*Determination of Lanthanum, Samarium and Europium in Manganese Nodules by Neutron Activation**

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So far the determination of a trace amount of rare earth elements have primarily been carried out by X-ray fluorometric, emission spectrometric or absorption spectrometric methods; but none of these methods have given satisfactory results. After the atomic pile has become available for wide use, ever growing attention has been paid to the application of radioactivation technique to the determination of many trace elements. A number of reports have proved the validity of the same technique for the determination of a trace amount of rare earth elements because of its selectivity and the high sensitivity.

Brooksbank and Leddicotte[1] determined a number of rare earth elements in biological materials (bones), by making use of the chromatographic separation and successive countings of the eluates after neutron irradiation of the sample. Likewise, Cornish[2] reported the ion exchange separation method. Jakovlev[3] discussed an approach for the determination of the total content of rare earth elements in high purity materials (graphite, beryllium, bismuth and germanium) on the basis of the activity of samarium and europium estimated by analyzing the decay curves, without resorting to chromatographic separation. Nakai et al.[4] reported the determination of dysprosium samarium, and lanthanum in thorium metal and oxide, based on gamma-ray counting of the rare earth fraction obtained by anion exchange separation from the sample irradiated in JRR-1.

Various nuclides are formed when a minute amount of rare earth elements in rocks and meteorites are irradiated with thermal neutrons.

TABLE I. NUCLEAR DATA

Element	Clarke number	Radionuclide	Half life	Activity* dis./sec.
Sc	0.0005	^{46}Sc	85 days	$2.65\cdot10^{2}$
Y	0.0028	^{90}Y	64 hr.	$2.3\cdot10^{3}$
La	0.0018	^{140}La	40 hr.	$9.0\cdot10^{3}$
Ce	0.0046	^{141}Ce	33 days	$3.6\cdot10$
		^{143}Ce	33 hr.	$4.1\cdot10^{2}$
Pr	0.00055	^{142}Pr	19 hr.	$5.8\cdot10^{3}$
Nd	0.0024	^{147}Nd	11.3 days	$6.0\cdot10$
		^{149}Nd	2 hr.	$1.9\cdot10^{3}$
Sm	0.00065	^{153}Sm	47 hr.	$1.2\cdot10^{4}$
Eu	0.00010	^{152}Eu	9.3 hr.	$1.5\cdot10^{5}$
Gd	0.00064	^{159}Gd	18 hr.	$7.6\cdot10^{2}$
Tb	0.00009	^{160}Tb	73 days	$2.5\cdot10$
Dy	0.00045	^{165}Dy	2.3 hr.	$4.7\cdot10^{5}$
Ho	0.00011	^{166}Ho	27 hr.	$5.7\cdot10^{3}$
Er	0.00025	^{177}Er	7.5 hr.	$6.6\cdot10^{2}$
Tm	0.00002	^{170}Tm	120 days	$2.2\cdot10$
Yb	0.00027	^{175}Yb	4.2 days	$1.2\cdot10^{3}$
		^{177}Yb	1.8 hr.	$6.3\cdot10^{3}$
Lu	0.000075	^{177m}Lu	3.7 hr.	$8.3\cdot10^{3}$
		^{177}Lu	6.9 days	$8\ \cdot10^{2}$

* A (dps) = Clarke number $\cdot 10^{-2}\cdot$ $Ab.(1/M)6.03\cdot10^{23}\cdot\sigma\cdot S$

A: Activity at the end of bombardment

M: Mass number Ab: Isotopic abundance

S: Saturation factor: $(1-e^{-\lambda t})$, $t=10$ hr.

σ: Neutron capture cross section.

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[1] W. A. Brooksbank and G. W. Leddicotte, *J. Phys. Chem.*, **57**, 819 (1953).

[2] F. W. Cornish, *Brit. Atomic Energy Research Establishment Rept.*, AERE C/R-1224 (1953).

[3] J. V. Jakovlev, *Proceedings of International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955, Paper 632 (USSR), Vol. 15, pp. 54—59; *Anal. Abstr.*, **4**, 1112 (1957).

[4] T. Nakai et al., Presented at the 2nd symposium on radiochemistry, Kyoto, Nov., 1958.

Then, the nature and activity of the induced radionuclides which come into question when 1 g. of sample containing rare earth elements in its normal natural abundance ratio is irradiated for 10 hr. with thermal neutrons of its intensity of 10^{11}n/cm^2/sec., are shown in Table I. These radionuclides would decay according to Fig. 1. It is clear that the nuclides which should be considered are lanthanum-140, samarium-153, europium-152 and yttrium-90 when as long as 20 hr. are needed for chemical processing after the end of irradiation.

The gamma ray spectrum of the rare earth fraction would then be considered to be the sum of photopeaks produced by X-rays which are induced by K electron capture, and compton continuums, and photopeaks produced by complete gamma ray absorption and bremsstrahlungs induced by β-rays which are emitted by lanthanum, samarium, europium and long lived nuclides. Therefore, the decay curve obtained by measuring the activity at a fixed base bias under the same counting conditions is expected to be analyzed into a few components. The present paper reports the determination of lanthanum, samarium, and europium in manganese nodules by means of a comparison method based on the counting rate of the respective components analyzed as above.

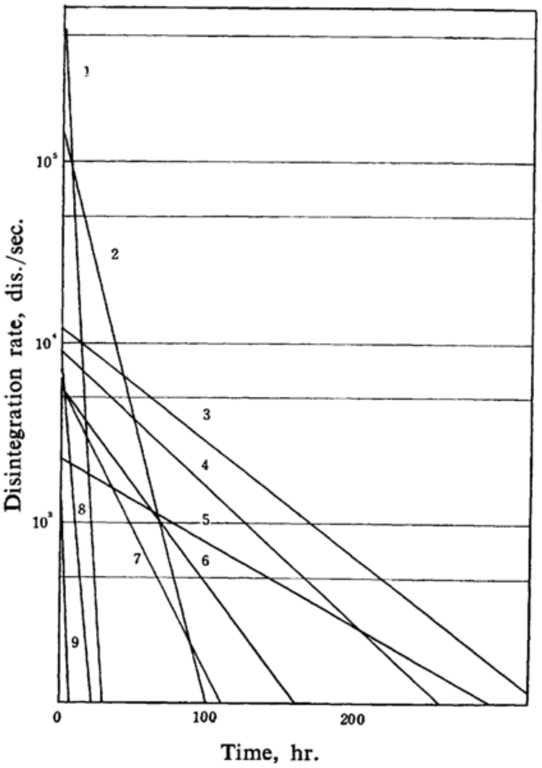

Fig. 1. Relative activities of rare earth radionuclides.

1 : 2.3 hr. Dysprosium-165
2 : 9.3 hr. Europium-152
3 : 47 hr. Samarium-153
4 : 40 hr. Lanthanum-140
5 : 64 hr. Yttrium-90
6 : 27 hr. Holmium-166
7 : 19 hr. Praseodymium-142
8 : 3.7 hr. Lutetium-177m
9 : 1.8 hr. Ytterbium-177

Experimental

Reagents and Samples. — Standard solutions of lanthanum, samarium and europium were prepared by dissolving respective metal oxides in nitric acid. The purity of these oxides listed by Johnson Mathey, was 99.99% for samarium oxide and 99.9% for europium and lanthanum oxides. These reagents were proved to be radiochemically pure by the activation analysis. Uranyl acetate (Merck) solution was used for the standard of uranium. All other chemicals used in this work were of c. p. or reagent grade.

Manganese nodule samples were offered by Professor E. D. Goldberg, Scripps Institution of Oceanography, La Jolla, California, to whom our thanks are due.

Irradition.—Manganese nodule samples of from 200 to 500 mg. were sealed in a silica tube and irradiated along with neutron monitors in the Japan Research Reactor-1 (JRR-1). The reactor was homogeneous, enriched uranium, water moderated and cooled type, and had a neutron flux of around $2\sim3\times10^{11}$ n/cm^2/sec. The flux monitors were prepared by evaporating a known amount (102, 3.5 and 0.35 μg) of lanthanum, samarium and europium in a silica tube or impregnating it into a filter paper wrapped in a vinyl bag. The irradiation lasted intermittently for 2∼3 days, 5 hr. each day.

Chemical Separation.—After neutron irradiation and a suitable decay time (about one day), the manganese nodule was dissolved in aqua regia. Any residue was fused with sodium peroxide, dissolved in hydrochloric acid, and added to the main solution. An aliquot of the solution (1/10 of the total volume) was used for the determination of the rare earth elements, and the remainder of the solution was reserved for the determination of elements other than the rare earths. Twenty milligrams of lanthanum carrier was added to the pipetted aliquot and the rare earth activity was carried down with lanthanum fluoride precipitate by adding hydrofluoric acid to the solution. Further purification was achieved by going through the standard lanthanum fluoride cycle[5] three times. The final lanthanum hydroxide precipitate which was decontaminated from any activities other than those of the rare earth elements was then dissolved in hydrochloric acid and diluted to a known volume. An aliquot of this solution was used for γ-ray counting and the remainder for the determination of the

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5) N. E. Ballou, "National Nuclear Energy Series, Radiochemical Studies: The Fission Products, Book 3", McGraw-Hill Book Co., Inc., New York (1953), p. 1673.

chemical yield by a conventional gravimetric method⁶⁾.

Counting. — The γ-rays and X-rays from the induced radioactive rare earth nuclides were detected and analyzed with the manual sweep scintillation spectrometer (Atomic Instrument Co., Model 510) equipped with a well type*, 1³/⁴ in. by 2 in., sodium iodide (Tl) scintillation crystal. The quantitative analysis for each rare earth element was made by comparing the lanthanum-140, samarium-153 and europium-152 activities of rare earth fraction which is separated from the irradiated manganese nodules with the correspondingly irradiated monitor of the respective element, after measuring the activity of each of the nuclides as mentioned later. Decay measurements of the rare earth activities from the manganese nodule samples and the flux monitors gave the same half-life for each nuclide.

Results and Discussion

The γ-ray spectrum of the rare earth fraction chemically separated and purified is shown in Fig. 2. Individual γ-ray spectra of lanthanum, samarium and europium obtained by the separate irradiation of the respective elements are shown in Fig. 3. These were measured at a channel width of 1 V. with the well type single channel scintillation spectrometer mentioned above. In this work, the counting rate at the peaks of 0.02, 0.09 and 0.5 MeV. for each sample were measured under exactly the same conditions.

Determination of the Lanthanum, Samarium and Europium Activities. — The activity of the rare earth fraction at the peak of 0.5 MeV. is attributed to 40 hr. lanthanum-140 plus long-lived components (Figs. 2 and 3). Therefore, the activity of lanthanum-140 at a given time can be determined by graphical analysis of the

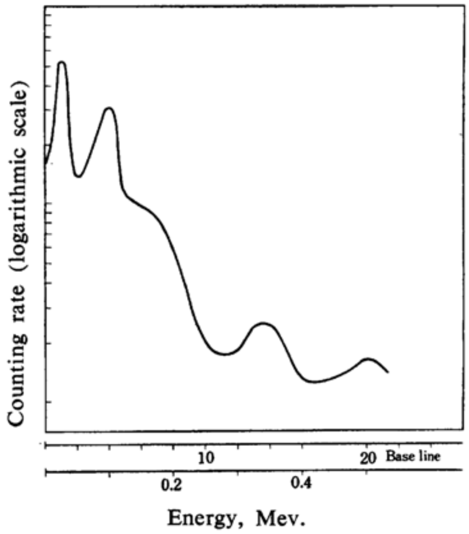

Fig. 2. Gamma-spectrum due to rare earth activities separated from neutron irradiated manganese nodule.

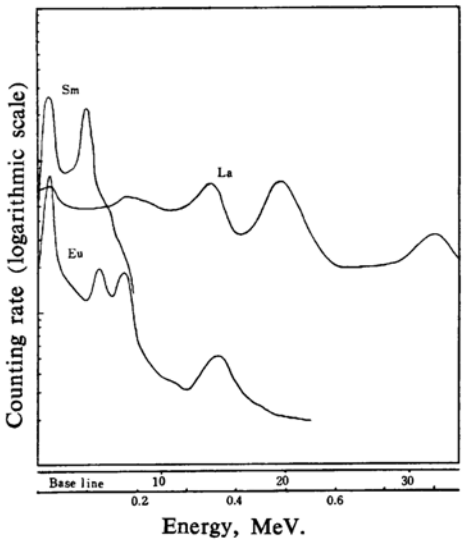

Fig. 3. Gamma-spectra of lanthanum-140, samarium-153 and europium-152.

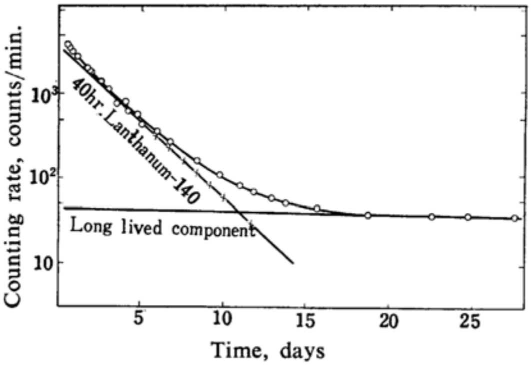

Fig. 4. Analysis of decay curve for the determination of lanthanum.

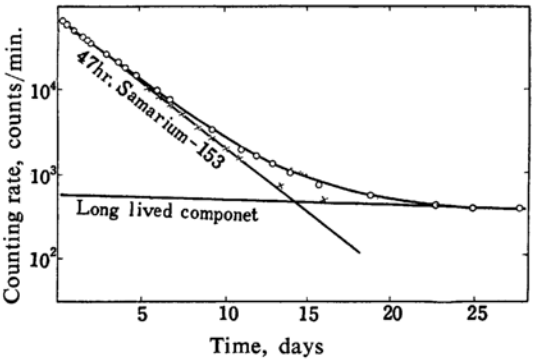

Fig. 5. Analysis of decay curve for the determination of samarium.

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6) W. F. Hillebrand, E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis", 2nd ed. John Wiley & Sons, Inc., New York (1953), p. 550.

* Hole 17mm$\phi\times$80mm, covered with aluminium can.

TABLE II. LANTHANUM, SAMARIUM AND EUROPIUM CONTENT OF MANGANESE NODULES (p. p. m.)

Sample	Location	Depth, m.	La	Sm	Eu
Horizon Guyot MP 26 A-3	19°N 169°W	1440～1540	234	33	9.6
			201	24	7.7
			270	35	9.4
			av. 235	av. 31	av. 8.9
Horizon Guyot MP 25 F-2	19°N 170°W	1870～1920	250	40	11.0
			378	60	19.6
			av. 314	av. 50	av. 15.3
Horizon Nodule	40°N 155°W	5500	357	108	19.6
			250	62	16.6
			av. 303	av. 85	av. 18.1

decay curve, a typical one of which is given in Fig. 4.

Just as in the case of lanthanum mentioned above, the activity of 47 hr. samarium-153 is estimated based on the decay curve at the 0.09 MeV. peak, as shown in Fig. 5.

The activity of around 0.025 MeV. peak is the sum of activities due to europium-152, lanthanum-140, samarium-153 and longer-lived nuclides (Figs. 2 and 3). Therefore, the activity of the 9.3 hr. europium-152 component can be analyzed by the graphical analysis of the decay curve at the peak, an example of which is shown in Fig. 6. If the activity of long-lived component (curve B) plus 40 hr. lanthanum-140 component (curve C) is deducted from the gross decay curve A, we obtain the curve D which corresponds to the composite of the activity of europium and samarium. Here the contribution of lanthanum-140 component (curve C) is calculated by the experimentally determined ratio of the counting rate at the peak of around 0.025 MeV. to that of 0.5 MeV. (the ratio is around 1, see Fig. 3). By analyzing the curve D, the decay curve of 9.3 hr. europium-152, curve E, is obtained.

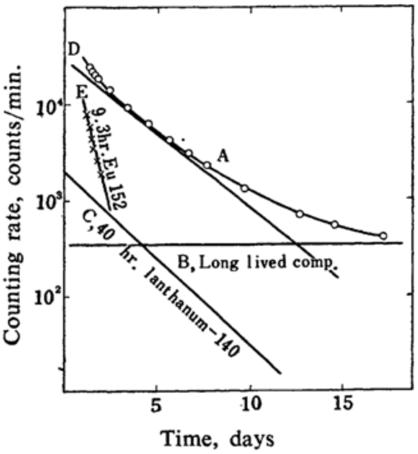

Fig. 6. Analysis of decay curve for determination of europium.

Determination of Lanthanum, Samarium and Europium in Manganese Nodules.—The amounts of lanthanum, samarium and europium in the sample are estimated by comparing the activities of each of the nuclides of the sample determined as above with that of the respective monitor. The results are summarized in Table II.

A possible interference of fission products of uranium in the manganese nodules should be taken into consideration, since lanthanum-140, samarium-153, and many other rare earth nuclides are produced by slow neutron fission of uranium. The interference should not be disregarded particularly in the case of lanthanum-140, because of the high fission yield of mass 140 chain. An experiment to examine this interference was performed by separating and measuring the fission product rare earths from an irradiated known amount of uranium. The uranium assay was carried out by utilizing the activity of fission product barium-140, on an aliquot of the reserved solution mentioned earlier. It was found that the interference with fission product rare earths from the uranium in the samples was negligibly small*.

The overall reproducibility of the method for manganese nodule samples is shown to be about 10～20%. Additional runs would probably increase the reproducibility of the method. As for the sensitivities of the method, as little as 1, 0.02 and 0.01 μg of lanthanum, samarium and europium respectively, could be detemined under the present experimental conditions.

Goldberg and Arrhenius⁽⁷⁾, and also Young⁽⁸⁾ gave 140 and 220 p.p.m. lanthanum respectively as the average for Pacific pelagic sediments by spectroscopic method. Our data indicate a

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* The result of uranium assay will be reported in a later paper. Tatsumoto and Goldberg (*Geochim. et Cosmochim. Acta*, **17**, 201 (1959)) gave 3.9, 3.6, 3.6 p. p. m. in Horizon Nodule by a spectrophotometric method.

7) E. D. Goldberg and G. O. S. Arrhenius, *Geochim. et Cosmochim. Acta*, **13**, 153 (1958).

8) E. J. Young, *Bull. Geol. Soc. Amer.*, **65**, 1329 (1954).

somewhat higher lanthanum content of the manganese nodules than pelagic sediments.

The relative abundance of the three elements was calculated for the three manganese nodules, which are tabulated in Table III. For reference, the abundance ratio of the three elements for crustal rocks, and the cosmic abundance ratio as given by Suess and Urey[9] are also included in Table III. It is seen that no essential differences in the relative abundance of the three rare earth elements are observed among the three different types of materials.

TABLE III. RELATIVE ABUNDANCE OF LANTHANUM, SAMARIUM AND EUROPIUM

Sample	Relative abundance		
	La	Sm	Eu
1a Horizon Guyot MP 26 A-3	1	0.13	0.038
1b Horizon Guyot MP 25 F-2	1	0.16	0.049
1c Horizon Nodule	1	0.28	0.060
2 Crustal rocks (Clarke No.)	1	0.33	0.056
3 Cosmic* (Suess, Urey)	1	0.332	0.093

* Atomic abundance ratio

Summary

The gamma spectrometric method has been developed for simultaneous determination of microgram amounts of lanthanum, samarium and europium without chemical separation of each other. The method was based on the chemical separation of rare earth mixtures from neutron irradiated samples and subsequent γ-ray scintillation counting of the isolated rare earth fractions. The sample was irradiated for 2～3 days, 5 hr. each day, in the nuclear reactor JRR-1 at a flux of the order of 10^{11}n/cm^2/sec. The rare earth mixture purified by lanthanum fluoride cycles was used for γ-ray counting at a given pulse height peak. The activity of each component could be evaluated by resolving the decay curves obtained, and the amount calculated by comparing the activity with that of each monitor.

We wish to express our hearty thanks to the staff of the Radiochemistry Group, Japan Atomic Energy Research Institute, for their help in making the irradiation. A part of the expense was defrayed from the Ministry of Education, to which our thanks are due.

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[9] H. E. Suess and H. C. Urey, *Revs. Mod. Phys.*, **28**, 53 (1956).