296. *Lanthanon Purifications by the Use of Hexa-antipyrine Lanthanon Iodides.*

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Fractional crystallisation of heavy hexa-antipyrine lanthanon iodide $[Ln(C_{11}H_{12}ON_2)_6]I_3$ yields efficiently pure lutetium material. The separation of thulium and lutetium is good, and that of thulium from erbium and yttrium very satisfactory though more difficult. Yttrium separates very slowly from erbium, and, uniquely, on the thulium side. Yttrium separates well from holmium, but holmium, dysprosium, and terbium are not efficiently separated. No separation of neodymium and praseodymium was observed.

THE good initial separation of lutetium from neighbouring earths obtained by a fractional precipitation of an iodide solution with antipyrine, followed by ten series of crystallisations of the resulting hexa-antipyrine lutetium iodide, has already been recorded (*J.*, 1950, 577). This work has now been extended, and the purification of both lutetium and thulium achieved with a satisfactory economy of effort. When the starting material is already spread into four or five fractions, less than 3000 crystallisations, and withdrawal of ytterbium by means of sodium amalgam, yields 99·9%-pure Lu_2O_3 33%, 99%-pure Tm_2O_3 11%, pure Yb_2O_3 2%, $(Lu,Tm)_2O_3$ intermediates 13%, $(Tm,Y,Er)_2O_3$ 9%, $(Y,Er)_2O_3$ 32%. The bulk of the originally associated erbium had been previously freed from thulium by 3000 bromate crystallisations, and the greater part of the ytterbium withdrawn by means of sodium amalgam. In view of the slight incompleteness of the withdrawal of ytterbium previously encountered by the author (*J.*, 1943, 8), it was considered inadvisable to attempt its final removal before further concentration by the antipyrine fractionation. However, an improved technique has demonstrated the possibility of withdrawal to below the limits of spectroscopic detection, so that it now becomes advisable to make this complete withdrawal before the antipyrine fractionation.

The surprising occurrence of yttrium between thulium and erbium also points to the desirability of eliminating all yttrium from the material by ferricyanide fractionation (Marsh, *J.*, 1947, 118) or by a process using ethylenediaminetetra-acetic acid.

Another fractionation series consisting of yttrium, holmium, dysprosium, and small amounts of terbium and gadolinium was studied. After 50 series (1500 crystallisations) a considerable amount of yttrium had been eliminated at the head, but progress in separating dysprosium and holmium was considered insufficient to indicate superiority of this mode of fractionation over other known methods. The fractionation is easy and safe, but the dimethyl phosphates are more efficient though much harder to crystallise. The separation of dysprosium and terbium is rather similar and not very satisfactory by either method. Traces of terbium tinted the oxides from most of the iodide fractions, though only a small amount of oxides from the tail was deeply coloured by it. Solutions in course of fractionation contain the equivalent of about 15 g. of oxide per l. in the antipyrine process, 40—50 as dimethyl phosphates, and over 500 as bromates. The advantage of the bromate method for large quantities is obvious even if a much larger number of crystallisations is required.

Only for lutetium and thulium is it likely that the antipyrine iodide salt possesses any advantage over known methods of purification, but for these two metals there is a clear case for its employment after they have had suitable preliminary concentration.

It is believed that the collection of yttrium between erbium and thulium here experienced has not previously been observed. The author has previously discussed the wandering of the position of yttrium through the lanthanon group (*J.*, 1947, 118, 1084) and pointed out that the electron density of yttrium is lower than that of the lanthanons and may permit of a relatively greater increase in size in passing from an ionic to a covalent state. However, the behaviour of yttrium is very erratic and does not follow a simple ionic–covalent transition. Owing to its lower atomic number the ion itself will be more compressible than lanthanon ions, and crystal structure considerations will introduce a constitutive factor not yet predictable, which may account for the variations. It is perhaps significant that the six antipyrine groups (156 atoms) are probably the largest and heaviest assemblage known to co-ordinate with the positive ions of these elements. As a result we may postulate a cramping effect upon the ions. An unusually small size of the yttrium ion would result from its higher compressibility where in general a compressive force is operative on the positive ions of a series of salts.

It has been noticed repeatedly that, especially on first setting up an iodide antipyrine series, a very insoluble product collects at the head in very small crystals of the usual type, but on further crystallisation these may suddenly change to long silky needles. It is thought that this may indicate a separation of isomeric forms of antipyrine, the insoluble needles being most probably associated with a concentration of *trans*-molecules. Antipyrine supplied from three or four different sources all showed the same phenomenon. It is known that antipyrine reacts at times according to more than one constitutional formula. On account of this phenomenon it is probably impossible to determine accurately the solubilities of the antipyrine salts of the series. Although the crystals present ten faces resembling a cubo-octahedron, as already reported, a crystallographic examination by Mr. H. M. Powell showed them to be in fact trigonal. After long boiling of solutions the habit is different, growth being in stout needles formed from a series of telescoped crystals. After long crystallisation, solutions tended to become slightly alkaline at the head and acid at the tail.

EXPERIMENTAL.

Two different modes of preparing the hexa-antipyrine lanthanon iodides have been used. (i) The oxides were dissolved in hydriodic acid to give a neutral solution which, however, contained free iodine. This solution was treated warm with a little antipyrine, producing with the iodine a dark red, highly insoluble precipitate, which became a tar at the b. p. The solution was then free from iodine. Successive quantities of antipyrine (1 mole per mole of iodide) were then added as previously described (*J.*, 1950, 577), and the resulting crystals were cropped. (ii) Owing to the much lower solubility of the complex salt than of lanthanon chlorides, iodides, or antipyrine, it is very satisfactory to prepare a neutral chloride solution and add to it the requisite quantity of potassium or ammonium iodide and antipyrine. Chlorides will then collect at the tail of the fractionation, but trouble from free iodine is not encountered. The thulium series was set up by the first method and the dysprosium series by the second. After fractionation the salt was decomposed by aqueous ammonia; the antipyrine and ammonium iodide solution was filtered from the hydroxides, evaporated, and kept for re-use.

Purification of Lutetium and Thulium.—The series having been set up from 110 g. of oxide rich in lutetium, 40 g. rich in thulium and 80 g. rich in erbium in about 20 flasks, with a total volume of about 17 l., daily fractionation was started. After 12 fractionations much erbium was withdrawn at the tail, and the remaining fractions spread. After 25 fractionations it became possible to start withdrawing pure lutetium at the head. When the hot, nearly saturated solution of the fifth fraction from the head showed no thulium absorption band at 685 mμ. through a 1-l. flask it was considered safe to withdraw the top fraction. Further spreading to about 30 fractions was now required. After 45 fractionations (1000 crystallisations) 90% of the erbium had been eliminated. Only the last three fractions were rose-coloured. At this stage the mother-liquors of alternate fractions were examined absorptiometrically in 1-cm. layers with a Beckman D.U. spectrophotometer with the following results :

Fraction	3	5	7	9	11	13	15	17	19	21	23	25
Erbium absorption [1]	—	—	—	—	—	0·002	0·004	0·009	0·020	0·040	0·060	0·065
Thulium absorption [2]	0·003	0·005	0·015	0·050	0·061	0·061	0·059	0·054	0·053	0·016	0·007	0·003

[1] Optical density at 525 mμ. (1 g. of Er_2O_3 per l. = 0·0135).

[2] Optical density at 685 mμ. (1 g. of Tm_2O_3 per l. = 0·0123).

The fractions were further spread to number 35 and now fitted into 400-ml. flasks. After 75 fractionations (2000 crystallisations) the bulk of the lutetium had been separated at the head. It was converted into acetate and treated in hot concentrated solution with sodium amalgam (Marsh, *J.*, 1943, 8). This removed several per cent. of ytterbium, and the bulk of the lutetium acetate crystallised on cooling. The remainder was recovered as hydroxide and again converted into acetate. A second sodium amalgam treatment yielded only a small amount of ytterbium; the fourth treatment yielded none. Each treatment consisted of using several successive portions of sodium amalgam, and in the later treatments these were allowed to react only very partially, so that much sodium remained in the mercury when it was separated from the acetate solution. The highly reactive ytterbium, having once passed into the mercury phase, was thereby protected by the even more reactive sodium present in quantity. The recovered lutetium oxide was carefully examined by arc-spectrography (by Johnson, Matthey & Co. Ltd.) but the extremely sensitive ultimate lines of ytterbium were not found. Examined in chloride solution with a hand spectroscope at a concentration equivalent to 670 g. of Lu_2O_3 per l. in 16-cm. depth, the thulium absorption band at 685 mμ. was weak but unmistakable, and comparable with 1 cm. of a solution of 10 g. of pure thulium oxide per l. Thus a thulium content of 0·1% is indicated in the lutetium preparation.

The collected erbium tails were at this stage put through ten series of crystallisations of 10—12 fractions. A little thulium became detectable at the head, but 75 g. of Er_2O_3 were obtained free from thulium. Another 150 g. of salts (oxide content 11%) were set aside containing a little thulium, and 37 g. of salt with considerable thulium content. The thulium fractionation was pursued through another 750 crystallisations. Some ammonium chloride was added to each fraction and is thought to have had a favourable effect on the separation. Heads and tails were collected as seemed desirable. The material was then examined by arc-spectrography. Fractions 37—56 amounted to about 250 g. of salts and ranged from almost pure lutetium (37) to almost pure thulium (56). The yttrium line, 3600·7 A., was faintly visible in fraction 49 and increased in strength down the series. A study of the erbium fractions showed very little variation of the yttrium content, but fraction 86 at the tail of the thulium series showed more yttrium than any of them. A spectrophotometric estimate of fraction 86 gave Tm_2O_3 31%, Er_2O_3 40%, indicating about 30% of yttrium oxide. Comparison was made with a sample of thulium oxide prepared by the late Prof. Sugden (*J.*, 1939, 139) : no trace of yttrium was found in this. Fractions 57—77 were substantially pure thulium and were converted into oxide (25 g.). The green erbium absorption band 525 mμ. was seen in 8·5 cm. of acetate solution (200 g. of Tm_2O_3 per l.) and matched by eye with 5 mm. of a solution of 2·73 g. of Er_2O_3 per l. Thus the erbium content is estimated at 0·3%. The thulium acetate solution was treated with sodium amalgam to withdraw a little ytterbium. An arc-spectrum examination (by Johnson, Matthey & Co. Ltd.) then showed the principal lines of yttrium, two or three faint ultimate lines of ytterbium and lutetium, and two very faint erbium lines.

Less than 3000 crystallisations have served to give large yields of substantially pure lutetium and thulium. It is believed that at some stages the separation suffered from working on too few fractions. A large multiplication of fractions is required in the early stages. In the case of thulium where both head and tail impurities require elimination, a series of 30—40 fractions is required.

The Dysprosium Series.—The oxides used consisted of (approx.) : Y 80 g., Ho 25 g., Dy 180 g., Tb, Gd, etc., 35 g. They gave a series of about 20-l. volume. After 15 series (250 crystallisations) the cold saturated solutions were examined with a Beckman spectrophotometer with the following results :

Fraction	9	12	15	18	21	24
Ho_2O_3, g./l.	0·9	1·3	0·9	0·4	0·5	0·5
Dy_2O_3, g./l.	1·2	3·8	5·1	5·8	6·0	6·9

Thereafter the fractions were increased to number about 32. After 50 series (1500 crystallisations) a similar estimation gave the following results :

Fraction	40	43	46	49	54	59	65	71	76
Ho_2O_3, g./l.	1·75	2·5	2·1	1·0	0·9	0·5	—	—	—
Dy_2O_3, g./l.	2·6	6·1	6·2	5·7	6·4	6·2	6·5	6·2	5·7

The fractions were united in pairs and converted into oxides which were analysed with the following results :

Fraction	38	40	42	44	46	50	54	58	62	66	70	74
Dy_2O_3, %	3	15	51	66	81	88	88	91	93	95	95	74
Ho_2O_3, %	5	17	29	24	22	14	12	7·2	5·2	3·2	2·5	2·5

These fractions totalled 210 g. Yttrium taken off at the head amounted to 80 g., and terbium, etc., at the tail to 30 g.

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