Spectrophotometric Determinatoin of Micro Quantities of Iron, Titanium and Aluminum when They accompany Each Other. Use of 8-Hydroxyquinaldine and Oxine

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Introduction

In general, iron, titanium and aluminum accompany each other, and the methods for separation and determination of these three metals are very essential. By the method described below, micro quantities of these three metals can be separated and determined by the use of 8-hydroxyquinaldine and oxine as reagents.

In the previous paper[1] presented by one of the authors, it has been reported that small amounts of iron and titanium can be extracted with chloroform as their chelate of 8-hydroxyquinaldine, and that by measuring the absorbancies of the extract at 380 and 580 mμ, these two metals can be determined simultaneously. At the same time iron and titanium are quantitatively extracted off and aluminum is perfectly left in aqueous phase. Therefore, after the above extraction aluminum can be determined photometrically without being effected by iron and titanium. using oxine as a reagent[2,3].

Apparatus and Reagents

All the apparatus and the reagents except for the following ones were the same as those had been used in the previous work[1].

Standard Aluminum Solution.—Several stand-

1) K. Motojima, This Bulletin, 29, 455 (1956).

2) E. B. Sandell, "Colorimetric Determination of Metals", 2nd Ed. (1950), p. 152.

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

ard aluminum solutions were prepared from pure potassium aluminum alum.

Oxine Solution (1% acetic acid solution).—In 5 ml. of glacial acetic acid 2 grams of pure oxine were dissolved by warming, and the volume was brought to 200 ml. with distilled water.

Procedure

Approximately 50 ml. of acidic solution containing not more than 50 micrograms of iron, titanium and aluminum respectively, 3 ml. of 8-hydroxyquinaldine solution and suitable amounts of ammonium hydroxide and ammonium acetate enough to adjust the pH to 5.3±0.2, is extracted with exactly 10 ml. of chloroform. Then, the measurements of two absorbancies at 380 and 580 mμ of the dry extract are made using blank as a reference, and iron and titanium are determined by the method mentioned in the previous paper[1]).

The aqueous layer is washed three times with 10 ml. of chloroform by shaking for about thirty seconds respectively. By this treatment iron, titanium and 8-hydroxyquinaldine will be quantitatively removed from the aqueous phase. Then the aqueous solution is transferred into a 100 ml. beaker with a few milliliters of rinsed water, treated with 3 ml. of 2 N sulfuric acid and heated on water bath to expel the chloroform which comes into the solution, and the volume is brought to about 35 ml. by evaporation.

After cooling, the solution thus resulting is treated with 3 ml. of oxine solution and a suitable amount of 2 N ammonium acetate enough to adjust the pH to 5.0±0.2, and transferred in a separatory funnel with a few milliliters of rinsed water, and the volume is brought to 50 ml. Then the extraction is made by vigorous shaking for a minute with exactly 10 ml. of chloroform. The chloroform layer is dried with a gram of anhydrous sodium sulfate and the absorbancy at 390 mμ is measured using blank as a reference. Aluminum is determined by the use of the calibration curve[3]).

Discussion and Results

If 8-hydroxyquinaldine extraction is made with 20 or 30 ml. of chloroform, double or triple amounts of iron and titanium can be determined respectively. When the amount of aluminum is more than 50 micrograms, the acidified solution from which iron and titanium have been removed by 8-hydroxyquinaldine extraction, is exactly diluted to suitable volume with distilled water using a volumetric flask, and an aliquot is taken for determination of aluminum. By this method up to a milligram of aluminum can be determined accurately.

TABLE

DETERMINATION OF IRON, TITANIUM AND ALUMINUM

Taken Microgram			Absorbancy Measured: 8-Hydroxyquinaldine Extraction		Absorbancy Measured: Oxine Extraction		Found Microgram		
Fe	Ti	Al	380 mμ	580 mμ	390 mμ	470 mμ	Fe	Ti	Al
0.0	5.4	25.0	0.124	0.004	0.656	0.011	0.1	4.7	25.4
0.0	10.8	25.0	0.275	0.011	0.678	0.012	0.1	10.3	26.2
0.0	21.6	25.0	0.549	0.000	0.674	0.014	0.0	21.6	26.0
40.0	0.0	25.0	0.338	0.291	0.617	0.014	37.9	0.2	23.8
40.0	5.4	25.0	0.486	0.308	0.612	0.004	40.0	5.3	23.9
40.0	10.8	0.0	0.605	0.303	0.005	0.007	39.4	10.2	0.0
40.0	10.8	10.0	0.633	0.318	0.279	0.008	41.4	10.6	10.7
40.0	10.8	25.0	0.629	0.311	0.640	0.001	40.5	10.8	25.0
40.0	10.8	50.0	0.638	0.319	1.210	0.011	41.5	10.8	47.1
40.0	21.6	0.0	0.905	0.311	0.004	0.006	40.5	21.7	0.0
40.0	21.6	10.0	0.910	0.305	0.284	0.008	39.7	22.2	10.9
40.0	21.6	25.0	0.910	0.302	0.665	0.018	39.3	22.3	25.5
40.0	21.6	50.0	0.900	0.312	1.240	0.021	40.6	21.4	48.0
40.0	32.4	0.0	1.160	0.308	0.010	0.014	40.0	31.8	0.0
40.0	32.4	10.0	1.190	0.306	0.280	0.009	39.8	33.1	10.7
40.0	32.4	25.0	1.190	0.322	0.651	0.005	41.9	32.4	25.4
40.0	32.4	50.0	1.200	0.319	1.210	0.005	41.5	33.0	47.2
0.0	5.4	200.	0.126	0.005	*1.270	0.017	0.1	4.8	197.
0.0	10.8	200.	0.277	0.012	*1.250	0.015	0.2	10.4	194.
0.0	21.6	100.	0.573	0.003	*0.631	0.018	0.0	22.4	97.
0.0	21.6	200.	0.549	0.000	*1.225	0.016	0.0	21.6	190.
40.0	5.4	200.	0.472	0.300	*1.235	0.016	39.0	5.1	190.
40.0	10.8	100.	0.639	0.313	*0.629	0.013	40.7	11.1	97.
40.0	10.8	200.	0.635	0.318	*1.255	0.030	41.4	10.7	194.
40.0	21.6	100.	0.915	0.305	*0.645	0.012	39.7	22.3	100.
40.0	21.6	200.	0.910	0.299	*1.220	0.016	38.9	22.4	189.

* Measurement was made for 25 ml. portion of the solution diluted to 100 ml.

The pH of the solution, after 8-hydroxyquinaldine extraction, is about 5.3 and at this pH aluminum tends to form hydroxide and give low analytical result; for this reason the solution should be acidified with sulfuric or hydrochloric acid before the determination of aluminum is carried out.

When the measurement of absorbancy of aluminum oxinate extract is made, it is desirable to measure the absorbancy of the extract at 470 mμ which is caused by iron oxinate, and, if necessary, make a correction for iron which seems to come accidentally into the solution during the procedure, by the method mentioned by one of the authors[3].

Relatively large amounts of alkali, ammonium, calcium and magnesium salts of acetate, chloride, nitrate and sulfate do not interfere with this procedure. Tartrate, fluoride and metal ions which form chloroform soluble chelate with 8-hydroxyquinaldine and oxine in acetic acid and acetate medium interfere with this method, and they should be absent.

A number of mixed solutions containing known amounts of iron, titanium and aluminum were prepared and these three metals were determined. Some of the results are shown in the following table, which seems to be quite satisfactory.

Conclusion

The method for separation and spectrophotometric determination of micro quantities of iron, titanium and aluminum with 8-hydroxyquinaldine and oxine was established. By this method, from 3 to 50 micrograms of iron, titanium and aluminium mixed in about 35 ml. of solution, are determined, rapidly and accurately.

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