tion of the excess of sulphur in an atmosphere of carbon dioxide at 250° has long been used with good results for accuracy in the hands of many analytical chemists.

But merely to bring the fact freshly to our minds again, I give here a dozen or more determinations made by starting with metallic antimony, with the temperature, time of heating in carbon dioxide atmosphere, and the acid used.

Wt. of Sb.		Temp.	Time, hrs.	Sb found.
0.1931	HCl acid	227°	0.5	0.1936
0.2040	" "	245°	0.5	0.2037
0.2287	" "	240°	0.5	0.2283
0.3685	" "	250°	0.5	0.3692
0.1414	" "	245°	0.5	0.1415
0.2400	" "	240°	0.5	0.2397
0.2586	HCl and Tar. acid	240°	0.5	0.2584
0.2405	" " " "	240°	0.5	0.2409
0.2035	" " " "	250°	0.5	0.2031
0.2060	" " " "	245°	0.5	0.2066
0.1592	" " " "	250°	0.5	0.1596
0.2214	" " " "	240°	0.5	0.2221

This is sufficient to show that quantitative results may be obtained. In no case is the error over 0.3 per cent. and usually from 0.1 to 0.2 per cent. even when calculated to metallic antimony, which is clearly close enough for any ordinary analytical work. To be sure, if the samples were to be heated much longer than 0.5 hour the error would rapidly increase and soon would become large owing to the volatility of the chloride.

It is not surprising that the results should be quantitative when the sulphide is heated only for a short time just long enough to volatilize the sulphur either free or combined as pentasulphide and to transform the sulphide to the black modification, for the equivalent molecular weights for Sb_2S_3—SbOCl and $Sb_4O_5Cl_2$ are 168.2, 171.45 and 157.9 respectively and thus not very widely apart, so that as far as the weight of the precipitate is concerned even several per cent. of SbOCl or even $Sb_4O_5Cl_2$ as an impurity would give a weight practically the same as though the antimony were all in the form of sulphide.

I am greatly indebted to Mr. Alva G. Austin for carrying out much of the detail of this work.

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A SCHEME FOR THE SEPARATION OF THE RARE EARTHS.

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In this communication, a comparatively simple scheme for the separation of mixtures of the rare earths is offered in the hope that it may prove of value to any one who is desirous of entering this very interesting field of research. The conclusions presented are the results of several years' investigation upon the various methods proposed for fractionation and of personal trial of the applicability of many other compounds which had not previously been employed for the separation of these elements. Only those methods which proved valuable will be mentioned.

It might be as well to state in the beginning for the benefit of those who have had little cause to study this subject, that there is no quantitative method for the separation of any of the rare earths. The true members of this family comprise those elements that are included in the cerium and yttrium groups and are characterized by their trivalency and by the fact that they form oxalates that are insoluble in dilute acids and in cold ammonium oxalate solution.

The nearest approach to a quantitative separation is found in the case of cerium. This is due to the fact that the properties of the metals of all these earths and their salts, with the possible exception of cerium itself, vary among themselves by very minute differences.

Bearing these observations in mind, the following scheme is presented: The mineral is decomposed, either by hydrochloric acid, sulphuric acid, potassium bisulphate, sodium hydroxide or hydrofluoric acid. When hydrochloric acid is used, the whole is evaporated to dryness to render the silica insoluble. It is then warmed with a little concentrated hydrochloric acid, after which the mass is treated with water and filtered. The filtrate may then be treated with either oxalic acid or ammonium oxalate. If the liquid contains considerable mineral acid, ammonium oxalate is to be preferred. When sulphuric acid or potassium bisulphate has been used to break up the mineral, it is necessary to stir with *cold* water to obtain the solution of the desired elements. Fusion with sodium hydroxide and washing with water gives a residue of oxides. These are dissolved in hydrochloric acid. Hydrofluoric acid decomposes many minerals, such as columbates, tantalates, etc., in the cold, giving a residue of rare earth fluorides while silicon, columbium, tantalum, etc., go into the solution. The insoluble fluorides are decomposed by means of sulphuric acid.

In the sulphate or chloride solutions obtained by one of the above methods, the earths are then precipitated by ammonium oxalate or oxalic acid as mentioned above.

Having obtained the earths in the form of oxalates, they are treated as follows:

Zirconium and Thorium.—Should the rare earth oxalates contain these elements they may be separated by boiling with a solution of ammonium oxalate when the whole of the zirconium and nearly all of the thorium pass into solution. The residue is filtered off and washed with ammonium oxalate solution. On the addition of an excess of hydrochloric acid to the filtrate, thorium oxalate alone is precipitated, while the whole of the zirconium is held in solution by the oxalic acid produced by the action of the hydrochloric acid on ammonium oxalate.

As zirconium oxalate is soluble in an excess of oxalic acid, this reagent alone may be used in the absence of thorium. In this connection it should be remembered that the oxalates of cerium and of the earths of the yttrium group, are somewhat soluble in hot concentrated ammonium oxalate solution so that varying amounts go into the solution. Thorium, however, can be separated easily from the yttrium earths which remain with it, by means of the double sulphate of thorium and potassium, which is insoluble in a solution of potassium sulphate, while the corresponding compounds of the yttrium group are soluble. The crude thorium oxalate is converted into sulphate and the cold solution is stirred with solid potassium sulphate. Sulphate solutions of the earths are the best to work with for this purpose, for if other compounds are used, care must be taken to keep the solution from being too concentrated since members of the yttrium group may be precipitated also.

After the removal of the yttrium earths, cerium earths are still present and thorium may be separated from these by means of the solubility of its oxalate in ammonium oxalate or, according to Glaser, by the solubility of thorium oxalate in ammonium acetate;[1] also by the method of Wyrouboff and Verneuil in which thorium is precipitated by hydrogen peroxide.[2] These methods are given under the separation of cerium and thorium, because under usual conditions they separate together from the rest of the rare earths.

In the next step, there are three alternatives which depend upon the composition of the oxalates as approximately determined from the solubility of the double sodium or potassium sulphates in potassium or sodium sulphate solution, *viz.*, (*a*) if containing 20 per cent. or more of the yttrium earths and only a trace of thorium; (*b*) if containing 20 per cent. or more of the yttrium earths together with thorium; (*c*) if containing less than 20 per cent. of the yttrium earths.

(*a*) When the material consists of 20 per cent. or more of the yttrium earths and practically no thorium, the oxalates are converted into sulphates by mixing with strong sulphuric acid and carefully igniting until fumes of sulphuric acid are no longer evolved. The residue is then powdered and dissolved in *ice-cold* water. The resulting sulphate solution is stirred with solid sodium sulphate which throws down the double sulphates of sodium and the cerium earths.[3]

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[1] THIS JOURNAL, 18, 782.

[2] *Bull soc. chim.* [3], 19, 219.

[3] Another method, which is simpler if the oxides will dissolve in acid, is to ignite

This precipitate contains some of the yttrium group of earths, while small amounts of samarium, gadolinium and europium remain in solution. The precipitate is separated by filtration and washed with a solution of sodium sulphate. The insoluble double sulphates consist chiefly of cerium, lanthanum, praseodymium, neodymium, samarium, europium and gadolinium together with small amounts of the yttrium earths in which the terbium, dysprosium and holmium contents are considerably increased. These double sodium sulphates constitute Fraction *A* of the table. The filtrate, on the addition of an excess of oxalic acid, throws down the oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and scandium together with some samarium, europium, and gadolinium. This precipitate forms Fraction *B* of the table.

(*b*) The composition of the oxalates in this case is very similar to (*a*), the only difference being the thorium content.

The sulphate or chloride solution is treated with sodium sulphate and the insoluble double sodium cerium group sulphates, forming Fraction *A*, filtered off. Since the sodium thorium sulphate is somewhat soluble in sodium sulphate solution, the filtrate is saturated with potassium sulphate, when the remaining thorium is precipitated as thorium potassium sulphate, insoluble in potassium sulphate solution. After separating the precipitate, the filtrate is treated with an excess of oxalic acid, the insoluble oxalates being filtered off and washed. This material is added to Fraction *B*.

(*c*) In this, the third and last alternative, the oxalates consist almost entirely of the cerium metals, and it is best to start the work of separation from the point *A*.

Cerium and Thorium.—The next operation consists of separating cerium together with thorium, if the latter is present, from the other elements forming Fraction *A*. This is best carried out by treating the nitrate solution with an excess of zinc oxide and potassium permanganate. If the material is in the form of the insoluble double sodium sulphates, it should be boiled with sodium hydroxide in excess. The resulting hydroxides are filtered off, well washed with hot water and dissolved in nitric acid. In dealing with oxalates that contain large amounts of lanthanum, praseodymium and neodymium, it is necessary only to ignite when the oxides, so obtained, will readily dissolve in nitric acid. As a

the oxalates and dissolve the oxides so obtained in hydrochloric acid or nitric acid, dilute the solution and treat with solid sodium sulphate until the double sulphates are precipitated. However, when oxalates rich in cerium are ignited, the oxides which are formed dissolve with great difficulty in hydrochloric or nitric acid and so in this case it is better to treat the oxalates with sulphuric acid as mentioned above. Extra care must be taken when the chlorides or nitrates in solution are stirred with solid sodium sulphate, for if the solution is too concentrated, metals from the yttrium group will be precipitated also.

rule, when cerium is present in large amounts, since the oxide dissolves with great difficulty, the oxalates are converted into sulphates. The sulphate solution is then poured into fairly strong and boiling sodium

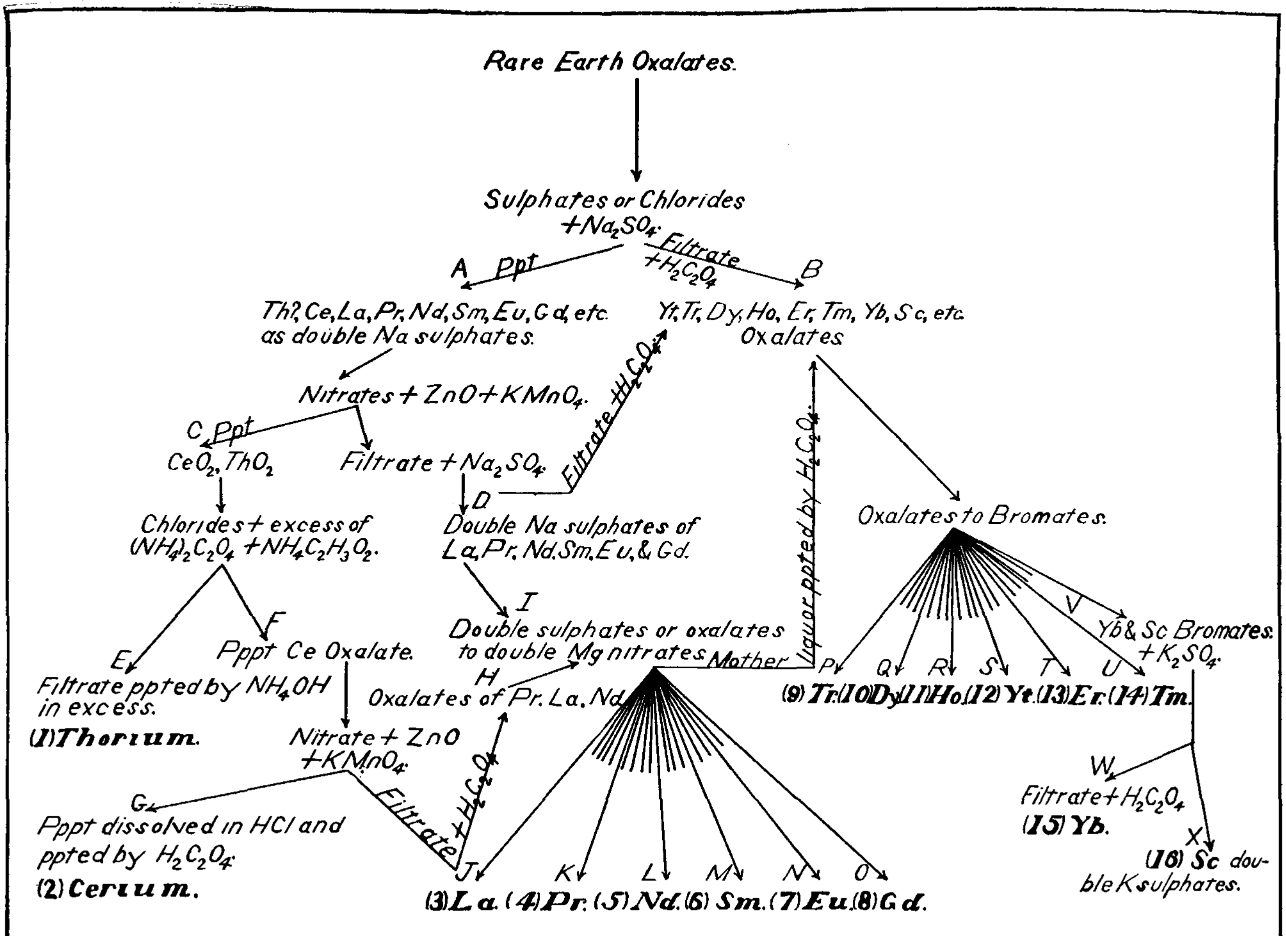

Diagram for Separation of Rare Earths.

hydroxide. The rare earth hydroxides formed under these conditions filter rapidly, and after washing with boiling water, are dissolved in nitric acid. The nitrate solution obtained by any of the above methods is neutralized, stirred rapidly by a motor and an *excess* of zinc oxide added. On the addition of potassium permanganate, cerium peroxide is precipitated and the addition is continued until the liquid after continued stirring remains red. This method leaves a little cerium in solution, which is separated later. The precipitate, consisting of cerium and manganese peroxides together with thorium and a small amount of lanthanum, praseodymium and neodymium, makes Fraction *C* on the diagram. The filtrate is saturated with sodium sulphate, causing a precipitate of the double sulphates of sodium with lanthanum, praseodymium, neodymium, etc. This, after filtering and washing with sodium sulphate solution, constitutes Fraction *D*. To this last filtrate, containing small amounts of the yttrium group, an excess of oxalic acid is added. The oxalates so obtained are united with those forming *B*.

Thorium.—Although thorium is not now considered as a rare earth, methods for its purification do not seem to be altogether out of place. The cerium peroxide contains large amounts of manganese, which is first removed by dissolving in strong hydrochloric acid and precipitating the earths by means of solid sodium sulphate until no more insoluble double sulphates separate. The liquid is then filtered and the precipitate washed with sodium sulphate solution. A portion of the thorium remains in the filtrate, but this can be separated either by means of oxalic acid or else by stirring with solid potassium sulphate.

The cerium sodium sulphate is boiled with an excess of sodium hydroxide, the residue filtered off, washed with boiling water and dissolved in nitric acid. The nitrate solution is then neutralized by means of ammonia, after which peroxide of hydrogen is added[1] and the whole boiled for a few minutes. Some of the filtered solution should then be tested by treating with an equal volume of hydrogen peroxide and boiling and the process repeated until no precipitate is thus obtained. The filtrate is reserved for the preparation of pure cerium. The thorium precipitate, having the composition $Th_4O_7N_2O_5$, is very impure and may have a yellow or even an orange color after standing for a short time.[2]

The crude thorium obtained above, may be purified by treating the nitrate solution with an excess of warm ammonium oxalate. The soluble portion can then be converted into the oxalate and treated again with warm ammonium oxalate.

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[1] Wyrouboff and Verneuil. *Bull. soc. chim.* [3], 19–20, No. 6 and *Chem. News*, 77, 245.

[2] It is highly important that the peroxide of hydrogen be free from phosphoric acid; otherwise an insoluble cerous phosphate may be thrown down with the thorium.

Thorium can be separated from cerium[1] by the solvent action of ammonium acetate on thorium oxalate. This as well as the ammonium oxalate method can be applied to the cerium precipitate. The whole is dissolved in strong hydrochloric acid and precipitated by means of oxalic acid. Glaser says: "Thorium is separated best by converting the oxalates into sulphates, the greater part of the free acid neutralized with ammonia, the solution boiled and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed but before the liquid has cooled), a solution of ammonium acetate is added. When cold, the entire cerium group is precipitated as oxalates while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration *F*; in the filtrate, precipitate thoria with ammonia in excess, filter and wash." All the thorium precipitates are accumulated at *E* on the diagram. Another treatment or two, with hydrogen peroxide in neutral nitrate solution, gives a very good thorium product.

Thorium can be obtained very pure in the following manner: Thorium hydroxide is first prepared by adding a slight excess of ammonium hydroxide to a solution of thorium nitrate and washing well the precipitate thrown down. This is then added to a solution of acetylacetone in absolute alcohol and the mass heated on the water bath for a short time, after which it is filtered and allowed to crystallize. The acetylacetonate is then placed in a very small retort and carefully distilled in a vacuum. The portion that condenses in the neck of the retort and in the receiver is dissolved in concentrated nitric acid, boiled for a short time, diluted with water, filtered and precipitated by means of oxalic acid. Thorium oxide obtained by igniting this oxalate is absolutely snow-white even after long ignition. A determination of the equivalent gave an atomic weight of 232.3. Thorium may also be purified by the sulphate method as follows: Anhydrous thorium sulphate is dissolved in ice-cold water until the liquid is saturated.[2]

The filtered liquid is then heated to 20° C., when nearly pure thorium sulphate separates. It is then dehydrated and the treatment repeated two or three times.

Cerium.—*F* is the starting point for the preparation of pure cerium. If Wyrouboff and Vereneuil's method for separating thorium has been used, the purification is easily carried out by slightly modifying the zinc oxide and potassium permanganate method. If other methods have been used it is best to convert the oxalates, etc., into nitrates. The liquid is neutralized by ammonia and treated with hydrogen peroxide in order to remove the last of the thorium. To the solution of cerium

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[1] Glaser, THIS JOURNAL, **18**, 782.

[2] According to Urbain ammonium acetate aids the solution.

nitrate, freed from thorium, sufficient ammonium nitrate is added to form the double salt. An excess of potassium permanganate is run in and only enough cream of zinc hydroxide added to precipitate most of the cerium, being sure to leave some in solution, for otherwise praseodymium and neodymium will accompany the precipitate. The whole is then heated by steam, filtered and washed with water containing a little ammonium nitrate. The precipitate is dissolved in concentrated hydrochloric acid, the solution diluted and the cerium precipitated with oxalic acid, *G*. The oxalate obtained by this method usually contains a little zinc and manganese, the latter coloring the oxide brown, so for the final purification the oxalate is treated with a slight excess of sulphuric acid and the whole heated until the fumes of sulphuric acid are no longer given off. The resulting sulphate is dissolved in cold water and the filtered solution heated on the water bath. The sulphate that separates is washed with boiling water. This material should give an oxide with only a pale yellow tint.[1]

The mother-liquor is treated with oxalic acid, the oxalate which is thrown down being worked up with the next lot. The filtrate from the cerium peroxide still contains cerium, which is removed by adding an excess of zinc oxide and more potassium permanganate should the color be discharged. The precipitate obtained here is mixed with *F*. The filtrate is precipitated with an excess of oxalic acid and the insoluble oxalates, consisting of lanthanum, praseodymium, neodymium, etc., constitute Fraction *H*.

Lanthanum, etc.—Fractions *H* and *D* contain lanthanum, praseodymium, neodymium, samarium, europium and gadolinium together with small amounts of the yttrium earths and some cerium.

These are best separated from each other by the fractional crystallization of certain double nitrates, such as those formed by the rare earth nitrates with ammonium, magnesium, manganese or nickel nitrate. For the separation of lanthanum and praseodymium the double ammonium nitrates are by far the best and for separating praseodymium from neodymium the manganese salts are to be preferred. However, where one is working on the large scale it is better to start with the double magnesium nitrates, as the more soluble portions crystallize more readily than is the case with the double ammonium nitrates.

The double magnesium nitrates,[2] $2[M'''(NO_3)_3].3[Mg(NO_3)_2] + 24H_2O$, 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 mag-

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[1] Praseodymium is a very common impurity found in cerium. This has been pointed out many times by different investigators, so that if very pure cerium is required, one must be on his guard against this substance.

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

nesium 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 of the solutions being such that half of the solid separates on cooling. Two fractions have thus been obtained and in subsequent fractionations the more soluble moves in one direction and the less soluble in the opposite. 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*, adding water or evaporating 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 crystallization 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 stage 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 saturate with solid sodium sulphate to separate the yttrium earths and impurities that have accumulated and interfere with the crystallization. The insoluble double sodium sulphates are converted back to the double magnesium nitrates in the same manner as already described and the solution will be found to crystallize readily on evaporation. The filtrate from the double sodium sulphates is precipitated with an excess of oxalic acid and the oxalates of the yttrium group which are thrown down are added to lot *B*. The neodymium bands finally become very weak in the most soluble fractions and these are set aside for the preparation of samarium, europium and gadolinium. After the samarium has been separated in this manner 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 neodymium. After the process has been continued a little 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:

1. Lanthanum and praseodymium.
2. Praseodymium and neodymium.
3. Neodymium.
4. Samarium, europium and gadolinium together with small amounts of terbium, dysprosium, etc.

Lanthanum.—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. To prepare the double salts, the oxides are dissolved 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 and evaporated until small crystals form on blowing over the surface of the liquid. A little water is sprayed over the surface and the whole set aside for twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. By this method lanthanum ammonium nitrate is soon obtained perfectly colorless and a saturated solution gives no praseodymium absorption spectrum even when observed through very thick layers. The lanthanum ammonium salt does not enclose anything like the amount of mother-liquor that the double magnesium compound does. Both cerium and praseodymium accumulate in the more soluble portion.

The colorless lanthanum salt is dissolved in water, the solution acidified and precipitated by means of oxalic acid. This oxalate is treated with a slight excess of concentrated sulphuric acid and the whole gently ignited until all free acid has been driven off. The sulphate is powdered and dissolved in water at about 1° until the liquid is saturated, after which it is filtered, placed in a water bath and gradually raised to 32°. The solution soon changes to a solid mass which is placed on a Buchner funnel and washed with hot water. The few grams that remain in solution are thrown out by means of oxalic acid. The crystallized sulphate may be rendered anhydrous and submitted once again to the sulphate method.

This lanthanum gives a fine white oxide.

Praseodymium.—There are two sources for praseodymium, firstly, from the more soluble portion obtained from the purification of lanthanum and secondly, from those fractions of the double magnesium nitrates which show a strong praseodymium spectrum. These are not mixed but treated separately.

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

In the first case the crystallization is carried on until no more colorless crystals separate, praseodymium accumulating in the more soluble fractions together with a little cerium.

In the second case the double magnesium salts are converted into the corresponding manganese compounds which are finally fractionally crystallized[1] from nitric acid of sp. gr. 1.3. 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. The oxalates obtained are washed, dried and ignited to oxides. The oxides are then dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by manganese carbonate, after which the two solutions are mixed. A precipitate of manganese peroxide is sometimes obtained at this point but it is easily removed by adding a little oxalic acid and warming. The least soluble portion, from this fractional crystallization that no longer gives any neodymium bands in the spectroscope, is dissolved in water, acidified and thrown down with oxalic acid. The fractions of praseodymium ammonium nitrate that are free from lanthanum are also dissolved and precipitated by oxalic acid. The praseodymium oxalate from the two sources is then united. This material may be impure, owing to the presence of cerium.

Cerium can be separated in several different ways. One method consists in treating the nitrate solution with potassium permanganate and a little sodium carbonate. A separation is obtained according to Wyrouboff and Verneuil[2] by adding a solution of sodium acetate to a solution of the nitrates and precipitating the cerium by hydrogen peroxide. The above methods throw down a certain amount of praseodymium also, so the precipitate should be worked up again.[3]

Neodymium.—Pure neodymium is obtained by continuing the crystallization of the neodymium magnesium nitrate obtained somewhat earlier. After a few more series of crystallizations the liquid assumes a beautiful bluish lilac color which is seen better when some of the solution is diluted with water. On observing the spectrum the absorption bands in the blue stand out clearly. When the solution contains samarium or praseodymium, these weaker neodymium bands are usually a little hazy. An excellent test of the purity of neodymium is found by observing the color of the oxide which is blue only when pure.

Samarium and Europium.—Samarium, europium and gadolinium are contained in the mother-liquors which are obtained during the fractionation of the double magnesium nitrates. The solutions are evaporated

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[1] Lacombe, *Bull. soc. chim.* [3], **31**, No. 10 and *Chem. News*, **89**, 277.

[2] *Bull. soc. chim.* [3], **19**, No. 6 and *Chem. News*, **77**, 254.

[3] Meyer and Koss, *Ber.*, **35**, 672, recommend magnesium acetate in place of sodium acetate.

and the residue fractionally crystallized from nitric acid[1] of 1.3 sp. gr. The addition of the isomorphous bismuth magnesium nitrate aids enormously in the separation of these elements as Urbain and Lacombe[2] have shown. Its solubility places it between samarium and europium and it also assists in the crystallization of the sirupy mother-liquors inasmuch as it carries down with it the more crystallizable portions. Samarium is obtained from the least soluble fractions. Europium is separated from the excess of bismuth magnesium nitrate which is found between the samarium and gadolinium fractions. The bismuth is thrown down by hydrogen sulphide and the mother-liquor precipitated by means of oxalic acid.

Gadolinium.—The fractions between europium and dysprosium, etc., consist mainly of gadolinium magnesium nitrate. These solutions are acidified and the gadolinium thrown down as oxalate. This is then washed and ignited to oxide. The resulting oxide is converted into the nickel nitrate[3] of the type $2Gd(NO_3)_3.3Ni(NO_3)_2 + 24H_2O$, which is then fractionally crystallized from nitric acid of density 1.3. Terbium is left in the most soluble portion.[4]

Fraction *B* contains oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and scandium. This material is converted into the anhydrous sulphate, the latter dissolved in cold water and poured over an excess of barium bromate.[5] The whole is well stirred and placed on the water bath. After the double decomposition is complete, *i. e.*, when the clear liquid gives no precipitate with barium bromate solution after diluting and boiling, the mass is filtered and evaporated until a drop removed on the end of a glass rod nearly solidifies when stirred on a watch glass. A little water is then sprayed on the surface and the whole submitted to fractional crystallization. The absorption spectrum soon shows that a rapid change is taking place. Small amounts of samarium and gadolinium are rapidly separated in the least soluble portion while the next fractions contain terbium and give oxides of a deep red-brown color. Dysprosium and holmium are more soluble than terbium. Yttrium places itself between holmium and erbium.[6]

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[1] Demarcay, *Loc. cit.*

[2] *Compt. rend.*, **137**, 792 and **138**, 84.

[3] Urbain, *Compt. rend.*, **140**, No. 9.

[4] The writer is applying the bromate method to a complicated mixture of samarium, gadolinium, terbium, dysprosium and holmium and is obtaining interesting results.

[5] James, THIS JOURNAL, **30**, 182 and *Chem. News*, **97**, 61.

[6] The writer, in a previous paper describing the serial order of the bromates, made an error in the position of yttrium. This element, as stated above, ranges itself in the fractions between holmium and erbium. The cause of the error was due to the fact that the material on which the serial order was worked out contained only a little yttrium and a fair amount of gadolinium. At the time, gadolinium was not suspected and the colorless bromate crystals were supposed to be due to yttria.

The most soluble portion contains erbium, thulium and ytterbium.

Terbium, Dysprosium and Holmium.—These elements are extremely difficult to separate. Operations with the bromates are still in progress. Terbium separates in the least soluble together with samarium and gadolinium. The separation of dysprosium from holmium is extremely slow and so much so that the bromate method is of no value for this work. Urbain recommends the fractionation of the double nickel nitrates from nitric acid of density 1.3 to separate samarium and gadolinium from terbium, dysprosium and holmium. The more soluble portion, consisting of terbium, etc., with some gadolinium, is converted into the simple nitrate and fractionally crystallized from concentrated nitric acid in the presence of bismuth nitrate. Terbium collects with the bismuth nitrate in the fractions between gadolinium and dysprosium. Fractional crystallization of the ethyl sulphates gives dysprosium. Small amounts only of dysprosium and terbium have been separated. The preparation of pure holmia has not yet been accomplished.

Yttrium.—Yttrium is obtained from the bromate fractions between holmium and erbium. Some fractions show holmium bands in addition to erbium. It is most easily prepared from the fractions that are free from holmium. The earths are precipitated from dilute boiling solutions of the bromates by the addition of boiling potassium hydroxide solution. The hydroxides are filtered off, washed and converted into the nitrates. Yttrium is then separated by the method of Muthmann and Rolig[1] as follows: The concentrated neutral nitrate solution is boiled and a thick cream of magnesium oxide added until the liquid no longer gives the absorption bands of erbium. The fractions that contain holmium in addition to erbium can be put through the same process. Yttrium oxide obtained by the bromate and magnesium oxide methods is snow-white and absolutely free from terbium, etc.

Erbium, Thulium, Ytterbium and Scandium.—These elements are separated from each other by the continued fractionation of the most soluble portion of the bromates. The erbium solutions become a beautiful rose tint. Thulium collects between erbium and ytterbium. The mother-liquor contains ytterbium with a very little scandium. The neutral solution is saturated with potassium sulphate when scandium potassium sulphate separates as it is insoluble in potassium sulphate solution. The filtrate on the addition of oxalic acid gives a precipitate of ytterbium oxalate.

The fractionation of the least basic earths is still being carried on with the object of preparing pure thulium for a determination of the atomic weight and also to confirm Urbain's lutecium.

In conclusion I again thank the Welsbach Company for large amounts

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[1] *Ber.*, **31**, 1718.

of material received through the courtesy of Dr. H. S. Miner. I also tender my thanks to the Christiania Minekompani, of Christiania, Norway, for many mineral specimens for examination.

NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
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ON VISCOSITY AND LUBRICATION.

BY CHARLES F. MABERY AND J. HOWARD MATHEWS.

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Excepting the work done in this laboratory during the last fifteen years in determining the composition of American petroleum, so far as we know, no attempts have been made to ascertain the composition of lubricating oils with reference to the hydrocarbons or even the series of hydrocarbons of which they consist.

Neither the composition of the oils nor the source of the petroleum from which the various products were manufactured have been relied on as a means of distinguishing differences in quality or durability, except a general distinction between straight hydrocarbon oils and compounded oils. Until comparatively recently, the refiner had to rely for high viscosity on mixtures of animal or vegetable oils with oils separated from petroleum, and the latter were obtained from Pennsylvania, Ohio, or other similar natural oils ordinarily referred to as paraffin oils, since they contained the solid paraffin hydrocarbons, C_nH_{2n+2}. Naturally, the refiner became convinced of the superiority of his compounded oils over straight hydrocarbon oils, and this idea has been maintained so persistently, it still prevails very generally with consumers of lubricating oils.

But within the last ten years, other varieties of petroleum have been found to yield lubricating oils with superior viscosity and wearing qualities which makes it no longer necessary to rely on compounded oils either for use on bearings or in cylinders. This is of especial importance with reference to cylinder oils, for it is well understood that the conditions of high temperatures and highly heated steam in cylinders lead to saponification of the animal or vegetable oil used in compounding, with consequent corrosion of the cylinder. As is well known, castor oil is one of the very best lubricating oils, especially for durability, but its general use is precluded by its high cost. It is now possible to prepare straight hydrocarbon oils fully equal in viscosity and wearing qualities to castor or any other high viscosity vegetable oil.

Viscosity is generally accepted as a standard of value in classifying lubricating oils, but it is not certain that it is reliable as indicating the durability and wearing qualities of oils differing widely in composition. There is little doubt that a confirmation of viscosity by chemical data