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# Determination of europium in minerals and rocks by neutron activation and $\gamma\gamma$ -coincidence spectrometry

ARTICLE *in* TALANTA · NOVEMBER 1969

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Typical results for solutions containing 50, 100 and 150 mg of manganese had a relative standard deviation of 0.3–0.4% and mean errors of +0.1%, –0.2% and –0.3% respectively.

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**Summary**—Precipitation of manganese, zinc and cadmium ammonium phosphates from homogeneous solution by decomposition of metal EDTA complexes by boiling with hydrogen peroxide in presence of phosphate has been investigated. Precipitation of Cd is not quantitative, but of Mn is complete in 2 hr, and of Zn in 6 hr.

**Zusammenfassung**—Die Fällung von Mangan-, Zink- und Cadmium-ammoniumphosphat aus homogener Lösung durch Zersetzung von Metall-EDTA-Komplexen durch Kochen mit Wasserstoffperoxid in Gegenwart von Phosphat wurde untersucht. Die Fällung von Cd verläuft nicht quantitativ; die von Mn ist nach 2 hr, die von Zn nach 6 hr vollständig.

**Résumé**—On a étudié la précipitation des phosphates doubles d'ammonium et de manganèse, zinc et cadmium en solution homogène par décomposition de complexes métal-EDTA par ébullition avec de l'eau oxygénée en présence de phosphate. La précipitation de Cd n'est pas quantitative, mais celle de Mn est complète en 2 h et celle de Zn en 6 h.

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Talanta, 1969, Vol. 16, pp. 1436 to 1439. Pergamon Press. Printed in Northern Ireland

### Determination of europium in minerals and rocks by neutron activation and $\gamma\gamma$ -coincidence spectrometry

(Received 6 March 1969. Accepted 2 April 1969)

SEVERAL neutron activation procedures for the determination of europium in geological material have appeared in the literature. Most methods have been based on radiochemical separation procedures used after decomposition of the sample. Recently instrumental methods based on measurement of  $^{152}\text{Eu}$ , with Ge(Li) detectors, have been applied to rocks.<sup>1,2</sup> The 9.2 hr isomer of  $^{152}\text{Eu}$  has been used in analysis of minerals rich in rare earths, either an NaI(Tl) detector<sup>3</sup> or a Ge(Li) detector<sup>4</sup> being used.

The aim of the present work was to develop a simple method for the routine determination of europium in connection with a rare earth prospecting programme. As no satisfactory Ge(Li) detector system was available in the laboratory when the present work started, it was decided to try  $\gamma\gamma$ -coincidence spectrometry following neutron activation of the samples.

Although  $\gamma\gamma$ -coincidence measurements represent a comparatively specific system for the determination of certain components in complex radionuclide mixtures, this technique has not been extensively used in activation analysis of geological material. Procedures for the determination of copper,<sup>5–7</sup> iridium and selenium,<sup>8</sup> and caesium and cobalt<sup>9</sup> have been described, but no applications to rare earth elements have been published so far.

TABLE I.—INTERFERENCE FROM EQUAL AMOUNTS OF SOME ELEMENTS IN THE DETERMINATION OF EUROPIUM BASED ON 9.3 hr  $^{152m}\text{Eu}$ .\*

	Single NaI detector, measurement of 41 keV X-ray <sup>a</sup>	$\gamma\gamma$ -Coincidence 122–841 keV, (gate: 122 keV)
$^{152m}\text{Eu}$	100	100
$^{152}\text{Sm}$	13	0.012†
$^{160}\text{Tb}$	0.08	0.008
$^{166}\text{Ho}$	3.1	<0.0002
$^{169}\text{Yb}_{-1.75}\text{Yb}$	0.3	<0.01
$^{177}\text{Lu}$	0.6	<0.0002
$^{56}\text{Mn}$	—	0.015
$^{72}\text{Ga}$	—	0.22
$^{140}\text{La}$	—	0.025

\* The values refer to measurements 24 hr after a 15-min irradiation.

† Probably due to  $^{152m}\text{Eu}$  impurity.

#### *Establishment of experimental conditions*

Three radioactive europium isotopes are formed by thermal neutron activation of Eu, *i.e.*, 9.3 hr  $^{152m}\text{Eu}$ , 13 y  $^{152}\text{Eu}$ , and 16 y  $^{154}\text{Eu}$ . In the present work, where a rapid acquisition of data was essential, the analysis was based on the short-lived  $^{152m}\text{Eu}$ . This nuclide decays partly by  $\beta^-$ -emission to  $^{152}\text{Gd}$  (75%), and partly by electron capture (EC) to  $^{152}\text{Sm}$  (25%). The actual possibilities of coincidence measurements are associated with the EC-branch, either by coincidence between the 41-keV K X-ray originating from the EC process and a subsequent  $\gamma$ -ray (abundances 14, 11 and 10% for the 122, 841 and 963 keV  $\gamma$ -rays respectively), or by 122-keV and 841-keV  $\gamma$ -rays in cascade (abundance 7%).

Testing of the various coincidences and evaluation of the various interferences to be expected from other radionuclides indicated the 122 keV–841 keV coincidence to be the best choice for the measurements. The possible interference from other rare earths emitting  $\gamma$ -rays in the 120 keV region was investigated, and the results are given in Table I, in comparison with similar figures obtained by a method previously used in the laboratory, based on NaI  $\gamma$ -spectrometry.<sup>3</sup> Nuclides having a  $\gamma$ -ray at about 840 KeV coincident with one or more other  $\gamma$ -rays would constitute a possible interference, by coincidences between a back-scattered or Compton-scattered  $\gamma$ -ray and a  $\gamma$ -ray totally absorbed in the detector. The most probable interfering nuclides of this kind, which were considered to be 2.58 hr  $^{56}\text{Mn}$ , 14.2 hr  $^{72}\text{Ga}$  and 40.2 hr  $^{140}\text{La}$ , were also tested. As shown in Table I, the elements investigated can usually be disregarded as sources of error, provided that the measurements are performed about 24 hr after the irradiation.

Angular correlation measurements in the region 90–180° showed that maximum intensity of the 122 keV–840 keV coincidence was obtained at an angle of 90° between the two detector axes, the relative counting rates being 100, 97, 89, 81 and 79 at 90°, 110°, 135°, 160° and 180°, respectively, as the angle between the detector axes.

### EXPERIMENTAL

#### *Counting equipment*

The detectors used were Harshaw integral line detectors with 50 × 50 mm NaI(Tl) crystals. They were mounted on a rack which made it possible to change the angle between the central axes of the detectors continuously in the range 90–180°. The detectors were connected *via* Hamner charge-sensitive amplifiers to a Hamner coincidence unit consisting of two linear double-delay line amplifiers, two jitter-free pulse-height analysers and a fast coincidence unit with a variable resolving time in the range 10–150 nsec. The output of the coincidence unit was used to gate a Tullamore 400-channel pulse-height analyser.

#### *Samples and standards*

As test material, five samples were selected which were considered to be representative of the series to which the method was to be applied. They were three apatites, a hematite and an iron-rich carbonatite. For standards, aliquots of dilute europium solutions were evaporated to dryness

on small polyethylene sheets and sealed in flat polyethylene bags; 10-mg samples of the test materials were weighed into flat polyethylene bags.

#### *Irradiation and measurement*

Samples and standards were irradiated for 15 min in the reactor JEEP II (Kjeller, Norway) at a thermal neutron flux of about  $2 \times 10^{11}$  n. mm<sup>-2</sup>. sec<sup>-1</sup>. The gamma-activity measurements were carried out 20–28 hrs after the irradiation. The samples were mounted in a perspex sample holder placed in the central axis of the detectors, which were kept at an angle of 90° relative to each other. During measurements the distance between detectors and sample was so adjusted that the dead time of the multichannel analyser in no case exceeded 40% when the pulses from either detector were fed via the preamplifier directly into the analyser. The counting time used was ordinarily 10 min. The area of the 0.841 MeV photopeak was evaluated according to the method of Covell.<sup>10</sup>

#### *Shielding effects*

As some rare earth elements show strong neutron absorption, the results of the present work may be subjected to errors associated with shielding effects. The following experiments were carried out to study this point:

The test samples were analysed for samarium, europium and dysprosium, partly by analysis of 10-mg aliquots of the solid samples, and partly by analysis of dilute solutions of each sample. The method employed for this was  $\gamma$ -spectrometry with an NaI-detector.<sup>9</sup> No significant difference between the results was observed, indicating that shielding effects were of minor importance in the concentration range covered by the test samples. This conclusion is supported by calculations according to the method described by Högdahl,<sup>11</sup> for the shielding effect due to gadolinium homogeneously distributed in a 10 mg sample. It appears that this element, which is likely to cause the most serious errors, may be present in concentrations up to 1000 ppm and still give less than 5% error due to thermal neutron shielding.

The possible self-shielding effect of europium was studied by adding known amounts of europium to the carbonatite test sample. The europium was added in increments of 50 ppm up to a maximum of 200 ppm, and the total content determined by the coincidence method for each addition. A plot of the total europium concentration as a function of the amount added gave a straight line which was extrapolated to zero addition. This gave a value of 37 ppm, which is in good agreement with the mean value 38.6 ppm for this sample. The result of this experiment indicates that the self-shielding effect of europium can be neglected in the concentration range studied.

### RESULTS AND DISCUSSION

Results for the europium content of the test samples are shown in Table II. The precision of the results is about 5%.

As shown in Table I, the interference from other elements by the present method is quite low. Interference from other rare earth elements should be insignificant in most geological samples. For samples with europium content of the same order as those analysed in the present work, possible interference from other elements can also be neglected in most cases. Neutron shielding effects also seem to be of little importance.

TABLE II.—EUROPIUM CONTENT OF FIVE TEST SAMPLES (ppm)

	Kodal apatite	Karlshus apatite	ödegaarden apatite	Hematite	Iron-rich carbonatite
	57.7	12.6	50.3	50.8	37.0
	55.8	13.2	49.3	56.3	40.5
	58.6	12.0	46.9	50.5	38.5
	61.0	12.1	50.5	52.6	38.2
	53.3	12.4	43.5	57.9	42.3
	60.3	13.9	47.0	59.1	37.8
	57.2	14.2	48.9	52.4	37.3
	55.2	12.5	47.2	50.8	39.4
	58.8	13.6	45.8	52.1	38.1
	53.9	12.8	47.6	51.0	36.9
Mean, ppm	57.2	12.9	47.7	53.4	38.6
Relative standard deviation, %	4.7	5.9	4.5	6.1	4.4

The present  $\gamma\gamma$ -coincidence method has proved to be a convenient method for the rapid determination of europium in a large series of mineral and rock samples, mostly in the 10–150 ppm concentration range. The sensitivity of the method for routine application is about 5 ppm. By extension of the counting period to several hours, europium concentrations below 1 ppm can be determined. In this case, however, the interference from  $^{56}\text{Mn}$  and  $^{72}\text{Ga}$  becomes important. In such cases use of a method based on a rapid radiochemical separation is recommended.

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**Summary**—Neutron activation followed by  $\gamma\gamma$ -coincidence measurements of 9.3 hr  $^{152}\text{Eu}$  is shown to be a convenient method for routine determination of europium in minerals and rocks. In the concentration range 10–150 ppm the method is free of interference from other elements, and neutron shielding effects do not interfere seriously in the analysis. The precision of the method is about 5%.

**Zusammenfassung**—Neutronenaktivierung und anschließende  $\gamma\gamma$ -Koinzidenzmessungen von  $^{152}\text{Eu}$  (9,3 h) wird als bequeme Methode zur Routinebestimmung von Europium in Mineralien und Gesteinen angegeben. Im Konzentrationsbereich 10–150 ppm ist die Methode frei von Störungen durch andere Elemente; Neutronenabschirmeffekte stören bei der Analyse nicht wesentlich. Die Genauigkeit ist ungefähr 5%.

**Résumé**—On montre que l'activation par neutrons suivie de mesures de coïncidence  $\gamma\gamma$  de  $^{152}\text{Eu}$  9,3 h est une méthode commode pour le dosage de routine de l'euporium dans les minerais et roches. Dans le domaine de concentrations 10–150 ppm, la méthode est exempte d'interférence d'autres éléments, et les influences de protection de neutron n'interfèrent pas sérieusement dans l'analyse. La précision de la méthode est d'environ 5%.

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*Talanta*, 1969, Vol. 16, pp. 1439 to 1441. Pergamon Press. Printed in Northern Ireland

#### Voltammetric oxidation of anthraquinones in acetonitrile and nitromethane

(Received 28 March 1969. Accepted 3 April 1969)

It is well known that quinones are reduced polarographically and voltammetrically in aprotic solvents in one-electron steps to the singly and doubly charged anions.<sup>1</sup> Fodiman and Levin<sup>2</sup> have used such reduction waves in the polarographic determination of anthraquinone derivatives. It has recently been observed in our laboratory that anthraquinones, but not benzoquinones, naphthaquinones and phenanthraquinones, can also be oxidized voltammetrically in acetonitrile and nitromethane to the singly charged cations. The voltammetric oxidations of anthraquinones have, therefore, been studied