[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

OBSERVATIONS ON THE RARE EARTHS. VII. THE SEPARATION OF HOLMIUM.

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A large part of the rare earth work which has been in progress in this laboratory during the past three years has been concerned with that portion of the Yttrium Group which includes dysprosium, holmium, yttrium and erbium. These four elements form salts whose solubilities in general increase slightly in the order given. The general plan of separation has been to carry out a thorough series of fractional crystallizations of the bromates as suggested by James and Bissel,[1] then to select those fractions which contain mainly two elements and to continue the separation by means of methods dependent upon some characteristics other than differences in solubilities. This plan has worked well for the more abundant of the rare earth elements like yttrium and erbium. But when applied to holmium the problem becomes more difficult because of the fact that it is one of the least abundant of the rare earth elements. Kremers and Balke[2] have shown that it was possible to obtain bromate fractions containing holmium and yttrium only. The bromate fractionation, however, fails to concentrate all the holmium, as is shown by the fact that Kremers, Hopkins and Engle[3] did not succeed in removing all the holmium from their dysprosium material. In addition to the scarcity of holmium and the difficulty of concentrating it, the purification of this element is hard to control since the last impurity, yttrium, has no absorption lines in the visible spectrum. Hence the progress of purification must be judged by means of the equivalents of the fractions, which consumes both time and material. The purpose of the present investigation was to continue the study of the purification of holmium, in an effort to find methods of separation by which the material could be obtained in a high degree of purity.

In general, only those yttrium-holmium fractions were used which were free from all but traces of other rare earths. Most of the material used in this work came originally from gadolinite, the preliminary treatment being described by Engle and Balke[4] and Kremers and Balke.[5]

Fractional Hydrolysis of the Phthalates.

Urbain[6] suggested that the best method for separating holmium and yttrium would depend on the difference in basicity of the two elements.

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[1] THIS JOURNAL, **36**, 2060 (1914).

[2] *Ibid.*, **40**, 600 (1918).

[3] *Ibid.*, **40**, 596 (1918).

[4] *Ibid.*, **39**, 53 (1917).

[5] *Ibid.*, **40**, 593 (1918).

[6] *Ann. chim.*, [8] **18**, 222 (1909).

Meyer and Wuorinen[1] employed the fractional hydrolysis of the phthalates for the separation of yttrium from the less basic members of the yttrium group. It was thought that a modification of this method could be employed for the separation of holmium from the more basic yttrium.

Material for this fractionation in Fraction 24, from the series by Engel and Balke, consisting of approximately 68 g. of a light yellow oxide, was shown by the absorption spectrum of a concentrated solution to be free from all earths yielding absorption bands excepting holmium. The atomic weight 97.7 showed a high yttrium content.

The oxides for this fractionation were dissolved in nitric acid and the hydroxides precipitated from a dilute hot solution by the addition of ammonium hydroxide. After being washed several times, the suspended hydroxides were added, a small portion at a time, to phthalic acid suspended in water. The phthalic acid was kept in excess to prevent the formation of an extremely insoluble basic compound. Meyer and Wuorinen[2] point out that, in order to secure the best separation, the concentration of the free phthalic acid should be such that hydrolysis will begin at about 50°. A small portion of the solution should be heated to determine the temperature at which the hydrolysis begins; if below 50°, more phthalic acid should be added, or, if above 60°, ammonium hydroxide should be added to neutralize the excess phthalic acid.

The phthalates, diluted so that there were about 10 g. of oxide for each liter of solution, were heated on a steam bath, the flask being shaken frequently to ensure uniform heating of the solution. For the first fraction, the temperature was raised gradually up to 50° and the basic phthalates were filtered off in the form of a flocculent precipitate. The precipitate was treated with nitric acid which liberated phthalic acid and gave a solution of the earth nitrates that could easily be filtered from the free acid. The earths were precipitated as oxalates and ignited to oxides. The second fraction was obtained by heating the solution at 62°. Six fractions in all were obtained by gradually raising the temperature of hydrolysis to 90°. The last fraction was precipitated by ammonium hydroxide. The atomic weight of each fraction was determined by the method of Gibbs.[3] The first 3 fractions had a value between 100.5 and 101.6, while the value in the last 3 fell off rapidly to 94.5 for the last fraction. This indicates some separation of holmium from yttrium.

In order to test the method further, Fractions 1 to 5, inclusive, were united to form Fraction C-b-1, while Fraction 7 constituted C-b-2. Each of these fractions was hydrolyzed in the manner described above except that only two fractions were obtained from each, a hydrolyzed

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[1] *Z. anorg. Chem.*, 80, 7 (1913).

[2] *Loc. cit.*

[3] *Am. Chem. J.*, 15, 546 (1893).

and an unhydrolyzed portion. The temperature was brought up to 85° or 87°. The hydrolyzed portion of C-b-1 became C-c-1, while the unhydrolyzed portion of C-b-1 and the hydrolyzed portion C-b-2 became C-c-2. The basic phthalate precipitate of the hydrolyzed portion of C-b-2 was treated with nitric acid, filtered from the phthalic acid, and precipitated with ammonium hydroxide. The washed hydroxides were dissolved in the unhydrolyzed portion of C-b-1, enough phthalic acid being used to secure solution. The unhydrolyzed portion of C-b-2 was converted to the oxide and weighed as C-c. These operations were continued by the method used by Baxter and Chapin in the purification of neodymium[1] and by Baxter and Stewart in concentrating praseodymium.[2] The principle involved in the method will be more easily understood by reference to the drawings of these authors.

Fraction C-d-3 was set out of the series as C-c-3 had been. The mean atomic weight of the four fractions in the last series, as well as the two fractions set out, showed a gradual decline from 107.7 to 92.3.

The original material used in this fractionation had an atomic weight of 97.7, or a holmium content of 12%, while the highest value obtained for the fractions corresponds to 25.4% holmium. The oxide of Fraction C-c-3 still retained a slight yellow color, while in a four-liter solution only one holmium line, $\lambda = 536$, was visible; C-e-1 was a light cream color, and the solution showed a strong holmium absorption.

Fractional Precipitation with Sodium Nitrite.

Hopkins and Balke[3] used, for the removal of both erbium and holmium from yttrium, a method suggested by Holden and James[4] which consists in a fractional precipitation by sodium nitrite from a dilute neutral nitrate solution. This method has also been used in this laboratory for the purification of erbium from yttrium,[5] and, because of the comparatively slight difference in the basicity of holmium and erbium, it was thought that the method could be applied to the purification of holmium from yttrium.

Material for this fractionation was obtained from the bromate series mentioned above. The oxide, approximately 100 g., was dissolved in nitric acid and the solution evaporated to drive off the excess acid. After dilution to about 8 liters, 60 g. of sodium nitrite, dissolved in a small volume of water, were added. The solution was heated as hot as possible on a steam bath and finally brought to boiling by passing in a vigorous blast of steam. Upon boiling for a few minutes a cloudiness and later

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[1] This Journal, 33, 1 (1911).

[2] *Ibid.*, 37, 516 (1915).

[3] *Ibid.*, 38, 2332 (1916).

[4] *Ibid.*, 36, 1419 (1914).

[5] Edward Wichers, *Doctor's thesis*, University of Illinois, 1917.

a rather granular precipitate formed that was easy to filter and wash. It was noticed that the steam escaping from the flask during the process of boiling had an acid reaction toward litmus, while the solution was slightly alkaline. The average time of boiling for each precipitation was one hour. The atomic weights showed a gradual decline from 98.1 for the first fraction to 88.7 for the ninth and 89.2 for the tenth fraction.

The atomic weight, absorption spectrum, and color showed Fraction 9 to be almost pure yttrium. It is supposed that the presence of some of the colored earths of the cerium group caused the color and slight increase in atomic weight in the last and most basic fraction. The atomic weight of the original material, 92.3, indicated a holmium content of about 4.8%, while the 98.1 of the first fraction shows that it is 12.5% holmium, an increase of 250% in holmium content.

The same method of fractionation was applied to the material of the same holmium content as that used in the fractional hydrolysis of the phthalates. As the series was smaller, 40 g. of sodium nitrite were used for the precipitation of each fraction, instead of the 60 g. of the larger series. Six fractions were obtained whose atomic weights varied from 103.3 in the first to 91.3 in the last fraction.

The atomic weight of the first fraction, 103.3, indicates a holmium content of 19.5%, the original material having 12%. The separation is not as rapid in this series as in the former, possibly because of the smaller sample.

This method of fractionation was also tried on 3 fractions of a bromate series described by Kremers and Balke.[1] The absorption spectrum of the combined fractions indicated the presence of holmium, dysprosium, praseodymium, and neodymium; the atomic weight, 128.3, showed that yttrium was present, while the light brown color of the oxide was probably due to the presence of a small amount of terbium.

This material was split into 7 fractions with atomic weights ranging from 143.7 in the first to 111.8 in the last. Sixty grams of sodium nitrite were added for the precipitation of each fraction. Fraction 1 was a cream color; the color increased in intensity to the light brown of Fraction 6; and Fraction 7 was a dark reddish brown, when ignited in the air, and a light gray when ignited in a stream of hydrogen. The absorption spectra revealed the presence of holmium, dysprosium, praseodymium and neodymium in all the fractions except the first, in which holmium and dysprosium alone could be detected. While Fraction 2 showed very faint lines of praseodymium and neodymium in its absorption spectrum, the intensity of the absorption lines increased progressively through the series. A concentrated nitrate solution of the last fraction was colored green and its absorption spectrum showed the presence of a rather large

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[1] This Journal, 40, 593 (1918).

amount of praseodymium. However, since Pr_4O_7 is black, the brown color of the oxide showed that terbium was present in large amounts. There was a change of 0.73% in the weight of the oxide before and after heating in a stream of hydrogen. Assuming all of the higher oxide found to be Tb_4O_7, it was calculated that there was present approximately 30% of terbium. The presence of a small amount of dysprosium in each of the fractions showed that holmium cannot be freed from dysprosium by this method.

The size of the holmium-rich fractions and the relative slowness of the concentration indicated that if reasonably pure holmium was to be obtained much larger amounts of material must be available. Accordingly this work is being continued with a large quantity of gadolinite hoping to secure holmium of atomic-weight purity.

Summary.

1. The purification of holmium is difficult because of its scarcity and close resemblance to dysprosium, on the one hand, and yttrium, on the other.

2. By means of 4 series of fractional hydrolysis of the phthalates the holmium content of a holmium-yttrium mixture was increased from 12% to 25.4%.

3. One series of fractional precipitation with sodium nitrite increased the holmium content 250% in material poor in holmium. The color of the oxide of the least basic fraction of a series containing holmium, dysprosium, praseodymium, neodymium, yttrium, and terbium, indicated that the terbium was about all removed and the absorption spectrum failed to reveal traces of either neodymium or praseodymium. The color of the oxide and absorption spectrum of the most basic fraction showed a concentration of terbium, praseodymium, and neodymium. Dysprosium cannot be removed by this method.

4. The fractional precipitation with sodium nitrite is considered the better of the two methods, (*a*) because the chemicals employed are cheaper, (*b*) because it is easier of operation, and (*c*) because an oxide of higher holmium content was obtained by one series of fractional precipitation with sodium nitrite than was obtained from material of the same atomic weight by one series of fractional hydrolysis of the phthalates.

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