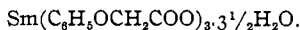
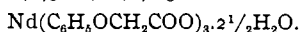


Calculated: Y, 14.71; C, 47.58; H, 4.66. Found: Y, 14.66; C, 47.80; H, 4.50.

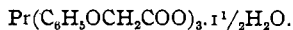
The *phenoxyacetates* of *Sm*, *Nd*, *Pr*, *La* and *Ce* were prepared in exactly the same manner as the yttrium salt. They were, however, much more insoluble than the latter and therefore could not be recrystallized from water.



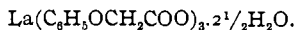
Calculated: Sm, 22.57; C, 43.20; H, 4.23. Found: Sm, 22.61; C, 43.30; H, 4.03.



Calculated: Nd, 22.47. Found: Nd, 22.51.



Calculated: C, 46.38; H, 3.90. Found: C, 46.14; H, 4.03.



Calculated: La, 21.82. Found: La, 21.83.



Calculated: Ce, 23.63. Found: Ce, 23.88.

*Thorium Phenoxyacetate*.—By working with a neutral solution of thorium, the authors found, on the addition of an excess of phenoxyacetic acid, that the thorium was almost quantitatively precipitated. On the other hand, the rare earths behave very differently and are not thrown out of solution, even though a great excess of the acid be added.

This reaction of phenoxyacetic acid on a *neutral thorium* solution affords a method for the separation of this element from the rare earths.

DUREAM, N. H.

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

## THULIUM I.<sup>1</sup>

BY C. JAMES

Received June 11, 1911.

Thulium was discovered by Cleve<sup>2</sup> in 1879 while trying to separate the element that gives a rose color to the salts of "old erbium." The earths used for this investigation consisted of some material obtained by Nilson while working upon ytterbia. These residues were separated during the use of "the fusion of the nitrate method" and consisted of those portions which were less basic than yttrium but more basic than ytterbium.

Cleve submitted this crude erbia to another long series of fractionations by again fusing the nitrates. This work yielded more basic, intermediate and least basic portions. Thalen examined these fractions spectroscopically for Cleve and showed that old erbia consisted of at least three elements. To the more basic part, which accompanied yttria, Cleve gave the name holmium, and to the least basic, the name thulium, derived

<sup>1</sup> Abstract given before the New York Section, March 10th.

<sup>2</sup> *Compt. rend.*, Sept. 1, 1879.

from Thule, the old name of Scandinavia. In this paper the oxide of thulium was said to be of a light rose color.

Soret<sup>1</sup> stated that he had observed differences in the absorption spectrum of various fractions of erbium supplied to him by Marignac, and, in the case of holmium, he had provisionally named this element X, as it appeared almost impossible to separate it. In addition it was well known that certain conditions somewhat modified the spectra.

Lecoq de Boisbaudran<sup>1</sup> was of about the same opinion as Soret. He maintained, however, that the thulium red band was rather broader than the ordinary red band of erbium.

Cleve<sup>2</sup> separated 1 ore of the oxide and found it to be white, while its solutions in acids gave colorless salts, which showed two absorption bands, one in the red and one in the blue, the blue band being broad only when the solutions were very concentrated. This material gave an atomic weight of 170.7.

Thalen<sup>3</sup> examined Cleve's purest thulium, which in solution in the form of the nitrate was nearly colorless. It gave a weak erbium absorption spectrum, brilliant lines belonging to ytterbium and about 15 new lines due to thulium. He said: "It seems that a new metal exists, though it must be admitted that it has not yet been separated from ytterbium and erbium."

Lecoq de Boisbaudran<sup>4</sup> recorded the presence of thulium in some fractions.

Krüss and Nilson, in 1887,<sup>5</sup> concentrated thulium, during some of their investigations upon rare earth minerals, so that the absorption bands were stronger than those of erbium. Finding in some solutions that the absorption bands did not show the same relative intensities, they came to the conclusion that thulium consisted of at least two elements: Thulium  $\alpha$ , the one giving the band  $h$  684.0, and thulium  $\beta$ , for the one giving the band  $h$  465.0. It is doubtful whether these chemists realized that concentration, acidity, etc., might modify the spectrum, as had been pointed out by some earlier workers.

Crookes,<sup>6</sup> in a paper on the rare earths, described a lot of spectroscopical researches in which a figure for the absorption spectrum of thulium was shown.

Krüss, in 1893,<sup>7</sup> obtained some fractions rich in thulium.

<sup>1</sup> *Compt. rend.*, Sept. 15, 1879.

<sup>2</sup> *Ibid.*, Aug. 9, 1880.

<sup>3</sup> *Ibid.*, Aug. 16, 1880.

<sup>4</sup> *Ibid.*, Sept. 7, 1885.

<sup>5</sup> *Ber.*, 20, 2134.

<sup>6</sup> *Chem. News*, 60, 39.

<sup>7</sup> *Ibid.*, 68, 148.

Astrid Cleve,<sup>1</sup> during the preparation of some ytterbium material, supposed that a violet color of certain fractions of fused nitrates was due to thulium; she also stated that this element was eliminated only with difficulty from ytterbium.

R. Marc,<sup>2</sup> in a communication on terbium, was of the opinion that thulium was a mixture of ytterbium and yttrium containing varying quantities of holmium and terbium.

C. Auer v. Welsbach,<sup>3</sup> describing a new method for the separation of the ytterbium earths, mentioned the fact that thulium concentrated between erbium and ytterbium, the thulium bands being of greatest intensity in the solutions colored only faintly pink.

About this time the author,<sup>4</sup> working with solutions of the rare earth oxalates in ammonium carbonate, observed that thulium concentrated in the more soluble fractions along with "ytterbium" and some erbium.

Bettendorff<sup>5</sup> considered that the rose color of erbium salts was due to thulium, since he found that the brighter the rose color, the stronger the bands of thulium.

Urbain,<sup>6</sup> in describing the separation of the element lutecium, stated that in fractionating old ytterbium, thulium separated in the least soluble portions.

The writer,<sup>7</sup> giving a new method for fractionating the rare earths, noticed that thulium could be rapidly concentrated in the bromate fractions between erbium and "ytterbium."

Hoffmann and Bürger,<sup>8</sup> when purifying Nilson and Krüss's erbium, found that dilute ammonium hydroxide removed thulium in addition to the ytterbiums.

Urbain<sup>6</sup> mentions the fact that the atomic weight of thulium is not above 168.5.

### Extraction.

Since thulium is very rare, it is absolutely necessary to commence with very large amounts of material. In this work the following minerals have been employed: Brazilian monazite (yttrium earths, derived from Brazilian monazite); xenotime; ytterspar (Norwegian xenotime, impure); euxenite; fergusonite (Norway, etc.); yttritanite; sipylite (columbate from Northern Norway); gadolinite (Norway and Sweden); also large amounts of oxalates from more soluble double potassium sulfates from

<sup>1</sup> *Z. anorg. Chem.*, **32**; *Chem. News*, **86**, 248.

<sup>2</sup> *Z. anorg. Chem.*, **27**, 304.

<sup>3</sup> *Monatsh.*, [8] **27**, 935.

<sup>4</sup> *THIS JOURNAL*, **29**, 495.

<sup>5</sup> *Ann.*, **352**, 88; *Chem. News*, **96**, 249.

<sup>6</sup> *Compt. rend.*, **145**, 759 (1907).

<sup>7</sup> *THIS JOURNAL*, **30**, 182; *Chem. News*, **97**, 61.

<sup>8</sup> *Ber.*, **41**, 308.

Carolina monazite, supplied by the Welsbach Co. through the kindness of Dr. H. S. Miner.

The best sources were found to be ytterspar, euxenite, and a columbate from an island in the north of Norway. Gadolinite varied very considerably, some varieties being fairly good, while most were rather poor in the erbium earths. Fergusonite contains only a very little of the desired elements. Yttrotitanite is very troublesome to work up. A specimen of samarskite, presented to the author recently by Prof. F. J. Metzger, Columbia University, was found to resemble euxenite with regard to its content of erbium metals. The details of the processes for the extraction of the mixed rare earths from the various minerals were as follows:

1. *Euxenite*.—The material was very finely ground and mixed with an excess of strong sulfuric acid in iron pots of about two gallons capacity. The mixture was then carefully heated until it frothed considerably, after which it was removed from the furnace and stirred rapidly, at which time a vigorous reaction took place. As soon as the evolution of gas began to slacken, the vessel was replaced in the furnace in such a manner that only hot gases from the fire could play upon it, in order that the sulfuric acid might not evaporate too rapidly. When the mass became hard, the iron pot was moved to a much hotter position and kept there until the excess of acid had been driven off. The furnace used was capable of taking four of these iron vessels at one time.

When the operation was successful, the residue had risen, very much like a cake during the baking process, and when in this condition was very readily removed by means of a hammer and chisel. If the operation was not successful, which was usually the case when the pot was left out too long, the whole settled down to a very hard mass which was only removed with great difficulty, so much so that the cast iron vessels were often broken. With very little practice the correct conditions were readily established. The decomposed mineral was powdered, placed in a churn containing water, the churn closed and the contents well agitated.

When the solution was completed, the churn was emptied into a tub and the latter allowed to stand for about twelve hours. After this period had elapsed, the metallic acids were found to have settled so that the clear supernatant liquid could be syphoned off and the rare earths precipitated by means of oxalic acid. The thick mass of columbic acid, etc., remaining at the bottom of the barrel was thrown upon a linen filter and washed with water. Washing by decantation was also very effective.

Sometimes, when the mineral had not been finely pulverized, the decomposition was not complete. In this case the residue was stirred with water and allowed to stand for a short time, after which the liquid, still containing the mineral acids in suspension, was run off from the

dense, undecomposed euxenite. The latter owing to its density rapidly settles. This coarser material was dried, reground and again worked up. The columbic and tantalic acids were allowed to deposit and the wash water was employed for the solution of more sulfated mineral.

Earthenware vessels were used for the precipitation. (These can be obtained in various sizes. Those possessing round bottoms can be heated by means of steam or calcium chloride baths.)

*Fergusonite and Samarskite.*—As fergusonite appeared to contain only small amounts of the erbium earths, and, since samarskite resembled euxenite, the writer did not operate upon more than several kilograms. The methods used to attack these substances were: (a) By boiling with sulfuric acid containing some potassium sulfate so as to increase the temperature. (b) Hydrofluoric acid.

When using sulfuric acid and potassium sulfate it was found necessary to stir well during the hardening, as otherwise the whole solidified to a cement-like mass. The result of the reaction after powdering was treated with ice-cold water, filtered and the clear filtrate precipitated with oxalic acid.

The hydrofluoric acid method was found to be an excellent one, inasmuch as the mineral need not be so finely ground. However, the cost was a great drawback, to obviate which the author prepared the acid on a large scale by using a capacious iron retort fitted with a leaden cover. The condenser consisted of a large lead pipe running through a barrel of water. The top of the condenser was so formed that water could drip in a sufficient quantity to form a concentrated, fuming acid.

*Columbates.*—Some columbates are attacked only with great difficulty by sulfuric and hydrofluoric acids while they are very rapidly decomposed by means of sodium hydroxide in the fused condition.

The mineral used resembled sipylite. It was much richer, however, in rare earths, since it contained about 43 per cent.

## ANALYSIS.

$\text{Cb}_2\text{O}_5$ (trace $\text{Ta}_2\text{O}_5$ ) . . . . .	42.42
$\text{SiO}_2$ . . . . .	4.27
$\text{WO}_3, \text{SnO}_2$ . . . . .	0.37
$\text{ZrO}_2$ . . . . .	0.41
Cu group . . . . .	1.38
$\text{U}_3\text{O}_8$ . . . . .	1.40
$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$ . . . . .	1.55
Yttrium earths . . . . .	39.91
Cerium earths . . . . .	3.57
$\text{ThO}_2$ . . . . .	1.10
$\text{CaO}$ . . . . .	1.25
$\text{MgO}$ . . . . .	0.07
Loss upon ignition ( $\text{H}_2\text{O}$ , He, etc.) . . . . .	2.00

---

 99.70

This mineral, which was of a reddish brown color, came from an island in the north of Norway. It possessed endothermic properties, since upon heating it soon began to glow. This glow rapidly passed through the mass. After cooling, it was observed that the mineral had become yellowish, more opaque, and could easily be powdered. Its sp. gr. before heating was 5.30 and after heating 4.62. The atomic weight of the yttrium earths was found to be about 110.2.

The analysis and other determinations were carried out very carefully by Mr. H. P. Corliss, to whom the author wishes to express his thanks.

In order to separate the earths, the mineral was first ignited, powdered, mixed with twice its weight of sodium hydroxide and carefully fused for about two hours. The liquid mass was then poured upon an iron plate. The cold melt was next broken in pieces and allowed to stand in contact with water, until it assumed the appearance of mud. It was then mixed with hot hydrochloric acid and the whole heated upon the water bath.

The columbic acid, etc., was then filtered off and the rare earths precipitated by means of oxalic acid.

*Yttrotitanite*.—Hydrochloric acid was used for attacking this substance. The mineral was finely powdered and heated with the acid for a considerable period. The acid liquid was filtered and the small amount of rare earths present precipitated as the oxalates. A large excess of acid was always avoided.

*Ytterspar*.—(Impure Norwegian xenotime.) The best method for decomposing this mineral was found to be as follows:

Sodium hydroxide was mixed with a little less than half its weight of water in an iron pot, the temperature raised to the boiling point and powdered ytterspar, equal in weight to the sodium hydroxide employed, was added. It was then stirred until the charge solidified, after which the temperature was raised to a low red heat. The result of the reaction was very friable and readily removed from the containing vessel. The crumbled material was mixed with water, boiled and filtered. The hydroxides, titanitic acid, gangue, etc., remaining upon the filter were well washed with boiling water. The green filtrate usually became thick, owing to the mass of crystals (phosphates) which separated as the liquid cooled. The hydroxides were treated with a slight excess of hydrochloric acid, the solution was filtered and the earths were separated by the use of oxalic acid.

*Gadolinite* was decomposed by heating with hydrochloric acid. The earths were obtained in the usual well-known way.

As the ytterspar earths contained only a very little of the elements of the cerium group, they were converted directly into the bromates in the following manner:

The crude oxides, obtained by igniting the oxalates, were dissolved

in hydrochloric acid, the solution diluted, filtered, and precipitated by oxalic acid. The oxalates were converted into sulfates by the action of concentrated sulfuric acid. The anhydrous sulfates were dissolved in cold water. The solution was then poured upon barium bromate covered with a layer of water and heated upon the water bath.<sup>1</sup> When the decomposition was complete, the barium sulfate was filtered off and the bromates fractionally crystallized.

The earths from euxenite, gadolinite, etc., which contained members of the cerium group, were first subjected to the sodium sulfate treatment.<sup>2</sup> After separating the insoluble double sulfates, the solution was precipitated by means of oxalic acid and the yttrium earth oxides, obtained by igniting the oxalates, were converted into bromates in a similar manner to the crude ytterspar oxides described above.

After the bromates had been fractionated for some time<sup>3</sup> it was found that nearly all the erbium had accumulated in the more soluble fractions, nearly all of which were quite free from the absorption bands of holmium and dysprosium. Since terbium was less soluble than dysprosium, and since the oxide had the pure rose tint of erbium, it was evident that the material was quite free from the terbium. The separation of ytterbium and lutecium from erbium was found to be very rapid. Five crystallizations of a mixture of erbium, thulium, ytterbium and lutecium, which possessed a fine rose color together with a strong erbium absorption spectrum, left most of the material in the mother liquor as a colorless liquid. The absorption bands of erbium and thulium were very faint, when observed through a saturated solution 5 cm. thick.

Thulium separated fairly rapidly and collected in the fractions between erbium and ytterbium as the crystallization was continued. Whenever the thulium bands became intense, the fraction was placed aside until no more would separate from the series. The less soluble fractions consisted of erbium with some yttrium.

The more soluble portion was then taken and again submitted to fractional crystallization. This portion was nearly colorless. It showed the absorption bands of thulium together with a very weak spectrum of erbium. It was apparent that by far the greater portion consisted of ytterbium and lutecium with perhaps traces of scandium. Of this crude material there was nearly three kilograms. The work was carried out in a room that possessed a fairly constant temperature of about 60° F.

<sup>1</sup> THIS JOURNAL, 30, 182.

<sup>2</sup> In using sulfate of sodium in place of sulfate of potassium care must be taken not to employ a great excess, otherwise some of the yttrium earths will be precipitated also. Yttrium sodium sulfate is rapidly decreased with regard to its solubility after the concentration of the sodium sulfate has reached a certain point. This problem has been partly studied, and the solubility curve, etc., will be published shortly.

<sup>3</sup> THIS JOURNAL, 30, 990.

Higher temperatures were not suited for the work, since they tended to prevent crystallization, of the more readily soluble fractions.<sup>1</sup> Casseroles were the vessels employed and the concentration was so gauged that the major portion separated in the crystallin form.

Since the more soluble bromates crystallize rather sluggishly, they were first crystallized once a day. However, when the most soluble portion had been removed, two operations could be carried out daily.

Because the salts form supersaturated solutions with extreme ease, it was absolutely necessary to start the crystallization with a crystal.

During the first few series of operations, erbium rapidly separated leaving the more soluble portions colored greenish. As the work proceeded, thulium concentrated in the fractions next to the least soluble erbium. When the mother liquors were found to be free from thulium they were placed aside. The color shown by these bromates in solution was of a yellowish green, which was afterwards found to be due to copper. Scandium occurred in these fractions in the merest traces only. This latter element was more inclined to separate with the erbium. This was, perhaps, due to the fact that the solutions became slightly basic. After all copper and other impurities had been removed, the fractions, more soluble than thulium, became colorless and formed good crystals.

The most interesting portion of the series was where the thulium accumulated. When free from erbium the solutions possessed a bluish green color. After sixteen weeks of this stage of the fractionation the colors of the various fractions, from the least soluble to the most soluble, were rose, yellow, bluish green, colorless and finally those colored yellowish green (copper). The yellow tint was due to admixture of erbium and thulium.

When the fractions became too small to recrystallize from water, a mixture of alcohol and water was used with good results.

After continuing the work it was observed that the thulium fractions did not change in color, simply remaining of a greenish tint when in solution. The presence of a very little erbium has a marked influence upon this color, since a trace turns it yellowish green, a little more renders it colorless and further addition pink. As the fractionation progressed it was evident that the alcohol was being slowly attacked by the bromates. This decomposition increased; the liquids became colored and smelled strongly of bromine and ethyl acetate. At this point the fractions were united according to color and precipitated as the oxalate. The oxalate was of a very pale green tint when moist. Artificial light increased this tint so that it became a delicate pale green color. The oxide, ob-

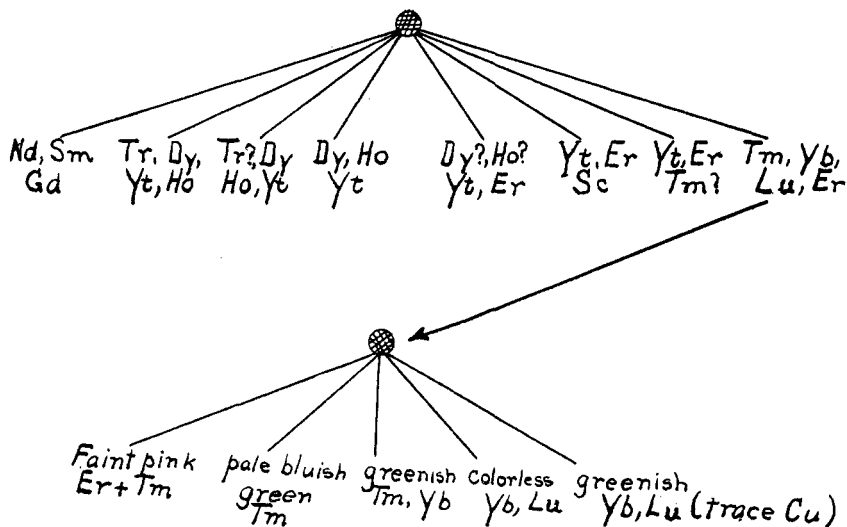
<sup>1</sup> The bromates should be free from impurities, since metals, which form bromates not isomorphous with the rare earths, cause the formation of tiny crystals so that it is practically impossible to drain off the mother liquor.



tained by igniting this oxalate, also showed this green tint and yielded a carmine glow, when heated carefully by a Bunsen burner.

The extraction of thulium commencing with the crude ytterbium earth bromates will be better understood by the following diagram:

CRUDE YTTRIUM EARTH BROMATES.



Some thulium oxide, containing ytterbium, was dissolved by heating with concentrated nitric acid for a short time, a large excess of concentrated nitric acid added and the boiling liquid fractionally precipitated by means of a boiling saturated solution of oxalic acid. Oxalic acid was added until a permanent precipitate formed, when the liquid was well stirred and cooled. The crystalline oxalate was removed by filtration and the filtrate again heated and treated with more oxalic acid solution and so on. The final mother liquor was evaporated nearly to dryness, taken up with water and all earths thrown out as oxalates.

After a number of series of precipitations had been carried out, some of the oxides from the first and last fractions were dissolved in concentrated hydrochloric acid and the spark spectrum photographed. The negatives obtained showed that there had been practically no fractionation, as the lines were identical in relative intensities.

The picrates were next tried. Thulium oxide similar to that used for the previous experiment was converted first into the hydroxide and then into the picrate. The solution of the picrate was then evaporated and fractionally crystallized. After six series, the first and last fractions were compared by the use of a spectrograph. The photograph showed scarcely any change in the lines.

One of the least soluble thulium bromate fractions, which contained a little erbium, was converted into the oxalate. This oxalate was fractionated by the oxalate-carbonate method. The results showed that this procedure was not rapid enough to be of any value.

In addition to these methods several others were tried, but none could be compared with the bromate method.

Since yttrium bromate comes between the bromates of praseodymium and neodymium, with regard to their solubility in water, and because the bromate of praseodymium is more soluble than the corresponding compound of yttrium,<sup>1</sup> it was considered that by crystallizing a mixture of erbium, thulium and praseodymium bromates, praseodymium would come between erbium and thulium. An experiment along this line showed that praseodymium rapidly accumulated in the least soluble fraction. However, by gradually feeding this substance through the most soluble fractions, they were kept larger and the erbium was swept out. Owing to the rapidity, with which praseodymium separated from erbium, it was thought advisable to try a mixture of the bromates of yttrium and praseodymium carrying small amounts of erbium and neodymium. The results were surprising, as the praseodymium again appeared in the fractions less soluble than yttrium. According to the solubilities, as previously mentioned, yttrium should be more soluble than neodymium but less soluble than praseodymium. The solubilities had been determined at 25°, while the crystallizations had been carried out at room temperature. The solubilities of lanthanum bromate and praseodymium bromate in yttrium bromate solution will be studied at the earliest opportunity.

A specimen of the purest thulium so far obtained by the bromate method was sent to Sir William Crookes who examined it by means of the spectrograph. He said: "Spectroscopic analysis shows very good thulium, and a trace of ytterbium. Only a very faint trace of calcium is present." The writer is extremely grateful to Sir William Crookes for his kindness in testing this and many other specimens.

These purest fractions were again converted into the bromate and fractionated first from water solution and then from aqueous alcohol. Later, a mixture of methyl and ethyl alcohols was tried. By employing methyl alcohol in place of water it was hoped that the decomposition of the bromates would be prevented. After working for a short time the liquid became colored, and a crystalline compound, insoluble in the mixed alcohols, was deposited. This compound was soluble in water, and evolved bromine when acidified with hydrochloric acid.

The various fractions were mixed according to their purity, the purest product being reserved for a determination of the equivalent,

<sup>1</sup> THIS JOURNAL, 31, 913.

which will form the main subject of the next paper on thulium. The fractions not quite so pure were used for the preparation of many compounds, some of which are given below.

The most important point proved by this work is that the element, giving the characteristic absorption bands of thulium, cannot be separated into simpler substances. After about 15,000 operations the absorption spectrum underwent no change.

### Compounds of Thulium.

*Thulium Oxide,  $Tm_2O_3$* , was prepared by igniting the oxalate. It forms a dense white powder with a faint green tint. This oxide dissolves slowly, if heated with strong acids, and, when carefully made to incandesce, emits a carmine colored glow.

Thulium hydroxide as usually obtained forms a precipitate which settles very readily, and filters nicely even when thrown down in the cold. This compound dissolves easily in dilute acids.

*Thulium Bromate,  $Tm_2(BrO_3)_6 \cdot 18H_2O$* , was obtained by decomposing barium bromate, covered with water, and heated upon the water bath, with a solution of thulium sulfate. As soon as the supernatant liquid failed to give a test for sulfuric acid, the barium sulfate was filtered off, and the filtrate concentrated. As the liquid cooled, the salt separated in pale, bluish green prisms belonging to the hexagonal system, and isomorphous with the other rare earths.

The bromate was obtained in nice small crystals by pouring a saturated solution into an excess of 95 per cent. alcohol. After standing a short time the liquid became full of crystals, which upon analysis gave the following results:

	$Tm_2O_3$ .	$Br_2O_5$ .	$H_2O$ (diff.).
Calculated ( $Tm = 168.5$ ).....	26.95	50.37	22.68
Found.....	27.08	50.34	22.58

Ammonium hydroxide was found to be the best precipitant. The thulium hydroxide must be well ignited, as otherwise the results run a little high. The oxalate gave figures that were slightly low, indicating a tendency of the oxalate to dissolve in dilute acid.

*Thulium Chloride,  $Tm_2Cl_6 \cdot 14H_2O$* .—Thulium oxide was dissolved in concentrated hydrochloric acid, and the solution evaporated until crystals formed upon the surface. It was then placed in a desiccator over sulfuric acid, until a quantity of the chloride had crystallized out. The crystals were pressed between thick filter paper under a press. The nearly dry chloride was finally freed from moisture over sulfuric acid. This compound which possessed a green tint was very soluble in water and alcohol. When 0.4 gram was dissolved in 100 cc., a distinct absorption band in the red could be seen using a layer 5 cm. thick.

Analysis—Calculated:  $Tm_2O_3$ , 48.06. Found, 48.26.

*Thulium Sulfate*,  $Tm_2(SO_4)_3 \cdot 8H_2O$ .—In order to obtain this salt, some oxide was dissolved in a slight excess of hydrochloric acid. The solution was diluted somewhat, an excess of sulfuric acid added, and the whole poured into an excess of 95 per cent. alcohol. The resulting product was very milky and after a few minutes crystals began to form. When it had stood for some time the sulfate settled. It was filtered off and washed with alcohol to remove all traces of hydrochloric and sulfuric acids. The anhydrous sulfate was easily obtained by carefully heating the hydrated compound nearly to redness. When the anhydrous compound was added to water, it formed a sticky mass at the bottom of the beaker, which, however, rapidly dissolved. The neutral sulfate solution seemed to be more astringent, but less sweet, than a corresponding solution of ytterbium.

The hydrated sulfate gave 18.80 per cent.  $H_2O$ , and the anhydrous salt 61.52 per cent.  $Tm_2O_3$ , upon analysis. These results show that the amount of water of crystallization is similar to that of most of the other rare earth sulfates, *viz.*,  $8 H_2O$ .

*Thulium Oxalate*,  $Tm_2(C_2O_4)_3 \cdot 6H_2O$ , is obtained as a white precipitate with a greenish tint by treating a slightly acid solution of thulium with a solution of oxalic acid. Using hot solutions an oxalate was prepared possessing the following composition:

	$Tm_2O_3$ .	$C_2O_3$ .	$H_2O$ (diff.).
Calculated.....	54.30	30.46	15.24
Found.....	54.20	30.35	15.45

This salt is soluble in potassium and ammonium oxalates, owing to the formation of double salts. These double oxalates have been used by Auer von Welsbach for separating the members of the yttrium group. The author found this procedure to be more troublesome and very much slower than the bromates.

*Thulium Acetylacetonate*,  $(CH_3COCHCOCH_3)_6Tm_2 \cdot 2H_2O$ .—This compound was prepared by precipitating a solution of thulium chloride by an excess of ammonium hydroxide, washing the precipitate first by decantation, then on a Buchner funnel, and finally dissolving the hydroxide in a warm mixture of absolute alcohol and acetylacetone. Thulium hydroxide dissolved with great ease in the above mixture. On evaporating the solution, the salt separated. This was purified by recrystallizing from absolute alcohol. It was not volatil in a vacuum.

The acetylacetonate gave 40.02 per cent.  $Tm_2O_3$  upon ignition, which indicates that there are two molecules of water of crystallization present.

Some thulium material carrying a little ytterbium (neoytterbium) was converted into the acetylacetonate and submitted to several series of fractional crystallizations. The most soluble and least soluble portions showed a slight difference in the spectrograph. Unfortunately this com-

pound readily undergoes hydrolysis and for this reason it cannot be used for purifying thulium.

The absorption spectrum of an alcoholic solution of the acetylacetonate differs from aqueous solutions of other salts, such as the nitrate and chloride. The difference is shown more especially by the blue band, which in the case of the acetylacetonate is most intense on the side towards the red, whereas the nitrate in aqueous solution gives the most intense part on the violet side.

*Thulium Phenoxyacetate*,  $(CH_2(C_6H_5O)COO)_6Tm_2 \cdot 6H_2O$ .—Thulium hydroxide was dissolved in a solution of phenoxyacetic acid in dilute alcohol. The clear liquid was evaporated, the crystals were separated upon a Hirsch funnel and washed with water. The crystallin mass was well stirred with 95 per cent. alcohol after which an equal volume of ether was added. The phenoxyacetate was again filtered and washed with ether. This compound is very voluminous, sparingly soluble in water and soluble in alcohol. By a simple ignition it was found that the thulium oxide amounted to 28.58 per cent.

*Thulium Nitrate*,  $Tm_2(NO_3)_6 \cdot 8H_2O$ .—This was obtained by dissolving thulium oxide in nitric acid and evaporating to a small bulk. After a slight excess of fuming nitric acid had been added, the nitrate crystallized out. This compound is deliquescent. When it was dried over sulfuric acid and analyzed, it gave the following results:  $Tm_2O_3 = 45.24$  per cent.; calculated  $Tm_2O_3 = 45.12$ . This compound therefore contains eight molecules of water of crystallization. Most of the rare earth nitrates contain ten or twelve molecules of water. Thulium nitrate resembles "old ytterbium" nitrate, since Astrid Cleve gave 8  $H_2O$  as the amount of hydration of the latter salt.

Thulium nitrate can readily be crystallized from nitric acid. The fractionation of the simple nitrates from nitric acid was first proposed by Demarcay and since then has been used with great success by Urbain and others. At this end of the series the nitrates are very soluble and strong nitric acid must be used during the fractional crystallization.

DURHAM, N. H.

---

## VOLHARD'S METHOD FOR THE ESTIMATION OF CHLORINE IN POTABLE WATERS.

BY A. T. STUART.

Received May 22, 1911.

The Volhard method, as is well known, requires the addition of an excess of standard silver nitrate solution to the sample under investigation. The precipitated silver chloride is filtered off and the excess of silver nitrate remaining in the filtrate is determined by titration with standard potassium thiocyanate, using a ferric salt as indicator.