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Determination of rare earth elements in the biological reference materials Pine Needles and Spruce Needles by neutron activation analysis

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Instrumental neutron activation analysis was applied to determine La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc in two biological reference materials: NIST 1575 Pine Needles and BCR-CRM 101 Spruce Needles. The purpose was to contribute to the reference data for these two reference materials. The results were obtained with a good precision (relative standard deviations less than 15%). For the Pine Needles reference material there are already some proposed values and our results showed, in general, a good agreement with the data published. The contribution of uranium fission products to La, Ce, Nd and Sm was evaluated and considered in the determination of these elements. Interferences in the determination of rare earth elements in biological materials are also discussed.

Introduction***

Rare earth elements (REE) are becoming more and more technologically significant due to their widespread utility as fine chemicals in modern industry.[1] The main areas of the applications of REE are in solid state laser and superconducting materials. The demand of REE for industrial applications is increasing rapidly, and concurrently the environmental contamination by REE in biological samples as plants and human organs may increase. With this, it will become essential to investigate their impact on humans and wildlife. Thus, REE analysis may be requested from laboratories working for environmental pollution control, medicine, food control, etc.

Investigations on REE in the environment depend on sensitive analytical techniques, due to the low concentration values of these elements especially in biological samples.[2] Even modern analytical techniques like ICP/MS and NAA may require a preconcentration step, especially for elements like Lu, which often occurs in $ng \cdot g^{-1}$ or $ng \cdot kg^{-1}$ levels. To assure the reliability of the data, a critical verification of analytical values must be performed and "quality control" must be the order of the day. The accuracy of analytical results is normally verified by application of the analytical procedure to certified reference materials. However, due to analytical difficulties, a very small number of certified biological reference materials for the REE are available.

In the present work, concentration values for the REE La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc were determined in the reference materials SRM-1575 Pine Needles (from the National Institute of Standards and Technology, NIST, USA) and BCR-101 Spruce Needles (from Institute for Reference Materials and Measurements, IRMM, Belgium). Pine Needles has information values for La, Ce, Eu and Sc, provided by NIST, and few literature data are published for the REE. However, there is a great discrepancy between the results for some elements like Tb, Nd, Yb and Lu.[3] This fact shows the importance of providing reliable results for this reference material. In the case of Spruce Needles, there are no proposed values for the REE, and the analytical data presented are a contribution to concentration values.

Instrumental neutron activation analysis (INAA), was used that has proved its worth in the instrumental analysis of biological samples.[4]

Experimental

Preparation of elemental synthetic standards

Aliquots of standard solutions with well known concentrations of REE to be analysed, were pipetted onto 1 cm^2 pieces of Whatman No. 40 filter paper and evaporated to dryness under an infrared lamp. The stock standard solutions of REE were prepared by dissolving their respective calcined oxides (Johnson Matthey Chemical Limited) with nitric acid and then diluting with distilled water, with the exception of Ce. In the case of Ce, standard solution of this element provided from NIST was used. Standard solution of uranium was prepared by dissolving U_3O_8 No. 6 from Compagnie Générale des Matières Nucléaires (COGEMA), France, with nitric acid. The quantity of the elements (in μg) in the standards irradiated were: La = 1.0, Ce = 4.0, Nd = 2.0; Sm = 0.50; Eu = 0.10, Tb = 0.150, Yb = 0.350, Lu = 0.150, Sc = 0.10 and U = 1.0.

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Procedure

Samples (about 200 mg) and standards were sealed in plastic envelopes and irradiated for 16 hours at a thermal neutron flux of 10^{12} n·cm^{-2}·s^{-1}, at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP). The measurements of the induced γ-ray activity were carried out with a GMX20190 hyperpure Ge detector, connected to an ADCAM 918A Multichannel Buffer (EG&G ORTEC) and to a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV γ-ray of ^{60}Co. Two series of countings were performed, the first one 5 days after irradiation, for the determination of La, Sm, Nd, Yb and Lu and the second one 15 days after irradiation, for the determination of Ce, Eu, Tb, Yb, and Sc. The counting times varied from 3 hours (for counting all the standards and the first series of counting of the samples) to 14 hours (for second series of counting of the samples). The γ-ray spectra were processed by the VISPECT computer program, developed at IPEN by Dr. Denis PICCOT, from Saclay, France.

The interference factors due to the contribution of uranium fission products in the analyses of La, Ce, Nd and Sm were experimentally determined. To obtain the correct concentrations of these elements, first the amount of U was determined and multiplied by the interference factor. The interference contribution was then subtracted from the concentration of the element measured. The following values (in μg of element/μg of U) were determined for interference factors: (0.017± 0.01) for ^{140}La for a decay time equal to 128.16 hours, (0.29±0.01) for ^{141}Ce, (0.24±0.01) for ^{147}Nd and (0.068 ±0.007) for ^{153}Sm.

Table 1 shows the radioisotopes used to calculate the concentrations of the analysed elements as well as their nuclear data. To evaluate the concentrations of REE in the samples, the counting rates (area of the photopeaks) corresponding to the γ-rays of the radioisotopes from samples and standards were compared.

The moisture content in the reference materials was ascertained by drying in an oven at 85 °C for about 6 hours. The following values (in %) of weight loss were used for correcting the final results: 5.17 for Pine Needles and 4.65 for Spruce Needles.

Results and discussion

The results obtained for REE in Pine Needles and Spruce Needles are shown in Table 2 together with information values for Pine Needles provided from NIST and also literature values presented by MARKERT and DE LI,[4] for comparison.

Table 1. Radioisotopes with main γ-ray energies and half-lives

Element	Radioisotope	Gamma-ray energy, keV	Half-life
La	^{140}La	328.6; 1595.4	40.27 h
Ce	^{141}Ce	145.4	32.5 d
Nd	^{147}Nd	91.4; 531.0	11.06 d
Sm	^{153}Sm	103.0	47.1 h
Eu	^{152}Eu	121.8; 1407.5	12.2 a
Tb	^{160}Tb	879.4	73.0 d
Yb	^{169}Yb	177.0	30.6 d
	^{175}Yb	197.8; 396.1	101 h
Lu	^{177}Lu	208.4	6.75 d
Sc	^{46}Sc	889.3	83.81 d
U	^{239}Np	106.1; .277.6	2.36 d

Our results obtained for Pine Needles agreed with the information or literature values. For most elements, the precision of the results was satisfactory, within the limits expected for trace element analyses. The relative standard deviations of the results, generally, varied from 4.8% to 15.0%. The precision was not so good for the elements Eu, Yb and Lu due to the low concentration values of these elements in the samples. Recently, WANG et al.[3] reported concentration values for REE in the reference material Pine Needles, where a great discrepancy between data can be observed. For Tb, there are concentrations ranging from 2 to 31 μg·kg^{-1} showing the analytical difficulties in the determination of this element. In this work, Tb was not detected in Spruce Needles, and fewer number of determinations of Nd, Yb and Lu were carried out. In some cases, the concentrations of these elements were not calculated because of the high counting statistical errors in the γ-ray peaks of the radioisotopes considered for the analyses.

The determination of REE in biological materials by INAA suffers interferences of some radionuclides such as ^{82}Br, ^{24}Na and ^{32}P, obtained after irradiation. The high activities of these radionuclides mask the less intense ones produced by REE. Some spectral interferences such as that from 889 keV γ-ray peak of ^{46}Sc in the 879 keV γ-ray peak of ^{160}Tb, or from ^{182}Ta radioisotope in the photopeaks of ^{169}Yb must also be considered, due to the low concentrations of Tb and Yb in this kind of matrix. The destructive method of neutron activation analysis could be applied when the determination of all REE is required and when the problem of interference becomes serious.

The interference of the fission products ^{140}La, ^{141}Ce,^{147}Nd and ^{153}Sm depends on the relationship between the concentrations of the uranium and the lanthanide elements as well as on the conditions of irradiation and, in the case of La, on the length of decay time.

Table 2. REE concentrations (in μg/g unless otherwise indicated) in the reference materials NIST 1575 Pine Needles and BCR 101 Spruce Needles obtained by INAA

Element	Pine Needles This work Mean ± s_d (s_r)	n	Reference[5,6]	Spruce Needles This work Mean ± s_d (s_r)	n
La	0.176 ± 0.019 (10.7)	15	(0.2)	0.092 ± 0.012 (13.0)	11
Ce	0.367 ± 0.018 (4.9)	13	(0.4)	0.203 ± 0.029 (14.3)	9
Nd	0.135 ± 0.021 (15.5)	6	0.17	0.188 ± 0.041 (21.8)	4
Sm	0.026 ± 0.002 (7.7)	13	0.030	0.011 ± 0.001 (9.1)	11
Eu, μg/kg	6.3 ± 0.8 (12.7)	8	(6)	4.5 ± 0.8 (17.7)	7
Tb, μg/kg	3.2 ± 0.2 (6.2)	8	5	not detected	
Yb, μg/kg	11.5 ± 2.4 (20.8)	9	12	11.9 ± 2.2 (18.5)	4
Lu, μg/kg	2.1 ± 0.3 (14.3)	8	2	1.1 ± 0.2 (18.2)	6
Sc	0.038 ± 0.002 (5.3)	13	(0.03)	0.023 ± 0.003 (13.0)	15

Figures in parenthesis correspond to information values from NIST.
s_d – standard deviation;
s_r – relative standard deviation;
n – number of determinations.

Results obtained in this work indicate the viability in using INAA for determination of the elements La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc in biological materials and that the uranium content in plant materials is generally very low and the contribution of uranium fission products is quite negligible.

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