Indirect Complexometric Titration of Beryllium with Ethylenediaminetetraacetic Acid

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Ethylenediaminetetraacetic acid (EDTA) has been used for volumetric determination of various metal ions, but it can not be used for a direct titration of the beryllium ion nor for that of the sodium and the potassium ion because these metal ions do not form stable EDTA complexes. Flaschka[1] reported the indirect titration method for sodium, and Pilleri[2] and one of the present authors[3] that for potassium. Pirtea and Mihail[4] reported that beryllium was determined gravimetrically, producing the precipitate $[Co(NH_3)_6]\cdot[(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$, by adding saturated hexammine cobaltic trichloride solution (Luteo salt) to beryllium carbonate solution. We studied the determination of beryllium ion concentration by volumetrically measuring the cobalt content in this precipitate. This method was proved to be quantitative and it was possible to separate and determine beryllium from iron (III), aluminum

1) H. Flaschka, *Mikrochemie ver. Mikrochim. Acta*, **39**, 391 (1952).
2) R. Pilleri, *Z. anal. Chem.*, **157**, 1 (1957).
3) T. Taketatsu, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 756 (1957).
4) T. I. Pirtea and G. Mihail, *Z. anal. Chem.*, **159**, 205 (1958).

and magnesium by using EDTA as a masking agent.

Experimental

Reagents.—Standard beryllium solution was prepared by dissolving the nitrate salt in distilled water and the concentration was determined gravimetrically as the oxide. The content (BeO) was 1.95 mg./ml.

Standard EDTA solution was obtained by dissolving the pure disodium salt of ethylenediaminetetraacetic acid dihydrate (Research Laboratory, Dojindo & Co., Ltd.) in distilled water. The concentration was determined by titrating standard zinc chloride solution with Eriochrome black T as indicator. The concentration was 0.01016 mol.

Hexammine cobaltic trichloride (Luteo salt) solution was prepared by Fernelius's method[5] and the supernatant liquid of the saturated solution was used in this experiment.

All other chemicals used were analytical reagent grades.

General Procedure.—An excess of ammonium carbonate was added to about 10 ml. of a slightly acidic solution containing 0.70 to 3.50 mg. of beryllium; a precipitate of basic beryllium carbonate was formed, which was then dissolved completely by stirring for a time. To this clear solution was added a few milliliters of saturated Luteo salt solution and an orange yellow precipitate[4] was obtained by stirring the solution. The solution containing the precipitate was stirred occasionally by a magnetic stirrer for several hours to make the precipitation complete. The precipitate was then filtered with a glass filter (1G. No. 4) and washed 2 to 3 times successively with 2 to 3 ml. of the following solutions: 0.2% Luteo salt solution, a mixture of ethanol and water (60 ml. +40 ml.) containing 2 to 3 drops of 0.2% Luteo salt solution, and absolute ethanol. The percipitate on the glass filter was dissolved in a small amount of 0.1 N hydrochloric acid. To decompose the Luteo salt in the solution obtained, one gram of sodium hydroxide was added to the solution and then the solution was boiled till the black-brown precipitate of cobalt (III) hydroxide was obtained. The solution containing the precipitate was acidified by adding hydrochloric acid and boiled to dissolve the cobalt hydroxide. By this procedure the valency of cobalt was reduced to II from III with hydrochloric acid and a solution containing cobalt (II) and beryllium ions was obtained. After the solution cooled, a small amount of malic acid was added to the solution and it was neutralized with aqueous ammonia (1:1, by volume). The cobalt in the solution was titrated with the standard EDTA solution by adding 0.2 g. of Murexide as indicator. The point at which the indicator attained its maximum violet color was as the end point.

1 ml. of 0.01 mol. EDTA solution
≡0.1803 mg. of berlliyum.

These procedures were carried out at 20~25°C except for boiling purposes.

Results and Discussion

In the general procedure described above, the following factors were specially considered; effects of the amount of ammonium carbonate, Luteo salt and malic acid, and of time allowed for the formation of the precipitate II*.

1) Relation between Ammonium Carbonate Added and the Time Required to Dissolve Basic Beryllium Carbonate.—When an excess of ammonium crabonate was added to about 10 ml. of solution containing 1.40 mg. of beryllium, basic beryllium carbonate was precipitated at first, but the precipitate was dissolved gradually by stirring, because beryllium carbonate complex was produced. The relation between the amount of ammonium carbonate added and the time required for dissolving the precipitate was studied and the results are shown in Table I. It is shown that the more the amount of ammonium carbonate, the shorter the time required for the dissolving of the precipitate.

TABLE I. RELATION BETWEEN THE AMOUNT OF AMMONIUM CARBONATE AND APPROXIMATE TIME REQUIRED TO DISSOLVE BASIC BERYLLIUM CARBONATE

Ammonium carbonate added, g.	Time for dissolving the precipitate, min.
0.5	>60
1.0	25~30
1.5	10~20
2.0	7~ 8
2.5	5~ 7
3.0	3~ 5
4.0	1~ 2

2) Effect of Luteo Salt Added.—To determine the optimum amount of Luteo salt added, various volumes of saturated Leuteo salt solution were added to the beryllium carbonate complex solution. In this case, all other conditions were kept constant. The results are shown in Table II.

It was found that the amount of the reagent added did not affect the determination of beryllium within the range 1 to 8 ml.

5) W. C. Fernelius, "Inorganic Syntheses", Vol. II, McGraw Hill Book Co., Inc., New York (1946), p. 217.

* The precipitate II means $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$

TABLE II. EFFECT OF LUTEO SALT ADDED

Be taken, mg.	Saturated Luteo salt solution added, ml.	Vol. of 0.01016 mol. EDTA titrated, ml.	Be found, mg.	Error, mg.
1.40	1.0	7.72	1.41	+0.01
1.40	2.0	7.79	1.43	+0.03
1.40	4.0	7.61	1.39	−0.01
1.40	5.0	7.72	1.41	+0.01
1.40	8.0	7.65	1.40	±0.00

3) Relation between the Amount of the Precipitate and That of Ammonium Carbonate Added.—Since the amount of ammonium carbonate added had an effect on the formation of the precipitate II., the relation between the amount of the precipitate formed and that of ammonium carbonate added was studied at various time intervals after Luteo salt was added. The results are shown in Fig. 1.

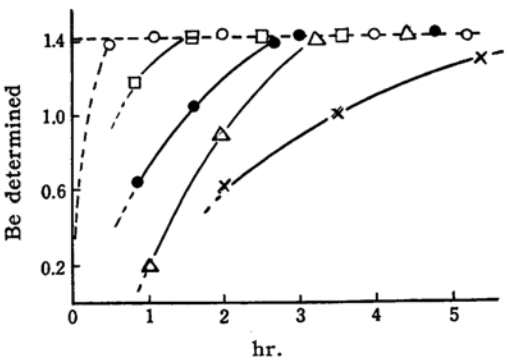

Fig. 1. Relation between beryllium determined v.s. time at various concentrations of ammonium carbonate added.

	Ammoium carbonate
—○—○—	1.0 g
—□—□—	1.5 g
—●—●—	2.0 g
—△—△—	3.0 g
—×—×—	4.0 g

When a small amount of ammonium carbonate had been added to the initial beryllium solution, the precipitate II was formed quantitatively as soon as Luteo salt was added. On the other hand, a longer time was necessary for the formation of the precipitate II with increase in the amount of ammonium carbonate. However, as it is convenient for the dissolution of the precipitate of basic beryllium carbonate to add a greater amount of ammonium carbonate as described above, 1.5 to 2.0 g. of ammonium carbonate was used in this experiment.

4) Effect of Malic Acid on the Titration of Cobalt. — When the titration of cobalt was carried out in an ammonium alkaline solution by using Murexide as indicator, beryllium precipitated as its hydroxide and the results, therefore, proved inaccurate. Since the hydroxide does not precipitate in general in the presence of malic acid, the effect of malic acid on the titration of cobalt was studied. The results are shown in Table III.

TABLE III. EFFECT OF MALIC ACID ADDED

Co taken, mg.	5% malic acid added, ml.	Vol. of 0.01016 mol. EDTA titrated, ml.	Co found, mg.	Error, mg.
3.64	0	6.08	3.64	±0.00
3.64	2	6.08	3.64	±0.00
3.64	4	6.08	3.64	±0.00
3.64	5	6.07	3.63	−0.01
3.64	10	6.05	3.62	−0.02

It is evident that the addition of 2 to 10 ml. of 5% malic acid solution did not give an error in the titration. But larger amounts of malic acid showed negative errors. Therefore, 2 ml. of 5% malic acid were used.

The results obtained from the titration of cobalt (3.64 mg.) with standard EDTA solution in the presence of 0.70 to 3.50 mg. of beryllium and 2 ml. of 5% malic acid are shown in Table IV. It was found that beryllium gives no effects in the titration of cobalt.

TABLE IV. TITRATION OF COBALT IN THE PRESENCE OF BERYLLIUM

Co taken, mg.	Be added, mg.	Vol. of 0.01016 mol. EDTA titrated, ml.	Co found, mg.	Error, mg.
3.64	0.70	6.08	3.64	±0.00
3.64	1.40	6.07	3.63	−0.01
3.64	1.40	6.09	3.65	+0.01
3.64	2.10	6.08	3.64	±0.00
3.64	3.50	6.07	3.63	−0.01

The optimum conditions for the general procedure were concluded as follows: the amount of ammonium carbonate added, 1.5 to 2.0 g.; the volume of saturated Luteo salt solution added, 2 ml.; the time allowed for the precipitate II to form, about 3 hr. after Luteo salt was added; the volume of 5% malic acid added, 2 ml.

5) Determination of Various Concentrations of Beryllium under the Optimum Conditions. — Various concentrations of

beryllium were determined by following the general procedure under the optimum conditions and the results are shown in Table V. Thus, it was concluded that the indirect titration of beryllium was satisfactorily carried out.

TABLE V. DETERMINTION OF VARIOUS CONCENTRATIONS OF BERYLLIUM AT THE OPTIMUM CNDITIONS

Be taken, mg.	Vol. of 0.01016 mol. EDTA titrated, ml.	Be found, mg.	Error, mg.
0.70	3.90	0.71	+0.01
0.70	3.84	0.70	±0.00
1.40	7.63	1.40	±0.00
1.40	7.68	1.41	+0.01
2.10	11.36	2.08	−0.02
3.50	19.02	3.48	−0.02

6) The Determination in the Presence of Iron (III), Aluminum and Magnesium. — After EDTA solution (0.1 mol., 5 ml.) and ammonium chloride (0.5 g.) were added to the sample solution containing iron(III), aluminum and magnesium, aqueous ammonia (1 : 1, 1 ml.) was added to the solution. At that time only beryllium hydroxide was precipitated. Then, 2 g. of ammonium carbonate was added to the solution and beryllium hydroxide was dissolved by stirring. The subsequent determination of beryllium was carried out by the procedure described above. In this case, iron, aluminum and magnesium were completely separated from beryllium when the precipitate II was formed and filtered. The results are shown in Table VI.

It is shown that the determination of berylium in the presence of these metals was carried out satisfactiorily. Therefore, this procedure is considered useful for a practical analysis of beryllium.

TABLE VI. DETERMINATION OF BERYLLIUM IN THE PRESENCE OF IRON(III), ALUMINUM AND MAGNESIUM

Be taken, mg.	Other metals added.	mg.	Vol. of 0.01016 mol. EDTA titrated, ml.	Be found, mg.	Error, mg.
1.40	Fe^{3+}	2.0	7.70	1.41	+0.01
1.40	Fe^{3+}	4.0	7.60	1.39	−0.01
1.40	Fe^{3+}	8.0	7.58	1.39	−0.01
1.40	Al^{3+}	1.7	7.64	1.40	±0.00
1.40	Al^{3+}	3.4	7.60	1.39	−0.01
1.40	Al^{3+}	6.8	7.55	1.38	−0.02
1.40	Mg^{2+}	2.1	7.65	1.40	±0.00
1.40	Mg^{2+}	8.3	7.69	1.41	+0.01

Summary

When Luteo salt was added to beryllium carbonate complex solution, the precipitate $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$ was obtained. In this experiment, the indirect determination of beryllium was tried by the titration of the cobalt content in the precipitate with EDTA. The following procedures were examined mainly; the formation of the precipitate II, the decomposition of the precipitate and titration of cobalt in the presence of beryllium. In the optimum conditions, 0.70 to 3.50 mg. of beryllium were determined quantitatively. This method could be applied to separation and determination of beryllium from iron(III), aluminum and magnesium by using EDTA as a masking agent.

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