Optional Method for Lithium.

The solution of the lithium in the ether-alcohol is evaporated to dryness on a steam bath and finally dried in an oven at 110° C. for 15–20 minutes. The residue is taken up in 5–10 cc. alcohol, warming if necessary. This solution is diluted with about 50 cc. of water. If a slight sediment remains, the liquid is filtered through a Gooch crucible and washed with water. A few drops of phenolphthalein are added to the filtrate (the reaction should be acid) and the liquid titrated with tenth-normal alkali. The chlorides are precipitated as the silver salt and from the weight of the latter there is subtracted the amount corresponding to the hydrochloric acid determined in the titration. The factor used for converting AgCl into LiCl was 0.2958.

Where the total quantity of mixed chlorides is greater than 0.5 g., proportionately larger quantities of solvents are necessary in the first precipitation. The second precipitation is carried out in exactly the same manner as for 0.5 g. of salts indicated in the method. More accurate results have been obtained, however, with quantities of total chlorides not exceeding 0.5 g.

WASHINGTON, D. C.

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

THE PURIFICATION AND ATOMIC WEIGHT OF YTTRIUM.

[SECOND PAPER.]

BY B. SMITH HOPKINS AND CLARENCE W. BALKE.

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A preliminary paper on this subject by Egan and Balke appeared in THIS JOURNAL in April, 1913, in which the sources of material, the preliminary processes of purification and the trial determinations of the atomic weight were discussed. Since the publication of this paper, the work has progressed steadily and the purpose of the present communication is to report progress on the problem.

Historical.

The atomic weight of yttrium has been determined by a large number of investigators. The results obtained previous to 1873 are of little value since the material used certainly contained considerable quantities of rare earths other than yttrium. Some of these early investigators, however, obtained numbers which are surprisingly close to the accepted value.

In 1873 Cleve and Höglund[1] published a memoir in which six determinations of the ratio Y_2O_3 to $Y_2(SO_4)_3$ are recorded, the mean value obtained being 89.58. The material used in this series was known to contain a small amount of terbium, which the authors attempted in vain to remove

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[1] *K. Svenska Vet. Akad. Handlingar*, Bb. 1, No. 8 (1873).

by the slight solubility of terbium formate and double potassium sulfate. Nine years later Cleve published another paper[1] in which he described the further purification of his material. The small amount of terbium was removed by fractional precipitation of the nitrate with oxalic acid. By this means four fractions of constant molecular weight were obtained, and with this material twelve determinations of the atomic weight of yttrium were made by observing the gain in weight when the dry oxide, was converted to anhydrous sulfate. The average value obtained in this second series was 89.12.

Jones[2] determined the atomic weight of yttrium in 1894, using material prepared by Professor Rowland, who used the method of fractional precipitation with potassium ferrocyanide. This material was estimated, by examination of its spectrum, to contain less than 0.5% of other elements. Two series of ten determinations each were made; in one the oxide was dissolved in sulfuric acid and the excess acid expelled by heating; in the other the crystallized sulfate was ignited to the oxide with the blast lamp. The results obtained were 88.96 for the first series and 88.98 for the second. These results were criticised by Delafontaine,[3] but Jones' reply[4] was insistent and his results practically determined the international value until recently.

In 1900 Muthmann and Böhm published[5] the result of a single determination, in which the sulfate was ignited to the oxide, obtaining the value 88.97, which agrees exactly with that obtained by Jones.

In 1901 G. and E. Urbain[6] in discussing the purification of yttrium material, stated that a final fraction gave an atomic weight of 88.6, but no information is supplied concerning the method used or the purity of the material.

In the same year Bodman[7] published the results of three determinations, obtaining the value 91.57 from the transformation of the oxide to the sulfate.

K. T. Postius, in his dissertation presented to the Technische Hochschule at Munich in 1902, describes seven determinations of the ratio $Y_2O_3 : Y_2(SO_4)_3$ with an average value of 88.35. In expelling the excess acid from the sulfate he used temperatures from 350° to 370° only.

Buill[8] in 1905 obtained the value 89.70 from two determinations of

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[1] *K. Svenska Vet. Akad. Handl.*, No. 9 (1882); *Compt. rend.*, **95**, 1225 (1882); *Bull. soc. chim.*, **39**, 120 (1883).

[2] *Am. Chem. J.*, **17**, 154 (1895).

[3] *Chem. News*, **71**, 243 (1895).

[4] *Ibid.*, **71**, 305 (1895).

[5] *Ber.*, **33**, 42 (1900).

[6] *Compt. rend.*, **132**, 136 (1901).

[7] *Bihang. Svensk. Vet. Akad. Handl.*, [2] **26**, No. 3 (1901).

[8] *Z. anorg. Chem.*, **47**, 464 (1905).

the same ratio, making use of the microbalance. In this paper there is also an interesting study of the effect of heating yttrium sulfate in an electric furnace for 15-minute periods. He found that the neutral sulfate when heated for this length of time was stable between the temperatures of 450° and 650°; that the material was completely transformed into the basic salt corresponding to the formula $Y_2O_3.SO_3$ at 900–950°; and that above these temperatures the material began to break down into the oxide, the decomposition becoming complete at 1100°.

Feit and Przibylla[1] departed from the usual method of determining the atomic weight of yttrium by using a titration method. The oxide was dissolved in an excess of 0.5 *N* sulfuric acid and the excess acid titrated with 0.1 *N* sodium hydroxide, using methyl orange as an indicator. The proportion of oxygen in the oxide and in turn the atomic weight of yttrium were calculated from the data obtained. The average of their six determinations gave yttrium an atomic weight of 89.35.

A. Bettendorff[2] in 1907 obtained yttria of a high degree of purity by fractional precipitation with potassium ferrocyanide. His purest fraction was shown by spectrographic study to be free from other rare earths. A single determination, the details of which are not given, showed his product to have an atomic weight of 88.76.

In 1913 Meyer and Wuorinen[3] discussed at length the results obtained by various investigators and compared several of the methods used in obtaining pure yttria. By using a combination of methods they prepared a product of a high degree of purity with which the atomic weight was determined by the synthesis of the sulfate. The authors found that the excess of sulfuric acid could not be expelled even at a temperature of 500°. Instead of trying to drive off the excess acid they proceeded as follows: The weighed oxide was dissolved in a small excess of sulfuric acid; the solution was evaporated to dryness; the sulfate was then heated to a temperature of 450° to 500° and weighed; finally the amount of acid retained by the salt was determined by titration with decinormal sodium hydroxide, using methyl orange as an indicator. The acidity determined in this way was calculated as SO_3 and subtracted from the weight of the yttrium sulfate, giving a corrected weight from which the atomic weight was determined. Two determinations were made, giving an average of 88.6.

The Ratio.—A review of the methods which have been used in determining the atomic weight of yttrium shows that the sulfate was used in some manner in every case, and that in the majority of investigations the synthesis of the sulfate was relied upon to give the desired ratio. In two

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[1] *Z. anorg. Chem.*, **50**, 262 (1906).

[2] *Ann.*, **352**, 88 (1907).

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

cases the values were based upon the decomposition of the sulfate, and in two others they depended upon titration methods. A comparison of the values obtained from the synthesis of the sulfate shows that Bodman's value, 91.57, is the highest, and Postius', 88.35, the lowest. It is perhaps worthy of note also that these two investigations were nearly or quite contemporaneous. It would seem that the difference in the results is much too great to be accounted for wholly by the varying purity of the material used, since if Postius' results are correct then Bodman's product must have contained about 6.5% of erbia or an equivalent amount of other rare earths. ·This quantity would certainly be detected by the means used in proving the purity of the material and it would seem that this wide variation must be explained in some other way than by differences in the purity of the material employed.

After repeated efforts to obtain concordant results with the sulfate method, we are led to the conclusion that the method is not ideal for three reasons. First, the anhydrous sulfates are extremely hydroscopic and Nilson has shown that they cannot be weighed in a perfectly anhydrous condition if removed from a phosphorus pentoxide desiccator of the ordinary type, and Bunsen declares that a thin glass weighing tube is not sufficient to protect the sulfates from the moisture of the air. It seems that all investigators have not had this point in mind in their manipulation. A second difficulty with the sulfate method as generally carried out, is the impossibility of telling when the excess sulfuric acid has been expelled. It is customary to follow the method suggested by Cleve and heat to constant weight and then if the residue dissolves to a clear solution to consider that only the normal anhydrous sulfate remained. It is obvious that this test is a good one to discover when the heating is carried too far and too much SO_3 has been expelled, but it is of no value in determining when some acid still remains in the sulfate. If the heat is applied suddenly, as with a flame, we would expect the center of the mass to remain acid for some time after the outer layer had become neutral or basic. Brauner and Pavlicek,[1] in a similar study of the effect of heating lanthanum sulfate, state that in 27 experiments not a single case was discovered in which the mass was homogeneous, the tendency being for the outer layers to become basic, the middle portions neutral, and the central upper layers acid. When such a mass is dissolved in water two facts should be noted: (1) a clear solution may be obtained but its reaction to indicators is a matter of chance; (2) a portion of the mass which is basic should dissolve more slowly than the rest and this experience was noted by Jones[2] who explained the phenomenon by supposing that a hydrate of lower solubility had been formed. We have had a similar ex-

[1] *Trans. Chem. Soc.*, 81, 1243 (1902).

[2] *Am. Chem. J.*, 17, 160 (1895).

perience with nearly every sample of heated sulfate which has been dissolved in water and we are led to believe that the less soluble portion is the basic outer layer which finally dissolves in the acid from the inner portions.

A third reason for questioning the accuracy of the sulfate method comes from the fact that it is impossible to obtain constant weight except at some definite temperature. As long ago as 1887 Bailey showed[1] that on heating "didymium" sulfate containing some free sulfuric acid up to and above 360°, no equilibrium could be obtained, but each increase in temperature is followed by a further loss in weight. Brauner and Pavlicek[2] reported the same experience with lanthanum sulfate, and showed that a temperature of 600° or more is needed to expel all the acid. Brill claims[3] that normal yttrium sulfate is stable between the temperatures of 450° and 650°. It is to be noted, however, that Brill heated his material for 15-minute periods only. In order to discover whether or not the sulfate would continue to remain constant in weight if kept for long periods at a definite temperature we have performed two tests. Two samples of the oxide from different sources were weighed out in platinum crucibles and converted into the sulfate in the usual manner.[4] These sulfates were then heated in an electric muffle, the temperature being determined by a recently calibrated pyrometer. At the end of the heating periods the hot crucibles were placed in weighing bottles whose stoppers were apparently tight, and the bottles put in a roomy sulfuric acid desiccator. When cold the stoppers of the bottles were opened for a moment and the bottles containing the crucibles weighed by substitution, the tare being a similar bottle containing an empty platinum crucible which was treated exactly like the crucibles containing the sulfates. The results are given in the following table, the weights being the values obtained in air:

TABLE I.

			Crucible I.		Crucible II.	
No.	Temp.	Hours.	Sulfate.	Atomic weight.	Sulfate.	Atomic weight.
1	470°	4	0.73574	91.97	0.78520	91.41
2	470°	16	0.73503	92.19	0.78486	91.51
3	485°	14	0.73503	92.19	0.78461	91.58
4	525°	12	0.73358	92.64	0.78477	91.54
5	575°	6	0.73382	92.56	0.78450	91.62
6	580°	7	0.73341	92.69	0.78442	91.64

These results show that there is generally a loss in weight when the sulfates are heated for long periods. The cases in which there is a gain in weight are probably due to the absorption of moisture by the hydroscopic

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[1] *Trans. Chem. Soc.*, 51, 683 (1887).

[2] *Ibid.*, 81, 1250 (1902).

[3] *Z. anorg. Chem.*, 47, 464 (1905).

[4] THIS JOURNAL, 35, 370 (1913).

sulfate. The sulfates from both crucibles were dissolved in water and showed some basic salts present, hence the gradual loss in weight was not due at all stages to the giving off of occluded sulfuric acid, but to the loss of SO_3 from the yttrium sulfate. It is difficult to say just where the heating should have been discontinued in order to give the normal salt and the true atomic weight.

On account of the divergent results and the unreliability of the ratio depending on the synthesis of the sulfate, it seems highly desirable that some entirely different ratio should be used. Encouraged by the early results obtained with the ratio Y_2O_3 to $2YCl_3$, this method has been carefully studied and we believe it to be the most satisfactory ratio yet proposed for the determination of the atomic weight of yttrium.

Experimental.

Preparation of Material.—The sources of material, the early treatment and the general methods of procedure have been presented in the preliminary paper[1] and will not be repeated here. An extensive study was made of three methods of purification and the results obtained will be discussed. In this study two methods were used to observe the effect of the treatment. The first was by means of the absorption spectra of the solutions, and the second was by watching the changes in the atomic weight of the material. For the latter work a portion of each fraction was carefully purified by dissolving the oxide in pure hydrochloric acid, reprecipitating twice with redistilled ammonia and twice with a hot solution of pure oxalic acid, each precipitate being thoroughly washed by several liters of boiling water. No effort was made in these trial determinations to remove the alkali metals, which probably accounts in part, at least, for the fact that the trial values run uniformly lower than the actual values.

In making the trial determinations of the atomic weights three methods were used. In the early part of the investigation the synthesis of the sulfate was tried but it was abandoned because of the difficulty of obtaining concordant results. A second method was then tried as follows: A weighed sample of the rare-earth oxide was dissolved in a known amount of 0.1 *N* sulfuric acid; there was added a quantity of a 5 *N* neutral solution of potassium oxalate slightly in excess of the amount needed to precipitate the rare earth present; and finally the excess of sulfuric acid was determined by titration with 0.1 *N* potassium hydroxide, using phenolphthalein as an indicator. This method is rapid and gives quite satisfactory results, although the presence of a rare-earth precipitate in the acid solution makes it difficult to obtain a sharp end point.

The third trial method used in observing the effect of the purification methods upon the yttria is as follows: Two samples of rare-earth oxalate

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[1] THIS JOURNAL, **35**, 365 (1913).

are weighed out, one in a small Erlenmeyer flask and the other in a platinum crucible. It is absolutely essential that these two samples be uniform in composition. The sample in the crucible is ignited to the oxide and the percentage of oxide in the oxalate determined. The sample in the flask is dissolved in a slight excess of dilute sulfuric acid and the amount of oxalic acid determined by titration with twentieth normal potassium permanganate. Then the percentage of oxalic acid in the oxalate is calculated and the atomic weight determined by the proportion

$X + 24 : 108 =$ percentage of oxide : percentage of oxalic acid.

In order to make sure that the oxalate contained no water-soluble substances which would reduce the permanganate, samples were soaked for 50 hours in conductivity water, at the end of which time the water contained no reducing substance. While this method is somewhat more laborious than the preceding, it has been used more than either of the others for the reason that it gives more concordant results. A comparison of the three methods is shown in Table II, in which are recorded the atomic weights of certain fractions determined by more than one method.

TABLE II.

	Atomic weight determined by		
Sample.	$KMnO_4$ titration.	KOH titration.	Sulfate.
1	89.30	90.12	.....
2	89.70	91.07	.....
3	88.88	89.70	.....
4	89.34	90.26	.....
5	93.76	.....	94.10
6	93.22	94.56	94.70
7	89.34	90.47	90.28

This table shows that the values obtained by the permanganate titration are somewhat lower than those obtained by the other methods and are probably no nearer the true value, but this method is preferred to the others because we have found it more reliable and hence more serviceable in determining the progress of the work. That the results from this method are too low is made evident by comparing the values obtained by its use with the atomic weights obtained by the use of the chloride method.

The Chromate Method.—An attempt was made to remove other less basic earths from yttrium by repeated treatment with the chromate method. The process was carried out exactly as described in the preliminary paper.[1] The fractions obtained in the previous chromate treatment were divided into five groups according to their atomic weight and each group was put through the chromate fractionation in a separate flask. The material used for this work contained considerable quantities of erbium and holmium and probably contained small amounts of other

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[1] THIS JOURNAL, **35**, 366 (1913).

rare earths, especially thulium, dysprosium and possibly terbium. Six fractions were precipitated with potassium chromate and the seventh and largest fraction was thrown down by potassium hydroxide. The results are shown in Table III.

TABLE III.

Flask.	Weight of oxide.	Av. at. wt.	Fractions obtained.	Atomic weight of last fraction.
I	160	92.9	7	90.3
II	160	92.4	7	89.2
III	153	90.8	7	89.1
IV	160	....[1]	7	90.1
V	160	94.3	7	91.3

A second run was made in the same manner, using the last fractions from Flasks II and III in Flask I2 and the last fractions from Flasks I and IV in Flask II2; Flask III2 contained the seventh fraction from Flask V, together with a quantity of yttria of about the same atomic weight. The results are shown below:

TABLE IV.

Flask.	Weight of oxide.	At. wt. of orig. subs.	Fractions obtained.	At. wt. last fraction.
I2	160	89.15	8	89.35
II2	160	90.20	8	90.20
III2	160	91.35	8	90.90

These results show that the limit of efficiency of the chromate method had been reached since both Flasks I2 and II2 show the same atomic weight as the original material within the limits of experimental error of the sulfate method which was used to determine these values. Accordingly it was determined to take the material from the last fractions of the second run and try the efficiency of the fractional precipitation with dilute ammonia. The absorption spectra of the last fractions showed a slightly decreased intensity of the holmium lines, considerably less erbium and none of the other rare earths. This method apparently is not able to remove the last traces of either erbium or holmium.

The Ammonia Method.—Fractions 7 and 8 from both Flasks I2 and II2 and Fraction 8 from Flask III2 were combined, giving 386 g. of yttrium oxalate, the average atomic weight of the yttrium being 90.31. This was ignited to the oxide, dissolved in HCl, evaporated to dryness and dissolved in about 5 liters of water. To this solution dilute ammonia was added, the mixture allowed to stand for 24 hours, the precipitate filtered out and the solution evaporated to its original volume, when the process was repeated. This material was subjected to 42 fractionations in this manner, the precipitates giving purified oxalates which averaged 3.1 g. in weight. The ammonia added was so dilute that there was no cloudiness when the solutions were first mixed, but on standing a faint precipi-

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[1] Flask IV contained no material with higher atomic weight than 92, but the average atomic weight was not determined.

tate appeared. The early fractions were precipitated by two liters of ammonia which was 0.0125 *N;* then the strength was decreased to 0.01 *N* and the volume of precipitant increased to three liters. Fractions from this series are designated as H fractions.

In exactly the same way 37 fractions were obtained from a solution representing 246 g. of the purest oxalate obtained in the work described in the preliminary paper. When a saturated solution of the chloride of this material was examined with the spectroscope, no trace of holmium or dysprosium could be seen, but faint lines of erbium were visible. It was estimated to contain about 0.5 % of erbium salts. The fractions prepared from this material are designated as E fractions and the atomic weights obtained from various fractions of the two series are shown in Table V.

TABLE V.

	Atomic weights.	
	H series.	E series.
Fraction 1	94.7	91.2
Fraction 10	92.7	89.7
Fraction 15	91.8	89.8
Fraction 20	90.7	....
Fraction 25	90.2	88.7
Fraction 30	89.9	88.7
Fraction 35	89.9	88.7
Fraction 40	89.9	....

Fractional precipitation by dilute ammonia is slow, but is capable of removing the less basic earths from yttrium when they are present in considerable quantities. This method seems to be useless for removing the last traces of both erbium and holmium. That the E series gave material of lower atomic weight than the H series is undoubtedly due to the fact that the latter contained considerable holmium while the former was free from this element.

Sodium Nitrite Method.—An extensive study of the effects of fractional precipitation by sodium nitrite was made. This method suggested, by Holden and James,[1] consists in adding a strong solution of sodium nitrite to the nearly neutral solution of the rare-earth nitrates. We have found it expedient to modify in certain features the procedure recommended by Professor James and so our practice is given in full. A quantity of rare-earth oxide weighing from 80 to 110 g. was dissolved in pure nitric acid and the solution evaporated to dryness, care being taken not to overheat any portion. The residue was dissolved in water and made up to about 3 liters, then heated to boiling and a strong solution of sodium nitrite was added drop by drop from a separatory funnel while bumping was prevented by passing in a lively stream of steam. The boiling

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[1] THIS JOURNAL, **36**, 1419 (1914).

was continued from 30 to 90 minutes after the addition of the nitrite, then the solution allowed to stand, usually overnight, and the precipitate filtered out. The precipitate was dissolved in nitric acid and purified in the usual manner, while the process was repeated with the mother liquor. The nitrite used was of the C. P. grade, whose purity was proven by the U. S. P. test. The usual amount of nitrite added at a time was 35 g. dissolved in 70 cc. of water, but larger or smaller amounts were added, depending upon the number of fractions desired from any run. During the progress of the study it was discovered that if the rare-earth solutions were sufficiently dilute the nitrite could be added in the cold without the immediate formation of a precipitate, but upon boiling the mixture for a few minutes a cloudiness appeared and finally a precipitate settled out. This procedure was followed during the latter part of the study of this method since it seemed to give a slightly more rapid separation. We have also found it advisable to continue the fractional precipitation with sodium nitrite until all of the rare earth is thrown out of solution in place of precipitating the final fraction with oxalic acid.

The material first used in testing this method consisted of 80 g. of yttrium oxide which were obtained by adding oxalic acid to the mother liquor from the H ammonia series. The fractions are marked N fractions and the results are shown in Table VI.

TABLE VI.

Fraction.	Wt. of oxalate.	Color of oxalate.	At. wt.
N_1	7.5	Slight pink	89.34
N_2	16.5	Very slight pink	89.07
N_3	30.4	Less than N_2	88.78
N_4	19.3	Almost white	88.95
N_5	32.3	White	88.88
N_6	26.4	White	88.85
N_7	24.5	White	87.65
N_8	1.7	White	87.56

The first fractions show an atomic weight lower than the original material, because the permanganate method was used to determine these atomic weights, while the values given in Table V were determined by titration with potassium hydroxide. It is to be noted that Fractions 3 to 6 yield atomic weights which are nearly or quite constant within the limit of error of the method used while Fractions 7 and 8 show a sharp and pronounced decrease. Fraction 8 was too small in quantity to permit an extended study of its composition but an effort was made to discover why Fraction 7 had so low a value. It was at first supposed that the purification of the sample used in determining the atomic weight had not been thoroughly done, so a fresh sample was put through the purification process. This portion gave an atomic weight of 87.77. Then it was thought that possibly these last fractions, being precipitated from solutions which were becoming heavily loaded with sodium salts, had dragged down enough sodium to account for the low value. So another sample was very thoroughly purified including two precipitations with ammonium sebacate in order to free the yttria from sodium compounds. The mateiral purified in this way gave yttrium an atomic weight of 87.75. Finally the material was tested for scandium by adding a saturated solution of K_2SO_4 to a nearly saturated solution of the rare-earth chloride but no trace of scandium could be detected. Efforts to detect a similar drop in the end fractions of other runs have not been wholly successful, although attention should also be directed to the fact that a similar drop in atomic weight in the last fraction is to be observed in many of the tables given by Holden and James.[1] We are not now prepared to offer an explanation of this peculiar phenomenon.

In order to test further the efficiency of the nitrite method of fractional precipitation, Fractions 3, 4, 5 and 6 of the N series were combined, giving 106.2 g. of material with an average atomic weight of 88.87. This was fractionated again, six fractions being obtained and designated as O fractions, which are described in Table VII.

TABLE VII.

Fraction.	Wt. of oxalate.	Color of oxalate.	Atomic weight.
O_1	10.1	Very slightly yellow	89.18
O_2	18.2	Faint pink tint	89.42
O_3	14.5	White	88.69
O_4	23.7	White	88.46
O_5	17.8	White	88.42
O_6	4.6	White	88.48

Solutions of Fractions 4, 5 and 6 showed no trace of absorption lines, so it was concluded that both erbium and holmium had been eliminated.

A quantity of yttria equivalent to 37 g. was collected from the last fractions of the E ammonia series (Table V) and subjected to the nitrite fractional precipitation. The original solution showed very slight traces of erbium but there seemed to be no other rare-earth admixture. The results are shown in Table VIII.

TABLE VIII.

Fraction.	Wt. of oxalate.	Color of oxalate.	Atomic weight.
R_1	16.3	White	88.58
R_2	36.3	White	88.50
R_3	9.0	White	88.40
R_4	6.8	White	88.45
R_5	1.4	White	88.42

Solutions from the last three fractions showed no visible absorption lines. The oxide obtained from the later fractions is pure white except for a very faint brownish tint which appears wherever the oxide is heated in contact with platinum.

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[1] THIS JOURNAL, 36, 1418–23 (1914).

To test the efficiency of the nitrite fractionation when less pure material is used, 639 g. of yttria from a separate series of bromate fractionations[1] and 583 g. of yttria from the early fractions of the chromate series (Tables III and IV) were converted into the nitrate, which was dissolved in 30 liters of water and neutralized with a dilute solution of sodium hydroxide. This solution contained in a 65 liter evaporating dish was heated over a steam bath and live steam was introduced directly into the solution by means of a perforated block tin coil connected with high pressure steam. A porcelain baffle plate prevented splashing during the heating. Six fractions averaging 364 g. in weight were obtained, the color of the fractions changing gradually from a distinct pink in the first to pure white in the sixth. The original material showed an atomic weight of 91.85 and the lines of both erbium and holmium were distinctly visible. The atomic weight of the yttrium in the sixth fraction was 89.73 and this material, equivalent to 135 g. of the oxide, was again fractionated by the nitrite method, thirteen fractions being obtained. A faint pink color was apparent in the first three fractions, but the others were pure white. The atomic weight of the yttrium in the fourth fraction was 89.75, this value decreasing gradually to 88.73 in the thirteenth fraction. The lines of both holmium and erbium were still faintly visible in these later fractions, but we are convinced not only that the nitrite method of fractionation produces pure yttria, but also that it serves as a rapid and convenient method of removing both erbium and holmium whether they are present in large or small quantities.

The Hydrated Yttrium Salts.

With the hope of finding the hydrated salts of yttrium sufficiently stable under some conditions to be used in atomic weight determinations, samples of $Y_2(SO_4)_3.8H_2O$ and $YCl_3.6H_2O$ were prepared. For the preparation of the former, 22.4 g. of oxalate from H ammonia fractions 17, 22, 24, 27 and 28 (Table V) were ignited to the oxide, dissolved in HCl, a small excess of H_2SO_4 added, the solution evaporated to dryness, and the residue heated in an electric furnace at 525° for four hours. The crystals were dissolved in water by the aid of an agitating machine and the solution evaporated to crystallization. The crystals were thoroughly drained from the mother liquor in a powerful centrifuge and the crystallization repeated. Finally the crystals were allowed to dry in air for 24 hours. These crystals were then divided into five parts and each part was placed in a porcelain crucible. One of the parts was heated until it was certain that a portion of the water of hydration had been expelled. Each of the other crucibles was placed in a weighing bottle and the bottle with cap removed was placed in a desiccator. One desiccator had an opening to the air but contained no desiccating agent, the second contained sulfuric

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[1] The bromate fractionation was performed by Dr. E. W. Engle.

acid, the third calcium chloride, and the fourth contained the partially dehydrated sulfate. In this manner it was hoped to discover the conditions under which the hydrates would be stable. At intervals the weighing bottles were closed and the weight determined as shown in Table IX.

TABLE IX.

Date.		In air.	Over H_2SO_4.	Over $CaCl_2$.	Over partly dehydrated sulfate.
Jan.	3	....	18.3387	17.2310	16.9220
Jan.	6	15.5649	18.3376	17.2293	16.9205
Jan.	8	15.5649	18.3381	17.2300	16.9212
Jan.	12	15.5641	18.3371	17.2290	16.9201
Jan.	14	15.5642	18.3373	17.2291	16.9203
Jan.	19	....	18.3367	17.2284	16.9196
Jan.	22	15.5637	18.3367	17.2285	16.9197
Jan.	24	15.56401	18.33717	17.22882	16.92013
Feb.	4	15.56394	18.33719	17.22874	16.91979
Feb.	7	15.56388	18.33701	17.22807	16.91961
Mar.	7	15.56373	18.33667	17.22784	16.91948
Mar.	24	15.56366	18.33672	17.22786	16.91944
Apr.	5	15.56352	18.33648	17.22771	16.91953

In a similar manner 17.2 g. of yttrium oxalate from ammonia fractions E 12, 13, 18 and 21 (Table V) were converted into $YCl_3.6H_2O$ and their stability tested in air, over sulfuric acid, over calcium chloride, and over the partially dehydrated yttrium chloride. The weights are shown in Table X.

TABLE X.

Date.		In air.	Over H_2SO_4.	Over $CaCl_2$.	Over partly dehydrated chloride.
Feb.	4	13.4313	14.8756	13.8957	13.5841
Feb.	5	13.4321	14.8761	13.8967	13.5849
Feb.	6	13.4317	14.8761	13.8963	13.5846
Feb.	7	13.43159	14.87592	13.89627	13.58393
Feb.	16	13.43138	14.87568	13.89611	13.58378
Feb.	25	13.43132	14.87574	13.89618	13.58370
Mar.	7	13.43145	14.87563	13.89618	13.58368
Mar.	24	13.43130	14.87563	13.89614	13.58369
Apr.	5	13.43125	14.87546	13.89608	13.58366

The hydrates did not seem to be stable under any of these conditions, consequently this effort was abandoned.

The Atomic Weight.

Preparation of Reagents.—The reagents used in the final treatment of the yttria preparatory to determining the atomic weight were all carefully purified in this laboratory. Hydrochloric acid was distilled in glass; nitric acid was distilled in quartz and kept in a quartz bottle; ammonia was freshly distilled as needed from a quartz flask into conductivity water contained in quartz. Ammonium sebacate was prepared by suspending the purest sebacic acid in conductivity water into which ammonia was distilled until the acid had dissolved; then the sebacate was recrystallized twice, the crystals being thoroughly freed from the mother liquor with the centrifuge. Oxalic acid was purified in the following manner: C. P. crystals were dissolved in water containing a small amount of nitric acid; the solution was evaporated to crystallization on the steam bath and then stirred constantly until cold. The fine crystals were freed from the mother liquor in a large centrifuge and recrystallized twice from dilute nitric acid solution, and twice from pure water. The oxalic acid prepared in this manner left no weighable residue on ignition.

The Yttrium Material.—The fractions selected for use in the determination of the atomic weight were O fractions 4, 5 and 6 (Table VII) and R fractions 3, 4 and 5 (Table VIII). The three O fractions were mixed, ignited to the oxide, then dissolved in redistilled hydrochloric acid and reprecipitated twice with freshly distilled ammonia. The precipitates were filtered out on a Büchner funnel and washed with several liters of boiling water, care being taken to keep the precipitate hot and flocculent. Then the yttrium material was precipitated twice from an acid solution with pure oxalic acid, twice with ammonium sebacate, and finally with oxalic acid. The yttria was converted into the chloride in a platinum dish, the solution evaporated and left in a vacuum desiccator to crystallize. Only the first crop of crystals were used in the atomic weight work.

The R fractions were purified in a similar manner, except that they were not mixed and the transformation to the chloride was omitted.

The purification of the yttrium material and the preparation of the reagents were made in a room in which no other work was permitted. Great care was exercised to keep the atmosphere of the room free from laboratory gases and the material free from dust.

The Determinations.—The apparatus used was similar in principle to that previously described.[1] The drying trains for gases were modified so that all reagents were applied in towers filled with glass beads, making a more compact apparatus. The quartz reaction flasks[2] used were somewhat smaller and lighter than those previously employed. When in use the flask was surrounded by an asbestos oven, which served partly to protect it from the laboratory atmosphere. Within the oven was placed an electric furnace which was provided with a double winding of nichrome wire in such a manner that by the use of external resistance any temperature between that of the room and 1000° or more could be maintained. In order to hasten as much as possible the process of dehydration the gases entering the reaction flask were preheated by passing through a glass coil enclosed within the oven.

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[1] THIS JOURNAL, **35**, 373 (1913).

[2] *Ibid.*, **35**, 373 (1913).

The manipulation was exactly the same as that described in the preliminary paper, except that after the oxide was weighed in the flask, it was dissolved in redistilled hydrochloric acid before the flask was attached to the drying train. This procedure shortened the time during which the flask was exposed to the laboratory atmosphere. Weights were made by substitution, using as tare a quartz flask differing in weight from the reaction flask by only a few milligrams. The weights were recently standardized and in all but the first two determinations the weighings were made in a special insulated balance room. The values obtained are shown in Table XI, correction having been made for air displacement.

TABLE XI.

No.	Material.	Weight of oxide.	Weight of chloride.	Atomic weight.
1	O_{4-6}	0.56492	0.97718	88.89
2	O_{4-6}	0.51059	0.88348	88.80
3	R_5	0.64232	1.11092	88.92
5	R_4	0.82157	1.42087	88.93
6	R_3	0.68246	1.17975	89.06
7	O_{4-6}	0.54164	0.93688	88.89

The fourth determination was lost. No reason is known for the low value in the second except that some difficulty was experienced in getting complete dehydration in this case, due probably to the fact that an attempt was made to shorten the process by dehydrating the crystals formed from the strongly acid solution instead of dissolving them in water and dehydrating the crystals formed from a nearly neutral solution. The high value obtained from R_3 may be due to the fact that this fraction was not quite as pure as the others. The R fractions give slightly higher values than the O fractions, but the rather close check obtained from these different fractions would indicate that the yttria is of a high degree of purity. These results have an average of 88.91, which is somewhat higher than the accepted value (88.7).

The advantages claimed for this method are as follows: (1) the use of a ratio which is independent of the sulfate; (2) simplicity in manipulation; and (3) the fact that there are no transfers during the process.

There are several sources of error which have been carefully guarded against. The length of time which is needed to complete a determination makes it necessary for the reaction flask to be exposed to the laboratory atmosphere for several days, during which condensations might easily take place upon the surface. In order to prevent this the flask was tightly inclosed in the drying oven, the lead tubes were kept covered, and the dehydration was finished within as short a time as possible. After the chloride had been fused the flasks were carefully wiped with a clean linen cloth. Care was then exercised to remove any electrification which might have been caused by the friction.

The volatility of yttrium chloride was a matter of some concern, and for this reason the fusion of the chloride was always made with the direct flame. In this way the temperature was raised quickly to the fusion point and as quickly lowered again. The exit tubes were always examined closely for evidences of a deposit and in no case was there the slightest indication of a deposit on the tube B[1] or the upper part of the side neck near D′. There was a slight deposit on the lower portions of this side neck, but since the tube B was included in the weighed portion of the flask it is improbable that any material was lost through volatilization.

In order to learn if fused yttrium chloride adsorbs HCl as it cools, a simple modification of the usual procedure was undertaken. After the chloride was fused in an atmosphere of hydrogen chloride, it was customary to allow it to cool to about 350° and then replace the HCl with nitrogen as the cooling continued. In the last determination (No. 7) the fused chloride was allowed to cool to room temperature in the atmosphere of HCl. In this way it was expected that the acidity of the chloride would be increased if HCl had been adsorbed. There was no increase in acidity, hence it was concluded that there was little or no adsorption.

Summary.

1. Determinations of the atomic weight of yttrium by the synthesis of the sulfate are not reliable since the value may be made to vary widely by changing the length of time and the temperature of ignition.

2. In preparing pure yttria three methods of fractional precipitation were applied to partially purified material.

(*a*) Fractional precipitation with potassium chromate is effective for removing considerable quantities of other rare earths from yttrium but will not remove all the erbium or holmium.

(*b*) Fractional precipitation with dilute ammonium hydroxide is tedious and does not produce pure yttria.

(*c*) Fractionation with sodium nitrite is both a rapid and effective means of freeing yttrium material from admixtures of erbium and holmium.

3. Solutions of materials prepared by the use of all three of these methods gave no visible absorption lines and seemed to be pure yttria.

4. The hydrates $Y_2(SO_4)_3.8H_2O$ and $YCl_3.6H_2O$ are found to be too variable to permit of their use in atomic weight work.

5. The atomic weight of yttrium was determined by the ratio Y_2O_3 : $2YCl_3$ using material from six different fractions. The average of the values obtained is 88.9.

The work is to be continued with two points in view: (1) to study further the purity of the yttria, and (2) to attempt to apply other ratios to the determination of the atomic weight of yttrium.

URBANA, ILL.

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[1] See figure, THIS JOURNAL, **35**, 373 (1913).