A COMPARISON OF THE EFFICIENCIES OF BROMATES AND NITRATES IN THE SEPARATION OF THE RARE EARTH ELEMENTS FROM ONE ANOTHER

by

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A. INTRODUCTION:

Increased interest is being taken in the elements of the Rare Earth Group owing to their growing importance in industry and to the fact that they offer interesting studies from the viewpoint of atomic structure, origin etc. In every case, however, progress is retarded owing to the extreme difficulty with which they may be separated from one another. The isolation or identification of the individual members of this group covers a period of some 130 years, the first member being discovered in 1794 whereas the existence of the last was only demonstrated in 1926.[1.]

During this period a great many methods have been used for the separation and purification of the elements, methods involving in the main part differences in the solubilities of simple or double salts of the elements, or differences in the basicities of the oxides. As a result the individual members of the entire group have been isolated in sufficient amounts to allow of their identification as elements, even though very few have

1. Harris with Hopkins--J.A.C.S., 48, 1585.

been prepared in a state of atomic purity in any quantity, and these only after extensive fractional crystallizations.

The methods used have naturally varied with each investigator and as a result the literature is filled with conflicting statements as to the relative solubilities, etc., and whereas separation of the elements has been accomplished by various means, there is no claim made as to the method used being the most efficient one. The result has been therefore to use for preliminary separations, methods that have been shown to be fairly successful, and the general separation, the final purification generally depends on the person who is working on the particular problem.

B. HISTORICAL:

During the concentration of illinium it was obvious that although a great deal of data was available regarding methods for producing a separation of the rare earth elements from one another, any thing in the way of a comparative study of these methods was lacking.

Preliminary separation of cerium group earths is generally accomplished by the fractional crystallization of a double salt, usually the double magnesium nitrate. In the case of the yttrium group earths, fractionation of the bromates appears to be the method most frequently used

although the simple nitrates have also been recommended. Our own interest, as has been pointed out in previous papers, is directed chiefly towards the finding of a more efficient method for the concentration of illinium than was used for its isolation. Consequently our efforts have been directed towards a comparative study of the effect of crystallizing as many different salts as possible in the hope that some one salt might prove more effective in permitting of a concentration of a particular element than the others. In every case therefore identical material was used, and the conditions of crystallization maintained as nearly the same in all cases as possible. The effect of the fractionation was in each case observed by comparing the absorption spectra of solutions made up from a definite volume of saturated solution from each fraction. The results from such a study of the spectra obtained from various series of salts of the cerium group earths have been reported[2,3], and it was possible from such a comparative study to note that certain salts are more effective in bringing about a rapid separation of certain elements than are the others. Consequently a great deal of time may be saved by selecting the salt to be used for preliminary separation as carefully as that for the final purification.

A similar investigation as to the relative effects

2. Pearce with Harris--T.R.S.C., Sec. III, 1930, 145.
3. Wylie with Harris--T.R.S.C., Sec. III, 1931, 107.

of the fractional crystallization of salts of the rare earths obtained from gadolinite was carried out. The salts used were the simple nitrates and the bromates as these have proved more effective in the separation of the yttrium group earths.

The fractional crystallization of the bromates was introduced by James[4] in his classical work on the yttrium group earths. In his later paper on the "Separation of the Rare Earths" he suggests four different methods for attacking the crude oxalates, depending on the concentration of the latter. For the separation of the crude yttrium earths he recommends the fractional crystallization of the bromates. He converted the oxalates to the anhydrous sulphates by treating them with a slight excess of sulphuric acid and heating until all fumes of sulphuric acid ceased to be evolved. The ignited sulphates were dissolved in cold water and a fairly strong solution of them were added to barium bromate, covered with a layer of water and heated on a steam bath. The whole was filtered when decomposition was completed and the barium sulphate well washed with hot water. The clear liquid was evaporated until crystals formed and the mother liquor and crystals were fractionally crystallized.

Using this method James found that Samarium and

4. C. James--J.A.C.S., 1908, 30,182; 1912, 34,757.

Gadolimium rapidly separated in the least soluble crystals, followed by Dysprosium, Holmium and Yttrium, whereas the most soluble fractions contained practically pure Erbium.

This method has been used extensively since by rare earth workers in the Yttrium group.

Fractional crystallization of the nitrates was first used by Demarcay[5] who found that this method was particularly effective when the mixture of earths contained no element of atomic weight less than that of dysprosium. Baur and Marc[6] found the method very efficient for separating gadolinium from yttrium and it has since been used extensively by Urbain and others.

C. EXPERIMENTAL:

Starting with the crude ore, the rare earths were extracted and after purification samples of these were taken and converted into bromates and nitrates. Fractional crystallization of the two series was carried out in order to determine which salt brought about the better separation of members of the yttrium group.

The material used had its source in Norwegian Gadolinite. The earths were extracted with hydrochloric acid or concentrated sodium hydroxide followed by nitric acid extraction, these extractants having been shown to be the most efficient ones for this mineral.[7] The liquor

5. Demarcay--Comp. Rend., 1896, 122, 728.
6. Baur & Marc--Ber., 1901, 34, 2460.
7. Harris-Pearce --T.R.S.C., Sec. III, 1929, 61.

containing the earths was then diluted, and the earths precipitated as the hydroxides by ammonia.

The mixture was filtered, washed thoroughly, and then taken into solution in the minimum amount of nitric acid. The resulting solution was diluted, heated, and the oxalates precipitated by the addition of excess of saturated oxalic acid solution. These were filtered, washed several times with water and again filtered, dried and ignited to the oxides in a muffle.

Since the presence of cerium renders the preparation of the bromate difficult, owing to the acid character of solutions of cerium sulphate, it is necessary to remove even the small amounts of cerium which are present in gadolinite. The oxides were extracted with nitric acid containing a little hydrogen peroxide and the small amounts of insoluble material filtered out. The filtrate was diluted to several times its original volume and brought to neutrality by the addition of ammonia. Marble chips and solid potassium bromate were now added and the solution brought to boiling. After allowing the mixture to cool, the basic cerium was filtered out and the earths in the solution precipitated as the hydroxides with ammonia.

These were washed thoroughly by decantation and then dissolved in nitric acid. The solution was then evaporated until the nitrates crystallized out followed

by their solution in water and the precipitation of the earths as oxalates with subsequent ignition to the oxides.

D. PREPARATION OF THE SALTS.

Samples of the purified oxides weighing 250 grams were taken in each case.

SERIES A.A. NITRATES.

The oxides were moistened with water and then warmed with concentrated nitric acid until solution was effected. The solution was then evaporated until crystallization was almost complete upon cooling to room temperature. The salt was then crystallized from concentrated nitric acid until a series of eight fractions had been built up, new fractions being started with sixth, eleventh, sixteenth, twenty-fourth, forty second and fiftieth pourings, making a total of fifty-two crystallizations in the case of fraction one, and two in the case of fraction seven.

SERIES B.B. BROMATES.

In a paper published by Harris[8] it was pointed out that the classical method for the preparation of the bromates is that of James. It was also shown however, that difficulty is encountered when this method is used for the preparation of the bromates of the cerium

8. J.A.C.S., 53, 2475, 1931.

group earths, when large amounts of the more basic members are present. At the same time the method involving as it does the decomposition of the sulphate radical by the oxalate ion, is objectionable from the standpoint of the copious evolution of fumes, and the necessity for the solution of the resulting sulphates in ice water.

The method by Harris eliminated these objectionable features, and so it was deemed advisable to attempt to apply it to the yttrium group earths.

The second sample of oxides was moistened with water to allow of ready penetration by the acid and then treated with small portions of sulphuric acid (1:3) allowing the liquor to reach neutrality before subsequent addition of acid. When the point had been reached at which the liquor remained acid, the mixture was gently heated until neutrality was again attained. The addition of acid was then carried out on a hot plate until a faintly acid solution persisted. When such a condition was reached the mixture was evaporated to dryness. When dry, the sulphates were removed and pulverized, and ignited in small portions with frequent stirring over a strong flame until all excess acid had been removed and the anhydrous salt obtained. This was quickly transferred to a dry, previously weighed container, roughly weighed and trans-

ferred immediately while still hot to a bell jar which was evacuated.

From the weight of the sulphates the amount of water necessary for their solution was calculated and measured into a large beaker. When cool the sulphates were removed in small portions and sprinkled with vigorous stirring into the water where they dissolved fairly readily giving a solution neutral to litmus.

A saturated solution of barium bromate was prepared; the sulphate was added to this in small portions making sure there was always an excess of barium ion in solution and the solution was kept at 100° and stirred mechanically. When all the sulphate solution was added, the barium sulphate precipitate was filtered out.

The solution of rare earth bromates thus obtained was evaporated slowly on a steam bath until crystals formed, then the bromates were placed in the cold and allowed to crystallize.

F. PREPARATION OF SAMPLES:

As was reported in previous papers, in order to compare the relative separations over the entire series at the final crystallization and to ascertain if possible the relative amounts of the various earths in each fraction, each series was taken and acid or water added to the fractions and recrystallization effected so that the

volumes of liquor and crystals were approximately the same. Since the acid radical has a marked effect on the absorption spectra of rare earth solutions it was deemed advisable to convert the salts in each case to the nitrates for spectroscopic examination. The individual fractions of the two series were therefore maintained at constant temperature for several hours in order to permit of equilibrium between the solid and liquid being reached. 10 c.c. samples of the saturated solutions were then withdrawn, transferred to large beakers and evaporated to dryness. The residues were taken up in water and the earths precipitated as the hydroxides by means of ammonia. The precipitates were washed with water, dissolved in a little nitric acid, the solution diluted and the rare earth oxalates precipitated from hot solution by means of oxalic acid. These were then ignited to the oxides. The oxides after weighing, for reference purposes, were moistened with a little water and dissolved in concentrated nitric acid and evaporated to dryness. They were taken up in water containing a little hydrogen peroxide and evaporated several times to expell acid. 5 c.c. of distilled water were added to each dried sample and warmed slightly to effect solution. Except in the cases of fractions seven and eight of the nitrate series, clear solutions were obtained. In these samples, however,

a basic salt precipitated and was filtered out. Consequently with the exception of these two fractions, each sample represented the amount of rare earths contained in 10 c.c. of the original salt solution and now contained in 5 c.c. of solution as the nitrate. The solutions were photographed through a 5 c.m. cell. The absorption bands recorded were compared to the spectrum of a standard iron arc, and also to the absorption obtained from standard solutions of neodymium, samarium, erbium and holmium, photographed through the same cell.

F. DISCUSSION OF RESULTS:

The photographs obtained from the solutions discussed above are reproduced in Plate I. An iterpretation of these absorption spectra is more complicated than in the case of a series composed of elements of the cerium group alone. In the series discussed in this paper, in addition to having members of the yttrium group earths present small amounts of cerium group elements are present causing overlapping of absorption bands. Likewise, several members of the yttrium group earths yield solutions that have but little or no absorption in the visible region of the spectrum. It thus is possible at this stage to obtain only a general idea as to the relative effectiveness of each salt in producing separations of individual members of the rare earth group.

The solutions of the bromates varied in colour from colorless in the first fraction, to a dark pink in the third one, fading away to a very pale tint in the last two. The oxalates from fraction 1 were white, from 2 and 3, pink, from 4 and 5, white, and from 6, 7 and 8 pink.

The absorption spectra indicates that there is a rapid concentration of neodymium and samarium in the head fractions, whereas the erbium concentrates in the least soluble fractions. A preliminary study of absorption bands would indicate the concentration of Europium in Fraction 1, Samarium, Terbium and Neodymium in Fractions 2 and 3, Dysprosium in Fraction 4, Holmium in Fraction 5, a colourless earth (possibly yttrium) in Fraction 6 and Erbium in Fractions 7 and 8.

The bromates would appear to be of most use in separating Neodymium amd Samarium from Holmium, Yttrium and Erbium in a preliminary fractionation of a series containing all of the Yttrium Group earths together with some of the Cerium Group.

The final solutions from the nitrates varied from almost colourless in Fraction 1 to a deep pink in Fraction 5. Fraction 6 showed a slight orange colour, Fraction 7 a deep orange, and Fraction 8 a deep yellow colour. In photographing the absorption Spectra of these solutioms

it was impossible to obtain uniform intensity in the last three fractions owing to total absorption from yellow to violet. In the photographs produced, the lower figure represents the results obtained by prolonged exposure of the three lower fractions. The intensity of the bands in these cases cannot therefore be used for comparision with the other exposures.

The nitrates bring about a totally different order or separation to that produced by the fractional crystallization of the bromates. Terbium, Europium, Dysprosium and Samarium appear to concentrate in the head fractions followed by Holmium, Erbium and finally Neodymium, although it is difficult to interpret the Spectra of the last three fractions as indicated previously.

The value of the nitrates would appear to be in the rapid separation of Samarium from Neodymium in an Yttrium group mixture in which these elements are present. It would also prove an effective means of separating Terbium, Europium and possibly Gadolinium from such a mixture.

G. SUMMARY:

A preliminary study of the effect of crystallization of identical material as the bromates, and as the nitrates has been made.

The order of solubilities of the salts in each series differs. For the rapid separation of Erbium, or of Neodymium and Samarium from an Yttrium group mixture the bromates are to be recommended for the preliminary separation.

The nitrates appear to offer a splendid means for the rapid concentration of Europium, Terbium and Gadolinium from a general mixture.

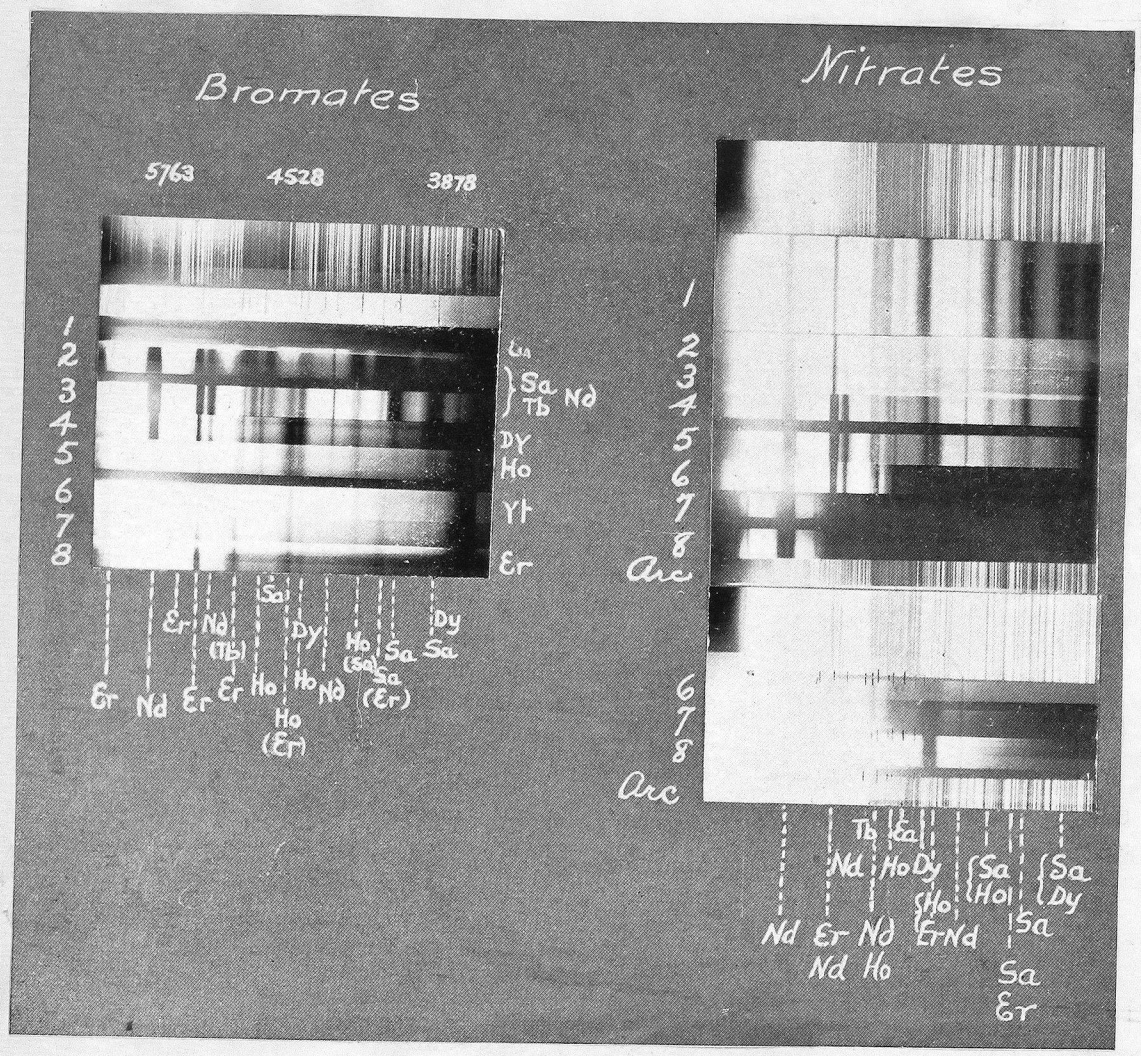

Figure 1

Figure 2

PLATE I

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4/5/33.