

CHARACTERIZATION OF THE MEDITERRANEAN SEA MUSSEL REFERENCE MATERIAL (IAEA-437)

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Abstract

The characterization of a new Reference Material (RM) for radionuclides in mussel (*Mytilus galloprovincialis*) from the Mediterranean Sea (IAEA-437) is described and the results of the certification process are presented. Four radionuclides (⁴⁰K, ²³⁴U, ²³⁸U, and ²³⁹⁺²⁴⁰Pu) have been certified, and information values on massic activities with 95% confidence intervals are given for nine other radionuclides (¹³⁷Cs, ²¹⁰Pb(²¹⁰Po), ²²⁶Ra, ²²⁸Ra, ²²⁸Th, ²³⁰Th, ²³²Th, ²³⁵U, and ²⁴¹Am). The IAEA-437 RM is intended to be used for quality assurance/quality control of radionuclide analyses of mussel samples using radiometric and mass spectrometry techniques (ICP-MS, AMS), for the development and the validation of analytical methods, for the development of reference methods and for training purposes.

Keywords: Radionuclides, Mediterranean Ridge, Pollution, Instruments And Techniques, Monitoring

Introduction

In collaboration with CIESM, an inter-laboratory comparison exercise using Mediterranean Mussel Reference Material was previously organised to test the performance of laboratories in analytical quality control [1-2]. More data from expert laboratories have been obtained during 2008-2009 allowing to assign the true values and the uncertainties of different radionuclides in this specific matrix of marine sample, and in consequence to permit to issue a new Certified Reference Material for Marine Environmental Study.

Experimental

The work was performed on a mussel tissue sample, which is commonly found and consumed seafood, and is widely used as bio-indicators in marine pollution studies. They were collected from the Mediterranean Sea in the framework of the CIESM (Commission Internationale pour l'Exploitation Scientifique de la Mer Méditerranée) Mediterranean Mussel Watch Program. About 1080 kg of mussel sample (*Mytilus galloprovincialis* species) was collected in Anse de Carteau, Port Saint Louis du Rhône (43°20'S, 5°10'E), France, by the Institut de Radioprotection et de Sureté Nucléaire (IRSN, France) in June 2003. More detail of description of the material could be found in [1-2]. Of 34 laboratories received the sample, a total of 24 sets of results were received from participants and included in the evaluation report of the interlaboratory comparison exercise [2]. Because of very low-levels of radionuclide activities in the sample, 16 more samples were sent to 5 members of CELLAR (Collaboration of European Low-Level Underground Laboratories) and to 11 expert laboratories in 2007. High quality data from the interlaboratory comparison exercise, and additional data from the CELLAR and expert laboratories were included in the certification process, results of which are reported in the present paper.

Results and discussion

Homogeneity tests: The homogeneity of the sample was checked by measuring the activities of ⁴⁰K, ¹³⁷Cs, ²³⁵U, ²³⁸U, ²³⁹⁺²⁴⁰Pu and ²⁴¹Am on 5-17 bottles taken at random. Gamma-spectrometric measurements were performed on 100 g of mussel. The activity concentrations of ²³⁵U, ²³⁸U, ²³⁹⁺²⁴⁰Pu and ²⁴¹Am were determined by ICP-MS and alpha spectrometry on 0.5 to 100 g of mussel sample, respectively. Homogeneity was determined using one-way analysis of variance. The coefficient of variation was below 15% for gamma, alpha-spectrometrically determined radionuclides (with activity concentration less than 1 Bq kg⁻¹). The "between samples" variances showed no significant differences from the "within sample" variances for all analysed radionuclides. The material was thus considered sufficiently homogeneous for the tested radionuclides at the range of weights used.

Certification process: The certification process was carried out following the ISO Guide 35 [3] using the most precise and accurate data from interlaboratory comparison exercise and additional data from CELLAR and expert laboratories. For data sets comprising 5 or more accepted laboratory means, the median activities for the sets of individual data – after rejection of outliers – were chosen as the best estimations of the property values [4]. Evidence on metrological traceability to the SI units was provided by all laboratories in their reports.

Only 4 radionuclides ⁴⁰K, ²³⁴U, ²³⁸U and ²³⁹⁺²⁴⁰Pu were certified in the certification process. The mean, median values with 95 % confidence intervals, the number of accepted means which were used to calculate the certified activities are given in Table 1. Information values are given for 9 radionuclides: ¹³⁷Cs, ²¹⁰Pb(²¹⁰Po), ²²⁶Ra, ²²⁸Ra, ²²⁸Th, ²³⁰Th, ²³²Th, ²³⁵U

and ²⁴¹Am. The mean, median values with 95 % confidence intervals, the number of accepted means which were used to calculate the activities are given in Table 2.

Tab. 1. Certified mass activities in IAEA-437 Mussel from the Mediterranean Sea (Reference date: 1 November 2003)

Radionuclide	Mean ± Std. Dev. (Bq kg ⁻¹ dw)	Median (Bq kg ⁻¹ dw)	95% Confidence Interval (Bq kg ⁻¹ dw)	N ^a	N ^b
⁴⁰ K	373 ± 20	373	360 – 380	21	91
²³⁴ U	2.3 ± 0.1	2.3	2.2 – 2.4	9	42
²³⁸ U	1.86 ± 0.09	1.87	1.80 – 1.92	14	57
²³⁹⁺²⁴⁰ Pu	0.0078 ± 0.0006	0.0076	0.0071 – 0.0082	11	45

N^a: Number of accepted laboratory means which were used to calculate the certified mass activities and the corresponding confidence intervals. N^b: Total number of assays.

Tab. 2. Information mass activities in IAEA-437 Mussel from the Mediterranean Sea (Reference date: 1 November 2003)

Radionuclide	Mean ± Std. Dev. (Bq kg ⁻¹ dw)	Median (Bq kg ⁻¹ dw)	95% Confidence Interval (Bq kg ⁻¹ dw)	N ^a	N ^b
¹³⁷ Cs	0.16 ± 0.06	0.14	0.11 – 0.23	9	67
²¹⁰ Pb(²¹⁰ Pb)*	4.6 ± 1.1	4.2	4.0 – 5.4	26	71
²²⁶ Ra	0.26 ± 0.09	0.27	0.21 – 0.31	9	48
²²⁸ Ra	1.44 ± 0.29	1.48	1.00 – 1.80	7	24
²²⁸ Th	0.79 ± 0.17	0.79	0.71 – 0.96	9	58
²³⁰ Th	0.21 ± 0.09	0.16	0.15 – 0.40	6	21
²³² Th	0.13 ± 0.05	0.11	0.09 – 0.16	8	30
²³⁵ U	0.09 ± 0.02	0.09	0.07 – 0.11	9	34
²⁴¹ Am [†]	0.019 ± 0.010	0.020	0.008 – 0.034	5	39

N^a: Number of accepted laboratory means which were used to calculate the information mass activities and the corresponding confidence intervals. N^b: Total number of assays.

* Two corrections for ²¹⁰Pb and ²¹⁰Pb determination should be applied during a storage time: (i) a correction for ²¹⁰Pb decay (the half-life 22.2y) and (ii) a correction for in-growth of ²¹⁰Pb from ²²⁶Ra.

[†] Values should be corrected for in-growth from ²⁴¹Pu.

Acknowledgments

The authors are indebted to their numerous colleagues who took part in the analytical works. Special acknowledgement is given to the Professor Frederic Briand, Director General of CIESM, for financial support provided for the Mediterranean Mussel Watch Program and to the Institut de Radioprotection et de Sureté Nucléaire (IRSN, France) for providing the mussel sample. The IAEA is grateful for the support provided to its Marine Environment Laboratories by the Government of the Principality of Monaco.

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