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.,
January 20, 1908.

YTTRIUM EARTHS.

[FIRST PAPER.]

BY VICTOR LENHER.

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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[1] 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[2] 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[3] was more successful in using this method

[1] Monatshefte, **5**, 508.

[2] THIS JOURNAL, **24**, 428.

[3] *Ibid.*, **29**, 495.

on gadolinite earths. James used the nitrate solution while Dennis and Dales used a chloride solution. The author in working in a nitrate solution with yttrium earths from monazite has found that various fractions acted quite differently toward magnesia, some showed marked differences in atomic weight and absorption spectra after treatment with magnesia, while others showed little change. It has been observed, moreover, that in order to work this method with any appreciable degree of success the magnesia must be freshly ignited. The various degrees of success with different methods can also be illustrated by the Welsbach method[1] of crystallizing the oxalates from an ammoniacal solution or by the James method[2] in which the "oxalate-carbonates" are crystallized from an ammonium carbonate solution of the oxalates. This method with gadolinite earths in the hands of James yielded first yttrium and successively fractions with higher atomic weight to ytterbium. In the author's hands, it has worked similarly with the yttrium earths from samarskite but on applying the same method to certain oxalates from monazite, atomic weight determinations showed that the elements with heavier atomic weight appeared first while the more soluble portion yielded fractions whose atomic weight was far below the more insoluble portions. In other words, we here have the same method producing opposite results with different mixtures of earths.

From time to time, it has been proposed to use salts of organic acids. The oxalates can be crystallized from either ammoniacal or ammonium carbonate solution, yielding a fairly rapid method of fractionation, or the oxalates can be crystallized from nitric acid solution yielding fractions of different atomic weights. The ethyl sulphates and the acetyl acetonates have been used by Urbain and others as means of separation in this group. The formates have been repeatedly used for fractionations. Salts of a number of organic acids have been prepared, but little has been done in the application of the derivatives as means of separation. Such salts as the tartrates, citrates and succinates have been prepared, but little has been attempted in the way of separation.

The tartrates and citrates of the yttrium earths appear as white gelatinous precipitates when a neutral salt of potassium, sodium or ammonium is added to a solution of the yttrium salt. In a similar manner, insoluble derivatives are formed with neutral salts of fumaric, maleic, tartronic, malic and malonic acids. The neutral succinates of the alkalis or ammonium deport themselves in a very interesting manner with the neutral nitrates of the yttrium earths.

When neutral ammonium or sodium succinate is added to a neutral nitrate solution of the yttrium earths and the solution allowed to stand,

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[1] Monatshefte, 27, 935.

[2] THIS JOURNAL, 29, 495.

a finely divided crystalline precipitate of the succinates appears. This insoluble precipitate forms slowly, in fact, in the cold a few hours are necessary to insure complete precipitation. On the other hand, when the solution is hot or boiling, complete precipitation is effected in much less time, from ten minutes to half an hour being sufficient time for complete formation of the insoluble succinates. The ready formation of this finely divided precipitate and the fact that the reaction is far from instantaneous appears to us as promising to be a satisfactory method for fractionation. The fact that it forms as slowly as it does, would indicate that there should be plenty of time for equilibrium to be established and the physical character of the salt and its insolubility enables it to be quickly filtered and readily washed.

That the yttrium earths form succinates was shown by Berlin in 1835.[1] He showed that with sodium succinate the yttrium earths form a fine crystalline powder. Ekeberg in 1802[2] thought that the yttrium earths were not precipitated by the alkaline succinates while beryllium was, which was contrary to the results found by Berlin and to the work of Cleve and Höglund[3] who showed that ammonium succinate precipitates yttrium but not erbium from nitrate solution, but out of a mixture precipitates both.

In the thorium cerium group, Berzelius showed in 1829[4] the formation of an insoluble succinate of thorium. This reaction has been later studied by Kaufmann[5] and Schilling.[6] The use of an alkaline succinate has been recommended as a means of separation of iron from the gadolinite earths by Gadolin, Vauquelin, Berzelius, Berlin, and Hermann, after Klaproth had shown that iron would be first precipitated from such a solution.

The yttrium earths from samarskite have been studied with the view of testing the applicability of the succinates as a means of separation in this group.

Treatment of Samarskite.

Fifteen pounds of samarskite, containing very little gangue minerals were treated with concentrated hydrofluoric acid according to the method of J. Lawrence Smith. The mineral dissolved with effervescence. The columbium and tantalum passed into solution while the earths appeared as insoluble fluorides. These insoluble fluorides were thoroughly washed with water by decantation, after which they were dried and treated with concentrated sulphuric acid. After the first copious evolution of

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[1] Pogg. Ann., 43, 108.

[2] Gilb. Ann., 14, 247; Ann. chim. phys., 43, 228.

[3] Ber., 6, 1468.

[4] Pogg. Ann., 16, 385.

[5] Dissertation Univ. Rostock, 1899.

[6] Dissertation Univ. Heidelberg, p. 141, 1902.

hydrofluoric acid, the mass was warmed and finally heated until the heavy fumes of the sulphuric acid came off. The pasty mass was allowed to cool; when it was extracted with water and the insoluble residue, which consisted of more or less of the oxides of columbium and tantalum, insoluble sulphates and a little undecomposed mineral was thoroughly washed with water by decantation. This sulphate solution of the earths and uranium was nearly neutralized with sodium hydroxide. Oxalic acid was then added, and the oxalates precipitated. These crude oxalates were ignited to oxides, dissolved in nitric acid, and treated with a hot saturated solution of potassium sulphate, with the addition of the solid salt. The soluble yttrium double sulphate solution was precipitated with oxalic acid, the oxalates were roasted to oxides, from the nitric acid solution of which it was again treated with potassium sulphate. Three such treatments with potassium sulphate from the nitrate solution were found necessary to completely remove the more insoluble group of earths and after three such treatments the didymiums could not be detected in a strong solution of the nitrates by means of their characteristic absorption spectra nor could cerium be detected by means of hydrogen peroxide.

Fractionation of the Succinates.

WITH R. C. BENNER.

About one hundred grams of the oxides were dissolved in nitric acid and the slight excess of free acid neutralized in ammonia. This neutral nitrate solution was diluted to a liter, brought to boiling and a saturated solution of neutral sodium succinate added in portions of 100 cc. By this means twelve fractions were obtained. After the addition of each portion of the sodium succinate, the solution was boiled fifteen minutes, after which the succinates were filtered and washed with 400 cc. of hot water. The fractions thus obtained were dried and ignited to oxide, small portions being taken for the determination of the atomic weight and the study of the absorption spectra.

SERIES I.

	Weight of fraction as oxide. Grams.	Atomic weight in R_2O_3.
1	22.2	114.2
2	15.8	111.83
3	10.0	110.06
4	8.8	111.30
5	9.0	108.5
6	7.1	107.2
7	7.0	105.6
8	6.1	104.4
9	7.0	101.0
10	6.4	97.0
11	4.0	95.8
12	3.0	....

The fractions thus obtained were combined and refractionated, selection being made of the portions whose atomic weights were close to each other; thus, for the second series, 2, 3 and 4 were combined and 5, 6, 7 and 8 were united while the lightest material, 9, 10 and 11, was similarly combined.

These oxides were dissolved in nitric acid, the excess of nitric acid removed by evaporation and in a dilution similar to that in Series I were fractionated by addition of sodium succinate in fractions as before. By again combining fractions of close atomic weight in three such series of fractionations the most soluble succinate fraction gave a nearly white oxide, whose nitrate solution showed only very weak absorption bands. The atomic weight of the element in the most soluble portion was 93, and the fraction corresponds to yttrium containing small amounts of samarium, europium and holmium as shown by the absorption spectra.

On the other hand, the third fraction at the other end of the series or the most insoluble portion gave a yellow earth whose atomic weight corresponded to 139. This oxide dissolved in nitric acid to a pink solution and showed absorption bands and was doubtless a mixture of yttrium with terbium. holmium. europium. samarium and erbium. Further study of these earths is being continued.

It has been considered well worth the while in making these studies on the samarskite earths and on the work which is in progress on the yttrium earths from monazite to determine the atomic weight in each fraction and also to study the absorption spectra.

The determination of the atomic weight for control purposes can be carried out sufficiently accurately by the estimation of the oxalic acid and of the earth oxide in the oxalate. While it is true that this method has some serious defects yet very good results can be obtained if it is properly handled.

Baxter[1] has recently shown in splendid detail that when the oxalates of neodymium, praseodymium, yttrium and certain other of the rare earths are precipitated in neutral or nearly neutral solution, they exhibit a strong tendency to carry down ammonium oxalate. This carrying down of ammonium oxalate by the insoluble oxalates of the yttrium earths is very pronounced and is difficult to prevent without going to the opposite extreme and making the solution too acid, in which case we have the factor of the solubility of the oxalate in acid appearing and the obviously incomplete precipitation of the oxalate. In the first case, the result due to the presence of additional oxalic acid in the precipitated oxalate would cause the atomic weight to be too low, while if considerable free nitric acid is present. the more soluble yttrium oxalate in incompletely precipitated and the result is to obtain a high atomic

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[1] This Journal, 28, 1684.

weight, due to the greater solubility of yttrium oxalate in nitric acid than of those earths of higher atomic weight.

The most accurate method for the precipitation of the oxalate of the yttrium earths which has come to the attention of the author has been to use a gram or less of the nitrate in very slightly acid solution and to use a dilution of about 500 cc. The oxalate is precipitated from the boiling solution by means of a dilute solution of pure oxalic acid.

In conclusion, the author wishes to acknowledge his appreciation of the courtesy of Mr. H. S. Miner, of the Welsbach Co., of Gloucester, N. J., who has placed at our disposal a large quantity of rare earth residues from Carolinian monazite and who has been able to secure for us a quantity of rare minerals for the study of the chemistry of the metals of the yttrium group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

MODIFIED SPECTROSCOPIC APPARATUS.

BY GREGORY PAUL BAXTER.

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In examination of absorption spectra of dilute solutions in long tubes, the faintness of the spectra owing to the necessarily great distance of the source of light from the slit is frequently a disadvantage. A form of container which partially obviates the difficulty is easily constructed of the shape shown in Fig. 1 from a T of glass tubing of suitable diameter. The light passes through the tube B lengthwise and is focused upon the slit S by the solution in the tube A, which acts as a cylindrical lens, thus very much increasing the light intensity. If the tube B is long, the length of path of the outside and middle rays of the beam within the tube is essentially the same, so that absorption is nearly equal in all parts of the beam. Hence this form of apparatus does not possess the disadvantage of a simple cylindrical vessel in which the outside rays pass through a relatively shorter length of solution.

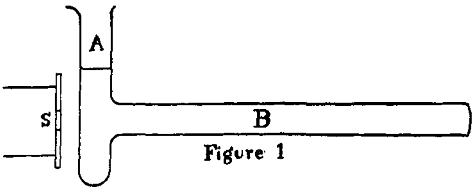

Figure 1

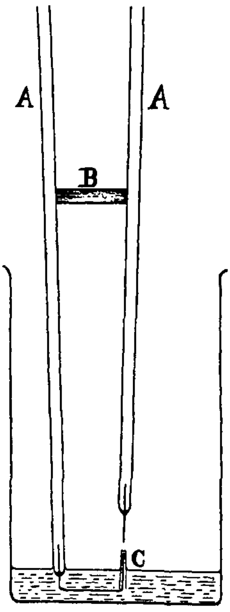

Figure 2