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

TERBIUM.

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This element was first described by Mosander during his researches upon yttria, just previous to 1843, under the name of erbium. He stated that the oxide was orange-yellow and the salts colorless.

Later, several chemists, employing the fusion of the nitrate method, failed to obtain the original erbium of Mosander, so the name erbium was given to terbium, which gave a rose colored oxide.

Delafontain maintained the existence of old erbium, or terbium as it was now called. He recommended samarskite[1] as a source of terbium, and described the preparation of a terbia of a dark orange-yellow color. The salts prepared from it were said to be colorless and to show only a trace of the absorption of didymium.

Marignac[2] fractionated 300 g. of gadolinite earths and obtained three sets of oxides: white yttria, rose erbia, and intermediate oxides of a more or less deep yellow color. He separated the didymium from these and showed that the color must be due to a third gadolinite oxide originally mentioned by Mosander and later denied by Bunsen and Bahr, and Cleve and Hoglund. Marignac's terbia, purified by the potassium sulfate method and the oxalic acid method, consisted of a dark orange-yellow powder.

Cleve[3] confirms Marignac's conclusions with regard to the existence of terbia.

Lecoq de Boisbaudron[4] pointed out the complicated nature of terbium oxide. He said that it contained variable proportions of yttria, holmia, ytterbia, samaria, erbia and the yellow earth. Such material was submitted to many fractionations. The resulting products when tested by the spectroscope showed the possibility of the existence of three terbiums, which he designated by $Z\alpha$, $Z\beta$, and $Z\gamma$. $Z\beta$ gave a very deep reddish brown terbia. The solution of the chloride gave only a weak absorption spectrum composed of the bands of dysprosium and of a band which appeared to belong to a new element. The same band (λ487.7) appeared as strongly in the paler colored terbias, and he, therefore, concluded that it was due to another terbia which he provisionally named $Z\delta$. He was unable to fractionate further, since all the material was used up.

Boisbaudron[5] examined a sample of impure mosandria, and found that it consisted of yttrium α and terbia as Marignac had supposed.

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[1] *Ann. chim. phys.*, **14**, 238 (1887).

[2] *Ibid.*, 247.

[3] *Bull. soc. chim.*, **31**, 195 (1879).

[4] *Compt. rend.*, **102**, 153 (1886).

[5] *Ibid.*, 647.

Hoffmann and Kruss[1] showed that terbia (of this date, 1893), which cannot be split up further by means of the double sulfate or formate methods, may be fractionated by solution in aniline chloride.

Marc[2] worked upon terbium material, obtained by Weiss during the preparation of didymium from monazite by the chromic acid method of Muthmann and Bohm, and came to the conclusion that, although his terbia was colored deep brown, only a few per cent. of the element causing this was present. He also said that the solution of the oxide gave an absorption band $\lambda 464$–461.

Emma Portratz,[3] in a paper on terbium and some of its compounds, describes the oxide as being of a brownish orange color like some varieties of ocher.

Feit[4] worked on the yttrium earths from monazite and obtained a crude oxide, which he supposed contained about 12% of terbia.

Urbain,[5] by three different methods of fractionation, obtained a dark colored earth between gadolinium and dysprosium, whose solutions showed the absorption band $\lambda 488$. He kept, provisionally, the name $Z\delta$, given by Boisbaudron to the element possessing this property. The results of Marc were not duplicated. The latter stated that the salts of terbium possessed a pink color, while Urbain showed that a common colored impurity of terbium was dysprosium. The compounds of this latter element communicate a green tint to those of terbium. Urbain obtained about 100 g. of the crude dark oxides. This material was submitted to a further long and careful fractionation,[6] which gave 7 g. of an oxide, that could not be divided by continued fractionation. It gave a dark brown oxide by ignition of the oxalate, and a black oxide when the sulfate was calcined at 1600°. The oxide corresponded to the formula Tb_4O_7. The solution of this oxide showed the absorption spectrum of $Z\delta$, the inverse spectrum of $Z\beta$, the spark spectrum of Demarcay's Γ, and the phosphorescent spectrum of a meta element of yttrium and to $G\beta$ (Crookes). The atomic weight was found to be 159.22.

Urbain[7] states that Boisbaudron's $Z\alpha$ is identical with dysprosium.

Urbain and Jantsch,[8] in describing some new compounds of terbium and dysprosium, state that terbium can be weighed as the oxide Tb_4O_7 if it has not been heated to too high a temperature.

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[1] *Z. anorg. Chem.*, **4**, 27 (1893).

[2] *Ber.*, **35**, 389 (1902).

[3] *Chem. News*, **92**, 3 (1905).

[4] *Z. anorg. Chem.*, **43**, 267 (1905).

[5] *Compt. rend.*, **139**, No. 19 (1904).

[6] *Ibid.*, **141**, No. 12 (1905).

[7] *Compt. rend.*, **143**, 229 (1906).

[8] *Ibid.*, **146**, 127 (1908).

Urbain[1] concludes among other things that the elements Γ of Demarcay, Zβ and Zδ of Lecoq de Boisbaudron, Gβ, ionium, and incognitum of Sir William Crookes are identical with terbium.

Welsbach[2] fractionating the yttrium earths by means of the double oxalates with ammonium oxalate, observed that terbium was distributed between the gadolinium and dysprosium fractions. He said that the separation was tedious, but might be carried out satisfactorily. On each side of the terbium the fractions were colored deep ocher; also they gave no optical test for terbium. From this he concluded that old terbia consisted of three elements, which he provisionally named TbI, TbII and TbIII. TbI was closely related to gadolinium, and TbIII to dysprosium.

Separation.—The methods used originally gave an oxide containing only a few per cent. of terbium oxide. These processes include: fusion of the nitrates; precipitation by potassium sulfate; precipitation of oxalates from a strongly nitric acid solution; the formic acid method.

When the nitrates are partially decomposed by heat, poured into water, boiled until clear and allowed to cool and crystallize, the least basic element separates first in the form of a crystalline basic nitrate. This method is not to be recommended for the extraction of terbium.

Terbium potassium sulfate and terbium sodium sulfate are very much less soluble than the corresponding double sulfates of yttrium and erbium, etc. They are more soluble than those of the cerium metals. Owing to the similar solubilities of the double sulfates of gadolinium and dysprosium, and also to the fractional precipitation nature of the method, it is very tedious.

The fractional precipitation of the oxalate from a highly acid solution of the nitrate is practically useless.

Terbium formate is very much less soluble than yttrium formate, and the formates might be used for the separation of yttrium and terbium, if it were not for the fact that they form a double compound. Philippium formate was found to be yttrium terbium formate.

Later, Boisbaudron recommended the use of very dilute ammonium hydroxide. Urbain says this method is very tedious. He advises the following: fractional crystallization of the double nitrates with nickel; fractional crystallization of the simple nitrates in the presence of bismuth nitrate; fractional crystallization of the ethylsulfates.

The double nickel nitrate method[3] gave gadolinium nickel nitrate, in a very pure state, as the least soluble portion. The most soluble fractions gave very dark colored oxides, whose solutions showed a strong spectrum of dysprosium, a feeble spectrum of holmium, and an almost

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[1] *Chem. News*, **100**, 73 (1909).

[2] *Chem. Ztg.*, **35**, 658.

[3] Urbain, *Compt. rend.*, **139**, No. 19 (1904).

imperceptible band of Zδ. These solutions possessed an olive color. The middle fractions gave oxides, paler in color, and the solutions when examined by the spectroscope revealed only the band belonging to Zδ.

The Fractionation of the Simple Nitrates in the Presence of Bismuth Nitrate.—Urbain found that the solubility of bismuth nitrate in nitric acid to be greater than the solubility of gadolinium nitrate, but less than that of dysprosium. Since bismuth nitrate is isomorphous with the nitrates of the rare earths, it would accumulate with the terbium and enlarge the amount of material, thus making it easier to carry on the fractionation. The above chemist found, after a careful study, that bismuth nitrate is less soluble than the nitrate of terbium. However, he was unable to separate quantitatively terbium from gadolinium, as he had done with europium and samarium by the addition of bismuth magnesium nitrate. Bismuth was separated from the terbium fractions by means of hydrogen sulfide. The terbium was then precipitated by the addition of a solution of oxalic acid.

Fractionation of the ethylsulfates rapidly separates terbium from most of the yttrium earths. This method has been extensively used by Urbain and Lacombe.

The authors, after due consideration, came to the conclusion that the only methods worth trying were the last three. The double nickel nitrate method must be a very good one, since, by it, Urbain obtained a pure white gadolinia. This process was tried, and some difficulty was encountered in the crystallizations. It requires considerable experience in order to get good crystals. It is also unfortunate that the liquid is so highly colored, for it prevents observations being made with regard to changes in color of the earth solutions themselves. In addition the absorption spectra cannot be studied.

The crystallization of the simple nitrates was not tried, since it does not work anything like as rapidly as the bromate method. The ethylsulfates are useful. It is a very great pity that they are so readily hydrolyzed.

The material, for the extraction of terbium oxide, consisted of gadolinium oxide containing terbium oxide. There were also present certain amounts of dysprosium and holmium oxides and traces of those of yttrium and erbium. The whole was converted into bromates by warming with bromic acid. The bromates so obtained were submitted to a long and careful fractionation.

After a few series of operations, the whole of the terbium and most of the holmium and dysprosium were found to be in the most soluble portion. As the work proceeded, a faint absorption band appeared in the blue, when the least soluble fraction was examined by means of the spectroscope. This was due to small amounts of europium, which showed that europium bromate was less soluble than gadolinium bromate.

Europium bromate would, therefore, appear to possess the lowest solubility of all the rare earth bromates. The solubility first of all decreases as we go up the series in the following order: lanthanum, cerium, praseodymium, neodymium, samarium, europium. After europium has been reached, the solubility commences to increase again in this manner: europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, lutecium, celtium, and scandium.

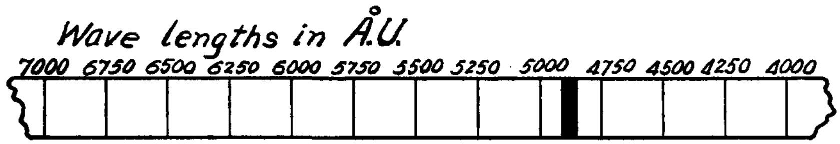
By the time a considerable number of series of operations had been carried out, the colors of the oxides of the fractions were observed to show very much light upon the rapidity of fractionation. The least soluble—gadolinium bromate—gave a nearly white oxide. All gadolinium was removed from the series, as soon as it gave an almost white oxide. With increase of solubility the color of the oxides rapidly changes. They became darker and darker until a maximum was reached, after which the colors became paler. The most soluble fractions gave a buff colored oxide. These portions were removed when this condition had been attained. From these results it can be seen that terbium is rapidly separated from gadolinium by means of the bromate method. The separation of terbium from dysprosium is not as simple as in the case of the previous element. Perhaps the ethylsulfates would be the best salts to use for this portion of the work. The results of the application of this method will be described later on.

The fractions that gave the darkest colored oxides showed only one absorption band—that of $Z\delta$ or terbium. The more soluble portions of the terbium showed the absorption bands of dysprosium in addition, while the less soluble portions gave very faint neodymium bands, the latter indicating the fact that neodymium bromate comes between the bromates of terbium and gadolinium. It would, therefore, be reasonable to conclude that by the careful use of neodymium the separation of terbium and gadolinium could be carried out quantitatively. Neodymium can, of course, be readily separated from terbium by many well known methods, such as by crystallizing the double magnesium nitrates with bismuth magnesium nitrate. Only three or four operations are necessary. Neodymium magnesium nitrate passes into the least soluble fractions, since it is practically insoluble in bismuth magnesium nitrate. The bismuth magnesium compound comes next, while the terbium magnesium nitrate collects in the mother liquor.

A statement, made somewhat recently, by another worker with regard to the bromate method, led one to understand that there was considerable difficulty in separating yttrium from gadolinium. Yttrium bromate comes between the bromates of erbium and holmium with regard to their solubilities. It will, therefore, naturally tend to divide itself into two portions, one accompanying the erbium and the other the holmium and dysprosium. Therefore as soon as a fraction, less soluble than dysprosium, no longer gives the dysprosium absorption spectrum, it is free from yttrium. Since, in addition, terbium and neodymium come between dysprosium and gadolinium, the separation of yttrium and gadolinium must be extremely good. When we have a fraction containing yttrium more soluble than holmium and free from the absorption bands of this element, it is free from gadolinium.

The original bromates used in this work comprised many kilograms. As large amounts of gadolinium bromate were, however, rapidly removed from one end, and fair quantities of the bromates of erbium, yttrium, holmium, and dysprosium from the other, the bulk of material undergoing fractionation quickly decreased. The whole of the erbium was removed in the most soluble portion after a few crystallizations. This was followed by yttrium and holmium with some dysprosium. Finally the holmium bands became very faint, and later dysprosium, with a little terbium, formed the most soluble fractions of the series.

By this time the fractions had become reduced to about 10 g. in each. About 30 g. of very pure terbium oxalate, giving a black oxide, were obtained. Thirty grams of an oxalate not quite so pure were also separated.



Visible absorption spectrum of terbium.
Concentrated solution of $Tb(NO_3)_3$

D.W.B.

The crystallization of the chlorides from hydrochloric acid was used in the endeavor to separate small amounts of terbium from dysprosium. The chlorides formed very nice crystals, and the mother liquor could easily be drained off. The rate of fractionation seemed to be about the same as in the case of the nitrates. The oxide from the least soluble was darker than that from the most soluble portion. This showed that terbium chloride like terbium nitrate passed into the least soluble fractions.

When a mixture of gas and air was directed upon terbium peroxide, or upon gadolinium oxide containing terbium peroxide, heated almost to redness, the mass immediately became incandescent, and the gas usually took fire.

A strong solution of terbium nitrate gave an absorption spectrum consisting of one band in the blue as shown in the figure on preceding page.

The authors conclude from their results that there is only one terbium. By means of the bromate process, terbium is comparatively rapidly separated from gadolinium; and neodymium, if present, comes between the two. This work agrees with that of Urbain and not with that of von Welsbach.

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THE RADIUM : URANIUM RATIO IN CARNOTITES.[1]

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I. Introduction.

The constancy of the ratio of radium to uranium in the uranium minerals, and its significance in the theory of the origin of radium have been recognized for some time. For its experimental demonstration we are indebted to the early work of Boltwood,[2] Rutherford,[3] Strutt,[4] McCoy,[5] and Eve.[6]

At a somewhat later period it began to be recognized that certain uranium minerals of secondary origin, of which autunite ($Ca(UO_2)_2(PO_4)_2.8H_2O$) is one of the chief representatives, show a ratio below that of pitchblende. In 1909, Mlle. Gleditsch[7] announced that she had found a sample of French autunite showing only about 80% of the normal ratio. A low ratio was confirmed in 1910 by A. S. Russell,[8] who, also in a sample of French autunite, found only 27% of the normal ratio, while Soddy and Pirret,[9] about the same time, found a sample of Spanish autunite with 44.5% of the pitchblende ratio.

To account for these low ratios in a sense consistent with the Rutherford and Soddy theory of radioactivity, two different explanations have been proposed. The first supposes that the secondary minerals are too young for the quantity of radium to have accumulated to the maximum equilibrium value shown in the older minerals such as pitchblende. The second mode of explanation assumes that the secondary minerals, owing to a looser mechanical structure, are more subject to a *leaching process* by water and that radium is more readily removed than uranium, which results in a low ratio of the former to the latter.

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[1] Published by permission of the Director of the Bureau of Mines.

[2] Boltwood, *Phil. Mag.*, **9**, 599 (1905); *Am. J. Sci.*, **18**, 97 (1904); **25**, 269 (1908).

[3] Rutherford and Boltwood, *Am. J. Sci.*, **20**, 55 (1905); **22**, 1 (1906).

[4] Strutt, *Proc. Roy. Soc. Lond.*, (*A*) **76**, 88 and 312 (1905).

[5] McCoy, *Ber.*, **37**, 2641 (1904); THIS JOURNAL, **27**, 391 (1905).

[6] Eve, *Am. J. Sci.*, **22**, 4 (1906).

[7] Mlle. Gleditsch, *Compt. rend.*, **148**, 1451; **149**, 267 (1909).

[8] A. S. Russell, *Nature*, **84**, 238 (1910).

[9] Soddy and Pirret, *Phil. Mag.*, **20**, 345 (1910); **21**, 652 (1911).