The Spectrophotometric Determination of Titanium with Xylenol Orange[1]

By Makoto OTOMO

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Titanium(IV), in a slightly acidic solution buffered with acetic acid and sodium acetate, reacts with xylenol orange to give red or reddish-violet complexes, each consisting of one molecule of the reagent to one atom of titanium. The red complex formed by adding an excess of xylenol orange to a titanium solution is applicable to the spectrophotometric determination of titanium. The present paper will describe the conditions which permit the spectrophotometric determination of titanium at microgram levels and the results of a study of complex formation.

Experimental

Stock Solution of Titanium.—Titanium dioxide, prepared by igniting the precipitates which result from the hydrolysis of titanium tetrachloride (E. Merck Co., Ltd.), was fused with about five times as large a mixture of ammonium sulfate and sulfuric acid. The fused mass, after cooling, was dissolved in 6 N sulfuric acid and then diluted with distilled water to make the solution about 0.1 M in titanium sulfate. The resultant solution was standardized by the volumetric method described by Ishimaru.[2] A working standard solution was prepared by diluting the above solution with distilled water.

Perchloric Acid and Sodium Perchlorate.—In a study of complex formation, perchloric acid and sodium perchlorate solutions were used to maintain constant the hydrogen ion concentration and the ionic strength. The latter was prepared from reagent grade perchloric acid and sodium carbonate.

The other reagents and apparatus used were the same as those reported previously.[3] All experiments were carried out at 25±0.5°C.

Standard Procedure.—To a solution in a 25 ml. volumetric flask, which contained up to 40 μg. of titanium, were added 10 ml. of an acetate buffer (pH 3 to 4.5) and 4 ml. of a 1×10^{-3} M solution of xylenol organge. The solution was diluted to the mark with water and then mixed. After about 30 min., the absorbance of the solution was measured at the desired wave length (502 or 532 mμ), using a reagent blank as the reference.

Results and Discussion

Preliminary experiments showed that the variation in pH value had no significant effect on the absorption spectra of the solution,

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[1] This work was first presented at the Tôhoku-Hokkaido Branch Meeting of the Chemical Society of Japan, Hakodate, July, 1962.

[2] S. Ishimaru, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kwagaku Kwaishi*), **59**, 667 (1938).

[3] M. Otomo, This Bulletin, **36**, 137 (1963).

provided the pH of the solution was maintained below 5 and a sufficient excess of xylenol orange was used.

Absorption Spectra.—Figure 1 gives the absorption spectra of solutions containing 35 μg. of titanium and xylenol orange added in various amounts, 3.5×10^{-5} to 1.44×10^{-4} M. There are two absorption bands; the intense absorption band with its maximum at about 440 mμ is due to the xylenol orange, which increases in intensity with the addition of the reagent, while the absorption found at the longer wavelengths seems to be due to the overlap of the titanium-xylenol orange complex band with that of the xylenol orange. It is found that the latter band at about 555 mμ slightly shifts toward shorter wavelengths with the increasing amounts of xylenol orange and that, at the same time, the intensity of the absorbance at this wavelength decreases gradually; for example, when the concentrations of xylenol orange are kept at 3.2×10^{-5}, 4.0×10^{-5}, and 4.8×10^{-5} M, the absorption maxima are found at 555, 552 and 550 mμ respectively. The further addition of xylenol orange causes disappearance of the absorption maximum, giving small shoulders. Further, an isosbestic point can be observed at 532 *mμ*, where the absorption curves for different solutions with a fixed amount of titanium cross each other, suggesting that titanium reacts with xylenol orange to form at least two absorbing entities which are in equilibrium with each other and also with the free xylenol orange. Similar phenomena have also been observed in the xylenol orange complexes of aluminum,[4] gallium[5] and thallium.[5]

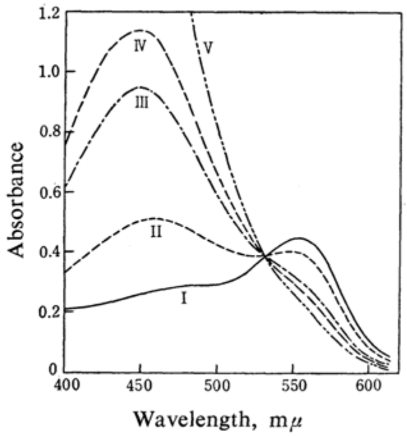

Fig. 1. Absorption spectra of Ti-XO complex at pH 3.0.
Ti: 35 μg., XO: I, 3.2×10^{-5} M; II, 4.8×10^{-5} M; III, 7.2×10^{-5} M; IV, 9.6×10^{-5} M; V, 1.44×10^{-4} M.

When, however, more than 3.5 ml. of a 1×10^{-3} M solution of xylenol orange is added and the same amount of this solution is used as the reference, the maximum absorption was always found at about 502 mμ (see Fig. 2), strongly suggesting the existence of only one form of the complex under the conditions so far studied.

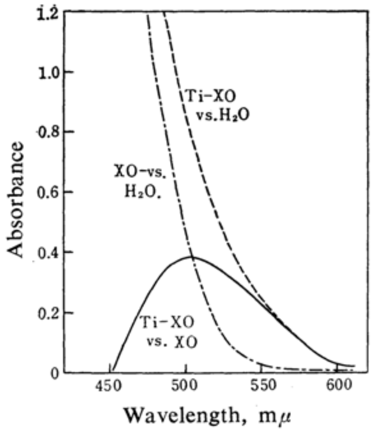

Fig. 1. Absorption spectra of XO and its Ti complex at pH 3.0.
Ti: 35 μg., XO: 1.6×10^{-4} M

The Effect of pH Value.—The effect of pH value on the color development was examined by measuring, at 502 mμ, the absorbance of a colored solution containing 25 μg. of titanium and 4 ml. of a 1×10^{-3} M solution of xylenol orange, the pH being adjusted to the desired value by means of an acetate buffer solution. From the curve shown in Fig. 3, it is found that the maximum and constant absorbance is obtained over the pH range 3 to 4.5. At a pH of less than 1.5, the complex does not

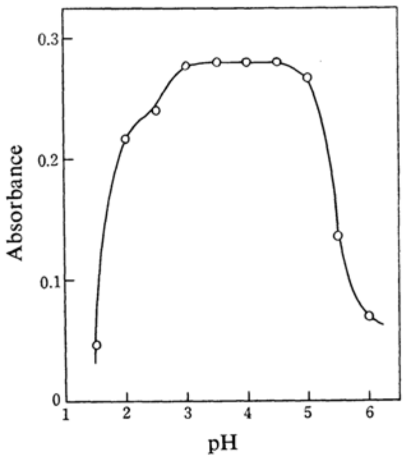

Fig. 3. Effect of pH on color development.
Ti: 25 μg., XO: 1.65×10^{-4} M

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[4] M. Otomo, This Bulletin, **36**, 809 (1963).
[5] M. Otomo, unpublished work.

give any red coloration. At a pH above 4.5, the absorbance at 502 mμ decreases sharply with the increasing pH value, probably because of hydrolysis of the titanium. A constant absorbance was also obtained at 532 mμ (isosbestic point) provided the pH of the solution was kept between 3 and 4.5.

The Effect of the Addition of the Reagent.—The effect of reagent concentration on the color development was studied with solutions containing 25 μg. of titanium and varying amounts of a 1×10^{-3} M solution of xylenol orange. The absorbance measurement was made at three wavelengths, 502, 532 and 552 mμ. The results are shown in Fig. 4. When more than 3.5 ml. of the reagent solution is added, the absorbance at neither 502 mμ nor 532 mμ is affected by the further addition of the reagent. On the other hand, the absorbance at 552 mμ decreases sharply with the additional reagent unless a large amount of the reagent is used.

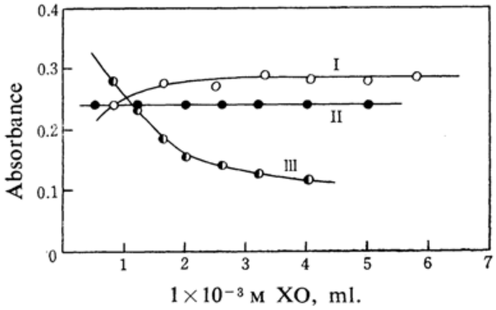

Fig. 4. Effect of addition of reagent (at pH 4.0).
Ti: 25 μg., I: 502 mμ, II: 532 mμ, III: 552 mμ

The Effect of the Standing Time.—The red color of the titanium-xylenol orange complex is stable for at least several hours.

Calibration.—Figure 5 shows that the plots of the absorbance-titanium concentration obey Beer's law over the ranges up to 25 μg. of titanium at 502 mμ and up to 40 μg. of titanium at 532 mμ. The absorbance measurements were made with solutions in which the pH value was adjusted (1) to 4.0 for the measurements at 502 mμ, and (2) to 3.0 for the measurements at 532 mμ. The latter pH value was chosen to minimize the interferences from other cations, which formed complexes with xylenol orange at the higher pH values to give positive errors. The apparent molar extinction coefficients were calculated as 18000 at 502 mμ and 11700 at 532 mμ, respectively.

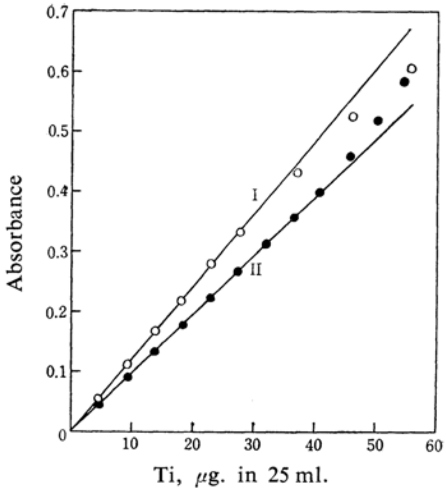

Fig. 5. Calibration curves.
XO : 1.6×10^{-4} M, I : 502 mμ, II : 532 mμ

The Effect of Diverse Ions. — Such anions as chloride, nitrate and sulfate do not interfere, even when present in large amounts. Large amounts of oxalate and tartrate give erroneous results, because they reduced the absorbance of the solution, probably by forming complexes with titanium. Since fluoride, phosphate and EDTA ions can form some stable complexes with titanium, they give large negative errors, even when added in small amounts.

Of the 26 cations tested, aluminum, iron(III), tin(II), thorium, yttrium vanadium(IV) interfere with the titanium determination by forming colored solutions.

Complex Formation.—The appearance of an isosbestic point, which has already been shown in Fig. 1, suggests that two complexes, one a red complex with its absorption maximum at 502 mμ and the other a reddish-violet one with its absorption maximum at about 555 mμ, are in equilibrium with each other. On the basis of the above suggestion, a study was made to determine the composition of the two complexes and to calculate the formation constants. In order to calculate the formation constants, however, it must be considered that xylenol orange is a polybasic acid* and that, therefore, the stability of the complexes is greatly dependent on the pH value under investigation. In all the solutions used in this study, therefore, the perchloric acid concentration was maintained constant at 0.020 M and the ionic strength was kept constant at 0.50.

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* The stepwise acid dissociation constants of xylenol orange have been determined by Řehák and Körbl[6] as $pk_1=2.58$, $pk_2=3.23$, $pk_3=6.37$, $Pk_4=10.46$, and $pk_5=12.28$.

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

The Red Complex with its Absorption Maximum at 502 mμ.—This complex is formed when xylenol orange is added in excess to a titanium solution. Although numerous methods have been developed for interpreting spectrophotometric data as they are presented in various cases, none is directly applicable to this particular system. Consequently, a method has been developed which is a modification of that of McConnell and Davidson.⁷⁾

Assuming that the formation of the red complex is in accordance with the following equation:

$$\mathrm{TiO^{2+}} + n\mathrm{XO} \rightleftarrows \mathrm{TiO(XO)}_n + np\mathrm{H^+}$$

the equilibrium constant, K, may be given by:

$$K = [\mathrm{TiO(XO)}_n]\,[\mathrm{H^+}]^{np}/[\mathrm{TiO^{2+}}]\,[\mathrm{XO}]^n \qquad (1)$$

where XO is the total unbound xylenol orange, $\mathrm{TiO(XO)}_n$ is the total titanium-xylenol orange complex, and p is the number of hydrogen ions liberated from one molecule of xylenol orange by the chelation. Unknown charges are omitted. The species of titanium(IV) present at the acidity and concentration level used is $\mathrm{TiO^{2+}}$ according to the notations of Musha and Ogawa⁸⁾ and of Sone and Tanaka.⁹⁾ The apparent formation constant, K', may be expressed as:

$$K' = K/[\mathrm{H^+}]^{np} = x/(a-x)(b-nx)^n \qquad (2)$$

where x is the molar concentration of the complex, and a and b are the initial molar concentrations of titanium and xylenol orange respectively. If a large excess of xylenol orange is present, the value of $b-nx$ will essentially equal the initial concentration of xylenol orange, b. The formation constant may then be written:

$$K' = x/(a-x)b^n \qquad (3)$$

If the molar extinction coefficient of xylenol orange is represented as $\varepsilon_{\mathrm{XO}}$ and that of the complex, as ε_{C}, the absorbance of the solution, D, at any wavelength may be written:

$$D = (\varepsilon_{\mathrm{C}} - n\varepsilon_{\mathrm{XO}})x + \varepsilon_{\mathrm{XO}}b \qquad (4)$$

If the absorbance is measured against the solution containing the same amount of xylenol orange as b, D may be reduced to:

$$D = (\varepsilon_{\mathrm{C}} - n_{\mathrm{XO}})x \qquad (5)$$

Solving for x and substituting it into Eq. 3 yields:

$$D = (\varepsilon_{\mathrm{C}} - n\varepsilon_{\mathrm{XO}})a - D/K'\mathrm{b}^n \qquad (6)$$

The values of D obtained at various concentrations of xylenol orange are plotted against D/b^n. With the correct choice of n, this should give a straight line, the slope of which is $-1/K'$, and the intercept, $(\varepsilon_{\mathrm{C}} - n\varepsilon_{\mathrm{XO}})a$. Values of n equal to one-half and two were tried unsuccessfully. Only a choice of n equal to one made the data interpretable. Thus, the only complex present is a 1 to 1 complex. Some of the results are shown in Fig. 6.

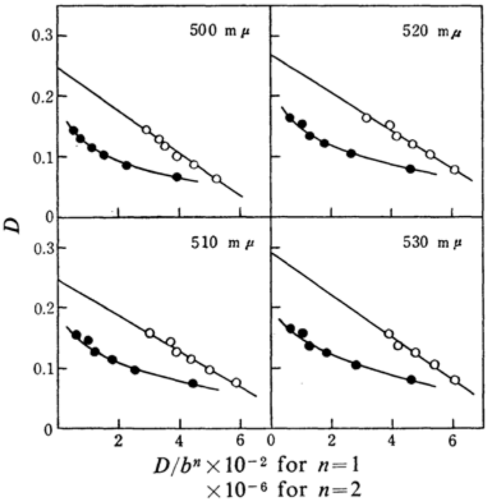

Fig. 6. Plots of D vs. D/b^n.
$\mathrm{HClO_4}$: 0.020 M, μ: 0.50 M $\mathrm{NaClO_4}$, a: 1.935×10^{-5} M
-○-: $n=1$, -●-: $n=2$

This graphical technique for evaluating the formation constant, K', was applied to data obtained at eight wavelengths, at 10 mμ intervals from 500 to 570 mμ. These eight values of K' were averaged to give a mean value of $K' = 2.9 \times 10^3$, with a standard deviation of 0.3×10^3.

Further, two other methods, one of which has been described by Andrews and Keefer¹⁰⁾ and the other of which has been reported previously by the present author,¹¹⁾ were applied for the calculation of the formation constant. Both methods showed that a 1 to 1 complex is also formed in the presence of excess xylenol orange. As the mean values for K', 3.1×10^3 and 2.9×10^3 were obtained respectively; these are in good agreement with the value obtained above.

The Reddish-Violet Complex with Its Absorption Maximum at 555 mμ.—This complex is formed by adding titanium in excess to a solution of xylenol orange. The method of

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7) H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3164 (1950).

8) S. Musha and K. Ogawa, *J. Chem. Soc. Japan*, (*Nippon Kagaku Zassi*), **78**, 1686 (1957).

9) K. Sone and M. Tanaka, "Teisei Bunsekikagaku," A Translation of Charlot, "L'Analyse Qualitative et les Réaction en Solution" (In Japanese), Kyoritsu Shuppan, Tokyo (1958), p. 263.

10) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.* **74**, 1891 (1952).

11) M. Otomo, This Bulletin, **36**, 889 (1963).

Frank and Oswalt[12] was applied here: if a 1 to 1 complex is formed, the following equilibrium may exist:

$$TiO^{2+} + XO \leftrightharpoons TiO(XO) + qH^+$$

$$K' = [TiO(XO)]\,[H^+]^q/[TiO^{2+}]\,[XO] \qquad (7)$$

where q is the number of hydrogen ions liberated from one molecule of xylenol orange by the chelation. At a constant acidity, the following relation may finally be derived:

$$ab/(D - \varepsilon_{XO}b) = (a+b)/(\varepsilon_C - \varepsilon_{XO}) + 1/K'(\varepsilon_C - \varepsilon_{XO}) \qquad (8)$$

where a and b are the initial molar concentrations of titanium and xylenol orange respectively. D is the absorbance of the solution, ε_{XO} and ε_C are the molar extinction coefficients of xylenol orange and the complex respectively, and K' is the apparant formation constant. If the first assumption is correct, on plotting the values of $ab/(D-\varepsilon_{XO}b)$ at various concentrations of titanium against the values of $a+b$, a straight line with slope $1/(\varepsilon_C - \varepsilon_{XO})$ and intercept $1/K'(\varepsilon_C - \varepsilon_{XO})$ should be obtained. Some of the results obtained are summarized in Fig. 7. From this figure, it is clear that a straight-line relationship is completely satisfied between $ab/(D-\varepsilon_{XO}b)$ and $a+b$, showing that a 1 to 1 complex is also formed. The formation constant, as a mean value of the values found at ten wavelengths between 520 and 610 mμ, was found to be 1.9×10^4, with a standard deviation of 0.5×10^4.

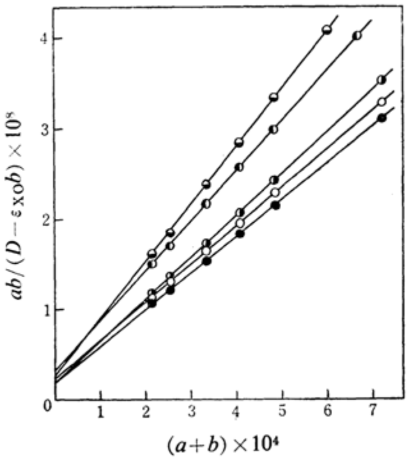

Fig. 7. Plots of $ab/(D-\varepsilon_{XO}b)$ vs. $(a+b)$.
$HClO_4$: 0.020 M, μ : 0.50 M $NaClO_4$
XO : 2×10^{-5} M, -◒- : 520 mμ
-◑- : 530 mμ, -●- : 550 mμ
-○- : 560 mμ, -◐- : 580 mμ

From the foregoing results, it may be concluded that, depending on the amount of the reagent, titanium forms either of two 1 to 1 complexes, a red complex with its absorption maximum at 502 mμ and a reddish-violet one with its absorption maximum at 555 mμ, the latter being more stable than the former. It was also found that the experimental data are satisfied only by assuming the existence of mononuclear 1 to 1 complexes. Although two interesting models of the position of the chelation ring in the xylenol orange complexes of niobium(V) and thallium(III) have been described by Cheng et al.[13] and by Busev et al.[14] respectively*, it is not possible to obtain definite information on the structure of these titanium-xylenol orange complexes on the basis of the experimental results described in the present paper and of the unpublished result. The present author is also, therefore, investigating the structural configuration of these complexes; the results will be presented elsewhere.

Summary

A new method for the spectrophotometric determination of titanium has been described. This method is based on the formation of the colored complex between titanium and xylenol orange in a slightly acidic solution. The effects of pH and the reagent concentration on the color development of the complex have been thoroughly investigated, and experimental conditions which make possible the determination of titanium at microgram levels have been devised. The compositions of the two 1 to 1 complexes have been determined from the data of spectrophotometric measurements. The apparant formation constants of these complexes have also been calculated.

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Department of Chemistry
Faculty of Literature and Science
Hirosaki University
Hirosaki, Aomori

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[12] H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

[13] K. L. Cheng and B. L. Goydish, *Talanta*, **9**, 987 (1962).

[14] A. I. Busev and V. G. Tiptsova, *Zhur. Anal. Khim.*, **15**, 573 (1960).

* They both suggested that the chelation occurs through at least the displacement of the phenolic hydrogen atom.