

## 142. Rare-earth Metal Amalgams. Part IV. The Isolation of Europium.

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Europium is concentrated rapidly by shaking its acetate (<1% Eu) with sodium amalgam, thus forming a samarium-europium amalgam and leaving gadolinium, etc., in solution (Part II; J., 1942, 398). The action of acetic and sulphuric acid on the amalgam is to give a pure samarium acetate solution and a samarous-europous sulphate precipitate. Nitric acid then selectively oxidises samarium, leaving europous sulphate (90%). This, when converted into acetate and then into amalgam and treated with concentrated hydrochloric acid, yields pure  $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$  crystals. If pure samarium is not desired, the acetate (<1% Eu) is shaken with a little sodium amalgam and sulphuric acid, and europous sulphate (20%) results. The solubility of this sulphate is less in acetate than in chloride solutions, and the stability of samarous sulphate is greater. An advantage is thereby gained over McCoy's technique for europium purification. Applications of zinc, barium and samarium amalgams to europium purification are also described.

YNTEMA (*J. Amer. Chem. Soc.*, 1930, **52**, 2782), using electroreduction, first showed that europium could be purified by precipitation of the bivalent sulphate. McCoy effected reduction by means of amalgamated zinc, but neither method was suited to quantitative separation from low concentrations. McCoy later reduced chloride solutions with zinc dust, and by co-precipitation with the less soluble but isomorphous barium sulphate obtained a large supply of purified europium material from a source, mainly samarium and gadolinium, but containing 0.5% of europium. His first concentrate does not appear to have contained more than 10% of europous sulphate, the rest being barium sulphate and much other rare-earth sulphates. Repeated reduction of chloride solutions with amalgamated zinc, followed by precipitation of bivalent sulphate, failed to remove the last few parts per 1000 of other rare earths, but later it was shown that europium of at least 70% content on reduction of a concentrated trichloride solution with amalgamated zinc yielded the dichloride, which was precipitated in a pure state on addition of concentrated hydrochloric acid (*ibid.*, 1935, **57**, 1756; 1936, **58**, 2279; 1937, **59**, 1131).

The method of concentrating europium now recommended makes use of acetate solutions. Europous sulphate is much less soluble in these than in chloride solutions. Moreover, samarous sulphate, being also less soluble and less ionised, is more stable in them and can be used as a co-precipitant of the europium in place of the hitherto-used barium sulphate, from which the recovery of europium is troublesome. A third advantage lies in the avoidance of the use of zinc dust, for finely divided metals render bivalent sulphate precipitates unstable.

From a crude rare-earth mixture, samarium and europium are removed together as amalgam by treatment with sodium amalgam (Part II, *loc. cit.*). If the original earths were largely samarium, europium, and gadolinium, gadolinium of good purity will constitute the non-amalgam-forming residue in the treated acetate solution. The samarium-europium amalgam is decomposed by mixed acetic and sulphuric acids to give mainly pure samarium(III) acetate and impure (20%) europium(II) sulphate. If, however, the isolation of europium alone is desired, the crude rare-earth solution is treated with small amounts of sulphuric acid and sodium amalgam. In presence of a strong acid, samarium-europium amalgam formation is small, and in the above reaction a precipitate of mixed europous and samarous sulphates results, similar to that yielded by treatment of the mixed amalgam with sulphuric-acetic acid. The reduction of the acetate solution with sodium amalgam may be repeated till removal of europium is quantitative, but the first treatment gives the bulk of the europium at a concentration of 20–30%. Treatment of such a concentrate with cold dilute nitric acid results in selective oxidation of samarous sulphate and formation of samarium nitrate solution, which is then filtered from europous sulphate, but retained for reworking for a small amount of europium present in it.

The greater part of the europium is now sufficiently concentrated to apply McCoy's method of purification by precipitation as  $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ , but if the europium has not been through an amalgam stage at the first step, and thereby had all earths other than samarium removed, amalgam formation is advantageous now. The amalgam is then treated with concentrated hydrochloric acid and yields europium(II) chloride crystals and samarium(III) chloride solution.

It was observed that an acetate solution containing a trace of neodymium in much europium lost the neodymium absorption spectrum when the europium was reduced to the bivalent state on first being treated with sodium amalgam. When the europium had been extracted from the solution as amalgam with more sodium, the neodymium absorption spectrum reappeared. There is evidently an equilibrium,  $\text{Nd}^{III} + \text{Eu}^{II} \rightleftharpoons \text{Nd}^{II} + \text{Eu}^{III}$ , and  $[\text{Nd}^{III}][\text{Eu}^{III}]/[\text{Nd}^{II}][\text{Eu}^{II}] = \text{const}$ . When  $[\text{Eu}^{II}]$  is large, a high proportion of neodymium will become bivalent. Conversely, as has been noted in previous Parts, the yields of amalgams are very adversely affected

by large amounts of non-reducing earths, so that it may be impossible to remove the last trace of a potentially bivalent material from admixture with them; *e.g.*, high  $[\text{Nd}^{2+}]$  will stabilise small amounts of  $\text{Eu}^{3+}$ , or high  $[\text{Lu}^{3+}]$  small amounts of  $\text{Yb}^{3+}$  (Part III; this vol., p. 8). If the bivalent ion can be removed as rapidly as formed and before decomposition, *e.g.*, by precipitation as sulphate, then the more stable bivalent element may be removed from solution quantitatively, and with an efficiency varying with the insolubility of the sulphate. Since in the bivalent state the characteristic absorption bands of the rare-earths are lost, it follows that in concentrated bivalent solutions absorption-spectrum tests for traces of other earths become unreliable.

It has been noted in previous work that the bivalent ion of ytterbium or samarium is much more stable in neutral than in acid solution; *e.g.*, if the amalgams are treated with acid, at first only trivalent salts are formed,  $2\text{Sm}^{2+} + 2\text{H}^+ \longrightarrow 2\text{Sm}^{3+} + \text{H}_2$ ; but as  $[\text{H}^+]$  decreases, the colour of the bivalent ion develops in the solution. This is of interest in connection with the difficulty experienced in obtaining high-purity europium by repeated precipitations of its bivalent sulphate with magnesium sulphate (McCoy, *loc. cit.*). The europous solution stabilises quantities of the cerium earths in the bivalent state and they are then co-precipitated with the europium; but by precipitation of europous chloride with concentrated hydrochloric acid the equilibrium was altered so that nearly pure  $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$  was deposited. Bivalent europium alone possesses appreciable stability in strongly acid solutions.

Most of the present work has been done with artificial mixtures of europium and samarium containing 1% of the former, *i.e.*, a proportion of europium to samarium not more than that occurring in monazite. It is found that europium forms amalgams rather more readily than samarium, doubtless owing to the greater stability of the europous ion. Quantitative separation of europium can therefore be achieved without obtaining a fully quantitative samarium extraction. Conversely, from the mixed amalgam on attack by acetic acid, europium passes into solution relatively more quickly than samarium. This is in accord with the reduction potentials (Noddack and Brukl, *Angew. Chem.*, 1937, 50, 362), *viz.*,  $\text{Sm}^{2+} \rightarrow \text{Sm}(\text{metal}) = -2.010 \text{ v.}$ ;  $\text{Eu}^{2+} \rightarrow \text{Eu}(\text{metal}) = -2.510 \text{ v.}$  on the hydrogen scale for 0.01M-sulphate solutions. That europium amalgam is not always more reactive than samarium amalgam is shown by the fact that the former remains mirror-bright in open air for 10 minutes, and the latter for only a fraction of a second. The stability of europium amalgam in air affords an excellent indication of its purity.

The solubility of europous sulphate in saturated europium sulphate solution (*ca.* 30 g./l. of anhydrous salt) is 0.19 g./l., that of samarous sulphate being 0.075 g./l. (Holleck and Noddack, *ibid.*, p. 819). The solubilities are therefore of the same order as that of strontium sulphate in water (0.11 g./l.), and considerably greater than that of barium sulphate (0.0011 g./l.), but these sulphates are much more soluble in certain salt solutions. A study of europous sulphate in rare-earth chloride and acetate solutions has therefore been made, and shows it to be much more soluble in the chlorides than in the acetates. In the latter, the solubility is sufficiently small to allow an almost quantitative precipitation without the use of barium sulphate as co-precipitant, which McCoy found necessary when using chloride solutions. Moreover, the europium separation may be facilitated by co-precipitation of samarous sulphate. Samarium precipitation does not occur to any great extent in chloride solution, for the higher solubility and ionisation allow the samarous ion to reoxidise as quickly as it is formed. It is easy, however, to prepare samarous sulphate by acting on samarium amalgam with dilute sulphuric or acetic-sulphuric acid.

Several methods of separating samarium and europium on decomposition of the mixed amalgam ( $\text{Eu}/\text{Sm} = 1/100$ ) have been tried.

(1) By allowing the amalgam to stand in contact with acetic acid containing a little sulphuric acid at room temperature for 18–20 hours, 50–60% of the europium was recovered as nearly pure sulphate (II).

(2) By carrying out the foregoing treatment in a hydrogen atmosphere, the yield was increased to over 90% of the europium.

(3) By acting on the amalgam with acetic and sulphuric acids at 65° in a hydrogen atmosphere with shaking, europous sulphate was recovered at a concentration of about 20%, accompanied by much samarous sulphate, but in nearly quantitative yield. The samarium sulphate was then oxidised and dissolved by cold dilute nitric acid, leaving the europous sulphate nearly unaffected and about 90% pure.

(4) Under the conditions of (3) but in the presence of a zinc salt, the bivalent sulphates are rendered less stable by the finely divided reduced zinc which is formed. According to the quantity of zinc, the formation of samarous sulphate may be restrained or the yield of bivalent sulphate may vanish. The action of dispersed metallic zinc in decomposing bivalent sulphate is similar to a phenomenon noted by the author (J., 1937, 1367), *viz.*, that traces of metallic salts in ytterbium sulphate solutions on electroreduction gave rise to a grey cloud which very much reduced the stability of the ytterbous sulphate. McCoy found lead to behave similarly in oxidising europous chloride. Even violent shaking, with consequent dispersion of mercury, may bring about the same result.

(5) If an acetate solution of samarium and europium is treated with zinc amalgam (2%) and a little sulphuric acid and kept acid with acetic acid while steam is blown through, a precipitate of mixed europous-samarous sulphate is formed and a concentrated samarium solution is left with a europium content of 0.02%. No samarous sulphate will be precipitated in the absence of europium. The reduction potentials for 0.01M-sulphate solutions have been determined by Noddack and Brukl (*loc. cit.*) as  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+} = -0.71 \text{ v.}$ ;  $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+} = -1.72 \text{ v.}$

(6) When no more europium can be eliminated by method (3), if a little barium amalgam is added to the

reaction mixture, barium sulphate will be slowly precipitated and carry with it the last of the europium. The treatment with barium may be repeated as long as the precipitate is obtained in a filterable condition : in the absence of europium it becomes too fine to be retained.

(7) Pure samarium amalgam may be used as the reducing agent in the same way as sodium amalgam (method 8) : it has the advantage of not introducing impurity.

(8) A perfect elimination of europium from samarium is made by treating the mixed acetates with dilute sodium amalgam and a little sulphuric acid. A good concentration of europous sulphate is effected at once. This method introduces some sodium acetate but has much in its favour : it is easy and certain. Successive crops of sulphates are taken till soon it is found that the crop is pure samarous sulphate, and the main bulk of samarium is free from europium.

A modification of McCoy's precipitation method for  $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$  allows of its application at europium concentrations below 70%. By acting on impure europium amalgam with concentrated hydrochloric acid, precipitates have been formed even in presence of 90% of samarium. The europium precipitation, however, is not quantitative, and the samarium chloride retains some 5% of europium. Samarium chloride will itself be precipitated if the concentration of hydrochloric acid becomes too high. One or two repetitions may be required to produce europium of the highest purity.

#### EXPERIMENTAL.

*Estimation of Europium in Samarium.*—Solutions were mixed and precipitated with oxalic acid, wherefrom samarium oxide standards with 3.3, 1, 0.33, 0.1, 0.033, 0.01, and 0.003% of europium oxide were prepared. Comparisons of other samarium oxide samples were made with the above from graphite arc spectrograms taken on a medium quartz-prism spectrograph and examined with the aid of a Hilger spectrocomparator. The two sensitive lines of europium at this dispersion are beset by samarium lines :  $\text{Eu } \lambda 4205.046$  (intensity 200) by  $\text{Sm } 4205.361$  (int. 8), and  $\text{Eu } 4129.735$  (int. 150) by  $\text{Sm } 4129.987$  (int. 10). The most suitable europium line for detection and comparison purposes was 3819.66 (int. 500). According to the Massachusetts Institute of Technology Tables, this should be beset by  $\text{Sm } 3819.678$  (int. 10), but this samarium assignment appears to be in error.

*Ease of (a) Formation and (b) Decomposition of Samarium-Europium Amalgams.*—(a) Samarium acetate (23 g.) and europium acetate (0.23 g.) were treated in solution with sodium (5 g.) in mercury, and the bulk of the rare-earths exchanged into amalgam. Another 0.5 g. of sodium extracted a further quantity of rare earth (0.635 g. of oxide) which contained only 0.02% of europium oxide. A final extraction with 0.3 g. of sodium yielded 0.185 g. of samarium oxide free from europium. The residual acetate on recovery yielded 0.14 g. of samarium oxide free from europium but showing some gadolinium arc lines.

(b) Some mixed amalgam (Sm 99%, Eu 1%) was decomposed with dilute acetic acid. Samples of amalgam were withdrawn at five stages in the reaction, and their total earth content recovered. Arc spectra showed that the relative proportion of europium in the amalgam fell regularly from 1% at the start to nil near the end, *i.e.*, europium reacts preferentially to samarium.

*The Solubility of Europous Sulphate.*—(1) *In acetate solution.* A solution of samarium acetate (= 10 g. of oxide) in water (65 ml.) was heated in a flask in brine (107°) stirred by a jet of steam. Saturated liquid (2%) zinc amalgam (10 ml.), acetic acid (1 ml.), magnesium sulphate (1 g.), and europium acetate (= 20 mg. of oxide) were added. A slight orange precipitate soon formed. It was concluded that the solubility of europous sulphate was equivalent to 0.2 g./l. of oxide. The samarium acetate solution at no time held sufficient europous salt to give a definite bleaching action on litmus paper.

(2) *In chloride solution.* Samarium chloride solution with europium acetate equivalent to 0.1 g. of oxide under similar conditions gave no precipitate, but the solution bleached litmus readily. The solubility of europous sulphate in samarium chloride must exceed seven times that in samarium acetate.

*Separation of Europium (1%) from Samarium.*—The mixed amalgam was first prepared from mixed acetates. The following is typical of this preparation : The acetates (45.8 g. = 20 g. of oxide) were dissolved in boiling water (90 ml.) and shaken with 0.3% sodium amalgam in successive portions of 175, 25, and 25 ml., acetic acid (2—2.5 ml.) being added during the reaction to prevent formation of a basic precipitate. The remaining samarium acetate (= 1 g. of oxide) was recovered, and contained only a trace of europium. The amalgam was washed once by running through water and then decomposed by various methods.

(1) Amalgam (= 10 g. of oxide), water (100 ml.), acetic acid (12 ml.), and sulphuric acid (0.2 ml.) were left in a separating funnel; reaction was complete in 18 hours, and a layer of sulphate lay on the mercury. It yielded 65 mg. of oxide which gave on solution an absorption spectrum of europium in which only a trace of samarium was visible; hence, about 60% of the europium in the amalgam had been recovered.

(2) Amalgam (= 19.2 g. of oxide), water (200 ml.), acetic acid (25 ml.), and sulphuric acid (0.2 ml.) were placed in a separating funnel which was then closed with a Bunsen valve to maintain a hydrogen atmosphere and set aside for 20 hours. The initial temperature was 35°. During the first and the last hour the funnel was shaken a few times. A greyish-orange precipitate of bivalent sulphates, a little mercury, and a few crystals of samarium acetate were separated. The precipitate yielded 0.18 g. of oxide. Some sulphate adhered to the funnel walls; this with the acetate crystals yielded another 0.145 g. of oxides, mainly samarium. The 0.18 g. of oxide was made into 0.6 ml. of solution and examined in a 1-cm. layer. The samarium absorption spectrum was compared with a standard and indicated 20%. The arc spectrum of the 0.145 g. showed it to contain much more than 3% of europium, and the oxide from the samarium acetate filtrate showed 0.06% of europium oxide. Residual samarium (0.64 g. of oxide) in the mercury amalgam was found to contain 0.1% of europium. Hence, 94% of the europium input is found in the two concentrates (0.325 g.), and 6% in the remaining samarium oxide (18.3 g.).

(3) Amalgam (= 18 g. of oxide), boiling water (162 ml.), acetic acid (18 ml.), and sulphuric acid (0.2 ml.) were placed in a separating funnel as in (2). The initial temperature of 65° was maintained by the heat of the reaction till the amalgam was nearly exhausted. The funnel was continuously shaken, and two additions each of 1 ml. of 10% sulphuric acid made in the course of the reaction (25 mins.). The acetate solution was filtered with suction. The orange residue and precipitate adhering in the funnel yielded 0.91 g. of oxide. The residual samarium in the mercury amounted to 0.93 g. of oxide and contained 0.2% of europium. The samarium acetate filtrate (16 g. of oxide) contained only about 6 mg. of europium [see method (6) for its removal]; 97% of the europium was concentrated in 5% of the material in this one reaction.

(4) Method (3) was repeated but during the early part of the reaction 15 mg. of hydrated zinc sulphate were added

This at first restrained the formation of samarous sulphate. The total yield of oxides from precipitated sulphates was reduced to 0.62 g. The colour of the sulphates was duller. The sulphate residue was separated and treated with cold 2N-nitric acid; it reacted immediately with effervescence, leaving a pale buff residue, which was at once filtered off. The filtrate yielded 0.44 g. of oxide, mainly samarium, and the residue 0.18 g. of oxide, mainly europium. In another experiment, but with 33 times as much zinc sulphate, a heavy grey cloud was produced but no europium.

In the following methods, acetate solutions were treated directly with reducing agents, and amalgam formation did not play an essential part.

(5) The samarium acetate solution from which europium had been incompletely separated by method (1) was placed in a flask in a boiling brine bath (107°) with 10 ml. of saturated liquid zinc amalgam (2%), and steam was blown through it for  $\frac{1}{2}$  hour. An orange-red precipitate formed, yielding 170 mg. of oxide. The remaining samarium acetate contained 0.02% of europium.

(6) The samarium acetate solution after treatment by method (3) was at once treated at its b. p. with 1 ml. of saturated barium amalgam (0.04 g. of Ba) in 5 ml. of mercury. A coloured precipitate was formed, and filtered off. A second treatment gave a smaller precipitate, which became filterable after a short time. The precipitates were digested with nitric acid and yielded 25 and 13 mg. of oxide respectively. Both were mainly samarium but contained perhaps 10% of europium. After an interval the solution was treated with zinc amalgam and steam (method 5) without result. Four more treatments each with 2 ml. of barium amalgam were given. Filtration from the sulphate precipitates was difficult, and the yields of 20, 9, 12, and 6 mg. of rare-earth oxides include much samarium from the unwashed filter-papers. Contents of 10, 3, 2, and 0.2% of europium oxide, respectively, were found. No trace of europium was then detectable in the arc spectrum of the samarium acetate.

(7) Samarium acetate (45 g., 0.1% of Eu), water (200 ml.), and sulphuric acid (0.2 ml.) were treated with samarium amalgam (50 ml.) at 70–75°. A precipitate, at first white but later orange, was formed. More samarium amalgam and sulphuric acid were added, and crops (0.22, 0.10, and 0.03 g.) of oxide were obtained. These contained much europium. By starting with a europium-free samarium amalgam, it would appear that an increased quantity of europium-free samarium should be producible by this means without introducing any impurity.

(8) Samarium acetate (135 g.) in 450 ml. of solution at 60° and 50 ml. of mercury were treated with 0.5 ml. of sulphuric acid and 0.33 g. of sodium in 10 ml. of mercury. Two further portions of sodium were added before any precipitate was formed. A trace of zinc reduced the stability and yield until it was removed with the first precipitate. The reaction mixture was shaken gently (too vigorous shaking gave a precipitate which could not be efficiently filtered off, and a vigorous reaction also tended to emulsify small quantities of mercury which, like zinc, reduced the stability of the sulphate). Pure samarous sulphate precipitates appeared more stable than mixed samarous-europous precipitates. After the filtration, the acetate solution was reheated and returned to the mercury, more sodium amalgam and sulphuric acid added, and another crop of insoluble sulphates obtained. This procedure was repeated several times, as shown in the table. The colour of the first four crops was different from that of later ones. The former contained the bulk of the europium. All were converted into oxides. Arc spectroscopy showed a rapid falling off in europium content in the later crops, and complete absence in the last. Only a little samarium (0.66 g. of oxide) was found in the mercury

*Fractionations from samarium acetate = 60 g. of oxide.*

Na, g.	H <sub>2</sub> SO <sub>4</sub> , ml.	AcOH, ml.	M <sup>++</sup> SO <sub>4</sub> , as g. of oxide.	Remarks.
1	0.5	—	0.12	Grey-brown, unstable; Zn
0.4	0.5	—	0.40	Rust colour; much Eu
1	0.5	—	1.29	Brick red; much Eu
0.4	—	0.3	0.27	Red; much Eu
0.4	0.5	1.0	1.25	Bright red; 5% Eu
0.4	0.5	—	1.59	" 0.3% Eu
0.4	0.5	—	0.86	" 0.003% Eu
0.4	—	—	0.07	" no Eu
			5.05	
			Sm <sub>2</sub> O <sub>3</sub> (purified, Eu-free) :	
			54.3 <i>ex</i> acetate solution	
			0.66 <i>ex</i> amalgam	

at the conclusion, and this was europium-free. The bulk of the samarium acetate was recovered by crystallisation, and was readily separable from the more soluble sodium acetate with which it was now mixed. The sulphuric acid used (3 ml.) was sufficient to combine with at least 8 g. of oxide to produce mixed europous-samarous sulphate, whereas only 5 g. of oxide were so recovered. Some sulphuric and acetic acid underwent reduction, and a ginger-like odour was always noticeable.

*Purification of Europium by Precipitation of EuCl<sub>2</sub>·2H<sub>2</sub>O.*—(a) *Initial Eu < 99%.* Europium oxide (20 g.) which had been reduced 6 times by amalgamated zinc and precipitated with magnesium sulphate was made into acetate and dissolved in water; sodium (11 g.) in amalgam was added in three portions, together with acetic acid (5 ml.) during the reaction. A green colour developed, but was lost after the last sodium extraction. A final extraction with 0.7 g. of sodium yielded 24 mg. of oxide, apparently good europium. Recovery of earths from the acetate mother-liquor amounted to 70 mg. Gadolinium, samarium and much europium were found in these by arc spectroscopy; the presence of neodymium, cerium, and praseodymium or terbium was also detected. The europium amalgam was washed once by passage through water. It reacted rapidly with air, indicating the presence of samarium, but not with water. It was then treated with concentrated hydrochloric acid in a separating funnel fitted with a Bunsen valve. 60 ml. of acid were used at first, but produced a green solution. Another 40 ml. were added and the colour was lost through fuller precipitation. When the reaction was complete, the solution was cooled in an ice-bath and filtered. The filtrate yielded 0.8 g. of oxide, and washings of concentrated hydrochloric acid another 0.8 g. of oxide. Samarium arc lines but not absorption bands were easily seen in filtrate spectra. Amalgam made from the main crop of purified europium remained mirror-bright for 10 minutes in open air, in striking contrast to the behaviour of less pure amalgam or to that of samarium or ytterbium amalgam. The arc spectrum showed no certain indication of samarium, which is the last impurity to be removed after this second amalgam formation.

(b) *Highly impure europium material (Sm 70%).* The mixed amalgam was formed in the usual manner, and treated with concentrated hydrochloric acid (20 ml.). A precipitate was formed and showed on solution at most a doubtful trace of samarium absorption bands indicative of < 0.025 g. of samaria in 0.61 g. of oxide. The filtrate yielded 1.28 g. of samaria; arc spectroscopy showed 3–10% of europium in this. The treatment had therefore recovered some 80%

of the original europium substantially pure. Treatment of some 10% europium material resulted in the recovery of two-thirds of it pure. It is possible to precipitate samarium chloride almost quantitatively with hydrochloric acid (saturated at 0°), but not to obtain a quantitative precipitation of europium(II) chloride by hydrochloric acid before samarium(III) chloride begins to precipitate if there is a large proportion of it present. Nevertheless, for europium preparations of more than 10% content the above process leads to a rapid concentration.

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