BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2764—2767 (1972)

The Extraction and Spectrophotometric Determination of Titanium(IV) with Tiron[1]

Yoshinobu WAKAMATSU* and Makoto OTOMO**

*Department of Industrial Chemistry, Hachinohe Technical College, Hachinohe-shi, Aomori

**Department of Synthetic Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya-shi

(Received March 13, 1972)

A method has been described for the spectrophotometric determination of titanium(IV), which is based on the extraction of the titanium(IV)-Tiron chelate into *n*-butanol in the presence of 1,3-diphenylguanidinium salt. The extracted species containing titanium, Tiron, and diphenylguanidine in a molar ratio 1:2:4, has an absorption maximum at about 385 nm. The maximum extraction is obtained when the pH of the initial aqueous phase is controlled to about 3.0 to 4.0. Beer's law is obeyed up to 25 μg titanium per 10 m*l* of *n*-butanol. The molar absorptivity of the extracted species is 1.4×10^4 at 385 nm. Molybdenum(VI) and chelating agents interfere with the determination of titanium.

As is well known, Tiron, disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid, forms water soluble chelates with many metal ions and has been used as a colorimetric reagent for several metal ions,[2–6] or as a masking agent[7] or a metallochromic indicator[8] in complexometric titrations. Recently, Busev *et al.*[9] applied the reagent to the selective extraction-spectrophotometric determination of molybdenum (VI), on the basis of the extraction of the ion-association complex formed between the molybdenum-Tiron chelate and 1,3-diphenylguanidinium cation. A similar method was also applied to the determination of iron(III).[10]

Because of its superior extraction efficiency, 1,3-diphenylguanidinium salt has recently been used in many analytical procedures with advantage. In our previous works, the anionic metal-chelates of Methylthymol Blue,[11,12] Xylenol Orange[13] or Indoferron[14–16] have been extracted into suitable organic solvents in

---

1) Presented at the 20th Annual Meeting of the Japan Society for Analytical Chemistry, Tokyo, October, 1971.

2) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).

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

4) J. H. Yoe and F. Will, *Anal. Chim. Acta*, **8**, 546 (1953).

5) Y. Oka, N. Nakazawa, and H. Harada, *Nippon Kagaku Zasshi*, **86**, 1158 (1965).

6) T. Yotsuyanagi, K. Goto, and M. Nagayama, *ibid.*, **88**, 1282 (1967).

7) H. Flaschka and R. Puschel, *Z. Anal. Chem.*, **143**, 300 (1954).

8) Y. Sasaki, *Bunseki Kagaku*, **16**, 1199 (1967).

9) A. I. Busev and G. P. Rudzit, *Zh. Anal. Khim.*, **19**, 569 (1964).

10) A. I. Busev, G. P. Rudzit, and I. A. Tsurika, *ibid.*, **25**, 2151 (1970).

11) M. Otomo, *Nippon Kagaku Zasshi*, **89**, 503 (1968).

12) Y. Wakamatsu and M. Otomo, *ibid.*, **90**, 595 (1969).

13) M. Otomo and Y. Wakamatsu, *ibid.*, **89**, 1087 (1968).

14) Y. Wakamatsu and M. Otomo, *Bumseki Kagaku*, **19**, 537 (1970).

15) Y. Wakamatsu and M. Otomo, *Research Rep., Hachinohe Tech. Coll.*, **5**, 72 (1970).

16) Y. Wakamatsu and M. Otomo, *Bunseki Kagaku*, **20**, 862 (1971).

the presence of 1,3-diphenylguanidinium chloride. The extraction mechanisms of the ion-association complexes thus formed have also been investigated by a spectrophotometric method. The present paper will describe the spectrophotometric determination of titanium(IV), which is based on the extraction of the titanium-Tiron-1,3-diphenylguanidinium association complex into *n*-butanol. The extracted species, containing titanium, Tiron and diphenylguanidine in a molar ratio 1:2:4, has an absorption maximum at 385 nm and the molar absorptivity of about 1.4×10^4. By this method, up to 25 μg of titanium can be determined within the experimental error.

Experimental

Reagent. About 0.01 M titanium(IV) solution was prepared by dissolving the hydrolysis products of titanium tetrachloride in 6 N sulfuric acid and diluting with distilled water. The resultant solution was standardized by the complexometric titration.[17] A working standard solution was prepared by diluting the above solution with distilled water to a desired concentration.

A 5×10^{-2} M Tiron solution was prepared by dissolving the Dotite Tiron in distilled water without further purification.

A 0.5 M 1,3-diphenylguanidinium chloride (DPG-Cl) stock solution was prepared by dissolving 1,3-diphenylguanidine (Guaranteed Reagent, Tokyo Kasei Co., Ltd.) in calculated amounts of hydrochloric acid and diluting with distilled water.

All other chemicals used were of guaranteed reagent quality.

Apparatus. The absorbance measurements were made with a Hitachi Model 124 recording-spectrophotometer with 10-mm quartz cells and a Hitachi Model EPU-2A spectrophotometer with 10-mm glass cells. The shaking was done with an Iwaki Model V–D shaker with a time switch. The pH measurements were made with a Toa Denpa Model HM-5A glass electrode pH meter.

Standard Procedure. To a sample solution containing up to 25 μg of titanium in a 50 m*l* separating funnel were added 2 m*l* of a 5×10^{-2} M Tiron solution and 10 m*l* of a 0.1 M DPG-Cl solution which had been adjusted to pH 3.6 with monochloroacetic acid and sodium acetate solutions. The solution was diluted with water to 20.0 m*l* and shaken for 5 min. with 10.0 m*l* of *n*-butanol. The absorbance of the organic phase was then measured at 385 nm using a reagent blank as the reference.

Results and Discussion

Absorption Spectra. The absorption spectra of the association complex extracted into *n*-butanol are shown in Fig. 1, along with that of the reagent blank. At any pH values examined, the absorption maximum of the extracted species is found at about 385 nm. The extracted species was stable for at least several hours.

The Effect of pH. The effect of pH of the aqueous phase on the extraction was examined. The results are shown in Fig. 2. The maximum extraction is reached at pH 3.0 to 4.0 when the association complex is extracted into *n*-butanol from the aqueous solution containing 9.6 μg titanium, 5.0×10^{-3}M Tiron and 1.3×10^{-1}M DPG-Cl. This pH range is shifted to 3.3 to 4.0 for 19.2 μg titanium.

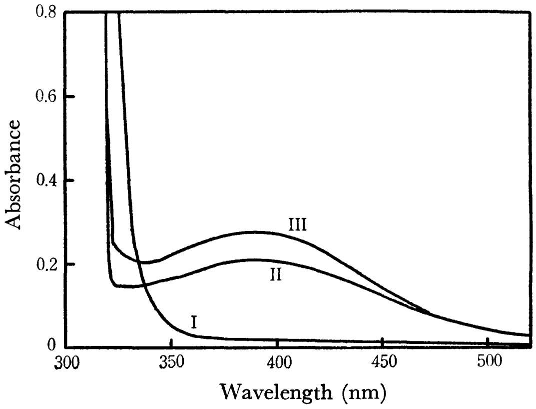

Fig. 1. Absorption spectra of the systems Tiron-DPG and Ti(IV)-Tiron-DPG in *n*-butanol.
Ti: 9.6 μg, Tiron: 5.0×10^{-3} M, DPG-Cl: 0.13 M, I: Tiron-DPG, pH 3.6, II: Ti-Tiron-DPG, pH 2.4; III: Ti-Tiron-DPG, pH 3.6

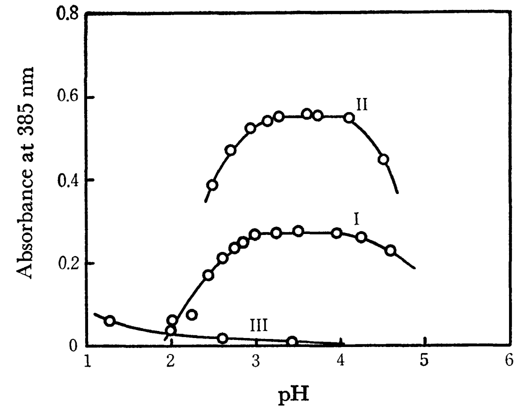

Fig. 2. Effect of pH on the extraction of Ti(IV)-Tiron-DPG.
Tiron: 5.0×10^{-3} M, DPG-Cl: 0.13 M, Ti: I; 9.6 μg, II; 19.2 μg, III; 0.

The Effect of the Tiron Concentration. The effect of the Tiron concentration on the extraction was investigated by varying the Tiron concentration, while other variables being held constant. The absorbance

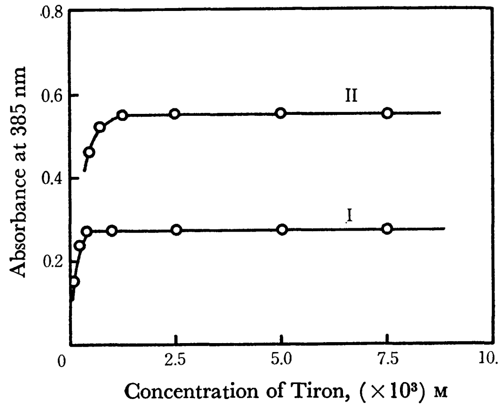

Fig. 3. Effect of Tiron concentration on the extraction of Ti(IV)-Tiron-DPG.
pH: 3.6, DPG-Cl: 0.13 M, Ti: I; 9.6 μg, II; 19.2 μg

---

[17] K. Ueno, "Chelatometric Titration (In Japanese)", Nankodo, Tokyo (1965), p. 315.

of the organic phase was constant when the Tiron concentration in the initial aqueous phase was more than 2.0×10^{-3}M, as is shown in Fig. 3.

The Effect of the DPG-Cl Concentration. The absorbance of the organic phase remained essentially constant provided that the DPG-Cl concentration of the initial aqueous phase was more than about 9.0×10^{-2}M. The titanium-Tiron chelate could not be extracted into the organic phase in the absence of DPG-Cl. The absorbance of the organic phase was not affected by further addition of DPG-Cl at least up to 0.2M.

The Effect of the Shaking Time. The shaking time was varied from 0.5 to 30 min. It was found that shaking for 3 min sufficed; for safety, a shaking time of 5 min was selected. The aqueous phase after one extraction was colorless,indicating that only one extraction is needed for complete extraction of the association complex.

Choice of Solvent. The titanium-Tiron-DPG association complex can be extracted into such aliphatic alcohols as *n*-butanol, isobutyl alcohol and *n*-amyl alcohol, but not into hydrocarbons, halogenated hydrocarbons, esters and ketones. *n*-Butanol was chosen as the solvent which gave the highest absorbance.

Calibration Curve. A calibration curve for the determination of titanium was prepared under the optimum conditions. A good linear relationship was obtained over the concentration range 0 to 25 μg of titanium per 10 m*l* of *n*-butanol. The molar absorptivity of the extracted species was approximately 1.4×10^4 at 385 nm. This value is about 1.4 times as high as that obtained by the direct reaction in aqueous solution without DPG-Cl. The proposed method is comparable in sensitivity with the Xylenol Orange[18] or the chromotropic acid method.[19]

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 summarized in Tables 1 and 2. Molybdenum(VI) interfered at all concentrations investigated, giving positive errors. Iron(III) up to about 10-fold excess did not interfere with the determination when nitrilotriacetic acid (NTA) (2×10^{-3}M) was added as a masking agent before extraction. The interference of the larger amounts of iron(III) may be prevented by addition of a suitable reducing agent. Of the anions tested, chloride, nitrate, sulfate, and phosphate ions, even at high concentrations, did not interfere with the determination. However, chelating agents such as ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CyDTA) interfered seriously, giving negative errors.

The Composition of the Extracted Species. The composition of the extracted species was studied by a graphical method, in which all the equilibrium concentrations and distribution ratios were estimated by measuring the absorbances of the organic or aqueous phases at suitable wavelengths.

Table 1. Effect of metal ions
Ti (IV): 1.5×10^{-5} M (14.4 g), Tiron: 5.0×10^{-3} M, DPG-Cl: 0.13M, pH: 3.6

Metal ion	Mole ratio to Ti	Ti found (μg)
Mg(II)	20	13.5
Zn(II)	20	14.1
Cu(II)	20	16.3
Cd(II)	20	14.2
Pb(II)	20	13.0
Ni(II)	20	14.3
Co(II)	20	14.4
Cr(III)	20	13.6
Al(III)	20	13.7
Fe(III)	2	14.5
	5	16.0
	10	14.8[a]
Th(IV)	20	14.9
V (IV)	10	17.7
	20	23.3
Zr(IV)	10	13.8
	20	8.5
U (VI)	20	16.9
W (VI)	5	16.8
	10	23.6
Mo(VI)	1	15.8
	5	21.2

a) NTA (2×10^{-3}M) was added as masikng agent.

Table 2. Effect of anions and complexing agents
(Conditions: the same as those in Table 1)

Anion or complexing agent	Mole ratio to Ti	Ti found (μg)
Cl^-	1000	14.4
NO_3^-	1000	14.2
SO_4^{2-}	500	13.9
	1000	12.7
$C_2O_4^{2-}$	10	12.8
	50	11.4
$C_2H_4O_6^{2-}$	50	12.1
	500	8.3
PO_4^{3-}	1000	14.2
NTA	30	14.4
	100	13.0
CyDTA	0.5	11.2
	1	9.2
EDTA	0.5	9.0

In Fig. 4, log (distribution ratio of Tiron, D_{Tiron}) is plotted against log (DPG-Cl concentration in the organic phase/chloride ion concentration in the aqueous phase, $[\text{DPG-Cl}]_0/[\text{Cl}^-]$), the Tiron and the hydrogen ion concentrations being kept constant. The slope of straight line portion shows that the ratio Tiron: DPG is 1: 2. Considering the acid dissociation constants ($K_{\text{OH},1}$ and $K_{\text{OH},2}$) of Tiron, it is reasonable to say that Tiron is combined with two DPG cations through its two sulfonate groups to give an extractable neutral species, $H_2R(DPG)_2$.

The number of moles of Tiron in the titanium-Tiron-DPG association complex was determined by plotting log (distribution ratio of titanium, D_{Ti}) against log

---

[18] M. Otomo, This Bulletin, **36**, 1577 (1963).

[19] A. V. Endredy and F. Brugger, *Z. Anorg. Allgem. Chem.*, **249**, 263 (1942).

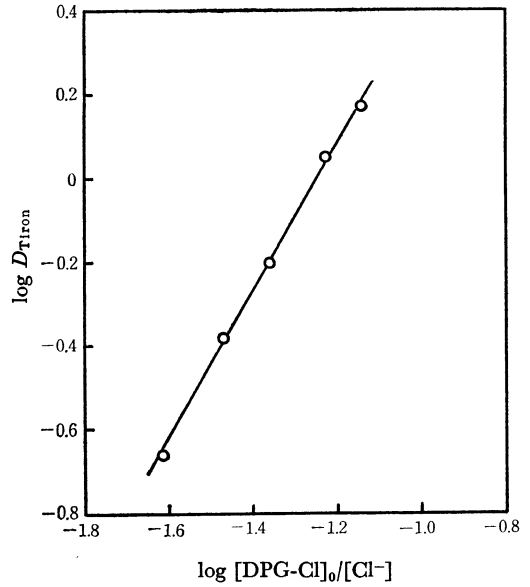

Fig. 4. Relationship between log D_{Tiron} and log [DPG-Cl]$_0$/[Cl$^-$] for the Tiron-DPG system.
Tiron: 5.0×10^{-4} M, pH: 3.6

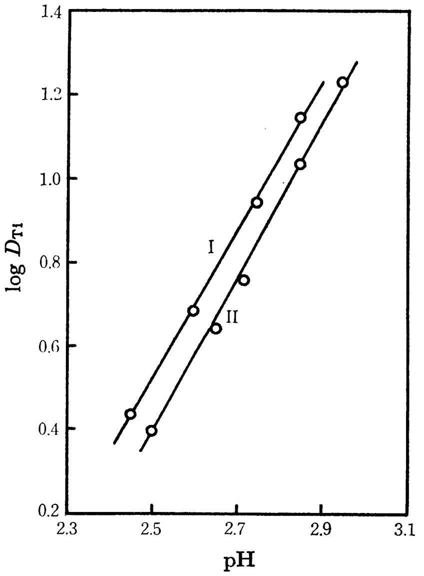

Fig. 6. Relationships between log D_{Ti} and pH for the Ti(IV)-Titon-DPG system.
Tiron: 5.0×10^{-3} M, DPG-Cl: 0.13 M, Ti: I; 1.0×10^{-5} M, II; 2.0×10^{-5} M

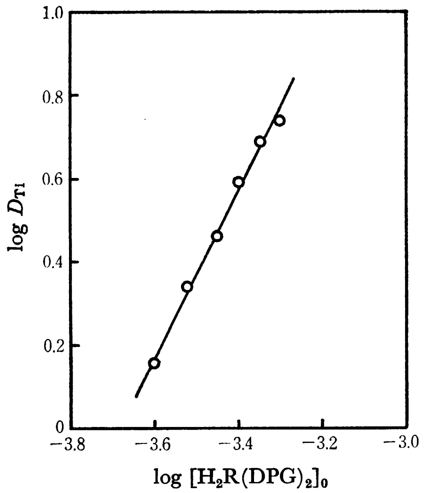

Fig. 5. Relationship between log D_{Ti} and log [$H_2R(DPG)_2$]$_0$ for the Ti(IV)-Tiron-DPG system.
Ti: 2.0×10^{-5} M, pH: 3.6

(Tiron-DPG concentration in the organic phase, [$H_2R(DPG)_2$]$_0$); all other variables were kept constant. The slope of 1.8 (Fig. 5) indicates that two molecules of Tiron combines with one atom of titanium. Evidently the composition of the extracted species is Ti: Tiron: DPG=1:2:4.

The pH dependence of the extraction was then examined by plotting log D_{Ti} against pH value of the aqueous phase. The curves shown in Fig. 6 indicates that two protons are concerned with the extraction process.

Since titanium(IV) exists predominantly as TiO^{2+} under the experimental conditions,[20] it may be assumed that the original complex is an anionic titanyl(IV)-Tiron species, $TiO(HR)_2^{4-}$, which combines with four DPG cations to form a neutral ion-association complex. From the foregoing observations, it seems natural that the extraction equilibrium expression is given in the simplest form

$$TiO^{2+} + 2[H_2R(DPG)_2]_0 \rightleftharpoons [TiO(HR)_2(DPG)_4]_0 + 2H^+$$

and that the distribution ratio of titanium is therefore expressed by

$$\log D_{Ti} = \log [TiO(HR)_2(DPG)_4]_0/[TiO^{2+}]$$
$$= \log K + 2 \log [H_2R(DPG)_2]_0 + 2\mathrm{pH}$$

where K is a constant including the acid dissociation constants of Tiron, the distribution coefficients of DPG-Cl, $H_2R(DPG)_2$, and $TiO(HR)_2(DPG)_4$, the formation constants of $H_2R(DPG)_2$ and $TiO(HR)_2(DPG)_4$, and the equilibrium constant of the reaction between titanium and Tiron.

The authors wish to thank Miss Tomiko Takebe for her laboratory work.

---

[20] S. Musha and K. Ogawa, *Nippon Kagaku Zasshi*, **78**, 1686 (1957).