04 to 0.06 N, the absorbance of the solution remained constant for several ten minutes.

The Effect of the Amount of Hydrogen Peroxide.—It was found that the amount of hydrogen peroxide considerably affects the position of the absorption maximum and the stability of the color. These relations are summarized in Table I. The maximum and constant absorbance is obtained when 0.2 to 5 ml. of a 0.3% solution of hydrogen peroxide is added. Under these conditions, an absorption maximum is found at 532 mμ and the absorbance of the solution remains constant for about 30 min. When a too small amount of hydrogen peroxide is added, the color is indeed stable for a long period, but too low an absorbance is obtained. With a large amount of hydrogen peroxide, on the other hand, a relatively higher absorbance is obtained, but the color becomes somewhat unstable.

TABLE I. EFFECT OF AMOUNT OF HYDROGEN PEROXIDE

Titanium taken, 23.2 μg.
Xylenol orange, 1.65×10^{-4} M
Perchloric acid, 0.05 N

H_2O_2 added	ml.	Absorption maximum mμ	Absorbance at absorption maximum	Period of time min.*
0.03%,	0.1	520	0.221	30∼ >80
	0.25	525	0.254	20∼>100
0.3%,	0.1	525	0.274	20∼>100
	0.25	532	0.282	15∼ >45
	1	532	0.284	15∼50
	5	535	0.282	15∼50
3%,	1	535	0.275	20∼50
	3	535	0.271	20∼50
	5	535	0.263	20∼50
	8	535	0.265	10∼30

* In which the absorbance of the colored solutions being kept constant.

The Effect of the Addition of Xylenol Orange.—The maximum color development was obtained when 3.5 to 6 ml. of a 1×10^{-3} M solution of xylenol orange was used. Under these conditions, no visual shift in the position of the absorption maximum was observed.

The Order of the Addition of Reagents.—Varying the order in which the reagents were added had no significant effect on the results. In all cases, the color was completely developed within 15 min.

Beer's Law.—As is shown in Fig. 4, the calibration plot obeys Beer's law over the concentration range investigated, 7 to 70 μg. of titanium. The molar extinction coefficient is found to be 15000 at 532 mμ and the sensitivity, 0.003 μg. per cm². This sensitivity is comparable with that of the thymol method[8]

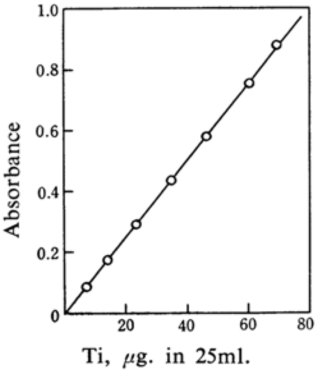

Fig. 4. Calibration curve at 532 mμ.
H_2O_2: 0.3% soln. 0.5 ml., XO: 1.65×10^{-4} M, $HClO_4$: 0.051 M

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[8] V. Lenher and W. G. Crawford, *J. Am. Chem. Soc.*, 35, 138 (1913).

TABLE II. EFFECT OF CATIONS ON TITANIUM DETERMINATION

Titanium taken, 32.4 μg. (0.68 μmol.)
Cations added, each 0.5 μmol.

Cation	Titanium found μg.	Deviation μg.
Aluminum (III)	32.4	± 0
Bismuth (III)	55.4	+23.1
Calcium (II)	32.5	+ 0.1
Cadmium (II)	32.8	+ 0.4
Cerium (III)	32.4	± 0
Cobalt (II)	32.4	± 0
Chromium (III)	32.4	± 0
Copper (II)	33.0	+ 0.6
Iron (III)	54.3	+21.9
Gallium (III)	64.0	+31.6
Mercury (II)	33.0	+ 0.6
Lanthanum (III)	32.4	± 0
Magnesium (II)	33.0	+ 0.6
Manganese (II)	32.6	+ 0.2
Molybdenum (VI)	32.5	+ 0.1
Neodymium (III)	32.3	− 0.1
Nickel (II)	32.5	+ 0.1
Lead (II)	32.5	+ 0.1
Palladium (II)	36.0	+ 3.6
Tin (IV)	47.0	+14.6
Thorium (IV)	71.0	+38.6
Thallium (III)	45.4	+13.0
Uranium (VI)	32.3	− 0.1
Vanadium (IV)	34.4	+ 2.0
Tungsten (VI)	32.5	+ 0.1
Zinc (II)	32.4	± 0
Zirconium (IV)	55.4	+23.0

TABLE III. EFFECT OF ANIONS ON TITANIUM DETERMINATION

Titanium taken, 32.4 μg.
Xylenol orange, 1.63×10^{-4} M
Hydrogen peroxide added, 0.3% soln. 1 ml.
Perchloric acid, 0.05 N

Anion		Titanium found	Deviation
Present	Added μmol.	μg.	μg.
Chloride	500	32.5	+0.1
Fluoride	0.5	32.3	−0.1
	1	30.7	−1.7
	2.5	26.6	−5.8
Nitrate	500	32.3	−0.1
Sulfate	100	32.4	±0
	200	32.2	−0.2
	500	30.7	−1.7
Oxalate	0.1	32.3	−0.1
	0.2	31.3	−1.1
	1	23.5	−8.9
Phosphate	20	32.3	−0.1
	50	31.8	−0.6
	140	29.8	−2.6
Tartrate	10	32.5	+0.1
	50	31.6	−0.8
	100	29.4	−3.0
Citrate	25	32.5	+0.1
	50	31.7	−0.7
	150	29.5	−2.9
NTA	0.1	31.1	−1.3
	0.25	28.1	−4.3
EDTA	0.1	29.1	−3.3
	0.25	23.8	−8.6

or that of the chromotropic acid method,[9] and it is much higher than that of the tiron method[10] or that of the resoflavine method.[11]

The Effect of Diverse Ions.—Separate tests were made to elucidate the interference of various cations as well as that of anions on the determination of titanium. The results are shown in Tables II and III.

Complex Formation.—Some attempts were made to establish the nature of the complex in solution and to determine the composition of the complex.

(1) The Mole Ratio Method.—The mole ratio method was employed to determine the molar ratio of xylenol orange to the titanium-hydrogen peroxide complex. A known aliquot of a titanium solution was treated preliminarily with an excess of hydrogen peroxide to form the yellow titanium-hydrogen peroxide complex. Varying amounts of a xylenol orange solution were then added, and the absorbance of the mixture was measured at 15 wavelengths between 420 and 600 mμ. The concentration of perchloric acid was held constant at 0.048 N. Some typical plots are shown in Fig. 5. It is seen that changes in the slope occur at a mole ratio of 1, indicating the presence of a 1 : 1 complex between xylenol orange and the titanium-hydrogen peroxide complex.

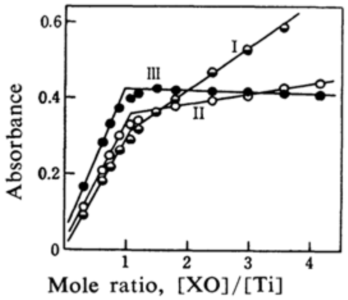

Fig. 5. Mole ratio method applied for Ti-H_2O_2-XO complex.
Ti : 2.713×10^{-5} M, H_2O_2 : 8.2×10^{-3} M
$HClO_4$: 0.051 M, I : 510 mμ, II : 530 mμ, III : 550 mμ

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[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York (1950), p. 577.

[10] J. H. Yoe and A. R. Armstrong, *Anal. Chem.*, **19**, 100 (1947).

[11] G. Charlot, *Anal. Chim. Acta*, **1**, 244 (1947).

(2) The Application of the Method of Lewis and Skoog.—In order to determine the combining ratio of titanium, a spectrophotometric method described by Lewis and Skoog[12] was applied in which the perchloric acid concentration was high enough for the complex formation to be quite incomplete. The concentration of perchloric acid was held constant at 0.4 N. Under these conditions, it is possible to assume that the equilibrium concentrations of the reactants are not appreciably different from their initial concentrations. The reaction producing the absorbing species is assumed to be

$$m\,\mathrm{Ti} + n\,\mathrm{H_2O_2} + p\,\mathrm{XO} \rightleftharpoons (\mathrm{Ti})_m(\mathrm{H_2O_2})_n(\mathrm{XO})_p$$

The equilibrium constant for this reaction can be expressed in terms of the apparent molar extinction coefficient, ε_c, of the complex and the absorbance, D, of the color-developing solution, which is measured against the reference solution containing the same amounts of perchloric acid and the reactants.

$$K'_{\mathrm{Ti}} = (D/\varepsilon_c)/[\mathrm{Ti}]^m[\mathrm{H_2O_2}]^n[\mathrm{XO}]^p \qquad (1)$$

If the conditions are now chosen so that the reaction does not proceed very far to the right, the initial concentration of the reactants, $[\mathrm{Ti}]_i$, $[\mathrm{H_2O_2}]_i$ and $[\mathrm{XO}]_i$, can be substituted for the equilibrium concentration.

Thus,

$$K'_{\mathrm{Ti}} = (D/\varepsilon_c)/[\mathrm{Ti}]_i^m[\mathrm{H_2O_2}]_i^n[\mathrm{XO}]_i^p \qquad (2)$$

which may be written as

$$\log D = m\log[\mathrm{Ti}]_i + n\log[\mathrm{H_2O_2}]_i + p\log[\mathrm{XO}]_i + \log K'_{\mathrm{Ti}}\varepsilon_c \qquad (3)$$

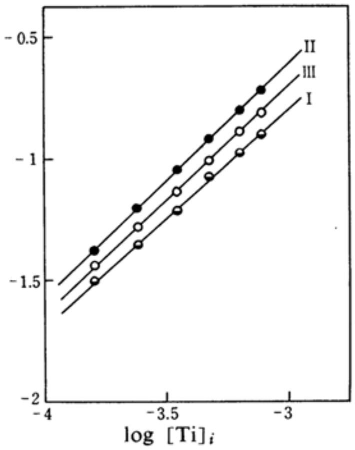

Fig. 6. Plots of log D vs. log$[\mathrm{Ti}]_i$. $[\mathrm{H_2O_2}]_i$: 1.64×10^{-3} M, $[\mathrm{XO}]_i$: 1.55×10^{-4} M, $\mathrm{HClO_4}$: 0.40 M, I: 510 mμ, II: 530 mμ, III: 550 mμ

If $[\mathrm{H_2O_2}]_i$ and $[\mathrm{XO}]_i$ are held constant, a plot of log D vs. log $[\mathrm{Ti}]_i$ should yield a straight line with slope m. When the experimental data were treated in this way, a good straight line with a slope of 0.95 (as an average at six wavelengths between 510 and 560 mμ) was obtained. Some of these data are plotted in Fig. 6.

(3) The Combining Ratio of Hydrogen Peroxide.—It now becomes necessary to determine the combining ratio of hydrogen peroxide. An interesting spectrophotometric method, which makes possible the interpretation of the experimental data for systems involving three components, was recently described by Newman and Hume.[13] This method, however, is not directly applicable to the present system, involving titanium, hydrogen peroxide and xylenol orange. Therefore, a modified method was developed. Assuming the following equilibrium:

$$\mathrm{Ti} + \mathrm{XO} + n\,\mathrm{H_2O_2} \rightleftharpoons \mathrm{Ti\cdot XO\cdot(H_2O_2)}_n$$

the equilibrium constant, $K'_{\mathrm{H_2O_2}}$, may be defined as;

$$K'_{\mathrm{H_2O_2}} = [\mathrm{Ti\cdot XO\cdot(H_2O_2)}_n]/[\mathrm{Ti}][\mathrm{XO}][\mathrm{H_2O_2}]^n \qquad (4)$$

If two species, xylenol orange and the complex, are absorbing and if the absorbance is measured against the solution containing the same amounts of the reactants except for hydrogen peroxide, the following relationship may hold:

$$D = \varepsilon_c[\mathrm{Ti\cdot XO\cdot(H_2O_2)}_n] \qquad (5)$$

where D is the observed absorbance and ε_c is the apparent molar extinction coefficient of the complex. The initial concentrations of titanium, xylenol orange and hydrogen peroxide in any given experiment are, respectively:

$$[\mathrm{Ti}]_i = [\mathrm{Ti}] + [\mathrm{Ti\cdot XO\cdot(H_2O_2)}_n]$$
$$[\mathrm{XO}]_i = [\mathrm{XO}] + [\mathrm{Ti\cdot XO\cdot(H_2O_2)}_n] \qquad (6)$$

and

$$[\mathrm{H_2O_2}]_i = [\mathrm{H_2O_2}] + n\,[\mathrm{Ti\cdot XO\cdot(H_2O_2)}_n]$$

If the initial concentration of xylenol orange is considerably higher than that of titanium, the equilibrium concentration of xylenol orange may be assumed to equal its initial concentration. Substituting Eqs. 5 and 6 into Eq. 4, rearranging it, and then taking logarithms,

$$\log\{D/([\mathrm{Ti}]_i\,\varepsilon_c - D)\} = \log K'_{\mathrm{H_2O_2}} + \log[\mathrm{XO}]_i + \log\{([\mathrm{H_2O_2}]_i - nD)/\varepsilon_c\}^n \qquad (7)$$

If the proper value of n is assumed, a plot of

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[12] C. Lewis and D. A. Skoog, *J. Am. Chem. Soc.*, **84**, 1101 (1962).

[13] L. Newman and D. N. Hume, ibid., **79**, 4571 (1957).

$$\log\{D/([\mathrm{Ti}]_i\ \varepsilon_c - D)\}\ \text{vs.}\ \log\{([\mathrm{H_2O_2}]_i - nD)/\varepsilon_c\}^n$$

should yield a straight line with a unit slope. When the experimental data were treated in this way and the value of n was assumed to be one, a good straight line with a slope of 0.9 ± 0.03 was obtained. Values of n equal to one-half and two were tried unsuccessfully. These findings hold for solutions containing a fixed amount of titanium (2.709×10^{-5} M) and xylenol orange (1.653×10^{-4} M) and varying amounts of hydrogen peroxide (0.286 to 4.090×10^{-4} M). In all the experiments, the concentration of perchloric acid was held constant at 0.048 N.

(4) Conclusion.—From the foregoing results, it is possible to conclude that a 1 : 1 : 1 complex is formed as a result of the reaction of titanium with hydrogen peroxide and xylenol orange.

The formation constant, K_c, of the complex can be calculated from Eq. 3, using the data obtained in section 2 and the step-by-step acid dissociation constants of xylenol orange[14] (see also Ref. 7). The results, along with the apparent molar extinction coefficients at six wavelengths, are summarized in Table IV. The value of the formation constant agrees approximately with that (1.8×10^{37}) calculated from Eq. 7.

TABLE IV. FORMATION CONSTANT, K_c, AND APPARENT MOLAR EXTINCTION COEFFICIENT, ε_c, OF THE COMPLEX

Wavelength, mμ	ε_c	K_c*
510	14000	4.0×10^{37}
520	14500	4.7×10^{37}
530	14800	5.4×10^{37}
540	14200	5.7×10^{37}
550	12600	5.4×10^{37}
560	10300	4.0×10^{37}
	Av.	4.8×10^{37}

* An average value at six different concentrations of titanium.

Summary

Although almost no color reaction occurs when titanium is treated with a solution of xylenol orange at pH below 2, the addition of hydrogen peroxide as a third reactant yields a new, red complex with an absorption maximum at about 535 mμ. On the basis of the above reaction, a new method for the spectrophotometric determination of titanium has been described. The color stability is affected by the amount of hydrogen peroxide and xylenol orange. When, however, 0.2 to 5 ml. of a 0.3% solution of hydrogen peroxide and 3.5 to 6 ml. of a 1×10^{-3} M solution of xylenol orange are used for less than 70 μg. of titanium and a total volume of 25 ml., the color obtained is stable for at least 30 min. Beer's law is obeyed over the 7 to 70 μg. range of titanium. The mole ratio method and the two spectrophotometric methods have been employed to determine the composition of the complex. It has been concluded that a 1 : 1 : 1 complex is formed under the conditions investigated.

The author wishes to acknowledge the kind guidance and the many helpful suggestions of Professor Kôichi Tonosaki.

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[14] B. Řehák and J. Körbl, *Collection Czechoslov. Chem. Communs.*, 25, 797 (1960).