purely mathematical. Feilmann[1] has discussed the approximation of atomic weights to integral and semi-integral numbers.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE RARE EARTHS OF THE CAROLINA MONAZITE SANDS.

BY C. JAMES.

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According to some writers, the yttrium earths, derived from the monazite sands of Carolina, contain an element, which prevents the rapid fractionation of this mixture. It occurred to the writer that it would be extremely interesting to apply the bromate method to these earths. It is true that the yttrium metals from monazite have been submitted to this method, but in previous work they were added to euxenite earths and the whole treated together. The conditions were therefore different and no conclusions could be drawn.

The material used in this work was obtained by treating a solution of monazite earths with potassium sulfate. The latter salt was added in an insufficient quantity to precipitate all the cerium metals. It was hoped that, by leaving a fair amount of neodymium, etc., in solution, nearly all the samarium and gadolinium, contained in the original mineral, would be left unprecipitated. The filtrate was treated with oxalic acid and the resulting oxalate was the starting point for this study.

These earths were prepared in this manner by Dr. H. S. Miner, to whom the author desires to express his sincere thanks.

The oxalates were converted into oxides by ignition, after which they were dissolved in nitric acid. Since cerium was present in considerable amount, some of the original oxalate was boiled with the solution to reduce all cerium in the ceric condition. The nitrate solution was then poured into large earthenware vessels, and the whole allowed to settle. The clear liquid was syphoned off and mixed with magnesium nitrate. (The magnesium nitrate was prepared from ignited magnesite by dissolving it in nitric acid. The neutral solution was then treated with a slight excess of magnesite at the boiling point. This threw down the small quantities of iron and aluminium that were present. These hydroxides were separated from the solution by filtration through cloth.)

The double magnesium nitrates were fractionally crystallized from water acidified with nitric acid. Lanthanum, cerium and praseodymium rapidly passed into the less soluble fractions. The intermediate crystals carried nearly all the neodymium together with very small quantities of praseodymium. The mother liquors, which crystallized badly, owing to the accumulation of iron and aluminium in addition to

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[1] *Proc. Chem. Soc.*, 28, 283.

the yttrium earths, showed fairly weak absorption bands of neodymium, stronger bands of samarium and bands of medium strengths of dysprosium, holmium and erbium. The thulium red band was not distinct.

These mother liquors were diluted and all the earths precipitated as oxalates by adding a boiling solution of oxalic acid. The precipitate was filtered off, washed and ignited to oxide.

According to previous work carried out by the writer, the above oxides should be very rich in samarium and gadolinium. As the spectroscope revealed the presence of considerable samarium, it was deemed advisable to separate most of these elements before the study of the yttrium earths should be carried on. In order to accomplish this the oxides were dissolved in nitric acid and the simple nitrates obtained in this way were submitted to fractional crystallization from nitric acid of 1.3 sp. gr. The spectroscope indicated that neodymium was inclined to spread itself over a wide range of fractions. Large amounts of material formed the less soluble portions and these appeared to consist almost entirely of samarium, gadolinium and neodymium. The absorption spectrum showed the presence of the first and last, and judging by the intensities there must have been a lot of earth in the mixture, giving no absorption bands. The spectra of dysprosium, holmium, erbium, and thulium were absent. Probably nearly all the europium and a good deal of the terbium, which the original earths contained, passed into this portion of nitrates.

The mother liquors from the less soluble nitrate crystals showed a spectrum containing strong bands of dysprosium, holmium and erbium. Thulium was extremely weak. Small quantities of neodymium and samarium and probably a minute amount of gadolinium (europium and terbium) remained with the yttrium earths.

The nitrate solution containing the yttrium metals was diluted and precipitated by means of oxalic acid. The whole was allowed to stand for some time, so as to make sure that the precipitation was complete. The oxalates were filtered off, washed, dried and converted into anhydrous sulfates by mixing with a slight excess of sulfuric acid and heating, with considerable stirring, until fumes of the acid ceased to be evolved.

The ignited sulfate was dissolved by stirring with cold water in a copper vessel which was surrounded by cold water. Copper was used, since it is a good conductor of heat and prevented a rapid increase in temperature due to the hydration of the sulfates. The stirring was best carried out by a propeller of copper fitted about an inch from the bottom. This propeller was connected by a copper shaft to a small wooden pulley wheel, which could be worked by a hot air motor. When working upon a smaller scale, a large round bottom flask immersed in cold water and stirred by means of an air blast was found to be very efficient.

The sulfate solution was gradually added to barium bromate covered with water and contained in very large porcelain dishes.[1] The mass was well stirred and, when the supernatant liquid proved to be free from sulfates, it was filtered. The barium sulfate remaining upon the filter was thoroughly washed. The original filtrate and wash water were evaporated to crystallization and the whole fractionally crystallized from water solution.

NOTE.—When very rare substances are converted into bromates, by treating barium bromate with a sulfate, it is important to remember that the resulting barium sulfate entrains a varying amount of the sulfate of the rare earth. Hence it is often necessary to regain this material by one of the well known methods.

When four fractions had formed, the first and last were examined by their absorption spectra. The least soluble fraction (1) contained neodymium and samarium, and owing to its pale color probably gadolinium was present in quantity. The bands of erbium, holmium and dysprosium were practically absent. Fraction 4—the most soluble—showed an entirely different spectrum; only the merest trace of neodymium was visible; the bands of erbium, holmium and dysprosium were strong; thulium could also be detected by its absorption spectrum.

After continuing the fractionation for a longer period, it was observed that the small amounts of ytterbium (ytterbium, lutecium and celtium) and thulium had passed into the most soluble fraction. This was then removed from the series. By studying the remaining fractions by means of the spectroscope, it could be seen that erbium, together with yttrium, was rapidly separating from holmium, dysprosium and yttrium. Yttrium coming between the erbium and holmium earths, naturally accompanies both. In the fractions following dysprosium, neodymium was found. As the least soluble end was reached, the bands of samarium became stronger.

It can be seen from the above that these Carolina earths can be separated just as easily as those from another mineral, such as gadolinite. The fractions between dysprosium and samarium appeared to be especially interesting, since neodymium seems to insert itself between some members of the yttrium earths. This should be somewhere near the point where terbium would accumulate. Since the separation of gadolinium, terbium, dysprosium and holmium is somewhat difficult, the fractionation of this portion of the series was kept going for a few weeks more. Two series of operations could be carried out during the day. As soon as the least soluble fractions showed only traces of neodymium, they were placed aside. The mother liquors were removed when the absorption bands became weak, since this indicated a concentration of yttrium. The removal of the latter element could be followed by observing the intensity of the dysprosium and holmium absorption, which increased with

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[1] James, THIS JOURNAL, 30, 182.

the concentration of these elements. Finally, when dysprosium began to pass into the mother liquor in considerable quantity, each fraction was carefully examined.

The fraction having the greatest solubility gave very strong bands of holmium and dysprosium. Erbium and neodymium were absent. The next casserole contained a similar mixture together with a trace of neodymium. The crystals following showed a marked increase of the neodymium content, while the absorption spectrum of holmium was much fainter than that of dysprosium. In the next fraction neodymium was very intense, dysprosium strong, and holmium just visible. Further along the series neodymium remained intense, but dysprosium was not seen. As the least soluble end was approached, the spectrum of samarium made its appearance, and as this became stronger, neodymium rapidly faded away.

It was decided first to examin thoroughly the neodymium that came nearest to the fraction showing only a faint holmium spectrum. The crystals were dissolved, and the resulting solution diluted and stirred with solid sodium sulfate. The double sulfates were filtered off, the filtrate poured into boiling sodium hydroxide and the whole filtered. The hydroxides remaining upon the funnel were washed, dissolved in nitric acid and precipitated by oxalic acid. The oxalates, upon ignition, gave a deep brown colored oxide, which, when in solution in nitric acid, showed a fairly strong dysprosium spectrum; that of neodymium was weak and the holmium absorption in the green was just perceptible. Therefore, judging from the color of the oxide and the absorption spectrum, the yttrium earths consisted of gadolinium with much dysprosium, a little terbium and traces of holmium. The writer is of the opinion that the bromate method would be of great service for the concentration of terbium. And in order to settle the question, an investigation is being commenced, using many kilograms of terbium material.

The results of this study indicate that Carolina monazite contains, in addition to lanthanum, cerium, praseodymium, and neodymium, fair amounts of samarium, gadolinium, and yttrium; very small amounts of dysprosium, holmium and erbium; and minute amounts of europium, terbium, thulium and ytterbium, etc. It is also interesting to note that erbium occurs in much smaller quantities than holmium and dysprosium. This fact probably accounts for the apparent anomaly, found by some workers upon certain fractions, as shown by the equivalent determination, when compared with some other mineral such as gadolinite or euxenite.

The writer would recommend the oxalates from the more soluble double sulfates as a source for samarium, gadolinium, europium, terbium, dysprosium and holmium.

NOTE 1.—A similar article will shortly appear upon the rare earths contained in samarskite from Sankara Mica Mine of Mysore, India. The author desires to express his thanks to the Syndicate for their generosity in supplying him with a very large amount of this mineral.

NOTE 2.—It becomes necessary to correct another point with regard to the bromate method of fractionation. In order to observe how the separation of holmium and dysprosium is proceeding, one must convert into the nitrates before observing the absorption spectrum, and the solution should be concentrated. This work upon the Carolina monazite has shown that the bromate method is after all a very good one for the separation of these elements. It possesses the advantage that no hydrolysis takes place, as is the case with the ethyl sulfates, even when one uses great care.

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THE ACTION OF SULFUROUS ACID UPON THE SULFIDES OF IRON, ZINC AND MANGANESE.

BY WILLIAM E. HENDERSON AND HARRY B. WEISER.

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It is a well known fact that the sulfides of iron, zinc, and manganese, when freshly prepared, are readily soluble in a concentrated solution of sulfur dioxide, while those of nickel and cobalt are difficultly soluble. As early as 1833, Berthier[1] employed this reaction as a means of freeing the hydrates of titanium and zirconium from ferrous sulfide, and Delffs[2] recommends the same process, although neither investigated the character of the reaction.

An inspection of the literature discloses the fact that while there are many references to the reaction, and a number of suggestions as to the products formed, there is little recorded experimental work relating to it. Mendelejeff[3] and Dammer[4] state that the product of the reaction is ferrous dithionate. Rammelsberg[5] says that when a stream of sulfur dioxide is conducted into a suspension of manganese sulfide in water, the products are the thiosulfate and sulfur. Guerout[6] expresses the opinion that the products are the thiosulfate and the sulfite, but records no experimental data and is not quoted in the handbooks.

In view of this uncertainty it seemed desirable to make a study of the reaction, especially as there is much confusion in regard to most of the thio acids and their salts and the reactions in which they are supposed to be formed, and many of them are in need of further study. The results of a preliminary investigation are recorded in the following pages.

[1] *Ann.*, 5, 246.

[2] *Jahresb.*, 1851, 174.

[3] "Principles of Chemistry," Vol. II, p. 171.

[4] "Anorg. Chem.," Vol. II, p. 564.

[5] *Pogg. Ann.*, 56, 305.

[6] *Compt. rend.*, 75, 1276.