Poster Presentation

RADIONUCLIDES OF NATURAL ORIGIN IN A BRAZILIAN MUSSEL REFERENCE MATERIAL

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Abstract

Certified reference materials are important tools for the quality assurance of analytical results. However there are several constraints for their widespread use in developing countries such as lack of technological development or difficult access to imported goods. Another issue is that analyte level differences between imported certified reference materials and local laboratory samples may be a concern in the measurement process. This contribution presents the activity concentrations of ^{234}U, ^{235}U, ^{238}U and ^{232}Th determined by alpha spectrometry after a radiochemical separation procedure and ^{40}K and ^{210}Pb determined by gamma-ray spectrometry in a *Perna perna* mussel reference material produced in Brazil. The activity concentrations obtained were included as information values in the certification process of the reference material.

1. INTRODUCTION

Certified reference materials are used for quality assurance of analytical results, method validation, quality control and to establish the metrological traceability of measurement results [1]. Their production is a complex task involving several steps such as preliminary tests, sampling, sample preparation, particle size and humidity adjustment, property characterization and certification [2]. Due care in the production process is essential in order to guarantee that the properties of interest are well established and that certified values are accompanied by appropriate expanded uncertainties that take into consideration not only the characterization process but also the stability and the homogeneity of the material [2].

Biological reference materials prepared from animal tissues such as mussels and oysters are useful in the quality assurance of environmental and nutritional studies. These materials usually present certified values for chemical elements and species, organic pollutants, toxins and microorganisms. However, few biological reference materials are available for naturally occuring and/or artificial radionuclides such as IAEA-437 mussel and IAEA-414 fish flesh reference materials [3–5].

Uranium and thorium series radionuclides are ubiquous in the marine environment. They may originate from natural processes as well as from anthropogenic activities such as mining industries and disposal of radium rich products such as phosphogypsum [6]. These radionuclides are prone to bioaccumulation in marine organisms and have implications for environmental biomonitoring studies [7]. Observed concentrations of the radionuclides ^{210}Po, ^{210}Pb or ^{232}Th in the biota are subject to environmental conditions as the salinity or temperature of marine water, season of the year and to biological parameters such as size (shell length and soft tissue weight) or sexual maturation, which complicates result interpretation [7, 8].

From a human health perspective, the determination of naturally occuring radionuclides and associated activity concentrations, particularly for alpha emitters, is important for the estimation of the intake levels from the consumption of marine foodstuffs such as mussels or oysters [9, 10].

This study presents the activity concentrations of ^{234}U, ^{235}U, ^{238}U, ^{232}Th, ^{210}Pb and ^{40}K in a *Perna perna* mussel reference material produced in Brazil as a contribution to the quality assurance of radionuclide measurements performed in the country.

2. METHODS

2.1. Mussel reference material production

For the preparation of the Brazilian mussel reference material, 164 kg of *Perna perna* (Linnaeus, 1758) mussels were purchased from a single producer, from Cocanha Beach in Caraguatatuba City, São Paulo State north shore. Soft tissues were homogenized in a domestic blender adapted with titanium blades. This process yielded approximately 36 kg of material which was freeze dried in a Thermo Savant Modulyo D freeze dryer, resulting in 5.4 kg of freeze dried material. The material was ground in the blender and the portion with particle size above 105 μm was discarded. The powder was homogenized for 72 h in a Y type homogenizer. Then the bulk material was bottled in 171 bottles containing approximately 13 g each. Afterwards the material was irradiated with a gamma dose of 5 kGy to enhance its stability [11].

2.2. Alpha spectrometry

The alpha spectrometry methods used are described in detail elsewhere [12–14]. Subsamples of approximately 5 g were burnt to ash at 450°C for 24 h in a muffle furnace. Then the ash samples were dissolved with three acids (nitric, perchloric, and hydrofluoric). The solution was evaporated and reconstituted with 8 mol/L nitric acid.

After sample digestion, ^{229}Th and ^{232}U radiotracers were added in order to determine the chemical recuperation. Thorium and uranium radionuclides were separated and purified using specific ion exchange resins (DOWEX 1x2 and UTEVA, respectively) for sequential chromatography extractions and were electrodeposited on polished silver plates. An Alpha Analyst spectrometer with 12 passivated implanted planar silicon (PIPS) detectors (counting efficiency 18%), and Genie 2000/Alpha Analyst spectroscopy systems, from Canberra Industries was used for radionuclide quantification. Samples were measured for 200 000 s. Alpha particle energies of 4.90 MeV for the ^{229}Th tracer and 4.01 MeV for ^{232}Th were used to quantify thorium. Alpha particle energies of 4.31 MeV for the ^{232}U tracer, 4.74 MeV for ^{234}U, 4.47 MeV for ^{235}U, and 4.19 MeV for ^{238}U were used to quantify uranium.

For expanded uncertanties estimation, the GUM software was employed using parameters associated with alpha spectrometry and the main uncertainty sources were identified for this radioanalytical method. Most sources of uncertainty in radioanalytical measurements, such as the sources in the intercomparison exercise, were classified as a normal probability distribution. The uncertainty of the detector efficiency was estimated from a series of repeated observations by calculating the standard deviation of the mean (approximately 20 experimental measurements for uranium and 20 experimental measurements for thorium) [15, 16].

2.3. Gamma-ray spectrometry

Reference material subsamples of approximately 30 g were kept in sealed plastic vials. A Canberra model GX4510 high purity germanium (HPGe) detector was used for ^{40}K detection via the 1461 keV photopeak and ^{210}Pb was detected using the X ray characteristic photopeak at 46.5 keV after a self-absorption correction. Genie 2000 software was used for data acquisition and treatment. The spectrometer was calibrated in energy using ^{152}Eu and ^{210}Pb certified sources (IRD/CNEN-RJ) and the calibration in efficiency was performed using standard solutions of the same radionuclides added to alumina Suprapur, kept in a vial with the same geometry as that of the samples. The average counting period was 250 000 s.

3. RESULTS AND DISCUSSION

Table 1 presents activity concentrations obtained for the mussel reference material on a dry mass basis. As results were reported by only one laboratory, the values were considered as informative rather than certified values. It was observed that while the activity concentrations of uranium series radionuclides were of the same order of magnitude as the ones reported for IAEA-437 and IAEA-414 reference materials, ^{40}K and ^{210}Pb presented much lower activity concentrations and ^{232}Th presented activity concentrations approximately 10 times higher if compared with IAEA-437 mussel reference material.

TABLE 1 INFORMATIVE VALUES OF ACTIVITY CONCENTRATION FOR THE MUSSEL REFERENCE MATERIAL (DRY MASS BASIS).

Radionuclide	Activity concentration, Bq/kg
^{40}K	0.0446 ± 0.0031
^{210}Pb	0.106 ± 0.032
^{232}Th	1.59 ± 0.62
^{234}U	1.39 ± 0.52
^{235}U	0.067 ± 0.065
^{238}U	1.25 ± 0.54

Note: Reported uncertainties are expanded uncertainties with a coverage factor $k = 2$ which gives a level of confidence of approximately 95%. Reference date for decay correction: 23 April 2009.

4. CONCLUSIONS

This study presents the informative values for the activity concentration of ^{234}U, ^{235}U, ^{238}U and ^{232}Th determined by alpha spectrometry after a radiochemical separation procedure and activity concentrations of ^{40}K and ^{210}Pb determined by gamma ray spectrometry in a *Perna perna* mussel reference material produced in Brazil. The reference material is intended to be used as a contribution to the quality assurance of radionuclide measurements performed in biological samples of marine origin in the country.

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