# 4. *Rare-earth Metal Amalgams. Part III. The Separation of Ytterbium from its Neighbours.*

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Lutecium and thulium acetate solutions have no amalgam-forming power when treated with sodium amalgam. Ytterbium acetate forms an amalgam readily and is thus very satisfactorily separated from them, and obtained pure itself. The amalgam is very reactive, and more electropositive than samarium amalgam.

The behaviour of ytterbium acetate on treatment with sodium amalgam differs in several respects from that of samarium acetate (Part II, J., 1942, 523). Ytterbium amalgam is more reactive towards water and air, and less heat is liberated during the reaction $Yb^{\cdot\cdot\cdot} + 3Na \longrightarrow Yb + 3Na^{\cdot}$ than in that of samarium with sodium, which, however, goes more completely in the above direction. This leads to the view that ytterbium amalgam is more electropositive than samarium amalgam, and approaches more nearly to sodium amalgam, though it is much less stable than the latter. As the reduction takes place in two stages, $E^{\cdot\cdot\cdot} + Na \longrightarrow E^{\cdot\cdot} + Na^{\cdot}$ and $E^{\cdot\cdot} + 2Na \longrightarrow E + 2Na^{\cdot}$, the stability of the bivalent ion is an important factor in amalgam formation. For ytterbium this stability is much greater than for samarium, but is more than counterbalanced by the reactivity to water of the amalgam itself. The maximum equivalent yields obtained per equivalent of sodium have been 75% for ytterbium and 90% for samarium.

The elimination of ytterbium from its neighbours does not follow the same lines as that of samarium from neodymium and gadolinium, because the neighbours of ytterbium are devoid of amalgam-forming power. The fact that gadolinium had slight amalgam-forming power enabled it to act as a vehicle carrying with it into amalgam the last trace of samarium, yet the bulk of gadolinium was left pure as acetate. The balanced reaction between sodium and ytterbium salts and amalgams makes it impossible to remove the last trace of ytterbium from solution by amalgam formation: 0·01% or more always remained in the non-reducing earth. It is also important that sodium amalgam should be used sparingly at high efficiency, *i.e.*, in as alkaline a solution as possible without hydroxide formation occurring. A too liberal use and a vigorous reduction under more acid conditions only results in the accumulation of sodium acetate in solution, and the consequent back reaction. Frequent removal of sodium acetate is important.

By adding samarium acetate and removing samarium as amalgam, nearly all of the small amount of ytterbium which could not be removed directly was removed with the samarium. Lutecium with a ytterbium content of 0·001% has been thus prepared. This compares favourably with Welsbach's preparations of lutecium containing 1·18% of ytterbium used by Hönigschmid and Wittner (*Z. anorg. Chem.*, 1939, **240**, 284) for the latest determination of the atomic weight.

On the other hand, the purification of ytterbium is even simpler than that of samarium because, provided no early or middle members of the rare earth series be present in the crude material, nothing but ytterbium will pass into amalgam, and the fractional decomposition required in the case of samarium amalgam to eliminate the 1% of neighbouring rare earths which enter the samarium amalgam can be omitted. Ytterbium recovered from a mixture in which thulium and lutecium preponderated was spectroscopically free from them, which places a limit of the order of 0·01% of either present. This is in striking contrast to the findings of Jantsch, Skalla, and Grubitsch (*Z. anorg. Chem.*, 1934, **216**, 75) on the reducibility of anhydrous chlorides by hydrogen at 900° in gold vessels, *viz.*, that thulium and lutecium took the fourth and the fifth place after the three earths which form stable dichlorides, while lanthanum took last place. In view of the structure of the thulium atom, dichloride formation would not be surprising, but in the present work no thulium reduction has been observed. The reduction of lutecium cannot be accounted for by the same mechanism as operates for the three easily reducible earths, *viz.*, the fall of a valency electron to the *N*-shell, because in lutecium this shell is complete. The gold–thulium and gold–lutecium alloys have not been analysed qualitatively, and an element of doubt as to their composition must exist unless the absence of ytterbium in them is proved, more especially as the proportion of metal passing into alloy was not above 25% in either case.

The demarcation between the attack of sodium in amalgam by water or acid and the attack of ytterbium, especially if the latter is at a fairly high concentration, is not entirely sharp. As sodium co-precipitates badly with ytterbium oxalate and causes the latter to become partially soluble, special care to eliminate it must be taken. The absence of ammonia or ammonium salts is necessary, for neither oxalate nor hydroxide precipitations are complete in their presence, and serious loss of material may result.

Ytterbium amalgam remains liquid up to higher concentrations than samarium amalgam. It is thus possible to handle larger amounts of the metal with the same quantity of mercury. The great reactivity of the concentrated amalgam, however, sets an upper limit at 1% to the strength which can be handled.

## Experimental.

*Purification of Ytterbium.*—Ytterbium oxide (97%), prepared by three or four precipitations as ytterbous sulphate (Marsh, J., 1937, 1367), was dissolved in acetic acid after several hours on a water-bath, and the acetate crystallised 270 g.). This salt was dissolved in 1·25 times its weight of boiling water and treated hot with sodium amalgam. There was an immediate production of the orange-yellow colour of the ytterbous ion in concentrated solution. At first, in neutral solution hydrogen liberation was abundant, but it soon slackened and the solution became basic. Hydroxide, blackened by dispersed mercury, was formed, and simultaneously the yellow colour faded to green and then disappeared.

Additions of acetic acid were therefore made to keep the solution somewhat yellow and prevent the formation of hydroxide, but the reaction was kept less vigorous than initially with the solution slightly basic (pH 8—9).

125% of the sodium requirement for the reaction $Yb^{\cdot\cdot\cdot} + 3Na = Yb + 3Na^{\cdot}$ gave a 98% yield of ytterbium as amalgam. The exchange was very ready and developed little heat. With good shaking the reaction was completed in 2 minutes with least loss of the amalgam through attack by water. Hydroxide formation was prevented by adding sufficient acetic acid. Separation of the solution and mercury was then easy. The mercury was run through two lots of water to wash it from acetate. This brought about decomposition of 1—2% of the amalgam. The washed amalgam was treated with the theoretical amount of dilute hydrochloric acid to decompose the excess of sodium in it. The small amount of ytterbium thereby extracted was precipitated with sodium hydroxide. The amalgam was then treated with excess of hydrochloric acid and shaken till calomel formation began. The first extract of ytterbium hydroxide was added to the chloride solution, which was then concentrated to a syrup. From this, any sodium present crystallised out as chloride, which was then filtered off. The ytterbium solution after dilution was precipitated as oxalate, and the latter ignited to oxide.

In one experiment (see following table) ytterbium acetate (107 g.) was dissolved by boiling in 133 ml. of water in a 1 l. flask. 250 Ml. of sodium amalgam (Na, 30 g.; Hg, 333 ml.) were added, with the addition during the reaction (2 mins.) of 3 ml. of acetic acid; the amalgam was then separated and washed. The acetate solution was next treated with acetic acid (3 ml.) and the remaining amalgam (83 ml.), and during the reaction (2 mins.) with more acetic acid (4 ml.). The solution was then diluted (1·5 l.) and precipitated with alkali. The hydroxide was dissolved in the necessary minimum of acetic acid, and the rare-earth acetate solution thus freed from sodium acetate was treated with sodium (2 g.) in mercury (30 ml.) and acetic acid (3·5 ml.). Some colour developed towards the end of the reaction. The solution was again precipitated as hydroxide, and the process repeated, after which the remaining earths were once more precipitated as hydroxides, but were subsequently dissolved in nitric acid and precipitated as oxalates and ignited.

*Purification of Ytterbium* (97%).

| Input. | | | | | Output. | | |
|---|---|---|---|---|---|---|---|
| Earth, g. | Na, g. | HOAc, ml. | $H_2O$, ml. | Hg, kg. | $Yb_2O_3$, g. | Earths, g. | Washings, g. |
| 50 | 30 | 10 | 133 | 4·5 | 46·68 | — | 0·77 |
| | 2 | 3·5 | 10 | 0·4 | 0·44 | — | — |
| | 2 | 2·0 | 10 | 0·4 | 0·20 | 1·50 | — |
| | | | | | 47·32 | 1·50 | |

The main crop of amalgam after treatment with acid and precipitation as oxalate yielded 46·68 g. of ytterbium oxide. The last ytterbium (0·73 g. of oxide) to be extracted by acid was compared by arc spectroscopy (medium quartz spectroscope) with the main bulk. No rare-earth lines other than those of ytterbium were detected in either. The second and third ytterbium oxide crops (0·44 and 0·20 g.) were not pure white. The residue (1·50 g.) was buff and contained all the yttrium earths. No trace of absorption spectrum was found in 25 cm. of 600 g./l. of ytterbium oxide in solution as chloride from the main crop, but the erbium spectrum was visible in 1 cm. of 7·5 g./l. of oxide from the residue. This indicates: erbium, in residue, 16%; in ytterbium, $<0{\cdot}008\%$.

In another experiment 100 g. of 97% ytterbium acetate (= 46·73 g. of oxide) were treated with the theoretical quantity of sodium (22·7 g.) in amalgam. Acetic acid (7 ml.) was required during the reaction, and 34·2 g. of ytterbium oxide, or 73%, were recovered pure. A similar efficiency was obtained in a third experiment using 60 g. of acetate.

*Purification of Lutecium.*—A number of small bromate fractions which had been recrystallised several thousand times showed thulium absorption bands at the head, and contained varying quantities of ytterbium. Magnetic measurement (for which the author thanks Prof. Sugden) showed 1—2% at the tail. The tail fractions (5·27 g. of oxide) were converted into acetate (11·75 g.). This was dissolved in 15 ml. of boiling water and treated in a tap-funnel with sodium (0·25 g.) in mercury (7 ml.). There was much effervescence and a green colour developed. Four further similar treatments were given, during which 2 ml. of acetic acid were added (see table). A green colour developed each time. The amalgams were then shaken with 2N-hydrochloric acid till calomel formation began. The acid extracts were treated with excess of alkali, and the hydroxide precipitates collected. The fourth and the fifth treatment gave only small yields; the total was 108 mg. of ytterbia. Most of the lutecium acetate crystallised from its solution overnight; the solubility at room temperature is small. The mother-liquor was decanted, diluted, and rendered alkaline. The resulting hydroxide was collected on a toughened filter, transferred to the tap-funnel, and redissolved in the necessary amount (1 ml.) of acetic acid. The lutecium acetate crystals were then added, and the whole brought into solution (20 ml.) at boiling point. Five more extractions each with 0·25 g. of sodium yielded another 12 mg. of ytterbia. The lutecium was then recovered as acetate or hydroxide as before, and again treated in hot acetate solution with 0·25 g. of sodium in mercury. Only a slight yield of ytterbium oxide (1—2 mg.) was obtained. A quantity of samarium acetate (112 mg.) equivalent to 50 mg. of samarium oxide was now added to the lutecium acetate solution, which was then extracted twice by a total of 0·28 g. of sodium in amalgam. Two further lots of samarium acetate were added and nine extractions made. The last gave a very small yield of oxide. The total yields for the last eleven extractions amounted to 150 mg., *i.e.*, to just the amount of samarium oxide so far added. Two more lots of samarium acetate and 13 more extractions were made as shown.

*Purification of Lutecium.*

(Sodium was eliminated after each step except that corresponding to the third line.)

| Input. | | | | | Output. | | |
|---|---|---|---|---|---|---|---|
| Earth, g. | $Sm_2O_3$, mg. | Na, g. | HOAc, ml. | Hg, kg. | $Yb_2O_3$, mg. | $Sm_2O_3$, mg. | $Lu_2O_3$, g. |
| 5·37 | — | 5 × 0·25 | 2 | 5 × 0·1 | 108 | — | |
| | — | 5 × 0·25 | 2·5 | 5 × 0·1 | 12 | — | |
| | — | 0·25 | — | 0·1 | 1 | — | |
| | 50 | 2 × 0·14 | 0·6 | 2 × 0·05 | — | 150 | |
| | 50 | 4 × 0·14 | 1·2 | 4 × 0·05 | — | | |
| | 50 | 5 × 0·14 | 1·5 | 5 × 0·05 | — | | |
| | 50 | 4 × 0·14 | 1·2 | 4 × 0·05 | — | 100 ? | |
| | 50 | 6 × 0·14 | 1·8 | 6 × 0·05 | — | | |
| | — | 3 × 0·14 | 0·9 | 3 × 0·05 | — | 2·2 | 5·12 |

The last three yielded only 2·2 mg. of oxide. This was proved by arc spectroscopy to be samarium oxide with only a trace of ytterbium. Hence, in all, 35 extractions were made. The first 11 yielded 121 mg. of ytterbium oxide. During the next 24, 0·25 g. of samarium oxide was added and then recovered. Finally, 5·12 g. of lutecium oxide were recovered. The arc spectrum of this material showed at most a faint trace of the ytterbium lines at λ 3289, which had not been reduced materially during the last 13 extractions.

60 Mg. of the purified lutecium oxide were dissolved in nitric acid, and ytterbium nitrate added to produce, on precipitation as oxalate and ignition, lutecium oxide samples containing 1, 0·33, 0·1, 0·033, 0·01, and 0·0033% of added ytterbium oxide. At the lowest concentration the ytterbium doublet at λ 3289 was clearly seen in the arc spectrum. The ytterbium lines at λλ 3694 and 3988 were only seen at 0·01% concentration or more. No samarium or thulium sensitive lines could be identified in the original lutecium oxide. The amount of either, therefore, probably did not much exceed 0·01%. The ytterbium content was below 0·0033% and may be estimated at 0·001%.

In another fraction containing lutecium, ytterbium, and thulium acetates (9·8 g.), three extractions each with 0·5 g. of sodium yielded 0·31 g. of ytterbia. After elimination of sodium, two more extractions, each with 0·25 g. of sodium, yielded a further 4 mg. of ytterbia. Eleven more extractions were made during which 0·7 g. of samaria (as acetate) was added and 3·0 g. of sodium were used. The elimination of ytterbium was not so complete as was obtained by using 0·15 g. of samaria and 1·5 g. of sodium in eleven extractions in the previous experiment. When there was only a little to be extracted, the recovered samarium was found spectroscopically to be richest in ytterbium. Its use probably leads to some real increase in purity, because it is more easily removable from solution by amalgam formation than ytterbium. A purer lutecium spectrum results, but on the other hand, more samarium than ytterbium may escape detection in the arc.

*Behaviour of Thulium and Cerium.*—In an experiment with 24 g. of acetate chiefly lutecium but with perhaps 25% of thulium, successive yields of ytterbium of 890, 140, 50, 18, 6, 6, 0 mg. were obtained on extraction with sodium amalgam. The first crop of ytterbium oxide failed to show the sensitive arc lines of thulium or lutecium. Thulium, like lutecium, is therefore non-reducible. The arc spectrum showed about 0·01% of ytterbium remaining in the acetate. 1 G. of cerous acetate was added and an attempt made to extract the remaining ytterbium along with the cerium. The strongest ytterbium arc lines were found in each of the four cerium oxide samples recovered, but there was thereafter no appreciable decrease observable in the ytterbium content of the lutecium–thulium mixture. It does not therefore appear that cerium can be used as a satisfactory vehicle for the elimination of ytterbium.

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[*Received, October* 12*th*, 1942.]