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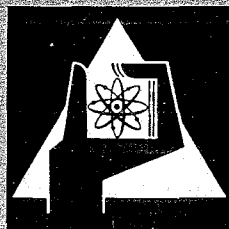
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Rapid Radiochemical Separations

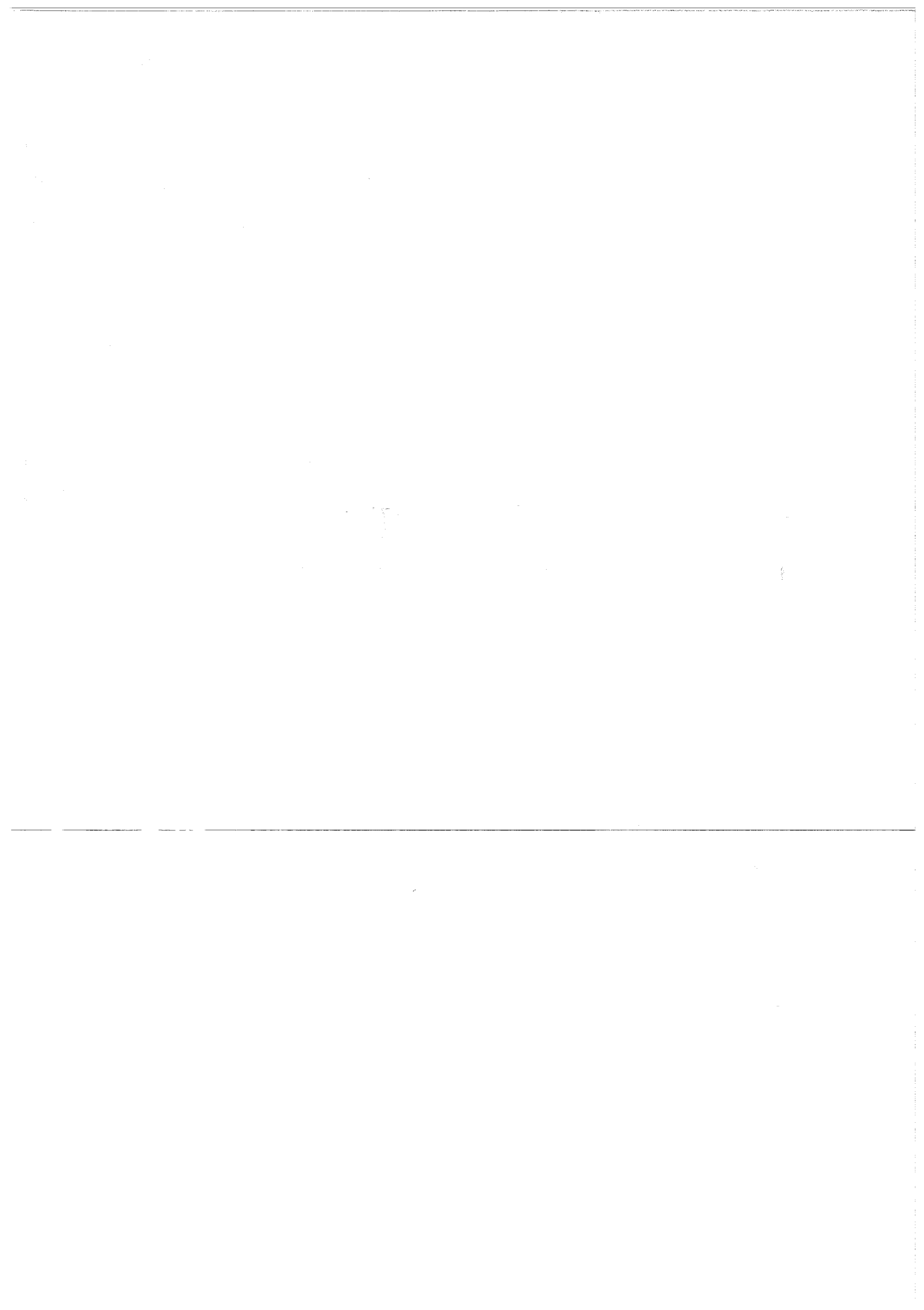
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Rapid Radiochemical Separations

II. Separation of Europium from other Lanthanides

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- Summary** The rapid chemical separation of europium from neighbouring lanthanides was investigated. Details are given of a procedure by means of which europium has been separated in about 50% yield from irradiated samarium targets within one minute. The separation factor with respect to samarium is about 10^3 , and with respect to other lanthanides one to several orders of magnitude greater.
- Zusammenfassung** Ein Verfahren zur schnellen Trennung des Europiums von den benachbarten Lanthaniden wurde entwickelt. Nach dieser Methode kann Europium mit 50% iger Ausbeute innerhalb von 1 Minute aus einem bestrahlten Samarium-Target abgetrennt werden. Der Trennfaktor gegenüber Samarium beträgt etwa 10^3 , während er gegenüber allen anderen Lanthaniden jeweils mindestens um eine Größenordnung besser ist.
- Résumé** Nous avons développé une méthode chimique rapide pour séparer l'euporium des terres rares voisines. L'euporium est séparé en une minute avec 50% de rendement, d'une cible de Sm irradiée. Le facteur de séparation est à peu près 10^3 vis à vis du Sm, et supérieur d'un ou plusieurs ordres de grandeur pour les autres terres rares.

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In the course of an investigation of shortlived isotopes of the elements samarium ($Z = 62$) and europium ($Z = 63$), with known and expected half-lives of between one and ten minutes, the need arose for methods by which these elements could be rapidly separated from neighbouring lanthanides as well as from one another.

Various methods have been proposed for isolating europium from mixtures of lanthanides [1]. With respect to the principle on which the separation procedures are based, these methods can be divided into two groups. To one group belong all those methods which exploit the small differences in the chemical properties of the tripositive lanthanide ions for separation purposes. Such procedures are time-consuming and are consequently unsuitable for rapid radiochemical separations. On the other hand shorter separation times can be achieved with methods belonging to the second group, which are based on the reduction of Eu^{3+} to Eu^{2+} . Since the chemical properties of Eu^{2+} are very similar to those of Ba^{2+} and Sr^{2+} , Eu^{2+} can easily be separated from tripositive lanthanide ions. Although Eu^{2+} , in contrast with Sm^{2+} , is stable even in fairly concentrated HCl for relatively long periods of time [2] it is very rapidly oxidised to Eu^{3+} by molecular oxygen. Precautions must therefore be taken to exclude air from the system during such a Eu separation. Isolation of Eu by this method thus requires two steps: (a) selective reduction of Eu^{3+} to Eu^{2+} and (b) separation of Eu^{2+} from tripositive lanthanide ions.

Experimental

The carrier solutions used, each containing 10 mg lanthanide/ml, were prepared by dissolving 99.9% pure lanthanide oxides in dilute acetic or hydrochloric acid. All other chemicals were of reagent grade quality. 0.1% sodium amalgam and 0.5% zinc amalgam were prepared by direct interaction of weighed amounts of the respective metals. Barium amalgam was prepared by electrolysis of a saturated solution of BaCl_2 at a mercury cathode. The Ba content of the amalgam was adjusted to 0.5% by subsequent addition of Hg.

p_{H} measurements on radioactive solutions were made with indicator paper, those on all other solutions with a glass-electrode p_{H} meter. p_{H} values were adjusted by addition of either NaOH or HCl.

The nuclides ^{154}Eu , ^{153}Sm and ^{147}Pm were used as radioactive tracers. Activity measurements were made with a methane flow counter and a well-type NaI scintillation counter.

Reductions were carried out by vigorously shaking together measured quantities of the metal amalgam with measured volumes of aqueous solutions of varying composition in 50 ml glass separatory funnels fitted with 10 cm glass tubes. Systems composed of 5 ml amalgam and 6 ml aqueous solution containing 5 mg Eu, 2 mg Sm and various anions and complexing agents were found to be convenient. The Eu amalgam, containing 1 ml Ba amalgam, was decomposed by

shaking it vigorously with 5 ml pre-cooled 12 M HCl in similar separatory funnels fitted with similar glass tubes.

Reduction of Eu

Comparison of redox potentials of lanthanides (Table 1) indicates that Eu^{3+} can be selectively reduced to Eu^{2+} by means of suitable reducing agents, such as Zn amalgam. Such selective reductions, however, are fairly slow reactions. Thus we found that only about 5% of the Eu^{3+} was reduced by 0.5% Zn amalgam in 30 seconds. Some 5 minutes were required to achieve a more or less complete reduction, as has also been found by PEPPARD et al [3].

The conversion of Eu^{3+} to Eu^{2+} can, however, be accelerated by making use of a two-step procedure, via Eu amalgam. By shaking aqueous solutions containing Eu^{3+} with alkali-metal amalgam, Eu amalgam can be obtained. When this is decomposed with a suitable acid (e.g. HCl), an aqueous phase containing Eu^{2+} is produced.

The extraction of lanthanides from dilute hydrochloric acid and acetic acid solutions by means of Na amalgam was investigated by MCCOY [4], and later by MARSH [5] and by BARRETT et al [6]. They found that the extraction yield decreased with increasing atomic number of the lanthanide, except in those cases where a divalent state is known. Thus Sm, Eu and Yb are extracted with an efficiency of nearly 100%. Under the conditions studied, however, mutual separation of these three elements are not possible.

Recently GANTNER and MÜNDEL [7] showed that the addition of citric acid to the aqueous phase caused a decrease in the extraction yield of Sm, but not of Eu. ONSTOTT et al [8] also found that the rate of extraction of Pm from citrate solutions by Li amalgam decreased with increasing citrate concentration.

These observations led us to surmise that the depressing effect of citrate on the amalgam extraction of lanthanides could be due to its complexing properties. As a result of chelation the concentration of the lanthanide

1. For details see:

- a) T. MOELLER, "The Chemistry of the Lanthanides", Reinhold Publishing Corporation, New York, 1963.
- b) F. H. SPEDDING, and A. H. DAANE, Eds., "The Rare Earths" John Wiley and Sons, New York, 1961.
- c) P. C. STEVENSON, and W. E. NERVIK, "The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium", USAEC, NAS-NS 3020, 1961.
- d) R. C. VICKERY, "Analytical Chemistry of the Rare Earths", Pergamon Press, London 1961.
2. J. F. NACHMAN and C. E. LUNDIN, Eds., "Rare Earth Research", p. 30, Gordon and Breach, New York, 1962.
3. Reference 2, pp. 15-27.
4. H. N. MCCOY, J. Amer. Chem. Soc. **63**, 1622 (1942).
5. J. K. MARSH, J. Chem. Soc., **1942**, 398, 523; **1943**, 8, 531.
6. M. F. BARRETT, D. SWEASY and N. E. TOPP, J. Inorg. Nucl. Chem. **24**, 571 (1962); **25**, 1273 (1963).
7. H. MÜNDEL and E. GANTNER, Radiochim. Acta **4**, 119-124 (1964).
8. E. I. ONSTOTT, W. H. SMYRL and R. F. MACANDER, LADC-6084, 1963.

ions is reduced and the redox potential consequently becomes more negative. Since the redox potential of Eu is significantly smaller than that of Sm (Table 1) this complexing effect can be expected to influence the amalgam extraction of Eu to an appreciably lesser extent than that of Sm.

Table 1. *Compilation of some oxidation potentials* [10]

Reactions	E° (volts)	
	For metals	For amalgams
Na \rightleftharpoons e ⁻ + Na ⁺	- 2.71	- 2.09
Ba \rightleftharpoons 2 e ⁻ + Ba ²⁺	- 2.90	- 1.57
Pm \rightleftharpoons 3 e ⁻ + Pm ³⁺	- 2.42*	
Sm \rightleftharpoons 3 e ⁻ + Sm ³⁺	- 2.41	- 1.80
Eu \rightleftharpoons 3 e ⁻ + Eu ³⁺	- 2.41	- 0.75
Gd \rightleftharpoons 3 e ⁻ + Gd ³⁺	- 2.40	
Sm ²⁺ \rightleftharpoons e ⁻ + Sm ³⁺	- 1.5**	
Eu \rightleftharpoons 2 e ⁻ + Eu ²⁺		- 1.10
Zn \rightleftharpoons 2 e ⁻ + Zn ²⁺	- 0.76	- 0.76
Eu ²⁺ \rightleftharpoons e ⁻ + Eu ³⁺	- 0.43	
H ₂ \rightleftharpoons 2 e ⁻ + 2 H ⁺	0.00	
4 (OH) ⁻ \rightleftharpoons 4 e ⁻ + 2 H ₂ O + O ₂	+ 0.41	
2 H ₂ O \rightleftharpoons 4 e ⁻ + 4 H ⁺ + O ₂	+ 1.23	

* Estimated.

** Reported values vary between 1 and 2 volts.

Proceeding on this assumption we investigated the effect of other complexing agents. EDTA proved to be very effective. The results obtained with this ligand are summarised in Table 2. The yields found for the extractions from acetic acid and citric acid solutions respectively are in good agreement with the values found by MARSH [5] and by GANTNER and MÜNDEL [7]. It is also evident from Table 2 that as a result of the presence of EDTA in the aqueous phase during the extraction a substantial enrichment of Eu with respect to all other lanthanides, including Sm, is achieved in the amalgam phase.

Table 2. *Extraction yield (%) as a function of the composition of the aqueous phase, initially at p_H 1, for a contact time of 5 seconds*

Composition of aqueous phase 5 mg Eu ³⁺ , 2 mg Sm ³⁺	Element		
	Eu	Sm	Pm
+ 2 mmole chloride	> 95	> 95	7
+ 2 mmole acetate	> 95	> 95	7
+ 2 mmole chloride + 0.1 mmole citrate	95	55	< 0.1
+ 2 mmole chloride + 0.025 mmole EDTA	85	15	~0
+ 2 mmole chloride + 0.05 mmole EDTA	77	6	~0
+ 2 mmole chloride + 0.10 mmole EDTA	70	2	~0

The influence of contact time and of the initial p_H of the aqueous phase on the extraction yield were also investigated. It was found that in the p_H range of about 0.5–3 optimal extraction was achieved with a contact time of about 5 seconds. Increasing the con-

tact time to 10 seconds caused no further increase in the extraction yield; on the contrary, a decrease was observed. An example of the results of a series of experiments to determine the dependence of the extraction yield on the initial p_H of the aqueous phase is given in Table 3. The maximum at about p_H 1 can

Table 3. *Extraction yield (%) as a function of the initial p_H of the aqueous phase containing 5 mg Eu³⁺, 2 mg Sm³⁺, 1 mmole acetate, 0.05 mmole EDTA, and HCl or NaOH to adjust the p_H , for a contact time of 5 seconds*

p_H :	0	0.5	1	2	3	4
Eu extracted:	15	55	75	50	40	10

be explained as follows: at low p_H values hydrogen ions are more readily reduced than lanthanide ions, while at higher p_H values the lanthanides are present in the form of hydrolysed ionic species [6, 9] which are not so readily reducible. Due to the reaction of Na amalgam with water the p_H of the aqueous phase increases rapidly during the extraction, e. g. from 1 to 10 for a contact time of 5 seconds. This explains why an increase in contact time does not result in increased extraction yields.

When the lanthanide amalgams are decomposed with HCl all lanthanides, except Eu, are present in the resulting aqueous phase as tripositive ions. In the case of Sm and Yb dipositive ions are actually formed first, but these are rapidly oxidised further to tripositive ions by the hydrogen ions. The corresponding oxidation of Eu²⁺ to Eu³⁺ proceeds much more slowly. The decomposition of Eu amalgam as a function of time was investigated experimentally. The results for its decomposition with 12 M HCl in absence of air are given in Table 4.

Table 4. *Lanthanide (%) present in various fractions after decomposition of the amalgam with cold 12 M HCl, in absence of air, as a function of contact time*

	Europium				Samarium
Contact time (seconds)	30	15	10	5	5
In amalgam phase	0.5	1	2.5	10	0.5
In BaCl ₂ · 2 H ₂ O-precipitate	55	72	80	80	2

Separation of Eu²⁺

PEPPARD et al. [3] have described a method for the separation of Eu²⁺ in dilute acid solution from all tripositive lanthanide ions in which the latter are extracted by means of organic phosphates or phos-

9. G. BIEDERMANN and L. CIAVETTA, *Acta Chem. Scand.* **15**, 1347 (1961).10. a) H. N. MCCOY, *J. Amer. Chem. Soc.* **58**, 1577 (1936).b) H. A. LAITINEN, *J. Amer. Chem. Soc.* **64**, 1133 (1942).c) A. TIMNICK and G. GLOCKLER, *J. Amer. Chem. Soc.* **70**, 1347 (1948).

d) E. V. KLEBER, Ed., "Rare Earth Research", p. 51, Macmillan, New York, (1961).

e) Reference 1(a), p. 19.

f) Reference 6.

phonates. As mentioned earlier, the rather long separation time of 5 minutes by this method is due to the slow reduction of Eu^{3+} to Eu^{2+} by Zn amalgam. Our attempts to accelerate this reduction step by substituting Ba amalgam or Na amalgam for Zn amalgam were unsuccessful for three reasons. In the course of the reduction the p_{H} of the aqueous phase increased so strongly that it was impossible to maintain optimal extraction conditions; as a result there was also a tendency towards emulsion formation which made phase separation very difficult. In addition yield losses due to partial reduction of Eu^{3+} to Eu amalgam were unavoidable.

GANTNER and MÜNDEL [7] investigated several precipitation reactions for bringing about an Eu^{2+} separation. They showed that co-precipitation of Eu^{2+} with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was very effective. In order to precipitate Eu^{2+} immediately upon its formation and thus avoid the possibility of its oxidation to Eu^{3+} they added Ba amalgam to the Eu amalgam before decomposing the latter with concentrated HCl. We confirmed the results obtained by these authors, and also investigated the Eu yield in the precipitate as a function of contact time during decomposition by this method. Results are given in Table 4. For comparison the yield obtained for Sm during a contact time of 5 seconds is also included in the table.

Procedure for the Rapid Separation of Eu from Lanthanide Mixtures

(e.g. irradiated samarium targets)

On the basis of the results obtained in the above investigations the following procedure has been developed:

Step 1: Bubble high-purity nitrogen gas through 5 ml 12 M HCl contained in a 50 ml glass separatory funnel (a) for 2 minutes to remove molecular oxygen. Close (a) with a tight-fitting glass or plastic stopper and cool in ice for 10–15 minutes.

Step 2: Prepare the following solutions:

Solution A: 2.5 ml 1 N HCl + 0.5 ml Eu-carrier solution + 0.2 ml Sm-carrier solution. (Carrier solutions contain 10 mg lanthanide per ml in 1 N HCl.)

Solution B: 2 ml 1 N NaOH + 1 ml 0.1 M EDTA (disodium salt).

Step 3: Dissolve the irradiated samarium target (ca. 0.1 mg Sm_2O_3) in Solution A, and immediately add Solution B. (The resulting Solution C has a p_{H} of approximately 1.)

Step 4: Add Solution C to 5 ml 0.1% Na amalgam contained in a 50 ml glass separatory funnel (b), fitted with a 10 cm long ground-glass jointed glass tube.

Step 5: Shake (b) vigorously for 5 seconds to extract the Eu into the amalgam. (The supernate turns greenish-yellow, due to the presence of unextracted Eu^{2+} .)

Step 6: Add 1 ml 0.5% Ba amalgam to the contents of (b).

Step 7: Run off the amalgam phase into the cold, nitrogen-flushed HCl in (a) – prepared in Step 1 –, exchanging the stopper for a glass tube similar to that used in Step 4.

Step 8: Shake (a) vigorously for 5 seconds. (Hydrogen gas is evolved and a white precipitate composed of NaCl, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ is formed. There is a temperature increase of several degrees.)

Step 9: Run off the mercury phase.

Step 10: Filter the precipitate under suction in a chimney-type filtering apparatus through a glass-fibre paper disc (e.g. Whatman GF/A).

Step 11: Wash the precipitate with 2 ml ethyl alcohol.

Step 12: Mount the precipitate for counting, or, if a further purification of Eu is required, dissolve the precipitate in 2 ml water and repeat the whole procedure.

The operations from Step 3 through Step 11 can be performed in about one minute. The yield for Eu is around 50%. The separation factor for Eu with respect to Sm is about 1000, and with respect to Pm and other neighbouring lanthanides at least one or more orders of magnitude greater.

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