Fractional Distillation of Hydrazine Hydrate.—As a blank experiment, it was deemed advisable to study the fractional distillation of hydrazine hydrate in the absence of dehydrating agents, in the same apparatus and under conditions similar to those governing the preceding experiments. It has been shown by Scott[1] "that at 100° in a vacuum hydrazine hydrate in vapor is dissociated into hydrazine and water to the extent of 58 per cent., and that at 140° this dissociation is complete." From these facts it is, of course, to be expected that the first fractions obtained by distilling hydrazine hydrate should contain less, and that the middle fractions should contain more than 64.0 per cent., of hydrazine (theory for N_2H_4 in $N_2H_4.H_2O$ = 64.0 per cent.). The results obtained by Mr. Welsh were as follows:

Experiment 1.—Two hundred and fifty grams of hydrazine hydrate (Raschig, 100%) were distilled, in a slow, steady current of hydrogen, in the apparatus already described. The first six 25 cc. fractions were found to contain the following respective percentages of hydrazine: (1) 56.87, (2) 61.50, (3) 62.23, (4) 63.43, (5) 65.03, (6) 65.22.

Experiment 2.—The preceding experiment was duplicated, and the distillate was divided into 10 fractions, the first 9 containing about 25 cc. each, and the tenth somewhat less. Analysis showed the percentages of hydrazine to be respectively as follows: (1) 56.64, (2) 60.19, (3) 61.77, (4) 62.97, (5) 64.36, (6) 65.62, (7) 72.27, (8) 67.22, (9) 68.05, (10) 68.82.

Summary.

In the foregoing paragraphs has been described a convenient form of glass apparatus for the preparation of anhydrous hydrazine by the action of any suitable dehydrating agent upon hydrazine hydrate. The action upon hydrazine hydrate (1) of barium oxide, according to the method of de Bruyn, (2) of barium hydroxide, and (3) of sodium hydroxide, according to the procedure of Raschig, has been studied under comparable conditions. As a blank experiment, pure hydrazine hydrate has been subjected to fractional distillation in the same apparatus and under conditions similar to those prevailing in the other experiments.

CORNELL UNIVERSITY,
ITHACA, N. Y.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE STEARATE SEPARATION OF THE RARE EARTHS.

BY C. W. STODDART AND C. W. HILL.[2]

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Introduction.—One of the principles of separating the rare earths by

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[1] *J. Chem. Soc.*, 85, 913-8 (1904).

[2] The investigations covered by these papers were undertaken at the suggestion of Professor Victor Lenher whom the authors wish to thank for his advice and encouragement. They were originally presented as theses for the doctor's degree by their respective authors.

Thanks are also due Mr. H. S. Miner, of the Welsbach Company, for the material employed.

fractional precipitation depends on the slight differences in basicity of the earths. Any reagent which forms insoluble compounds with the earths may be used; but if the reagent in question has weak acidic or basic properties, it is of distinct advantage. When, for example, a salt of a strong base and a weak acid is added in dilute solution to a mixture of the rare earth nitrates, the strong base tends to unite first with the nitric acid radical of the weakly basic earths, since the salt of the weak acid is readily decomposed in the presence of the stronger acid. The rare earth metal is then free to unite with the weak acid to form an insoluble compound. As the fractionation proceeds the more strongly basic earths react, and as a result a much better separation is effected than in the case of a precipitant of stronger basic character.

Stearic acid is a weak organic acid of the fatty series, is of high molecular weight, and forms easily handled precipitates with the rare earths. It was therefore chosen as a reagent for attempting the fractionation of these difficultly separated elements.

Method of Fractionation.—The fractionation of rare earth mixtures as stearates was accomplished by the addition of an alcoholic solution of potassium stearate to a neutral solution of the earth nitrates, in quantity sufficient for the precipitation of only a fractional portion of the earths present.

The oxides of the earths were dissolved in nitric acid, the excess of acid removed by evaporation, and the syrupy residue taken up with water. It was found that if the stearate was added rapidly the precipitate was hard and lumpy, due to complete local precipitation where a large quantity of stearate came suddenly in contact with the earth nitrate. If, however, the stearate was added drop by drop, and the solution vigorously stirred, the precipitate was loose, fine-grained, easily washed, and the separation was excellent. Consequently the method finally adopted was to add, drop by drop, a hot alcoholic solution of potassium stearate to a cold, dilute, neutral solution of the earth nitrates. The mixture was agitated by a glass stirrer driven at high speed by a small electric motor. The stirring was continued several hours after the addition of the precipitant.

By using a Buchner funnel with two thicknesses of filter paper, it was possible to wash the precipitate rapidly. The filtrate was evaporated to the original volume and cooled before the addition of the next portion of stearate. The washed precipitate was ignited for atomic weight determination. (NOTE.—When fractions are to be combined without determination of the atomic weight, as in the case of large amounts of materials and several similar series, the precipitated stearates suspended in water may be decomposed by nitric acid. The free stearic acid can be removed mechanically, and the resulting nitrate solution combined with others. This permits of very rapid fractionation.)

The first fraction of a series was always smaller than the others, and the precipitate had a tendency to be hard and lumpy, notwithstanding the care used in adding the precipitant slowly. This was due to the liberation of free stearic acid by the slight excess of nitric acid often remaining in the earth solution. It was found advizable, therefore, when the solution was acid, to add a small amount of stearate and remove the free stearic acid before proceeding with the separation.

The use of a mechanical stirrer changed the nature of the precipitate from a coarse, curdy texture to a fine, light material. Time is another factor entering into the more complete separation of the rare earths. If the mixture of precipitate and solution is stirred for a considerable length of time, a secondary decomposition takes place which materially changes the chemical composition of the precipitate. This fact is shown by the two experiments conducted as follows:

Seven-tenths of a gram of an oxide, the elements of which had an average atomic weight of 109.6, were dissolved in nitric acid, the solution evaporated, and the residue diluted with water to two liters. To this was added the thoroughly washed precipitate of earth stearates which had an average atomic weight of 97.4. This mixture was stirred for about twelve hours. At the end of this time the precipitate had changed physically from a coarse, curdy mass to a very fine-grained, light, fluffy material. The precipitate was removed, washed thoroughly, and the average atomic weight of the elements found to be 102.8. This increase in atomic weight from 97.4 to 102.8 showed that a very decided secondary decomposition had taken place between the solid stearate and the nitrate solution.

In another instance a mixture which indicated an atomic weight of 126 yielded a first fraction, the earth element of which had an atomic weight of 127.1. The atomic weight of the element of the same fraction stirred for forty-eight hours was changed to 135.2.

Preparation of the Stearate Solution.—Pure stearic acid which had a melting point of 69°-70° was used for the first fractionations. Later it was found that commercial stearic acid with a melting point of 55° was satisfactory. This material was approximately 50 per cent. stearic acid and 50 per cent. palmitic and oleic acids. Since the commercial acid is very much cheaper, and at the same time just as effective, its use is of great advantage.

The potassium stearate solution was prepared by dissolving stearic acid in 95 per cent. alcohol, neutralizing with a solution of potassium hydroxide, using phenolphthalein as indicator, and diluting with water to make a 50 per cent. solution. One cubic centimeter of the solution contained about two-tenths of a gram of stearic acid.

Determinations of Atomic Weight and Absorption Spectra.—The atomic weight determinations were made by the Gibbs method of analyzing the oxalates, which was sufficiently accurate for this work.

Absorption spectra of 10 per cent. nitrate solutions through layers of solution 17.5 mm. thick were obtained by means of a Steinheil grating spectroscope. Comparisons were made with samples of rare earth salts prepared by Waldron Shapleigh and Eugene Demarçay.

Experimental Note.—It was observed during the washing of the precipitated stearates that the material tended to separate in the long cylinder employed, part of the precipitate floating on the surface and part of it sinking to the bottom. This suggested the possibility of a separation based upon the differences in specific gravity of the stearates of the various earths present. A mixture of yttrium earths with didymium and erbium earths was converted into nitrates and carefully precipitated as stearates. The precipitate was washed, suspended in water, and agitated continuously for a week by means of the rapidly revolving mechanical stirrer. It was then placed in an alcohol-water solution of a specific gravity which allowed the stearates to settle to the bottom. Water was added until three fractions had been obtained. Sodium chloride solution was added to separate the fourth and fifth fractions. The specific gravities (by hydrometer) of the solutions from which the fractions were removed and the atomic weights of the earth elements are tabulated below.

	Atomic weight.	Sp. gr. of solution.
Mixture	120.3	.....
Fraction 1 (small)	121.6	0.900
Fraction 2	120.8	0.950
Fraction 3	120.6	0.951
Fraction 4	120.8	1.040
Fraction 5 (remaining)	120.1	.....

There is evidence of a slight separation, especially with the first fraction which was small. The separation is not good in comparison with that obtained by other methods applied to the same mixture of earths, although it might be more striking with other mixtures. Opportunity has not been afforded the writers to repeat the experiment, nor to employ other mixtures of the rare earths.

I. THE STEARATE SEPARATION OF THE YTTRIUM GROUP (BY C. W. STODDART).

Yttrium Earths from Monazite.

Preparation of Oxides.—The material employed was in the form of oxalate from monazite, which was ignited, converted into nitrates, and the yttrium earths separated from the cerium earths by precipitating the latter as the double potassium sulfate in a saturated solution of potassium sulfate. The cerium earths were in such excess that a considerable quantity of yttrium earths was carried down with them either by inclusion or adsorption, although the presence of an excess of nitric acid prevented this adsorption to a very considerable extent. By treating the cerium earth double sulfate with additional water it was found possible to recover a further portion of the yttrium earths.

In this way several lots were obtained, amounting in all to six per cent.

of the original roasted oxalates. The atomic weights of the different lots varied from 117.4 to 132.2, the latter containing some didymium. It was possible to tell with considerable accuracy when the characteristic absorption bands of didymium had disappeared, by using a hand spectroscope on an eight-inch layer of the filtrate from the cerium earth double sulfates.

Separations Effected.—The first fractionation was made on 10 grams of yttrium earth oxide with an atomic weight of 118.1. Nineteen fractions were removed by adding various amounts of an aqueous solution of potassium stearate. Table I gives the atomic weights of the fractions.

TABLE I.—ATOMIC WEIGHTS OF THE FIRST SERIES OF FRACTIONS.

Number of fraction.	Atomic weight.	Number of fraction.	Atomic weight.
1	124.5	11	120.7
2	127.0	12	123.1
3	129.2	13	121.6
4	119.7	14	118.9
5	125.4	15	118.9
6	125.3	16	113.3
7	123.3	17	107.9
8	123.3	18	102.7
9	124.4	19	103.7
10	120.5	..	...

The atomic weights do not diminish regularly from first to last, due in great measure to the changes in methods of fractionation. The precipitate in many instances was not homogeneous, owing to complete local precipitation having taken place where the precipitant was added too rapidly. Apparently such a large number of fractions is unnecessary, but the fact is clearly brought out that the stearate method is able to separate the rare earth oxides of atomic weight 118.1 into fractions varying from 129.2 to 102.7.

The second fractionation was carried out on 10 grams of earth oxide with an atomic weight of 117.4, using a solution of potassium stearate in 95 per cent. alcohol, and adding it drop by drop from a burette, it being necessary to warm the burette from time to time to keep the solution liquid. After the addition of the precipitant the mixture was shaken violently in a flask. Six fractions were removed, the atomic weight of each being as follows: 122.8, 119.8, 116.8, 115.6, 106.7, 103.7. From these results it is to be noted that approximately the same degree of separation may be effected in six fractions as in nineteen, if the conditions are slightly changed.

In order to try the method on a larger scale, 50 grams of rare earth oxides of atomic weight 118.1 were dissolved in nitric acid and fractionated with alcoholic potassium stearate. Each part of the first series was fractionated again and suitable fractions combined. In this way sixteen fractions were obtained and united according to their atomic weights into four portions, the atomic weights of each being 123, 120, 114, and 112.

The separation effected here was not particularly good. Sufficient time had not been allowed for equilibrium to be established. The precipitate was in many cases so coarse that some of the solution was occluded. Consequently, it was at this point that the method of fractionation was changed to the use of the mechanical stirrer and a solution of potassium stearate in 50 per cent. alcohol. Moreover, it was found that instead of obtaining fractions of equal weight, if several small fractions were first removed, the heavier earths could be separated more rapidly and a large fraction left, with materially lighter atomic weight. For example, with ten grams of oxide there were removed four fractions of 1.5 grams each, and one fraction of 4 grams.

With these improvements in method, the four portions mentioned above, having atomic weights of 123, 120, 114, and 112, were separated into numerous fractions, the various fractions in the different groups united according to the color of the ignited stearates and refractionated. The colors varied from dark brown to light buff. Thirty-three fractions were thus obtained. Three were united whose color was almost white and whose atomic weight was 92. This lot was separated into four fractions, the last one having an atomic weight of 90.6, and was practically pure yttrium. The quantity, however, was so small that further fractionation was impossible, although there is no doubt that yttrium of atomic weight 89 could have been obtained very easily from this material.

Absorption Spectra.—Twenty-nine of the thirty-three fractions in the last series were examined for absorption bands. Table II gives the wave

TABLE II.—ABSORPTION SPECTRA OF THE FIRST STEARATE FRACTION, OF THE TWENTY-NINTH STEARATE FRACTION, AND OF ERBIUM NITRATE (SHAPLEIGH'S).

First fraction.		Twenty-ninth fraction.		Erbium nitrate.	
		444.2	very faint		
				452.0	very faint
458.0	fairly strong	462.3	very faint	457.4	fairly strong
463.7				464.1	very faint
493.7	very faint	495.1	very faint	493.5	very faint
496.4	fairly strong			496.8	fairly strong
529.1	very faint	529.4	haze	527.6	very faint
435.7	strong	532.6	fairly strong	533.0	strong
544.7	fairly strong	545.3	faint	545.6	faint
				550.5	very faint
580.2	faint	579.2	faint	579.5	fairly strong
589.9		590.9		590.2	
647.5	fairly strong	648.4	faint	649.3	faint
651.1					
				657.3	very faint
661.7	fairly strong	664.3	very faint	661.7	faint

lengths for the first fraction and for the twenty-ninth fraction whose atomic weight was 101.4. In comparison there is given the spectrum of a sample of erbium nitrate prepared from monazite by Dr. Waldron Shapleigh.

Examining the table it may be seen that most of the lines are those of erbium, or at least of earths very closely associated with erbium, such as samarium, holmium, and europium. The lines fade markedly as the fractionation progresses, but persist throughout the series until there is obtained the last fraction which had an atomic weight of 90.6. This portion gave absolutely no absorption spectrum.

Yttrium Earths from Gadolinite.

To test the separation of the yttrium earths from gadolinite, about 8 grams of oxide, freed from the cerium group by precipitation of the latter with potassium sulfate, were separated into five fractions. The first fraction had an atomic weight of 109.6, the last fraction of 97.4. This material contained a higher percentage of yttrium than did the monazite earths, and the progress of the fractionation indicated a rapid approach to the separation of this element from its companions.

Behavior of Yttrium Earth Stearates towards Anhydrous Solvents.—In order to test the solubility of the stearates of the rare earths in anhydrous compounds and subsequently to investigate the ability of the latter to extract them differentially, a portion of the earth oxide of atomic weight 118.1 was dissolved in nitric acid, evaporated to a thick syrup, diluted with water, and all the rare earths precipitated by potassium stearate. The precipitate was filtered, washed, dried and pulverized.

A part of this substance was placed in a Schleicher and Schüll paper thimble in a Soxhlet extractor and subjected to extraction with *ether* for some time. Only stearic acid was removed. This was present in the original mass in the free state, having been liberated from the potassium salt by the excess of nitric acid in the original solution.

Benzene extracted a portion of the rate earths. A determination of the atomic weight of the extracted material gave 116.6, of the part remaining in the thimble, 117.5.

Carbon tetrachloride extracted a portion which gave an atomic weight of 116.9. The fraction remaining behind was 117.4 in atomic weight. Further treatment extracted practically all of the rare earth stearates.

Carbon disulfide extracted nothing but stearic acid.

Alcohol extracted only stearic acid.

Xylene extracted a portion whose atomic weight was 117.8. All of the material was soluble finally.

Toluene dissolved all of the material.

Chloroform extracted only stearic acid.

Melted *naphthalene* and *anthracene* dissolved all of the material, as did hot *olive oil.*

From these results it can be seen that yttrium earth stearates are soluble in anhydrous compounds of relatively high boiling points, but there is no one rare earth stearate markedly different in solubility from the rest.

Discussion of Results.

In the year 1896, Drossbach[1] obtained by fractional precipitation with sodium hydroxide, and also by fractional crystallization of the sulfates, a white oxide whose element had an atomic weight of approximately 100. Also in 1896 Schützenberger and Boudouard,[2] by alternating the basic nitrate method with fractional crystallization of the sulfates, obtained a white oxide whose atomic weight was 102. Since these investigators were unable to decompose this fraction further, they assumed that they had an element whose atomic weight was approximately 100. In 1897 Urbain and Boudischovsky[3] by using the acetyl-acetonate method obtained several fractions whose atomic weights averaged about 100.

In 1900, however, Urbain[4] was able to carry the fractionation further with the ethyl-sulfate method, obtaining one portion whose atomic weight was 152, on one hand, and pure yttrium on the other. He claimed that the product obtained by Drossbach, Schützenberger and Boudouard, as well as by himself previously, was a mixture of pure yttrium and the terbium earths. In all the above cases the material employed was from monazite.

Referring back to the last fractions of the first two series by the stearate separation on page 1080, it will be noticed that the atomic weights were 103.7 in both cases. This may be the same fraction obtained by the investigators mentioned above. It is to be observed that this fraction of approximately 102 (average) is obtained only from monazite yttrium earths. In the stearate separation on the gadolinium earths no such fraction was obtained.

The earths of the yttrium group are characterized by such a similarity one with another, that by any method their separation is difficult. In the case of the yttrium earths from monazite, however, this difficulty of separation apparently reaches a climax when the mixture has an atomic weight of approximately 102. This particular fraction is so difficult of separation that, as seen above, some of the previous investigators went so far as to think that they had discovered a new element. The later work of Urbain, however, dispelled their illusion.

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[1] *Ber.*, **29**, 3, 2452.

[2] *C. r.*, **122**, 697.

[3] *Ibid.*, **124**, 618.

[4] *Ann. chim. phys.*, **19**, 184.

It is customary in preparing pure yttrium to use alternately various methods, since most reagents are unable to carry the separation beyond a certain point. A different reagent is necessary to effect a further separation. The fraction from monazite earths having an atomic weight of 102 presents more than ordinary difficulties of separation, even when the methods are changed. It is to be noted that the use of potassium stearate, however, as a means of separating these earths is in itself sufficient to carry the fractionation from the original material down to pure yttrium without using any other reagent. It is true that there is a momentary pause at the fraction of atomic weight 102, indicating a combination whose separation causes more than ordinary difficulty.

In explaining the cause of this difficulty in separating the fraction whose atomic weight is 102, two possibilities suggest themselves:

First, that there is a new element in monazite very closely allied with yttrium and so near like it in properties that it is very difficult to separate them. In passing, Crookes' victorium[1] might be mentioned. This element, which Crookes claims to have separated from samarskite, gadolinite, cerite, and other similar minerals, has an atomic weight of approximately 118, and is very like yttrium in properties. The presence of a new element, however, has been disproved by the work of Urbain, mentioned above.

Second, that there is formed a pseudo-compound of yttrium with other members of the group—a compound which gives an atomic weight of 102 for the element. The average atomic weight of the other members of the group is 166 and calculating with this average figure it would mean a compound of four parts yttrium to one part of the other members of the group.

Conclusions.

1. The stearate method is of distinct advantage over existing methods in many ways. The precipitate formed is easily filtered and washed, the precipitant cheap, the separations sharp and distinct. For the preparation of pure yttrium from monazite it is decidedly the best method known, and yttrium is one of the most difficult rare earths to separate pure. Only one reagent is necessary, and few fractionations are required, thereby saving a great amount of time, as well as of material, in a large number of manipulations. There is a brief pause in the progress of the fractionation at the portion which has an atomic weight of approximately 102.

2. The stearate method applied to the yttrium earths from gadolinite effects a rapid separation without the pause at the fraction having an atomic weight of 102.

3. Yttrium earth stearates are soluble in anhydrous compounds of

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[1] *Chem. News*, 80, 49.

relatively high boiling point, but they are not extracted differentially by such solvents.

II. THE FRACTIONATION OF THE GADOLINIUM EARTHS AS STEARATES (BY C. W. HILL).

The experimental work here described was undertaken with the purpose of studying the adaptability of the stearate method to the fractionation of the gadolinium earths. The available material was Welsbach residues from monazite, and gadolinite. The treatments of the rare earths from the two sources are considered separately.

Separation of Rare Earths from Monazite.

The rare earths obtained from monazite as oxalates, ignited and converted into nitrates, were fractionally crystallized from the nitrate solution as the double magnesium nitrates, crystallization being continued until magnesium nitrate separated out. The crystallized part contained the major portion of the cerium, lanthanum, and the didymiums. From the remaining solution, three large fractions of insoluble double potassium sulfates were crystallized. The earths remaining in solution were treated as described on page 1087.

Insoluble Double Sulfate Portion. — The earths in the last insoluble double sulfate fraction were converted into hydroxides by boiling with sodium hydroxide. The hydroxides, after being washed, were dissolved in nitric acid, and the earths reprecipitated from the dilute nitrate solution by dilute ammonia, washed free from alkali and dissolved in formic acid.

Five large fractions of formates were obtained by the slow evaporation of the formate solution, and the earths remaining in solution were precipitated by ammonia. The earths in the large first formate fraction were converted into nitrates, hydroxides, and formates successively, and fractionated partly as formates (three fractions) and as hydroxides (last four fractions). The earths in the other formate fractions were precipitated fractionally with dilute ammonia. The atomic weights determined were:

SERIES I.

Formate fractions.	I.	II.	III.	IV.	V.	VI.
Subdivisions...	143.5	137	134	132	138.1	119.9
	...	...	...	...	132.4	...
	...	...	...	...	131.1	...
	...	...	...	...	...	...
	...	...	...	...	...	...
	135.1	...	...	...	...	...
	63.0	...	...	...	...	...

The last fraction of formate fraction I, showing an atomic weight of

63, gave a white oxide, and its solution showed no absorption spectrum. It consisted of yttrium and scandium.

The fractions derived from the large formate fractions I and II were separated further by fractional precipitation of the stearates. Thirty-three fractions thus obtained were combined into six groups according to the color of the oxides and their relation to the other fractions, the more soluble of one group being combined with the less soluble portion of the group following (Series II).

The six groups were fractionated further as stearates into twenty-eight fractions, the atomic weights being as follows:

SERIES III.

138.0	146.9	144.7	150.8	144.8	146.5
...	...	...	...	...	...
...	...	...	...	...	...
...	...	...	147.5	...	...
...	128.9	131.6	...	...	...
...	...	...	...	124.6	...
113.6	...	...	...	...	...

In the first part of the work the atomic weights of only the extreme fractions were determined. This course is not advizable, since the first fraction of a group is usually lower in atomic weight than the second, and often approximates an average of the group. It is to be expected, with the earths under consideration, that the didymiums will be present to a greater extent in the first fractions of a series and that the atomic weight of some intermediate fraction will be greatest. The atomic weights in many of the tables confirm this statement. It is therefore necessary in accurate work to determine the atomic weights of practically all the fractions of a series.

The fractions last described were combined according to their atomic weights into eight groups, the atomic weights of which approximated 148, 145, 142, 140, 137, 132, 128, 124. The first three groups after removal of the cerium by hydrogen peroxide and ammonia were taken for further separation as stearates. The atomic weights of the different groups and fractions are given. Each group was obtained by combination of fractions of the preceding group which had nearly the same atomic weight.

	SERIES IV.			SERIES V.		
At. wt. of group.....	(148)	(145)	(142)	(146)	(144)	(140)
At. wt. of fractions..	145.8	146	148.4	146.2	148	144
	...	...	...	147.5	139.9	143.3
	...	...	...	147.4	...	143.2
	...	121.6	...	...	...	142.1
	131.3	...	137.6	120.1	...	141.3
				118.9	...	...
				...	...	126

	Series VI.			Series VII.		
At. wt. of group....	(147.6)	(143)	(144)	(153.1)	(146.6)	(143.4)
At. wt. of fractions	153.1	150.4	145.3	152.3	151.2	149.8
	146.6	150.2	143.1	150.3	145.7	137.1
	142.9	143.4	140.9	147.8	...	...
			133.7			

	Series VIII.		Series IX.	Series X.
At. wt. of group..........	(150)	(147)	(149.5)	(153)
At. wt. of fractions........	149.1	149.8	151.8	153.3
	151.3	142.8	153.2	153.0
			153.0	
			149.8	

The fractions had now become so small that it was considered advizable to combine them with fractions of the same atomic weight and absorption spectra, which had been obtained from the soluble double sulfate portion from monazite.

Series X showed a constant atomic weight of 153. The oxide had a light chamois color. The spectrum lines of a ten per cent. solution of the nitrate were:

Europium.		Samarium.		Erbium.	
464	strong	471	faint	484.3	fairly strong
534.5	strong	478		486.8	
592	faint				
		496.5	haze	543.6	fairly strong
		500		545	
		559	very faint	666	very faint

The earth was europium with only the faintest traces of samarium and a small amount of erbium.

Fractions from Series VIII and IX having the atomic weight of 149.8 were found to be constant. The absorption spectrum of a 20 per cent. nitrate solution was composed of strong lines of samarium, a few lines of erbium of medium strength, and one stronger one of praseodymium.

Samariun.		Erbium.		Praseodymium.	
463	faint	483–485	medium	595–604.5	strong
470–475	medium	542–544.8	medium		
497–501.5	strong	666.6	very faint		
531–535	medium				

The earth was therefore fairly pure samarium, being especially free from other members of the gadolinium group.

Soluble Double Sulfate Portion.—The earths remaining in solution after the removal of the insoluble double potassium sulfates, as described on page 1085, were precipitated as oxalates, converted into oxides and fractionated as chromates.[1] The earths of the first insoluble chromate fraction thus obtained (at. wt. 134) were separated as chromates into four

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[1] Muthmann and Boehm, *Ber.*, 33, 42.

fractions having the atomic weights 141, 145, 131, 122 in order of precipitation. Cerium was present in the first fraction and was separated as ceric hydroxide.

The first three fractions were fractionated as stearates, the atomic weights of the successive groups and fractions being:

SERIES A.

At. wt. of group.........	141	145	131
At. wt. of fractions.......	142.7	150.1	134.1
	143.5	150.0	133.1
	145.7	150.2	130.9
	139.4	146.3	...
	...	136.6	...

SERIES B.

At. wt. of group.........	143	146	150
At. wt. of fractions.......	149.6	150.8	153.2
	144.4	150.2	156.0
	...	147.9	147.8

SERIES C.

At. wt. of group...	...	...	150.5	147.8	144.4
At. wt. of fractions	154.0	152.2	154.0	154.7	151.0
	152.8	151.9	150.4	149.9	146.1
	151.5	148.9	151.8	146.0	134.6
	142.5	...	147.7	134.5	...

SERIES D.

At. wt. of group...	154	152.8	152.2	151.8	151.0	144.4
At. wt. of fractions	156.0	152.6	154.0	153.0	155.5	145.2
	153.3	152.5	151.4	151.0	151.8	143.0

Series D contained some of the most pure fractions from the insoluble double sulfate portion (page 1087) as well as those from Series C.

The second group of the series had an atomic weight of 152.8 and yielded two fractions of atomic weight 152.6 and 152.5. The limit of the efficiency of the stearate separation had therefore been reached for this particular earth in the quantity at hand—about three grams. Spectroscopic examination revealed the presence of a very slight trace of erbium, with a larger amount of samarium, although the atomic weight was near that of pure europium—152—, and the spectrum lines of this element are strong. The lines of the absorption spectrum of a 10 per cent. nitrate solution were:

Europium.		Samarium.		Erbium.	
465	faint	471	strong	484.3	faint
529	faint	478		486.8	
534.5	medium	498	medium		
592.6	strong			543	faint
597				546.5	
				666	

Fractions having the atomic weight of 156 and 155.5 gave an absorption spectrum of erbium and samarium (extremely faint) with practically the same lines as above with varying intensity. The gadolinium was not so nearly pure as the europium.

Europium had therefore been obtained, which contained only the slightest traces of erbium, with a very small quantity of samarium, while by the same method (page 1087) another sample had been obtained which contained some erbium with only the slightest traces of samarium. There can be no doubt as to the efficiency of the stearate separation, although it did not appear advizable to effect the complete removal of erbium and samarium from the two samples of europium until larger portions of the earth could be obtained.

The samples of europium were obtained from the original monazite material after 59 series of fractionations yielding 204 fractions as shown below:

Double magnesium nitrates—1 series of 3 fractions.
Double potassium sulfates—1 series of 3 fractions.

Insoluble double sulfate portion.			Soluble double sulfate portion.		
Separated as	Series.	Fractions.	Separated as	Series.	Fractions.
Formates......	7	21	Chromates.....	1	4
Stearates.......	32	120	Stearates......	17	53
	—	—		—	—
	39	141		18	57

Separation of Rare Earths from Gadolinite.—Rare earths were obtained from twenty-five pounds of gadolinite from Norway by treatment of the mineral with hydrochloric acid, and precipitation of the earths as oxalates from acid solution. The earths were fractionated into 18 portions as double potassium sulfates. The didymiums were practically all removed in fraction 12. The last three fractions yielded white oxides. The double sulfate fractions were converted into hydroxides which were then dissolved in formic acid. The 18 sulfate fractions were then divided by careful evaporation of the formate solution into 59 fractions. These were grouped according to the color of the oxide and absorption spectra into 8 groups, the atomic weights of which were afterwards found to be 138.6, 121.1, 108, 105, 102, 100, 98.6, 99.9.

The four fractions of higher atomic weights were fractionated as double potassium sulfate, the atomic weights being:

At. wt. of group...........	138.6	121	108	105
At. wt. of fractions.........	135	136	120.2	118.3
	...	...	107.8	107.4
	133	...	105.0	101.0

These fractions were combined according to their atomic weights and the three heavier groups, after removal of the cerium, were fractionated as stearates. The atomic weights were:

At. wt. of group	136	135	133
At. wt. of fractions	138.2	136.1	140.9
	135	135.6	134.5
	127.2	124.8	...

The heavier fractions contained so small an amount of the earths desired in our work, erbium and samarium showing very faintly in the spectra, that the separation was not carried further.

Note.

The Stearate Separation of the Cerium Earths.—The effectiveness of the stearate separation when applied to the earths of the cerium group is shown by Series V (page 1086) where groups of the atomic weights of 140, 144, and 146 were fractionated. It is also indicated by certain groups in Series VII and IX in the insoluble sulfate portion, and by Series A, B, C, and D (page 1088) in the soluble sulfate portion.

Spectroscopic examination of the groups and fractions indicated a partial separation of the didymiums, while cerium was concentrated in the first fractions as shown by the hydrogen peroxide and ammonia test.

While none of the members of this group was isolated, the separations effected in this group, while seeking members of the intermediate group, leave little doubt as to the efficiency of the stearate separation in the cerium group.

Summary of Experimental Work.

After division as potassium double sulfate, the rare earths from monazite were fractionated as stearates, until the gadolinium earths were concentrated and separated. Eighteen series of 57 fractions from the soluble double sulfate portion yielded a fraction of constant atomic weight of 152.5 which was practically pure europium. A second sample of europium (atomic weight 153), containing a trace of erbium, was separated from the insoluble double sulfate portion by 39 series of 141 fractions. The separation at the same time yielded a sample of impure gadolinium of atomic weight 156, which contained some erbium, samarium, and europium, and also a sample of samarium of atomic weight 149.8.

The rare earths were extracted from twenty-five pounds of gadolinite and fractionated by 31 series of 129 fractions. The mineral contained quantities of the gadolinium earths too small to warrant their separation.

In the entire work 90 series of fractionations yielded 333 fractions, of which 159 were analyzed and the atomic weight of the earth determined.

Conclusions.

The experimental work described demonstrates that:

1. The gadolinium earths may be concentrated and separated by their fractional precipitation as stearates.

2. The stearate method is also applicable to the separation of the members of the cerium group.

MADISON, WIS.