

oxide is found to be 0.7 mg. of La_2O_3 per liter at 25° . The data from the conductivity and volumetric methods agree within 10%.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]
**THE QUANTITATIVE DETERMINATION OF LANTHANUM BY
PRECIPITATION AS OXALATE OR AS HYDROXIDE AND THE
HIGHER OXIDE FORMATION OF LANTHANUM**

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The Determination of Lanthanum by Precipitation as Oxalate.—As lanthanum oxalate carries down alkali oxalates² oxalic acid must be used as a precipitating agent. The determination can be made volumetrically or gravimetrically. All experiments have been carried out with lanthanum chloride solutions. Pure³ lanthanum chloride ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) was prepared and a standard solution of this product made up in a known weight of water. The latter was standardized by gravimetric chloride and lanthanum determinations according to precision methods, and contained 0.2946 equivalent of LaCl_3 per 1000 g. of solution (chloride analysis). In all further experiments a known volume was pipetted out and weighed. All reagents used were purified and tested for purity according to precision methods.

Volumetric Determination.—(a) The excess of oxalic acid is titrated in an aliquot part of the filtrate. (b) After washing out with water the precipitate is dissolved in warm dilute sulfuric acid and titrated according to the standard procedure with permanganate.

Ten-cc. portions of the stock solution of lanthanum chloride were pipetted into iodine flasks of known weight. Afterward the flasks were reweighed, varying amounts of a pure 0.05 molal oxalic acid solution were added and the flasks and contents again weighed. After standing overnight, weighed portions of the filtrates were titrated with a standard permanganate solution added from a weight buret. In all cases the titration error was determined by experiment. The precipitated lanthanum oxalate was collected on a filter and washed with cold water until the filtrate turned methyl orange the same shade as the water. The precipitate was

¹ From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Th. Sheerer, *Ann. phys. chim.*, [II] 56, 479 (1842); G. P. Baxter and R. C. Griffin, *THIS JOURNAL*, 28, 1684 (1906); G. P. Baxter and H. W. Daudt, *ibid.*, 30, 563 (1908); compare next paper in this series, where an interpretation of this so-called coprecipitation has been given.

³ Cf. I. M. Kolthoff and Ruth Elmquist, *THIS JOURNAL*, 53, 1217 (1931).

then dissolved in dilute sulfuric acid and titrated with permanganate. The results are given in Table I. From Expts. 1-4 it is evident that a relatively large excess of oxalic acid must be added in order to get a quantitative precipitation of lanthanum oxalate. Moreover, the high values in Expts. 2, 3 and 4 obtained by titrating the filtrates (Columns 4 and 5) show that oxalic acid is carried down by lanthanum oxalate, the amount increasing with the quantity of precipitant. This occlusion, however, is much less than with alkali oxalates.

In order to get good results a large excess of oxalic acid must be used in the precipitation, and the precipitate washed for a long time with water in order to remove the adsorbed oxalic acid. Even after the filtrate gives an intermediate color with methyl orange, the precipitate still contains oxalic acid and about 175 cc. more wash liquid is required to remove the last traces of oxalic acid.

Precise results are obtained according to the following procedure (Expt. 5, Table I): 50 cc. of normal oxalic acid is added to 10 cc. of the lanthanum chloride solution. The precipitate is collected and washed until the filtrate turns methyl orange the same shade as that of the wash water. The lanthanum oxalate is dissolved and titrated. The results are accurate to 0.1%.

Experiments 5 (Table I) have been carried out according to the above procedure; 275 cc. of water was used to wash out all the oxalic acid. As the solubility of lanthanum oxalate in water amounts to 0.023 milliequivalent per liter,³ the error due to solubility in our case cannot be greater than 0.2%, and in reality it was much smaller, since the filtration was rapid and permitted only momentary contact between liquor and precipitate.

TABLE I
VOLUMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS OXALATE

Expt.	M. equiv. La taken	M. equiv. oxalic acid added	M. equiv. La found from titration of filtrate	Deviation from calcd. value, %	M. equiv. La found from titration of ppt.	Deviation from calcd. value, %
1	2.990	4.332	2.960	-1.00	2.951	-1.30
2	2.996	5.005	3.002	+0.20	2.990	-0.20
3	2.999	7.508	3.016	+ .57	3.012	+ .43
4	2.989	10.201	3.133	+4.81	2.984	- .17
5a	2.993	50			2.991	- .07
5b	2.994	50			2.995	+ .03
5c	2.992	50			2.988	- .13

In the literature⁴ it is reported that the volumetric determination of lanthanum by titration of the lanthanum oxalate gives high results. This must be attributed to an incomplete removal of oxalic acid from the precipitate.

⁴ G. Krüss and A. Loose, *Z. anorg. Chem.*, **4**, 161 (1893); W. A. Drushel, *Am. J. Sci.*, [IV] **24**, 197 (1907).

Since sodium oxalate (and other alkali oxalates) are carried down to a considerable extent by lanthanum oxalate and cannot be removed by washing the precipitate, the experiments described in Table I have been repeated in the presence of 2 and 3 g. of sodium chloride added as a 1 *N* solution. The results showed a slight coprecipitation of sodium oxalate or bioxalate. According to the precise procedure (Expt. 5) the results were accurate to within 0.2%.

The Gravimetric Determination of Lanthanum by Precipitation as Oxalate.—Twenty-five to 100 cc. of a 1 *N* oxalic acid solution was added to 10 or 40 cc. of the standard lanthanum solution (weighed portion) with constant stirring. After standing overnight the precipitate was filtered, washed and dried at temperatures between 50 and 300°. No temperature was found at which any hydrate of lanthanum oxalate reached constant weight. The oxalate decomposes before the last portion of the water has been removed.⁵ Therefore the filter and precipitate were ignited in an electric furnace, in which the oxalate was transformed into oxide. It was found that the lanthanum oxide absorbs water from the atmosphere very readily. When the relative humidity of the air is low (about 20%), the oxide does not increase in weight during the weighing, but when it is high (60% or more) its weight increases rapidly when the oxide is exposed to the air. Therefore for accurate work it is recommended that the crucible containing the oxide, after being cooled in a desiccator, be weighed in a weighing bottle with well-fitted cover. At 700° the oxide is slow in coming to constant weight; after heating for twenty-four hours at this temperature the weight was 6% too high. This result is not in harmony with the statement of Backer and Klaassens,⁵ who find that on heating lanthanum oxalate the formation of the oxide is quantitative at 600°. It was found that after heating the oxalate for five to eight hours at temperatures between 800 and 900°, a quantitative formation of the oxide takes place; the weight does not change upon prolonged heating at these temperatures. It is recommended that the ignition temperatures should not exceed 850°; at 1000°, the oxide, after having reached a minimum weight, increases its weight upon further heating. A similar phenomenon has been noted by P. H. M.-P. Brinton and L. A. Sarver,⁶ though they did not investigate the influence of the temperature upon this effect. It is possible to obtain perfectly constant results if the ignition temperature is kept between 800 and 850°.

⁵ After this work was finished, a paper was published by H. J. Backer and K. H. Klaassens, *Z. anal. Chem.*, **81**, 104 (1930). These authors state that at 250° lanthanum oxalate is obtained in the anhydrous form and that the weight is constant. At temperatures above 300° they noticed a decomposition of the oxalate under evolution of carbon monoxide and carbon dioxide. Between 400 and 500° again a constant weight was found, corresponding to the composition La_2CO_5 (basic carbonate), and it is recommended that this compound be used as a weighing form of lanthanum oxalate.

⁶ Sarver and Brinton, *THIS JOURNAL*, **49**, 943 (1927).

The results given in Table II were obtained by weighing the crucible containing the oxide in a closed weighing bottle after constant weight had been attained at 800°.

TABLE II
GRAVIMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS OXALATE AND WEIGHING AS OXIDE

M. equiv. La taken	M. equiv. H ₂ C ₂ O ₄ added	M. equiv. La found	Deviation from theo- retical value, %
10.425	100	10.453	+0.25
11.684	100	11.698	+ .15
11.691	100	11.713	+ .19
11.639	100	11.658	+ .16
11.609	100	11.625	+ .14

The results are consistently 0.15% high. Comparing the results with those reported in Table I (5a, 5b and 5c) it may be inferred that the volumetric method gives more precise results. As the latter is much easier to perform, and gives results in a much shorter time it is preferable to the gravimetric method.

The Determination of Lanthanum by Precipitation as Hydrous Oxide

Volumetric Determination.—Though lanthanum hydroxide behaves like a strong base, its solubility in water is so small that the saturated solution does not react alkaline to thymolphthalein as indicator. Therefore the direct titration of lanthanum chloride with sodium hydroxide (or with an excess of the latter and back titration) was tried using thymolphthalein as an indicator. The end-points were indistinct and the results very unsatisfactory. Later the interesting fact was found that a suspension of lanthanum oxide in water assumes a dark blue-violet color upon addition of thymolphthalein, though the clear saturated solution remains colorless. The indicator is hydrolytically adsorbed by the solid strong base.

In the following experiments a weighed portion of a standard 0.05 *N* sodium hydroxide solution (carbonate free, kept in paraffin-coated flasks) was added to a weighed amount of the stock solution of lanthanum chloride. The next day weighed portions of the filtrate (the first few cc. were discarded) were titrated with 0.05 *N* hydrochloric acid, using methyl orange as an indicator. The acid and base were standardized according to precision methods, and the titration error was corrected for in an experimental way. In all experiments weight burets were used. The precipitates were washed with a mixture of 50% alcohol and water until the wash liquid was free from alkali when tested with phenol red. They were then dissolved in a weighed excess of standard acid and the excess titrated back.

As shown by Expts. 1 and 2 in Table III, the results are low. The deviation is due to basic chloride formation, which was proved by quantitative chloride determinations in the filtrate and in the precipitate. Better

results might be expected if the lanthanum chloride were added slowly to an excess of sodium hydroxide. Experiments 3, 4, 5 and 6 in Table III were carried out in this way. The last two experiments show that good results are obtained if the lanthanum solution is added slowly to a large excess of sodium hydroxide (about five times the theoretical amount) and the precipitate is titrated after having been washed with a mixture of 50% alcohol and water. No basic chloride is formed. The chloride in the filtrates and wash liquids of Expts. 5 and 6 was determined gravimetrically; the results were 0.10 and 0.15% higher than the theoretical figures.

TABLE III

VOLUMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS HYDROXIDE

Expt.	M. equiv. La taken	M. equiv. NaOH added	M. equiv. La found from filtrate	Deviation from calcd. value, %	M. equiv. La found from titration of ppt.	Deviation from calcd. value, %
1	2.985	3.179	2.897	-2.95	2.891	-3.15
2	2.999	4.974	2.941	-1.93	2.950	-1.63
3	3.001	3.185	2.957	-1.47	2.978	-0.77
4	2.989	4.287	2.951	-1.27	2.973	- .54
5	2.984	15	2.986	+ .13
6	3.001	15	3.007	+ .20

Precipitation of the Hydrus Oxide by an Excess of Ammonia.—Carbonate-free ammonia was prepared by distillation over calcium oxide and the solution was kept in a paraffin-coated flask. An excess of ammonia was added to the lanthanum chloride solution and the precipitate after having been washed was titrated in the way described. In all cases the results were low on account of basic chloride formation, the deviation being larger when the ammonia was added to a hot solution of lanthanum chloride than at room temperature. The speed of addition of ammonia has also an influence; the results are better when it is added quickly (deviation in the various cases between 1.5 and 3.8% from the theoretical value). By gravimetric chloride determinations it was found that no basic chloride is formed when lanthanum chloride is added slowly to an excess of ammonium hydroxide. A series of experiments was next run in which 10 cc. (weighed portion) of the approximately 0.3 *N* lanthanum chloride was added slowly to about 30 to 40 cc. of 1 *N* ammonia. The precipitate was collected the next day and washed with a mixture of 50% alcohol and water until free from ammonia. The results obtained agreed within 0.1% with the theoretical figures.

Gravimetric Determination.—Since it was found that the last procedure gives a quantitative precipitation of hydrus lanthanum oxide free from chloride, 40-cc. weighed portions of the approximately 0.3 *N* lanthanum chloride stock solution were added with constant stirring to about 80 to 100 cc. of *N* ammonia. The next day the precipitates were filtered and

washed with a dilute solution of ammonium hydroxide to decrease the solubility. After ignition to constant weight in an electric furnace at 800°, the precipitate was weighed in a closed weighing bottle.

The results are accurate within 0.3% as indicated by the figures in Table IV.

TABLE IV
GRAVIMETRIC DETERMINATION OF LANTHANUM BY PRECIPITATION AS HYDROUS OXIDE
BY AMMONIA

M. equiv. La taken	M. equiv. La found	Dev. from calcd. value, %
11.666	11.674	+0.07
11.633	11.657	+ .21
11.574	11.610	+ .30
11.619	11.656	+ .3
11.648	11.673	+ .22

T. O. Smith and C. James⁷ found higher results when they precipitated lanthanum chloride with sodium hydroxide and ignited to oxide than when they used the oxalic acid method. With ammonium hydroxide the results were found to lie between the two. This can be easily explained by the formation of a basic chloride in the direct precipitation with base.

Higher Oxide Formation of Lanthanum.—In the discussion of the gravimetric determination of lanthanum reference has been made to an increase in weight obtained upon the ignition of lanthanum oxide at high temperature. This phenomenon was first noted by R. Hermann,⁸ who reported a gain of 0.24%. H. Tschiesche⁹ however, found no variation in weight upon heating lanthanum oxide and decided that Hermann's results were erroneous. Neither investigator reported the temperature at which the ignitions were made. Sarver and Brinton⁶ next observed that lanthanum oxide shows a well-defined tendency to descend to a minimum in weight and then to register small gains of approximately 0.1 to 0.2 mg. upon subsequent ignitions. After heating lanthanum oxide for three hours at 500° under a pressure of 300 pounds, H. A. Pagel and P. H. M.-P. Brinton¹⁰ found an increase in weight of only 0.02%. They concluded that no higher oxide of lanthanum exists. On the other hand, P. Melikoff and L. Pissarjewsky¹¹ report having obtained a peroxide to which they assigned the formula $\text{La}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ by adding hydrogen peroxide and potassium hydroxide to solutions of lanthanum nitrate.

Since the work described in the present paper indicated the existence of a higher oxide, an extensive study of its formation at high temperatures has been made. Though it has not been possible to find the exact con-

⁷ Smith and James, *THIS JOURNAL*, **36**, 909 (1914).

⁸ Hermann, *J. prakt. Chem.*, **82**, 385 (1861).

⁹ Tschiesche, *ibid.*, **107**, 65 (1869).

¹⁰ Pagel and Brinton, *THIS JOURNAL*, **51**, 42 (1929).

¹¹ Melikoff and Pissarjewsky, *Z. anorg. Chem.*, **21**, 70 (1899).

ditions (temperature) at which it is formed, there is hardly any doubt that peroxides are formed when lanthanum oxide is ignited at very high temperatures in the air.¹²

The results described in Table V have been obtained by heating lanthanum oxide at various temperatures in an electric muffle furnace (gas burners should be avoided, as the oxide will be contaminated by sulfur trioxide upon long heating). The oxide was obtained from hydrous lanthanum oxide, the latter being prepared by slowly adding a solution of lanthanum chloride to an excess of ammonia. The precipitate was ignited at 800° to constant weight.

The experiments have been carried out with five different samples of lanthanum oxide. In all cases an increase in weight amounting to 10.2 to 10.8% was noticed upon prolonged ignition at white heat. Identical results were obtained with lanthanum oxide obtained from the oxalate.

If the sesquioxide were converted into the higher oxide, La_2O_5 , an increase in weight of 9.81% would result.

TABLE V
INCREASE IN WEIGHT OF LANTHANUM OXIDE UPON HEATING AT HIGH TEMPERATURES

Time, hours	Condition	Increase in weight of 0.1655 La_2O_3 in %	Increase in weight of 0.2585 g. of La_2O_3 in %
10	Red heat	0.0	0.0
5	Light red heat	.0	.0
14	Light red heat	1.03	1.21
14	White heat	1.94	7.34
14	White heat	9.45	8.85
18	White heat	10.06	9.88
12	White heat	10.48	10.25
15	White heat	10.48	10.25

In other experiments three different types of oxide were used: one from hydrous oxide, one from oxalate and one from pure lanthanum nitrate. Another muffle furnace was used, as the former was burned out. After a long period of heating at white heat the increase in weight was 18.5 to 19.7%. These values closely check the theoretical gain in weight (19.63%) which would result if the higher oxide La_2O_7 were formed.

Four other sets of experiments were run in which the temperature was measured by means of an electric pyrometer. The results were irregular; after an increase in weight of 5.65% had been noticed, the increase in weight dropped again to about 2% on longer heating. It seems that the formation of higher oxide is slow at temperatures of 1100°. Other furnaces were built; the addition of a trace of a cerium salt¹³ and of platinum salt

¹² For a detailed discussion of all experiments, see thesis of Ruth Elmquist, pp. 73-88.

¹³ R. Marc, *Ber.*, 35, 2370 (1902), stated that the presence of a trace of cerium catalyzes the higher oxide formation of praseodymium.

as a catalyst was tried,¹⁴ but at present no definite information on the conditions of formation of the higher oxide has been obtained.

The results so far, however, show definitely that lanthanum oxide heated for long periods of time at very high temperature in an electric furnace and exposed to the air can be transformed into the higher oxides La_2O_5 and La_2O_7 .

Summary

1. A precise volumetric procedure has been described for the determination of lanthanum as lanthanum oxalate. The oxalate can be estimated gravimetrically as oxide if ignited to constant weight in an electric furnace at 800 to 900° and weighed in a well-closed weighing bottle.

2. In the precipitation of lanthanum chloride with sodium hydroxide or ammonia basic chloride is formed. This is avoided by adding the lanthanum solution slowly to an excess of the base. Use of this fact is made in the volumetric and gravimetric determinations of lanthanum by precipitation as hydrous oxide.

3. Lanthanum oxide heated for long periods of time at white heat in an electric muffle furnace in air can be transformed into higher oxides La_2O_5 and La_2O_7 .

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LANTHANUM ALKALI OXALATES¹

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The fact that alkali oxalates are carried down by lanthanum oxalate was first observed by Th. Sheerer.² G. P. Baxter and R. C. Griffin³ stated that ammonium oxalate, but not oxalic acid, was carried down in considerable quantities by rare earth oxalates and that occlusion of ammonium oxalate was made negligible by acidifying the solution with twice the equivalent amount of nitric acid. G. P. Baxter and H. W. Daudt⁴ reported that potassium oxalate was occluded to the same extent as ammonium oxalate (5–18%) but that sodium oxalate was occluded only slightly even in neutral solution. Since the occluded oxalate was determined after washing the lanthanum oxalate, part of the occluded salt may be removed from the precipitate. For this reason a series of experi-

¹⁴ Ref. 12, p. 82–87.

¹ From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Sheerer, *Ann. phys. chim.*, [II] 56, 479 (1842).

³ Baxter and Griffin, *THIS JOURNAL*, 28, 1684 (1906).

⁴ Baxter and Daudt, *ibid.*, 30, 563 (1908).