The Photometric Determination of Titanium with Acetylacetone

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Many methods have been published concerning the determination of titanium in various substances.[1] The most widely-used method is that based on the yellow complex formed upon the addition of hydrogen peroxide to acidic solutions of titanium. Several factors can affect the results obtained by this procedure; these factors include the quantity of salts present in the solution, the quantity of peroxide used, and the temperature of the solution to which peroxide is added. The method is also subject to much interference, including that of niobium, which forms a red color with peroxide. Niobium frequently accompanies titanium in minerals.

One of the most sensitive and selective methods for the determination of titanium is based upon the measurement of the absorbance of the titanium thiocyanate complex at 432 mμ. after extraction from a hydrochloric or sulfuric acid solution by tri-*n*-octylphosphine oxide dissolved in cyclohexane.[2] The extracted complex follows Beer's law up to at least 1.7 μg. Ti/ml. Niobium and molybdenum are also known to interfere.

Acetylacetone has been of interest in analytical chemistry for many years because of its great ability to form complexes with many metals. Its use in complex formation for the solvent extraction of metals was given an excellent treatment in a monograph on the subject of metal solvent extractions,[3] in which the solvent extraction procedure utilizing acetylacetone was applied to titanium(IV). Acetylacetone forms a complex with titanium(III) which is intensely red in an acidic solution and blue in neutral and basic solutions. The color and absorbances of titanium(III) acetylacetonate containing 2.0 mg. of titanium in 50 ml. of solution at varying pH values are shown in Table I. The absorbances were measured with a Hirama Filter Photometer using 1 cm. cells. This reagent seemed very desirable for use as an analytical reagent for titanium because of its apparent ease of application, and because of the few ions which may be expected to interfere. Early attempts in this laboratory to utilize this complex for the quantitative determination of titanium were unsuccessful because of the instability of the color, which faded to a considerable extent within a few minutes after the addition of the reagent. This fading was somewhat delayed by the addition of stannous chloride, and a further delay in the fading process was accomplished by adjusting the pH to the range 1.5 to 2.5. Even with these innovations, however, the stability of the color was insufficient for use as an analytical procedure. It was then found that the addition of a few granules of zinc metal to the final solution delayed the fading sufficiently to allow the method to be generally applied.

TABLE I

pH	Lower than 1.5	1.5~2.5	Higher than 2.5
Color	red	red	Becomes more bluish with increasing pH values
Absorbance at 517 mμ	0.20 (at pH 0.5)	0.29	0.28 (at pH 4)

A spectrophotometric curve covering the visible region for titanium(III) acetylacetonate containing 1 mg. of titanium in 50 ml. of solution is shown in Fig. 1. The molar extinction index calculated for the maximum at 500~510 mμ is 350.

Complexing acids were investigated for the purpose of maintaining in solution titanium(III), tin(II), and other ions likely to be encountered in an analysis. The most desirable reagent for this purpose was found to be citric acid. The pH most suited to color development could be obtained by the addition of citric acid only; there was no necessity of adding any additional reagents to adjust the pH.

It was found that additions of EDTA, ascorbic acid, and thioglycollic acid as a means of eliminating interferences were unsuccessful because the intensity of the color of the titanium(III)-acetylacetonate complex was lower in their presence.

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[1] M. Codell, "Analytical Chemistry of Titanium Metals and Compounds," Interscience-Wiley, New York (1959), p. 87.

[2] J. P. Young and J. C. White, *Anal. Chem.*, **31**, 393 (1959).

[3] G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chmistry," Wiley, New York (1957), p. 158.

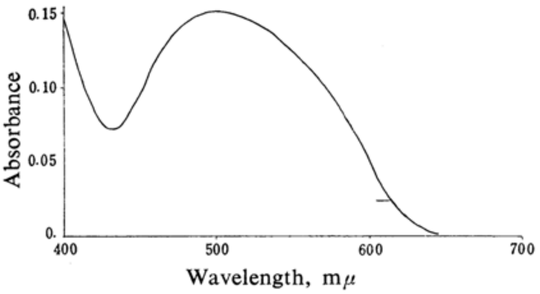

Fig. 1. Absorbance curve of titanium(III)-acetylacetonate.

The Procedure for Silicate Minerals.—Transfer a sample containing 0.2 to 20 mg. of titanium to a platinum dish, and add 10 ml. of sulfuric acid (1 to 1) and 5 ml. of concentrated hydrofluoric acid. Evaporate to fumes of sulfuric acid. Wash the sides of the dish with a small amount of water and again heat to fumes. Repeat the washing and fuming once more to insure the expulsion of all the fluoride. Transfer to a 100 ml. volumetric flask and dilute to 50 ml. Filter, ignite the residue, and fuse with about 2 g. of potassium bisulfate. Dissolve the melt in 10 ml. of sulfuric acid (1 to 10). Transfer the solution to the filtrate. If the titanium content is more than 7 mg. and dilute to a definite volume; then take an aliquot containing 1 to 5 mg. of titanium and add sulfuric acid sufficient to make the total content about 5 ml. of concentrated acid. Adjust the volume to 20 ml. If no aliquot has been taken, evaporate the solution to 20 ml. To the solution in a 100 ml. Ehrlenmeyer flask, add 1 g. of zinc (20 mesh). Let stand for about 10 min. In the presence of more than 20 mg. of iron, allow the solution to stand for 20 min. Add 5 ml. of a stannous chloride solution (5%). Add ammonium hydroxide (1 to 1) until the first faint permanent precipitate forms. Add 10 ml. of a 20% citric acid solution and 5 ml. of a 10% acetylacetone solution, and transfer the solution to a 50 ml. volumetric flask. Add several garnules of zinc metal (approximately 0.1 g.) and dilute to the mark with water. Within 45 min., measure the absorbance of the solution at 510 mμ, and estimate the titanium content by comparison with a calibration curve prepared by the absorbance measurement of a series of standard solutions containing known amounts of titanium, solutions prepared by adding 10 ml. of sulfuric acid (1 to 1) to aliquots of the stock solution contained in a 100 ml. Ehrlenmeyer flask and following the procedure for silicate rocks from the point where 1 g. of zinc is added. A stock standard solution of titanium containing 1 mg./ml. is prepared by heating titanium dioxide with a mixture of sulfuric acid and ammonium sulfate over an open flame and diluting the mixture with 1 : 10 sulfuric acid. A calibration curve prepared in this manner is shown in Fig 2. The results of the titanium analysis of two rock samples are shown in Table II.

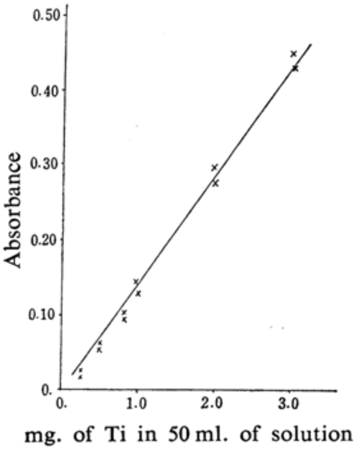

Fig. 2. Calibration curve.

TABLE II. ANALYSIS OF ROCK SAMPLES

Rock	Ti % found	Rock	Ti % found
	0.315		0.465
Granite	0.305	Silica ore	0.443
(2% Fe)	0.300	(0.8% Fe)	0.437
	0.299		0.415
	0.288		
	0.31 (by the H_2O_2 method)		0.45 (by the H_2O_2 method)

The Procedure in the Presence of Niobium Oxide.—Transfer a sample not exceeding 40 mg. of niobium to a platinum crucible. Fuse with 2 g. of potassium bisulfate and dissolve the melt in 10 ml. of sulfuric acid (1 to 1). Transfer the solution to a 100 ml. Ehrlenmeyer flask and dilute to 20 ml. Add 1 g. of zinc and proceed as directed above. The results of the analysis of titanium in titanium-niobium mixtures are shown in Table III.

TABLE III. DETERMINATION OF Ti IN THE PRESENCE OF 30 mg. Nb

Ti added, mg.	Ti recovered, mg.
3.0	3.2, 3.1, 3.0
2.0	2.1, 2.1

The Procedure in the Presence of Chromium, Vanadium and More than 25 mg. of Iron.—Dissolve the sample as directed in either of the above procedures. Transfer to an electrolytic beaker, dilute to 100 ml., adjust the sulfuric acid concentration to 5%, and electrolyze the solution at a mercury cathode for 15 min., using a current of 5 amp. Remove the solution, evaporate to 20 ml., add 1 g. of zinc, and proceed as directed under the

TABLE IV. DETERMINATION OF Ti AFTER TREATMENT WITH A MERCURY CATHODE

Ti presence, mg.	Ions added, mg.	Ti recovered, mg.
3.00	Fe 100	2.87
3.00	Fe 50	3.02
3.00	Cr 30	2.92
3.00	V 30	2.86

first procedure. The results of the analysis of titanium after treatment with a mercury cathode are shown in Table IV.

Summary

A new method has been proposed for the determination of small amounts of titanium in various substances. Acetylacetone forms an intensely-colored red complex in an acid solution with titanium(III), but this complex had not previously been used for the photometric estimation of titanium, probably because of the great instability of its color. A process has now been proposed for stabilizing the color. Up to 30 mg. of niobium and 30 mg. of iron do not interfere. Interference is encountered from chromium and vanadium, and in their presence, or in the presence of more than 30 g. of iron, a mercury cathode separation must be made. The method has been applied to quantities of titanium as small as 0.2 mg. in 50 ml. of solution.

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