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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 10$^{th}$ 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