Atomic Weight of Samarium (*continued*).

No. of analysis.	Fraction.	$SaCl_3$ in vacuum. g.	Ag. in vacuum. g.	Ag. added. g.	Corrected weight of Ag. in vacuum. g.	Ratio $SaCl_3:3Ag$.	Atomic weight of samarium.
8.......	14:15	4.47775	5.64295	0.00070	5.64365	0.793414	150.41
9.......	14:15	3.33781	4.20662	0.00050	4.20712	0.793374	150.40
	Average of series						150.45
			Final Series.				
10.......	6:7	4.65174	5.86126	0.00002	5.86128	0.793639	150.48
11.......	6:7	5.13023	6.46373	0.00204	6.46577	0.793445	150.42
12.......	8:9:10	4.52826	5.70641	0.00086	5.70727	0.793420	150.41
13.......	8:9:10	6.65425	8.38568	0.00060	8.38628	0.793469	150.43
14.......	11:12:13	6.02908	7.59642	0.00027	7.59669	0.793628	150.49
15.......	11:12:13	5.09858	6.42431	0.00089	6.42520	0.793528	150.45
16.......	14:15	4.68220	5.90040	0.00071	5.90111	0.793444	150.42
17.......	14:15	4.32763	5.45310	0.00241	5.45551	0.793258	150.36
	Average of series						150.43
	Average of both series						150.44

Summary and Conclusions.

The preparation of a very pure samarium material has been described, and its purity proven by spectroscope and analysis.

The possibility of the occlusion of samarium chloride, samarium nitrate or silver nitrate by silver chloride is thought to have been extremely remote because of the special mixing method employed and because of the great dilution of the reacting materials, since the concentration was far less than that used by Baxter and his students. These investigators used a similar method in analyzing similar materials (neodymium chloride and praseodymium chloride) and they found no trace of occlusion.

A considerable disagreement of results in the Preliminary Series is thought to have been due to the diameter of the quartz fusion tube. This was entirely too great when compared with the volume of the sweeping gas. In order to prevent backward diffusion in the final series, a smaller tube was employed. The discordant result of analysis 17 is not explained.

The average value 150.43 of the final series is almost identical with the general average 150.44 of both series.

Durham, N. H.

[Contribution from the Chemical Laboratory of the University of Illinois.]

OBSERVATIONS ON THE RARE EARTHS. IV.

THE PURIFICATION OF GADOLINIUM.

By Louis Jordan and B. Smith Hopkins.

Received July 15, 1917.

The object of this work was to study some methods for the separation of gadolinium from rare earth mixtures and for the purification of gadolinium rich material with the view of obtaining gadolinium of a fairly high degree of purity.

The methods which have been used in the purification of gadolinium are best shown by a brief statement concerning its history.

The discovery of gadolinium, first designated as Y_α, among the earths of samarskite was announced by C. Marignac[1] in 1880. The earths from samarskite whose nitrates were most stable on fusion were divided into four fractions by precipitation with potassium sulfate. One of these fractions contained terbium, ytterbium and a new earth whose solution showed no absorption lines, whose oxide had a pale yellow-orange color and whose equivalent was a maximum of the equivalents of the earths on either side in the potassium sulfate fractionation. The new earth, to which the name gadolinium was later applied,[2] was separated from terbium and ytterbium by the fusion of the nitrates. In 1890, Lecoq de Boisbaudran[3] described the purification of gadolinium by fractional precipitation with dilute ammonium hydroxide.

In 1892, Bettendorf[4] announced the separation of gadolinium from earth material from the mineral orthite, which contained didymium, samarium, gadolinium and terbium. Didymium was separated by the fusion of the nitrates, the samarium was removed by precipitation with a saturated solution of potassium sulfate, and the terbium was removed by fractional precipitation with dilute ammonium hydroxide. It was observed that when the yellow gadolinium oxide was heated gently in an atmosphere of hydrogen, it became colorless without change of weight but when strongly ignited in hydrogen it seemed to undergo a partial reduction, assuming a faint grayish hue.

Benedicks[5] obtained fairly pure gadolinium oxide by fractional crystallization of the simple earth nitrates in nitric acid and later by fractional precipitation with dilute ammonia.

Demarcay[6] used the method of fractional crystallization of the double magnesium nitrates, while Marc[7] obtained some good material by fractionation with potassium sulfate and dilute ammonia.

In 1903 and 1904, Urbain and Lacombe[8] introduced the use of bismuth magnesium nitrate whose solubility lies between that of the double nitrates of samarium and europium. In this manner samarium was entirely removed and only small amounts of europium and terbium remained in the

[1] *Ann. chim. phys.*, [5] 20, 535 (1880).

[2] Boisbaudran, *Compt. rend.*, 102, 902 (1886); *Chem. News*, 53, 225.

[3] *Compt. rend.*, 102, 902 (1886); *Chem. News*, 53, 225.

[4] *Ann.*, 263, 167 (1891); 270, 376 (1892).

[5] *Z. anorg. allgem. Chem.*, 22, 393 (1900).

[6] *Compt. rend.*, 131, 343 (1900).

[7] *Z. anorg. allgem. Chem.*, 38, 121 (1904).

[8] *Compt. rend.*, 137, 792 (1903); 138, 84, 627 (1904).

gadolinium. Later, Urbain[1] further purified this material by recrystallizing the double nickel nitrates in strong nitric acid, obtaining from the insoluble end several fractions which gave perfectly white oxides. The values obtained for the atomic weights of these fractions are approximately constant.

Brauner[2] pointed out that apparently all the gadolinium prepared by workers up to the time of Urbain's work contained some earth of atomic weight less than 157 and that the best of all the early determinations is the earliest of all, that of Marignac.

Sources of Material.

The material for the present work came in part from cerium group earths, in part from yttrium group earths. Europium, gadolinium and terbium form a transition group between the earths of the cerium and yttrium groups, these three earths often being designated as the terbium group. In the usual separation of the cerium and yttrium earths with potassium or sodium sulfate, the gadolinium is divided between the two groups. It follows that either or both groups may be taken as the source of gadolinium material.

The gadolinium material from cerium group sources was taken from Fractions 13 to 18 of a double magnesium nitrate series with bismuth magnesium nitrate that had been run for some time by other workers in this laboratory. These fractions were more soluble than those containing the bismuth and the absorption spectrum showed weak lines of samarium. After removal of the bismuth and magnesium, these six fractions gave about 200 g. of an orange-brown oxide. A concentrated solution of this oxide in nitric acid showed a very distinct absorption spectrum of samarium and a faint but distinct line $\lambda = 525\ \mu\mu$ indicating the presence of europium. The color of the oxide indicated the presence of terbium although no terbium absorption was observed. The average atomic weight of this material, determined by the potassium permanganate titration method as described below, was 157.20. While the accepted value for gadolinium is 157.3, this material was not as pure gadolinium as the atomic weight might at first indicate. The chief impurities, samarium (at. wt. 150.4) and terbium (at. wt. 159.2), tend to neutralize each other. Some of this orange-brown oxide was ignited in an atmosphere of hydrogen to make certain that the color was due to the presence of terbium. It is usually stated that a white oxide colored brown by a small amount of terbium will become pure white on igniting in hydrogen. Strong ignition of this oxide in hydrogen changed the color to a distinct gray, not white. But more gentle heating in hydrogen gave a perfectly white oxide. This behavior

[1] *Compt. rend.*, **140**, 583 (1905).

[2] *Z. anorg. allgem. Chem.*, **50**, 249 (1906).

of gadolinium oxide containing a small amount of terbium was first noted by Bettendorf.[1]

Gadolinium material from yttrium earths was obtained by combining the least soluble fractions from five bromate series. Two of these series were composed of material from which the cerium earths had been removed by precipitation with potassium sulfate. The other three series were made up of earths as extracted from the mineral gadolinite without any treatment to remove cerium group elements. The insoluble end from each of these series, therefore, contained in addition to the gadolinium, a considerable amount of neodymium, less praseodymium and some samarium. The fractions from all five series, twelve fractions in all, were combined into two fractions according to the depth of the red (neodymium) color and by comparison of the absorption spectra, the lighter red fraction being the richer in gadolinium and containing samarium, the deeper colored fraction containing a considerable amount of neodymium and some holmium and dysprosium. These two fractions together contained the equivalent of about 250 g. of earth oxides. The oxide from Fraction 1 was orange-brown, that from Fraction 2 a dark orange-brown. The atomic weights for these fractions were determined: Fraction 1, 154.36; Fraction 2, 152.9.

The Determination of Equivalents.

The method of Feit and Przibylla[1] for the determination of the atomic weights was tried but was not found as convenient as the potassium permanganate titration method of Gibbs.[2] This latter method was the one used in determining values for the atomic weights of earths in this work. The method is very accurate, enabling checks within a tenth of a unit in the atomic weight.

Fractional Crystallization of Dimethyl Phosphates.

The fractionation of the rare earth dimethyl phosphates was suggested as a method of value in the separation of gadolinium by James and Morgan[3] as a result of their work on some crude gadolinium material. They state that comparatively pure gadolinium, judging by the light color of the oxide, was obtained in a very short time. These authors give the order of increasing solubility of the earth dimethyl phosphates as Yb, Er, Y, Gd, Sm, Nd, Pr, Ce and La. This order is the reverse of the more usual one in which lanthanum is at the insoluble end and ytterbium one of the most soluble of all the earths. Further, the earth dimethyl phosphates are very much less soluble in water at 80–90° than at ordinary temperatures.

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[1] *Loc. cit.*

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

[3] THIS JOURNAL, 36, 10–16 (1914).

Dimethyl phosphoric acid was prepared as suggested by James according to the method of Hugo Schiff.[1]

The material converted to the dimethyl phosphates was about 33 g. of the oxide described above as obtained from cerium group earths in a double magnesium nitrate series. The earth oxide was added to a dilute solution of the dimethyl phosphoric acid and went into solution in the cold with a little shaking. This solution was heated on the steam bath to 80°. A small quantity of a gelatinous percipitate formed which was insoluble on cooling the solution. This precipitate was filtered off. The solution was again heated till a precipitate formed, this time entirely soluble on cooling the solution, showing it to be earth dimethyl phosphates. This solution was then evaporated till a crop of crystals of sufficient size for the first fraction had formed, the liquid poured off, again evaporated to crystallization and the first crop of crystals dissolved in cold water to form Fraction 1. The solution was divided into six fractions. This series was run in the following manner: The fractions were heated gradually to 80° on a steam or water bath with frequent stirring, the earth dimethyl phosphates crystallizing out nicely. When sufficient precipitate had formed, the fraction was heated for a few minutes without stirring in order that the crystalline precipitate might form a more compact mass that would allow better draining of the liquor from the crystals in pouring the fractions. The fractions were poured while still hot, the mother liquor being strained through an ordinary Gooch crucible (without asbestos) into the next more soluble fraction. Loose crystals of the earth dimethyl phosphates in the liquid were thus retained in the bottom of the crucible and returned to the fraction from which they were poured. The fractions were then set aside and on cooling the crystals went entirely into solution.

The progress of the fractionation could be judged from the absorption spectrum of the cold saturated solutions of the fractions. After only three series of fractionations the most soluble fraction was a light yellow and showed quite distinct lines of samarium. As the fractions at the insoluble end became too small for convenient fractionation they were set out of the series. After fifteen series of crystallization had been carried out the fractions remaining were numbered 6 to 12.

These fractions were diluted and the earths precipitated as oxalates from a hot solution strongly acid with nitric acid, the oxalates dried and ignited to the oxides. The oxide was then taken up in nitric acid and again precipitated as oxalate to make certain of the removal of all phosphates. The strong nitric acid solution of the oxide before the second precipitation was observed for absorption spectrum. The lines observed compared with those observed in the saturated dimethyl phosphate solution and it is these latter that are referred to below in Table I. The atomic

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[1] *Chem. Zentralb.*, 1857, pp. 761–63.

weights of the material in these fractions were determined in the usual manner.

TABLE I.

Dimethyl Phosphate Fractionation.

Fract. No.	Wt. of oxide, g.	Color of oxide.	Color sol. $R_2(Me_2PO_4)_6$.	Absorp. shows.	At. wt.
1......	0.20	Dark orange-brown	White	.....	..
2......	0.40	Dark orange-brown	White	.....	..
3......	0.25	Dark orange-brown	White	.....	157.98[1]
4......	0.74	Dark orange-brown	White	.....	..
5......	0.72	Orange-brown	White	.....	..
6......	0.65	Light orange-brown	White	.....	..
7......	4.58	Light orange-brown	White	No. abs.	157.46
8......	4.95	Light yellow-brown	White	Sm (barely visible)	157.27
9......	4.73	Light yellow-brown	White	Sm (very faint)	157.25
10......	4.29	Light yellow-brown	Faint yellow	Sm (faint)	157.29
11......	3.90	Cream color	Yellow	Sm (distinct)	156.94
12......	6.00	Cream color	Golden yellow	Sm (strong) Eu (sharp)	156.41

The dark orange-brown color of the oxides at the insoluble end of this series indicates the concentration of terbium in the least soluble fractions as does also the atomic weight, considerably higher than that of the original oxide, 157.20. The value 157.98 for Fraction 3 corresponds to a 3% content of terbium. The light color of the oxide of Fraction 12 shows the absence of any considerable amount of terbium and the strong absorption lines indicate the concentration of samarium and europium in this fraction. The atomic weight of the most soluble fraction 156.41 corresponds to about 12% samarium.

Fractions 8, 9 and 10 showed only faint absorption lines for samarium at $\lambda = 465\mu\mu$ and $475\mu\mu$, the two strongest of the samarium lines. This fact, together with the light color of the oxide as compared with the original material, would seem to indicate that these oxides contained only small amounts of either samarium or terbium. A better indication of the purity of the material is the practically constant atomic weight of these three successive fractions, leading to the conclusion that there was no longer any separation of earths of different atomic weights by this method of fractionation. The constant atomic weight of these fractions and the closeness of the value obtained to the present accepted value for gadolinium (157.3) indicate a fairly high degree of purity in this oxide. It should be pointed out, however, that it was the experience of Hopkins and Balke[2] that the determination of equivalents of yttrium material by

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[1] Fractions 1, 2 and 3 were combined for the atomic-weight determination given under Fraction 3.

[2] THIS JOURNAL, **38,** 2332 (1916).

the potassium permanganate method gave values for the atomic weight that were about 0.5 of a unit lower than the values obtained on the same material by a careful application of the oxide-chloride ratio.

Fractional Crystallization of the Bromates.

James and Bissell[1] found that the fractional crystallization of the bromates gave them a rapid concentration of terbium in the fractions more soluble than the neodymium bromate. A white oxide of gadolinium was obtained from the fractions less soluble than the neodymium. With this in mind, the material described above as from yttrium group sources was fractionated as the bromates. As before stated, this material contained a considerable amount of neodymium. It was hoped that by its concentration between the terbium and gadolinium, it would be possible to remove from the oxide taken the terbium that was present in amounts sufficient to color the oxide orange-brown.

The two original fractions of bromates were made into a series of 10 to 12 fractions and carried through some fifty series of crystallizations. The fractions at the completion of the work were numbered 14 to 29. Table II shows the composition of these fractions as determined by the absorption of the saturated solution of the bromates.

TABLE II.

Fractionation of Bromates.

Atomic weight of original material: Fract. 1, 154.36.
Fract. 2, 152.9.

Fract. No.	Color of bromates.	Absorption shows.	Color of oxide.	Atomic weight.
14...........	Light yellow	Sm		
15...........	Light yellow	Sm		
16...........	Nearly colorless	Sm Nd	Pale cream	
17...........	Nearly colorless	Sm Nd		
18...........	Flesh color	Nd Sm	Cream	
19...........	Flesh color	Nd Sm		
20...........	Pale pink	Nd Sm	Cream	155·57
21...........	Pale pink	Nd Sm Dy		
22...........	Pale pink	Nd Dy Sm	Light orange-brown	
23 to 20......	Pink to red	Nd Pr Dy Ho		

Fractions 18 to 22 were selected as those probably containing the best gadolinium material. The most of the samarium was in the fractions less soluble than the neodymium with the dysprosium and terbium in the more soluble fractions. The earths were recovered from the fractions as the oxides according to the method described by Engle and Balke.[2]

Fraction 20 was converted to the sulfate and treated with a saturated potassium sulfate solution in the attempt to remove some of the samarium and neodymium still present in the oxide. The atomic weight of the material thus treated showed a small rise, 155.94 as compared with 155.57

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[1] THIS JOURNAL, **36**, 2060 (1914); **38**, 873 (1916).

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

of the original Fraction 20. The absorption of the purified portion of Fraction 20 still showed neodymium but only very faint indications of samarium even in a concentrated solution of the nitrates.

The oxide from this purified material was lighter colored, more nearly white, than the oxides from those fractions of the dimethyl phosphate series that were considered to contain the most pure gadolinium. This indicated that the bromate fractionation was the more efficient of the two methods in removing the last traces of terbium. The small amount of neodymium and samarium present is more easily removed from gadolinium than the last traces of terbium.

Fractional Precipitation with Sodium Glycolate.

Jantsch and Grünkraut[1] studied the rare earth glycolates and determined the solubilities of a number of these salts. The order of increasing solubility is given as: Y, La, Ce, Pr, Nd, Sm and Gd. The gadolinium glycolate was found to be more than twice as soluble as the samarium glycolate, the next most soluble. These authors also studied the fractional precipitation with sodium glycolate of a mixture of earths containing Pr, Nd, Sm, Ho, Y and Er and obtained a marked separation. Because of the very great solubility of gadolinium glycolate in comparison with the other earths, it was decide to try the precipitation with sodium glycolate on some of the gadolinium material from the same source as that used for the study of the dimethyl phosphates.

Sodium glycolate was prepared according to the method of Holzer.[2] A neutral solution of the nitrates of the gadolinium rich oxide was prepared by dissolving the original oxide in nitric acid, precipitating the earths as hydroxides with ammonium hydroxide, washing thoroughly, and carefully dissolving up these hydroxides suspended in water by the addition of nitric acid. The solution could be neutralized by the addition of dilute sodium hydroxide if too much acid were used. A drop of methyl orange was added to the earth nitrate solution and also to the sodium glycolate solution in order to be certain that the solutions were entirely neutral. The earth nitrate solution was diluted till it contained about 8 g. of earth oxide in a liter.

To the hot solution of the nitrates the sodium glycolate solution was added. If both solutions were entirely neutral, the addition of the sodium glycolate formed a cloudiness just as it mixed with the nitrate solution but this precipitate dissolved almost immediately. As more of the glycolate solution was added this first precipitate dissolved more and more slowly. When the turbidity was permanent, some excess of the sodium glycolate was added and the whole solution heated for about an hour on the steam bath. On removing and cooling an exceedingly fine granular

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[1] *Z. anorg. allgem. Chem.*, **79**, 305 (1913).

[2] *Ber.*, **16**, 2955 (1883); also L. Vanino, "Handbuch d. Prap. Chime," **2**, 126.

precipitate settled nicely to the bottom of the flask. This precipitate filtered easily and was dried and ignited directly to the oxide. A second precipitate was removed in the same manner, but the third addition of sodium glycolate failed to produce any further precipitate. The remaining solution was acidified with nitric acid and the rest of the earths precipitated with oxalic acid. By far the greater part of the earths was obtained in this last fraction. There was almost no difference in the color of the oxides from these three fractions, all equally orange-brown. Hence there was little, if any, concentration of the terbium by this method, but the atomic weight of the first fraction showed a rapid concentration of samarium. Samarium lines were only barely visible in the absorption of a concentrated nitric solution of Fraction 3. The constant atomic weight of Fractions 2 and 3 indicate practically complete removal of samarium. The atomic weight of Fraction 1 corresponds to the presence of about 8% samarium.

TABLE III.

Precipitation with Sodium Glycolate.

Atomic weight original = 157.20.

Fraction No.	Absorption shows.	Atomic weight.
1	Sm	156.70
2		157.47
3	Sm (barely visible)	157.46

Summary.

1. The dimethyl phosphate fractionation very rapidly and completely concentrated the europium and samarium and removed them from the gadolinium. The most of the terbium was separated in the insoluble fractions of the series. The method did not remove the last traces of terbium that still colored the gadolinium oxide a light yellow-brown. Gadolinium oxide of considerable purity was obtained from the middle fractions of this series.

2. Gadolinium material giving an oxide colored orange-brown by terbium was fractionated as the bromates in the presence of neodymium. The method was more tedious than the dimethyl phosphate method but almost completely removed even the last traces of terbium from the gadolinium and furnished a light cream, almost colorless, oxide. This oxide still contained a small quantity of neodymium and samarium. The first method studied would seem to be an effective method for removing these earths.

3. Precipitation of a neutral nitrate solution of the earths with sodium glycolate rapidly removed samarium from gadolinium but did not appreciably concentrate the terbium.

4. The above results suggest the following procedure for the separation of gadolinium from rare earth mixtures: The cerium should be removed by the potassium bromate method and the mixed rare earths fractionally

crystallized as the bromates without having been separated into the cerium and yttrium groups. The insoluble end of the bromate series will contain only europium, samarium, gadolinium and neodymium. These fractions may be converted to the dimethyl phosphates and fractionated. The gadolinium should be easily obtained very pure from the least soluble fractions. Precipitation with sodium glycolate may take the place of the dimethyl phosphate fractionation or may be employed for the removal of the last traces of samarium remaining in the gadolinium from the dimethyl phosphate series.

URBANA. ILL.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK AND THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

A STUDY OF THE TEST FOR TARTRATES DEPENDING UPON THE FORMATION OF THE COPPER-TARTRATE COMPLEX.

BY L. J. CURTMAN. A. LEWIS AND B. R. HARRIS.

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The test described by Böttger,[1] depending upon the solubility of cupric hydroxide in alkaline solutions of alkali tartrates, appears to offer a simple and reliable means for the detection of tartrates. But it was observed in preliminary experiments, the object of which was a systematic procedure for the identification of tartrates, that in actual practice, the formation of the copper-tartrate ion was affected by a number of variables which could not be predicted from a theoretical consideration of the reaction. It became apparent, moreover, that the influence of these variables was of such importance that it would be necessary to make a thorough study of certain phases of the reaction before it could be safely used in systematic analysis.

The first aim was to determine the sensitiveness of the test under a set of definitely specified conditions.

Procedure I.—A definite volume of a standard potassium tartrate[2] solution was measured into a small beaker. 1.5 cc.[3] of 10% sodium hydroxide and 1 cc. of 0.5 *N* copper sulfate were added. The mixture was stirred thoroughly one minute and transferred to a filter. The filtrate, received in a test tube was treated with strong ammonium hydroxide in excess. The results are given in Table I.

The coloration obtained with 1 mg. was detectable only by very close comparison with the blank.

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[1] "The Principles of Qualitative Analysis," Smeaton's translation, **1906,** 159.

[1] $K_2C_4H_4O_6.{}^1/_2H_2O$ was used.

[2] Experiment showed that this amount of sodium hydroxide provided a safe excess over that required to completely precipitate the quantity of copper used.