# **109.** *The Purification of Lutecium by Fractionation of Hexa-antipyrinelutecium Iodide.*

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It is demonstrated that fractionation of hexa-antipyrinelutecium iodide, $[Lu(C_{11}H_{12}N_2O)_6]I_3$, gives a very rapid purification. This is ascribed to a large complexing, rather than a solubility, differential. The separations of thulium and erbium, and of holmium and dysprosium, have also been noted.

The favourable results obtainable by lanthanon tri(dimethyl phosphate) fractionation prompt a search for other compounds of a similar nature. Freed's suggestion (*J. Amer. Chem. Soc.*, 1931, **53**, 3906) that the use of non-solvated ions would permit of better fractionation than occurs with solvated ions would appear to be exemplified by the dimethyl phosphates. Few salts of the lanthanons, however, crystallise in the anhydrous state, and in these cases the metal ion appears to be complexed with some group other than water. Thus the six oxygen atoms attached to methyl groups of $Ln[PO_4Me_2]_3$ are probably complexed with the metal. The antipyrine addition compounds of the lanthanons are a noteworthy class of anhydrous salts (Kolb, *Z. anorg. Chem.*, 1913, **83**, 144; Riabtschikov and Terentieva, *Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **51**, 291), and from the solubility measurements of Wilke-Dörfurt and Schiliephake (*Z. anorg. Chem.*, 1928, **170**, 129) all the evidence points to a further resemblance to the dimethyl phosphates in that the lanthanum salts are the most soluble of the series. From published work the iodides seem most likely to constitute a favourable medium for fractionation. The solubility range is considerable, there being a 6·4-fold increase for lanthanum over the molar value for yttrium, the solubilities being 4·44 and 29·5 g./100 g. of water, respectively, at room temperature. A 26-fold increase occurs in the case of the dimethyl phosphates. The hexa-antipyrine lanthanon iodides form compact cubo-octahedral crystals, whereas the dimethyl phosphates give a fibrous pulp which generally requires filtration, thus much reducing the efficiency. Moreover, hydrolysis is too pronounced for erbium and elements of higher atomic number to be dealt with efficiently as dimethyl phosphates, whereas the antipyrine iodide compounds are stable.

By the aid of these compounds a crude lutecium product has shown a very rapid purification, and it seems probable that thulium and erbium may also be separated with reasonable efficiency. The separation of holmium and dysprosium has not proved so effective, though further work is required before it can be said definitely whether the method is useful or not, in this case.

The separation does not appear to be based upon solubility differences alone, for these are only moderate. It must depend rather upon the complexing strengths of the metals with antipyrine. The complex is much less soluble than its components, and normal lanthanon ions exist in its solution, indicating some dissociation, since oxalic acid gives the usual oxalate precipitate. The fractionation therefore is based on the crystallising out of the more strongly complexing elements. These are the more weakly basic and give slightly the less soluble complexes. Hexa-antipyrinelutecium iodide collects at the insoluble end of the series, thus providing a means of purification utilising the well-known principle that impurities are eliminated at the tail fraction preferably to the head. This is especially valuable, since lutecium is the end member of the series. The solubility of the iodide complex is such that only 10—20 g./l. of oxide are present in the fractionation series when hot, so that it is rather bulky. The solubility in methanol is considerably greater, and the same types of crystals are obtained. A mixed solvent might therefore prove useful, but a short fractionation in methanol indicated that separation was much less pronounced in this solvent. The older methods of lutecium fractionation, by bromates or double ammonium oxalates, concentrate lutecium at the tail. The bromates are so soluble and the mother-liquors so viscous that the fractionation is difficult.

The initial fractional precipitation of some crude lutecium iodide by antipyrine gave a head fraction containing $Tm_2O_3$, 6·1; $Er_2O_3$, 0·7%, whereas the tail (fraction 9) contained 43% and 32%, respectively. Ten series of crystallisations produced a head with $Tm_2O_3$, 1·4%; $Er_2O_3$, nil; and a tail with 49% and 42%, respectively. Further work on a larger scale is in hand.

## EXPERIMENTAL.

The lanthanons from a quantity of Norwegian gadolinite were fractionated by double sulphate precipitation till the oxide was free from any brown tint due to the presence of terbium. The terbium-free material was then fractionated by precipitation of basic salts till most of the yttrium had been removed but the thulium retained. The concentrate of weak bases was converted into acetate, and ytterbium removed by sodium amalgam. The residue was then fractionated as bromate, and tail fractions were taken off as soon as they became almost colourless; these consistituted the material used in this investigation.

10 G. of the crude lutecium oxide were dissolved in hydriodic acid (*d* 1·7) and excess of acid and iodine driven off on the water-bath. The salt was taken up in 400 ml. of hot water, and 20 ml. of antipyrine solution (400 g./l.) were added. A crop of hexa-antipyrinelutecium iodide was collected next day. Seven further crops were collected on subsequent days. The solution was concentrated to 100 ml. after the sixth crop, and a small residue (0·13 g. of oxide) was recovered from the final mother-liquor. After recrystallising twice, the first crop was converted into oxide (0·17 g.). The remaining crops were dissolved in boiling water, about 100 ml. being required for each. They crystallised on cooling and the mother-liquors were examined with a Beckman spectrophotometer (Model DU), thus affording an estimate of thulium and erbium present. The series was then fractionated systematically ten times in 8—10 fractions, the tail fractions being allowed to become small. Head and tail fractions were then again recovered as oxide (1·0 and 0·2 g.). The series of mother-liquors were again examined spectrophotometrically. The two sets of heads and tails were made up as chloride solutions (33·3 g./l. of oxide, except the head fraction after fractional crystallisation, which was 150 g./l.). All were examined in 1-cm. cells using the bands λλ 940, 684, and 524 mμ. for Yb, Tm, and Er estimations, respectively, checked against standard chloride solutions. In the case of the mother-liquors the assumption was made that a calibration with chloride solutions was admissible for estimating the antipyrine complex in solution. Some yellow colour had developed in fractions 13 and 14 so that here erbium estimates are probably high. The results are set out below.

Initial split.

| Fraction : | 3. | 4. | 5. | 6. | 7. | 8. | 1. | 9. |
|---|---|---|---|---|---|---|---|---|
| $Tm_2O_3$ .................... | 0·81 | 1·06 | 1·55 | 3·16 | 4·46 | 5·20 g./l. | 6·1% | 54% |
| $Er_2O_3$ ....................... | 0·20 | 0·40 | 0·60 | 1·22 | 2·31 | 3·80 g./l. | 0·7% | 32% |

After ten series of crystallisations.

| Fraction : | 6. | 7. | 8. | 9. | 10. | 11. | 12. | 13. | 14. | 5. | 15. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Tm_2O_3$ | 0·24 | 0·73 | 1·55 | 2·2 | 3·0 | 3·3 | 3·9 | 3·0 | 3·0 g./l. | 1·4% | 49% |
| $Er_2O_3$ ... | 0·00 | 0·00 | 0·07 | 0·41 | 0·41 | 0·75 | 1·8 | 3·5 | 5·4 g./l. | nil | 42% |
| Volume | 90 | 90 | 90 | 70 | 70 | 70 | 60 | 30 | 20 ml. | 2·4% of $Yb_2O_3$ | |

*Holmium and Dysprosium.*—A mixture of holmium and dysprosium oxides (3·5 g.) was given a similar treatment to that described above for the initial split into hexa-antipyrinelutecium iodide fractions. The first crop and final mother-liquor were recovered as oxides (0·1 g. each). The oxide of the head fraction was a deep cream, but the tail a bright brown, indicating a good concentration of terbium oxide in the tail fraction. Chloride solutions were prepared (33·3 g./l. of oxide) and examined spectrophotometrically with the following results: $Ho_2O_3$, Head 15·1%, Tail 7·2%. $Dy_2O_3$, Head 52·5%, Tail 54%.

*Solubilities.*—3·190 G. of mother-liquor from fraction 6 of the hexa-antipyrinelutecium iodide, after standing for 2 days at room temperature after the series of ten fractionations, were evaporated to constant weight on the water-bath and yielded 0·124 g. of solid = 4·05 g./100 g. of water; $Lu_2O_3$ = 4·82 g./l. A similar determination on the head fraction of the dysprosium material gave 6·15 g./100 g. of water; $Dy_2O_3$ = 6·86 g./l.

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