Europium Determination In Some Rare Earth Elements
by Isotope Dilution Method

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The determination of europium in samarium and gadolinium by isotope dilution method is described. This allows a comparatively precise determination of europium without separating it from other rare earth elements.

1. Introduction

One of the difficulties associated with the elementary chemical analysis of rare earth elements is the separation of these elements. The isotope dilution method, using a mass spectrometer of the surface-ionization type, has been investigated by the present authors in order to obtain greater reliability in the determination of small amounts of europium in samarium and gadolinium. This method constitutes the first step in future investigations of the analysis of other rare earth mixtures.

Isotope dilution technique1),2),3) involves the addition of a known quantity of an enriched isotopic tracer of the element to be determined to a weighed portion of the sample to be analyzed. The sample is dissolved beforehand in an appropriate solvent. Tracer and sample are mixed and brought to equilibrium, chemical extraction of the element in question follows. This extraction need not be quantitative; in some cases the extraction is not necessary. The concentration of the element in the original sample can be calculated from the change in the isotopic composition of the element in question. This change is caused by the addition of the tracer isotope and determined mass spectrometrically.

2. Experimental

2.1 Preparation of Solutions

2.1.1 Europium Standard
0.0381 g of natural europium (Johnson Matthey) was weighed as europium sesquioxide after being heated to a constant weight at 840°C. The oxide was dissolved in nitric acid and diluted to a concentration of 0.2808 mg of europium per gram of solution. This solution was used to calibrate the tracer. The isotopic composition of this sample was 47.86±0.23% and 52.14±0.23% for Eu^{151} and Eu^{153}, respectively.

2.1.2 Europium Tracer
A solution of enriched Eu^{151} (Oak Ridge National Laboratory) was prepared with a concentration of about 0.26 mg/g in 1 N nitric acid. The tracer had the following isotopic composition; Eu^{151} 91.85±0.07% and Eu^{153} 8.15±0.07%.

2.1.3 Solution under Investigation
Samarium and gadolinium sesquioxides of the Johnson-Matthey* and the Lindsay** were used as samples. To prepare each sample solution, each oxide was heated to a constant weight at 840°C, dissolved in nitric acid and diluted to the following concentrations:

- Johnson-Matthey samples: samarium 4.966 mg/g soln., gadolinium 3.663 mg/g soln.,
- Lindsay samples: samarium 5.691 mg/g soln., gadolinium 4.849 mg/g soln.

2.2 Mass Spectrometer
The instrument used in this investigation was a CEC type 21-702 B mass spectrometer which is a first order direction focusing instrument with a 60° sector-type magnetic field and twelve inches radius, having a surface ionization ion source. In this source a small amount of the sample was coated on two sample holding filaments of tantalum ribbon. These filaments were heated to the temperature where evaporation of the sample occurs; a third filament of rhenium ribbon was used as the ionizing filament. Electrical scanning was accomplished for europium ions by varying the ion acceleration voltage from 8.6 to 8.9 KV at a constant magnetic field of 4.9 KG. About forty measurements of the isotope ratio were accomplished for each sample.

2.3 Analysis
2.3.1 Calibration of the Tracer
From the isotopic abundance in the tracer and the natural abundance of europium it is clear that the abundances of Eu^{153} in the tracer and in the sample are greater than that for Eu^{151} in the same solutions; if then Eu^{153} is used as tracer isotope the sensitivity given in the analysis will be better. Using this criterion, six aliquots of the tracer solution were mixed with aliquots of europium standard solution. About 0.5 µg of europium of each mixture sample were evaporated to dryness on tantalum ribbons. The Eu^{153}/Eu^{151} ratio was determined for each case.

2.3.2 Determination of Europium in Solutions under Investigation.
From each of the four solutions in question, two aliquots were taken and mixed with aliquots of the tracer solution. After mounting a small amount of sample solution on tantalum ribbons and evaporating the mixture, the ratio Eu^{153}/Eu^{151} was determined for each case.

3. Results and Discussion
The quantity of europium in the sample in question was calculated using the equation given by Hintenberger for two isotopes:

\[ x - y \times \frac{B_{12}}{C_{12}} - \frac{C_{12}}{A_{12}} \times \frac{a_2}{b_2} \times \frac{M_x}{M_y} \]

where:
- \( x \) amount in grammes of the element in question in the sample,
- \( y \) amount in grammes of the element in question added as tracer,
- \( A_{12} \) ratio of the isotopes 1 to 2 in the sample,
- \( B_{12} \) ratio of the isotopes 1 to 2 in the tracer,
- \( C_{12} \) ratio of the isotopes 1 to 2 in the mixture,
- \( a_2 \) abundance of the enriched isotope in the sample,
- \( b_2 \) abundance of the enriched isotope in the tracer,
- \( M_x \) atomic weight of the element in question in the sample,
- \( M_y \) atomic weight of the element in question in the tracer.

Results are shown in Tables I, II and III.

The purpose of the work described in this paper
is to determine europium in samarium and gadolinium without separating europium from other rare earth elements. No interference in the mass spectrum occurs as europium has no isobar of samarium and gadolinium. To minimize contamination, glass wares were used only once, washed with nitric acid and rinsed thoroughly with redistilled water. New filaments terminal and filament ribbons were used for each experiment, since past experience has shown that in this case the mass spectrometer utilized in this research does not present memory effects.

According to Jamieson and Schreiner\(^5\) the ideal mixing ratio is such that the abundance of the tracer isotope in the mixture is the geometric mean between the abundances of the same isotope in the sample and in the tracer solutions. However, in the present investigation the separation of europium from samarium and gadolinium was not performed and Eu\(^{153}\) was used as \(\text{hypothetical} \) tracer, consequently the amount of tracer used was smaller than the theoretical value given by Jamieson and Schreiner's equation.

From the results obtained it can be concluded that the application of the isotope dilution method to the determination of europium in samarium and gadolinium without isolating europium may give accurate results for samples containing europium down to 0.01%.

**References**