Spectrophotometric Determination of Micro Quantities of Titanium with 8-Hydroxyquinaldine

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Introduction

Titanium forms slightly soluble chelate with oxine and this chelate can be extracted with chloroform, giving a yellow colored solution which has an absorption maximum at 385 mμ. This property can be used for the photometric determination of a small amount of this metal[1]. On the other hand, Gardner[2] has described a method based on a measurement of the color intensity of a chloroform solution of peroxidised titanium oxinate extracted from the solution containing hydrogen peroxide. These two methods are very sensitive, but the reactions are not very selective and, especially, the former method is affected seriously by small amounts of the aluminum and iron which are most likely to accompany titanium. In the method to be described below, 8-hydroxyquinaldine, one of the derivatives of oxine, is used as a reagent, and the method employed by the author for the spectrophotometric determination of beryllium with this reagent[3] is applied to this metal. By this method from 3 to 50 micrograms of titanium in about 35 ml. of solution can be determined without being affected by a few milligrams of aluminum. Moreover, small amounts of iron and titanium can be determined simultaneously in the similar way used for the simultaneous spectrophotometric determination of iron and aluminum with oxine[4].

Apparatus

A Beckman Model DU type spectrophotometer (Shimadzu, QB-50) with 1 cm. glass cell was used for all absorbancy measurements. A glass electrode pH meter (Horiba, Model M) was used for pH measurement. Separatory funnel, automatic measuring pipette and all other glass wares were the same ones used in the previous investigations[3,4].

Reagents

Standard Titanium Solution.—In 30 ml. of hot concentrated sulfuric acid, 3 g. of meta-titanic-acid (about 75% TiO_2) purified by reprecipitation, was dissolved and, after cooling, it was diluted to 1 liter. After suspended insoluble titanium

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[1] K. Motojima, Unpublished work.

[2] K. Gardner, *Analyst*, **76**, 485 (1951).

[3] K. Motojima, This Bulletin, **29**, 71 (1956).

[4] K. Motojima, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **76**, 903 (1955).

oxide was filtered off with a fine filter paper, the titanium content was determined gravimetrically as the oxide. Working solutions were prepared by exactly diluting this solution with 0.5 N sulfuric acid. Each 10 ml. of these solutions contained 10.8 and 21.6 micrograms of titanium.

Standard Ferric Iron Solution.—Several ferric iron standard solutions were prepared by dissolving pure ammonium iron alum in 0.1 N sulfuric acid.

8-Hydroxyquinaldine Solution.—1% 8-hydroxyquinaldine acetic acid solution was prepared[3].

Chloroform.—Purified chloroform[3] was used.

Other Reagents.—The other reagents were prepared from reagent grade chemicals.

Experimental

Absorption Spectra.—Absorption spectra of titanium chelate of 8-hydroxyquinaldine extracted with chloroform were studied. The data obtained are shown in Fig. 1. From these curves, it is seen that this chelate in chloroform has an absorption maximum at the wave length of 370 mμ, and at the same time, the reagent alone in this solvent has a considerable absorption at this wave length. Accordingly, the wave length of 380 mμ has been chosen for the analytical purpose.

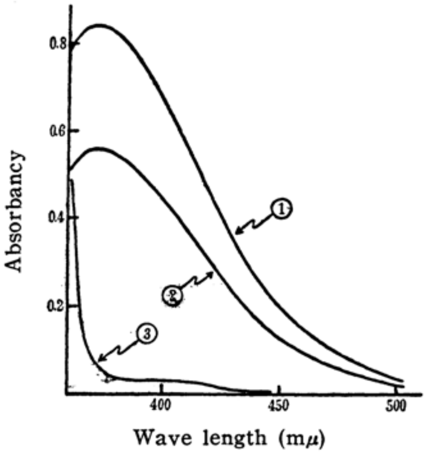

Fig. 1. Absorption spectra of titanium chelate of 8-hydroxyquinaldine in chloroform.
①: 32.4 micrograms of Ti,
②: 21.6 micrograms of Ti,
③: blank.

Effect of pH upon Extraction.—The proper pH for the efficient extraction of titanium was determined. A series of several solutions each containing 21.6 micrograms of titanium in about 35 ml. was treated with 3 ml. of 8-hydroxyquinaldine solution and suitable amount of ammonium acetate or ammonium hydroxide enough to fall within a pH range from 2 to 11. After the volume of the solution was brought to 50 ml., extraction was made with exactly 10 ml. of chloroform. Then, the absorbancy of the extract dried with anhydrous sodium sulfate, was measured at 380 mμ versus chloroform. On the other hand, measurement of pH was made on the aqueous layer after extraction. The results obtained are shown in Fig. 2. Extraction is seen to be almost complete over a pH range from 5.0 to 9.0, and the approximately constant absorbancies are obtained in the pH range from 5.0 to 6.0. A similar experiment was made about the reagent, and it was found that the blanks were reasonably constant in the pH range from 4.0 to 10.0. So that the pH range from 5.0 to 6.0 has been chosen as the optimum range for this method.

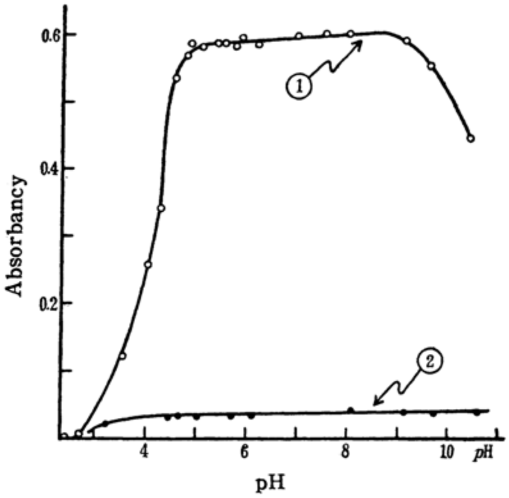

Fig. 2. Effect of pH upon extraction.
①: 21.6 micrograms of Ti,
②: blank.

Amount of Reagent.—Approximately 50 ml. of solutions each containing 43.2 micrograms of titanium and varying amounts of 8-hydroxyquinaldine solution, were extracted with exactly 10 ml. of chloroform respectively, at a pH of 5.3±0.2, and the absorbancies of these dried extracts were measured at 380 mμ, versus chloroform. A similar set but with no titanium present was also done. The results are shown in Table I.

TABLE I

EFFECT OF AMOUNT OF REAGENT

8-Hydroxyquinaldine Added, ml.	Absorbancy Measured		Correct for Blank
	Ti is present	Blank	
0.5	0.404	0.017	0.387
1.0	0.855	0.017	0.838
1.5	0.980	0.015	0.965
2.0	1.100	0.027	1.073
2.5	1.130	0.031	1.099
3.0	1.135	0.033	1.102
3.5	1.150	0.039	1.111
4.0	1.135	0.046	1.089
5.0	1.155	0.047	1.108

When more than 2.5 ml. of reagent solution is added, the absorbancies, after correction for the blank reading are reasonably constant. Therefore, 3 ml. of 8-hydroxyquinaldine solution has been selected as a sufficient amount of reagent.

Effect of Temperature and Digestion.—After five, fifteen, thirty and sixty minutes of digestion at various temperatures, from 10° to 80°C, extractions were made respectively, in case of high temperature, solution being cooled to room temperature before extraction. And it was found that since the absorbancies of their dried extracts were reasonably constant, no digestion was necessary.

Shaking Period.—The complete extraction of titanium chelate of 8-hydroxyquinadline with chloroform seems to be attained by vigorous shaking for thirty seconds.

Stability.—The absorbancy of the dried chloroform extract of titanium chelate, stored in a glass bottle with a glass stopper and protected from sunlight, was found to remain unchanged for a week.

Spectrophotometric Procedure and Preparation of Calibration Curve

About 35 ml. of acidic solution containing not more than 50 micrograms of titanium, is treated with 3 ml. of 8-hydroxyquinaldine solution and suitable amounts of 2 N ammonium hydroxide and 2 N ammonium acetate solution enough to attain the pH to 5.3±0.2. The solution is transferred to a separatory funnel with a few milliliters of rinsed water and the volume is brought to 50 ml. Then extraction is made with exactly 10 ml. of chloroform by vigorous shaking for a minute. The chloroform layer is drawn off into a small glass bottle with a glass stopper, containing 1 g. of anhydrous sodium sulfate, and is shaken to remove droplets of water. The absorbancy of this extract is measured at 380 mμ using blank as a reference. Titanium is determined by the use of the calibration curve prepared by the same treatment of a series of known amount of this metal.

The calibration curve obtained is shown in Fig. 3. As will be seen from this curve, a close approximation to a linear relationship between titanium concentration and the absorbancy is obtained up to 50 micrograms or more.

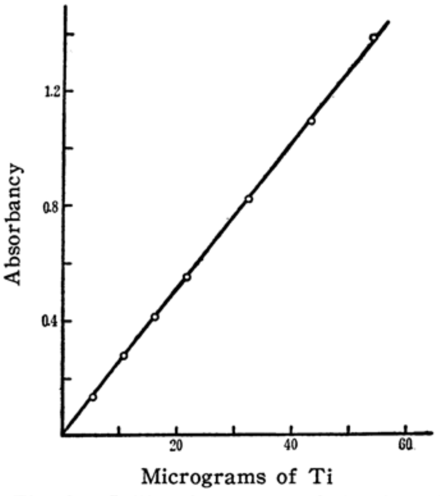

Fig. 3. Calibration curve of titanium (at the wave length of 380 mμ).

Interfering Substances

Relatively large amounts of alkali, ammonium, calcium and magnesium salts of acetate, chloride, nitrate and sulfate, and less than about 10 mg. of aluminum do not interfere with this procedure. Tartrate produces a serious effect and gives a low result. Such metals as bithmus, cobalt, copper, iron, nickel, vanadium and zirconium which form chloroform soluble chelate with 8-hydroxyquinaldine in acetic acid and acetate medium interfere with this method, and these metals, except a small amount of ferric iron, should be absent.

Ferric iron yields a dark blue chloroform solution under the same condition and interferes seriously with this method, but when its amount is less than about 100 micrograms, titanium and iron can be determined simultaneously by a method similar to that presented by the author[3,4].

Simultaneous Spectrophotometric Determination of Titanium and Iron

Ferric chelate of 8-hydroxyquinaldine in chloroform has two absorbancy maxima at 470 and 580 mμ, and Beer's law is obeyed at both 380 and 580 mμ, respectively. On the other hand titanium chelate has no absorption at 580 mμ. Therefore, both titanium and iron can be determined simultaneously, by the very same treatment mentioned above, and by measuring the absorbancies at 380 and 580 mμ and applying the following formulas[5].

$$C_{\mathrm{Fe}}=\frac{A_{580}}{a_{580}^{\mathrm{Fe}}}$$

$$C_{\mathrm{Ti}}=\frac{a_{580}^{\mathrm{Fe}}\cdot A_{380}-a_{380}^{\mathrm{Fe}}\cdot A_{580}}{a_{380}^{\mathrm{Ti}}\cdot a_{580}^{\mathrm{Fe}}}$$

Where, C_{Fe}, C_{Ti}: iron and titanium present, in microgram,

A_{380}, A_{580}: absorbancies measured at 380 and 580 mμ,

a_{380}^{Ti}, a_{380}^{Fe}, a_{580}^{Fe}: absorbancy indexes of titanium and iron at 380 and 580 mμ (the absorbancy per microgram of these metals).

In this experiment the values of these absorbancy indexes obtained are as follows:

$$a_{380}^{\mathrm{Fe}}=0.0088 \qquad a_{580}^{\mathrm{Fe}}=0.0077$$

$$a_{380}^{\mathrm{Ti}}=0.0254$$

the values of a_{380}^{Fe} and a_{580}^{Fe} are slightly lower than that when extraction is made in ammoniacal medium[3], because these values slightly increase in proportion to the pH at which extraction is made. Nevertheless, their changes are negligible when extraction is made at the pH range from 5 to 6.

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[5] E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience Publisher Inc., New York (1950) p. 70.

Several mixed solutions containing known amounts of titanium and iron in various ratios were prepared and these two metals were determined. Some of the results are shown in Table II, which seem to be quite satisfactory.

TABLE II
SIMULTANEOUS DETERMINATION OF TITANIUM AND IRON

Taken Microgram		Absorbancy Measured		Calculated Microgram	
Ti	Fe	380 mμ	580 mμ	Ti	Fe
5.4	20.0	0.324	0.161	5.5	20.9
5.4	40.0	0.481	0.308	5.1	40.1
5.4	60.0	0.657	0.466	5.3	60.6
5.4	80.0	0.830	0.623	4.6	81.0
5.4	100.0	0.990	0.774	4.2	100.7
10.8	20.0	0.450	0.160	10.6	20.8
10.8	40.0	0.626	0.311	10.7	40.5
10.8	60.0	0.810	0.476	10.5	61.9
10.8	80.0	0.975	0.614	10.9	79.9
10.8	100.0	1.125	0.765	9.9	99.5
21.6	20.0	0.724	0.164	21.1	21.3
21.6	40.0	0.875	0.312	20.5	40.6
21.6	60.0	1.090	0.473	21.8	61.6
21.6	80.0	1.270	0.627	22.0	81.5
32.4	20.0	1.025	0.164	33.1	21.3
32.4	40.0	1.160	0.315	31.5	41.0
32.4	60.0	1.350	0.471	32.0	61.3

Conclusion

The spectrophotometric method for determination of micro quantities of titanium with 8-hydroxyquinaldine was established. By this method from 3 to 50 micrograms of titanium in about 35 ml. of solution can be determined; therefore the sensitivity of this method is almost equal to that of the tiron method established by Yoe and his coworker⁶⁾, but is much better than that of the ordinary hydrogen peroxide method⁷⁾. A few milligrams of aluminum do not interferes with this method. Moreover, the method for simultaneous determination of micro quantities of titanium and iron was studied.

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

7) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed. (1950), p. 572.