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HICKS.

Observations On The Rare Earths: A Study
Of The Relative Efficiency Of The Sodium Sulfate
And Potassium Sulfate Separation Of Cerium
And Yttrium Earths.

OBSERVATIONS ON THE RARE EARTHS: A
STUDY OF THE RELATIVE EFFICIENCY
OF THE SODIUM SULFATE AND
THE POTASSIUM SULFATE
SEPARATION OF CERIUM
AND YTTRIUM
EARTHS.

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY JOHN FREDERICK GROSS HICKS

ENTITLED OBSERVATIONS ON THE RARE EARTHS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

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*Required for doctor's degree but not for master's.

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Observations on The Rare Earths: A Study of the Relative
Efficiency of the Sodium Sulfate and the
Potassium Sulfate Separation of
Cerium and Yttrium Earths.

This investigation was undertaken as a portion of a larger investigation on the general subject of the rare earths, and had for its purpose the determination of which method of separation, that employing sodium sulfate, or that employing potassium sulfate, afforded the best separation of the cerium and yttrium earths, both from the standpoint of rapidity and completeness. Both of these methods have been discussed freely in the literature, and but little data is available to show which of the two is the better for general use. James states that the sodium sulfate method is better "when used with care", but gives no experimental data to support this statement; however, he does state that an excess of sodium sulfate causes some of the yttrium earths to pass into the precipitated cerium earths, owing to the fact that their double sulfates with sodium become more and more insoluble as the concentration of sodium sulfate increases. On the other hand, it has been the experience of other workers in this laboratory that while the potassium sulfate, when working on a large scale, gave a precipitate which was somewhat difficult to handle, the precipitate was much more readily freed from adherent alkali-salts than was the precipitate formed by sodium sulfate under similar conditions. It was therefore thought worth while to investigate the two methods by carrying them out in parallel, using exactly similar solutions of the earths, under exactly the same conditions, and to compare the results obtained both from the standpoint of precipitated material (atomic weight), and the purely mechanical

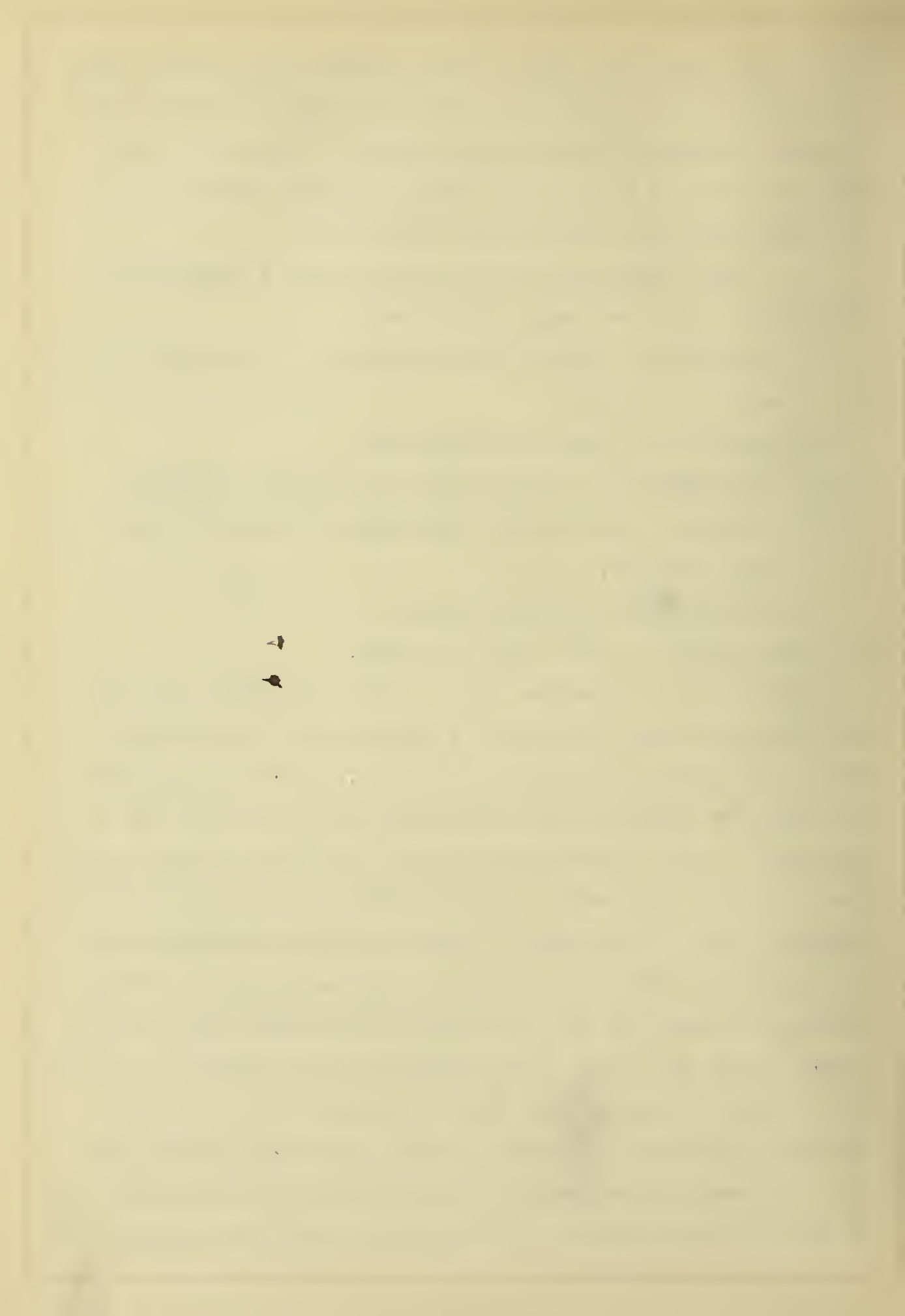


side of the operation, that is, the rapidity and ease with which each method was carried out to completion. The author here takes occasion to express his deep appreciation of the advice and assistance rendered by Dr. C. W. Balke, at whose instance and under whose direction the work was carried out.

The experimental work conducted may be conveniently classified under five heads, as follows:

- I. Precipitation of mixed earth-oxalates, and subsequent treatment of the same.
 - II. Sulfating the mixed earth-oxalates.
 - III. Precipitation of alkali-cerium earth double sulfates.
 - IV. Conversion of all double alkali-earth sulfates to pure earth-oxalates,
 - V. Determination of Atomic Weights.
- I. Precipitation of mixed earth-oxalates:

The source of the earths used in this investigation was gadolinite, which was received in a condition of a pasty mass of silica and earth-chloride solution mixed; it has been prepared by a previous worker in this laboratory from the mineral by acting upon it with boiling hydrochloric acid. This mass was extracted repeatedly with water, care being taken to keep the solution slightly acid at all times, in order to prevent hydrolysis of the earth-chlorides to basic salts, which are insoluble. When a sufficient amount of the earth-chlorides had been extracted (as indicated by the amount of the oxalates precipitated), the earths were roughly separated from iron by precipitation with a hot solution of oxalic acid, with constant stirring; this also served as a means of separation from any thorium and zirconium which might have been present. as the solutions were partly neutralized



with ammonia before adding the oxalic acid, the resulting ammonium oxalate dissolving the precipitated thorium and zirconium oxalates, although a slight loss of earths is unavoidable in this instance. The precipitated earth-oxalates were allowed to settle, washed repeatedly by decantation, until the washing showed no test for chlorides, dried by suction, then over the steam-bath, and finally powdered, after which they were sulfated.

II. Sulfating the earth-oxalates:

The completely dried oxalates were mixed with sufficient concentrated sulfuric acid to give a thick paste, transferred to eight-inch evaporating dishes, and heated in small reverberatory furnaces made for the purpose, until sulfuric anhydride was no longer evolved. These small reverberatory-furnaces were made from twelve-inch lengths of ten-inch "asbestos-magnesia" pipe-covering, the two longitudinal halves being wired tightly together, the whole being first coated thickly with a syrupy solution of sodium silicate, and then with a paste of magnesia and silica with borax-water, air-dried for several days, and then at a gentle heat for a day or two. The top of the furnaces consisted of a thick piece of asbestos-board, with a two-inch hole in the center to permit of the exit of the sulfuric anhydride fumes. Three holes, each one and one-half inches in diameter, and equally distant from each other, were cut half-way down the sides of the furnaces; these served for the admission of air above the sulfating-dishes, and also for the insertion of iron rods, which formed a triangle inside the furnace,- upon this triangle was placed an iron-wire gauze, covered with asbestos-paper, which served for a support for the sulfating-dishes. The whole was mounted on two fire-bricks, to insure free bottom-draught, and heat was supplied by a five-inch

Fletcher burner. With these furnaces a bright red heat could be attained in a very few minutes, and a dishful of sulfating mixture could be run through in from one to two hours.

Upon removal from the furnaces, the sulfates had a reddish or a red-brown color (due to the presence of ferric oxide); sometimes, however, this color was observed only at the bottom of the sulfated mass, and in such cases the sulfates above had a pale pink or yellowish-white color, and were often nearly pure white at the top. After cooling, the powdered sulfated mass was stored until a sufficient quantity had been collected for solution and subsequent treatment.

The sulfates were dissolved in water containing floating ice (they being much more soluble in cold water than in warm), and a small amount of sulfuric acid (125 cc per 100 litres) to prevent hydrolysis (an exceedingly important precaution), and this acid apparently aided in dissolving the sulfates also. The powdered sulfates were sprinkled in small quantities at a time on the surface of the water, and rapidly stirred in, until no more of the salt was taken up. As the sulfates sank rapidly, it was found advantageous to use rather deep vessels (decanting-jars) to effect their solution and this together with the constant stirring insured a maximum amount of the sulfates being dissolved. It was also noted that if any considerable amount of the sulfates settled upon a piece of ice, a hard stone-like mass resulted, which did not afterward dissolve, even upon pulverizing; this was probably a basic sulfate formed by hydrolysis at the (localized) elevated temperature, when the anhydrous sulfates came in contact with the ice. At any rate, heat was given out in sufficient quantity to rapidly melt the ice, with the formation of a little steam, and with a hissing sound as the sul-

fates came in contact with the ice. When a small filtered sample of the solution failed to dissolve an appreciable amount of the anhydrous sulfates, the whole was allowed to settle over night, and the clear liquid siphoned off. The residue was washed on to a filter with ice-water, dried, re-sulfated (as above) and stored. During the process of solution, the temperature ranged from three to nine degrees Cent., although, of course, it did rise during the night, - in the morning, the supernatant liquid usually showed a temperature of from fifteen to nineteen degrees Cent.

The solution of sulfates was now transferred to two large (65-litre) porcelain dishes, thoroughly mixed by pouring litre portions from one vessel to another, with constant stirring, the object being to secure two solutions of uniform composition. One hundred litres of this solution were now transferred to two similar dishes to those previously used, but each provided with a mechanical stirring-device, so that a sample of fifty litres was contained in each dish. Each fifty-litre portion was made by taking one litre of the solution from each of the first two dishes, and mixing them in the other dishes, with constant stirring, until the hydrometer showed a constant specific gravity of 1.148 at 19.5 deg. for each dish. After four or five hours' further stirring, the same figures were obtained, when the two solutions were considered to be of exactly the same concentration.

For the sake of brevity, the two solutions will be designated I (treated with sodium sulfate) and II (treated with potassium sulfate, since this is the only difference in the whole experimentation. The absorption-spectra were observed through a layer twelve centimetres in thickness, the atomic weight of the mixed earths was taken, and a test made for cerium (hydrogen peroxide-

ammonia) and also for thorium (potassium iodate-nitric acid) was made; this procedure was also followed throughout for the cerium earths and for the yttrium earths, after they had been separated from each other. The results of these observations follow:

Spectroscopic Examination:

670 very faint
 653 sharp
 648 weak
 645 weak
 640 weak
 585) very
 to) intense
 570) band
 550 very faint
 545 very faint
 540 well-defined d
 535 well-defined
 525) very intense
 522) band
 520) indistinct limits
 518) band medium intensity
 515 weak
 510 weak
 492 weak
 490 weak
 487) very intense
 482) band
 480 very faint
 475 indistinct
 470 indistinct
 468 well-defined
 455 weak
 452 weak
 450 weak
 445 weak
 442 very faint
 435? ?

Atomic weight determination:

Original Material:

I. Sodium Sulfate Treatment

1. $\text{CaO}_3 = 39.70$
 $\text{R}_2\text{O}_3 = 47.16$
 Atomic Weight = 103.04
2. $\text{CaO}_3 = 39.72$
 $\text{R}_2\text{O}_3 = 47.09$
 Atomic Weight = 104.04

Original Material:

II, Potassium Sulfate Treatment:

1. $\text{CaO}_3 = 39.68$
 $\text{R}_2\text{O}_3 = 47.12$
 Atomic Weight = 104.38
2. $\text{CaO}_3 = 39.64$
 $\text{R}_2\text{O}_3 = 47.19$
 Atomic Weight = 104.31

Cerium test: strongly positive

Thorium test: small quantity.

III. Precipitation of the Alkali-Cerium Earth Double Sulfates:

These are salts of the type $\text{R}_2\text{SO}_4 \cdot \text{R}_2''(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$; the procedure in the case of solutions I and II was precisely the same, with the exception that solution I was saturated with sodium sulfate and solution II was saturated with potassium sulfate, as already stated.

The alkali-sulfate was added in the solid condition, and in a fine state of division, in portions of about 100 grammes each,

(7)

with constant stirring, using as a check the appearance of the neodymium line 575 in the absorption-spectrum; when this became hazy or very faint, the alkali sulfate was added in smaller amounts and at longer intervals, until this line became quite difficult to distinguish, when the addition of the alkali-sulfate was stopped, and the whole was stirred for several hours, allowed to settle, and a spectroscopic examination made of the supernatant liquid, an atomic-weight determination made on the precipitated cerium-earths and the thorium and cerium-tests made exactly as in the case of the original material. It is of interest to note in this connection that the sodium-sulfate-treatment caused a complete elimination of the line 575, while this was not true of the potassium sulfate treatment when the same weight of material had been added in both instances (2900 grams); the equivalent quantity (2520 grams) was then added, with a like result. Longer stirring was of no use, and addition of the potassium sulfate up to 3800 grams produced little or no improvement. As the mechanical stirrer was so geared that the stirring-device in the sodium-sulfate material rotated more rapidly than that in the potassium sulfate (R. P. M. = 64 and 56 respectively), the latter was stirred two days longer in the hope that a more thorough mixing would result favorably; it did not, however, and there was a distinct haze at the position 575 after this last stirring, when the matter was given up as useless. It may be well to note that these solutions were of fifty litres each, and the stirring-devices of eight-inch radius, projecting six inches into the liquids, and rotating at the speeds mentioned above. It is also of interest to note that in the case of the potassium sulfate treatment, the liquid was about saturated with that salt, but the liquid from the other dish would still dissolve appreciable

quantities of sodium sulfate, observations being taken on five cc. test-tube samples at room-temperature, which, throughout the entire experimentation ranged from fifteen to twenty three degrees.

Although the line 523 is the most characteristic in the absorption-spectrum of neodymium, it was thought best to use the line 575 as a check for the above operation in view of the fact that erbium (yttrium earth) gives a line very close to that point on the scale; now erbium, being one of the yttrium earths, will not be precipitated as a double sulfate with the alkali sulfates, hence this line should not be removed, and the presence of a line at or near 523 might prove a source of serious error in an operation of this sort, as its persistence might lead to the continued addition of alkali sulfate in an effort to remove it. In the case of sodium sulfate, this would lead to serious results, in view of the fact that an excess of sodium sulfate causes the precipitation of some of the yttrium earths, as their sulfates become less soluble as the concentration of alkali sulfate increases; this, of course, leads to a less perfect separation of the two groups.

After the completion of the reaction with the alkali sulfates, and the settling out of the double sulfates of the cerium metals, the supernatant liquor was siphoned off (and reserved for the precipitation and study of the yttrium metals), and the precipitated material thrown upon a Büchnerfunnel, washed thoroughly with a saturated solution of sodium sulfate (the particular one with which it had been precipitated), sucked as dry as possible, dried completely on the steam-bath, powdered, and quartered down to about 100 grams, and stored for determination of the atomic weights of the mixed cerium earths.

Four principal differences were to be noticed in the two

methods of separation of the cerium earths, as follows:

1. The potassium double sulfates were in greater quantity than the sodium double sulfates.
2. The potassium double sulfates packed together in a hard stony layer, removable from the dish only with great difficulty, and coming off it in such large pieces that it could not be satisfactorily washed with potassium sulfate solution, but had to be dried and powdered before this could be accomplished; this was not true of the sodium double sulfates in the slightest degree, as they formed a rather coarsely-crystalline powder, and could be readily washed out of the large dish with a stream of saturated sodium sulfate solution from an ordinary wash-bottle, the whole operation requiring somewhat more than half a litre of the wash-solution. The double sulfates in both cases were of a violet-pink color; they were washed with five litres of saturated alkali-sulfate solution.
3. Potassium sulfate fails to completely remove the check-line 535 from the absorption-spectrum; in the case of sodium sulfate, the line is completely eliminated. Potassium sulfate added for fifty litres of solution, 3800 grams; sodium sulfate for the same quantity of the same solution, 2900 grams; potassium sulfate solution practically saturated; sodium sulfate solution will easily dissolve appreciable quantities of this salt.
4. Differences in Absorption-spectra and atomic weight of precipitated material, as follows: (The absorption-spectra were taken on chlorides obtained from the sulfates, their solubility being too low to permit of good observations on even a saturated solution of the double sulfates of the cerium metals and the alkalis.

The results on the cerium-earth double sulfates follow:

Spectrum-analysis:

Sodium Double Sulfates:	Potassium Double Sulfates:
670 sharp	670 sharp
653 sharp	653 sharp
645 weak	645 weak
640 weak	
585) very intense band	585) very intense band
570)	570)
545 very faint	545 well defined
540 very faint	540 very faint
535 well defined	535 well defined
525) very intense band	525) very intense band
518)	520)
515) very intense band	512) very intense band
508)	510)
	487 sharp
482) very intense band	482 well defined
480)	
475) very intense band	
473)	

Atomic Weight determinations:

Sodium Double Sulfates:	Potassium Double Sulfates:
1. $C_2O_3 = 35.53$	1. $C_2O_3 = 30.73$
$R_2O_3 = 50.47$	$R_2O_3 = 44.55$
Atomic Weight = 131.15	Atomic Weight = 132.57
2. $C_2O_3 = 35.56$	2. $C_2O_3 = 30.65$
$R_2O_3 = 50.49$	$R_2O_3 = 44.60$
Atomic Weight = 129.34	Atomic Weight = 133.15

Cerium test: strongly positive.

Thorium test: positive; stronger than with original material.

IV. Preparation of pure oxalates for atomic weight determinations:

(1) For the Cerium earths:

The double sodium or potassium sulfates were boiled with a concentrated solution of sodium or potassium hydroxide respectively, until completely converted to hydroxides, and then washed by repeatedly boiling with water until the hydroxides settled with difficulty, when they were dissolved in hydrochloric acid, and reprecipitated with ammonia, washed five times by boiling and decantation, and the whole process (dissolving in hydrochloric acid and reprecipitating with ammonia) repeated until

the hydroxides failed to give a flame-reaction for either sodium or potassium (as the case might be), and then twice more. A decided difference was noticed here,- the adherent sodium salts were much more difficult to wash out than the adherent potassium salts under the same conditions. For example, after boiling the double sodium ~~for~~ sulfates with sodium hydroxide, it required twelve successive boilings with two litres each to remove sufficient electrolyte (NaOH) from a half-kilogram sample of sodium double sulfates to cause the precipitated hydroxides to "go colloidal", and the precipitation with ammonia and dissolving in hydrochloric acid treatment was repeated seven times before a negative test for sodium was obtained in the flame. In the case of the adherent potassium salts, however, it required but seven treatments with boiling water to render the hydroxides colloidal, and but four hydrochloric acid-ammonia treatments to result in a negative flame-test for potassium. This does not take into consideration the two extra precautionary treatments already mentioned. On the one hand, this indicates the superiority of the sodium sulfate treatment in so far as the saving of time in handling material at the start is concerned, but on the other hand, the easier removal of adherent potassium salts would seem to about compensate for the added work involved in the removal of the adherent sodium salts; in fact, the two operations (precipitation and conversion to alkali-free hydroxides) involves but little difference in time for the two methods.

The alkali-free hydroxides, prepared by either method, were dissolved in hydrochloric acid, diluted with double the volume of water, and precipitated with oxalic acid which had been recrystallized twice from water containing a little nitric acid, the precipitated oxalates allowed to settle, washed by decantation

until the washings were colorless, then twice more; they were then redissolved in hydrochloric acid containing a little nitric acid, diluted with water, and reprecipitated exactly as before, washed ten times by decantation, and the whole operation repeated three times more, making a total of five precipitations with oxalic acid and about fifty-five washings with water. The water from the last washes responded negatively for iron with both potassium ferrocyanide and potassium ferricyanide. The purified oxalates were dried over a steam-bath, thoroughly mixed, quartered down to about one hundred grams, and these samples transferred to weighing-bottles, dried at 108 - 112 deg. for about twenty hours, remixed, and again dried over night at 109 - 113 deg., and allowed to stand over night in a desiccator over concentrated sulfuric acid, and used for atomic weight determinations. They showed a very slight momentary test for sodium in the flame, which was traced to the oxalic acid.

(2) The Yttrium earths:

These being found in the supernatant liquor from the insoluble double sulfates of the cerium earths, the boiling with alkali hydroxide could, of course, be omitted; the yttrium earths were directly precipitated from their solution with ammonia, and treated precisely as has been described before, and it may be noted that the same difference in removing adherent potassium and sodium salts was noticed as before, - the potassium salts being much more readily washed from the precipitated hydroxides of the yttrium earths as well as the cerium earths. The oxalates of the cerium earths, and also of the original material, prepared by either separation, were white in color, while those of the yttrium earths had

a slight pinkish tinge, which was probably a little more pronounced in the case of the sodium sulfate method than in that of the potassium sulfate. The results on the yttrium earths follow:

Spectrum analysis:

Sodium Sulfate treatment:

653 sharp
648 weak

545 very faint
540 well defined
535 well defined
523 very faint, almost absent
492 indistinct
487 well defined

Potassium Sulfate Treatment:

653 sharp

575 very faint
545 faint
~~540 well defined~~
535 well defined
523 sharp
520 faint
492 faint
487 sharp

Cerium test: positive; nearly as strong as for the cerium earths.

Thorium test: negative.

Atomic Weight determinations:

Sodium Sulfate treatment:

1. $C_2O_3 = 41.61$
 $R_2O_3 = 47.39$
Atomic Weight = 99.00

2. $C_2O_3 = 47.36 - 41.56$
 $R_2O_3 = 47.36$
Atomic Weight = 99.07

Potassium Sulfate treatment:

1. $45.40 - C_2O_3 = 45.40$
 $E_2O_3 = 52.16$
Atomic Weight = 100.08

2. $C_2O_3 = 45.38$
 $R_2O_3 = 52.22$
Atomic Weight = 100.28

V. Determination of Atomic Weights:

These were determined by means of the oxide-oxalate ratio, the percentage of "oxalic anhydride" being determined by titration with potassium permanganate, and that of earth-oxide by ignition to constant weight, using the equation

$$(2R + 48) : 216 :: \text{percent } R_2O_3 : \text{percent } C_2O_3,$$

where R is the atomic weight of the earth, 216 the molecular formula weight of "oxalic anhydride" and 48 that of the O_3 in the earth oxide respectively. Results of atomic weight determinations are tabulated below for the sake of comparison.

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1950

Summary of atomic weight determinations:

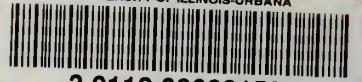
Sodium Sulfate Treatment				Material	Potassium Sulfate Treatment			
No.	C ₂ O ₃	R ₂ O ₃	At. Wt.		No.	C ₂ O ₃	R ₂ O ₃	At. Wt.
1.	39.70	47.16	103.04	Original	1	39.68	47.12	104.38
2.	39.72	47.09	104.04	Original	2	39.64	47.19	103.31
1.	35.53	50.47	131.15	Cerium	1.	30.73	44.55	132.57
2.	35.56	50.49	129.34	Cerium	2.	30.65	44.60	133.15
1.	41.61	47.39	99.00	Yttrium	1.	45.40	52.16	100.08
2.	41.56	47.36	99.07	Yttrium	2.	45.38	52.22	100.28

Conclusions:

Sodium sulfate precipitates the cerium earths more completely than potassium sulfate, and this precipitate entrains decidedly less erbium and allied earths; the separation is more rapid in general, and affords a precipitate which is much more easily handled than that made by the potassium sulfate treatment, as well as involving the use of the lesser amount of the cheaper material. The only disadvantage of the sodium sulfate method, and this is at the same time a decided advantage in the potassium sulfate treatment, lies in the fact that the adherent sodium salts are considerably more difficult to remove than the adherent potassium salts under the same conditions, it requiring about twice the labor to remove the former as is involved in removing the latter. Concerning the action of thorium under the two treatments, both are equally efficient in removing that element completely from the yttrium earths, and in the case of cerium itself, both seem equally incapable of separating it from these elements, the test for cerium being almost as pronounced with the yttrium earths as with the cerium earths: a satisfactory method of separating cerium completely with the cerium earths, thereby removing the necessity of precipitating it from the yttrium earth solution with potassium bromate and heat (in neutral

solution) has yet to be devised.

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