Radiochemical determination of Europium and application of the method in marine samples

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Abstract - A radiochemical method for determining europium, at the nanogram level, in dry or ashed biological tissues has been developed. By this technique, the rare earth group is first isolated by ion exchange from the neutron irradiated sample and then ^{152m}Eu is counted on the 121.8 keV photopeak which, in this case, is practically free from interfering γ-rays using a Ge(Li) detector. The whole bodies and the main parts of four benthic organisms from the Aegean sea have been analysed for europium.

Résumé - Une méthode radiochimique a été developpée pour doser l'europium, au niveau de nanogramme, dans les tissues biologiques sechés ou calcinés. Par cette technique, l'ensemble des terres rares est d'abord isolé de l'échantillon irradié aux neutrons, par des résines échangeuses d'ions et ensuite le ^{152m}Eu est compté sur le photo pic 121.8 keV qui, en cette cas, est libre de l'interférence d'autres rayons-γ en utilisant un détécteur Ge(Li). Les corps entiers et les parties principales de quatre organismes benthiques de la mer d'Egée ont été analysés pour doser l'europium.

Introduction

The determination of rare earths and/or europium in several matrices like rocks, sediments, blood cells, marine organisms[1] etc., is usually connected with a special interest for the corresponding field of application on research. In the field of marine radioecology europium is a significant element since waste discharge from nuclear activities are entering the marine environment. The radioisotopes of europium having half lives of years may affect the marine biosphere by which they are taken up rapidly. Sediments were found[2] to contain radioisotopes of europium and this fact leads to the investigation of the stable europium content in benthic organisms, assuming that the principle of the stable isotope exchange with radioisotopes is holding. Therefore, four common in the Aegean sea benthic organisms have

been selected for this study. The method of analysis should be rapid enough for treating series of samples and very sensitive, taking in consideration the low levels expected. In this case the neutron activation analysis seems to be the most sensitive, provided that chemical purification before counting is taking place. Methods for separating the rare earth group from other elements[3] or the rare earths from each other[3] are not lacking and also the analysis of rare earths by activation has been reviewed[4]. However, convenient methods for determining europium in tissues were not encountered in the literature. Therefore, a method adapted to our requirements has been developed.

Experimental

The sample (100 mg about of dry or ashed tissues) and standard are irradiated at 5.10^{13} n/cm^2.sec flux for 30 minutes. Two hours later the dry tissues are digested with HNO_3, HCOOH and H_2O_2 in presence of europium carrier and the solution is converted to 8 M HCl (ashed tissues are dissolved directly in 8 M HCl) for fixation on DOWEX 1 X 8 100-200 mesh, 6 mm X 90 mm resin. The column is eluted with 9 ml 8 M HCl and the effluent is converted to 2M HCl solution which is passed through a DOWEX 50 X 8 100-200 mesh 6 mm X 60 mm resin. The column is eluted successively with 9 ml 2 M HCl, 15 ml 1.75 M HNO_3 and finally with 12 ml 6 M HNO_3. The last fraction is only kept and ^{152m}Eu is counted on the 121.8 keV photopeak by a 37 cm^3 Ge(Li) detector connected with a 4000-channel analyser. The standard, diluted to the same volume as the sample, is counted also and compared with the sample.

Results and discussion

This method is based on an our previous work[4] dealing with the determination of Mn, Sr and Ba, and leading, also, to the isolation of the rare earths. The objectives of this work in relation to the previous one are quite different and they have been achieved in considerably shorter time. The ion exchange procedure result to a solution containing the rare earths with Se, Y and a small percentage of Hf and Cr. Although a further purification of the fraction or isolation of ^{152m}Eu would be possible, this was not found necessary if a Ge(Li) detector was to be used. By investigating the nuclear data[6] of the nuclides eventually present when europium is counted on the 121.8 keV photopeak, it was found that only ^{147}Nd, ^{161}Tb, ^{169}Yb and ^{171}Er could interfere with the counting at the region 114 to 130 keV. The activity of the three of them are supressed by a factor at least 10^5 in the region 114 to 130 keV compared with that of europium. This factor

is induced only by the choice of the irradiation time in connection with the nuclear properties of their isotopes. For the same reason ^{171}Er is supressed by a factor 10^3 and when present it can be recognised by the 308 keV γ-ray which is not emitted by other nuclide in consideration except from ^{169}Yb being without importance. Thus the determination of europium in tissues is practically free from any interference as far as it concerns the counting. The same is valid for the chemistry. It was found that major constituents of a biological matrix (i.e. 300000 ppm Ca) do not affect the ion exchange separations. Moreover the digestion of tissues proved effective without adding high boiling acids which make the conversion of the solution to hydrochloric difficult.

TABLE 1

Europium content in some benthic organisms from the Dodecanese area of the Aegean sea

Parts of the organism	ppm of Eu in dry matter			
	Spondylus gaederopus	Chama placentina	Pinna nobilis	Arca noae
Whole body	0.020	0.044	0.020	0.030
Muscles	0.030	0.0090	0.016	0.016
Mantle-Gills	0.017	0.061	0.011	0.034
Stomach-Intestine	0.012	0.048	0.020	0.023
Gonades	-	0.039	0.023	0.011
Hepatopankreas	-	-	0.012	0.017
Byssus	-	0.026	0.014	0.056

The method has been applied in the analysis of the whole bodies and the main parts of four benthic organisms which were collected from the Dodecanese area of the Aegean sea (Table 1). These results are the mean values from three groups of 12 organisms, each group being analysed in duplicate. The precision was found 9% and the sensitivity of europium 0.4 ng.

This method has been published in extenso elsewhere[7].

References

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20. Papadopoulou C., Hadzistelios I. - Radiochemical determination of Europium and application of the method in marine samples.

Discussion

Guary J.C. (IAEA, Monaco) : Why did you combine the mantle and gills which are physiologically very different and may have quite different levels of europium ?

Papadopoulou C. : The main goal of this work was to find out a radiochemical method for the determination of Eu and we show some distribution in organs disregarding their physiological significance.

Guegueniat P. (France) : I am interested in Europium in sea water; I bring some values of Europium we got in La Manche: 90-150 x 10^{-3} µg/l in open sea water; 1 or 2 x 10^{-3} µg/l in coastal sea water (comment).

Papadopoulou C. : Our values for benthic species of mollusks we analysed are between 0.0090-0.060 ppm Eu in dry matter.