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A NEW METHOD FOR THE PREPARATION
OF
RARE EARTH BROMATES

by
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Chemistry.*

Head of the Dept. of Chemistry.

ACKNOWLEDGEMENT

This work was carried out under the supervision of Dr. J. Allen Harris, and it is to him that I wish to express my indebtedness for his keen interest and constant sound advice.

ABSTRACT

The preparation of the oxides of the cerium and yttrium sub-groups is discussed, and a new method is proposed for the preparation of rare earth bromates, involving the use of calcium bromate instead of barium bromate.

The solubility of calcium bromate was measured roughly, and was found to be 102.5 gms per 100 ml of saturated solution at 19°C.

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A NEW METHOD FOR THE PREPARATION OF RARE EARTH BROMATES

I. INTRODUCTION

The value of the bromates as a method of separation of the rare earths has long been recognised. They are especially useful as a means for the preliminary separation of the elements of the Yttrium Group, and use was made of them during the search for Illinium.¹

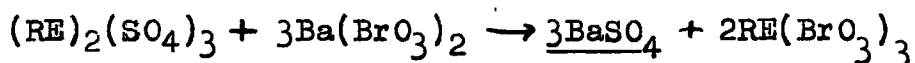
The solubilities of the bromates, in order of decreasing solubility are roughly as follows: Erbium, Lanthanum, Praesodymium, Yttrium, Holmium, Dysprosium, Neodymium, Terbium, Illinium, Samarium, Gadolinium, and Europium.²

James³ advanced the first synthesis of the rare earth bromates in 1908 and since then several other methods have been proposed. The main ones are as follows : -

1. James' Method³

The dried earth oxalates are heated with concentrated sulfuric acid, are warmed to expel excess acid and are heated strongly to convert them to the anhydrous sulfates.

These are now pulverized and sifted into ice water and the resulting solution is thoroughly stirred with freshly precipitated barium bromate, filtered and concentrated.



2. Harris' Method⁴

This method is an adaption of James method. The rare earth oxides are slowly digested with successive small portions of dilute sulfuric acid so that the resulting mixture is only feebly acid. The mixture is then evaporated to dryness and ignited to expel the excess acid. The resulting sulphates can then be dissolved in water at room temperature and precipitated with a saturated solution of barium bromate.

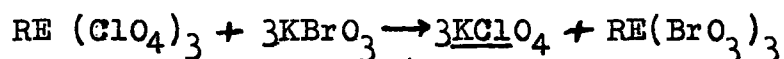
3. Pearce's Method⁵

The rare earth oxides are dissolved in dilute hydrochloric acid, the hydroxides are then precipitated with dilute ammonia washed by decantation, and then dissolved in just enough dilute sulfuric acid to dissolve the precipitate. The bromates are then prepared by adding solid barium bromate and heating, with constant stirring, until precipitation is complete. The mixture is filtered and concentrated.

4. Moeller and Kremer's Method⁶

The rare earth oxides are dissolved in perchloric acid and, on the addition of potassium bromate, potassium per-

chlorate is precipitated leaving the rare earth bromates in solution.

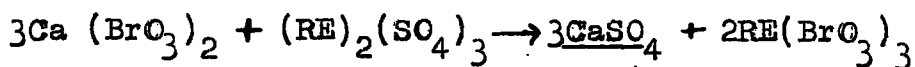


In the preparation of all rare earth bromate solutions, the solution must be as nearly neutral as possible, otherwise, during fractionation, in the final concentration, decomposition invariably results if the solution is at all acid. It is for this reason that elaborate precautions are taken in all the above procedures to cut down acidity.

The first two methods are time consuming, and comparatively large volumes of solution have to be used because of the very poor solubility of barium bromate. Large quantities of irritating fumes are also produced. In the third method barium bromate is added in the solid form, but in the author's experience it was found that the resultant barium sulfate tended to precipitate around the barium bromate, severely inhibiting the reaction, and necessitating prolonged heating and stirring, or the use of a large excess of expensive barium bromate, to bring the reaction to completion. The fourth method is faster, requiring less volume of solution, but even so potassium bromate is not very soluble. The main advantage of this method is its speed and the fact that potassium perchlorate occludes salts to a far less extent than does barium sulfate. This, however, is in part offset by the relative solubility of potassium perchlorate.

Reference to Table I shows that calcium bromate is much more soluble than barium bromate and it was thought that if

this reagent could be substituted the volumes of solution required would be considerably decreased. Calcium sulphate is more soluble than barium sulphate but it will be noticed that it is less soluble than potassium perchlorate, and (on fractionation) any calcium sulfate that did carry through would concentrate rapidly in the least soluble fraction. The solubility of calcium bromate is about 103 gms/100 gms of water at 20°C, so that any carried through should concentrate with samarium and gadolinium in the less soluble fractions.



An added advantage of this method would be that the acidity of the solution need not be controlled to such a fine extent originally, since, prior to the addition of the calcium bromate the solution of rare earth sulfates can be neutralized by the addition of precipitated calcium carbonate. Here the only product is calcium sulfate, and as this is going to be precipitated in the next step, the small amount formed by the neutralization can be filtered out with the main bulk of the precipitate.

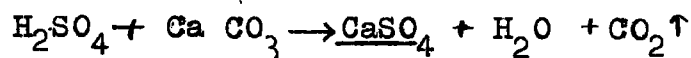


TABLE I
TABLE OF SOLUBILITIES (a)
 gms of solute in 100 gms H₂O

	0°C	20°C	25°C	35°C	45°C	100°C
BaSO ₄	1.15x10 ⁻⁴	2.4x10 ⁻⁴				
CaSO ₄	1.76x10 ⁻¹	2.0x10 ⁻¹				1.62x10 ⁻¹
KClO ₄	7.5 x10 ⁻¹	1.80				21.8
Ba(BrO ₃) ₂ [*]	2.86x10 ⁻¹	6.52x10 ⁻¹				54x10 ⁻¹
Ca(BrO ₃) ₂ ^{*ø}		103.				
KBrO ₃	3.1	6.9				50.0
La(BrO ₃) ₃	184.6	363.0	462.1	1061.5		
Pr(BrO ₃) ₃	88.55	167.9	196.1	278.5	434.5	
Y(BrO ₃) ₃			168			
Dy(BrO ₃) ₃			V.S.			
Nd(BrO ₃) ₃	66.35	128.6	151.3	205.8	289.9	
Tb(BrO ₃) ₃	66.42	117.1	133.2	172.9	227.1	
Sm(BrO ₃) ₃	49.78	100.6	117.3	157.2	214.1	
Gd(BrO ₃) ₃	50.18	95.58	110.5	144.5	195.6	

^{*} Gms per 100 gms. saturated solution

^ø Own determination. Ca(BrO₃)₂ H₂O

(a) Rare earth solubilities taken from
 James J. Am. Chem. Soc. 49 132 (1927).

Remainder from
 Handbook of Chemistry and Physics 30th Edition
 1947.

All rare earth bromates are of the form
 RE(BrO₃)₃ · 9H₂O

II. PREPARATION OF MATERIALS

1. Rare Earths

The starting material used was Gadolinite from Norway.

1.1 Kg batches (3 in all) were added slowly to $2\frac{1}{2}$ litres of hot concentrated hydrochloric acid. The red doughy mass that was formed was heated for 24 hours, the acid lost by evaporation being replaced. The mix was then diluted to 3 litres, filtered, and washed with 6 litres of hot water. The residue was re-extracted with hydrochloric acid and the resultant filtrate was united with the first. This filtrate was now diluted with water until the concentration of free acid was about 0.1N, then was heated to about 80°C , and hot saturated oxalic acid solution was added until precipitation was complete. The oxalates were filtered off, washed thoroughly with hot water, and roasted to the oxides in an electric furnace. The total yield of oxides from 3 batches was 574 gms.

This batch of oxides was now combined with 386 gms of oxides of Gadolinite earths.

The combined oxides were then treated with concentrated nitric acid. A vigorous reaction resulted but a large amount of insoluble material was left which would not dissolve, even on repeated extraction with nitric acid and hydrogen peroxide. This was filtered off and assumed to be Ce O_2 .

The resultant solution was brownish in color and it is of interest to note that if hydrogen peroxide was added to this solution of nitrate a deep reddish orange solution resulted. This was found to be due to the presence of titanium, and it was found necessary to reprecipitate the oxalates to free them entirely of this element. This will be further discussed on page 12.

The resultant solution of nitrates had a volume of about 5 litres, and was ascertained to be about 5N in free acid by titration of a 1 ml sample with 0.1N sodium hydroxide. The solution was diluted to 10 litres and solid sodium sulfate was slowly sifted into the cold solution with constant stirring. A yellow precipitate soon formed. The addition of sodium sulfate was kept up until the 5200 Å Neodymium band was only faintly discernible through a 5 cm layer of the solution, using a hand spectroscope.⁷ The spectroscope used was made by Reichert, Austria.

The precipitate consisting of cerium group sulfates was filtered off, but was not washed.

Purification of Sub Groups

A. Cerium Group

The next task was to remove the cerium completely from the precipitated sulfates. Several methods are available notably the potassium bromate⁸ and the permanganate phosphate⁹ methods. It was decided to use the latter as it gave a quantitative separation and was less time consuming.

The sulfate precipitate was treated with 15N ammonium hydroxide until the appearance of the precipitate indicated that it had been converted to the hydroxides. This precipitate was washed by decantation, was dissolved in dilute nitric acid and the oxalates precipitated. The oxalates were roasted to the oxides and then the oxides were dissolved in dilute nitric acid so that the resultant solution was less than 2N in acid. A solution of disodium hydrogen phosphate was added and it was noticed that a yellowish gelatinous precipitate appeared almost immediately. This was probably a mixture of ceric and titanium phosphates.

Now a 0.5N solution of potassium permanganate was added and the mixture became thick with ceric phosphate. The mixture was heated for one hour and was then filtered. The filtrate was treated with hot concentrated oxalic acid and the resultant oxalates were filtered out and roasted to the oxides. It was found necessary to repeat this procedure twice more to remove the cerium completely. The final oxides which were dark brown in color, weighed 160 gms. All the sulfates obtained, incidentally, were not converted to the oxide.

It was found that disodium hydrogen phosphate was the best precipitating agent to use here. If phosphoric acid was used a white insoluble basic salt was formed which was very hard to filter out and was found on analysis to contain other earths besides cerium.

The average atomic weight of these earths was found by

the method based on the ratios; oxalate/oxide, oxalate/per-manganate.¹⁰ Results are tabulated in Table II. The value of 137.0 is slightly lower than the atomic weights of the other members of this group, but this may be explained if it is remembered that the "double sulfate split" is by no means quantitative, and some scandium will remain in the cerium group.

B. Yttrium Sub Group

The filtrate from the sodium sulfate precipitation was made basic with ammonium hydroxide and the resultant hydroxides were washed by decantation and dissolved in dilute nitric acid. The oxalates were then precipitated and converted to the oxides. The cerium was now removed by the same procedure as before, and again it was found that three precipitations were necessary. For this sub group it was found that either disodium hydrogen phosphate or phosphoric acid could be used as the precipitant, but that the disodium hydrogen phosphate gave best results. The resulting oxides weighed 190 gms, and were a light tan color.

The results of an average atomic weight determination done on this group are given in Table III. The very low value of 108.5 is due to the presence of scandium (At. Wt. 45.1) or yttrium (At. Wt. 88.92) or, more probably, both.

TABLE II
AVERAGE ATOMIC WEIGHT
CERIUM GROUP

Wt. Oxalate Titrated (Gms)	Vol. of KMnO ₄ (ml)	Normality of KMnO ₄	Wt. of Oxalate Ignited	Wt. Oxide Obtained
0.1622	44.75	0.0340	0.4075	0.2049
0.1518	41.75	0.0340	0.4032	0.2023
0.16465	45.30	0.0340	0.4087	0.2052

Relationship Used

$$\frac{RE_2O_3}{3C_2O_3} = \frac{2RE + 48}{216.06} = \frac{\text{gms oxide obt.}}{\text{gms oxalate ignited} \times \frac{\text{gms oxalate titrated}}{\text{Vol. KMnO}_4 \times N \text{ of KMnO}_4 \times G. \text{Equiv.}}}$$

1000 wt. C₂O₃

Results

- (i) RE = 136.8
(ii) RE = 136.9
(iii) RE = 137.0⁵

Value chosen as Average Atomic Weight 137.0

TABLE III
 AVERAGE ATOMIC WEIGHT
 YTTRIUM GROUP

Wt. Oxalate Titrated (Gms)	Vol. of KMnO ₄ (ml)	Normality of KMnO ₄	Wt. of Oxalate Ignited (Gms)	Wt. Oxide Obtained (Gms)
0.2097	56.05	0.0392	0.4115	0.1903
0.2341	62.50	0.0392	0.4262	0.1971
0.22135	59.05	0.0392	0.4989	0.2305

Same relationship used as before.

Results

(I) RE = 108.4

(II) RE = 108.5

(III) RE = 108.5⁵

Value chosen as average atomic weight 108.5

In the foregoing procedures it was noticed that, in the early stages, after precipitation of the oxalates with hot saturated oxalic acid, a yellow color always remained in the supernatant liquid. At first it was thought this was due to ceric cerium which was not reduced by the oxalic acid, but further investigation showed that this was not the case, and the color was shown to be due to the presence of ferric and titanic salts. This was done as follows:

Some of the cerium group sulfates were converted to the hydroxides before the removal of the cerium and precipitated as the oxalates. The mother liquor, which was a deep orange yellow color, was carefully decanted through a filter and was made basic with ammonium hydroxide. An orange gelatinous precipitate appeared, which was filtered out and dissolved in 6N hydrochloric acid. Half of this solution was diluted with water until the acid concentration was about 0.5 N, and on the addition of hot saturated oxalic acid no precipitate appeared, showing the absence of cerium or any other rare earth. The rest of the solution was extracted with ether. The ether layer was evaporated and on treating part of it with ammonium hydroxide, the typical red ferric hydroxide appeared. The blue ferric ferrocyanide was also obtained with potassium ferrocyanide, and the red complex with potassium thiocyanate, but this was not relied on because titanic salts give precisely the same color in the latter case. The water layer was found to contain titanium only by the following tests. The addition of hydrogen peroxide produced

a red solution, ammonium hydroxide gave only a white gelatinous precipitate, and potassium ferrocyanide gave only the brown titanous ferrocyanide.

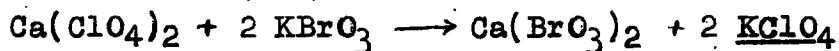
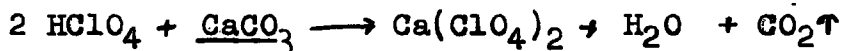
The oxalate precipitate was washed thoroughly with boiling water, was converted to the oxides, and the oxalates were then reprecipitated. This time a faint yellow color was apparent in the mother liquor, and this was found to be due almost entirely to titanium. A trace of iron, but no cerium, was found.

The oxalates were again washed thoroughly with boiling water, converted to the oxides and dissolved in nitric acid. The solution was quite yellow, but the addition of hydrogen peroxide to a few drops of this caused the yellow color to vanish completely. This indicates that, while ignition of oxides causes the formation of cerium dioxide, subsequent solution in nitric acid leaves a considerable amount of the cerium in the ceric condition. On precipitating the oxalates again the mother liquor was now found to be quite colorless. These tests show definitely that the yellow color was due to titanium and iron, which seem to be occluded to a considerable extent by the oxalates, but not to cerium. To ensure complete removal of impurities from the oxalates, at least two precipitations are indicated.

2. Calcium bromate

(a) Synthesis

To prepare the calcium bromate, use was made of the following reactions:



Method.

1000 ml of 60% perchloric acid is treated with excess calcium carbonate (about 550 gms) until all reaction has ceased. The solution is heated and the excess calcium carbonate is removed by filtration, Celite filter aid being added if it tends to run through the filter.

1800 gms of potassium bromate are now dissolved in boiling water and this solution is added slowly with constant stirring. The mixture is now cooled to 0°C being stirred mechanically all the time, and the potassium perchlorate is filtered off but is not washed. The filtrate is evaporated on a steam bath and a limited series of fractional crystallizations is set up., the least soluble fractions being discarded as they contain potassium perchlorate and potassium bromate. It is best to cool to 0°C before separating the crystals from the mother liquor to ensure as complete a removal of potassium salts as possible. The intermediate fractions are dried in a vacuum over concentrated sulfuric acid for a few days and are stored. Theoretical yield

1594 gms. Actual yield about 1300 gms.

(b) Determination of Solubility

No data on the solubility of calcium bromate could be found in any of the literature, so it was decided to determine it roughly for room temperature. The method used was as follows.

A saturated solution of calcium was prepared and was allowed to stand several days to reach equilibrium. A 10 ml portion was pipetted into a calibrated volumetric flask and diluted to the mark with distilled water. 10 ml portions of this solution were evaporated with 3 ml concentrated hydrochloric acid to destroy the bromate, 10 ml water and 30 ml of 0.5 M ammonium oxalate were added and then, slowly, with constant stirring, dilute ammonium hydroxide until the solution was basic. The precipitate of calcium oxalate was heated to 80°C on a water bath, allowed to stand for one hour and was then filtered and washed by decantation until free from chloride ion. The precipitate was dissolved completely in 30 ml of hot 3 N sulfuric acid, the filter was washed thoroughly with hot water, and the resultant solution was titrated with standard permanganate.

Results.

Flask at 23°C contains 499.30 ml.

Temperature at which saturated $\text{Ca}(\text{BrO}_3)_2$ sample
taken 19°C

N of KMnO_4	Vol KMnO_4 used for 10.0 ml sample	Soly. $\text{Ca}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ g/100 ml sat. soln.
----------------------	--	---

0.0260	50.4 ml	102.8
0.0260	50.1 "	102.2
0.0340	38.6 "	103.0
0.0340	38.2 "	102.0

Average Solubility - 102.5 g/100 ml sat. soln.
at 19°C

3. Spectrographic Data

The equipment used was the same as that used by Taylor,¹¹ the only alterations being:

(i) The arc and the Point-o-light were mounted on the same optical axis. When the poles of the arc were separated by an inch or so the Point-o-light could shine through unobstructed and so do away with the necessity of a reflecting mirror.

(ii) The arc assembly and the Point-o-light were encased in a plywood box. This kept direct light off the spectroscope and also preserved the operator's eyes.

Cut film, instead of plates, was used and excellent results were obtained. It was found that Kodak Super Panchro Press gave best results and with this film the exposure time for the arc could be cut to a fraction of a second and five second's exposure through a 1 cm absorption layer was ample.

In making all plates the usual standard procedure of converting the sample to the nitrate and then photographing the saturated solutions through a 1 cm layer, giving an exposure of five seconds, was followed.

Some "Specpure" samples of the rare earths were obtained from Johnson, Matthey and Mallory of Toronto, and absorption spectra of these are shown in Fig. 1.

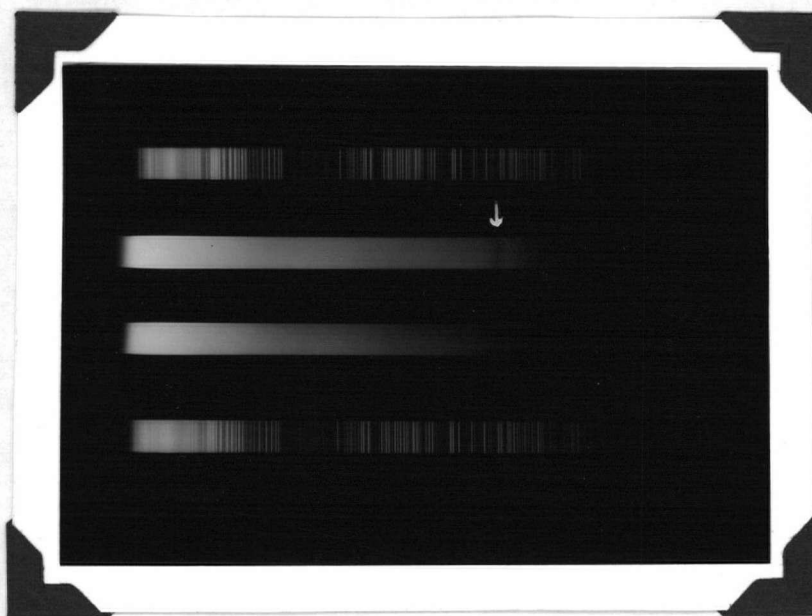
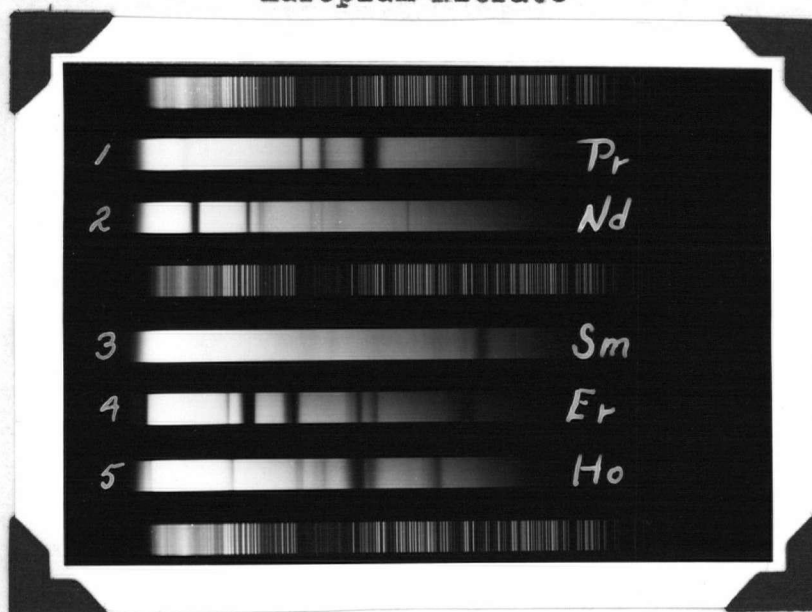
Fig. 2 shows absorption spectra of the nitrates of the cerium and yttrium groups, whose preparation is described

previously.

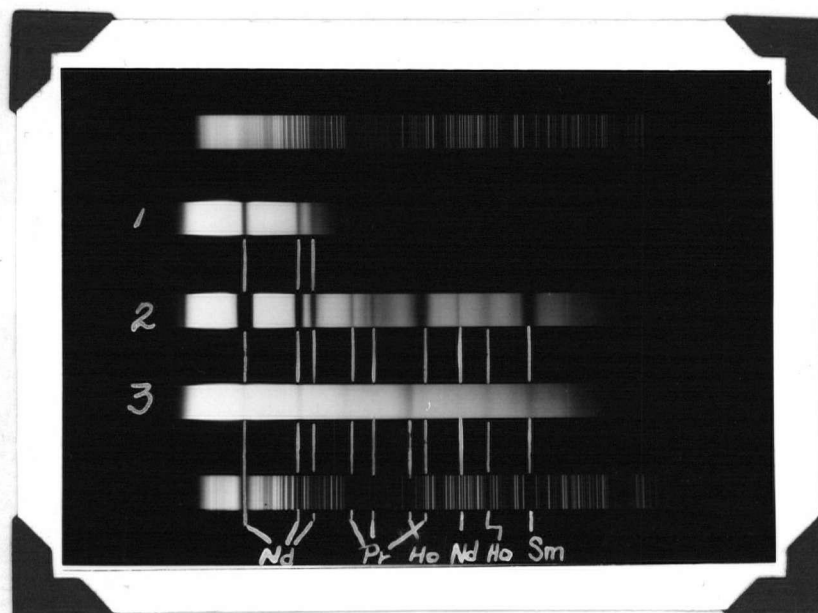
For the benefit of future operators the optimum settings for the spectroscope are:

Slit	0.005
Telescope	13.0
Plate Tilt	2.1
Arc current	3 amps
Exposures (Kodak Super Pan Press Film)	
Arc	1/2 to 1 sec
Absorbtion	5 secs

If the prism is set at 461.75 the spectra will be centered on the plate.

Fig. ISpectra of Pure Rare Earth NitratesEuropium Nitrate

1. Praesodymium Nitrate
2. Neodymium Nitrate
3. Samarium Nitrate
4. Erbium Nitrate
5. Holmium Nitrate

Fig. IISpectra of Cerium and Yttrium Group Nitrates

1. Original Sample
2. Cerium Group
3. Yttrium Group

III. PREPARATION OF BROMATES

(a) Cerium Group

100 gms of cerium group oxides were dissolved in 130 ml of concentrated nitric acid, giving a pink solution. This was made basic with ammonium hydroxide and the precipitated hydroxides were washed by decantation with distilled water until the supernatant liquor was only slightly basic. Pearce⁵ now recommends that the supernatant liquor be decanted off, but it was found that if the mixture is filtered, a considerable reduction in the volume of the bulky hydroxides is effected. If a large Buchner funnel and a Cenco Pressovac oil pump, as a source of vacuum, is used, filtration is quite rapid.

Just enough 6 N Sulfuric acid to dissolve the precipitate, (about 350 ml), was now added and a clear pink solution resulted. Inadvertently, at this point, too much acid was added and the solution was distinctly acid; however powdered calcium carbonate was sifted in and the solution rapidly regained neutrality, with no ill effects.

A concentrated water solution of 312 gms of calcium bromate was next added and the mixture was heated on a steam bath for an hour with constant stirring. The precipitate of calcium sulfate did not come down at once, but only after about five minutes of heating and stirring. The calcium sulfate was filtered off, washed with 500 ml of boiling water, and the resulting filtrate was evaporated on a steam bath.

By the color of the calcium sulfate it could be seen that some occlusion of rare earths had taken place, and, to determine how much, the precipitate was boiled with hydrochloric acid until all the bromates had decomposed. The rare earths were precipitated, converted to the oxides, and the weight of oxide was found to be 35 gms, showing that calcium sulfate occluded about 35% of the original oxides. This value is very high, but it should be pointed out that only 500 ml of wash liquid was used. In preparing the yttrium group bromates more wash liquid was used and less occlusion resulted. The oxides resulting from the occlusion were a very much darker brown color than the others. Their absorption spectrum is shown in Fig. III, Spectrum 1, and it will be noticed that neodymium and especially lanthanum seem to be concentrating there.

When the filtrate containing the rare earth bromates had reached a volume of about one litre, it could be seen that a considerable precipitate of calcium sulfate had separated. This was filtered off and evaporation was continued. When a volume of about 600 ml was reached, the accumulated calcium sulfate was again filtered off, and when the filtrate was cooled the bromates started to crystallize. As there was not enough time to carry out a complete series of fractionations, the bromates were divided into six rough fractions and the absorption spectrum of a representative sample of each was photographed. The results are tabulated in Table IV and the spectra are shown in Fig. III.

During the entire course of the crystallization a close check was kept on the acidity of the solution, and if it showed any signs of becoming too acid powdered calcium carbonate was sprinkled in until neutrality was regained. After two of these additions it was noticed that a slight brown sludge formed, which was filtered out and on analysis found to be mainly cerium. Absorption spectra (Fig. III Spectra 2 and 3) showed a small amount of scandium to be present also. It was probably the oxidation and subsequent hydrolysis of this cerium that caused the rise in acidity of the solution. The amount of cerium was not great, but the fact that it was there indicates that it had not been entirely removed by the permanganate-phosphate treatment. However, if the above procedure is followed this is not important, since, if an excess of calcium bromate is added and the solution is kept neutral, any small amount of cerium will be precipitated as the basic ceric salt and can be removed along with the calcium sulfate.

TABLE IV
CERIUM GROUP

Fraction	Color of Oxide	Elements indicated by absorption spectra
1	Brown	Pr, Nd, Sm, Ho.
2	Brown	Pr, Nd, Sm, Ho.
3	Light Brown	Pr, Nd, Sm, Ho.
4	Light Brown	Pr, Nd, Sm, Ho.
5	Cream	No RE giving absorption spec.
6	Cream	Nd (tr), Sm (tr)

Due to the rough nature of the fractionation not much data could be obtained on where the various salts were coming out, but it was noticed that as fraction 5 was being crystallized the appearance of the crystals and their mode of formation indicated that calcium bromate was coming out here in addition to the others.

(b) Yttrium Group

100 gms of the yttrium group oxides were treated in an exactly analagous manner to those of the cerium group, using stiochiometric quantities of reagents, with a slight excess of calcium bromate. Again it was found that, if the solution was too acid upon the formation of the sulfates, it could be easily restored to neutrality by the addition of powdered calcium carbonate. The precipitate of calcium sulfate was washed this time with 2 litres of boiling water, and it was found that only 20 gms of the oxide were occluded, and as these oxides were identical in color to the original they were not spectrographed.

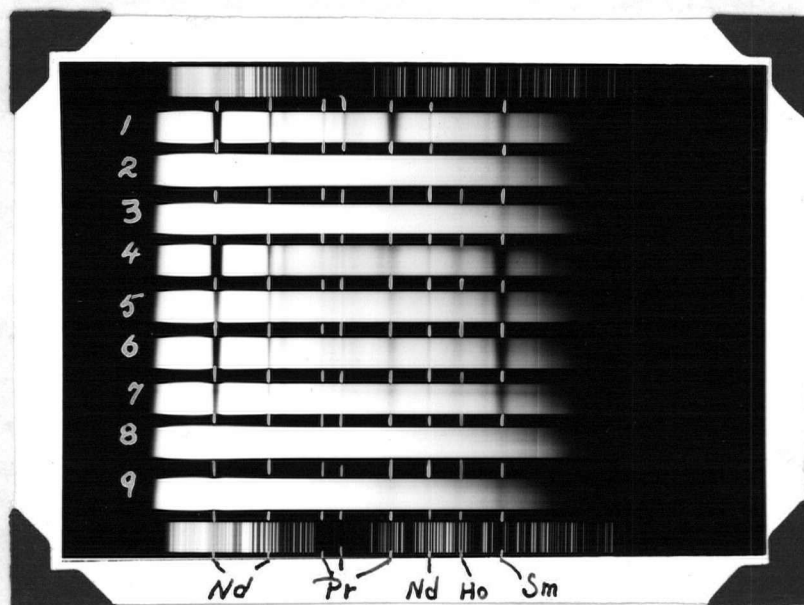
The solution of bromates was evaporated to a volume of about one litre and the accumulated calcium sulfate was filtered out. As this precipitate could be seen by its color to contain rare earths, it was boiled with one litre of water and filtered. The water extract was found to contain 9 gms of oxide and the residual calcium sulfate 6 gms of oxide. (Water extract, spectrum 1; Residue from calcium sulfate, spectrum 2, Fig. IV).

The remaining bromate solution was concentrated further on the water bath and was divided into six rough fractions. It was found necessary to add calcium carbonate only at the last fraction when the solution became slightly acid. A small amount of cerium was found in Fraction 2. Table V shows the results of each fractionation and absorption spectra are shown in Fig. IV.

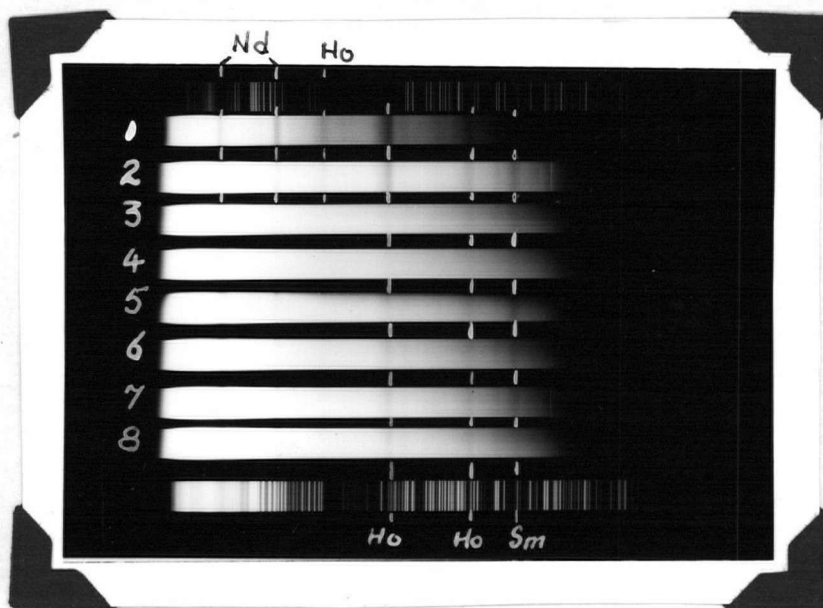
TABLE V
YTTRIUM GROUP

Fraction	Color of Oxide	Elements indicated by absorption spectra
1	Cream	Sm (tr) Ho (tr)
2	Yellow	Sm (tr) Ho (tr)
3	Yellow	Nd (tr), Sm, Ho.
4	Yellow	Nd (tr), Sm, Ho.
5	Yellow	Nd (tr), Sm(tr), Ho.
6	Pale Yellow	Ho. Sm

Fig. III
Cerium Group Fractions



- | | |
|---------------------------------|---------------|
| 1. Extract from CaSO_4 | 5. Fraction 2 |
| 2. } Residues after treatment | 6. " 3 |
| 3. } with CaCO_3 | 7. " 4 |
| 4. Fraction 1 | 8. " 5 |
| | 9. " 6 |

Fig. IVYttrium Group Fractions

- 1.) } Extracts from CaSO_4
 2.) }
 3. Fraction 1
 4. " 2

5. Fraction 3
 6. " 4
 7. " 5
 8. " 6

IV. DISCUSSION OF RESULTS

The foregoing results show that it is possible to prepare rare earth bromates using calcium bromate in the place of the barium salt. The main advantages of this method are : -

1. Calcium bromate is far more soluble than barium bromate and thus the reduction in volume of solution needed is considerable. The use of solid barium bromate is eliminated.

2. Since calcium carbonate may be sprinkled into the solution, the usual stringent precautions taken at the start, to prevent the solution becoming too acid, are eliminated. Of course the solution should be as neutral as possible, but time need not be wasted making sure it is entirely neutral.

3. The complete removal of cerium is not essential, as any small amount present will be precipitated as the basic ceric salt. This is in effect the James method for the removal of cerium⁸. Here again of course most of the cerium should be removed before the bromates are made, but complete removal is not essential.

4. Calcium bromate is cheaper than barium bromate. It is easy to prepare.

The main disadvantages are : -

1. Calcium sulfate is appreciably soluble. However it was noticed throughout this work that nearly all of the calcium sulfate tended to separate out before the bromates themselves crystallized.

2. Calcium sulfate tends to occlude salts to a high degree, although it is doubtful if it does so any more than does barium bromate.

Some other conclusions reached during the course of this work are : -

1. To ensure quantitative removal of cerium by the permanganate-phosphate method, care must be taken that the solution is not over 1 N in free acid, as, in acid concentrations greater than that the solubility of ceric phosphate is appreciable.

2. The writer was asked to track down the yellow color that remained in the solution after the oxalates were precipitated initially. This was shown to be due to the presence of titanium and iron.

Suggestions for further work.

Much work remains to be done on this problem and the main avenues of approach suggested are : -

1. Bromates of the cerium and yttrium groups should be prepared and thoroughly fractionated to determine where

the calcium sulfate and bromate separate out.

2. Further data should be obtained on the solubility of calcium bromate at temperatures ranging from 0°C to 100°C.

3. The optimum volume of wash water to be used for the washing of the precipitated calcium sulfate should be determined, in order to ensure the most thorough washing, with least solution of the precipitate.

4. The question whether calcium sulfate preferentially absorbs any of the rare earths should be studied further, since, if this is the case, a useful preliminary separation could be brought about.

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