Separation of a Small Amount of Titanium from Iron by Ion-Exchange Resin

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Introduction

In determining a small amount of titanium, the colorimetric method with hydrogen peroxide(1) has been most commonly used. But, if a sample contains much iron, the color of ferric ion intensifies that of the test solution.

W.F. Hillebrand(2) says that 0.1 g. of Fe_2O_3 in 100 cc. of solution corresponds to 0.02 per cent TiO_2 in the same volume of solution.

To avoid this interference, various devices have been offered. For example, the addition of the same amount of iron to the standard solution(3) is the simplest method. In the case when iron content is very high, however, this method would prove ineffective in determining titanium. P. Faber(4) recommended the addition of phosphoric acid to both the standard and the test solution in order to neutralize the effect of iron. However, since phosphoric acid weakens the yellow tint to some extent, the use of this method is not always desirable when the amount of titanium is very small.

For accurate analysis, therefore, sepatation of titanium from iron before the color development seems to be the most desirable. For such a purpose, the separation of iron as ferrous sulfide in presence of tartaric acid(5) has been in the most common use. For the satisfactory employment of this method, however, the double precipitation of ferrous sulfide is necessary, because a part of titanium is apt to coprecipitate with it. Moreover, the tartaric acid must be completely decomposed before development of the color.

The authors have studied the method of separation of both elements using an ion-exchange resin and found that even a large amount of iron could be removed as ferricyanide complex ion as described in the following.

Experimental

Apparatus and Reagent.—The cation-exchanger used was one of commercial phenolsulfonic acid polymers and between 30 and 70 mesh of size. Five or ten grams of the resin were conveniently equipped in a 50 cc. burette. The standard solution of ferric ion was prepared from Merck's ferric sesquichloride and that of titanium from Kahlbaum's titanium dioxide after bisulfate fusion.

Determination Method of Titanium.—In the experiment, the standard solutions of both ions were mixed together in various proportions, then following two ways of treatment were studied.

Method 1.—On treating the sample solution, in which iron concentration is rather high, with 50 per cent potassium or sodium cyanide solution, the iron is converted into both ferricyanide complex ion and ferric hydroxide percipitate, while titanium coprecipitates quantitatively as white titanium hydroxide owing to the excess of alkali cyanide. The precipitates are filtered off and dissolved with dilute sulfuric acid. This is diluted with water and passed through the column of resin previously saturated with hydrogen ion. Then, the resin is washed with about 200 cc. of 2*N*-KCN solution at the rate of 1 cc. per minute or less. The adsorbed iron is gradually eluted out as ferricyanide complex, while titanium remains without change. After washing the column thoroughly with water, adsorbed titanium is eluted with from 100 to 200 cc. of 10 per cent sulfuric acid. The aliquot portions of the eluent are used for colorimetric determinations of titanium as well as remaining iron. The results are shown in Table 1.

Table 1

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	Ti^{++++}	0.12	0.12	0
	Fe^{+++}	50.2	2.3	—
2	Ti^{++++}	0.68	0.68	0
	Fe^{+++}	67.2	0.3	—

If the concentration of iron is relatively low, all the iron is apparently converted into complex ion by previous treatment with the excess of concentrated potassium cyanide solution while titanium forms the precipitate. In such a case, a little dilute sulfuric acid just enough to dissolve the precipitate is added very cautiously and the solution is passed through the column of resin. After elution with 10 per cent sulfuric acid, titanium is determined as before. Table 2 shows the results of such experiments.

Table 2

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	Ti^{++++}	0.48	0.45	−0.03
	Fe^{+++}	0.88	trace	—
2	Ti^{++++}	0.68	0.66	−0.02
	Fe^{+++}	0.88	trace	—

Method 2.—Various mixed solution of iron and titanium are passed through the resin

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(1) A. Weller, *Ber.*, **15**, 2592 (1882).

(2) W.F. Hiilebrand, *Bull. U.S. Geol. Sur.*, **700**, 160 (1919).

(3) W.A. Noyes, *Journ. Anal. App. Chem.*, **5**, 39 (1891).

(4) P. Faber, *Chem. Zeit.*, **31**, 263 (1906).

(5) R. Fresenius, *Z. anal. Chem.*, **1**, 69 (1862).

without any previous treatment. The adsorbed iron is eluted out with from 300 to 500 cc. of 2*N*-NaCN solution as slowly as 1 cc. per minute or less. The elution and determination of titanium are conducted as described above. The results are listed in Table 3.

Table 3

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	Ti^{++++}	0.68	0.66	—0.02
	Fe^{+++}	0.88	0.08	—
2	Ti^{++++}	0.68	0.71	+0.03
	Fe^{+++}	8.78	0.16	—
3	Ti^{++++}	0.68	0.68	0
	Fe^{+++}	67.2	0.25	—

The results obtained by both Methods 1 and 2 seem to be satisfactory for the colorimetric determination of a small amount of titanium in a sample rich in iron.

Determination of Titanium in Limonite.—As an example of practical application of the method, the titanium content in the limonite from Asahida mine, Kumamoto Pref., Kyushu is determined. The spectroscopic analysis of the sample showed the presence of the following minor constituents.

Al, Be, Ca, K, Li, Mg, Mn, Na Si, Ti, V.

Of these, the content of vanadium was previously determined by E. B. Sandell's colorimetric method⁽⁶⁾ and obtained the value of 0.012 per cent as V. The iron content was 74.51 per cent as Fe_2O_3. Therefore, the test solution was prepared according to the following procedure. About 1 gram of the powdered sample was weighed and fused with sodium carbonate and the fused mass was leached with water. The residue was dissolved in a small volume of hot 10 per cent sulfuric acid and diluted to 250 cc., of which 50 cc. was used for titanium determination according to the Method 1.

To make sure, we took another portion of the test solution and separated iron as ferrous sulfide by the ordinary hydrogen sulfide method and determined titanium colorimetrically. The results of both experiments were in good agreement as indicated in Table 4.

Table 4

Method of Separation	Titanium Content, % TiO_2
Resin method	0.207
H_2S method	0.197

Discussion

As cation exchange resin is not resistant enough against alkaline solution, its repeated use will result in the decrease of exchange capacity and will not be desirable. By reason of that, Method 1 which requires less alkali cyanide solution as an eluting agent seems to be more preferable to Method 2 in case of a sample rich in iron.

Summary

Separation of a small amount of titanium from iron with cation exchange resin was studied using alkali cyanide solution as eluting agent of iron. Successful results were obtained even in case of high iron concentration. This method enables us to remove the interfering effect of the iron on titanium colorimetry with hydrogen peroxide.

As an examle of practical application, this method was tried in determining the titanium content of a limonite. The result agreed with that of the ordinary method of separation.

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(6) E.B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **5**, 336 (1936).