98. *Rare-earth Metal Amalgams. Part II. The Separation of Neodymium, Samarium, and Gadolinium.*

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By treating neodymium–samarium or samarium–gadolinium acetates with sodium amalgam, samarium, which readily forms an amalgam, is at once separated. Fractional decomposition of the samarium amalgam gives further purification, for this amalgam is much less stable than those of neodymium and gadolinium. In one operation the neodymium content in samarium is reduced from 70% to 0·01%.

It was shown in Part I (this vol., p. 398) that by reaction between sodium amalgam and rare-earth acetates widely differing amounts of rare-earth metal amalgams were formed. In the case of samarium practically quantitative transfer from aqueous acetate solution to mercury was brought about. This reaction has now been studied more fully and applied as a method for rare-earth purification. The separation of neodymium–samarium or samarium–gadolinium mixtures has been achieved with greater ease and completeness than by any of the known methods, but europium if present accompanies samarium in the separation. McCoy (*J. Amer. Chem. Soc.*, 1935, **57**, 1756; 1937, **59**, 1131; 1941, **63**, 3422) has, however, described three easy ways of separating these two elements, the latest of which makes use of the preferential amalgam formation by europium on electrolysis. Only small amounts of europium oxide were present in any of the earths used in the present investigation, so for the purposes of this communication europium and samarium may be regarded as a single element.

The conditions most applicable to the extraction of samarium by amalgam formation from neighbouring elements other than europium depend upon their relative amounts. If samarium greatly preponderates in a rare-earth mixture, it may be separated as amalgam from a slightly alkaline acetate solution by the use of sodium amalgam, the efficiency for the sodium–samarium exchange $3Na + Sm^{\cdot\cdot\cdot} = 3Na^{\cdot} + Sm$ being 90%. A p_H of 8—9 is favourable, *i.e.*, the solution should be almost at the point of hydroxide precipitation. When samarium is only present in small amount, however, it is best to carry out the reaction under conditions suited to give maximum production of amalgam of the element forming the main constituent of the rare-earth mixture. If this element is neodymium or gadolinium, a p_H of 4—5 is suitable. Care should be taken that about 10% of the sodium in the amalgam is left when the reaction is stopped; otherwise, some of the samarium may pass back from amalgam to solution at the end. It is impossible therefore to lay down precise conditions for treating rare-earth mixtures the composition of which will often be known only approximately. The reducing action may take only 1—5 minutes and cannot be brought under accurate control.

Separation of the rare-earth elements occurs both on amalgam formation and on amalgam decomposition. Samarium forms amalgam much more readily than neodymium or gadolinium, but the amalgam is less stable and by attack with water or dilute acid will react almost completely before there is any considerable decomposition of the other constituent. By this two-fold reaction neodymium has been reduced from 70% to 0·01% in a samarium preparation, and in two extractions about 80% of the samarium handled had the neodymium removed to this limit. In the case of gadolinium in samarium it is not possible to estimate traces with the same facility as traces of neodymium owing to the lack of suitable strong absorption bands, but the following considerations show that the separation is likely to be at least as good. The maximum yields of oxides from amalgam per g. of sodium which have been obtained are: Nd, 0·18; Gd, 0·018 g. Optimum conditions are similar in the two cases, but the yield of neodymium is ten times as great as that of gadolinium. No change in proportion of the two earths was, however, observable when their mixed amalgam was fractionally decomposed. Gadolinium and neodymium are therefore about equally stable in amalgam, but gadolinium forms less amalgam in the first instance. There is therefore every reason to think that the separation of samarium and gadolinium by amalgam formation is at least as efficient as that of neodymium and samarium.

The amount of residual samarium left in neodymium or gadolinium is also not easy to estimate, for the visible absorption bands are not sensitive, and observation of the band at 10869 A. is beyond ordinary resources. It was found that, while at first samarium could easily be separated from neodymium or gadolinium, yet soon the yield fell to almost zero. The amount remaining was not detectable by arc or absorption spectroscopy. In the case of gadolinium by 6 successive similar treatments with sodium the yield of samarium oxide recovered fell from 6 g. to 1 mg. (Table I), leaving 48 g. of purified oxide. There is no reason to suppose that more than a fraction of a mg. (or, say, 0·001%) of samarium remained with the gadolinium.

After a few treatments of a rare-earth acetate solution with sodium, the efficiency of the extraction falls off in accordance with the law of mass action. The accumulated sodium acetate also tends to salt out samarium or gadolinium acetate, and it is easy to recover 90% of them free from sodium acetate by crystallisation. Neodymium, on the other hand, gives a stable acetate tetrahydrate only at room temperature, and on warming, a less soluble salt is precipitated. Neodymium solutions must therefore be used cold. The separation from sodium is also less satisfactory.

Experimental.

Materials.—All the rare-earth materials had been fractionated as double magnesium nitrates, and the europium removed from the samarium–gadolinium intermediates by McCoy's method with a Jones reductor. Only small amounts of europium remained in any of the material used. The neodymium–samarium mixture was the head fractions from a samarium fractionation; it gave a brown oxide due to the presence of a little praseodymium but the spectrum showed only a trace of lanthanum.

Sodium amalgam was made by direct union and stored as a crystalline solid of about 2% strength. It was dissolved in mercury just before use to 0·25—0·33% concentration—the exact value should be known in order to gauge the equivalent amount of acetic acid.

The acetates were prepared as crystalline salts before use. Gadolinium and samarium are known to give tetrahydrates, but neodymium gives several hydrates and difficulty was experienced through the precipitation of a salt of lower solubility when a concentrated, cold acetate solution was heated.

Quantitative estimates of components of rare-earth mixtures have where possible been made by comparison of absorption spectra of solutions with standards.

Separation of Samarium and Gadolinium.—The mixed oxides (65 g.) of gadolinium (89%) and samarium (11%) were converted into acetate (143 g.), dissolved in 325 ml. of boiling water, and treated hot with sodium (7·5 g.) in mercury (175 ml.). During the reaction, which took only a few minutes, 12 ml. of glacial acetic acid were added. The reaction mixture was shaken gently in a 1-l. flask and then separated in a tap funnel. There was still some sodium remaining in the mercury. The samarium absorption spectrum at the conclusion indicated roughly 5 g./l. of oxide in solution.

The washed amalgam was shaken with water till the sodium was removed. It was then treated with 2N-hydrochloric acid and shaken till calomel began to form. The acid extract was treated with oxalic acid, and the resulting oxalate ignited, affording 6·1 g. of samaria. The above procedure was repeated after adding 300 ml. of water to the acetate solution; 20 ml. of acetic acid were used this time, and the solution finally had p_H 6 (B.D.H. universal indicator). No absorption spectrum was now detectable; yield of samaria, 0·89 g. A third extraction with sodium amalgam (6·4 g. Na) gave a further yield of 0·14 g. of oxide. The oxalate of this material was too pale to be that of pure samarium. The acetate solution was now concentrated to 300 ml. and set aside to crystallise; yield, 122 g. of rare-earth acetate. The mother-liquor containing all the sodium acetate was treated with sodium hydroxide, and gadolinium oxide (4·2 g.) recovered from it. This was not worked further. Frequent sodium acetate removal is desirable, as shown by an increased amalgam yield in the following extraction.

In the fourth extraction gadolinium acetate (122 g.), water (300 ml.), sodium (6·4 g.) in mercury (175 ml.), and acetic acid (20 ml.) were used. Only a little sodium remained in the mercury when it was separated from the acetates. The mercury was shaken with water. At first the sodium reacted, then the mercury broke into droplets and formed a mud. At this stage hydroxide precipitate began to appear in the water. After being shaken for a short time the sludge broke down and the mercury coalesced once more. The hydroxide which had now formed was collected. The mercury was again shaken with water; more hydroxide was formed, but no sludge. The mercury was finally shaken with hydrochloric acid till calomel formation started. It was found that the hydroxide (75 mg. of oxide) formed during the mercury sludge period gave a yellow oxalate and chloride solution, and strong samarium absorption spectrum, whereas the rare-earth oxide recovered subsequently gave a white oxalate and no absorption spectrum in chloride solution. The spectrum would have revealed 0·6% of samarium. Arc spectroscopy gave confirmatory results. The first crop hydroxide was found to have been samarium with a little europium and gadolinium, but the second crop was pure gadolinium.

In the fifth extraction 100 ml. more of water were used, but only 10 ml. of acetic acid. There was thus considerable sodium left in the amalgam when it was separated from the acetates. This gave greater protection to the samarium in the amalgam, for sodium suffers attack and removal almost quantitatively before any rare earth. The sodium was laboriously removed from the mercury by shaking with several changes of water, but eventually only a very little mercury sludge formation occurred. The hydroxide precipitate at this stage was too small to handle, so acid was added, and the total rare-earth extracted from the amalgam (62 mg. of oxide). The absorption spectrum of this oxide, examined as chloride, led to an estimate of a content of 10 mg. of samaria.

At this point the gadolinium acetate was again purified from sodium acetate and 5·1 g. of gadolinium oxide rejected. The sixth extraction was given in 250 ml. of hot gadolinium acetate solution. The rare earth obtained from the amalgam afforded 120 mg. of oxide. This was converted into chloride, and the absorption spectrum examined in 0·22 ml. (l = 6 cm.). The presence of 1 mg. of samarium oxide should have been detectable, and just about this amount appeared to be present. The foregoing results are summarised in Table I.

TABLE I.

The separation of samarium and gadolinium by extraction with sodium amalgam.

Extraction no.	1.	2.	3.	4.	5.	6.
Na used, g.	7·5	6·4	6·4	6·4	6·4	6·4
Acetic acid, ml.	12	20	20	20	10	17
Yield of Sm_2O_3, g.	6·1	0·9	0·14	0·075	0·010	0·001
Yield of Gd_2O_3, g.				0·090	0·052	0·120
Residue, Gd_2O_3, g.			4·2		5·1	48

Purification of Gadolinium.—This was effected in a similar manner to the later extractions of the samarium–gadolinium mixture (above), but the impurity was chiefly europium. Gadolinium acetate (140 g.) was treated in 250 ml. of boiling water with 6·4 g. of sodium in 175 ml. of mercury, and during the reaction 17 ml. of acetic acid were added. A little sodium remaining in the amalgam at the end of the reaction was removed by shaking with water. The mercury then formed a sludge. The hydroxide which had formed when the sludge broke down again yielded 141 mg. of oxide showing the green reflection bands of europium distinctly but not so strongly as pure europium oxide. The arc spectrum confirmed the presence of some gadolinium. Oxide (40 mg.) recovered from amalgam subsequent to sludge formation showed no reflection bands or absorption spectrum in 1 cm. of 200 g./l. of oxide in solution as chloride. The europium oxide content was therefore under 1·25%.

130 G. of gadolinium acetate crystallised out from the solution on cooling. It was given a second extraction with 6·4 g. of sodium as above. The oxide (85 mg.) recovered from amalgam gave no europium reflection or absorption spectrum. The main bulk of gadolinium was now found to be free from any trace of europium arc lines.

Purification of Samarium.—The sample of oxide used had been fully fractionated as double magnesium nitrate but came from the more soluble end of the samarium fractions. It might therefore contain a little europium or gadolinium.

Samarium acetate (80 g. = 35 g. of oxide), boiling water (200 ml.), and sodium (5·4 g. in 175 ml. of mercury) were shaken together gently till a dark red colour developed (1 min.), and the amalgam was then separated. It was slightly pasty and contained no sodium. Solid samarium amalgams result, and are troublesome to separate, if sodium amalgam exceeding 0·25% concentration is used to extract samarium from solutions where a high yield is to be expected. The solubility of samarium in mercury cannot be above 0·5%.

The foregoing reaction was repeated with the addition of 0·6 ml. of acetic acid at the start and 1 ml. during the course of the reaction (4 mins.). The solution was frothy all the time, indicating an alkaline state. Escaping hydrogen was not noticeable. The resulting samarium amalgam was a little pasty and the mercury showed a tendency to emulsify and form black clots with samarium hydroxide. The separated amalgam was treated with insufficient concentrated hydrochloric acid, and the strong, dark red colour of samarous salts developed as the solution became alkaline. Some of the red-brown solution was decanted and kept in a beaker. At first there was a rapid evolution of hydrogen and a green precipitate formed, but some colour persisted for more than an hour. The amalgam was extracted with more hydrochloric acid.

In making a third extraction of the acetate solution, only half the previous amount of sodium amalgam was used. Acetic acid (1·5 ml.) was added at the beginning. The whole of the sodium reacted in 2 mins. A fourth extraction similar to the third but without the addition of more acetic acid was made. The solution was frothy and much sodium remained. Rare earth (2·4 g. of oxide) still in solution as acetate was recovered as hydroxide and reconverted into acetate. This was then extracted four times with 0·4 g. of sodium in 25 ml. of mercury each time. The residue subsequently recovered as hydroxide gave a pale brown oxide and showed no samarium reflection bands. These separations are summarised in Table II.

TABLE II.

Purification of samarium by amalgam formation.

Extraction no.	1.	2.	3.	4.	5.	6.	7.	8.	Total.
Na used, g.	5·4	5·4	2·7	2·7	0·4	0·4	0·4	0·4	
Acetic acid, ml.	0	1·6	1·5	0	0	0·7	0	1	
Yield of Sm_2O_3, g.	12·0	12·9	4·7	1·4	0·75	1·11		0·15	33·0
Residue unamalgamated	0·1 g.	Washings, etc., 1·9 g.							

In this purification no attempt was made to separate samarium and gadolinium on decomposition of the amalgams. A very slight trace of gadolinium was found by arc spectroscopy in the samarium from the first extraction; the third and the fifth extraction showed small but increasing quantities. The residue was largely but not entirely gadolinium. The work was done before the importance of the fractional decomposition of the amalgams was realised, but it was shown later that the separation of samarium and gadolinium should be equally as good as the separation of samarium and neodymium.

Separation of Neodymium and Samarium.—The acetate used was derived at an early stage from the heads of a fractional crystallisation series of samarium magnesium nitrate. Besides neodymium it contained enough praseodymium to cause the derived oxide to be brown. Lanthanum was also detectable. The neodymium acetate prepared by evaporation at 30° of the solution of the oxide in acetic acid appeared similar in crystalline form to samarium acetate tetrahydrate, but was more soluble. On being heated, a concentrated solution would usually deposit a less soluble salt. The nearly boiling solutions used in other instances were therefore unsuitable. The acetate (120 g. = 50 g. of oxide) was dissolved in 300 ml. of cold water, and sodium (6·4 g.) in mercury (200 ml.) added, and in the course of the reaction 12 ml. of acetic acid. The reaction mixture was shaken gently in a 1-l. flask as before. The mercury was separated and washed twice with water and then shaken in a tap funnel with 2N-hydrochloric acid. The sodium was found to be exhausted. When with excess acid present the evolution of hydrogen slackened the acid was separated with its rare-earth content (Table III, Extraction 1, Crop 1). More acid was shaken with the mercury; extraction then appeared to be almost complete (Crop 2). The mercury was now shaken with water. Hydroxide formed but not a mercury sludge, so the water was acidified and withdrawn (Crop 3). The mercury was finally shaken with acid till calomel formation began (Crop 4).

The acetates were given a repetition of the previous extraction. The reaction was vigorous, but the mixture frothed towards the end. The mercury on withdrawal still held sodium. It was twice washed and then treated with 2N-hydrochloric acid till sodium was removed. On addition of alkali to the sodium solution, a little rare earth was found (Table III, Extraction 2, Crop 1). The amalgam was then treated with 2N-acid till extraction of samarium appeared complete (Crop 2). By shaking the mercury and water some hydroxide was formed (Crop 3). A final treatment of the mercury with acid gave a pale neodymium-coloured solution (Crop 4). A third extraction of the acetate solution was made on similar lines. Most of the crops were made into chloride solutions and the neodymium content estimated from the absorption spectrum, giving the results recorded in Table III.

TABLE III.

Separation of neodymium and samarium by sodium amalgam.

	Extraction 1.				Extraction 2.		Extraction 3.	
	Oxide, g.	Oxide colour.	Nd_2O_3, %.	Nd_2O_3, g.	Oxide, g.		Oxide, g.	
Crop 1	8·07	Sm_2O_3	0·01	0·001	0·035		0·042	
Crop 2	1·04	Sm_2O_3	0·04	0·0004	3·52	0·01% Nd_2O_3	0·60	4% Nd_2O_3
Crop 3	0·140	Buff	1·2	0·0017	0·36	Buff	0·16	Brown
Crop 4	0·144	Brown	50	0·072	0·24	Brown	—	
	9·4			0·075	4·155		0·80	

As the earth mixture was not in the first place binary, further separation would not have resulted in any pure neodymium; 1—2% of samarium was probably still present in the neodymium, but neodymium and sodium acetates do not separate with the same ease as gadolinium and sodium acetates by crystallisation from solution. For further treatment, precipitation of the neodymium as oxalate and reconstitution of the acetate would have been necessary. The recovery of pure samarium has however been most satisfactory, and further recovery would not be economic.

Relative Stability of Neodymium and Gadolinium Amalgams.—Gadolinium acetate (8 g.) and neodymium acetate (0·8 g.), dissolved in hot water (25 ml.) and treated with sodium (0·5 g.) in mercury (7 ml.) with addition of acetic acid (1·4 ml.), gave an amalgam. This might be expected to contain approximately equal quantities of neodymium, and gadolinium, the quantities of acetates mixed being inversely proportional to the amalgam-forming powers.

The amalgam was decomposed in four fractions, the first by water and the other three by 2N-hydrochloric acid. The four oxides were recovered and examined by arc spectroscopy. No difference in the relative amounts of the two earths in the first and the fourth fraction could be detected, but the first contained traces of europium. The four oxalates were similar in tint.

The amalgams of neodymium and gadolinium are therefore of similar stability, but as gadolinium forms amalgam less readily than neodymium the purification of samarium from gadolinium should be even more satisfactory than the separation from neodymium described above.

Purification of Neodymium.—The material had been subjected to 2000 crystallisations as double magnesium nitrate and came from a fraction near the tail of the neodymium salt and so might contain traces of samarium.

Neodymium acetate (65 g.) was dissolved in water (250 ml.) and treated with sodium (4 g.) in mercury (50 ml.) and acetic acid (11 ml.), reaction being vigorous; after being washed, the mercury was treated with 2N-hydrochloric acid, which reacted with the sodium amalgam present, and a little neodymium was also extracted. The rare earth was precipitated from the acid as hydroxide (giving 10 mg. of oxide). The arc spectrum showed it to be largely neodymium but to contain also considerable samarium. The mercury was then treated with concentrated hydrochloric acid and yielded 0·71 g. of neodymia. A second extraction yielded 0·014 g. of oxide as a first crop and 0·575 g. as a main crop. The two crops gave identical spectra; no samarium was detectable in either. All the samarium present in the specimen of neodymium had therefore been removed by the first extraction with sodium. This result would not be obtained, however, if there was not considerable sodium left in the amalgam when the reaction was stopped, for then samarium might pass back from amalgam to solution.

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