

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

OBSERVATIONS ON THE RARE EARTHS. X. THE PURIFICATION AND ATOMIC WEIGHT OF SAMARIUM.¹

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Introduction.

This investigation was undertaken as a part of a general program mapped out in 1911 for work on the purification and atomic weights of the different rare earth elements. The samarium material was purified to a high degree preliminary to the determination of its atomic weight. The ratios oxide to chloride, and oxide to chloride hydrate, were found to be unsatisfactory and were replaced by the ratio chloride to silver.

Purification of Reagents.

The water used was redistilled from alkaline permanganate and gave no test for chlorides in the nephelometer. The oxalic acid was prepared by twice recrystallizing c. p. acid from water acidified with nitric acid and once from water alone. The acid thus prepared gave no residue on igniting a 20 g. sample. c. p. nitric and hydrochloric acids were redistilled from a quartz flask as needed. Hydrogen chloride was prepared by dropping c. p. sulfuric acid into c. p. hydrochloric acid and drying the gas by passing it through beads moistened with sulfuric acid. Nitrogen was prepared by burning ammonia and air in a quartz tube containing copper gauze and was then purified by removing the water, carbon dioxide, arsine, etc. The air was purified in the same manner. The apparatus for the purification of hydrogen chloride, nitrogen and air has been previously described.² The silver used was very kindly donated by Dr. H. C. Kremers. Its preparation has been previously described by him.³

Preparation of Pure Samarium Oxide and Chloride.

(a) Separation of Samarium from Lanthanum, Praseodymium and Neodymium.—The source of the material used in obtaining the pure samarium material was some 400 pounds of cerium-earth double sulfates from the Welsbach Mantle Co. These sulfates contained all of the members of the cerium group, but as the original source of the material was monazite sand there was very little europium or gadolinium present. Most of the cerium had been removed for commercial purposes and the yttrium earths had been roughly removed by precipitating out the cerium earths as double sulfates with a saturated solution of sodium sulfate.

¹ Part of a thesis submitted by A. W. Owens to the Graduate School of the University of Illinois as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Kremers, H. C., THIS JOURNAL, 40, 598 (1918).

³ *Loc. cit.*

The double sulfates were boiled with a strong solution of sodium hydroxide until they were completely decomposed. The solution was diluted and the hydroxides were washed with boiling water until they were free from sulfates. In order to remove the remaining cerium, the hydroxides were dissolved in nitric acid, the solution was made nearly neutral, heated to boiling and potassium bromate added. As the red fumes of bromine appeared, marble dust was added to keep the solution nearly neutral and the solution was boiled until some of the filtered liquid failed to give a test for cerium with hydrogen peroxide. The small amount of cerium basic nitrate and the excess marble were filtered off. The rare earth oxalates from this solution were ignited to oxides and these were dissolved in dil. nitric acid. In order to convert these nitrates into the magnesium earth double nitrates for fractionation, as first recommended by Demarcay,¹ a quantity of nitric acid equal to the amount used in the solution of the oxides was neutralized with magnesium oxide, and the two solutions filtered and united. This solution was then fractionally crystallized for the separation of the samarium material. When the most soluble fractions, containing the bulk of the samarium, began to crystallize poorly, they were diluted, filtered, and the earths precipitated as oxalates in order to remove any impurities of the common elements which might be present.

When no more samarium appeared at the soluble end the fractionation was discontinued. The samarium oxalate was ignited, and the oxide was again converted into the magnesium samarium double nitrate as described above. In the second series of fractionations the most soluble fractions were set aside when no more absorption lines of neodymium were visible through 10 cm. of a saturated solution.

(b) **Separation of Samarium from Europium and Gadolinium.**—The material from the previous fractionation now contained some europium and gadolinium and possibly a very small amount of yttrium earths. After the yttrium earth nitrates had been removed, by running the samarium magnesium double nitrates through about 180 fractionations with 30% nitric acid, bismuth magnesium double nitrate was added at the soluble end. According to Urbain and Lacombe,² the bismuth magnesium double nitrate crystallizes between samarium and europium with gadolinium still more soluble than europium. After about 40 crystallizations of this series the first 6 determinations were made. Before making any further determinations it was thought advisable to fractionate the bismuth and samarium double nitrates still more, even though for some time the material had shown no other adsorption lines than those of samarium. The material was put through about 150 more crystalliza-

¹ *Compt. rend.*, 130, 1019 (1900).

² *Ibid.*, 137, 793 (1903).

tions before the final series of oxide-chloride determinations were made. The samarium chloride-silver determinations were made with the very best material.

(c) **Conversion into Oxide.**—The samarium material used for the atomic weight determinations was taken from the middle series of the samarium bismuth magnesium nitrates described above. The nitrates were thoroughly fused in a porcelain dish and the oxides and basic nitrates thus formed were dissolved in as little hydrochloric acid as possible. After evaporating this solution to a syrupy condition, it was poured into a large volume of distilled water. The bismuth oxychloride was allowed to settle and the supernatant liquid siphoned off. The cold solution containing the samarium chloride and magnesium chloride was saturated with hydrogen sulfide in a 10-liter flask, and was then digested on the steam bath until the brown coloration entirely disappeared and the bismuth sulfide settled out. The bismuth sulfide was filtered off and the solution again saturated with hydrogen sulfide. This was repeated until no further precipitation of bismuth sulfide was obtained. The hydrogen sulfide was removed by forcing filtered air through the boiling solution. The solution was made 1% acid with nitric acid and samarium oxalate precipitated out with hot dil. oxalic acid.

In precipitating samarium oxalate it was found best to do so from a boiling 1% nitric acid solution, using a boiling solution of dil. oxalic acid as the precipitant. By adding the oxalic acid until the precipitate first formed, just failed to redissolve and then cooling the solution rapidly it was found possible to obtain a very fine precipitate which was crystalline, settled rapidly, and washed well on a Büchner funnel. These oxalates were dried and ignited in platinum dishes in an electric oven in order to convert them into oxides. The oxides were then dissolved in nitric acid and the samarium precipitated as hydroxide by passing ammonia vapors into the flask while the solution was being agitated. The hydroxides were washed by decantation until they started to become colloidal and were then washed on a Büchner funnel. The oxalate and hydroxide precipitations were carried out alternately, 3 times for each sample. The oxalates were ignited at 800° for 6 hours and then at 900° for 2 hours. In this way it was hoped that all the carbonate first formed would be decomposed to the oxide.

(d) **Conversion into Anhydrous Chloride.**—The method of converting samarium oxide into anhydrous chloride was somewhat similar to that used by Baxter in preparing other rare earth chlorides. Instead of the bottling apparatus used by the latter, a quartz reaction flask, first described by Egan,¹ was used to obtain the transformation. This had the advantage that the oxide was changed to chloride in the apparatus in

¹ THIS JOURNAL, 35, 365 (1913).

which it was weighed and the chloride was also weighed in the same apparatus.

The samarium oxide, ignited as described above, was transferred to the previously weighed reaction flask while still hot, and the outlet and inlet tubes were inserted and their air-tight caps were adjusted. The reaction flask was then placed in a desiccator and the latter placed in the balance room for one hour. After loosening one of the caps to equalize the pressure, the flask was hung in the balance case and weighed at intervals of $\frac{1}{2}$ hour until it had come to equilibrium.

All weighings were made on a very sensitive Ruprecht balance used exclusively for atomic weight work, in a special cork-lined room, the temperature of which seldom varied more than 3° . All weighings were made by substitution, using a similar flask as tare. The weights were either of platinum or of gold-plated brass and were calibrated to 0.01 mg. All weights were corrected to vacuum before being used in any calculation. The specific gravity of the brass weights was taken as 8.4, of the platinum weights as 21.5, of the samarium oxide as 8.247,¹ of samarium chloride as 4.465,² of samarium chloride hydrate as 2.383,³ and of silver as 10.53. The atomic weights were taken as follows: oxygen, 16.0; chlorine, 35.46; silver, 107.88; and hydrogen, 1.008.

The oxide in the flask was moistened with water and then dissolved in pure hydrochloric acid. The oxide always dissolved to a clear amber-colored solution without any apparent effervescence or spattering. The reaction flask was then attached to the drying train by means of the two ground joints and enclosed in an electrically heated oven having glass sides through which the progress of the dehydration could be watched. This oven also protected the flask from the fumes of the laboratory during the time it was connected to the train. The oven was heated to 130° , and a brisk stream of air was passed through the flask thus driving off most of the excess water. The temperature was then dropped to 105° , and hydrogen chloride, passed in to cause the formation of samarium chloride hydrate, as this procedure allowed the excess solution to creep up the sides of the flask, and exposed a larger surface for dehydration. The first 5 molecules of water were removed below 105° , by a current of air and hydrogen chloride, in from 10 to 12 hours. This point was shown by the absence of moisture in the cooler portions of the exit tube. The proportion of hydrogen chloride was now increased and the temperature was gradually raised to 190° where the last molecule of water was expelled. Hydrogen chloride alone was now passed through the flask and the temperature gradually raised to 360° , where it was held for one hour. The oven

¹ *Chem. News*, 51, 145 (1885).

² *Compt. rend.*, 140, 1339 (1905).

³ *Chem. News*, 53, 45 (1886).

was then removed, the stream of hydrogen chloride was stopped, and the samarium chloride was fused either with a Bunsen flame or with an electric pot furnace. There was no evidence that the samarium chloride was appreciably volatile at its melting point. According to Matignon,¹ anhydrous samarium chloride melts at 686°. When free from oxychloride the samarium chloride melts to a reddish liquid which does not wet the bottom of the quartz flask. If, however, any oxychloride is present the melt wets the flask, attacks it, and fuses with much more difficulty. After the samarium chloride was fused the flask was cooled in an atmosphere of hydrogen chloride and then air was passed through the flask until all traces of hydrogen chloride were removed. By first adjusting the cap on the outlet tube, and then the one on the inlet tube, the flask could be sealed without admitting any undried air. The samarium chloride was weighed in a manner similar to that described for the oxide.

At first nitrogen was used in the early part of the dehydration, but this was found to be unnecessary. Furthermore, it was found that samarium chloride heated for some time in a current of nitrogen lost chlorine, and was reduced to samarous chloride (SaCl_2). According to Baxter, nitrogen prepared in this way contains some hydrogen and these experiments seem to confirm his statement for tests showed that hydrogen chloride was given off and not chlorine. The samarous chloride was a purplish brown crystalline mass and had the other properties ascribed to it by Matignon.² The use of nitrogen was discontinued, because of the danger of reducing the samaric chloride.

All the samples of samarium chloride dissolved completely in cold water. In order to test the hydrogen ion concentration of the samarium chloride solution, samples from a preliminary run were treated with the following indicators: rosolic acid gave yellowish pink; methyl orange gave yellow; congo red gave orange; phenolphthalein gave a colorless solution; and litmus gave red-violet. These results, according to Washburn, indicate a hydrogen ion concentration of about 10^{-8} .

The Ratio of Samarium Oxide to Samarium Chloride.

In about 1911 Prof. C. W. Balke and his associates began a series of atomic weight determinations on various elements of the rare earth family. As a few preliminary experiments showed that the oxide-sulfate and hydrated sulfate ratios were unreliable they decided to use the oxide-chloride ratio. Egan,³ Sears,³ Engle,⁴ Hopkins,⁵ Kremers,² and Wichers,⁶ have used this ratio for atomic weight determinations.

¹ *Compt. rend.*, 141, 1230 (1905).

² *Loc. cit.*

³ *THIS JOURNAL*, 36, 833 (1915).

⁴ *Ibid.*, 39, 53 (1917).

⁵ *Ibid.*, 38, 2332 (1916).

⁶ *THIS JOURNAL*, 40, 1615 (1918).

The first 6 determinations were made in 1913 with material from the middle of the best series. Although this material showed no other absorption spectra than that of samarium, one year was spent in making further fractionations from nitric acid of 1.30 sp. gr. As the results from the next 8 determinations were in no better agreement than those from the first 6, it was decided to obtain the oxide from different sources. Dr. Kremers found that the oxide chloride ratio gave consistently higher results than the chloride silver ratio in the determination of the atomic weight of dysprosium. Dr. Wichers found that it was impossible to prepare pure erbium oxide by the ignition of the oxalate. Samarium nitrate and samarium hydroxide were, therefore, used as the source of oxide in the next 8 determinations. These samples were ignited at 900° and then ground in an agate mortar, the process being repeated 3 times in order to obtain as pure an oxide as possible. These results were no better than the previous ones so this ratio was abandoned because of the difficulty of obtaining pure samarium oxide. The average atomic weight for the 22 determinations by this ratio was 153.0.

The Ratio Samarium Chloride Hexahydrate to Samarium Chloride.

Samarium chloride hexahydrate was prepared from the purest oxide and was recrystallized 5 times from a water solution. It was hoped that a dependable ratio might be obtained between samarium chloride hexahydrate and samarium chloride, but due to the difficulty of obtaining a hydrate of constant composition this ratio was found to be useless. The hexahydrate when exposed to dry air at 27° will lose water continuously and finally fall to a powder.

The Ratio Samarium Chloride to Silver.

The ratio of a rare earth chloride to silver was first used by Baxter and Chapin¹ to determine the atomic weight of neodymium and was later used by Baxter and Stewart² to determine the atomic weight of praseodymium. Stewart and James³ also used this ratio in their revision of the atomic weight of samarium.⁴ Egan tried to use this ratio in his determination of the atomic weights of yttrium, but for some unknown reason he failed to get concordant results. The ratio was not used again in this laboratory until it was successfully carried out by Kremers in his determination of the atomic weight of dysprosium.

In order to become familiar with the manipulations necessary in this ratio, a few determinations of pure fused sodium chloride against silver

¹ THIS JOURNAL, 33, 1 (1911).

² *Ibid.*, 37, 516 (1915).

³ *Ibid.*, 39, 2605 (1917).

⁴ At the time Stewart and James published their article entitled, "A Revision of the Atomic Weight of Samarium," the laboratory work on the present investigation was nearly completed, the first 13 determinations having been finished. Due to the stress of the times these results could not be published sooner.

were made. The results were quite comparable to those of Richards and Wells for the same ratio.

The anhydrous samarium chloride was weighed in the reaction flask, in which it had been dehydrated, and was dissolved in conductivity water. The solution was quantitatively transferred to a 1.5 liter glass-stoppered Jena Erlenmeyer flask, and diluted to 400 cc. Assuming the atomic weight of samarium to be 151.0, within a few tenths of a milligram of the calculated weight of silver was weighed out, and dissolved in dil. redistilled nitric acid in a liter Jena Erlenmeyer flask fitted with a column of bulbs, 50 cm. high, to retain any spray. The silver nitrate solution was diluted to 400 cc. and added gradually to the dilute samarium chloride solution while the latter was being violently agitated. After agitating for 3 hours in a motor-driven shaking machine, the solution was allowed to stand for 12 hours, and the clear supernatant liquid was then tested in a nephelometer for an excess of either chlorine or silver. All work which involved materials affected by light was done in a dark room. After testing the supernatant liquid, portions of standard silver nitrate or sodium chloride solutions were added from weighing pipets until exact equivalence was reached. The amount of silver used, as silver nitrate, was added to the amount originally weighed out, and the silver equivalent of the sodium chloride added was subtracted from the total silver. It was necessary to add sodium chloride when too much silver had been weighed out, or when too much silver nitrate had been added. After each addi-

THE RATIO OF SAMARIUM CHLORIDE TO SILVER.

No.	Frac- tion.	SaCl ₂ .	Ag weighed out.	Ag added.	Ag total.	SaCl ₂ 3 Ag.	Atomic weight.
1	42	6.47502	8.14202	+0.01608	8.15810	0.793692	150.49
2	42	4.03877	5.09024	-0.00941	5.08083	0.794903	150.90 (SaOCl)
3	43	4.25295	5.36673	-0.00745	5.35928	0.793567	150.45
4	43	4.34537	5.47543	+0.00120	5.47663	0.793442	150.41
5	44	3.84046	4.74751	+0.09251	4.84002	0.793480	150.42
6	45	3.32317	4.31449	-0.12629	4.18820	0.793460	150.42
7	32	2.96369	3.73081	+0.00423	3.73504	0.793480	150.42
8	33	3.34818	4.21583	+0.00353	4.21936	0.793527	150.44
9	34	3.27999	4.13128	+0.00205	4.13333	0.793546	150.44
10	35	3.00394	3.78617	+0.00152	3.78769	0.793396	150.40
11	36	2.36481	2.97873	+0.00097	2.97970	0.793640	150.47
12	37	3.68616	4.64535	+0.00042	4.64577	0.793444	150.41
13	38	3.17435	4.00033	-0.00013	4.00020	0.793548	150.44
14	39	2.81639	3.54905	+0.00027	3.54932	0.793501	150.43
15	40	3.13555	3.95087	+0.00068	3.95155	0.793500	150.43
16	41	2.91019	3.66900	-0.00154	3.66744	0.793520	150.44
17	42	4.15775	5.23920	+0.00053	5.23973	0.793504	150.43
18	43	3.32305	4.18985	-0.00033	4.18952	0.793650	150.47
19	44	2.06632	2.62794	+0.00156	2.62950	0.793430	150.41

Omitting No. 2, because SaOCl was known to be present, average = 150.43

tion the flask was shaken for 2 hours and was then allowed to stand from 8 to 12 hours before testing again.

The samarium chloride for determinations 1-4 was obtained from the last 4 determinations of the oxide-chloride ratio. In determinations 5-13 the anhydrous chloride was obtained by introducing a saturated solution of samarium chloride into the flask and dehydrating as described above. In determinations 14-19 the anhydrous chloride was obtained from the determinations of the ratio hydrated chloride to anhydrous chloride. Although the material for these last 6 determinations was purified more than the previous material, the atomic weights are virtually the same.

The results of this ratio are shown in the table on page 521.

Summary.

1. Samarium material was obtained from rare earth residues purchased from the Welsbach Mantle Co. The cerium was removed by means of bromine and marble. Lanthanum, praseodymium and neodymium were removed by fractionation of the rare earth magnesium double nitrates, first from a water solution and then from nitric acid of 1.30 sp. gr. Europium and gadolinium were removed by fractionation of the rare earth magnesium double nitrates along with bismuth magnesium double nitrate. The final purification was the alternate precipitation of samarium material as hydroxide and oxalate and 5 recrystallizations of this material as hydrated chloride.

2. The oxide-chloride ratio was found unsatisfactory due to the difficulty of obtaining pure oxide. Oxide was obtained by igniting the oxalate, nitrate and hydroxide, but the results were equally discordant.

3. The hydrated chloride-anhydrous chloride ratio was found unsatisfactory due to the difficulty of obtaining pure samarium chloride hexahydrate.

4. The anhydrous chloride-silver ratio was altogether satisfactory and these values are to be taken in preference to all others.

5. The results of this investigation confirm the results of Stewart and James as to the value of the atomic weight of samarium.