

in an open flask: it became dark yellow in about 1 hour owing to oxidation of the sulphide and consequent formation of polysulphide.—The experiment was repeated except that 1 mg. Ni as  $\text{NiNO}_3$  was also present; the excess of 10 per cent. NaOH was 4 or 5 cc.;  $\text{H}_2\text{S}$  was led into the solution for about 1 minute and the CoS filtered off: the filtrate was nearly colorless. This was saturated with  $\text{H}_2\text{S}$ : it became brown, the color being such as to indicate that very little of the nickel had been carried down with the cobalt.—This experiment was repeated except that the  $\text{H}_2\text{S}$  was led through the solution for 5 minutes before the CoS was filtered off: the filtrate was of a lighter brown than before, indicating that over half the nickel had been carried down with the cobalt.—The experiment was repeated except that the CoS was not filtered off till after 10 minutes: the filtrate was almost colorless, and remained so on saturating again with  $\text{H}_2\text{S}$ .—The experiment was repeated, the CoS being filtered off after half an hour: the filtrate was colorless and contained no nickel.—In a similar series of experiments in which a smaller excess of NaOH than 4 to 5 cc. was added, the filtrate was light brown after 1 minute, and nearly colorless after 5 minutes, thus showing that there is more danger of losing nickel when the excess of alkali is small, in which case the brown solution is formed more quickly.—This result that NiS is deposited on CoS after the separation of the latter was confirmed by several experiments.

Similar experiments were made with a mixture of 20 mg. Fe as  $\text{FeCl}_3$  and 1 mg. Ni, and with one of 20 mg. Mn and 1 mg. Ni: good tests for nickel were obtained in both cases.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## THE CARRYING DOWN OF SOLUBLE OXALATES BY OXALATES OF THE RARE EARTHS.

BY GREGORY PAUL BAXTER AND HERBERT WILKENS DAUDT.

Received January 22, 1908.

In a recent investigation<sup>1</sup> it has been shown that neodymium oxalate, when precipitated in neutral or nearly neutral solution by means of ammonium oxalate, carries down considerable quantities of this salt, and that the amount carried down increases with increasing concentration of molecular ammonium oxalate at the moment of precipitation. Furthermore, it was shown that neodymium oxalate has no tendency to carry down molecular oxalic acid, and that occlusion of ammonium oxalate may be prevented by diminishing the molecular concentration of the latter salt with a strong acid before precipitation. Other rare earth oxalates were found to exhibit a like tendency to occlude ammonium oxalate. Since it seemed probable that the carrying down of sodium and potassium oxalates<sup>2</sup> would vary with conditions of precipitation in a similar manner, the following investigation was undertaken to test this point.

The method employed was to precipitate the rare earth oxalate under different conditions, and to analyze the precipitated oxalate by deter-

<sup>1</sup> Baxter and Griffin, *THIS JOURNAL*, 28, 1684 (1906).

<sup>2</sup> The well-known fact that the oxalates of the alkalis are carried down by the oxalates of the rare earths was first noted by Sheerer. *Pogg. Ann.* [2], 56, 496 (1842).

mining the ratio of metallic oxide to  $C_2O_3$ . The atomic weight of the metal being known, the excess of  $C_2O_3$  could be calculated and hence the purity of the precipitate. Although all the rare earth oxalates contain crystal water, even after drying at an elevated temperature, the amount of this water is immaterial for the purpose in hand.

Since none of the rare earth specimens were pure, it was necessary to determine the average atomic weight of each specimen. This was done by the oxalate method first proposed by Stolba.<sup>1</sup> A hot solution of oxalic acid containing a small quantity of nitric acid was slowly added with constant stirring to a hot nitric acid solution of the rare earth until precipitation was complete. After the precipitate had been washed ten times by decantation with hot water, it was collected upon a porcelain Gooch crucible provided with a disk of filter paper in place of an asbestos mat, and was dried in an electric air-bath at about  $125^\circ$  for twenty-four hours. Shortly before being weighed out for analysis, the dried precipitates were thoroughly mixed by grinding in an agate mortar to insure uniformity in water content,<sup>2</sup> and all portions of the same material were weighed out at the same time, in order to avoid error from hygroscopicity.

The per cent. of oxide in the oxalate was determined by igniting weighed portions of about one-half gram in platinum crucibles, while the ratio  $C_2O_3$ : oxalate was found by dissolving weighed amounts of the oxalate in hot 2 *N* sulphuric acid and titrating the oxalic acid with standard potassium permanganate. From the ratio  $M_2O_3:3C_2O_3$  the average atomic weight of the sample was calculated, the following atomic weights being assumed: H = 1.008, O = 16.00, C = 12.00.

The permanganate solution was standardized with oxalic acid which had been allowed to come to constancy over sulphuric acid of the specific gravity 1.35. This oxalic acid had been three times recrystallized, with centrifugal drainage. Although the permanganate solution changed in concentration very slowly, re-standardization was carried out frequently.

In order to gain some idea of the extent to which the alkali oxalates are carried down by the rare earth oxalates under conditions most favorable for this effect, each material under investigation was precipitated by pouring a hot nearly neutral solution of the nitrate of the rare earth into a hot solution of from three to four times the equivalent quantity of each alkali oxalate. In this precipitation the solution of the rare earth nitrate was on an average about four-tenths normal and the solution of the alkali oxalate about six-tenths normal.

Next the same material was again precipitated in as nearly as possible

<sup>1</sup> Sitzber. böhm. Ges., Dec., 1878; also Chem. News, 41, 31 (1880).

<sup>2</sup> Gibbs, Proc. Amer. Acad., 28, 262 (1893).

the same way, except that about twice the equivalent quantity of nitric acid was added to the solution of the alkali oxalate before the precipitation. Although the dissociation of the first hydrogen of oxalic acid is very considerable,<sup>1</sup> that of the second hydrogen is small.<sup>2</sup> Hence, in the presence of a high concentration of the hydrogen ion the concentration of the oxalate ion and therefore that of the molecular alkali oxalate must be very low, so that little carrying down of the alkali oxalate is to be expected.<sup>3</sup>

With solutions as concentrated as the above it is of course probable that a small amount of soluble oxalate would be "included" in cells of mother liquor in the highly crystalline precipitates. This may be the reason for at least a portion of the small amount of alkali oxalate found even in precipitates formed by methods calculated to reduce occlusion to a minimum.

As in the previous investigation, the first element studied was neodymium. The sample used was not quite pure, its absorption spectrum showing, besides the bands of neodymium, traces of those of samarium and praseodymium. Other elements giving no absorption spectrum may have been present. The average atomic weight of the sample was found by analysis of the oxalate as described above.

	ATOMIC WEIGHT.				
	I.	II.	III.	IV.	Average.
Per cent. of Nd <sub>2</sub> O <sub>3</sub> . . . . .	53.87	53.81	53.77	. . . . .	53.82
Per cent. of C <sub>2</sub> O <sub>3</sub> . . . . .	34.29	34.36	34.30	34.37	34.33
	Ratio M <sub>2</sub> O <sub>3</sub> : 3C <sub>2</sub> O <sub>3</sub> =1.5677.		M=145.3.		

Although the average atomic weight of the sample is only slightly higher than the most probable atomic weight of neodymium, 144.5,<sup>4</sup> this result does not indicate with exactness the purity of the sample, for the atomic weights of the known impurities, praseodymium and samarium, lie on opposite sides of that of neodymium. The specimen undoubtedly consisted chiefly of neodymium, however.

A portion of the same material was next precipitated by pouring a hot nearly neutral solution of the nitrate into a hot solution of about three times the equivalent quantity of potassium oxalate. Portions of the carefully washed and dried precipitate, when held in the Bunsen flame, indicated the presence of considerable quantities of potassium. A fruitless attempt to expel all the potassium by prolonged ignition in the flame of a blast lamp, showed that some other method was necessary

<sup>1</sup> Ostwald, Z. physik. Chem., 3, 281 (1889).

<sup>2</sup> *Ibid.*, 9, 553 (1892).

<sup>3</sup> In the previous paper the effect of increasing the hydrogen ion concentration was erroneously imputed to the formation of molecular oxalic acid instead of the acid oxalate ion.

<sup>4</sup> v. Welsbach, Sitzb. Akad. Wiss. Wien, 112, 1037 (1904).

for the determination of the neodymium oxide. Accordingly, weighed amounts of the precipitate were first dissolved in either sulphuric or nitric acid, and, after the solution had been neutralized with freshly distilled ammonia, ammonium oxalate was added until precipitation appeared complete. More ammonia was then added until the solutions were slightly ammoniacal. After standing some time, the precipitates were washed several times with hot water, filtered, ignited and weighed. Occluded ammonium oxalate was, of course, volatilized during ignition. The oxalic acid was determined as before described.

NEUTRAL PRECIPITATION WITH POTASSIUM OXALATE.

	I.	II.	III.	Average.
Per cent. of $\text{Nd}_2\text{O}_3$ .....	46.76	46.76	46.70	46.74
Per cent. of $\text{C}_2\text{O}_3$ .....	37.71	37.61	37.66	37.66
Per cent. of $\text{C}_2\text{O}_3$ equivalent to 46.74 per cent. of $\text{Nd}_2\text{O}_3$ .....				29.82
Excess per cent. of $\text{C}_2\text{O}_3$ .....				7.84
Per cent. of $\text{K}_2\text{C}_2\text{O}_4$ carried down.....				18.10

The experiment with potassium oxalate was then repeated with similar solutions except that the potassium oxalate solution before precipitation was made acid with about twice the equivalent amount of nitric acid. It has already been shown that neodymium oxalate shows no tendency to carry down oxalic acid.<sup>1</sup> This new precipitate of neodymium oxalate gave no visible flame test for potassium, and analysis showed only 0.30 per cent. of potassium oxalate to have been carried down. The per cent. of neodymium oxide was found by ignition of weighed portions of the oxalate, finally with a blast lamp to expel traces of potassium. This method is later shown to give accurate results in the case of a precipitate formed with sodium oxalate.

The result of this experiment, in which the carrying down of potassium oxalate is a little less than two per cent. as large as in neutral solution, is in accord with the prediction, and also with the behavior of neodymium oxalate with ammonium oxalate previously observed, the excess of oxalate found not being greater than could be accounted for on the basis of inclusion.

When sodium oxalate in neutral solution was used as precipitant, the neodymium solution being added to a large excess of oxalate, the dried precipitate gave scarcely any flame test for sodium. The same surprising result was obtained in two successive repetitions of the experiment. One of the precipitates, upon analysis, proved to contain only a few tenths of a per cent. of sodium oxalate. The analyses for neodymium oxide were made by ignition of the oxalate with a blast lamp.

<sup>1</sup> Baxter and Griffin, *Loc. cit.*

In strongly acid solution with sodium oxalate as precipitant, exactly the same proportion of sodium oxalate was found in the precipitate. The neodymium oxide was determined by ignition. In one of the analyses the neodymium oxide, after being weighed, was dissolved in nitric acid and the neodymium was precipitated with ammonium oxalate. The weight of the oxide obtained by ignition of this latter precipitate agreed essentially with that of the original, showing that small quantities of the occluded alkalis may be volatilized completely by ignition.

Since the solubility of the oxalates of the rare earths in nitric acid is a variable one, and since our material was known to be a mixture, at the end of the experiments with neodymium, the average atomic weight of the material which had been through the preceding operations was redetermined, and was found to have diminished 0.3 to 145.0. It is to be noted that the effect of this diminution is to exaggerate slightly the occlusion. With sodium oxalate in acid solution for instance, the per cent. of sodium oxalate carried down, calculated upon the basis of the lower atomic weight, is 0.3 instead of 0.4.

## OCCLUSION BY NEODYMIUM OXALATE.

	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Per cent.	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Per cent.
Neutral precipitation.....	18.1	0.4
Acid precipitation.....	0.3	0.4

Lanthanum upon examination was found to behave similarly to neodymium. The material used was essentially free from elements whose solutions absorb in the visible region, and its atomic weight, determined as in the case of neodymium to be 139.1, was found to be very close to the probable value of this constant, 138.9.

Since the carrying down of ammonium oxalate by lanthanum oxalate was not investigated in the previous research, this point was taken up here. The precipitate formed by adding a nearly neutral solution of lanthanum nitrate to a large excess of ammonium oxalate proved to contain a considerable amount of ammonium oxalate. When, however, the ammonium oxalate solution was acidified with twice the equivalent quantity of nitric acid, only a trace of ammonium oxalate was found.

Similar results were obtained with potassium oxalate as precipitant, this oxalate being carried down in considerable quantities from neutral solution and very slightly from strongly acid solution. In the analyses of the precipitate from neutral solution the lanthanum oxide was determined by igniting weighed portions of the oxalate, leaching the oxide with water and filtering the wash water through a tiny filter, and finally igniting both oxide and filter paper. In analyzing the precipitate from acid solution the lanthanum oxide was determined by ignition only.

When sodium oxalate was used as precipitant, only small quantities

of this substance were found in the precipitates of lanthanum oxalate either from neutral or from acid solution.

OCCLUSION BY LANTHANUM OXALATE.

	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Per cent.	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Per cent.	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Per cent.
Neutral precipitation.....	5.4	2.3	0.5
Acid precipitation.....	0.2	0.1	0.8

It is noticeable that the carrying down of both potassium and ammonium oxalates by lanthanum oxalate is very much less than by neodymium oxalate under nearly the same conditions of precipitation.

The third material examined was of somewhat complex nature. A solution of gadolinite earths, which had been treated with potassium sulphate, was fractionated with magnesium oxide until about half the earths remaining had been precipitated. The magnesium oxide fractions, which seemed identical as far as spectroscopic evidence was concerned, were combined and fractionally crystallized from concentrated nitric acid until the greater part of the neodymium and praseodymium had passed into the mother liquors. A portion of this material, which consisted largely of samarium, was used in the following work. Subsequent prolonged fractional crystallization showed the presence of gadolinium, dysprosium, europium and holmium. This material was investigated in exactly the same way as in the cases of neodymium and lanthanum, by precipitating the oxalate in both neutral and acid solution with a large excess of ammonium, potassium and sodium oxalates. The average atomic weight of this material was found to be 149.3.

OCCLUSION BY SAMARIUM OXALATE.

	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Per cent.	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Per cent.	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Per cent.
Neutral precipitation.....	5.9	20.7	5.9
Acid precipitation.....	0.0	0.0	0.1

From the preceding table it can be seen that the carrying down of the precipitant in neutral solution and almost absolute purity of the precipitate from acid solution is in accord with the behavior of the elements previously studied—lanthanum and neodymium. It is further to be noted that the quantity of sodium and potassium oxalates found in the precipitates from neutral solution is markedly greater in all cases than was found with neodymium and lanthanum oxalates. This is in accord with the fact that elements of the yttrium and erbium groups in general show marked tendency to form soluble double oxalates with the oxalates of ammonium and the alkalis.

Finally, a sample of yttria was examined in a similar fashion. This sample was very crude, its atomic weight being found to be 102.7.

First, precipitation with potassium oxalate in strongly acid solution was investigated. Considerable quantities of potassium in the precipi-

tate were indicated by a strong flame test. Some difficulty was experienced in the determination of the yttrium oxide in the oxalate, owing to failure of all attempts to reprecipitate the oxalate completely from either neutral or slightly acid solution. The method finally adopted was that of leaching the ignited oxalate with hot water and collecting the small amount of suspended yttrium oxide upon a tiny filter paper, as previously described in the case of lanthanum. Even after filtration the decantate was cloudy, but repeated filtration through the same filter paper removed all but negligible amounts of the yttrium oxide. The washed oxide was dried upon the steam-bath, ignited and weighed, and its weight was added to the weight of oxide upon the filter paper after ignition. The filtrate was alkaline to phenolphthalein. Over seventeen per cent. of potassium oxalate was found.

Since the material had been precipitated in acid solution several times between the original determination of the atomic weight and the acid precipitation with potassium oxalate described above, the change in atomic weight produced by partial solubility of the oxalates in nitric acid was determined, and found to be considerable, the new value for the atomic weight being 104.7. Hence the calculated percentage of potassium oxalate carried down in the above case is probably slightly too low.

The fraction of material used in the above experiments was now mixed with a new portion of the original substance, and the average atomic weight of the mixture was found to be 103.2.

This new material was now precipitated with potassium oxalate in neutral solution under as nearly as possible the same conditions as before. The precipitated oxalate contained potassium oxalate in slightly greater quantities than when formed in acid solution.

Examination of the precipitates formed with sodium oxalate in both neutral and acid solutions showed that in both cases very small quantities of the precipitant were carried down.

Since yttrium oxalate was found to carry down large quantities of potassium oxalate even in strongly acid solution, an experiment was performed to determine whether this was the case with ammonium oxalate also. Baxter and Griffin have already found that yttrium oxalate, when precipitated from neutral solution, may carry down as much as 16.5 per cent. of ammonium oxalate. The precipitate of oxalate from acid solution gave a strong test for ammonia when treated with caustic soda, and was found to contain a somewhat lesser amount of occluded ammonium oxalate than the precipitate formed in neutral solution.

OCCLUSION BY YTTRIUM OXALATE.

	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Per cent.	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Per cent.	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Per cent.
Neutral precipitation.....	.....	18.0	1.0
Acid precipitation.....	13.6	17.5	0.9

Finally, in order to show conclusively that oxalic acid itself is not carried down by yttrium oxalate, a precipitate was formed by adding a solution of yttrium nitrate to a concentrated solution of a large excess of oxalic acid. Analysis of the precipitate showed not only that no carrying down of oxalic acid takes place but also that the average atomic weight of the material had increased to 106.1. The result of this rise in atomic weight, as previously stated, is to make the carrying down of precipitant appear less than it really is.

Since in all cases previously described the precipitates were formed in hot solution, in order to determine the effect of temperature upon the occlusion, precipitations with neodymium solutions were made at ordinary and at boiling temperatures with solutions otherwise identical. In one case a cold solution of neodymium nitrate was added to a cold saturated solution of a large excess of ammonium oxalate, and in a second case similar solutions were precipitated boiling hot. The precipitate from cold solution gave no test for ammonia when treated with sodium hydroxide and analysis of the precipitate gave no evidence of occlusion, while in the second case 2.1 per cent. of ammonium oxalate was found.

Similar experiments were then carried out with a cold saturated solution of potassium oxalate and with a similar solution at boiling temperature. The precipitate formed at the lower temperature was found to contain 10.0 per cent. of potassium oxalate while the one formed at boiling temperature contained nearly double this proportion, 17.5 per cent.

The effect of high temperature is very marked both with ammonium oxalate and with potassium oxalate. The smaller quantity of ammonium oxalate found even in the hot precipitation is due at least in part to the fact that the solutions of ammonium oxalate were more dilute, owing to the lesser solubility of this salt at ordinary temperatures.

The very considerable extent of the carrying down of the oxalates of the alkalis and ammonium by all the rare earth oxalates investigated, points to the formation of double salts as the cause of the phenomenon rather than to ordinary solid solution. Although the foregoing experiments may not indicate the limiting values of the occlusion under the conditions most favorable and least favorable for the phenomenon, it is interesting to tabulate the molecular ratios between the occluded and occluding oxalates.

A glance at the following table shows that in no case does the carrying down of a soluble oxalate exceed the proportion of one molecule of alkali oxalate to one of rare earth oxalate. One might conclude from this fact that stable insoluble double salts containing more than one



molecule of alkali oxalate to one of rare earth oxalate do not exist, although the grounds for such a conclusion are not by any means final.

MOLECULAR RATIO OF OCCLUDED OXALATE TO RARE EARTH OXALATE.

	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .		K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .		(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	
	Acid.	Neutral.	Acid.	Neutral.	Acid.	Neutral.
Nd <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> . . . . .	0.02	0.02	0.01	0.79	0.01 <sup>1</sup>	0.71 <sup>1</sup>
La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> . . . . .	0.04	0.02	0.00	0.09	0.01	0.27
Sm <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> . . . . .	0.00	0.30	0.00	0.94	0.00	0.32
Y <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> . . . . .	0.04	0.04	0.69	0.73	0.65	0.82 <sup>1</sup>

It is somewhat difficult to explain the unexpected behavior of yttrium oxalate, when precipitated from acid solutions, the occlusion being only slightly diminished thereby. The oxalates of the earths of the yttrium and erbium group, however, show considerable tendency to form *soluble* double oxalates with the oxalates of the alkalis and ammonium, indicating a more marked tendency toward double salt formation than is possessed by the oxalates of the neodymium group. Since even in the presence of a high hydrogen ion concentration the oxalate ion concentration and hence that of alkali oxalate must be appreciable, the carrying down of alkali oxalate is still possible where the tendency in this direction is strong. The fact that the occlusion by yttrium oxalate is not greater in neutral solution may be explained on the hypothesis previously stated that there is no tendency to form insoluble double oxalates containing more than one molecule of alkali oxalate to one of yttrium oxalate.

The following general conclusions seem to be justified from the foregoing results:

(1) The oxalates of the rare earths show marked but varying tendencies to carry down the oxalates of the alkalis and ammonium.

(2) This tendency increases with increasing concentration of molecular alkali oxalate at the moment of precipitation.

(3) Potassium and ammonium oxalates are carried down to a much greater extent than sodium oxalate. Precipitation with sodium oxalate in most cases gives precipitates only slightly contaminated with this substance even in neutral solution.

(4) The carrying down of the soluble oxalates is greater at high than at low temperatures.

(5) By conducting the precipitation in the presence of a quantity of a strong acid considerably more than equivalent to the alkali oxalate, thus very much reducing the concentration of molecular alkali oxalate, the carrying down is in many cases almost wholly prevented. In the case of yttrium, the diminution in occlusion is slight.

(6) In order to produce as pure as possible a precipitate of a rare earth oxalate by means of an alkali oxalate or ammonium oxalate, precipita-

<sup>1</sup> From the results of Baxter and Griffin, *Loc. cit.*

tion should be conducted in cold dilute solution in the presence of a quantity of a strong acid considerably more than equivalent to the oxalate added.

We are greatly indebted to the Welsbach Light Company for some of the rare earth material.

CAMBRIDGE, MASS.  
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## YTTRIUM EARTHS.

[FIRST PAPER.]

BY VICTOR LENHER.

Received December 28, 1907.

The methods which we have at our disposal for the separation of the earths of the yttrium group may be classified under the following heads: (1) Fractional precipitation; (2) Fractional crystallization; (3) Fractional decomposition of such salts as the nitrates by heat.

Under fractional precipitation, we have methods which depend largely on the differences in basic properties, such as the fractional precipitation by ammonia, magnesia, etc. The speed by which separations are effected by use of this principle depends largely on how quickly the system can be brought into equilibrium.

In the methods of fractional crystallization we must depend necessarily on the differences in solubility of various salts and as a rule with the mixtures which are found in the rare earth minerals; the solubilities of a given salt of the various metals are not widely different. On this account separation by the crystallization of the nitrates or double nitrates is not rapid, while with the chromates accurate conditions must be observed, in which case this method gives splendid results.

The decomposition of the nitrates by heat is slow, but can, by patience, be carried out with success. The basic nitrate method of Welsbach<sup>1</sup> which can be applied to the yttrium group is a combination of this method and that of fractional precipitation. It is more rapid and successful than either method alone.

The successful use of any of the methods for separating the metals of the yttrium group depends largely on the ratios of the various constituents present in the mixtures, as well as on the character of the elements to be separated. We note, for example, that Dennis and Dales<sup>2</sup> in their study of the yttrium earths from sipylite find that magnesia, as a precipitating agent, causes little change in the atomic weights and absorption spectra, while James<sup>3</sup> was more successful in using this method

<sup>1</sup> Monatshefte, 5, 508.

<sup>2</sup> THIS JOURNAL, 24, 428.

<sup>3</sup> *Ibid.*, 29, 495.