Determination of Titanium(IV) Using *o*-Hydroxyhydroquinonephthalein and Tween 20

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Synopsis. A new, simple and sensitive spectrophotometric method for the determination of titanium(IV) was studied using *o*-hydroxyhydroquinonephthalein(Qn.Ph.) and Tween 20. The analytical species of interest have an absorption maximum at 595 nm and obeyed Beer's law over the range 0.3—2.4 μg of titanium(IV) in final 10 ml solution. This method was highly sensitive in comparison with Sandell sensitivity of 0.00025 μg/cm² for titanium(IV) at an absorbance of 0.001 at 595 nm against water and the molecular extinction coefficient of the Qn.Ph.–titanium (IV) complex was 1.91×10^5 l mol^{-1} cm^{-1}.

Various spectrophotometric methods for titanium-(IV), such as tiron,[1] diantipyrylmethane(DAM),[2,3] *N*-benzoy-*N*-phenylhydroxylamine(NBNPA),[4] and trioctylphosphine oxide[5] methods, have been reported. However, most of these methods are not selective, simple, rapid and sensitive.

On the other hand, we have already reported the simple and sensitive spectrophotometries for the determination of various metal ions using *o*-hydroxyhydroquinonephthalein(Qn.Ph.).[6-8]

In this paper, fundamental conditions for the color reaction between Qn.Ph. and titanium(IV) in the presence of various surfactants, and spectrophotometry of titanium(IV) were studied.

Experimental

Apparatus. The absorbance was measured with a Shimadzu Model 202 and 240 recording spectrophotometers using matched 1.0-cm quartz cells. For pH measurements a Toa Dempa Model HM-5 pH meter was used.

Reagents. A 1.0×10^{-3} M (1 M=1 mol dm^{-3}) Qn.Ph. methanol solution was prepared according to the previous report.[6] A stock solution of titanium(IV) was prepared by dissolving of 167 mg titanium dioxide in 10 ml of 97% sulfuric acid, and diluted to 100 ml with water. The working solution was made by suitable dilution of this stock solution as required. A 5% Tween 20 soultion was prepared by dissolving the respective compound in water. All other reagents used were of analytical grade.

Standard Procedure. A solution containing 0.3—2.4 μg of titanium(IV) was placed in a 10-ml measuring flask, 1.0 ml of 5% Tween 20 solution, and 0.5 ml of 1.0×10^{-3} M Qn.Ph. solution were added. The pH of the solution was adjusted to pH 4.7 with 0.2 M sodium acetate–acetic acid buffer (Walpole buffer) solution.

Then the solution was diluted to 10 ml with water, mixed well, kept at 60 °C for 60 min, and cooled for 5 min in water. The absorbance of the Qn.Ph.–titanium(IV) solution was measured at 595 nm against water. The concentration of titanium(IV) was determined using the calibration graph.

† Application of Xanthene Derivatives for Analytical Chemistry. Part XXIV. The previous paper is: I. Mori, Y. Fujita, K. Sakaguchi, and S, Kitano, *Bunseki Kagaku*, **31**, 475 (1982).

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra of the Qn.Ph.–titanium(IV) complex solution and Qn.Ph. solution in the presence of Tween 20 or hexadecyltrimethylammonium chloride (HTAC) as dispersion agent, respectively. It is evident that the Qn.Ph.–titanium(IV) complex exhibits a considerable bathochromic shift in the presence of nonionic surfactant such as Tween 20, and that the complex shows maximum absorption at 595 nm against water.

Effect of pH. The aqueous solution was adjusted to various pH values with Walpole buffer solution. The maximum and constant absorbance was obtained in the pH range from 4.4 to 4.9. Subsequent measurements were carried out at pH 4.7.

Effect of Various Dispersion Agents and Stability of the Complex. The color reaction rate between Qn.Ph. and titanium(IV) was slow in the absence of surfactants. On the other hand, in the presence of nonionic surfactants such as Tween 20 this color reaction was completed in about 45 min by heating at 60 °C, and the reaction was stable with highest sensitivity. In the presence of nonionic surfactants such as poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), Triton X-100 or

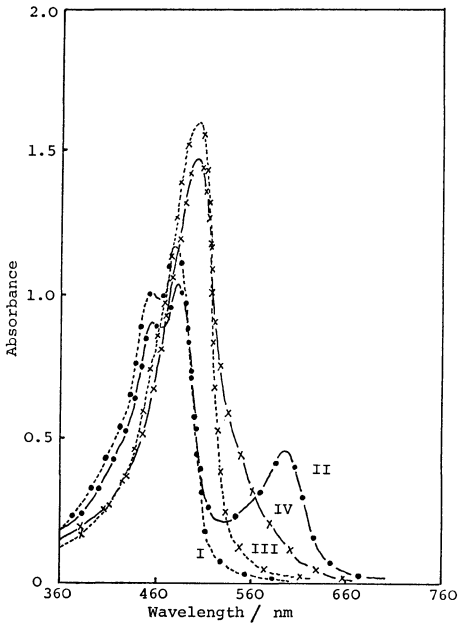

Fig. 1. Absorption spectra of Qn.Ph. solution and Qn.Ph.–Ti(IV) complex solution at pH 4.7.
Ti(IV): 2.5×10^{-6} M, Qn.Ph.: 5.0×10^{-5} M, Tween 20: 1.0 ml of 5% Tween 20 solution, HTAC: 4.0×10^{-3} M; reference: water, curve I: Qn.Ph.–Tween 20, curve II: Qn.Ph.–Ti(IV)–Tween 20, curve III: Qn.Ph.–HTAC, curve IV: Qn.Ph.–Ti(IV)–HTAC.

Table 1. Effect of foreign ions

Foreign ions	Added as	Added (μg)	Absorbance at 595 nm
—	—	—	0.478
Fe(III)	Sulfate	0.3	0.478
Al(III)	Nitrate	0.3	0.478
Th(IV)	Nitrate	0.3	0.470
Sn(IV)	Sulfate	0.2	0.464
Zr(IV)	Nitrate	0.6	0.442
Co(II)	Nitrate	15.9	0.470
Zn(II)	Nitrate	1.6	0.470
Pb(II)	Nitrate	0.3	0.442
Ni(II)	Nitrate	1.5	0.470
MoO_4^{2-}	Sodium	0.2	0.470
VO_3^-	Ammonium	0.1	0.460
F^-	Sodium	4.7	0.486
CN^-	Potassium	26.1	0.456
$S_2O_3^{2-}$	Sodium	1121.2	0.478
SCN^-	Ammonium	580.8	0.478
$C_2O_4^{2-}$	Sodium	88.0	0.470
$C_2H_2(OH)_2(COO^-)_2$	Acid	2961.4	0.478
$C_3H_4(OH)(COO^-)_2$	Acid	1891.0	0.478
Triethanolamine	—	1491.9	0.470

Ti(IV) taken: 1.2 μg; Qn.Ph.: 5.0×10^{-5} M; Tween 20: 1.0 ml of 5.0% Tween 20 solution; pH: 4.7; Reference: Water.

gelatin this color reaction increased rapidly and then decreased. The maximum and constant absorbance could be obtained over the range of 0.75 to 3.0 ml of 5% Tween 20 solution. The absorbance of the Qn. Ph.–titanium(IV) complex solution was constant and stable at least for 90 min at room temperature.

Calibration Curve. The calibration curve for the determination of titanium(IV) was prepared according to the standard procedure. Beer's law was hold in the concentration of 0.3—2.4 μg of titanium(IV) in final 10 ml. The molar absorptivity of the complex was estimated to be 1.91×10^5 l mol^{-1} cm^{-1} at 595 nm. The Sandell sensitivity was 0.00025 μg/cm^2 titanium(IV).

The precision was estimated for 1.8 μg/10 ml of titanium(IV), and the relative standard deviation was 0.46% for 8 determinations.

Effect of Foreign Ions. Interferences by various foreign ions for the determination of titanium(IV) were examined. The tolerance limit was taken as the amounts required to cause ±2% error in the absorbance. Iron(III), copper(II), aluminum(III), thorium-(IV), molybdenum(VI), vanadium(V), tin(IV), lead-(II), cyanide, sulfide, *etc.* caused a decrease in the absorbance at 595 nm. The interference of copper(II) could be overcome by addition of sodium thiosulfate solution, and that of iron(III) by addition of L-ascorbic acid solution as masking agents, respectively.

Composition of the Complex. The stoichiometry of the Qn.Ph.–titanium(IV) complex was evaluted by the continuous variation and the molar ratio methods. The results were estimated to be a defined 1:2 ratio

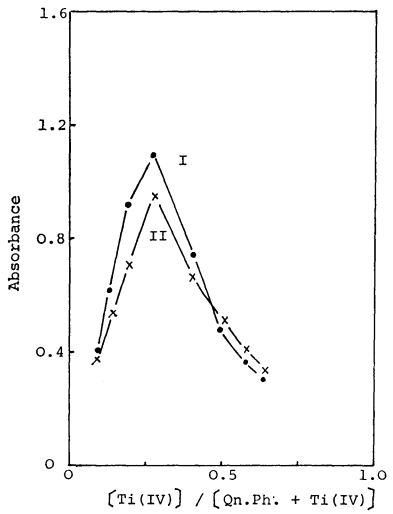

Fig. 2. Continuous variation method.
[Ti(IV)+Qn.Ph.]=2.5×10^{-5} M, Tween 20: 1.0 ml of 5% Tween 20 solution, pH: 4.7, reference: water, curve I: absorbance at 595 nm, curve II: absorbance at 580 nm.

of titanium(IV) to Qn.Ph.

Conclusion. The color reaction between Qn.Ph. and titanium(IV) complex was studied in the absence or presence of nonionic surfactancts such as Tween 20. And then, a simple and sensitive procedure for the determination of titanium(IV) using Qn.Ph. and Tween 20 was studied. The calibration curve was linear over 0.3—2.4 μg of titanium(IV) concentration. The molecular extinction coefficient of the Qn.Ph.–titanium(IV) complex was 1.91×10^5 l mol^{-1} cm^{-1}. It's sensitivity of this method was about ten times greater than DAM method,[2,3] and two fold greater than NBNPA method.[4] Therefore, this method is recommendable for the determination of microgram amounts of titanium(IV) in pigments and metallic luster agents.

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