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Certified reference materials for radionuclides in Bikini Atoll sediment (IAEA-410) and Pacific Ocean sediment (IAEA-412)

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HIGHLIGHTS

- Two new reference materials for radionuclides in marine sediments characterized.
- Massic activities of natural and anthropogenic radionuclides were certified.
- Aimed at QA/QC analysis and method validation for radionuclides in marine sediments.

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ABSTRACT

The preparation and characterization of certified reference materials (CRMs) for radionuclide content in sediments collected offshore of Bikini Atoll (IAEA-410) and in the open northwest Pacific Ocean (IAEA-412) are described and the results of the certification process are presented. The certified radionuclides include: ^{40}K, ^{210}Pb (^{210}Po), ^{226}Ra, ^{228}Ra, ^{228}Th, ^{232}Th, ^{234}U, ^{238}U, ^{239}Pu, $^{239+240}$Pu and ^{241}Am for IAEA-410 and ^{40}K, ^{137}Cs, ^{210}Pb (^{210}Po), ^{226}Ra, ^{228}Ra, ^{228}Th, ^{232}Th, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu and $^{239+240}$Pu for IAEA-412. The CRMs can be used for quality assurance and quality control purposes in the analysis of radionuclides in sediments, for development and validation of analytical methods and for staff training.

1. Introduction

Accurate and precise determination of radionuclide concentrations in marine samples is important for marine radioactivity assessments and for the study of oceanographic processes. To ensure such data is of suitable quality for these purposes, the IAEA´s Environment Laboratories (IAEA-EL) in Monaco have conducted inter-laboratory comparison exercises on determinations of radionuclides in marine samples for almost fifty years as part of their contribution to the IAE's programme of Analytical Quality Control Service (AQCS), now renamed as '*IAEA's Reference Products for Science and Trade*' (Povinec and Pham, 2001; Sanchez-Cabeza et al., 2008). An important part of this activity was the production of reference materials (RMs), which were usually products of worldwide inter-laboratory comparison exercises. The IAEA's Reference Products for Science and Trade programme has recently focused on the production of certified reference materials (CRMs) (ISO, 2006; Povinec and Pham, 2001; Sanchez-Cabeza et al., 2008; Pham et al., 2006, 2008, 2014) to improve the accuracy and precision of analyses, and to demonstrate traceability to appropriate national and international standards. Certified Reference Materials are essential for method development and validation; they can indicate the need to improve or change existing methods as well as the need for further staff training. In fact, analytical validation methods should only be accepted on the basis of inter-laboratory comparison and proficiency tests performed on selected CRMs (ISO/IEC, 2005; Povinec and Pham, 2001; Sanchez-Cabeza et al., 2008). Reference materials and CRMs should be available for all important marine matrices, such as sediment, biota, sea water, suspended matter, etc.

The production of a new reference material is a long process, including the identification of needs, sample collection, pretreatment, 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 uncertainties), and finally issue.

This work was performed on sediment materials collected offshore from Bikini Atoll and in the open northwest Pacific Ocean. Participating laboratories were requested to determine as many radionuclides as possible by γ-spectrometry, α-spectrometry, β-counting and/or mass spectrometry. Characterization study was completed and the materials will be issued as CRMs for radionuclides in sediment matrix.

2. Experimental

2.1. Description of the material

A total mass of 60 kg of wet sediment sample was collected by box coring down to 24 m of sediment depth at 11°26'N, 165°20'E (water depth 4500 m) offshore of Bikini Atoll on the 10th November 1997. Similarly, 200 kg of wet sediment sample was sampled by box coring down to 35 m of sediment depth at 22°22'N, 152°40'E (water depth 5600 m) in the northwest Pacific Ocean on the 16th November 1997. In both cases a sub-core sampling from the sediment box was carried out using plastic tubes of 10 cm in diameter. Detailed information on sampling has been published elsewhere (Povinec et al., 2003).

The sediments were air dried and then dried at 75 °C in an oven. The samples were then ground, sieved through a 250 μm sieve, homogenized by mixing under nitrogen, bottled and sealed in glass bottles (100 g units) and coded as IAEA-410 for the Bikini Atoll sediment and in polyethylene flasks (100 g units) and coded as IAEA-412 for the Pacific Ocean sediment. In total, 150 bottles of IAEA-410 and 175 bottles of IAEA-412 were produced. All bottles were sterilized in a 25 kGy radiation field (^{60}Co). The average moisture content of the material was determined by drying several test portions of 1 g in an oven at 75 °C for 24 h, and was found to be 2–3%.

2.2. Sample dispatch and data feedback

The test materials were distributed to the selective thirty laboratories in February 2013. Each participant received a single bottle of each type of sediment. Twenty-seven laboratories reported their results. For each radionuclide analysed, the following information was requested from participating laboratories:

- average weight of sample used for analysis;
- number of analyses;
- massic activity (Bq kg^{-1}) corrected for blank, background, etc.;
- estimation of the combined uncertainties;
- description of chemical procedures and counting equipment;
- standard solutions used for analysis;
- chemical recoveries (if any), and
- counting time and decay corrections.

The reference date for reporting activities was set at 1st January 2013.

2.3. Data treatment and criteria for certification

The certification process was carried out following the ISO Guide 35 (ISO, 2006) and ISO Guide 34 (ISO, 2009). The obtained data were first checked for compliance with the certification requirements, and then for their validity based on technical reasoning. All accepted set of results were used for robust statistical calculation. Robust statistics as described in ISO Guide 13528 (ISO, 2005) were used for the determination of the assigned values, where the robust mean and robust standard deviations were calculated as per Algorithm A as described in Annex C.1 of ISO 13528.

A certified value was assigned when at least 5 independent

results were available and the relative expanded uncertainty was less than 15%. For the radionuclides where these criteria were not fulfilled, the robust mean and relative expanded uncertainties were given only as information values.

3. Results and discussion

3.1. Homogeneity tests

For both sediments, the material's homogeneity was evaluated for ^{40}K, ^{137}Cs, ^{210}Pb (^{210}Po), ^{214}Bi, ^{214}Pb, ^{226}Ra, ^{228}Th, ^{230}Th, ^{232}Th, ^{238}U, ^{235}U and $^{239+240}$Pu activities based on measurements by high-resolution low-background γ-spectrometry, α-spectrometry and mass spectrometry. The first homogeneity test between bottles was done for 14 bottles chosen randomly at different masses of samples (100 g for γ-spectrometry and between 1.5 and 10 g for α-spectrometry and mass spectrometry). The second test within bottles was done for another 10 aliquots (of one bottle) at 0.5–3 g of sample for ^{239}Pu and ^{240}Pu analysis by accelerator mass spectrometry (AMS) and 0.5 g of material for ^{238}U and ^{235}U determination using ICP-MS, respectively. Homogeneity was tested by using one-way analysis of variance. The coefficient variation was below 15% for all radionuclides determined, depending on their activity range. The between samples variances showed no significant differences from the within sample variances for the radionuclides tested. The material can be considered homogeneous based on the heterogeneity tests at the mass levels down to 0.5–100 g depending on radionuclides of interest. An additional homogeneity test for major and trace elements (P, S, Cl, K, Ca, Fe, Ni, Cu, Zn, As, Br, Sr, I, Ba and Pb) was done by XRF (X-ray fluorescence) analysis on 4 g samples. The coefficient of variation was below 10% for XRF determined elements.

3.2. Radionuclides with certified and information values

3.2.1. IAEA-410 (sediment from Bikini Atoll)

The list of certified and information values for different radionuclides in IAEA-410 is shown in Table 1, where certified values are given for ^{40}K, ^{210}Pb (^{210}Po), ^{226}Ra, ^{228}Ra, ^{228}Th, ^{232}Th, ^{234}U, ^{238}U, ^{239}Pu, $^{239+240}$Pu and ^{241}Am, and information values are given for ^{137}Cs, ^{230}Th, ^{234}Th, ^{235}U, ^{238}Pu and ^{240}Pu. As the sample was collected at offshore the Bikini Atoll, elevated levels of plutonium and americium isotopes were expected mostly due to the influence of atmospheric nuclear weapons tests carried out (by the US between 1946 and 1958, with the first megaton detonation in 1952 (Carter and Moghissi, 1977) on Bikini and Enewetak Atolls.

Table 1
Massic activities (certified and informative), in Bq kg^{-1}, in IAEA-410 Sediment from Bikini Atoll. (Reference date: 1 January 2013).

Radionuclide	Certified value[a] [Bq kg^{-1}]	Expanded uncertainty[b] [Bq kg^{-1}]
^{40}K	115	6
^{210}Pb(^{210}Po)[c]	217	14
^{226}Ra	194	22
^{228}Ra	8.1	0.6
^{228}Th	8.3	1.0
^{232}Th	8.7	1.2
^{234}U	10.0	1.4
^{238}U	10.1	1.4
^{239}Pu	2.42	0.26
$^{239+240}$Pu	4.68	0.48
^{241}Am	4.12	0.28
	Information value	
^{137}Cs	0.186	0.034
^{230}Th	4.4×10^2	0.8×10^2
^{234}Th	10.7	2.8
^{235}U	0.56	0.16
^{238}Pu	0.072	0.020
^{240}Pu	2.27	0.40

[a] This value is the robust mean and is reported on a dry mass basis.
[b] Expanded uncertainty with a coverage factor $k=2$.
[c] ^{210}Pb and ^{210}Po are considered to be in equilibrium.

Table 2
Massic activities (certified and informative), in Bq kg^{-1}, in in IAEA-412 Sediment from the Pacific Ocean. (Reference date: 1 January 2013).

Radionuclide	Certified value[a] [Bq kg^{-1}]	Expanded uncertainty[b] [Bq kg^{-1}]
^{40}K	561	14
^{137}Cs	6.50	0.28
^{210}Pb(^{210}Po)[c]	100.9	4.4
^{226}Ra	27.4	2.6
^{228}Ra	36.7	1.8
^{228}Th	38.3	3.8
^{232}Th	36.3	2.0
^{235}U	1.38	0.20
^{238}U	31.2	3.2
^{239}Pu	0.358	0.016
^{240}Pu	0.240	0.016
$^{239+240}$Pu	0.611	0.028
	Information value	
^{230}Th	26	6
^{234}Th	37	8
^{234}U	29	6
^{238}Pu	0.0199	0.0040
^{241}Am	0.30	0.10

[a] This value is the robust mean and is reported on a dry mass basis.
[b] Expanded uncertainty with a coverage factor $k=2$.
[c] ^{210}Pb and ^{210}Po are considered to be in equilibrium.

3.2.2. IAEA-412 (sediment from Pacific Ocean)

The list of certified and information values for radionuclides in IAEA-412 is shown in Table 2, where certified values are given for ^{40}K, ^{137}Cs, ^{210}Pb (^{210}Po), ^{226}Ra, ^{228}Ra, ^{228}Th, ^{232}Th, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu and $^{239+240}$Pu radionuclides, and the information values are given for ^{230}Th, ^{234}Th, ^{234}U, ^{238}Pu and ^{241}Am. As the sample was collected in the northwest Pacific Ocean, elevated levels of long-lived anthropogenic radionuclide such as ^{137}Cs, ^{239}Pu and ^{240}Pu were expected mostly due to the influence of atmospheric nuclear weapons tests carried out on Bikini and Enewetak Atolls (Carter and Moghissi, 1977). However, the $^{239+240}$Pu concentration in this sediment sample is much lower compared to the one collected offshore Bikini Atoll (Table 1 and Table 2) and vice versa, the ^{137}Cs concentration in sediment sample IAEA-412 is higher than the one found in IAEA-410, showing that plutonium is much more reactive in sediment than cesium (or both radionuclides have been transported by Kuroshio current from Atolls (with the biggest test named Bravo, 15 Mt TNT) to the northwest Pacific).

It is worthy to notice that for $^{239+240}$Pu, a reasonable agreement was obtained between the results obtained by alpha-particle spectrometry and mass spectrometry for both samples: The combined ^{239}Pu and ^{240}Pu values obtained by the laboratories using ICP-MS and AMS were in agreement with the $^{239+240}$Pu values obtained by alpha-spectrometry (Table 1 and Table 2).

3.3. Disequilibrium in natural decay series

Disequilibrium was found for the ^{238}U series, especially for sediment from Bikini Atoll with ^{230}Th levels much higher than ^{234}U, ^{226}Ra and ^{210}Pb (^{210}Po) levels. This is expected, as thorium is a particle reactive element and its bioavailability is relatively low. No disequilibria were found for the ^{232}Th thorium series in any of the two sediments.

4. Conclusion

The certification process, carried out following the ISO Guides 34 and 35, for new reference materials for radionuclides in sediments collected from the Bikini Atoll (IAEA-410) and Pacific Ocean (IAEA-412) has been performed through characterization study. The CRMs can be used for Quality Assurance/Quality Control of analysis of radionuclides in sediments, as well as for development and validation of analytical methods, and for staff training purposes. The CRMs are available from the IAEA in 100 g units and can be ordered through the IAEA website (http://nucleus.iaea.org/rpst/).

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