Complexometric Titration of Rare Earth Elements. Dissolution of the Rare Earth Oxalate with Ethylenediaminetetraacetic Acid and Back Titration with Magnesium Sulfate

By Seizo MISUMI and Tomitsugu TAKETATSU

(Received March 23, 1959)

Complexometric titration of the rare earth ions in solution has been studied widely by many investigators[1-3]. The rare earth oxalate is usually precipitated from a weak acid solution and used for the gravimetric determination of the rare earth elements. Oxalic acid is the most excellent precipitating reagent for the rare earth ion. However, according to the fact that the rare earth oxalate was dissolved in alkaline solution by adding the excess of ethylenediaminetetraacetic acid (EDTA), Marsh[4] studied the fractional precipitation of the rare earth elements, using a different solubility of each rare earth-EDTA-oxalate complex anion in successive decreases of pH of solution. The present authors found that the rare earth ion, in the presence of a large amount of the oxalate ions, could be determined by back titration of the excess of EDTA with standard magnesium sulfate solution using Eriochrome black T as indicator under certain conditions. Thus, the rare earth ion was precipitated as the oxalate, the precipitate was separated and an excess of standard EDTA solution was added to dissolve the precipitate. After the oxalate was completely dissolved, the excess of EDTA in the solution was back titrated with standard magnesium sulfate solution, using Eriochrome black T as indicator. The conditions of dissolution of the rare earth oxalate and of the back titration were studied in detail and the optimum conditions were obtained for the determination of the rare earth elements. This procedure affords good and accurate results for the determination of 1 to 5 mg. of rare earth elements contained in solution under certain conditions. Especially, it is more rapid and rather simpler than the usual gravimetric procedure.

Experimental

Preparation of Standard Solution and Reagents.—*Standard EDTA solution.*—A certain quantity of disodium ethylenediaminetetraacetate dihydrate (analytical grade pure) was dissolved in distilled water and standardized by titration with standard zinc chloride solution, using Eriochrome black T as indicator. Concentration of the standard EDTA solution: 0.01030 mol./l.

Standard magnesium sulfate solution. — The weighed pure magnesium sulfate heptahydrate was dissolved in distilled water and standardized by titration with standard EDTA solution, using Eriochrome black T as indicator. Concentration of the standard magnesium sulfate solution: 0.01131 mol./l.

0.5% *Eriochrome black T (E. B. T.) solution.*— A half gram of E. B. T. and 4.5 g. of hydroxylamine hydrochloride were dissolved in absolute ethanol and the total volume was filled up to 100 ml. with ethanol.

Buffer solution. — Ammonium chloride-ammonium hydroxide buffer was used. Each equivalent quantity of 1 mol. ammonium chloride solution and 1 mol. ammonium hydroxide solution were mixed.

Rare earth chlorides were prepared from the pure rare earth oxides which were all of extra pure grade, specially purified with ion-exchange resins. La_2O_3: more than 99.99%, CeO_2: more than 99.99%, Pr_6O_{11}: more than 99.99%, Nd_2O_3: more than 99.99%, Sm_2O_3: 99.98%.

All other reagents were of analytical reagent grade.

Apparatus.—Two or five ml. microburette (corrected) was used. One drop was equal to 0.005 or 0.006 ml. Micro glass filters (No. 4) and beakers were all boiled in 2% alkaline EDTA solution for about three hours and allowed to stand overnight and washed with distilled water thoroughly before use. The measurements of pH were carried out with the glass electrode pH meter EHM-1 Type of Hitachi & Co.

A sample solution, containing 1 to 5 mg. of the rare earth ion, was taken, the crystalline rare earth oxalate was precipitated, filtered and separated. An excess of the standard EDTA

1) G. Schwarzenbach, "Die Komplexometrische Titration", Ferdinand Enke Verlag, Stuttgart, (1955), p. 61.
2) H. Flaschka, *Mikrochim. Acta*, **1955**, 55.
3) G. Brunisholz and R. Cohen, *Helv. Chim. Acta*, **39**, 324 (1956); ibid., **39**, 2136 (1956).
4) J. K. Marsh, *J. Chem. Soc.*, **1950**, 1819.

solution was added and then the solution was made alkaline with dilute aqueous ammonia. The oxalate was completely dissolved as the rare earth-EDTA-oxalate complex anion[4]. By back titration of the excess of EDTA in the solution with standard magnesium sulfate solution, the rare earth was determined indirectly. The basis of calculation is derived from the fact that the rare earth-EDTA-oxalate complex is known as the 1 : 1 complex[4], which contains one gram atom of rare earth and one molecule of EDTA.

Results and Discussion

Back Titration in the Presence of Oxalate Ion.—Rare earth oxalate was dissolved as the complex anion with an excess of EDTA (HY^{3-}) in the solution and this reaction is supposed to proceed as follows: that is,

$$R_2(C_2O_4)_3+2HY^{3-} \rightarrow 2[RHYC_2O_4]^{2-}+C_2O_4^{2-}$$

in alkaline solution, where R^{3+} indicates the tripositive rare earth ion. When the excess of EDTA in the presence of the rare earth complex ion was back titrated with standard magnesium sulfate solution, using Eriochrome black T as indicator, the interference of the oxalate ion in solution was studied. To the aqueous solution of lanthanum or cerium chloride (content of rare earth ion: 2~4 mg.), about 10 to 70 mg. of oxalic acid was added and the crystalline rare earth oxalate was precipitated. Then an excess of standard EDTA solution was added and the solution was made alkaline with dilute ammonia water solution to dissolve the oxalate completely. After the pH was accurately adjusted to 10.0~10.5 with dilute ammonia water, 5 drops of 0.5% Eriochrome black T solution were added and the excess of EDTA remaining in solution was back titrated with standard magnesium sulfate solution till the blue color of the solution changed into red at the end point. The results are shown in Table I.

It had been supposed that the great excess of the oxalate ions would cause the end point of back titration to be ambiguous. But for 1 to 5 mg. of the rare earth ion, it was found that the addition of 30 mg. of oxalic acid did not interfere with the titration at all. Therefore, provided that the rare earth oxalate can be precipitated, separated and dissolved completely with a known amount of standard EDTA solution, the back titration of the excess of EDTA with standard magnesium sulfate solution is readily carried out in the presence of the oxalate ions and the rare earth-EDTA-oxalate complex ions in solution.

Studies on Various Conditions for the Determination of the Rare Earth Element.—Further, the conditions for this procedure for the determination of the rare earth elements were studied concerning the following matters, i. e.,

a) The process for the precipitation of crystalline rare earth oxalate. The crystalline oxalate was precipitated from a solution of rare earth chloride.

b) The amount of EDTA added for the complete dissolution of the oxalate. The use of 5 ml. of 0.01 M standard EDTA solution was optimum.

c) The amount of the buffer solution added to the solution obtained. The use of 2 ml. of the buffer solution was optimum.

d) The temperature for dissolution of the oxalate with the EDTA solution. 50 to 60°C (5 min.) was the best temperature

TABLE I. EFFECT OF VARIATION IN AMOUNT OF OXALIC ACID ADDED ON THE BACK TITRATION

Lanthanum taken=2.333 mg. pH=10.2~10.5

Oxalic acid added, mg.	La found, mg.	Error, mg.	%	Remarks
10	2.325	−0.008	−0.34	end point sharp
15	2.333	±0.000	±0.00	〃
20	2.333	±0.000	±0.00	〃
30	2.325	−0.008	−0.34	〃
40	2.317	−0.016	−0.69	lacks sharpness
50	2.317	−0.016	−0.69	〃
70	2.270	−0.063	−2.70	obscure

Cerium taken=3.595 mg. pH=10.2

Oxalic acid added, mg.	Ce found, mg.	Error, mg.	%	Remarks
20	3.586	−0.009	−0.25	end point sharp
30	3.576	−0.019	−0.53	〃
40	3.567	−0.028	−0.78	lacks sharpness

for the complete dissolution.

e) Adjustment of the pH for micro titration. The pH 10.2~10.5 was the optimum value which must be accurately kept.

f) On the indication of accurate end point of the back titration with standard magnesium sulfate solution in the presence of oxalate ion, using Eriochrome black T as indicator. The end point was defined to be accurately at the point where the blue color changed completely into the red color.

As the result of these experiments, the optimum conditions are found as follows.

Recommended Procedure.—1) *Precipitation and filtration of the crystalline rare earth oxalate.* — 10 ml. of a weak acid aqueous solution of the tripositive rare earth elements (content of R^{3+} ion: 1~5 mg.) is warmed at 60°C for a few minutes and 20 ml. of the saturated oxalic acid solution is added. The solution is warmed at the same temperature for several hours and then left to stand overnight. Large crystals of the rare earth oxalate are completely precipitated. The precipitate is filtered slowly with the micro glass filter (No. 4) by suction and washed with a saturated oxalic acid solution.

2) *Dissolution of crystalline rare earth oxalate.*—The precipitate is put into a small beaker together with the glass filter, about 25 ml. of distilled water is added and the mixture is warmed at 50~60°C for a few minutes. Then an excess of 0.01 M standard EDTA solution and 2 ml. of 2 N ammonia water are added and the mixed solution is warmed again carefully at 50~60°C for about 5 minutes. The precipitate is thus completely dissolved by this process. After complete dissolution of the precipitate, the solution is cooled rapidly and the glass filter is removed by washing with the distilled water which is added to the original solution.

3) *Back titration with standard magnesium sulfate solution.*—The pH of the solution obtained, must be correctly adjusted to 10.5 with 2 ml. of the buffer solution and dilute ammonia water. Then the total volume of the solution is filled up to about 60 ml. with distilled water. As this indicator, 5 drops of 0.5% E. B. T solution are added and the excess of EDTA in the solution is back titrated with 0.01 M standard magnesium sulfate solution. At the end point, the blue color changes completely into red.

The results obtained by this procedure are given in Table II.

TABLE II. MICROTITRATION OF SOME RARE EARTH ELEMENT

Element	Taken mg.	Found mg.	Error mg.
La	0.935	0.914	−0.021
	2.332	2.332	±0.000
	4.688	4.704	+0.016
Ce	1.798	1.815	+0.017
	3.595	3.605	+0.010
	5.393	5.322	−0.011
Pr	2.582	2.557	−0.025
Nd	1.617	1.627	+0.010
Sm	1.140	1.167	+0.027

It is especially necessary to notice the following matters in this procedure.

a) Determination of the tetrapositive cerium. In the complexometric titration of cerium in alkaline solution, to prevent the oxidation by the tetrapositive ion, it is necessary, in general, to add a reducing agent (e. g., one such as ascorbic acid), but in the presence of the oxalate ion, owing to its reducing property, addition of the reducing agent was not required and the procedure could be applied also to the determination of the tetrapositive cerium ion.

b) Addition of ethanol to the solution for back titration. Wünsch[5] added ethanol for the determination of scandium by complexometric back titration. Generally, in the case of the usual back titration for the determination of rare earth ions, addition of ethanol makes the end point evidently clearer with E. B. T as indicator, but in the presence of the oxalate ion, on the contrary, low value was obtained by adding ethanol.

c) Treatment of the glass vessels with alkaline EDTA solution. As Flaschka and Amin[6] reported, it was seen that the glass vessels were attacked slightly by concentrated EDTA solution and if so, there must be a tendency that a slightly high value for the determination would be obtained. Therefore, the glass vessels which were used in this experiment, were boiled with 2 percent alkaline EDTA solution and left to stand overnight and washed thoroughly with distilled water before use. In this way, such errors, owing to EDTA, were not recognized at

5) L. Wünsch, *Collection Czechoslov. Chem. Communs.*, **20**, 1107 (1955).
6) H. Flashka and A. M. Amin, *Mikrochim. Acta*, **1953**, 410.

all and the value found was accurate and reproducible.

This procedure of complexometric titration to determine the small amount of the rare earth from the oxalate is rapid and precise and more excellent than the usual gravimetric method in its accuracy.

Summary

The processes for dissolution of the oxalate and complexometry to determine the small amounts of rare earth rapidly and accurately, were studied. Crystalline rare earth oxalate was precipitated and filtered. The precipitate was dissolved completely with EDTA in alkaline solution and the excess of EDTA in solution was back titrated with standard magnesium sulfate solution. By this procedure, rare earth in the range of a content about 1 to 5 mg., was determined rapidly with a good accuracy.

The authors desire to thank the Ministry of Education for its financial support of this research.

Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka