

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

EUROPIUM.

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Received June 21, 1911.

By fractionally crystallizing the nitrates of a mixture of the rare earths, very rich in samarium and gadolinium, from concentrated nitric acid, Demarçay¹ obtained a new nitrate more soluble than gadolinium and less soluble than samarium. This element, which differed from all the rare earths by its characteristic spectrum, he provisionally named Σ .

In 1900² the discoverer obtained this earth in a pure condition and found that the oxide was white, with a pink tinge. The salts were of a pale rose color and gave the following absorption spectrum: 590, 570, 535, 525, 465, 395.5, 385.5, 380.5. None of these bands were strong, however. A year later Demarçay³ obtained the element in a fairly pure condition and named it europium. He also found that the crystallization of the double magnesium nitrate gave a more rapid separation.

Some years previous to Demarçay's work, Lecoq de Boisbaudran⁴ had observed three lines in certain samarium solutions, which did not occur in Cleve's pure material. These lines were later found to coincide with those given by europium. Crookes, in 1885, discovered the phosphorescent spectrum of europium, and gave the element the provisional name Sub.

Urbain and Lacombe⁵ showed that isomorphous bismuth magnesium nitrate came between samarium and europium with regard to its solubility in fairly strong nitric acid. This method enabled them to obtain several grams of europium, in a very pure condition from a comparatively large amount of samarium and gadolinium (610 grams oxides).

In order to obtain a sufficient quantity of this earth for further study, the writers worked up very large amounts of material. This material comprised the following: oxides from insoluble double sodium sulfates from about 200 kilograms of yttrium minerals; all the samarium and gadolinium oxides derived from about 200 kilograms of Brazilian monazite; and about 110 kilograms of oxides obtained from the more soluble double potassium sulfates coming from very large amounts of Carolina monazite.

These crude oxides were first converted into double magnesium nitrates in the following manner: concentrated nitric acid and the oxides were gradually mixed in a large porcelain dish, care being taken not to allow the liquid to become alkaline. All cerium in the ceric condition was reduced by addition of rare earth oxalates of similar metallic content to

¹ *Compt. rend.*, 122, 728.

² *Ibid.*, 130, No. 22.

³ *Ibid.*, 132, No. 24.

⁴ *Ibid.*, 114, 575.

⁵ *Ibid.*, 138, 628.

the oxides. About two bottles of concentrated nitric acid were used in each batch. The solution was finally made as nearly neutral as possible, poured into a large earthenware vessel and allowed to stand until it became clear. This operation took about twelve hours. An equal amount of acid was neutralized with crude magnesium oxide. The magnesium nitrate solution was made slightly basic by heating with a little more of the oxide. The precipitate of iron and aluminium hydroxides was then filtered off. The filtrate was acidified and mixed with the rare earth nitrate solution. The mixed liquids were evaporated until such a concentration was obtained that half of the material separated out in a crystalline state upon cooling. The mother liquor was poured off and evaporated further. The double nitrates that separated were recrystallized three times, after which they were drained and placed aside. When the mother liquors began to crystallize badly, owing to increase in the impurities, they were diluted and precipitated with oxalic acid. The oxalates were filtered off on large Büchner funnels, thoroughly washed with water and ignited in fire-clay crucibles placed in a large furnace.

The oxides obtained in the above manner contained small quantities of lanthanum, cerium and praseodymium, large quantities of neodymium and fair amounts of samarium, gadolinium and yttrium earths. This material was converted into the double magnesium nitrate in a similar way, as described above, with the exception that pure magnesium oxide was used. These double magnesium nitrates were fractionally crystallized according to the usual method with 30 per cent. nitric acid as the solvent. After the crystallization had proceeded for a short time, it was found that the neodymium, lanthanum, cerium and praseodymium rapidly collected in the least soluble portion. The intermediate fractions consisted chiefly of the pale yellow samarium compound while the most soluble portions were rich in gadolinium and were colored very pale pink by the erbium metals. As soon as the crystals of the simple nitrates of the yttrium elements made their appearance, it was deemed advisable to commence the addition of the isomorphous bismuth magnesium nitrate. Five kilograms of bismuth were converted into the double nitrate. This salt was added in portions of about 1 kilogram to the most soluble fraction, such procedure rapidly eliminating all traces of samarium and europium. When the yttrium earths were entirely freed from samarium and europium they were separated from the series.

With regard to the yttrium earths, it was found that erbium and yttrium separated first, holmium next and lastly dysprosium and terbium. It proved to be practically impossible to free gadolinium entirely from terbium by the magnesium nitrate method. A crystallization of the simple nitrates caused yttrium, erbium, holmium, and dysprosium to pass rapidly into the most soluble part.

The fractions containing lanthanum, cerium, praseodymium and neodymium were set aside as soon as they were freed from all traces of samarium. Samarium was gradually removed after a large number of crystallizations, at which time it was considered certain that all europium had passed further along the series.

These operations were carried out in very large porcelain dishes. As these dishes were uncovered the top crystals deliquesced, causing the samarium to pass beyond its correct position in the series. Because of this difficulty and since the fractions had decreased in bulk considerably, the series was removed from the dishes and placed in casseroles, which were covered with large watch-glasses. From now on the solvent used was nitric acid of about 50 per cent. concentration. Hitherto the only visible sign of europium was a fine sharp absorption band in the blue, shown by the gadolinium fractions next to samarium.

As the work proceeded, the europium band was observed to become stronger in the fractions between samarium and gadolinium. Later the two bands in the green made their appearance. The fractions kept getting smaller and smaller, since all mother liquors that gave no europium absorption had been removed. At this period nearly all the samarium had been separated. After continuing the work a little longer, the fractions which consisted almost entirely of bismuth magnesium nitrate were mixed according to their absorption spectra. The liquids were diluted, precipitated with hydrogen sulfide and filtered. The filtrate was precipitated with oxalic acid and the europium oxalate filtered off and washed. About 100 grams of this compound were obtained. Each precipitate was then ignited to the oxide, the oxide dissolved in nitric acid, and the resulting solution tested with the spectroscope. The solutions of the europium material nearest to the samarium were found to be still slightly contaminated with that element.

It was decided to submit the whole material to more series of crystallizations. For this purpose it was again converted back to the double magnesium nitrate and mixed with bismuth magnesium nitrate. When the europium was found to be free from samarium, it was dissolved in water, saturated with hydrogen sulfide and the clear filtrate was once again precipitated with oxalic acid. This europium oxalate was then washed, dried and stored for the study of its compounds.

In this work, which required two years, about 30 kilograms of the crude double nitrates of samarium and gadolinium were extracted and fractionated. About 5 kilograms of pure samarium oxalate and about 4 kilograms of nearly pure gadolinium oxalate were prepared.

The authors hope to publish the second part of this paper in the near future.