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THE SEPARATION OF THE RARE EARTHS.

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Since writing a scheme for the separation of rare earths in 1908, many new methods have been introduced and others modified. Furthermore, since communications asking for reprints still arrive, the author has considered it advisable to bring the methods of separation up to date.

The operations herein dealt with concern only the rare earth elements, La, Ce, Pr, Nd, Sm, Eu, Gd, Tr, Dy, Ho, Er, Tm, Yb, Lu, and Ct together with Yt and Sc, it being considered that other metals, such as thorium, zirconium, etc., have been removed, if found occurring in the oxalate precipitate. A description of the working up of rare earth minerals will be found included in a paper on thulium.[1]

There are four different methods for attacking the crude oxalates, which depend upon the composition of the latter: (*a*) If the mixture is chiefly composed of lanthanum, much cerium, praseodymium, neodymium, samarium, europium and gadolinium, it should be converted into the neutral nitrates and boiled with potassium bromate and marble, as required for the separation of cerium. (*b*) If only a little cerium is present, the oxides should be converted into double magnesium nitrates, which are then fractionated, the cerium being separated from the fractions where it is found to occur. (*c*) Should the mixture be composed of gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, yttrium and scandium it is best to commence with the fractional crystallization of the bromates. (*d*) When the cerium and yttrium metals occur together, one must commence with the sodium sulfate treatment, which is the first operation shown on the diagram.

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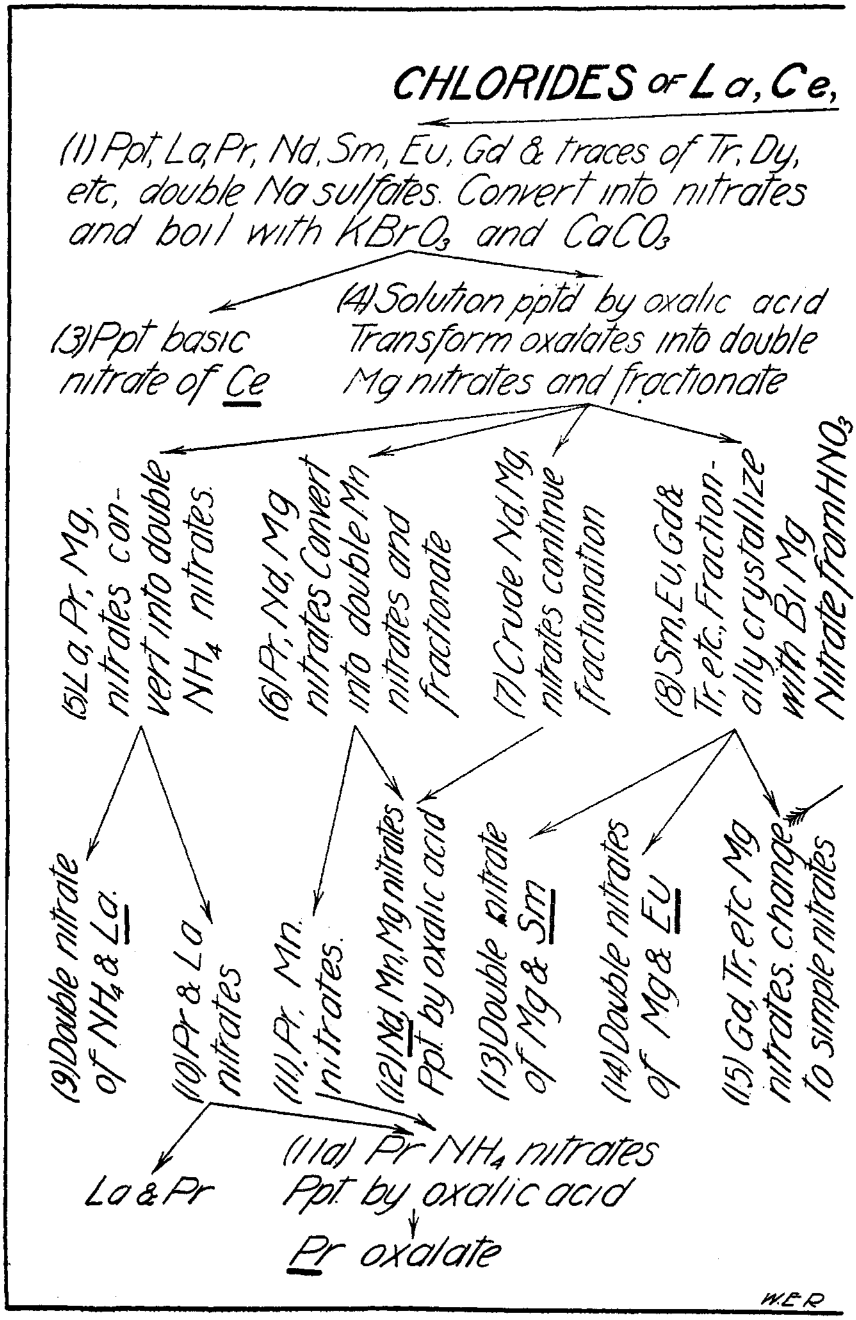
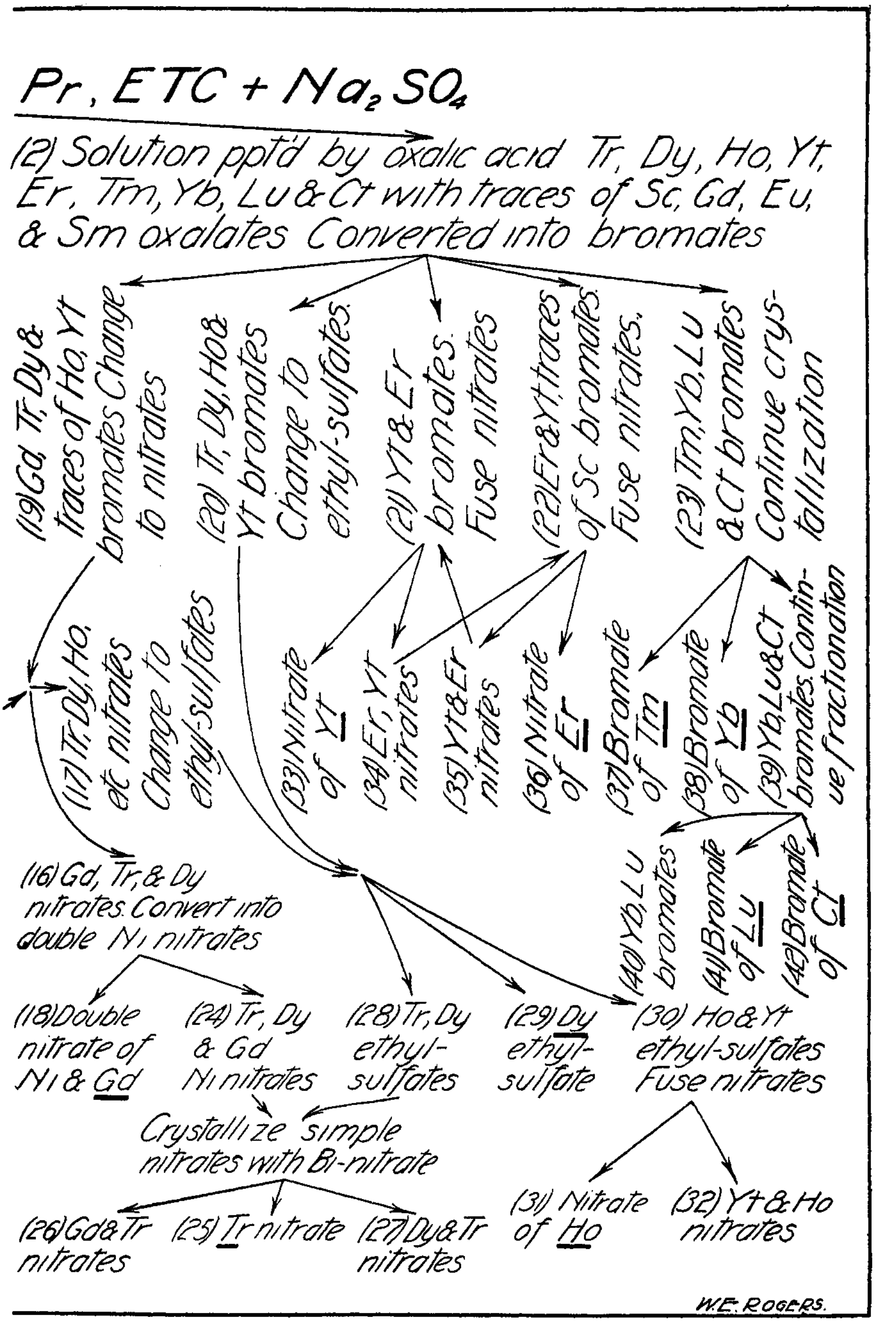
[1] THIS JOURNAL, 33, 1332.


CHLORIDES OF La, Ce,
(1) Ppt. La, Pr, Nd, Sm, Eu, Gd & traces of Tr, Dy, etc, double Na sulfates. Convert into nitrates and boil with $KBrO_3$ and $CaCO_3$
(3) Ppt basic nitrate of Ce
(4) Solution pptd by oxalic acid Transform oxalates into double Mg nitrates and fractionate
(5) La, Pr, Mg, nitrates convert into double NH_4 nitrates.
(6) Pr, Nd, Mg nitrates Convert into double Mn nitrates and fractionate
(7) Crude Nd, Mg, nitrates continue fractionation
(8) Sm, Eu, Gd & Tr, etc., Fractionally crystallize with Bi Mg Nitrate from HNO_3
(9) Double nitrate of NH_4 & La.
(10) Pr & La nitrates
(11) Pr, Mn. nitrates.
(12) Nd, Mn, Mg nitrates Ppt. by oxalic acid
(13) Double nitrate of Mg & Sm
(14) Double nitrates of Mg & Eu
(15) Gd, Tr, etc Mg nitrates. change to simple nitrates
La & Pr
(11a) Pr NH_4 nitrates Ppt. by oxalic acid
Pr oxalate
W.E.R.


Pr, ETC + Na_2SO_4
(2) Solution ppt'd by oxalic acid Tr, Dy, Ho, Yt, Er, Tm, Yb, Lu & Ct with traces of Sc, Gd, Eu, & Sm oxalates Converted into bromates
(19) Gd, Tr, Dy & traces of Ho, Yt bromates Change to nitrates
(20) Tr, Dy, Ho & Yt bromates Change to ethyl-sulfates.
(21) Yt & Er bromates. Fuse nitrates
(22) Er & Yt traces of Sc bromates. Fuse nitrates.
(23) Tm, Yb, Lu & Ct bromates Continue crystallization
(17) Tr, Dy, Ho, etc nitrates Change to ethyl-sulfates
(33) Nitrate of Yt
(34) Er, Yt nitrates
(35) Yt & Er nitrates
(36) Nitrate of Er
(37) Bromate of Tm
(38) Bromate of Yb
(39) Yb, Lu & Ct bromates. Continue fractionation
(16) Gd, Tr, & Dy nitrates. Convert into double Ni nitrates
(40) Yb, Lu bromates
(41) Bromate of Lu
(42) Bromate of Ct
(18) Double nitrate of Ni & Gd
(24) Tr, Dy & Gd Ni nitrates
(28) Tr, Dy ethyl-sulfates
(29) Dy ethyl-sulfate
(30) Ho & Yt ethyl-sulfates Fuse nitrates
Crystallize simple nitrates with Bi-nitrate
(26) Gd & Tr nitrates
(25) Tr nitrate
(27) Dy & Tr nitrates
(31) Nitrate of Ho
(32) Yt & Ho nitrates
W.E. ROGERS.

Separation of Yt and Ce Group.—The solution in the form of the chloride or sulfate is stirred with sodium sulfate crystals until the praseodymium and neodymium bands disappear. Sodium sulfate is better than potassium sulfate when used with care. The solubilities of the yttrium earth sulfates increase with the addition of sodium sulfate until the latter reaches a certain concentration, after which the former rapidly decrease. When all the cerium group double sulfates (1) are precipitated, they are filtered off and washed with sodium sulfate solution. The filtrate is acidified, and the rare earths thrown out by means of oxalic acid (2).

Separation of Ce.—The double sodium sulfates (precipitate 1) are boiled with strong sodium hydroxide until thoroughly decomposed. The mass is diluted, filtered and washed with boiling water until free from sulfates. The hydroxides are dissolved in nitric acid, the solution made nearly neutral, heated to boiling and potassium bromate added.[1] When the red fumes of bromine make their appearance, a few lumps of marble are added to keep the liquid nearly neutral. (Recent experiments show that powdered marble, added very gradually, can be used with great advantage, when working upon the large scale.) The whole is then boiled until some of the filtered liquid fails to give the hydrogen peroxide test for cerium. The marble (if in the lump condition) is removed and the precipitate of basic ceric salts is allowed to settle as much as possible, after which it is filtered off and washed with water acidified with nitric acid (precipitate 3). The filtrate can either be precipitated in the cold by oxalic acid, or else heated to boiling and the hydroxides separated by means of an excess of sodium hydroxide. The hydroxides or oxalates form precipitate 4. In case oxalic acid is used to throw out the rare earths, it is advisable not to use too much potassium bromate in the early part of the operation, as otherwise much oxalic acid is used up by the oxidation and quantities of bromine are liberated. When large quantities of cerium are present, the boiling should be continued until only a little remains in solution; under these conditions the cerium basic salt, after washing with acidified water, is obtained in a very pure state. The small amount of cerium remaining in solution can then be removed by continuing the boiling as described above.

If necessary, the cerium can be purified by repeating the process, or as follows: The precipitate is dissolved in concentrated nitric acid by the aid of a *very little* alcohol. The orange red liquid obtained in this manner is diluted, and boiled with lump marble. The solution must not be allowed to become alkalin by boiling too long. The precipitate is filtered off and the solution is then treated with potassium bromate, etc., to remove the remaining portion. The basic salts may be further purified by dissolving in hydrochloric acid, adding a slight excess of sulfuric

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[1] James and Pratt, THIS JOURNAL, **33**, 1326.

acid and heating. The crystallin cerium sulfate is separated, and washed with alcohol. The sulfate is then rendered anhydrous, made into a cold saturated solution, and the pure hydrated sulfate thrown down by heating.

Separation of La Group.—The cerium-free earths (4) if in the state of oxalates are ignited to oxides. For roughly separating these earths upon the large scale the crystallization of the double magnesium nitrates is employed. These compounds crystallize more readily than the double ammonium nitrates. The magnesium double salts,[1] $2R'''(NO_3)_3.3Mg(NO_3)_2.24H_2O$, are prepared by dissolving the rare earth oxides in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by magnesium oxide, after which the two solutions are mixed and evaporated until, upon blowing on the surface, small crystals form. Water is sprayed over the surface and the whole allowed to crystallize for about twenty-four hours. The mother liquor is then poured off and evaporated further, while the crystals are heated with water until dissolved, the correct amount to use being soon learned by experience. Both fractions are again allowed to crystallize for a like period, the concentration being such that half of the solid separates upon cooling. In the subsequent fractionations the more soluble moves in one direction and the less soluble in the opposit. After the crystallization of the second series is complete the liquid from the most soluble portion is poured off and evaporated, while the liquid from fraction I is used as the solvent for the crystals forming fraction II, water being added or evaporated as may be necessary. The least soluble portion, fraction I, is again dissolved by heating with water. The above is repeated many times. When the fractions at either end become too small to work they should miss one series of operations and then be added to the next lot.

After a few series of crystallizations, the least soluble portion becomes very light colored, later growing nearly colorless, and finally takes a faint green tinge. When the fractions at this end no longer show the characteristic absorption bands of neodymium, they should be placed aside and mixed together according to the amount of praseodymium contained therein; in other words, fractions of the same color are united.

The most soluble portion changes very rapidly. It soon takes a yellow color and shows a samarium spectrum together with the bands of dysprosium, holmium and erbium. Sometimes at this point the liquid refuses to crystallize or else a precipitate may form. If either of these things happens, it is best to dilute with water and precipitate with oxalic acid in order to separate the impurities that have accumulated and interfere with the crystallization. The insoluble oxalates are converted back to the double magnesium nitrates in the same manner as already described.

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[1] Demarçay, *Compt. rend.*, **130**, 1019.

The neodymium bands finally become very weak in the mother liquors from the most soluble fractions. These are then set aside for the preparation of samarium, europium and gadolinium. When the samarium has been separated the more soluble portion of the remaining fractions rapidly turns to a beautiful amethyst and when this occurs, it is separated from the rest as crude neodymium. After the process has been continued for some time longer, it will be found that the material has been split up into four groups according to the order of their solubilities. Commencing with the least soluble we have: (5) Lanthanum and praseodymium magnesium nitrates. (6) Praseodymium and neodymium magnesium nitrates. (7) Crude neodymium magnesium nitrate. (8) Samarium, europium and gadolinium magnesium nitrates together with the simple nitrates of terbium, dysprosium, holmium, yttrium, etc.

Separation of La.—Lanthanum and praseodymium are best separated from each other according to the method of Auer von Welsbach[1] which consists of the fractional crystallization of the double ammonium nitrates of the type $M'''(NO_3)_3.2(NH_4NO_3) + 4H_2O$. These compounds are crystallized from water containing nitric acid to the extent of one-tenth the weight of the dissolved solid. The double salts are obtained by dissolving the oxides in the required amount of nitric acid, and for every three parts of acid required for the oxides two additional parts are neutralized by ammonium hydroxide. The resulting solutions are mixed, filtered if necessary, and evaporated until small crystals form on blowing over the surface of the liquid. A little water is then sprayed over the hot solution and the whole set aside to crystallize. The time required for large amounts is about twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. The lanthanum is rapidly obtained in a colorless condition. A saturated solution gives no praseodymium absorption spectrum even when very thick layers are used. The lanthanum ammonium salt encloses only a small amount of mother liquor, while the double magnesium compound carries large quantities. Both cerium and praseodymium pass into the more soluble fractions (10).

The lanthanum may be further purified by dissolving in water and precipitating by means of oxalic acid. This oxalate is treated with a slight excess of sulfuric acid, and the whole gently ignited until nearly all the free acid has been driven off. The sulfate is powdered and dissolved in water at about 1°, with rapid stirring, until the liquid becomes saturated, after which it is filtered and placed in a water-bath which is gradually raised to about 32°. The solution rapidly becomes solid, owing to the separation of hydrated lanthanum sulfate. It is filtered upon a Büchner funnel and washed with hot water. The small quantity that

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[1] *Monatsh.*, 6, 477.

remains in solution is then thrown out by means of oxalic acid. The crystallized sulfate may be again converted into the anhydrous state by heating, and the solution of this, prepared in the cold, precipitated by heating again. This lanthanum material (9) should give a fine white oxide.

Though the crystallization of such compounds as the metanitrobenzenesulfonates and bromates may give satisfactory results, the old method of Auer von Welsbach is the best general procedure.

Separation of Pr.—Praseodymium can be obtained from two sources: (*a*) From the more soluble lanthanum fractions (10). (*b*) From the mixed praseodymium and neodymium double magnesium nitrates (6). These are treated separately. Praseodymium containing lanthanum is purified by continuing the fractional crystallization of the double ammonium nitrates. The process is continued until no more lanthanum ammonium nitrate separates from the less soluble portions of the series. In this method the praseodymium accumulates in the most soluble portions. By fractionating the bromates the order is reversed, since lanthanum bromate is very much more soluble. At a temperature of 30° the latter compound crystallizes with great difficulty.

In the second case, where praseodymium and neodymium occur together, it is best to convert the double magnesium nitrates into the corresponding manganese compounds $2[M'''(NO_3)_3][.3Mn(NO_3)_2] + 24H_2O$. In order to do this the magnesium double salts are dissolved in water, the solution acidified and the rare earths thrown down by oxalic acid. These oxalates are washed, dried and ignited to the oxides. The oxides are dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by manganese carbonate. Any peroxide remaining undissolved can be brought into solution by the addition of a few drops of dilute oxalic acid solution to the hot double nitrates. The manganese double salts are crystallized from nitric acid having a sp. gr. 1.3. This fractionation is carried on until the spectrum of neodymium disappears. A very concentrated solution of the nitrate should give no trace of the bands of the latter element even when observed through a thick layer.

The double nitrate (ammonium or manganese) is dissolved in water and precipitated with oxalic acid. This oxalate is free from all rare earth metals with perhaps the exception of traces of cerium. There are several methods for removing this element such as: (*a*) Boiling the almost neutral nitrate solution with potassium bromate and marble. Instead of marble a little precipitated calcium carbonate may be added occasionally as long as there is any effervescence. (*b*) Potassium permanganate and sodium carbonate. Since praseodymium is thrown down also to a slight extent the precipitates require working up again.

Praseodymium oxalate is shown at 11.

Separation of Nd.—The crude double magnesium neodymium nitrate forming (7) is the starting point for the preparation of pure neodymium salts. The mother liquors together with the most soluble crystals from the double manganese fractionation can also be used. Moreover, this last double salt can be used for the purification of neodymium with results equal to if not surpassing those of the magnesium salts. In the case of the double magnesium nitrates water is used as the solvent, which makes the process cheaper and more convenient to handle than nitric acid.

After more series of crystallizations have been carried out, the liquid assumes a beautiful bluish lilac color which is better seen when some of the liquid is diluted somewhat. The absorption bands in the blue stand out clearly. An excellent test of the purity of neodymium is found by observing the color of the oxide, which is blue when pure.

By crystallizing the bromates, the order of the solubilities is reversed; neodymium becomes the least soluble, while praseodymium passes into the mother liquors.

Pure neodymium material is found at (12) upon the diagram.

Sm and Eu Separation.—Fraction (8) contains not only samarium and europium but large quantities of gadolinium, yttrium, dysprosium and erbium earths. The double magnesium salts are crystallized from 30% nitric acid. The fractions rapidly change in their appearances, the least soluble showing the yellow tint due to samarium while the most soluble portions begin to crystallize badly owing to the quantities of yttrium earths present. At this point it is best to commence the addition of the isomorphous bismuth magnesium nitrate, which, as Urbain[1] has pointed out, places itself between samarium and europium. When working upon the large scale, the bismuth salt is crystallized through the mother liquors in portions of one kilogram at a time. This rapidly removes all europium from the yttrium earth nitrates. After crystallizing many times, the mother liquor, which shows a strong spectrum of dysprosium, holmium and erbium, is placed aside. The series is then allowed to expand to twenty or more fractions. Samarium is removed from the least soluble end, after a very large number of crystallizations, when it is considered certain that all europium has passed further along the series. As soon as the gadolinium fractions next to the samarium show a fine sharp absorption band in the blue—due to europium—nitric acid of about 50% is used as the solvent. By this time most of the samarium has been removed in a pure condition (13) and in addition nearly all the yttrium, dysprosium, erbium earths, together with quantities of gadolinium from the opposit end. Since the fractions now take up only a comparatively small space, it is best to transfer all to large casseroles, which can be covered with

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[1] *Compt. rend.*, 138, 84.

watch glasses and so prevent a considerable amount of inconvenience and deliquescence. As the work proceeds, the europium band is observed to become stronger in the fractions between samarium and gadolinium. Later, the two bands in the green make their appearance. The fractions become smaller and smaller, since all mother liquors beyond one or two that give no europium spectrum have been removed. Only traces of samarium should be left by this time. Finally the samarium bands disappear and the remaining fractions consist almost entirely of bismuth magnesium nitrate. The fractions containing no gadolinium are mixed, diluted and all bismuth thrown out by means of hydrogen sulfide. The clear filtrate is next treated with oxalic acid, and the europium oxalate separated upon a Büchner funnel, washed and dried (14).

All the more soluble portions consisting of gadolinium together with varying amounts of yttrium, etc., form (15).

Separation of Gd.—The earths from fraction (15) are converted into oxalates. These are ignited to oxides and dissolved in nitric acid. The simple nitrates are then fractionated from strong nitric acid.[1] Gadolinium and terbium collect in the first crystals, dysprosium, holmium and yttrium come next, while yttrium, erbium, etc., accumulate in the mother liquors. These mother liquors are precipitated with oxalic acid, and the insoluble oxalates added to fraction (2). The intermediate nitrates consisting of dysprosium, holmium and yttrium form lot (17).

The least soluble nitrates comprising gadolinium and terbium (16) cannot be purified by the continued crystallization of the double magnesium nitrates since the oxide remains of a yellow color, even after many thousand operations. The crystallization of the simple nitrates effects a separation very slowly. Apparently the best method for obtaining a white gadolinia is that of the double nickel nitrate of the type $2Gd(NO_3)_3.3Ni(NO_3)_2 + 24H_2O$.[2] This salt is crystallized from nitric acid of sp. gr. 1.3. Terbium collects in the more easily soluble crystals (24). The position of gadolinium is shown in the diagram at 18.

Separation of Crude Yt Earths.—Fraction 2, consisting of dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, and small amounts of gadolinium and terbium together with yttrium and scandium, is converted into the anhydrous sulfates by treating the oxalates with a slight excess of sulfuric acid and heating until all fumes of sulfuric acid cease to be evolved. The ignited sulfates are dissolved in cold water. The fairly strong solution is then gradually added to barium bromate covered with a layer of water and heated upon the steam bath.[3] The mass is well stirred until decomposition is complete, *i. e.*, when some

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[1] Demarçay, *Compt. rend.*, 122, 728.

[2] Urbain, *Ibid.*, 140, No. 9.

[3] James, THIS JOURNAL, 30, 182.

of the clear liquid gives no precipitate with barium bromate solution after diluting and boiling. It is necessary to dilute and boil, owing to the fact that a strong solution of the rare earth bromates causes a precipitate of barium bromate itself. The whole is next filtered, and the barium sulfate well washed with hot water. If the barium bromate is not in a very fine state of division, a large amount remains unattacked. The clear filtrate is evaporated until a drop removed upon the end of a glass rod nearly solidifies when stirred upon a watch glass. A little water is then sprayed upon the surface and the dish placed aside to crystallize. The mother liquor and the crystals are fractionally crystallized. The absorption spectrum soon shows that a rapid change is taking place. Samarium and gadolinium rapidly separate in the least soluble crystals (19) together with terbium. The next fractions are colored yellow and contain dysprosium, holmium and yttrium with very small quantities of terbium (20). The bromate that follows consists almost entirely of yttrium contaminated with very small quantities of dysprosium, holmium and erbium. Further along the series the bands of dysprosium and holmium disappear and the only impurity found is erbium (21). Practically the whole of the erbium is contained in the portions more soluble than yttrium (22). The erbium absorption is extremely intense and the solutions possess a beautiful rose red color. The mother liquors (23) are nearly colorless or possess only a very faint pink tint. The absorption spectrum shows only a trace of erbium together with a strong spectrum of thulium. This fraction consists almost entirely of ytterbium, lutecium and celtium.

Scandium occurs only in traces in the minerals usually worked up. Probably nearly all is lost during the oxalate precipitations, due to the fact that scandium oxalate is not entirely insoluble in water. The solubility is increased rapidly by free acid. During the fractional crystallization of salts, scandium tends to collect in the mother liquors. However, if the solutions become basic, it is likely to be found in the fractions further down the series. In the case of the bromates, the solutions gradually become basic owing to a slight decomposition. When this is the case, the mother liquors are free from scandium, while the erbium fractions contain small quantities. If dysprosium and holmium fractions are carefully examined, it will in all probability be found there as well. The various methods for the purification of scandium will be given towards the end of this paper.

The bromates forming (19) are converted into the simple nitrates, and fractionated from strong nitric acid similarly to the more soluble earths derived from the samarium-europium process. However, in this case, the least soluble goes to 24 and the more soluble to 17.

Separation of Tr.—Practically all the terbium concentrates in 24. In addition to this element, there are also present gadolinium and dysprosium. Three methods have been used to separate this mixture: (*a*) Crystallization of the simple nitrates. (*b*) Fractional precipitation by ammonium hydroxide. (*c*) Crystallization of the ethylsulfates.

When the simple nitrates are used, it is best to add a quantity of bismuth nitrate, which is isomorphous with the rare nitrates and, as Urbain has shown, comes between gadolinium and dysprosium along with terbium. By fractionally crystallizing the nitrates from nitric acid for a few thousand times, it is found that bismuth nitrate accumulates in the middle fractions accompanied by terbium. Gadolinium is removed in the least soluble (26) portions, while dysprosium is removed in the mother liquors (27). The middle fractions are diluted and saturated with hydrogen sulfide. The bismuth sulfide is filtered off and the filtrate precipitated by means of oxalic acid. The terbium oxide obtained by igniting the oxalate (25) forms a black powder which in solution gives a characteristic absorption spectrum.

Fractional precipitation with very dilute ammonium hydroxide gradually concentrates terbium in the fractions slightly more basic than dysprosium.

When working with the ethylsulfates, terbium places itself between gadolinium and dysprosium.

Separation of Dy.—So far, the only really satisfactory method for the separation of pure dysprosium material is the crystallization of the ethylsulfates as proposed by Urbain. Fractions 17, 20 and 27 carry nearly all the dysprosium present in the original material. There are two methods by which the ethylsulfates may be prepared: (*a*) Action of the rare earth sulfate in solution upon barium ethylsulfate in a similar condition. (*b*) By mixing alcoholic solutions of the rare earth chlorides and sodium ethylsulfate.

When the writer endeavored to prepare the ethylsulfates by using the barium salt, the precipitates obtained often required days to filter. They were very difficult to wash, and, in addition, the barium sulfate, thrown down, entrained quantities of the rare dysprosium and holmium sulfates. It can readily be seen from this that the preparation of large quantities of material takes a very long time and also there is a loss of valuable material. These difficulties are all removed when we employ alcoholic solutions of the rare earth chloride and sodium ethylsulfate both hot and concentrated.

The fractions rich in dysprosium are precipitated with oxalic acid, the resulting oxalates filtered off and ignited to oxides. These oxides are then dissolved in hydrochloric acid. Small portions of oxides are then added until the solution becomes very slightly basic, after which the solution is evaporated to such a consistency that it would solidify upon cooling. When it has cooled down considerably, but while still liquid, it is poured into a quantity of 95% alcohol. This last operation requires considerable care, if the mass is very hot. Because the salt is somewhat basic, the alcoholic solution is very turbid. This solution is now cleared by gradually adding concentrated hydrochloric acid drop by drop. Sodium ethylsulfate in alcohol, very hot and strong, is poured in and the whole well stirred. After heating for a while upon the water bath the crystallin precipitate of sodium chloride is filtered off, washed with hot alcohol and the filtrate set aside to crystallize. The mother liquor is poured off and the crystals well drained. The liquid and crystals are systematically fractionated for a very long time. The small quantity of terbium separates in the first few fractions, together with some dysprosium (28). Pure dysprosium (29) comes next, and these fractions are followed by dysprosium and holmium. The most soluble portions are found to contain holmium and yttrium (30).

Separation of Ho.—Holmium has never been obtained in a very pure form. Small quantities may be freed from dysprosium, but then again the fractions so obtained are very rich in yttrium and carry a little erbium. The fusion of the nitrates is as yet the best method for separating yttrium from holmium. However, this method calls for more material than is usually obtained. Probably two or three years may elapse before this element is obtained in the form of a pure compound. Fraction 30 upon the diagram must be converted into the nitrate and fractionated as described under yttrium. This should eventually give a pure basic holmium nitrate (31) while yttrium nitrate and some holmium nitrate (32) will remain as the more stable portion.

Separation of Yt.—The best sources for yttrium are found in fractions 21 and 35, *i. e.*, if the latter has been obtained.

Many methods have been described for the purification of yttrium such as: The chromate method; the decomposition of the nitrate by fusion; the action of magnesium oxide upon a concentrated boiling solution of the nitrate; etc.

The chromate method is very useful, if terbium is present as an impurity. However, under usual conditions (when bromates or ethylsulfates have been used) it is absent. Muthmann and Böhm's chromate method, one of the best, is as follows:

The oxides are dissolved in chromic acid solution, 40 grams R_2O_3 are contained in each liter. The liquid is then treated with potassium chromate solution until it becomes cloudy. It is placed in a retort, heated to boiling, and rapidly stirred with a current of steam. Another tube passing through the cork carries a stopcock by means of which the potassium chromate solution can be added and controlled. Six fractions are usually taken. Fractions I and II are obtained by employing 10% potassium chromate solution. To get the remaining fractions, potassium chromate of 5% strength is used. By regulating the burner underneath the retort, the volume can be kept constant. This method is excellent when one is working upon a small scale. The writer finds that a neutral earth nitrate solution, to which potassium dichromate has been added, works as well as the chromate solution.

When there are large quantities of yttrium material to be purified the old method of fusing the nitrates is undoubtedly the best. If terbium is present as an impurity, a pure white yttrium oxide cannot be obtained. In order to carry out this method the oxides are dissolved in nitric acid, the solution evaporated and the nitrates fused until a portion has decomposed. When working on a large scale, porcelain dishes are used, while casseroles are found very convenient for smaller amounts. During the decomposition, the evolution of red fumes is allowed to proceed until the surface assumes a glazed appearance. This point is easily ascertained by experience. The decomposition should never be allowed to advance so that the mass becomes of a thick creamy nature. The best method for obtaining a solution of the melt is to pour the fused mass into a sufficient quantity of cold water. Great care, however, is required and stirring usually aids the operation very much. A large amount of cold water must be avoided, since it is desired that the solution should be concentrated after about five minutes' boiling. As the fused nitrate is gradually added to the water, the temperature rapidly rises and the whole suddenly begins to boil violently. When the dish, which contained the melted salt, has cooled sufficiently, a little water is added and the whole heated until the glassy mass has disintegrated, after which it is added to the main bulk. The latter is then boiled for five minutes and set aside to cool.

Under the best conditions the entire mass goes into solution; especially is this true of the yttrium end of the series. Upon cooling it will be found that the basic nitrate separates in a crystallin form. At the opposit end, the least basic portion of the fractions, there always remains an insoluble basic nitrate, unless the decomposition is stopped at an earlier stage, *i. e.*, when there is a copious evolution of red fumes.

In case a precipitate remains, it is highly important that it be well agitated by thoroughly boiling. After cooling, the precipitate (fraction B) is filtered off, redissolved in nitric acid and again fused. The filtrate (fraction A) is also boiled down and fused. This second series gives two filtrates and two precipitates. The filtrate from fraction B is mixed with the precipitate from fraction A with the result that the second series contains three fractions, etc.

Pure yttrium nitrate, which is eventually obtained, forms lot 33 upon the diagram while the less basic portion forms 34.

Separation of Er.—Fractions 34 and 22 contain practically the whole of the erbium found in the original mineral. It contains a considerable amount of yttrium with perhaps traces of scandium, thulium and holmium. Yttrium is best separated by fractionally decomposing the nitrate by fusion. Since erbium nitrate decomposes easily, the temperature is not raised quite so high as in the case of nearly pure yttrium. The least basic portion, obtained after a large number of series, consists of erbium basic nitrate (36). The yttrium concentrates in more basic fractions, which, when united, form 35. The best method for removing scandium is to crystallize the nitrates from nitric acid (fairly strong). Holmium and thulium are separated, if still found contaminating the material, by converting back to the bromate and employing fractional crystallization from water. This last method also causes yttrium to pass into the less soluble crystals.

According to work carried out by the author, erbium is not nearly so common as many are led to believe. During concentration, the material rapidly becomes less, the erbium solutions become more rose colored and the absorption spectrum appears very intense.

Separation of Tm.—For the preparation of pure thulium material the most soluble fractions, obtained during the original bromate crystallizations, are used. These contain thulium, ytterbium, lutecium and celtium with traces of erbium. The solution is nearly colorless. It shows the absorption bands of thulium and mere traces of those of erbium. Usually, however, the greater portion consists of the ytterbium metals. The fractionation of the bromates is carried on in a room which has a temperature of about 16°. Higher temperatures are inconvenient, owing to the formation of very concentrated solutions. Casseroles form the best containers, and the concentration should be such that the greater portion separates in the solid condition upon cooling. From the fact that supersaturated solutions tend to form with extreme ease, the crystallization must necessarily be started by a tiny crystal.

During the first few series, erbium rapidly separates in the least soluble portion, after which, the other fractions become colored greenish. As soon as the mother liquors fail to give any thulium absorption bands, when examined in a saturated solution of about 10 cm., they are placed aside for the preparation of ytterbium, etc. Thulium is found to collect in the fractions between erbium and ytterbium. The solutions become colored a faint bluish green and show a very intense absorption spectrum consisting of three bands. If very great care is taken, dilute alcohol can be used as solvent for a short time—best towards the end of the work. However, it soon shows signs of being attacked by the bromate.

Thulium is very rare, and in order to obtain a few grams of the oxide in a pure condition, one must commence with large quantities of suitable mineral.

Yb, and Lu, Ct.—Ytterbium, lutecium and celtium are contained in the mother liquors from the purification of thulium (38). They can be fractionated by means of the bromates, if the solution be not allowed to become basic. One must deal with large amounts owing to their great solubilities. Urbain recommends the use of the nitrates from nitric acid.

Celtium is said to occur in gadolinite, from the crude earths of which it can be separated by repeatedly crystallizing the simple nitrates from nitric acid. It separates in the mother liquor, being more soluble than lutecium.

Scandium.—Scandium occurs in few minerals to any extent, such as wiikite from Lake Ladoga, Finland,[1] also in orthite from the same locality,[2] also in residues from the working up of certain tungsten minerals. This element is easily detected by means of its spectrum, as Crookes has pointed out, and, when found to occur in any fractions or in minerals in quantity, can be separated by methods of R. J. Meyer. (*a*) The hydrochloric acid solution is precipitated with sodium silicofluoride.[3] (*b*) Scandium can also be separated by sodium thiosulfate. Meyer says the separation is almost quantitative; no trace of scandium remains in the filtrate; the precipitate contains thorium (if present) and only very small amounts of the yttrium earths, which can be removed by repeated precipitation with thiosulfate. This method is better than the sodium silicofluoride.

(*c*) Separation of thorium and scandium by means of sodium carbonate: The concentrated chloride solution is poured into a solution of sodium carbonate containing 20% of anhydrous carbonate. One liter of sodium carbonate solution is used for every 10 g. of scandium oxide. The scandium dissolves entirely on stirring and warming. It is then boiled rapidly for half an hour, when the double carbonate is precipitated as a powder. The volume of the solution should be kept constant during the boiling. After the crystallin powder has settled, the liquid is poured off, and the precipitate washed by boiling with 20% sodium carbonate solution for 15 minutes—this is repeated three times. The double carbonate is dissolved in two liters of cold water; four hours and constant stirring are required for this purpose. The liquid is then filtered, acidified with hydrochloric acid and the hydroxide thrown down by ammonium hydroxide while boiling. The scandium hydroxide is filtered off and well washed with boiling water until free from alkali. If necessary, the operation is performed again. Finally the chloride solution is precipitated with oxalic acid.

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[1] Crookes, *Proc. Roy. Soc.*, 80, (*A*), 516.

[2] R. J. Meyer, *Sitzungsber. K. Akad. Wiss.*, Berlin, 1911, 379.

[3] *Z. anorg. Chem.*, 67, 398.