

This hydroxyl derivative may or may not condense with itself with the elimination of a molecule of water. The corresponding phenyl compound does, however.<sup>9</sup> Trimethyl germanium bromide is rapidly oxidized by sodium peroxide and by hot chromic acid, but only slowly by ammoniacal 30% hydrogen peroxide. Hot, concentrated sulfuric acid liberates bromine.

When a sample was dissolved in benzene and dry ammonia gas was bubbled through the solution, a white crystalline precipitate appeared. This was shown by analysis to be ammonium bromide. The filtrate from this precipitate was allowed to evaporate at room temperature. When only a few drops remained, the material had an odor similar to that of the original material. However, when a drop on a stirring rod was brought in contact with a drop of water, the odor of ammonia was noticed. This liquid fumed strongly when concentrated hydrochloric acid was added. It is assumed from this experiment that trimethyl germanium bromide reacts with ammonia to form an amine which is volatile and readily hydrolyzed by water.

### Summary

The preparation, purification and some chemical and physical properties of trimethyl germanium bromide are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## THE SEPARATION OF EUROPIUM BY ELECTROLYTIC REDUCTION. OBSERVATIONS ON THE RARE EARTHS. XXXV

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The existence of a bivalent europium chloride was announced by Urbain and Burion<sup>1</sup> who prepared it by reduction of the anhydrous trichloride with hydrogen at 400–450°. Jantsch, Alber and Grubitsch<sup>2</sup> extended the study of the bivalent compounds of europium. They found that europium bichloride is quite stable in solution. The bi-iodide was found to be still more stable. The sulfate is a fine, white crystalline compound, insoluble in water and difficultly soluble in acids. The bichloride of samarium, described by Matignon and Cazes<sup>3</sup> and by Jantsch, Rüping and Kunze,<sup>4</sup> reacts with water and, more rapidly, with acids, evolving hydrogen and undergoing oxidation to the trivalent state. The bivalent sulfate is a red compound, sparingly soluble.

<sup>9</sup> Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

<sup>1</sup> Urbain and Burion, *Compt. rend.*, **153**, 1155 (1911).

<sup>2</sup> Jantsch, Alber and Grubitsch, *Monatsh.*, **53**, **54**, 305 (1929).

<sup>3</sup> Matignon and Cazes, *Compt. rend.*, **142**, 83 (1906).

<sup>4</sup> Jantsch, Rüping and Kunze, *Z. anorg. allgem. Chem.*, **161**, 210 (1927).

These facts suggested the possibility of separating europium from the other rare earths by electrolytic reduction in the presence of the sulfate ion.

### I. Experimental Procedure

Five grams of mixed rare earth oxides containing samarium, europium and a small percentage of gadolinium was dissolved in hydrochloric acid. The excess acid was evaporated and the solution was diluted to 125 cc.; 2 cc. of sulfuric acid (sp. gr. 1.84) was added. It was found that the addition of more sulfuric acid would result in the precipitation of trivalent sulfates. Visual examination of the solution through a seven-centimeter layer showed the absorption spectra of samarium and of europium.

This solution was put into the cathode compartment of the electrolytic cell (Fig. 1). The anode compartment was filled to the same level with dilute sulfuric acid of approximately molar concentration. A current of 0.18 ampere, corresponding to a current density at the cathode of 0.01 amp./sq. cm., was used. The voltage drop between electrodes was 65 volts.

After electrolyzing for six hours, an appreciable amount of a granular, white precipitate, later identified as bivalent europium sulfate, had formed. This was removed for analysis. On continuing the electrolysis more precipitate was formed. After electrolyzing for about twenty-four hours, no more appeared and the reduction was assumed to be complete. The solution now showed none of the absorption bands of europium.

### II. Analysis

(a) **Gravimetric.**—The portion of the precipitate reserved for analysis was collected in two portions for duplicate analyses on sintered glass crucibles. The precipitate was washed with air-free water until the washings gave no precipitate with ammonium hydroxide, then with alcohol and finally with anhydrous ether. It was dried at 65°. After weighing, it was again heated at the same temperature for an hour; no gain or loss in weight occurred.

The europium sulfate was then dissolved in dilute nitric acid. The reaction with nitric acid yielded nitrogen dioxide, indicating that an oxidation occurred. The spectrum of this solution showed the absorption bands of europium and none of samarium. After diluting the nitric acid solution to 150 cc., the excess acid was neutralized with ammonium hydroxide and the solution was then made acid with nitric acid, two or three drops of

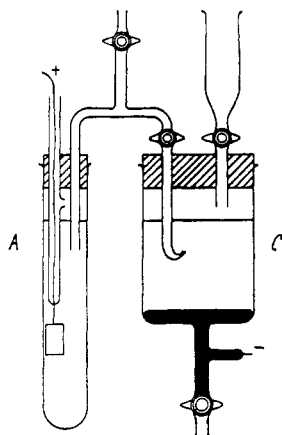


Fig. 1.—The electrolytic cell. C, Cathode compartment with mercury cathode; A, anode compartment with platinum anode.

concentrated acid in excess being added. The europium was precipitated as oxalate, ignited and weighed as oxide. The oxide obtained was a very pale pink in color. The sulfate was determined as barium sulfate. The results of the analysis are given in Table I. The precipitate is shown to have the composition  $\text{EuSO}_4$ .

TABLE I  
ANALYSIS OF PRECIPITATED EUROPIUM SULFATE

	I	II
1 Weight of $\text{EuSO}_4$ taken, g.	0.2128	0.1388
2 Weight of $\text{Eu}_2\text{O}_3$ found, g.	.1476	.0963
3 Weight of $\text{BaSO}_4$ found, g.	.2053	.1327
4 Weight of Eu (calcd. from No. 2), g.	.1275	.0832
5 Weight of $\text{SO}_4$ (calcd. from No. 3), g.	.0845	.0546
6 Weight of $\text{EuSO}_4$ found (4 plus 5), g.	.2120	.1378
7 Percentage error	0.4	0.7
8 Mol. ratio $\text{SO}_4/\text{Eu}$	1.049	1.039

(b) **Spectroscopic.**—Photographs of the arc spectra on carbon electrodes of (1) the original mixed oxides, (2) the oxide obtained in analysis No. 1 and (3) of an oxide prepared from the solution after electrolysis, were made. A Hilger E I quartz prism spectrograph was used. It was found that the precipitate consisted of europium with very little samarium (estimated at 1 or 2%). The solution after electrolysis was almost europium free. The presence of samarium in the precipitate may have been due either to a partial reduction or the mechanical inclusion by the precipitate.

The writer wishes to express his appreciation of the assistance of Mr. P. W. Selwood, who photographed the spectra.

### Summary

1. Bivalent europium sulfate may be precipitated from an acid solution by electrolytic reduction in the presence of the sulfate ion.

2. An analysis of the precipitate showed it to have the composition represented by the formula  $\text{EuSO}_4$ . This is a white crystalline compound, stable when heated in air at  $65^\circ$ , and insoluble in dilute acids. It is oxidized by dilute nitric acid.

3. Visual examination of the solution of the precipitate in nitric acid shows no samarium absorption bands. The solution after electrolysis showed none of the europium absorption bands.

4. The arc spectrum of the precipitated fraction indicates that it consists of europium with very little samarium. The solution is almost samarium free.

The use of this reaction for the isolation and the purification of europium is being further investigated.