

A new reference material for radionuclides in the mussel sample from the Mediterranean Sea (IAEA-437)

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Received: 30 November 2009 / Published online: 7 January 2010
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Abstract 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 (^{40}K , ^{234}U , ^{238}U , and $^{239+240}\text{Pu}$) have been certified, and information values on massic activities with 95% confidence intervals are given for nine radionuclides (^{137}Cs ,

^{210}Pb (^{210}Po), ^{226}Ra , ^{228}Ra , ^{228}Th , ^{230}Th , ^{232}Th , ^{235}U , and ^{241}Am). Results for less frequently reported radionuclides (^{90}Sr , ^{129}I , ^{238}Pu , ^{239}Pu , and ^{240}Pu) are also reported. The RM can be used for quality assurance/quality control of the analysis of radionuclides in mussel samples, for the development and validation of analytical methods and for training purposes. The material is available in 200 g units.

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Keywords Reference material · Mussel Mediterranean Sea · Natural radionuclides · Anthropogenic radionuclides · Massic activity

Introduction

Accurate and precise determination of radionuclide concentrations in marine samples is important for marine radioactivity assessments and for the use of radionuclides in the study of oceanographic processes. To address the problem of data quality, the IAEA's Marine Environment Laboratories (IAEA-MEL) in Monaco have conducted interlaboratory comparison exercises on radionuclides in marine samples for last 40 years as part of their contribution to the IAEA's programme of Analytical Quality Control Service (AQCS), now renamed as IAEA's Programme of Reference Materials [1, 2]. An important part of this activity was the production of Reference Materials (RMs), which were usually products of worldwide interlaboratory comparison exercises. The IAEA's AQCS programme for radionuclides in the marine environment has recently focused on the production of Certified Reference Materials (CRMs) [3–7], to improve the accuracy and precision of analyses carried out by the laboratories and

thus the quality of data, and to provide traceability to SI standards. They are valuable for method development and validation: they can indicate the need to improve or change existing methods and/or the need of further training. In fact, reference methods should only be accepted on the basis of interlaboratory comparison tests performed on selected CRMs. RMs and CRMs should be available for all important marine matrices, such as sediment, biota, sea water, suspended matter, etc....

Collection and preparation of large volume samples (over 100 kg) requires development of specific methods for their pre-treatment. The required long-term availability of RMs/CRMs (over 10 years) necessitates their long-term stability as well. The production of a new reference material is a long process, covering the identification of needs, sample collection, pre-treatment, physical homogenization, bottling, homogeneity test, distribution to laboratories, evaluation of data, preliminary reporting, additional analyses by expert laboratories, certification of material (including the determination of proper values and their expanded uncertainties), and finally issuing the RM.

This 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 [8]. The sample was collected from the Mediterranean Sea in the framework of the CIESM (Commission

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Internationale pour l'Exploitation Scientifique de la Mer Méditerranée) Mediterranean Mussel Watch Program. Participating laboratories were requested to determine as many anthropogenic radionuclides as possible by gamma-spectrometry, alpha-spectrometry, beta counting and mass spectrometry. The certification process was completed and the material was issued as a RM for radionuclides in mussel tissue.

Experimental

Description of the material

About 1,080 kg of mussel sample (*Mytilus galloprovincialis*) 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 Sécurité Nucléaire (IRSN, France) in June 2003. The shells were removed and the fresh soft parts (145 kg) and internal fluids (505 kg) were separated from the raw mussels.

The sample was reduced by freeze-drying to about 60 kg, finely ground to a powder, sieved at 200 µm, and homogenised in a nitrogen atmosphere. The samples were aliquoted in 200 g, then bottled in brown glass flasks under nitrogen gas. The bottles were sealed with polyethylene screw caps and labelled with the code IAEA-437. They were then sterilized at 10 kGy in an irradiation facility in accordance with ISO recommendations [3].

The average moisture content of the freeze-dried sample after bottling, determined by drying several aliquots in an oven at 80 °C to constant weight (1–2 days), was approximately 2.5%. Since moisture content can vary with ambient humidity and temperature, it was recommended to check the water content prior to analysis and to report all results on a dry-weight (dw) basis.

Sample dispatch and data feedback

The sample aliquots were distributed to participating laboratories during 2004–2005. Taking into account the limiting size of the sample, only 34 laboratories, on which half of them are partners of CIESM Mediterranean Mussel Watch Program, have received the sample. Each participant received 200 g of mussel powder. For each radionuclide analyzed, the following information was requested: (1) average weight of sample used for analysis; (2) number of analyses; (3) massic activity (Bq kg⁻¹ dw) corrected for blank, background, etc.; (4) estimation of the combined uncertainties; (5) description of chemical procedure and

counting equipment; (6) standard solutions used for analysis; (7) chemical recoveries if any, counting time and decay corrections.

A total of 24 sets of results were received from participants and included in the evaluation report of the interlaboratory comparison exercise [9]. Because of very low-levels of radionuclide activities in the sample, 16 more samples were sent to five 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.

Data treatment

The massic activities of anthropogenic and natural radionuclides in the sample were reported. Calculations are based on the assumption of non-parametric distribution of data to which distribution-free statistics are applicable. Laboratory means were calculated when necessary from individual results, and they are given either as arithmetic means with corresponding standard deviations when more than two results were reported, or as weighted means with weighted uncertainties in the case of only two results reported. The values below the detection limits are segregated from the results and the remaining values are checked for the presence of outliers using a Box-and-Whisker plot test. Median values are calculated from all results passing the test, rounded off to the most significant number of the uncertainty. These values are considered to be the most reliable estimates of the true values. Confidence intervals were taken from a non-parametric sample population representing a two-sided interval at 95% confidence limits. Expanded uncertainty with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95%, was also calculated according to the ISO-1993 and NIST Guidelines [10, 11].

Following the IUPAC [12] and ISO [13] recommendations for assessment of performance of laboratories, a Z-score methodology was used in the data evaluation. The Z-score was calculated as following:

$$Z = (X_i - X_a) / S_b$$

where X_i is the robust mean of massic activity values reported by laboratory i , X_a is the assigned value (a mean value of accepted results), and S_b is the target standard deviation. The right target value depends on the objective of the exercise. For radionuclide analysis, laboratories were required to have a relative bias below 20% ($S_b < 10\%$).

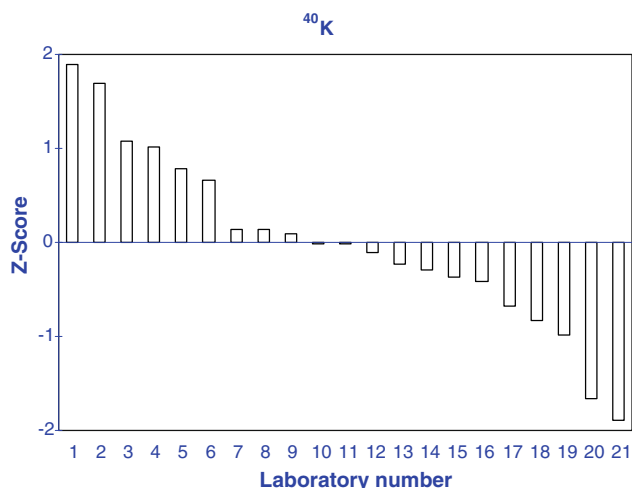


Fig. 1 Z-score values for ^{40}K in IAEA-437

The uncertainty of the assigned value (S_{tu}) was included in the target value for bias [14]:

$$Z = (X_i - X_a) / \sqrt{S_b^2 + S_{\text{tu}}^2}$$

The performance of laboratories in term of accuracy was expressed by the Z-score for each radionuclide. The performance of a laboratory is considered to be acceptable if the difference between the robust mean of the laboratory and the assigned value (in S_b units) is less than or equal to 2. A Z-score from 2 to 3 indicates that the results are of questionable quality, and the result of analysis is regarded as an outlier when $|Z| > 3$.

The Z-score distributions were symmetric (after excluding outliers) and usually with Z-scores below 2, indicating that the performance of the laboratories was satisfactory. A typical example of the Z-score for ^{40}K is shown in Fig. 1. The Z-score evaluation represents a simple method which informs participating laboratories on their performance.

Criteria for certification

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 five 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 [1–7]. They are reported as certified values when (i) at least five laboratory means were available, calculated from at least three different laboratories, (ii) the relative uncertainty of the median did not exceed $\pm 5\%$ for activities higher than $100 \text{ Bq kg}^{-1} \text{ dw}$, $\pm 10\%$ for

activities from 1 to $100 \text{ Bq kg}^{-1} \text{ dw}$ and $\pm 20\%$ for activities lower than $1 \text{ Bq kg}^{-1} \text{ dw}$.

An activity value was considered as an information value when at least five laboratory means calculated from the results of at least two different laboratories were available.

Expanded uncertainties with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95%, were calculated according to the ISO-1993 and NIST Guidelines [10, 11]. Evidence on metrological traceability to the SI units was provided by all laboratories in their reports.

Results and discussion

Homogeneity tests

The homogeneity of the sample was checked by measuring the activities of ^{40}K , ^{137}Cs , ^{235}U , ^{238}U , $^{239+240}\text{Pu}$ and ^{241}Am on 5–17 bottles taken at random. Gamma-spectrometric measurements were performed on 100 g of mussel. The massic activities of ^{235}U , ^{238}U , $^{239+240}\text{Pu}$ and ^{241}Am were determined by ICP-MS and alpha-spectrometry on 0.5–100 g of mussel sample. Homogeneity was determined using one-way analysis of variance. The coefficient of variation was below 15% for gamma and alpha-spectrometrically determined radionuclides (with massic activities 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.

An additional homogeneity test for major and trace elements (P, S, Cl, K, Ca, Fe, Ni, Cu, Zn, As, Br, Sr, I, Ba, Pb) for the mussel sample was done by XFR analysis of 4 g samples. The coefficient of variation was below 10% for XRF determined elements.

Radionuclides with certified values

Only four radionuclides ^{40}K , ^{234}U , ^{238}U and $^{239+240}\text{Pu}$ 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 and their expanded uncertainties are given in Table 1. The evaluation results in order of ascending massic activities, the distribution of medians and corresponding confidence intervals (95%) are shown in Figs. 2, 3, 4, 5.

^{40}K : Gamma-spectrometry was mostly used by participants to determine ^{40}K . The data representing 21 laboratory means were used in the certification process. The Z-score

Table 1 Certified mass activities in IAEA-437 mussel from the Mediterranean Sea (Reference date: 1 November 2003)

Radionuclide	Mean \pm SD (Bq kg ⁻¹ dw)	Median (Bq kg ⁻¹ dw)	Expanded uncertainty (Bq kg ⁻¹ dw)	95% Confidence interval (Bq kg ⁻¹ dw)	N ^a	N ^b
⁴⁰ K	373 \pm 20	373	9	360–380	21	91
²³⁴ U	2.3 \pm 0.1	2.3	0.06	2.2–2.4	9	42
²³⁸ U	1.86 \pm 0.09	1.87	0.05	1.80–1.92	14	57
²³⁹⁺²⁴⁰ Pu	0.0078 \pm 0.0006	0.0076	0.0004	0.0071–0.0082	11	45

N^a: number of accepted laboratory means which were used to calculate the certified massic activities, the expanded uncertainty with a coverage factor of $k = 2$ and the corresponding confidence intervals. N^b: total number of assays

Fig. 2 Data evaluation for ⁴⁰K in IAEA-437. The median (solid line) and corresponding 95% confidence intervals (dashed lines) are shown. The error bars correspond to the combined uncertainty reported by a laboratory

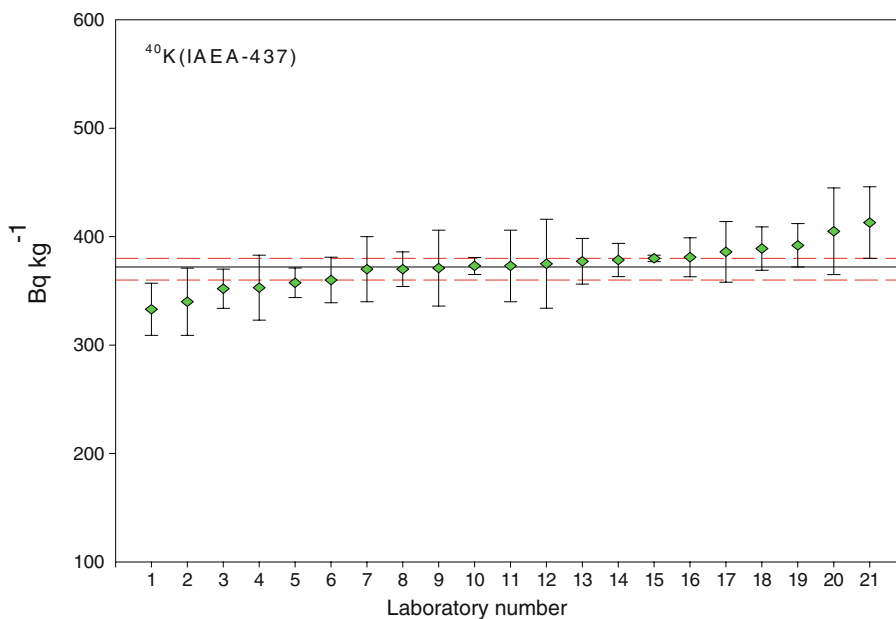
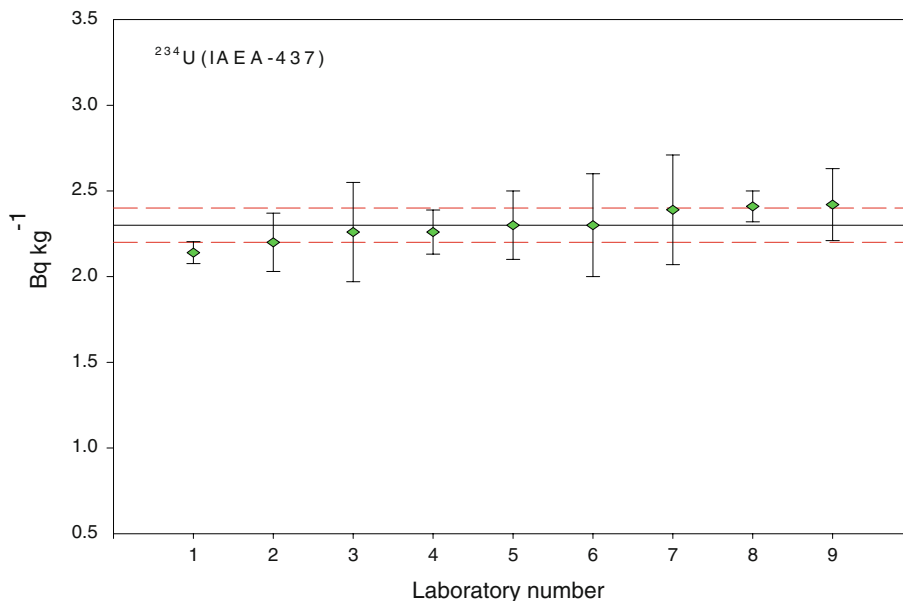


Fig. 3 Data evaluation for ²³⁴U in IAEA-437. The median (solid line) and corresponding 95% confidence intervals (dashed lines) are shown. The error bars correspond to the combined uncertainty reported by a laboratory



values were below 2 showing good performance by the laboratories (Fig. 1). The data show a good homogeneity, falling less than two standard deviations from the

distribution mean (Fig. 2). The median given as the certified value is 373 Bq kg⁻¹ dw, 95% confidence interval is 360–380 Bq kg⁻¹ dw.

Fig. 4 Data evaluation for ^{238}U in IAEA-437. The median (*solid line*) and corresponding 95% confidence intervals (*dashed lines*) are shown. The error bars correspond to the combined uncertainty reported by a laboratory

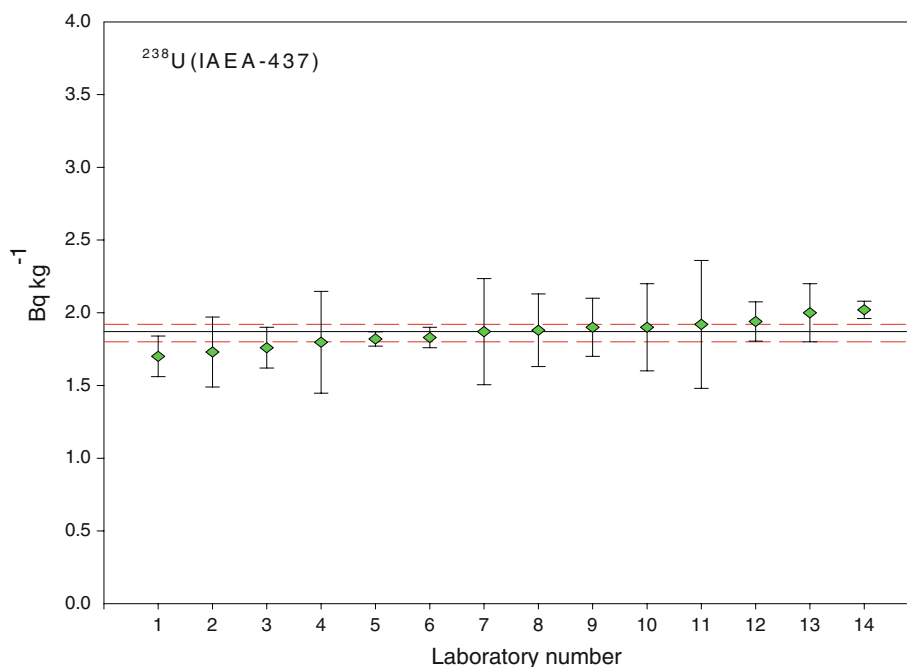
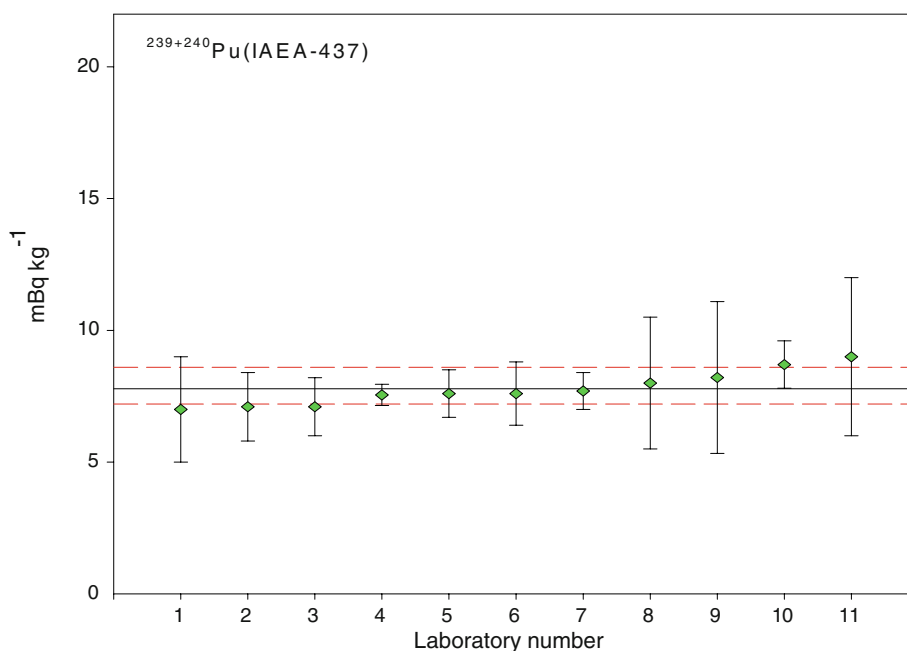


Fig. 5 Data evaluation for $^{239+240}\text{Pu}$ in IAEA-437. The median (*solid line*) and corresponding 95% confidence intervals (*dashed lines*) are shown. The error bars corresponding to the combined uncertainty reported by laboratory



^{234}U : Total dissolution followed by alpha-spectrometry, with the exception of one result obtained by ICP-MS, were used in the analysis. Nine laboratory means were accepted to be used in the certification process (Fig. 3). The Z-score values were below 1.5 showing very good performance of the laboratories. The median, given as the certified value is $2.3 \text{ Bq kg}^{-1} \text{ dw}$ (95% confidence interval is $2.2\text{--}2.4 \text{ Bq kg}^{-1} \text{ dw}$).

^{238}U : Data representing 14 laboratory means were used in the certification process (Fig. 4), of which five results were obtained by gamma-spectrometry including

underground low background spectrometry, six results were obtained by alpha-spectrometry and three by ICP-MS with prior radiochemical purification. The Z-score values were below 1.8 showing good performance by the laboratories. The median, given as the certified value is $1.87 \text{ Bq kg}^{-1} \text{ dw}$ (95% confidence interval is $1.80\text{--}1.92 \text{ Bq kg}^{-1} \text{ dw}$).

$^{239+240}\text{Pu}$: The majority of participants used conventional radiochemical methods based on sample treatment, ion-exchange separation followed by electro-deposition and alpha-spectrometry. Some laboratories combined ion-exchange separation with liquid-liquid extraction, or used

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

Radionuclide	Mean \pm SD (Bq kg ⁻¹ dw)	Median (Bq kg ⁻¹ dw)	Expanded uncertainty (Bq kg ⁻¹ dw)	95% Confidence interval (Bq kg ⁻¹ dw)	<i>N</i> ^a	<i>N</i> ^b
¹³⁷ Cs	0.16 \pm 0.06	0.14	0.04	0.11–0.23	9	67
²¹⁰ Po(²¹⁰ Pb)	4.6 \pm 1.1	4.2	0.6	4.0–5.4	26	71
²²⁶ Ra	0.26 \pm 0.09	0.27	0.06	0.21–0.31	9	48
²²⁸ Ra	1.44 \pm 0.29	1.48	0.22	1.00–1.80	7	24
²²⁸ Th	0.79 \pm 0.17	0.79	0.11	0.71–0.96	9	58
²³⁰ Th	0.21 \pm 0.09	0.16	0.08	0.15–0.40	6	21
²³² Th	0.13 \pm 0.05	0.11	0.03	0.09–0.16	8	30
²³⁵ U	0.09 \pm 0.02	0.09	0.01	0.07–0.11	9	34
²⁴¹ Am ^a	0.019 \pm 0.010	0.020	0.006	0.008–0.034	5	39

N^a: number of accepted laboratory means which were used to calculate the information mass activities, the expanded uncertainty with a coverage factor of $k = 2$ and the corresponding confidence intervals. *N*^b: total number of assays

^a The values should be corrected for in-growth from ²⁴¹Pu

only liquid–liquid extraction. Resins (a single TRU columns or double UTEVA + TRU columns) for the separation and subsequent electro-deposition for alpha-spectrometry (²³⁸Pu, ²³⁹⁺²⁴⁰Pu) and/or for direct ICP-MS and AMS (Accelerator Mass Spectrometry) analysis (²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu) were also used. The samples for mass spectrometry analyses were either leached from stainless steel discs after alpha-spectrometry measurements, or in some case analysed directly in mass spectrometers. A reasonable agreement was obtained between the alpha-spectrometry and mass spectrometry results. Eleven data sets obtained by alpha-spectrometry, ICP-MS and AMS were included in the evaluation (Fig. 5). The data show a good homogeneity, within two standard deviations of the distribution mean. The *Z*-score values were below 1.9 showing very good performances of the laboratories. The median, given as the certified value is 7.6 mBq kg⁻¹ dw (95% confidence interval is 7.1–8.2 mBq kg⁻¹ dw).

Radionuclides with information values

Information values are given for nine 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 and their expanded uncertainties are given in Table 2.

¹³⁷Cs: The data set was evaluated using nine laboratory means, which were obtained by gamma-spectrometry including the ones obtained by the CELLAR group. The data were homogenous within two standard deviations of the distribution mean. The *Z*-score values were below 1.7, showing good performance of the laboratories. The

median, given as the information value is 0.14 Bq kg⁻¹ dw (95% confidence interval is 0.11–0.23 Bq kg⁻¹ dw).

²¹⁰Pb(²¹⁰Po): Ten and 16 laboratory means were available for ²¹⁰Pb and ²¹⁰Po, respectively. Mostly gamma- and alpha-spectrometry (by ²¹⁰Po in-growth) were used for ²¹⁰Pb determination, and alpha-spectrometry for ²¹⁰Po determination. The precision of alpha-spectrometry was much better than that obtained by gamma-spectrometry. Taking into account the time elapsed between collection and analysis of the mussel sample, we assumed that ²¹⁰Pb and ²¹⁰Po were in secular equilibrium. The *Z*-score is below 1.8. The median given as the information value is 4.2 Bq kg⁻¹ dw (95% confidence interval is 4.0–5.4 Bq kg⁻¹ dw). The users should notice that relative uncertainty for ²¹⁰Pb(²¹⁰Po) determination is high and two corrections for their determination should be applied during a storage time: (i) a correction for ²¹⁰Pb decay (the half-life 22.2 y) and (ii) a correction for in-growth of ²¹⁰Pb from ²²⁶Ra.

²²⁶Ra: Nine laboratory means were evaluated. All ²²⁶Ra results were determined using gamma-spectrometry (including ²¹⁴Bi measurements) on which some laboratories still face a difficulty to determine this radionuclide due to improper calibration, background estimation and possible interferences in gamma-spectra. The *Z*-score values were below 1.9. The median given as information value is 0.27 Bq kg⁻¹ dw (95% confidence interval is 0.21–0.31 Bq kg⁻¹ dw).

²²⁸Ra: Seven laboratory means obtained by gamma-spectrometry were evaluated. The median given as information value is 1.48 Bq kg⁻¹ dw (95% confidence interval is 1.00–1.80 kg⁻¹ dw).

²²⁸Th: Nine laboratory means were obtained by gamma-spectrometry. The median given as information value is

0.79 Bq kg⁻¹ dw (95% confidence interval is 0.71–0.96 Bq kg⁻¹ dw). This is not really close to the ²²⁸Ra value (²²⁸Ra and ²²⁸Th are expected to be in equilibrium), however, because of different behaviour and bioavailability of these elements can make difference.

²³⁰Th: Six laboratory means were obtained by both gamma- and alpha-spectrometry. The median given as information value is 0.16 Bq kg⁻¹ dw (95% confidence interval is 0.15–0.40 Bq kg⁻¹ dw). This is close to the ²²⁶Ra result, as ²²⁶Ra and ²³⁰Th are expected to be in equilibrium.

²³²Th: Different techniques such as gamma-spectrometry, alpha-spectrometry and mass spectrometry were used in ²³²Th analyses, but those obtained by gamma-spectrometry are considered as outliers. Within eight laboratory means, two obtained by mass spectrometry and six by alpha-spectrometry were considered. The Z-score values are below 1.5, showing good performance of laboratories. The median given as information value is 0.11 Bq kg⁻¹ dw (95% confidence interval is 0.09–0.16 Bq kg⁻¹ dw).

²³⁵U: One result obtained by underground gamma-spectrometry and eight by alpha-spectrometry were used in the evaluation. The Z-score values were below 1.7. The median given as information value is 0.09 Bq kg⁻¹ dw (95% confidence interval is 0.07–0.11 Bq kg⁻¹ dw).

²⁴¹Am: Five results obtained by alpha-spectrometry were used for data evaluation. The Z-score values were below 1.5. The median given as information value is 20 mBq kg⁻¹ dw (95% confidence interval is 8–34 mBq kg⁻¹ dw).

Less frequently reported radionuclides

⁹⁰Sr: Three laboratory means obtained by radiochemical treatment (mostly precipitation, ⁹⁰Y extraction) and gas or scintillation counting were available for the evaluation. The average massic activity is 0.092 ± 0.003 Bq kg⁻¹ dw.

¹²⁹I: Three laboratory means obtained by AMS were available for the evaluation. The average massic activity is 0.8 ± 0.1 mBq kg⁻¹ dw.

²³⁸Pu: Three laboratory means obtained by alpha-spectrometry were available for the evaluation. The average massic activity is 0.47 ± 0.7 mBq kg⁻¹ dw.

²³⁹Pu: Two laboratory means obtained by ICP-MS were available for the evaluation. The average massic activity is 4.4 ± 0.4 mBq kg⁻¹ dw.

²⁴⁰Pu: Two laboratory means obtained by ICP-MS were available for the evaluation. The average massic activity is 3.0 ± 0.3 mBq kg⁻¹ dw. It would be valuable to notice that the combined ²³⁹⁺²⁴⁰Pu value of 7.4 ± 0.4 mBq kg⁻¹ dw obtained by these two laboratories using ICP-MS is in agreement with ²³⁹⁺²⁴⁰Pu values obtained by both alpha-spectrometry and ICP-MS methods mentioned above (Table 2).

Conclusion

A mussel sample from the Mediterranean Sea collected in 2003 has been certified for radionuclides according to ISO certification criteria. The sample has been issued as the IAEA-437 reference material.

The IAEA-437 has been certified for four radionuclides (⁴⁰K, ²³⁴U, ²³⁸U and ²³⁹⁺²⁴⁰Pu). Information values have been obtained for nine 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. The RM is available from IAEA in 200 g units and can be ordered through IAEA website (www.iaea.org).

Acknowledgements 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 Sûreté 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.

References

- Povinec PP, Pham MK (2001) *J Radioanal Nucl Chem* 248:211
- Sanchez-Cabeza JA, Pham MK, Povinec PP (2008) *J Environ Rad* 99:1680
- International Standard Organization (ISO) (2006) Guide 35 certification of reference materials—general and statistical principles. ISO, Geneva
- Povinec PP, Badia C, Baeza A, Barci-Funel G, Bergan TD, Bojanowski R, Burnette W, Eikenberg J, Fifield LK, Serradell V, Gastaud J, Goroncy I, Herrmann J, Hotchkis MAC, Ikaheimonen TK, Jakobson E, Kalimbadjan J, La Rosa JJ, Lee S-H, Liong Wee Kwong L, Lueng WM, Nielsen SP, Noureddine A, Pham MK, Rohou J-N, Sanchez-Cabeza J-A, Suomela J, Suplinska M, Wyse E (2002) *J Radioanal Nucl Chem* 251(3):369
- Pham MK, Sanchez-Cabeza JA, Povinec PP, Arnold D, Benmansour M, Bojanowski R, Carvalho F, Kim CK, Esposito M, Gastaud J, Ham GJ, Hegde AG, Holm E, Jaskierowicz D, Kanisch G, Llaurodo M, La Rosa J, Lee SH, Gascó C, Liong Wee Kwong L, Le Petit G, Maruo Y, Nielsen SP, Oh JS, Oregoni B, Palomares J, Pettersson HBL, Rulik P, Ryan T, Sandor T, Satake H, Schikowski J, Skwarzec B, Smedley PA, Vajda N, Wyse E (2006) *Appl Radiat Isot* 4:1253–1259
- Povinec PP, Pham MK et al (2007) *J Radioanal Nucl Chem* 273:383
- Pham MK, Sanchez-Cabeza JA, Povinec PP, Andor K, Arnold D, Benmansour M, Bikit I, Carvalho FP, Dimitrova K, Edrev ZH, Engeler C, Fouche FJ, Garcia-Orellana J, Gascó C, Gastaud J, Gudelis A, Hancock G, Holm E, Legarda F, Ikaheimonen TK, Ilchmann C, Jenkinson AV, Kanisch G, Kis-Benedek G, Kleinschmidt R, Koukouliou V, Kuhar B, La Rosa J, Lee SH, LePetit

- G, Levy-Palomo I, Liong Wee Kwong L, Llauro M, Maringer FJ, Meyer M, Michalik B, Michel H, Nies H, Nour S, Oh JS, Oregioni B, Palomares J, Pantelic G, Pfitzner J, Pilvio R, Puskeiler L, Satake H, Schikowski J, Vitorovic G, Woodhead D, Wyse E (2008) *Appl Radiat Isot* 66:1711
8. Thebault H, Rodriguez Y Baena AM, Andral B, Barisic D, Albaladejo JB, Bologna AS, Boudjenoun R, Delfanti R, Egorov VN, El Khoukhi T, Florou H, Kniewald G, Noureddine A, Patrascu V, Pham MK, Scarpato A, Stokozov NA, Topcuoglu S, Warnau M (2008) *Mar Pollut Bull* 57:801
 9. Pham MK, Sanchez-Cabeza JA (2007) Report on the worldwide intercomparison exercise IAEA-437: radionuclides in Mediterranean mussel. IAEA/AL/173, IAEA/MEL/79. IAEA, Monaco, 37 pp
 10. International Standard Organization (ISO) (1993) Guide to the expression of uncertainty in measurement. ISO, Geneva
 11. Taylor BN, Kuyatt CE (1994) Guidelines for evaluating and expressing the uncertainty of NIST measurement results; NIST technical note 1297, Washington DC, 20 pp
 12. Thompson M, Ellison SLR, Wood R (2006) *J Pure Appl Chem* 78(1):145
 13. International Standard Organization (ISO) (1997) Guide 43 proficiency testing and interlaboratory comparisons. ISO/IEC, Geneva
 14. Cofino WP, Wells DE (1994) *Mar Pollut Bull* 29:149