

526. *The Separation and Purification of Lanthanum. Part I. Hydroxide Precipitation.*

By R. C. VICKERY.

The application is studied of the air-borne ammonia separation of lanthanum. It is found that this method provides for very good separation, and at high concentrations of ammonium ions the introduction of cadmium into the system is not necessary.

It is known that lanthanum is the most basic of the rare-earth elements, and this characteristic is the basis of the most efficient procedures for its separation and purification from the other rare earths, although Bowles and Partridge (*Ind. Eng. Chem. Anal.*, 1937, **9**, 124) concluded that basicity methods were applicable only to the separation of quadrivalent cerium and lanthanum. Prandtl and his co-workers studied the "basic ammonia" precipitation of the rare earths, showing that equilibria were set up of the form $RCl_3 + 3NH_4OH \rightleftharpoons R(OH)_3 + 3NH_4Cl$, so that, in fractionating by this method, it is preferable to disturb the equilibrium by filtration at intervals. These workers also studied the influence on the equilibrium of bivalent ions which can bind part of the ammonia as complex ammine ions. With Rauchenberger, Prandtl (*Z. anorg. Chem.*, 1922, **120**, 120, etc.) stated the optimum conditions for this lanthanum separation: the solution of rare-earth and cadmium nitrates should attain a molecular ratio of 2 : 3, the precipitation being effected at 100° in 3—4*N*-ammonium nitrate solution by the addition of 1% ammonia solution; fractionation is preferred, about 5% of the oxides being precipitated at each operation in order to reduce adsorption on the hydroxide precipitates to a minimum. By this means lanthanum in good yield and purity was recovered from the final filtrate.

The major disadvantage of Prandtl's procedure has been the inevitable excessive dilution of the rare-earth solution. In the application of the basic ammonia separation to the heavier, yttrium-group earths, Trombe (*Compt. rend.*, 1942, **215**, 439) bubbled air, first through ammonia solution and then through the rare-earth solution. Such a technique, apart from avoiding the dilution effect, enabled a closer control of the pH of the solution and yielded dense, easily filterable precipitates. This technique has more recently been employed also by Sugden (this vol., p. 135) for the purification of yttrium.

In application to lanthanum purification, this air-borne ammonia process has yielded excellent results. The concentration of ammonia in the vapour introduced may be easily controlled by variation of the rate of air-flow, of the concentration of the ammonia solution, or, as is the author's usual practice, by variation of the concentration of ammonia in the air-flow as shown below. A further advantage of this application of Trombe's technique is that it is not necessary to introduce cadmium salts into the solution.

EXPERIMENTAL.

The apparatus employed was simple. 500 ml. of ammonia solution (*d* 0.880) were diluted to 1 l. and contained in a double-necked Woulff bottle through the stoppers of which passed two tubes, an inlet reaching to the bottom of the solution and an outlet receiving the ammonia vapour just below the level of the stopper. These tubes were by-passed by a tube carrying a stopcock, and the inlet tube was guarded by a soda-lime tube to remove carbon dioxide from the incoming air stream. The outlet tube passed to a wide-necked flask of 1½ l. capacity containing the rare-earth solution. A reflux condenser was also inserted through the stopper of the precipitation flask, a continuation of the inner tube of the condenser leading to suction. The ammonia delivery tube terminated in the reaction flask in a sintered-glass disc which ensured thorough dissemination of the ammonia vapour. The concentration of ammonia vapour reaching the rare-earth solution could be varied by adjustment of the stopcock which, when opened, allowed the incoming air to take the line of least resistance and pass straight through to the rare-earth solution without bubbling through the ammonia solution. The pressure attained by the vacuum pump was initially adjusted so that when the stopcock was fully opened air was just stopped passing through the ammonia solution.

The rare-earth nitrate solution employed was derived from a mixture of oxides from monazite sources; most of the cerium had been removed, and the mixture had been subjected to one double sodium sulphate separation for removal of the heavier rare earths; the mixed oxides showed on analysis by arc and absorption spectroscopy and chemical means: CeO₂, 1.0; Nd₂O₃, 46.0; La₂O₃, 36.5; Pr₂O₃, 14.5; other rare earths, 2.0%. The neodymium content was slightly higher than the normally accepted average for monazite concentrates but no explanation was available for this apart from random variation.

In each fractionation noted here, 100 g. of these mixed oxides were taken as nitrates, as starting material.

In preliminary work no attempt was made critically to evaluate the influence of ammonia concentration in the air-borne vapour, but it was found that the degree of separation of lanthanum and the ease of filtration of the hydroxides were greater with increasing dilution of the vapour—a similar finding was recorded by Sugden. The operative concentration of the ammonia vapour reaching the rare-earth solution was adjusted to *ca.* 20% of its concentration above the parent ammonia solution. Also, whereas

TABLE I.
 "Basic ammonia" process (after Trombe).
 (Stepwise sequence.)
 Lanthanum purity, %, of fractions, and final weights.

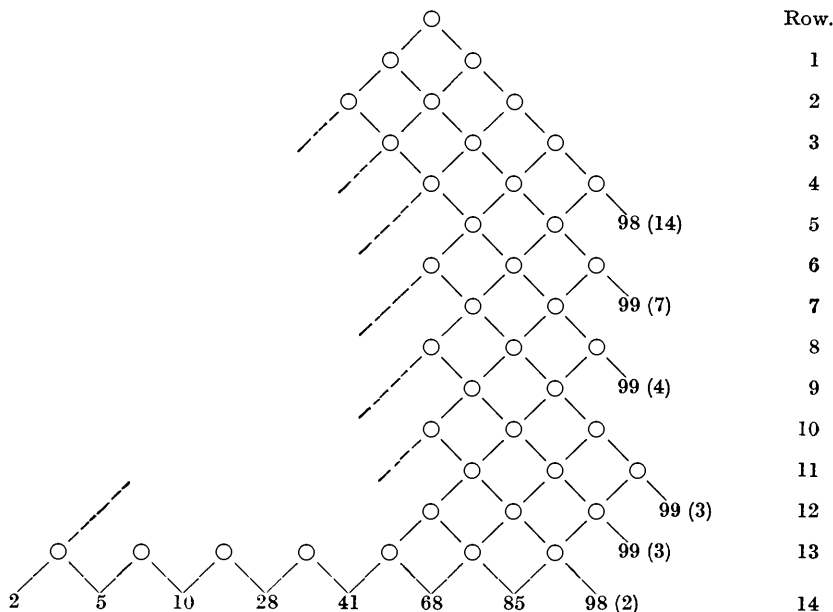
Row.	Fraction.										Filtrate.	Wt., g.
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.		
1	10	15	25	35	47	60	70	80	—	—	97	22
2	8	10	20	30	40	52	68	88	96	—	99	8
3	3	8	15	25	40	55	70	91	—	—	98	2
4	D	5	10	18	41	53	70	93	—	—	98	1
5		1	8	12	35	46	64	82	95	—	99	0.2
6		D	4	8	26	38	48	65	83	94	99	0.2
7			2	6	18	30	45	60	70	90	98	0.1
8			1	3	8	30	42	58	71	92	98	0.1
9			D	1	6	18	37	45	62	80	97	0.1

Recovery : 33.7 g. = 92.5%.

D = Discarded as free from La.

with higher concentrations of ammonia vapour the delivery tube and sintered-glass disc occasionally became choked with precipitated hydroxide, yet at lower concentrations this was not experienced.

Pyramidal series.



Recovery : 33 g. = 90.5%.

(Figures in parentheses indicate weights in g.; other figures indicate lanthanum purity, %.)

Stepwise and pyramidal fractionations were carried out, maintenance of the solution at constant volume being more or less attained by the reflux condenser. The optimum conditions stipulated by Prandtl and Rauchenberger being used, *viz.*, 215 g. of cadmium nitrate to every 100 g. of Ln_2O_3 in 15% nitrate solution 3N. to ammonium nitrate, precipitation being carried out at 100°, ammonia vapour at *ca.* 20% concentration (see above) was passed into the solution at a rate just sufficient to keep it well agitated. Sugden employed an ammonia concentration of 10 g./l. but did not state whether this was the air-stream concentration or that of the parent solution, and he used a vapour-stream flow-rate of 2 l./min. The flow-rate in the present experiments was not determined but was considered to approximate to this. Stepwise fractionation was made by precipitating and filtering off 10% of the oxides at each step, the filtrate being regassed. The 10 fractions thus obtained were redissolved and regassed, the filtrate from each fraction passing on to the next step (see Table I).

The pyramidal fractionation was carried out with each precipitation being carried to the disappearance of absorption spectra through 5-cm. of solution. It should be noted that in a 10% solution, such a condition normally represents La_2O_3 purity of 98—99%, but it must be remembered that although a 15% solution was used initially, by the time the absorbing elements had been removed, the oxide con-

centration was down to *ca.* 5%, which results in a lower purity indication, *i.e.*, 95—97% (see Figure). As the later fractions became predominantly lanthanum-containing, the purity indication became higher and more accurate as the concentration of La_2O_3 in the filtrate approached 10—15%. The purities of the oxides finally recovered from the filtrates were determined by arc spectroscopy.

A modification of this separational technique could, of course, have been to allow free evaporation of the solution which could have been adjusted to be nearly commensurate with the removal of rare earths from solution, thus yielding a more or less constant concentration of oxides in solution. This was attempted on occasion but, with progression, owing to accumulation of ammonium and cadmium salts in solution, the solutions became very viscous, which not only required a high degree of suction to be applied but also tended to deposit mixed crystals of ammonium and cadmium nitrates.

After the two above fractionations a further sequence was carried out, *i.e.*, a stepwise application of Trombe's method without the inclusion of cadmium nitrate in solution but with the ammonium-salt concentration increased to 4.5N., *i.e.*, 360 g. of ammonium nitrate per l., it having been reasoned that in previous runs increase in the content of this salt with progress of fractionation was the main variable and this must have an enhanced inhibitory effect on lanthanum precipitation. It was obvious, therefore, to attempt a reduction of the number of fractions by an increase in the concentrations of ammonium ions at the start. This is, of course, in line with Prandtl's findings. That this modification provided excellent results is shown in Table II, which also includes data on a similar run with the inclusion of cadmium nitrate in the correct concentration; it is readily seen that in the application of Trombe's technique at high ammonium nitrate concentrations the presence of cadmium ions is not a necessity for the rapid separation of lanthanum.

TABLE II.
Final filtrates.

Row.	4.5N-NH ₄ NO ₃ .			4.5N-NH ₄ NO ₃ + Cd(NO ₃) ₂ .		
	No. of fractions.	Final purity, %.	Wt., g.	No. of fractions.	Final purity, %.	Wt., g.
1	8	98+	28	8	97+	21
2	9	99+	4	9	98+	8
3	8	97+	1	9	98+	3
4	10	98+	1	10	99+	0.5
5	9	99+	0.3	10	98+	0.5
6	10	99+	0.3	10	99+	0.3
7	10	98+	0.3	9	99+	0.2
8	9	98+	0.1	10	98+	0.1
9	10	97+	0.1	10	98+	0.1
10	10	97+	0.1	10	97+	0.1

Recovery : 35.2 g. = 96.5%.

Recovery : 33.8 g. = 92.5%.

It may be concluded therefore that Trombe's modification of the ammonia separation is an advance on previous basicity techniques for the separation of lanthanum in so far as both ease of techniques and recovery are concerned. A notable point, which the author has found to apply also to other basicity techniques, is the increase in general efficiency at each end of a series, *i.e.*, fairly rapid removal of lanthanum from the head and its speedy purification from fractions of 70—80% purity. This increase in efficiency is the converse of what has been found in normal crystallisation techniques where purification is quite rapid up to *ca.* 75% of La_2O_3 . The author therefore employs initial concentration of lanthanum to *ca.* 75% by fractional crystallisation of the double ammonium nitrates, and removal of the head fractions by a gaseous basicity separation. Although the double magnesium or manganese salts are normally preferred for lanthanum crystallisation, the use of the ammonium salt avoids the intermediate purification necessary with these salts and requires only the addition of a little more ammonium nitrate to the solution to bring the ammonium-ion concentration to the required level.