of the acid with half its volume of water, however, a slow but steady decomposition of the tetrachloride ensues.

When ammonia is passed into germanium tetrachloride, much heat is evolved and a white precipitate is formed. This substance is now being subjected to further study.

Germanium tetrachloride is soluble in absolute alcohol, carbon disulfide, carbon tetrachloride, benzene, chloroform, and ether. It dissolves in acetone with the formation of a light orange colored liquid.

Summary.

This article deals with the preparation and purification of germaniun tetrabromide and germanium tetrachloride, the analyses determination of the boiling points, melting points, indexes of refraction, specific gravities, and some of the chemical properties of the two compounds, and the crystal form and electrical conductivity of germanium tetrabromide.

ITHACA, NEW YORK.

THE ATOMIC WEIGHT OF YTTRIUM.

BY H. C. FOGG AND C. JAMES.

This work was undertaken because the atomic weight of yttrium, the commonest member of the yttrium earths, varies considerably according to the results published by different workers. Among the publications concerning this work only those which appear to the writers to be of major importance are discussed below.

Clève[1] carefully purified yttria, first by means of the basic nitrate method, and finally by fractionally precipitating the oxalate from very acid solutions of the nitrate in order to remove the last traces of terbium. He found, as a result of 12 determinations by the synthesis of the sulfate, the value 89.12.

Jones[2] used yttrium oxide, very carefully purified by the sodium sulfate method to remove members of the cerium group and then by the ferrocyanide method to throw out erbium, etc. His ratio of yttrium oxide to sulfate gave an atomic weight of 88.96 as a mean of 10 determinations. A second series in which the sulfate was converted to oxide, yielded the value 88.98 as the average of 10 analyses.

Feit and Przibylla[3] by means of a volumetric method obtained 89.346 as a mean of 6 runs.

Meyer and Wuorinen[4] roughly separated the yttrium and cerium earths

[1] Clève, Compt. rend., 95, 1225 (1882).

[2] Jones, Am. Chem. J., 14, 154 (1895).

[3] Feit and Przibylla, Z. anorg. Chem., 50, 262 (1906).

[4] Meyer and Wuorinen, ibid., 80, 7 (1913).

by the use of sodium sulfate. The yttrium earths were then further purified by two new methods: (a) the fractional hydrolysis of the phthalates; (b) the precipitation as the iodate from dil. nitric acid solution. By synthesis of the sulfate they obtained 88.71 and 88.73. Later Meyer and Weinheber[5] working with material that had been extensively purified by the iodate method, obtained the values 88.75 as a mean of 6 determinations using the sulfate to oxide ratio, and 88.76 as a mean of 3 experiments involving the oxide to sulfate ratio.

Hopkins and Balke[6] purified their yttrium oxide by first submitting it to a series of crystallizations of the bromates, followed by the fractional precipitation of the basic nitrate by means of sodium nitrite. The results obtained from 6 runs of the oxide-to-chloride ratio gave an average of 88.91. Later Kremers and Hopkins[7] using the same material, studied the ratio of yttrium chloride to silver. As an average of 7 results they obtained the value 89.33.

With the exception of the last three sets of results, those given above were obtained from the sulfate-to-oxide ratio or *vice versa*. These processes have been justly criticized by various workers from time to time, as can be ascertained by reference to previous papers upon the subject. Of the three remaining sets, only one, the last, involves the use of a standard method, namely, the chloride-to-silver ratio.

The Extraction of Yttrium Oxide.

The material used in this work was derived entirely from Norwegian gadolinite in the following manner.

The mineral was finely powdered, decomposed by heating for some time with an excess of, 1 : 1 commercial hydrochloric acid, diluted with water, filtered and precipitated warm with a hot solution of oxalic acid. The washed and dried oxalates were converted into sulfates by heating with conc. sulfuric acid until white fumes ceased to be evolved. The sulfates were dissolved in cold water in a large copper tank provided with a mechanical stirrer. The resulting solution, which was not completely saturated, was poured over an excess of barium bromate, gently warmed, and well stirred. As soon as the decomposition was complete, the solution was removed by filtration. The residue, which consisted of barium sulfate and barium bromate, was treated with more rare earth sulfate solution. When an excess of sulfate ions was found to be present after long heating and stirring, it was concluded that practically all the barium bromate had been exhausted. The solution was removed from the barium sulfate and the latter well washed. The filtrate and wash water were then poured over a new lot of barium bromate. The mixture was gently heated and well stirred, as before, until no test for a sulfate could be obtained. The filtered liquid was then added to the former bromate solution and the processes repeated until all the rare earth sulfate was converted to bromate.

Crystallization of the Bromates.[8]—The bromates were then submitted to a long

---

[5] Meyer and Weinheber, *Ber.*, **46**, 2672 (1913).

[6] Hopkins and Balke, THIS JOURNAL, **38**, 2332 (1916).

[7] Kremers and Hopkins, *ibid.*, **41**, 718 (1919).

[8] THIS JOURNAL, **30**, 182 (1908).

series of fractional crystallizations. As the fractionation progressed, the erbium absorption spectrum began to fade in the least soluble, while that of thulium appeared in the most soluble fractions. When the erbium bands had completely disappeared from the least soluble fractions, they were removed from the series. When strong thulium bands appeared in the most soluble fractions, these were mixed together and set aside. After the work had continued for a considerable time, the absorption bands of the middle fractions gradually became weaker. When it became apparent that the material consisted mainly of yttrium, the fractionation was discontinued and the fractions divided into two sets, namely, (a) yttrium bromate with some holmium and dysprosium, and minute amounts of erbium; (b) yttrium bromate containing a very little erbium and practically no holmium.

Since yttrium is more easily separated from erbium than from holmium, the latter set (b) was selected for the continuation of the work, in which stage it was decided to employ the basic nitrates.

Precipitation as Basic Nitrates.[9]—The bromates were boiled with an excess of sodium hydroxide solution until thoroughly decomposed. The hydroxides were filtered off, washed with boiling water, and dissolved in nitric acid. The concentrated solution of nitrates was boiled and treated with dil. sodium hydroxide solution until minute crystals could be observed swirling through the liquid. The vessel was then removed from the burner and allowed to stand for 24 hours. The precipitate of basic nitrate which formed was filtered off and the filtrate treated with more dil. sodium hydroxide solution as above until several fractions had been obtained. The precipitates were dissolved in the least quantity of nitric acid and fractionated in the same manner. Whenever filtrates or solutions of precipitates appeared from their absorption spectra to have the same earth content, they were united. As soon as nearly all the erbium had been removed, which was shown by the bands becoming faint, the yttrium was precipitated in the form of the oxalate and stored until 6 or 8 kg. had been collected.

Precipitation as Basic Nitrate by Means of Sodium Nitrite.[10]—During this stage very slow precipitation was brought about by boiling dilute neutral nitrate solutions with sodium nitrite. The sodium nitrite was added in small amounts at a time and the boiling continued until the precipitate was considered sufficiently large. This was immediately filtered off and the liquid subjected to fractionation in the above manner until nearly all the yttrium had been removed, after which the liquid was rendered slightly acid with nitric acid and precipitated with oxalic acid. Each basic nitrate precipitate was dissolved in the least quantity of nitric acid, the solution diluted, neutralized with dil. sodium hydroxide solution while boiling, and further fractionated with sodium nitrite. Any fractions which appeared to be similar after a careful examination by the spectroscope were united. During this fractionation the purest yttrium, which collected in the last or most basic fractions, was placed aside when the absorption bands of erbium were scarcely discernible.

Fractional Precipitation as the Ferricyanide.[11]—Two hundred g. of oxide derived from the above nitrite fractionation was dissolved, carefully, in the least possible quantity of nitric acid, diluted to 2 liters and rendered neutral by the addition of a dilute solution of sodium hydroxide to the boiling liquid. Two hundred cc. of a 20% solution of potassium ferricyanide was added drop by drop while the whole was well stirred by a rapid current of steam. The volume of the solution in the flask was kept constant by the application of outside heat. After the potassium ferricyanide had been added, the liquid was kept boiling until the desired quantity of precipitate had formed. The

---

[9] This Journal, **43**, 1397 (1921).

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

[11] Ibid., **39**, 936 (1917).

red crystalline precipitate of ferricyanide was immediately filtered off, the liquid returned to the flask and the process repeated until 6 fractions had been obtained.   The remain-- ing yttrium which constituted Fraction 7 was removed by the addition of an excess of sodium hydroxide solution.   A similar run was made employing 250 g. of yttrium oxide.
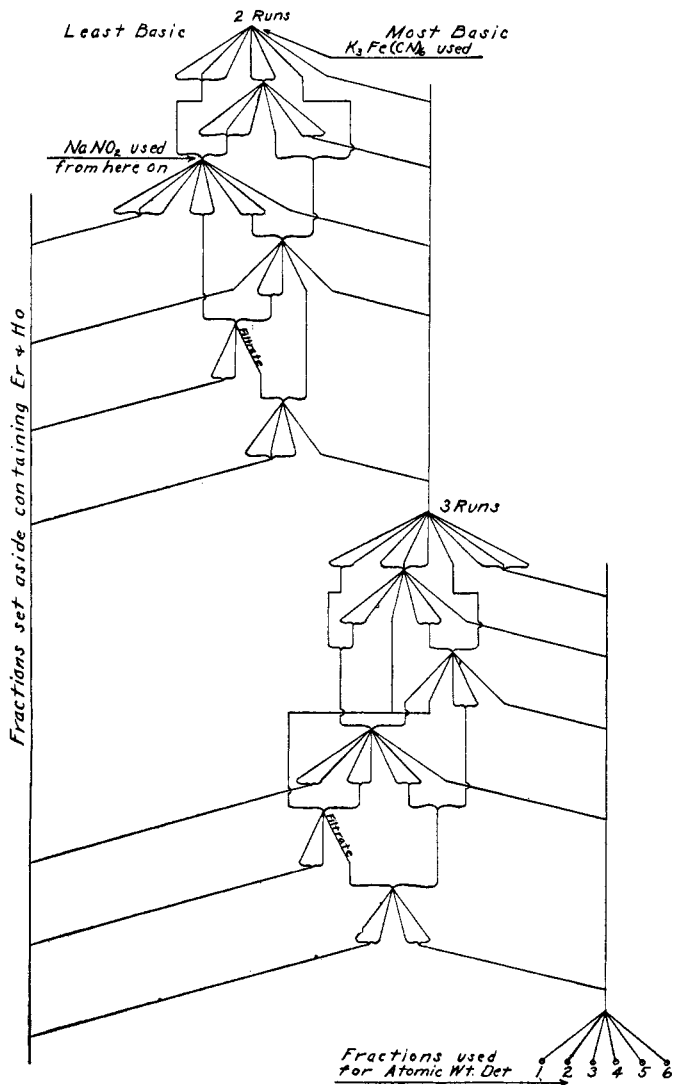

Fig. 1.

The precipitates were converted back to nitrates in the following manner.   After being transferred to porcelain casseroles, they were boiled with an excess of conc. sodium hydroxide solution until decomposed, as shown by the disappearance of the red color. The residues were filtered off, washed and ignited.   The resulting oxides were trans- ferred to beakers, moistened with water, dissolved in conc. hydrochloric acid and

evaporated nearly to dryness in order to expel the excess of acid. The chlorides were taken up with approximately 400 cc. of water, heated to boiling and precipitated as the oxalates. After standing for several hours the precipitates were removed by filtration, ignited to oxide, transferred to beakers, dissolved in nitric acid, evaporated to sirupy consistency, examined with a spectroscope and divided into 4 groups according to purity, namely, (a) Fractions 1, 2 and 3 from each series; (b) Fractions 4 and 5 from each series; (c) Fraction 6 from each series; (d) Fraction 7 from each series.

Group b was fractionated as before, taking 5 fractions with potassium ferricyanide and the last (No. 6) with sodium hydroxide. The precipitates were converted back to nitrates as in the previous case, and the fractions placed in the following groups: (e) Fractions 1, 2, and 3; (f) Fraction 4; (g) Fractions 5 and 6. Group e was then united with Group a; Group f with c; and Group g with d. This will be better understood by referring to the diagram.

Owing to the fact that the conversion of the ferricyanide to the nitrate was troublesome, and since the separation was no better than in the case of the sodium nitrite method, the latter was resorted to from this point on. The fractionation was therefore continued in a similar manner to the above except that 200 cc. of a 20% solution of sodium nitrite was used in place of potassium ferricyanide, and the precipitates converted back to nitrate by dissolving in the least amount of nitric acid. The work was carried through two stages, the purest material obtained in the first stage, which showed an extremely faint holmium band when examined through a thick layer of fused nitrate, being subjected to a similar process. The purest fractions obtained from this, which failed to give the slightest evidence of absorption bands of erbium or holmium, were united, and the whole broken up into 6 fractions as nearly equal as possible, by the above method.

During the fractionation it was observed that the most basic fractions gave a light cream colored oxide upon ignition, which was proved. to be due to praseodymium, as will be shown later.

Composition of the Precipitate Obtained during the Nitrite Fractionation.—This precipitate consisted of small, transparent, hexagonal plates, which after ignition gave an oxide having the same transparent crystalline appearance. A careful analysis of the material from two different fractions gave 63.54 and 63.44% of Y_2O_3, 14.93 and 14.77% of N_2O_5 and 21.53 and 21.79% of H_2O (by difference). This composition corresponds to a compound possessing the formula $4Y_2O_3.2N_2O_5.17H_2O$. A very small amount of nitrous anhydride was present and this was calculated and included as nitric anhydride. This nitrite content varied among the different fractions, so the writers assumed that it was merely occluded. A slight difference in the amount of water present would simplify the formula, inasmuch as it could be $2Y_2O_3.N_2O_5$ with 8 or 9 H_2O.

The ratio $Y_2O_3 : N_2O_5$ in this case is different from the ratio of the basic nitrate[12] $3Y_2O_3.4N_2O_5.20H_2O$. A study of the figures given on pages 877 and 878 of this reference indicates that there is a possibility that this more basic nitrate may exist at 25° and lie along the portion of the curve AB.

Purification of the Yttrium Material.—As previously mentioned it had been noticed that some of the most basic fractions gave an oxide which possessed a pale cream color. It was therefore obvious that a minute amount of an element giving a dark colored oxide must be present, i. e., praseodymium or terbium or both. Since the yttrium material had been submitted to a very long series of fractional crystallizations of the bromates, it was highly probable that all terbium had been removed, inasmuch as

[12] This Journal, 32, 873 (1910).

terbium bromate is one of the least soluble rare earth bromates. This leaves praseodymium as the other alternative. If this were so, there would also be the possibility of the presence of lanthanum, since this element gives a very soluble bromate·and in addition a strongly basic oxide.

A search was then made for suitable compounds showing a great divergence between the solubilities of yttrium and the most basic cerium earths. In order to make the process thoroughly efficient, it was necessary that the salts of the cerium earths be much more soluble than that of yttrium. The following compounds seemed to offer the best possibilities: (a) dimethylphosphates, (b) acetates, (c) p-sulfobenzoates, and (d) cacodylates.

Dimethylphosphates.[13]—Fraction 1 which was in the form of nitrate, was precipitated by oxalic acid, the oxalate washed, ignited and the resulting oxide dissolved in acetic acid. The excess of acid was neutralized by ammonium hydroxide, the whole heated to boiling and a hot neutral solution of ammonium dimethylphosphate added. The voluminous precipitate of yttrium dimethylphosphate was removed by filtration and washed with hot water. Two more fractions were obtained in like manner from the filtrate. The yttrium remaining in the mother liquor was thrown out as the oxalate. The colors of the oxides of the various fractions indicated that there had been no concentration of the earth with the colored oxide. A duplicate run confirmed these results.

Acetates.[14]—The oxide from Fraction 6 was dissolved in acetic acid and submitted to 31 series of fractional crystallizations. While this method concentrated the colored earth in the mother liquors, it was found to be too wasteful and tedious.

p-Sulfobenzoates.—The writers found that there was a considerable difference between the solubilities of the yttrium p-sulfobenzoates and those of the cerium earths. However, the fractionation of these salts failed to bring about any separation in this case. This subject is to be investigated at greater length in the near future.

Cacodylates.[15]—The mother liquors from the acetate crystallization of Fraction 6, which gave a chamois colored oxide, were evaporated to dryness to remove excess of acid, taken up with water and precipitated by means of ammonium cacodylate. The rare earth remaining in solution was precipitated as the oxalate. After both fractions had been converted to oxide, a great difference in color was immediately observed, the oxide from the precipitate being practically white, while that from the filtrate was a deep chocolate color. A solution of the latter in nitric acid showed weak praseodymium absorption bands. Since lanthanum cacodylate has never been obtained in a crystalline form, it was concluded that lanthanum would be found with the praseodymium in the filtrate. Inasmuch as the above results show that small amounts of praseodymium (and lanthanum) are rapidly removed from yttrium by precipitating the latter as cacodylate from acetate solution, this procedure was employed for the final purification.

[13] THIS JOURNAL, **36**, 10 (1914).
[14] Postius, *Dissertation*, München Polytech., **1902**, pp. 11–30.
[15] THIS JOURNAL, **35**, 127 (1913).

Each fraction was converted to oxide, dissolved in acetic acid, evaporated almost to dryness to remove excess of acid, taken up with water and diluted to 250–300 cc. The solution was then heated to boiling and treated with a slight excess of ammonium cacodylate. After a few minutes' heating and stirring a voluminous, crystalline precipitate formed. This precipitate was removed by filtration, washed, transferred to the original beaker, suspended in water and dissolved in a slight excess of acetic acid. When solution was complete, 5 to 10 g. of cacodylic acid was added, and the liquid boiled. At this point dil. ammonium hydroxide was added with thorough stirring until an odor of ammonia was perceptible. When this procedure was carefully carried out only a slight amount of rare earth was found to remain in solution. The precipitate was again removed by filtration and the process repeated one precipitation beyond the stage where a white yttrium oxide was obtained from the filtrate, in order to make sure that all the cerium earths were removed. The number of precipitations required varied from 3 to 6.

The Preparation of Yttrium Chloride.

Each final cacodylate precipitate was dissolved in hydrochloric acid, diluted to about 3 liters, heated to boiling and precipitated by the addition of a hot dilute solution of oxalic acid. The whole was allowed to stand over night, washed several times by decantation with boiling water to which a little oxalic acid had been added, and then filtered upon a hardened paper placed on a perforated porcelain plate in a glass funnel. The oxalate was transferred from the paper to a porcelain dish and ignited in an electrically heated quartz muffle furnace. The oxide was dissolved in redistilled dil. hydrochloric acid, diluted to about 3 liters and reprecipitated as the oxalate. After filtering and washing, the precipitate was detached from the filter paper and ignited in a Palau dish at a dull red heat. The oxide was again dissolved in hydrochloric acid and precipitated for the third time as oxalate. The oxide resulting from the ignition of this last oxalate precipitation was dissolved in hydrochloric acid, the solution diluted to about 3 liters, treated with an excesss of ammonium chloride and precipitated by means of redistilled ammonium hydroxide. The hydroxide was washed several times by decantation, placed on a Büchner funnel and again washed. This hydroxide was dissolved in hydrochloric acid and reprecipitated as above. The precipitate was redissolved in hydrochloric acid, diluted to about 3 liters, precipitated as the oxalate, and converted to oxide. This oxide was dissolved in hydrochloric acid, evaporated to small volume, transferred to a platinum dish and evaporated to dryness in a glass oven, after which it was heated to 110° for several hours. The residue was treated with water and acidified with dil. hydrochloric acid. The solution was carefully filtered, and the entire dehydration process repeated twice.

Some of the later dehydrations were carried out in the following manner. The chloride solution was evaporated in a platinum dish over a hot plate with constant stirring until it just became solid on cooling. The crystals were coarsely powdered, placed in a silica boat and carefully dehydrated in a current of pure dry hydrogen chloride, the temperature being gradually raised to 170–200°. The advantage of this method over the above is that the resulting dehydrated chloride is completely soluble in water, thus obviating the possibility of dissolving any silica by hydrochloric acid.

The solution of the chloride, resulting from the final dehydration, was diluted to about 200 cc. and treated with hydrogen sulfide, first in the cold and then boiling. No appreciable precipitate was obtained in any case, indicating that all arsenic had been previously removed. After filtration the liquid was diluted, heated to boiling and the oxalate precipitated by oxalic acid solution, filtered off, washed and gently ignited. The oxide was dissolved in dil. hydrochloric acid in a quartz dish and purified by two crystallizations of the chloride as follows. The solution was evaporated to the point of crystallization, cooled in ice and saturated with hydrogen chloride. The thick mass of crystals was transferred to a platinum Gooch crucible and the mother liquor removed by means of a centrifuge. The yttrium chloride obtained by the second crystallization was dried over fused potassium hydroxide in a vacuum desiccator.

The Preparation of Other Reagents.

The purification of the silver was described in an article upon the atomic weight of samarium.[16] The distilled water of the laboratory was further purified by two more distillations, first from alkaline permanganate and second from sulfuric acid, using tin condensers and well-seasoned Jena glass receiving flasks. The hydrochloric and nitric acids were twice distilled through quartz condensers, the first and last thirds being rejected.

The Dehydration of Yttrium Chloride.

Hydrated yttrium chloride, $YCl_3.6H_2O$, melts at 156–160°, loses 5 molecules of water at 100° and the six that 160°, giving the anhydrous salt which melts at about 686°.[17] The dehydration was carried out in a similar manner to that employed by Baxter and his co-workers.[18] The hydrated salt was coarsely powdered in an agate mortar, transferred to a platinum boat and placed in the bottling apparatus. After the air had been swept out by nitrogen and hydrogen chloride, the temperature was raised to and kept at 100° for an hour or so, after which it was raised to 125° to 135°. When moisture had ceased to be evolved, the temperature was

[16] This Journal, **39**, 2609 (1917).

[17] Matignon, Compt. rend., **134**, 1308 (1902); Ann. chim. phys., **8**, 433 (1906).

[18] Baxter, This Journal, **37**, 516 (1915).

increased to 170–180°, when more water was given off. At 250° nitrogen was shut off and only hydrogen chloride passed through the apparatus. At 280–300° the last amount of water was driven off. After the salt had been kept at 325° for an hour the heater was removed, the apparatus allowed to cool and the hydrogen chloride removed by a current of nitrogen. The salt was removed, ground in an agate mortar, returned to the apparatus and heated to 300–350° for some time in a stream of hydrogen chloride, after which the temperature was quickly raised until the chloride fused. The heating sleeve was removed, the apparatus allowed to cool, the hydrogen chloride swept out by nitrogen and this in turn by air. The boat was then bottled and placed in a desiccator, which was set near the balance.

Analysis.

The chloride, after weighing, was dissolved in about 200 cc. of water in a glass-stoppered Erlenmeyer flask, and then transferred to a 2-liter bottle where it was diluted to about 600 cc. All samples analyzed dissolved completely and quickly.

The silver, equivalent within a few tenths of a milligram to the yttrium chloride, was dissolved in dil. nitric acid in an Erlenmeyer flask fitted with a column of bulbs. When the oxides of nitrogen had been driven off, the solution was diluted to 250 cc. and added to the chloride solution with thorough mixing by rotation. The whole was kept, with frequent shaking, for at least 10 days and then tested nephelometrically, deficiency in either silver or chloride being made up by the addition of a solution of silver containing 1 g. per liter or from an equivalent solution of potassium chloride. When the solution was found to be nephelometrically equivalent, the bottle was allowed to stand with occasional shaking for a week or two and again tested to make sure that equilibrium had been reached. All weighings were made on a Staudinger balance and with weights reserved for this type of work. The weights were standardized by the method described by Richards.[19] The balance case contained, in addition to fused potassium hydroxide, radio-active material. The weighings were made by substitution using counterpoises almost exactly like the vessels themselves in size and weight. Vacuum corrections were applied as follows.

Material	Sp. Gr.	Vacuum corrections per g.
YCl_3	2.80[a]	+0.000287
Ag	10.49	−0.000031

[a] Matignon, *Ann. chim. phys.*, **8**, 433 (1906).

[19] Richards, THIS JOURNAL, **22**, 144 (1900).

TABLE I

Analysis	Fraction	Wt. of YCl$_3$ in vac. G.	Wt. of Ag in vac. G.	At. wt. of yttrium
1	2	2.32881	3.85660	89.06
2	3	2.62838	4.35335	89.03
3	5	2.70726	4.48289	89.08
4	6	2.57431	4.26298	89.07
5	4	2.42924	4.02481	88.97
6	2	2.99852	4.96557	89.06
7	3	3.13897	5.19903	89.03
8	5	4.20721	6.96662	89.08
9	1	2.45615	4.06741	89.06
10	2	2.60321	4.31174	89.03
11	3	2.86276	4.74036	89.08
12	6	2.10381	3.48514	89.00
13	1	1.53281	2.53937	88.98
14	2	2.05579	3.40596	88.98
15	3	2.70410	4.47765	89.08
16	2	2.19335.	3.63357	88.99
17	2	2.17992	3.61115	89.00
18	5	2.86866	4.75281	88.97
19	5	2.79189	4.62545	88.98
20	4	3.22857	5.34787	89.01
21	4	2.80721	4.64965	89.03

Av. 89.03

Summary.

It has been shown that in order to obtain very pure yttrium, it is essential to use, finally, such a method as the cacodylate in which the yttrium is precipitated, while the more basic cerium earths remain in the form of quite soluble salts.

The average atomic weight of 89.03, which agrees better with the average gravimetric analyses of yttrium salts, differs somewhat from the figure at present accepted by the International Committee.

DURHAM, NEW HAMPSHIRE.