neutral by means of ammonium hydroxide, and precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed.

The Gooch crucible containing the lanthanum together with the excess of bismuth magnesium nitrate was washed into a beaker, saturated with hydrogen sulfide to remove the bismuth and treated similarly to the yttrium. The results were as follows:

No.	Y_2O_3 taken.	Y_2O_3 found.	La_2O_3 taken.	La_2O_3 found.
1	0.08705	0.0892	0.08925	0.0883
2	0.08705	0.0876	0.1785	0.1782
3	0.1741	0.1752	0.1785	0.1731
4	0.1741	0.1758	0.1785	0.1779
5	0.1741	0.1767	0.1785	0.1764
6	0.1741	0.1735	0.1785	0.1791

This method is not all that could be desired either in point of accuracy or ease of manipulation, but is offered because of its superiority over the older potassium sulfate method. For separating holmium, dysprosium, etc., from lanthanum the error would probably be greater, owing to the fact that these elements have a slight tendency to form double magnesium nitrates. On the other hand, the separation should be much more perfect for the elements of the yttrium group possessing greater solubilities than yttrium itself.

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RARE EARTH REACTIONS IN NON-AQUEOUS SOLVENTS

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1. Introduction.

Very little systematic general analytical work has been done in solvents other than water. Only isolated cases are to be noticed in a review of the subject where application of some non-aqueous solvent has facilitated analytical separations. Among these might be mentioned the ether extraction of iron, the ether extraction of uranium, the separation of barium, strontium and calcium with alcohol, the ether separation of beryllium and aluminium, the pyridine and the amyl alcohol separation of lithium chloride from sodium chloride. Naumann[1] has studied several reactions, notably the action of hydrogen sulfide and ammonia with most of the common members of the second and third analytical groups in ethyl acetate, methyl acetate, pyridine and acetone, obtaining very interesting results. The solubility tables of Naumann have been found serviceable, but in error in a number of cases. A new enlarged solubility list will be published in future papers dealing with the analytical chemistry

[1] Naumann, *Ber.*, 32, 999; 37, 3600, 4328, 4609; 42, 3789.

of non-aqueous solvents. This paper is concerned with the domain of the rare earths, dealing essentially with the general reactions of neodymium, lanthanum, cerium and the yttrium group with various acids and bases.

The usual solvent employed is acetone although occasionally another solvent is utilized to obtain specific solubilities not obtainable in this medium. The acetone was carefully dehydrated over calcium chloride for several months and distilled when needed, only the product with constant boiling point being employed. The conditions for each reaction have been kept as nearly anhydrous as possible although small quantities of water are unavoidably introduced in some instances. In such cases the general effect of added water has been carefully considered.

Among the first reactions studied were those with the salts of the halogen acids and of nitric and sulfuric acids, inasmuch as their corresponding salts are as a rule soluble in water.

The iodides of neodymium, yttrium, lanthanum and cerium are readily soluble in acetone, the bromides moderately soluble and the chlorides quite insoluble. The nitrates of the earths are soluble, but the sulfates are insoluble in this medium. Hence solutions of the iodides, nitrates and to a more limited extent the bromides furnish good solutes for a study of the comparative reactions of the earths in acetone.

The iodide solutions were prepared by solution of the hydroxides in strong hydriodic acid, evaporation, extraction of the free iodine with carbon disulfide and solution of the resulting iodides in acetone. The bromide solutions were prepared in the same way omitting, however, the carbon disulfide treatment. The nitrates were dissolved directly in acetone.

In certain cases reactions do not take place with the nitrates or bromides, but do with the iodides; or do not with the nitrates, but do with the bromides; hence some of the general reactions have frequently been tried with more than one salt dissolved in acetone.

2. General Reactions.

A. Reactions with Common Acids and Study of the Halides.

Hydrochloric acid yields insoluble earth chlorides. The acid may be added either by passing the dry gas into the earth solution or by employing a solution prepared by diluting concentrated aqueous hydrochloric acid with a considerabe volume of acetone. Upon addition of hydrochloric acid white precipitates of the earth chlorides appear immediately in the form of an emulsion from which crystallization proceeds slowly and incompletely. The precipitates are soluble in large excess of the reagent. This solvent action is best shown by continuing the passage of gas for some time when complete solution is effected. Dilution with acetone reprecipitates the chlorides.

Yttrium group chlorides are not precipitated by such salts as cupric, stannous and ferric chlorides in acetone. However, acetone solutions of a number of common chlorides dissolve the solid yttrium group chlorides, which in the absence of chlorides of this character are practically insoluble. Zinc, bismuth, ferric, cupric, antimonous, stannous, cobaltous and mercuric chloride solutions in acetone dissolve the earth chlorides quite readily. Cadmium, arsenious, and uranyl chlorides act slowly but appreciably. Upon evaporation the copper, cadmium and cobalt chlorides give crystallin products.

Mercuric chloride in acetone added to an acetone solution of yttrium group iodides gives no precipitate immediately, but in a short time a white precipitate of the chloride forms which becomes heavier as more mercuric chloride is added. With excess of mercuric chloride the precipitate redissolves to a clear solution. Addition of yttrium iodide solution again causes a precipitate to form, but on the other hand an excess of the iodide also gives a clear solution. If the solution is concentrated mercuric iodide precipitates, but this can be avoided by dilution with acetone in which it is soluble. To ascertain the molecular proportions existing between $HgCl_2$ and YI_3 standard solutions of the two were prepared in acetone. By numerous titrations the following ratios were indicated to exist, although the results are only approximate inasmuch as the end points were rather obscure: $2YI_3.HgCl_2$, $2YI_3.3HgCl_2$, $YI_3.2HgCl_2$.

The formation of double chlorides indicated above was tried on mixed rare earth chlorides of both the cerium and yttrium groups. Cupric, bismuth, stannous and ferric chloride solutions in acetone were found to dissolve large quantities of the solid chlorides, although only a very slight amount was soluble in acetone alone. This strengthens the view that double chlorides are formed in solution. On account of the ready solubility of the chlorides in the corresponding solvent it has not been possible to effect a fractionation of the earths by this means.

Crystallization of double bromides was attempted by evaporating solutions of calcium, cadmium, sodium and bismuth bromides with the rare earth bromides in acetone solution. The products were of syrupy consistency and not crystallin. Attempts to crystallize double iodides gave similar results.

Silver nitrate in acetone gives a complete precipitation of the halogens from acetone halide solutions, although the first few drops of reagent cause no precipitate to form. Volhard's method for the estimation of silver or determination of chloride can be carried out in acetone by adding in the above reaction an excess of standard silver nitrate solution in acetone and titrating the excess of silver present with a standard acetone solution of ammonium sulfocyanate, using a ferric salt as indicator. Ferric

nitrate crystallized from fuming nitric acid, then dissolved in acetone can be employed. Thus prepared the ferric solution is only moderately permanent, the iron gradually precipitating. One can prepare a dilute solution of ferric chloride or sulfocyanate and use measured portions for the indicator. Naturally under these conditions a "blank" must be subtracted for the volume of silver nitrate necessary to react with the measured volume of indicator.

Hydrobromic acid precipitates the bromides from concentrated iodide but not from the nitrate earth solutions. When sodium iodide in acetone is added to a rare earth bromide acetone solution sodium bromide precipitates, the earth iodide remaining in solution.

Hydrofluoric, sulfuric, oxalic, citric and *mucic acids* precipitate the earths completely as the corresponding salts when acetone solutions of the acids are added to yttrium, neodymium, cerium, or lanthanum nitrates dissolved in acetone.

Tartaric and *phosphoric acids* precipitate the earths almost completely. The phosphates are soluble in large excess of acid. *Malic acid* gives almost complete precipitation upon standing.

Formic, lactic, maleic and *succinic acids* give incomplete precipitation of the four earths studied. Lactic acid precipitates the earths completely from the iodide solutions.

Hydrosulfuric, propionic, benzoic, salicylic, hippuric, cinnamic, or *stearic* acids do not precipitate the corresponding salts of yttrium, neodymium, lanthanum and cerium. However, the cinnamates, benzoates, hippurates and stearates are but very slightly soluble in acetone. Stearic acid gives partial precipitation of the earths from the iodide solutions.

Of the above list of reactions those of formic and lactic acids (see tartaric acid fractionation later) merit especial description, inasmuch as they show evidences of being good reagents for separation purposes.

Formic acid diluted with acetone and added to a cerium solution gives a small amount of a white precipitate instantly. On standing this precipitate gradually becomes heavier. Lanthanum precipitates in a like manner. Neodymium yields no precipitate at first with a moderate amount of formic acid, but upon standing a pink precipitate appears. A large excess of formic acid throws down a precipitate at once. No precipitate is obtained using any concentration of acid with the nitrates of the yttrium group in acetone even after allowing to stand for forty-eight hours. The precipitates of cerium, lanthanum and neodymium are slowly soluble in water. Undoubtedly formic acid could be used as a rapid means of fractionation of the mixed earths.

Lactic acid yields white gelatinous lactates with the nitrates of the yttrium earths. The precipitation is almost complete. The lactates are very soluble in water and very soluble in dilute ammonia. Stronger

ammonia (sp. gr. 0.9) dissolves the lactates forming two immiscible layers both containing yttrium. Warming reprecipitates the earths from the ammoniacal solutions. When lactic acid in acetone is added to a moderately strong solution of cerium nitrate no precipitate appears. Dilution and prolonged standing cause the lactates to settle out. The solubility of the cerium precipitate in water and its deportment with ammonia resemble yttrium. Neodymium precipitates like cerium. Lanthanum is more difficult to throw down with lactic acid, the precipitate forming much more slowly than with cerium or neodymium. The yttrium group precipitates so readily and the others so slowly that without doubt lactic acid can be applied as a rapid fractionation agent for the concentration of this group away from the others.

B. Reactions with Bases.

The reaction of a number of organic bases were tried in acetone with the earth nitrates but they gave no precipitates or general appearance of reaction. Among these were aniline, ethylaniline, acetamide, naphthylamine, diphenylamine, phthalamide, pyridine, quinoline and urea. Benzylamine gives partial precipitation. Phenylhydrazine added to a concentrated nitrate solution of the earths gives two immiscible layers, the lower layer containing practically all of the earths. The lower layer is slightly pink and is miscible with acetone, hence is not obtained in dilute solutions.

Ammonia Reactions.

When anhydrous NH_3 is passed into an acetone solution of yttrium nitrate, lanthanum nitrate, cerium nitrate or neodymium nitrate a heavy white precipitate forms which contains varying amounts of earths, nitric acid, ammonia and acetone, the first and last named being the highest in percentage composition. These precipitates are difficult to handle inasmuch as in many cases when desiccation is utilized to free the precipitates from the acetone held in loose combination, decomposition occurs yielding a dark colored mass which contains considerably more nitrogen than corresponds to the nitric acid and ammonia content.

The nitrates are not well adapted for the study of this reaction due to the difficulty of keeping the conditions sufficiently anhydrous. Naturally if water is present in appreciable amounts the hydroxides are formed in part at least. Decomposition due to oxidation is another factor with the nitrates. Some of the compounds obtained were semi-explosive when heated, hence the oxide value could not be obtained by direct ignition. This reaction is being further investigated.

Reactions with the Alkaloids.

Acetone is a good solvent for the alkaloids. When a number of the alkaloids are dissolved in acetone and the acetone solution added to an

acetone earth solution compounds are formed which contain the earth nitrate and the alkaloids, hence they appear to be a new type of alkaloidal compounds.

The quinine compounds of cerium, lanthanum, neodymium and yttrium are precipitated by the addition of an excess of acetone solution of quinine to the acetone earth solution as white amorphous bodies (the nitrates were employed). The precipitates in the case of yttrium, lanthanum and neodymium are soluble in the earth nitrates. The cerium compound is precipitated with the first drop of alkaloidal solution, hence is not soluble in excess of earth nitrate. All are soluble in water.

Solutions of lanthanum, cerium, neodymium and yttrium earth nitrates in acetone were treated separately with acetone solutions of quinine and the precipitates handled like those with brucine. The acetone is very difficult to remove from the quinine. The compounds $4LaONO_3.C_{20}H_{24}N_2O_2$, $4NdONO_3.C_{20}H_{24}N_2O_2$, $4YtONO_3.C_{20}H_{24}N_2O_2$, and $4CeONO_3.C_{20}H_{24}N_2O_2$ were indicated to exist.

Cinchonidine is sparingly soluble in acetone, hence ethyl alcohol was used as the solvent. An excess of reagent precipitates yttrium, lanthanum, and neodymium slowly. Warming hastens reaction, and precipitates cerium immediately. The precipitates obtained with the first three are soluble in excess of earth nitrates, but not so with cerium. All are white compounds, soluble in water.

Cocaine dissolved in acetone yields with the earth solutions white precipitates, soluble in water.

Sanguinarine is readily soluble in acetone and yields yellow compounds, forming readily with lanthanum, more slowly with cerium and neodymium and still more slowly with yttrium. The compounds are soluble in water. The precipitates have a tendency to turn red on standing.

Chelerythrine is readily soluble in acetone and gives yellow precipitates with the earths, with lanthanum quickly, with cerium not so rapidly, with neodymium more slowly and with yttrium still more slowly. The precipitates are soluble in water.

Piperidine is readily soluble in acetone. It gives white precipitates with the earths which are almost completely insoluble in acetone but are soluble in water.

Hyoscyamine is soluble in acetone. With the earths in excess no precipitate is formed but with alkaloid in excess white precipitates are obtained. All are soluble in water.

Brucine is readily soluble in acetone. With lanthanum, cerium and neodymium precipitation ensues immediately with the first drop of alkaloid added and gradually becomes heavier, although complete precipitation does not occur for several days with an excess of alkaloid

Yttrium requires an excess of alkaloid to start precipitation. The products are all white, except that of neodymium which has a pink tinge. All are soluble in water.

Weak acetone solutions of the nitrates of lanthanum, cerium, neodymium, and the yttrium group were treated with an excess of brucine dissolved in acetone. The precipitates were filtered and washed with acetone by suction then dried *in vacuo* over potassium hydroxide for several days. The precipitates retained a large amount of acetone which could be satisfactorily removed only by prolonged desiccation under diminished pressure.

Upon analysis the following ratios were found to obtain: $La(NO_3)_3.C_{23}H_{26}N_2O_4$, $2Nd(NO_3)_3.C_{23}H_{26}N_2O_4$, $Yt(NO_3)_3.C_{23}H_{26}N_2O_4$, and $Ce(NO_3)_3.C_{23}H_{26}N_2O_4$. The alkaloid may be functioned as indicated or as basic earth alkaloidal nitrates.

Morphine in acetone gives a white precipitate with the earths, requiring an excess of reagent in case of yttrium, lanthanum and neodymium, while with cerium the precipitate forms immediately with the first drop of alkaloid solution. The first three compounds are soluble in excess of earth nitrate. All are soluble in water.

Coniine is miscible with acetone in all proportions. Coniine gives a white precipitate with yttrium nitrate, requiring a larger excess of alkaloid than with the other three earths studied. When added to the earth solution in quantity just sufficient to give a permanent precipitate, the precipitate is soluble in water. When added in larger amounts so that the alkaloid is in excess the precipitate is not soluble in water. Neither precipitate is soluble in alcohol. This deportment indicates the formation of at least two compounds.

With lanthanum the reaction is similar except that the precipitate forms with less excess of alkaloid.

With cerium the reaction is also similar to that of lanthanum but does not show the water-soluble compound to such a marked degree.

With neodymium the reaction is analogous to that of lanthanum.

Strychnine is almost insoluble in acetone, hence a solution in ethyl alcohol was employed. With all four of the earths white precipitates are slowly formed. They are all soluble in water.

Leucine dissolved in warm ethyl alcohol (in which it is only slightly soluble) yields white precipitates soluble in water.

Cinchonine, narcotine and *piperine* give no precipitates with the four earths studied.

3. The Basic Nitrate Separation Using Acetone as the Medium of Extraction.

When a solution mixture of rare earth nitrates is evaporated to dryness and extracted with acetone complete solution is seldom effected,

a residue remaining in almost every instance. If the nitrates are heated after evaporation the amount of insoluble residue is increased until by moderately strong ignition the entire mass is converted to insoluble basic nitrate or oxide. This deportment of the nitrates is made use of in the well known aqueous basic nitrate schemes of fractionation and was tried using acetone instead of water for extraction.

Series I and II.

Thirty grams of yttrium earth oxides containing a very slight trace o didymium were dissolved in nitric acid and evaporated to dryness on the steam bath. The resulting nitrates were treated with acetone, the whole transferred to a flask and shaken until the residue was very finely divided and the extraction apparently complete. In no case was filtration made unless the residue had remained in contact with the acetone for two hours. The residue was filtered off, washed several times with acetone and converted to the oxide. Conversion to oxide by direct ignition gave some difficulty due to the tendency to fuse and not go to a dry powder. Hence the residue in each case was dissolved in nitric acid, the earths precipitated by oxalic acid from a dilute solution which was slightly acid and after filtration ignited to oxide. The washings and filtrate of the first extraction were evaporated to a stiff consistency with thorough stirring at the last, thus giving a slight amount of decomposition in as uniform a manner as possible and avoiding local decomposition. The residue was again extracted as before, etc. The ignited oxides were labelled in order 1, 2, 3, etc.

Examination of the resulting fractions showed rather inconsistent results. The conclusion was drawn that the heating was not regulated in a sufficiently uniform manner to insure good fractionation and a second series of fractions was obtained with this in mind. Although the fractions were more uniform in size, spectroscopic examinations and determinations of atomic weights did not show uniform results. From this it was concluded that the nitrates were not heated to a sufficiently high temperature.

Series III.

Yttrium earth material which originally came from fergusonite was employed. In this case decomposition was carried much further preceding extraction with acetone. Heating was continued with constant stirring using a heavy rod and casserole until the material was hard and in small lumps. The mass thus treated tends to swell up as decomposition proceeds but with a little care in stirring the mass can be kept fairly uniform and local decomposition avoided for the most part. The lumpy material is pulverized before acetone is added for extraction. One small and three larger fractions were obtained.

Fraction.	Quantity. Grams.	Color of oxide.	Equivalent wt.
1.........	0.3	Yellow.	Not determined, at least 75% CeO$_2$.
2.........	4.0	Almost white, very slightly pink.	115.8
3.........	3.5	Almost white, yellow tinge.	106.5
4.........	3.0	Chamois.	103.3

Spectroscopic Examination.

Fraction 1 not examined.

Fraction 2:

Comparative intensity.

(a)	653 650	Ebrium	Moderately strong.	2
(b)	642 641	Holmium	Very light band.	1
(c)	582 576	Didymium	Very light band.	0.5
(d)	540 538	Erbium	Well defined.	2
(e)	537 535	Holmium	" "	1.5
(f)	523 517	Erbium	Very heavy and well defined.	10
(g)	487 484	Erbium-Holmium	Moderate.	2
(h)	449 446	Dysprosium	Very heavy line.	9

Fraction 3:

Same lines as above only much weaker. (c) heavier.

Fraction 4:

(a), (b), (e), (d), and (g) completely gone. (c) much heavier.
(f) is a moderately light band with an intensity of about 2.
(h) is a moderately light band with an intensity of about 2.

572 570 } Neodymium. A light band. Intensity about 1.

This examination shows a concentration of erbium, holmium and dysprosium in the first fractions and didymium in the last. Cerium comes out before the members of the yttrium group. The equivalent weight determinations show a concentration of yttrium in the last fractions.

Series IV.

The fractions from Series II were united and refractionated in a manner similar to Series III, with the following results:

Fraction.	Color of oxide.	Equivalent weight.
1..........	Very light buff (slightly pink).	115.2
2..........	Much lighter than 1.	110.3
3..........	Somewhat darker yellow than 2.	109.3
4..........	Chamois.	107.0

Spectroscopic Examination.

				Intensity.
(a)	654 650	Erbium	Light band.	1.5
(b)	641 639	Holmium	Moderate.	2.5
(c)	536 534	Holmium	Moderate.	2
(d)	523 517	Erbium	Moderate.	2.5
(e)	486 484	Erbium-Holmium	Light.	1
(f)	460 456	Dysprosium	Heavy.	7

Fraction 2:

(d), (f), (e), and (c) lighter.

Fraction 3:

Very light line just discernable at 580-didymium. Line (b) about the same intensity as in 2, but other lines much lighter.

Fraction 4:

578 580 } Didymium. Moderately strong. Intensity about 2.

It has become the strongest band of the field except (f) which has now an intensity of about 3. Other lines are weak.

This series corroborates the results of Series III.

Conclusions.

The use of acetone as a medium of extraction in the basic nitrate fractionation of the members of the yttrium group works satisfactorily and can be employed for the purification of some of the members of this group. Erbium, holmium and dysprosium are thrown out in the first fractions and the yttrium last. Any cerium which may be present is concentrated in the first fraction and didymium in the last with the yttrium. In

fact the concentration of cerium in the first fraction is so marked that cerium can be obtained very quickly in a high degree of purity with this method starting with crude rare earth mixtures. The fact that didymium is concentrated toward the last is also worthy of especial mention inasmuch as cerium concentrates in the first fraction.

4. The Fractionation of Yttrium Earths by Precipitation with Tartaric Acid from Acetone Solutions.

When tartaric acid is added to an acetone solution of the earth nitrates in sufficient quantity to unite with only a small portion of the earths present a semi-flocculent white precipitate forms. If this precipitate is filtered from the mother liquor and tartaric acid added again the second precipitate is formed much more slowly and is more crystallin than the first. After two or three fractions have been removed it is noticed that considerable tartaric acid must be added in excess to start precipitation. Soon it is observed that the precipitate formed by the introduction of a considerable quantity of reagent will redissolve when the solution is agitated and then slowly crystallizes out on the sides and bottom of the containing vessel. Gentle disturbance will cause the crystallin tartrate layer to settle to the bottom in large leaflets and the clear solution can be decanted readily from the precipitate. The last several fractions do not form until a number of hours have elapsed. The last fraction is best precipitated by means of oxalic acid.

Preparation of Solutions.

(1) A saturated solution of tartaric acid in acetone. Tartaric acid is only moderately soluble in acetone, consequently solution is effected by adding an excess of acid to acetone and allowing the solution to stand for some time with occasional shaking.

(2) A dilute acetone solution of the earth nitrates. The oxides are dissolved in nitric acid and evaporated over a steam bath until the nitrates crystallize and are free from water. The resulting nitrates are extracted with acetone. If solution is not effected readily the residue should be transferred to a flask and allowed to remain in contact with the acetone for some time with occasional agitation. Should solution still be incomplete the residue is filtered out, again dissolved in nitric acid, evaporated and extracted again. Usually more or less of the basic salts are formed which seem to be insoluble in acetone, hence reconversion to normal nitrate is necessary before complete solution results. This acetone solution of the nitrates is then diluted with a convenient amount of acetone.

Completeness of Precipitation.—About 0.5 gram of mixed yttrium group oxides was dissolved in nitric acid, evaporated to dryness, dissolved in acetone as outlined above, diluted to 100 cc. with acetone and tartaric acid in acetone added slowly with constant stirring until precipitation

was apparently complete. The precipitate was removed by filtration and more tartaric acid added to the filtrate. A precipitate slowly formed. It was allowed to stand about twelve hours, again filtered and the filtrate tested for the presence of earths by the addition of ammonium oxalate and ammonia. A slight precipitate formed.

Occlusion occurs to some extent when the precipitant is added rapidly to the earth nitrate solutions for the first fractions. Consequently, until that stage of the fractionation is reached when the addition of the fractional amount of reagent produces no immediate precipitation, the addition of tartaric acid should be made slowly with constant agitation of the earth solution. The more dilute the solution the less is the occlusion effect.

In moderately dilute solutions then we have an almost ideal precipitate to handle—crystallin, easily filtered and slow forming, thus allowing a maximum opportunity for equilibrium to be established preceding the removal of each fraction.

Fractional Separations.

About 30 grams of yttrium group oxides from fergusonite were converted to nitrates, dissolved in acetone and diluted with acetone to about 400 cc. A solution of tartaric acid in acetone was added drop by drop from a buret with constant stirring until the solution became turbid due to the forming tartrate, then 10 cc. were added in excess. After thorough shaking and subsiding of the precipitate the solution was filtered. The residue was ignited to oxide and called fraction one. To the filtrate tartaric acid was added, 5 cc. in excess of the amount used for the first fraction, and the fractionation continued. Seven fractions were obtained in all. The filtrate from the seventh precipitation was treated with ammonium oxalate and ammonia and the resulting precipitate ignited to oxide, which constituted fraction eight.

Number of fraction.	Color.	Grams.	Equivalent weight.
1	Almost white, chamois tinge	2.5	155.8
2	Almost white, chamois tinge	4.0	140.7
3	Somewhat darker	4.5	139.1
4	Dark chamois	4.5	133.9
5	Dark chamois	5.5	134.0
6	Dark chamois	4.5	135.8
7	Dark chamois (lighter)	3.5	123.8
8	Almost white	1.0	112.3

Spectroscopic examination of 10% solutions showed a concentration of didymium, dysprosium, holmium and erbium in fractions 5, 6 and 7. Erbium seemed also to concentrate slightly in fraction 2. The equivalent weights show a concentration of ytterbium in the first and yttrium in the last fractions.

Fractions 2 and 3 were combined and refractionated giving the following fractions:

Number.	Color of oxide.	Equivalent weight.
1	Very light buff (almost white)	144.3
2	Very light buff (darker)	. . .
3	Very light buff (darker)	. . .
4	Almost white	. . .
5	Chamois	126.2
6	Light chamois	. . .
7	Light chamois	. . .
8	Light chamois	. . .
9	Lighter chamois	. . .
10	Light buff (pink tinge)	117.0
11	Much lighter buff	. . .
12	Very light buff (almost white)	110.5

Fractions 4, 5, 6 and 7 were combined and refractionated resulting as follows:

Number.	Color of oxide.	Equivalent weight.
1	Very light buff (almost white)	131.5
2	Much darker buff	134.2
3	Much lighter buff	138.8
4	Much lighter buff	130.0
5	Deep chamois	131.4
6	Much lighter chamois	126.8
7	Still lighter chamois	123.9
8	Light buff (pink tinge)	120.5
9	Very light buff	118.2
10	Very light buff (almost white)	113.6

The last five were small fractions. A slight accumulation of erbium was noted spectroscopically in fractions 2 and 3 of both series, but the main portion appeared to be concentrating in fractions 9, 10 and 11 of the first series and 7, 8 and 9 of the second.

Seven fractions which had been previously extracted from monazite were next fractionated, yielding fractions of the same general order as those above. Below are listed the first and last fractions.

Series I:
First fraction	Yellow to buff oxide	Equivalent weight	133.0
Seventh fraction	Almost white oxide	Equivalent weight	. . .

Series II:
First fraction	Deep buff oxide	Equivalent weight	128.8
Sixth fraction	Light yellow oxide	Equivalent weight	114.5

Series III:
First fraction	Light yellow oxide	Equivalent weight	121.3
Seventh fraction	Light yellow oxide	Equivalent weight	115.9

Series IV:
First fraction	Light yellow oxide	Equivalent weight	118.6
Sixth fraction	Very light buff oxide	Equivalent weight	110.7

Series V:

First fraction	Almost white oxide	Equivalent weight	115.9
Sixth fraction	Almost white oxide	Equivalent weight	110.5

Series VI:

First fraction	Almost white oxide	Equivalent weight	120.9
Fifth fraction	Almost white oxide	Equivalent weight	110.8

Series VII:

First fraction	White oxide	Equivalent weight	117.2
Sixth fraction	White oxide	Equivalent weight	113.1

Spectroscopic examination of these series showed that, of the earths giving absorption bands, holmium was the first to concentrate, followed by erbium and dysprosium, the last two being less separated than any of the others. Erbium seems to concentrate toward the first and also in the last fractions with the first few fractionations. However this seeming double behavior is in this case only temporary, as further fractionation removes the erbium from the early portion of the series and places it toward the end of the series with the remainder of the erbium. In a recent investigation of the action of picric acid as an agent for the fractionation of the earths from aqueous solutions Dennis and Bennet[1] observe that erbium tends to concentrate in two places in the series. This behavior is also characteristic of the tartaric acid fractionation in acetone. The atomic weight determinations indicated the accumulation of yttrium in the last fractions.

Some earths containing a little didymium originally from monazite were fractionated yielding 34 fractions which were united with the previous fractions according to (1) the relative order of precipitation, (2) color of oxides (3) spectroscopic absorption lines. They were then refractionated. One hundred and seventy-one fractions were obtained. Again the fractions were united and refractionated and 164 fractions resulted each series of which was subjected to spectroscopic examinations and to the determination of equivalent weights. The following end fractions are given inasmuch as they are representative of the entire set of series:

Series I:

First fraction	Almost white oxide	Equivalent weight	170.8
Fourth fraction	Almost white oxide	Equivalent weight	129.4

Series II:

First fraction	Almost white oxide	Equivalent weight	168.4
Tenth fraction	Dark chamois oxide	Equivalent weight	126.3

Series IV:

First fraction	Very light buff oxide	Equivalent weight	134.1
Twelfth fraction	Very light chamois oxide	Equivalent weight	110.5

Series IX:

First fraction	Buff, with slightly pink tinge	Equivalent weight	125.1
Thirteenth fraction	Chamois oxide	Equivalent weight	114.1

[1] Dennis and Bennet, This Journal, 34, 7.

Series XIII:
    First fraction   Almost white oxide   Equivalent weight   120.2
    Twelfth fraction   Almost white oxide   Equivalent weight   105.8
Series XIV:
    First fraction   Almost white oxide   Equivalent weight   115.8
    Ninth fraction   Almost white oxide   Equivalent weight   107.1
Series XVI:
    First fraction   Almost white oxide   Equivalent weight   107.6
    Seventh fraction   White oxide   Equivalent weight   93.2

Spectroscopically those earths giving absorption bands correspond to the order—holmium, erbium and dysprosium. From the equivalent weight determinations the conclusion can be drawn that ytterbium (lutecium and neoytterbium) is the first member of the group precipitated and yttrium last. Hence the serial order is ytterbium, holmium, erbium and dysprosium, yttrium.

Composition of the Precipitated Tartrates.—The precipitated tartrates carry down tartaric acid which is difficult to wash out with acetone. After thorough washing and drying by suction the tartrates contain only traces of acetone, in fact a negligible quantity. Ignition gives an oxide content which shows the precipitate to be acid. However, if the tartrates are dissolved in a measured volume of standard acid and the excess of free acid titrated with standard alkali using phenolphthalein as indicator, the tartrates give acidity in excess of the amount calculated as being possible from the percentage of oxide obtained. This deportment indicates that the earth tartrates become basic during titration, liberating free acid which is subsequently titrated.

Summary.

In this investigation a contribution to the systematic non-aqueous chemistry of the rare earths is given. A number of the reactions of the common acids and bases with the yttrium group, neodymium, lanthanum and cerium have been studied, utilizing acetone as solvent. In specific cases other solvents have been used. The reactions are of the same general order as those in aqueous solution except that the solubilities vary greatly, hence the results of interaction of reagent with earth are vitally different in many cases. In general it may be said that the earths form more compounds insoluble in acetone than in aqueous solution. In many instances compounds have been found to be insoluble in acetone and soluble in water, hence the use of a solvent like acetone furnishes a means of preparation which can not be attained with water as the reaction medium. Especially is this the case with certain compounds of the acids and the alkaloids. A new field of rare earth study is introduced by the preliminary work done with the alkaloids.

The basic nitrate scheme of fractionation using acetone as solvent

gives a rapid method for the separation of cerium from the mixed earths as well as fractionating the others at the same time.

A separation of the yttrium group using tartaric acid as the precipitant has been found to be very effective for fractional purposes. The serial order established is ytterbium (lutecium and neoytterbium), holmium, erbium and dysprosium and yttrium.

This investigation was undertaken at the suggestion of Professor Lenher who has kindly coöperated throughout the work. Gratitude is also expressed to Professor Fischer for suggestions especially during the alkaloidal study. To Mr. H. S. Miner of the Welsbach Company we are grateful for most of the material used.

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NOTE.

New Thermometers for Melting Point Determinations. — Uniformity in practise in making melting point determinations would be very desirable for even to-day there are too many cases where different observers disagree. The failure to agree is not always due to the quality of the material if we may have confidence in the analytical data given. Many forms of apparatus are in use as well as various kinds of thermometers. Other factors also enter in. The practise of reporting the corrected reading is a step in the right direction and its extension should be constantly urged.

In order to avoid the necessity of making corrections for the exposure of the mercury column I have devised a thermometer with a short scale, so that it may be completely immersed in the bath. The method of construction may be readily seen from the accompanying sketch. Owing to the compact form of the scale it was necessary to construct a set of seven thermometers, each with a milk glass scale of 50° with divisions in degrees. The length of the scale is 35 mm. The thermometer jacket is lengthened so that the total length is 20 cm. This permits of its suspension by means of a cork as in the Thiele apparatus which is a particularly good form to be used with this thermometer. The mercury bulb is small and compact and above it is a constriction to enable one to attach the capillary tube if that is desired. For the protection of the manufacture of the thermometers patent No. 507,320 has been entered in the German Patent Office. The thermometers may be obtained from C. Richter, 30 Lehrterstrasse, Berlin N. W. 5.

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