Food Chemistry 229 (2017) 159–164

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

A sequential determination of ^{90}Sr and ^{210}Po in food samples

S. Hurtado-Bermudez [a,*], J.L. Mas [b], M. Villa-Alfageme [c]

[a] Centro de Investigación Tecnología e Innovación, CITIUS, Av. Reina Mercedes 4B, 41012 Sevilla, Spain
[b] Dpto. Física Aplicada I, Escuela Universitaria Politécnica, Universidad de Sevilla, Spain
[c] Dpto. Física Aplicada II, ETSIE, Av. Reina Mercedes 4A, Universidad de Sevilla, 41012 Sevilla, Spain

ARTICLE INFO

Article history:
Received 12 June 2016
Received in revised form 8 September 2016
Accepted 16 February 2017
Available online 17 February 2017

Keywords:
^{210}Po
^{90}Sr
Sequential determination
LSC
Alpha-particle spectrometry
Seafood

ABSTRACT

The latest EU Council Regulation 2016/52/Euratom updates the emergency limits on radionuclides in foods including ^{210}Po and ^{90}Sr, two of the most important radionuclides for radiological dose from the ingestion pathway. A novel and straightforward method has been developed for sequential determination of ^{90}Sr and ^{210}Po in food samples using ultra low-level liquid scintillation counting and alpha-particle spectrometry. For ^{90}Sr analysis, the method makes use of stable strontium as yield tracer, and ^{210}Po is determined through self-deposition using ^{209}Po as a yield tracer. The quantification limit for this method is 25.0 and 2.0 Bq kg^{-1} for ^{90}Sr and ^{210}Po, respectively. The proposed radiochemical separation can be completed within 2 days for a batch of 12 samples. The radiochemical procedure was validated by its application for the measurement of IAEA certified reference materials, and through participation in a national intercomparison exercise. Results are also presented in seafood from the Mediterranean coast.

1. Introduction

The EU Council Regulation 2016/52/Euratom, and the regulations of other countries (Health Canada., 2000; U.S. Food and Drug Administration, 2004; FSCJ., 2011) and international organizations (United Nations FAO/WHO, 1995), establish a maximum tolerated concentration of radioactivity in food following a radiological emergency.

Amongst all of the radionuclides included in the EU regulation we focus on ^{210}Po and ^{90}Sr. ^{90}Sr is one of the most important radionuclide of anthropogenic origin in the marine environment. Furthermore, ^{210}Po is one of the most characteristic radionuclide of natural origin presents in marine ecosystems.

In the ^{238}U natural decay series, ^{226}Ra disintegrates in a number of successive short-lived daughter nuclides (^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po) before ^{210}Pb is formed. ^{222}Rn is a gas that is continually emitted from the earth's surface. The daughter products of ^{222}Rn are associated with particles and washed out of the atmosphere into the sea. In the environment, ^{210}Po ($T_{1/2}$: 138.4 days) is an alpha emitter which is mainly produced from the natural decay of ^{210}Pb ($T_{1/2}$: 22.3 years) through the decay of ^{210}Bi ($T_{1/2}$: 5.01 days) (Matthews, Kim, & Martin, 2007).

Additionally industrial activities can release ^{210}Po in the marine environment. During the EU Marina II project, studies regarding the radiological impact of NORM releases on the European marine systems (comprising gas and oil activities) were carried out (Betti et al., 2004). This study found a widespread distribution of ^{210}Po into the food chain through inhalation, direct uptake or ingestion.

Regardless of the origin of ^{210}Po, its measurement and detection in food is crucial because it is one of the most toxic radionuclides (Guérin & Dai, 2014), which gives rise to health impacts on humans and other organisms because it is an alpha-particle emitter, and contributing to most of the radiation dose received by marine life (UNSCEAR., 2008). Specifically, ^{210}Po is preferably accumulated in protein thus permitting its access to the food chain and increasing levels of ^{210}Po in protein-rich diets including seafood and meat (Watson, 1985).

Many methods have been developed for measuring the radioactivity concentration of ^{210}Po (Matthews et al., 2007). Conventional analytical methods are based on alpha-particle spectrometry and usually involve self-deposition on silver discs. In some sample matrices an extraction and separation step are necessary because interferences may appear from different radionuclides resulting in a massive source deposit or low Po recovery (Matthews et al., 2007).

Regarding ^{90}Sr, it has been considered a key radionuclide in a nuclear accident (i.e. recently Fukushima Daiichi NPP on 2011) because of its high generation rate during nuclear reactions. (Habibi, Boulet, Gleizes, Larivière, & Cote, 2015). Furthermore ^{90}Sr has a long biological and nuclear half-life (nuclear $T_{1/2}$: 28.9 years) becoming a hazardous radionuclide due to its similar

* Corresponding author.
E-mail address: shurtado@us.es (S. Hurtado-Bermudez).

http://dx.doi.org/10.1016/j.foodchem.2017.02.077
0308-8146/

metabolism than calcium. ^{90}Y, ^{90}Sr daughter nuclide, emits high-energy beta particles increasing the risk of developing bone cancer through its accumulation in bone tissue. This leads to the need of monitoring the ^{90}Sr content in food, and particularly in seafood, and to quantify the absorbed radiological doses through its ingestion.

The Commission Implementing Regulation (EU) 2016/6 of 5 January 2016 set out special restrictions on the import of food from Japan following the accident at the Fukushima nuclear power plant, and Council Regulation (Euratom) 2016/52 of 15 January 2016 established maximum authorized levels of radioactive contamination of food following a radiological emergency. The need to test additional foodstuffs demands the development of new analytical methods in order to quantify the selected radionuclides.

Many methods have been developed for measuring the radioactivity concentration of ^{90}Sr (Matthews et al., 2007; Vajda & Kim, 2010). The most popular methods used for the detection of ^{90}Sr in environmental samples involve liquid scintillation and proportional counter but they are time-consuming methods (Vajda & Kim, 2010).

The purpose of this work is to establish a sequential analytical method for the determination of ^{210}Po and ^{90}Sr radioisotopes in food. The method is based on the extraction chromatography with Sr-resin, followed by strontium precipitation as oxalate and polonium self-deposition, and finally their determination by liquid scintillation counting and alpha-particle spectrometry. The method validation and quality control of the proposed method was carried out using several reference materials.

2. Materials and methods

2.1. Instrumentation

An ultralow background liquid scintillation spectrometer, Quantulus 1220™ (PerkinElmer, Inc.), was used for Liquid Scintillation Counting (LSC). The detector background is reduced by means of combined passive and active shields. The classification of pulses produced by alpha or beta particles is carried out through a pulse shape analysis (PSA) circuit (Villa, Manjón, & García-León, 2003).

An alpha-spectrometry instrument (Alpha Analyst, Canberra) containing twelve independent chambers, each of them with a Passivated Implanted Planar Silicon (PIPS) detector inside, was utilized for the measurement of polonium sources. Each PIPS detector has a good alpha-peak energy resolution of 18 keV (as Full-Width at Half-Maximum FWHM), and an active surface area of 450 mm^2. The polonium sources were located at 1.5 mm from the PIPS detector in order to get high counting efficiency. Alpha spectrum analysis was performed by using Alpha Analyst software (Villa, Hurtado, Manjón, & García-Tenorio, 2007).

2.2. Reagents and analytical solutions

^{90}Sr samples were prepared for LSC through mixing with scintillation cocktail OptiPhase HiSafe III and placing into polyethylene vials (Packard BioScience).

Deionised water (DI water, Millipore) with 18.0 MΩ cm^{-1} resistivity, and Suprapure grade chemicals (HNO_3, H_2O_2, NH_3OH and HCl from Merck) were utilized for solution matrix matching, samples leaching, and chromatographic isolations, when required. Oxalic and ascorbic acid (Panreac, Spain) were analytical grade. Radiochemical yield was determined through analytical grade strontium nitrate $Sr(NO3)_2$ (Sigma-Aldrich). Chromatographic isolation of ^{210}Po and ^{90}Sr were carried out using 2 mL Sr resin columns (TRISKEM, France) placed on a 12-hole polycarbonate vacuum box with an attached pressure valve.

^{210}Po activity and radiochemical yield determinations were performed using a ^{209}Po standard solution (Eckert & Ziegler) of 100 ± 3 Bq g^{-1} (1366-12). The calibration of the LSC system was carried out with a ^{90}Sr standard solution of 107.1 ± 0.4 Bq g^{-1} (MRC-2006-011) obtained from CIEMAT (Spain).

Finally, the energy calibration of the alpha-particle spectrometer was performed with an electroplated alpha standard source of natural U prepared from an aqueous solution of uranyl nitrate hexahydrate ($UO_2(NO_3)_2{\cdot}6H_2O$) (Panreac, Spain). ^{241}Am standard electroplated source from PTB (Germany) containing 93.3 ± 1.9 Bq of (380–911) was used to determine the counting efficiency for each chamber and located at 1.5 mm from the detector. The obtained values range from 0.245 to 0.263 depending of the chamber. The uncertainty of the counting efficiency was less than 3% within a confidence probability of 95%.

2.3. Certified reference materials

The method presented in this work was validated by the analysis of certified reference materials (CRM) provided by the International Atomic Energy Agency (IAEA). The IAEA-437 is a reference material designed for the determination of anthropogenic and natural radionuclides in mussel (*Mytilus galloprovincialis* species) including ^{210}Po (median value of 4.2 Bq kg^{-1}). The IAEA-330 is a certified reference material for radionuclides in spinach including ^{90}Sr (20.1 ± 2.1 Bq kg^{-1}). And finally, the IAEA-414, a mixed fish species from eastern Irish Sea, is a reference material certified for ^{210}Pb (^{210}Po in equilibrium with a median value of 2.1 Bq kg^{-1}) and ^{90}Sr (with a median value of 0.28 Bq kg^{-1}).

2.4. Samples

Seafood samples (sea urchins, mussels and oysters) were taken along the southern Spanish Atlantic coast (Andalusia) and Ballearic Islands in the year 2015. All samples were stored in bags, kept cool using ice and transported to the laboratory. Then samples were placed in filtered seawater for a 24-h period, and afterwards they were cleaned and shucked with a knife in order to separate the soft parts. Each sample was weighed and then dried to constant weight at 60 °C and weighed again. Finally, the samples were homogenized and stored in plastic bags.

2.5. Analytical procedure

The radiochemical method started with sample pre-treatment consisting of digestion with hydrogen peroxide and nitric acid. The next step was the ^{210}Po and ^{90}Sr isolation using the chromatographic Sr columns. Finally, the ^{210}Po and ^{90}Sr sources were prepared in order to measure them with the appropriate technique. The radiochemical procedure is schematized in Fig. 1 and the steps are detailed as follows:

Step 1. *Pre-treatment of samples.* Firstly, if the samples were not previously lyophilized, they were freeze-dried, determining moisture content through weight loss due to drying, and subsequently ground to powder. Then the food samples were easily dissolved taking care of the operating temperature in order to avoid losses due to polonium volatilisation. It has been reported that polonium losses occur leaching biological materials above 100 °C, and more than 90% of the ^{210}Po may be volatilized if the temperature exceeds 300 °C (Martin & Blanchard, 1969). Therefore, a sequential procedure for simultaneous determination of ^{90}Sr and ^{210}Po should avoid previous sample calcination (at 500–600 °C) utilized in most of ^{90}Sr analysis procedures (Vajda & Kim, 2010).

Consequently a dry weight of 5 g from each food sample was put into a Teflon beaker. The high sample capacity of the proposed pre-treatment step outperforms other analytical techniques such