

## The Electrolysis of Rare Earth Acetates and the Separation of Europium as Amalgam from Other Rare Earths

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The method used for the preparation of europium and ytterbium amalgams<sup>1</sup> by the electrolysis of their acetates dissolved in aqueous tertiary potassium citrate has been extended to the other rare earths. In addition to the two elements above mentioned, samarium was the only other one that gave an amalgam. In this case the yield was very low compared with that of europium. Potassium amalgam is always formed whether or not it is accompanied by a rare earth amalgam.

The marked difference in electrical efficiency with which europium and samarium are deposited makes it possible to separate the former from the latter, as well as from other accompanying rare earths, by a single electrolysis.

This has been done with equal amounts of the two rare earths, as well as with various mixtures in which the europium formed five per cent. or less of the rare earths present.

If europium forms as little as 1% of the rare earths present, the solution bleaches litmus paper almost from the start of the electrolysis, due to formation of europous salts. After an hour or two, bleaching no longer takes place and it is found that practically all europium has been deposited. If europium is absent, litmus is not bleached even in the presence of much samarium.

With both elements present, if the electrolysis is stopped at the point where litmus is no longer bleached, the amalgam will contain nearly all the europium and be free from samarium.

If by chance the electrolysis is continued beyond the optimum point, a trace of samarium may accompany the europium. In this case a repetition of the electrolysis with the solution made from the amalgam by treatment with acetic acid and potassium citrate will yield a product free from samarium.

It might seem that ytterbium would be a disturbing factor since it also forms an amalgam and since  $\text{Yb}^{++}$  bleaches litmus. However, in the practical separation of the rare earths ytterbium scarcely need be considered, as this element is readily eliminated at an earlier stage by methods based upon marked differences in solubility of the

double potassium sulfates,<sup>2</sup> the ethyl sulfates,<sup>3</sup> or the bromates.<sup>4</sup>

### Experimental

The electrolyte consisted of 2 to 12 g. of rare earth acetates dissolved in a solution of two to three times its weight of tertiary potassium citrate. The solution was made alkaline to litmus by a small excess of potassium carbonate. The volume of the electrolyte was about 100 ml. The cathode was 200 g. of mercury. The anode was a spiral of heavy platinum wire. The vessel was a 150-ml. beaker with a sealed-in tube for electrical contact with the mercury. Power stirring was used. No porous cell was needed nor was an inert gas used to retard reoxidation by air.

After an electrolysis the electrolyte was decanted, the amalgam was washed well with water and treated with an acid either before or after elimination, as hydroxide, of the potassium, always present as amalgam, by treatment with water. The nature of the rare earths in the solutions so formed was determined by observation of their absorption spectra. The rare earths recovered from the amalgams were determined as oxides. The experimental results are shown in Table I.

TABLE I

Expt.	Weight and nature of acetate used	Amperes	Minutes	Weight and nature of oxides from amalgams	Yield, %
1	3 g. Sm	1.0	110	0.181 g. $\text{Sm}_2\text{O}_3$	13.6
2	3 g. Sm	1.1	62	.027 g. $\text{Sm}_2\text{O}_3$	2.0
3	5 g. Sm	1.2	120	.066 g. $\text{Sm}_2\text{O}_3$	3.0
4	5 g. Sm	1.2	120	.060 g. $\text{Sm}_2\text{O}_3$	2.9
5	5 g. Sm	1.2	120	.029 g. $\text{Sm}_2\text{O}_3$	1.4
6	3 g. Sm	1.2	133	.156 g. $\text{Sm}_2\text{O}_3$	11.9
7	6 g. R. E.	1.2	35	Trace	..
8	3.2 Gd-Er	1.0	60	Trace	..
9	3.2 Gd-Er	1.	60	None	..
10	{ 2 g. Sm 2 g. Eu	1.2	70	0.793 g. $\text{Eu}_2\text{O}_3$	90.0
11	{ 3 g. R. E. 2 g. Eu	1.2	90	.852 g. $\text{Eu}_2\text{O}_3$	94.8
12	{ 11.5 R. E. 0.6 Eu	1.0	40	.196 g. $\text{Eu}_2\text{O}_3$	74.0
13	5 Crude Eu	1.2	165	1.320 g. $\text{Eu}_2\text{O}_3$	60.0

**Expt. 3.**—The solution formed by treating the amalgam with hydrochloric acid bleached litmus paper slowly. The effect was traced to a very small amount of europium in the samarium used.

**Expt. 4.**—The electrolyte poured from the amalgam in expt. 3 was again electrolyzed. The bleaching caused by the solution of the amalgam was now slight.

**Expt. 5.**—The same electrolyte was electrolyzed a third time. The chloride from the amalgam showed no bleaching.

**Expt. 7.**—The rare earth acetate used contained all the earths precipitated from a monazite solution by sodium

(2) Marsh, *J. Chem. Soc.*, 1367 (1937).

(3) Urbain, *Compt. rend.*, 126, 835 (1898).

(4) James, *THIS JOURNAL*, 30, 182 (1908).

(1) McCoy, *THIS JOURNAL*, 63, 1622 (1941).

sulfate. The trace of rare earths recovered from the amalgam was probably europium or samarium.

**Expt. 8.**—The solution used contained the natural mixture of Gadolinium, Terbium, Dysprosium, Holmium, Yttrium, and Erbium extracted from monazite. A minute amount of europium probably accounted for the trace of rare earths recovered from the amalgam.

**Expt. 9.**—A second electrolysis of the same solution gave potassium amalgam free from rare earths.

**Expt. 10.**—The chloride solution from the amalgam showed the europium bands at 4650 and 5253 Å. distinctly. No samarium bands were visible. The electrolyte poured from the amalgam showed the two samarium bands at 4630 and 4760 Å. very plainly.

**Expt. 11.**—The rare earth acetate was like that used in Expt. 7. The acetate solution made from the amalgam was greenish-yellow. It bleached litmus instantly and after oxidation showed bands at 4650, 5253, 5257, and 5790 Å., all characteristic of europium. No other bands were visible.

**Expt. 12.**—This solution was made from the acetates produced from the rare earths of monazite from which most of the cerium had been removed. To this 5% of pure europium acetate was added. The amalgam yielded 74% of the europium taken. Its absorption spectrum showed no other elements present than europium.

**Expt. 13.**—The rare earths used were from a lot of partially refined europium. It contained neodymium and other rare earths. The yield of europium was 60% of the rare earths present.

The experiments summarized in the foregoing table seem to show that only three rare earths form amalgams by electrolysis of their acetate-citrate solutions in the manner here described. These rare earths, europium, ytterbium and samarium are those whose anhydrous halides are most easily reduced to bivalent salts by hydrogen at high temperatures.

Europic solutions are easily reduced by magnesium, aluminum, zinc, etc.<sup>5</sup>; ytterbic solutions are not reduced appreciably by zinc but are reduced by sodium amalgam. Samaric solutions seem to resist all attempts to reduce them to the samarous stage in a wet way.

The stability of the bivalent sulfates toward oxidation is in the same order. Europous sulfate,  $\text{EuSO}_4$ , is not appreciably changed by months of exposure to air; ytterbous sulfate is oxidized by air and also by water<sup>6</sup> in a few hours; while samarous sulfate is completely oxidized by water, with liberation of hydrogen in a few minutes.

The ease of reduction of trivalent salts and of oxidation

of bivalent ones stands in close relationship to the oxidation-reduction potentials of europium,<sup>7</sup>  $E_0 = 0.428$  v. and of ytterbium,<sup>8</sup> 0.578 v. The potential of the samarium electrode has not been measured but would doubtless exceed that of ytterbium.

The following additional experiments may also be recorded. Potassium amalgam, made by the electrolysis of a carbonate solution with 1 ampere for thirty minutes, was stirred with a solution of 2.5 g. of samarium acetate and 10 g. of potassium citrate for thirty minutes. The remaining amalgam yielded 0.0146 g. of  $\text{Sm}_2\text{O}_3$ , or 1.3% of the samarium taken. The yield was much lower than that found for europium or ytterbium treated with potassium amalgam.<sup>1</sup>

A solution of 4 g. of samaric chloride was run through a Jones reductor charged with amalgamated zinc. The resulting solution was not reducing, and gave no precipitate of samarous sulfate with a sulfate solution.

A solution of 2 g. each of europic and samaric acetates, plus 5 ml. of concentrated hydrochloric acid, was run through the reductor into a sulfate solution. Europous sulfate was formed in good yield and, when brought into solution as europic salt, showed europium absorption bands plainly with none of those of samarium. The filtrate from the europous sulfate showed the strongest samarium bands, with only a trace of those of europium.

It seems probable that lutecium does not form an amalgam by electrolysis of its acetate-citrate solution and is thus separated from ytterbium when the latter is deposited as amalgam<sup>1</sup> from a solution of the two elements. A confirmation of this view is under way by the examination of the emission spectra of the products of the reaction.

### Summary

1. By the electrolysis of aqueous solutions of europium, ytterbium or samarium acetates and potassium citrate, amalgams are formed, the yield decreasing in the order given.

2. The same elements, in like solutions, give amalgams when stirred with potassium amalgam.

3. None of the other rare earths similarly treated gave amalgams.

4. Europium and probably ytterbium can be separated from accompanying rare earths by means of their amalgams.

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(5) Pearce, *Chem. Rev.*, **16**, 131 (1935).

(6) Pearce and Selwood, *J. Chem. Education*, **13**, 224 (1936).

(7) McCoy, *This Journal*, **58**, 1579 (1936).

(8) Walters and Pearce, *ibid.*, **62**, 3330 (1940).