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Determination of ^{210}Po in low-level wild bilberries reference material for quality control assurance in environmental analysis using extraction chromatography and α-particle spectroscopy

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Abstract: Certified reference materials (CRM) are being widely used for quality control assurance in environmental analysis. For certain CRM, the analytes and/or the range of concentrations are not be available or certified at all. The Joint Research Centre – Institute for Reference Materials and Measurements (JRC-IRMM) of the European Commission has issued a CRM of Wild Berries (IRMM-426) in order to validate radionuclide measurement methods for activity concentrations of the natural radionuclide ^{40}K and the anthropogenic nuclides ^{90}Sr and ^{137}Cs, but not for ^{210}Po. The aim of the work was to determine low-level activity concentration of ^{210}Po in these wild berries. The activity concentration of ^{210}Po was assessed by α-particle spectroscopy after dissolution of the sample by wet digestion and chemical isolation of Po by extraction chromatography. According to the time elapsed since sample collection, the results here shown can be useful not only for ultra low-level analysis of ^{210}Po but also for ^{210}Pb in the reference material.

Keywords: ^{210}Po, wild berries, extraction chromatography, radioactivity in food, α-particle spectroscopy, quality control assurance.

1 Introduction

International regulations provide maximum guidance levels for radioactivity in food after a radiological emergency [1–4]. Following the nuclear accident at the Fukushima Daiichi Nuclear Power Station (NPS) in 2011, there is a need for certified reference materials (CRM) in wild foods subjected to radioactive fallout in order to validate reliable radiochemical methods. For this reason, IRMM has developed a CRM for the activity concentration of ^{40}K and the anthropogenic radionuclides ^{90}Sr and ^{137}Cs in wild bilberries.

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However, the activity concentrations for the natural decay chains are not certified in this matrix. This lack of information in CRMs is usual because they are chosen according to a certain set of targeted analytes. As a consequence, testing the robustness of the analytical techniques for a relatively wide set of target isotopes means in turns using different certified materials and even, sometimes, different sample matrices. As a consequence, the scientific communities are continuously providing additional information on these materials, in such a way that they are not certified (information or recommended values) but can be extremely helpful (see, for example, [5–7]).

Amongst all of the natural radionuclides we focus on ^{210}Po ($T_{1/2}$: 138.4 days), an α 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) [8]. The quantification of ^{210}Po is critical because its application to environmental sciences and dosimetry [9–15].

The purpose of this work is to determine the activity concentration of ^{210}Po in IRMM-426 low-level CRM. A previous radiochemical method was adapted and simplified [16]. The method was based on the extraction chromatography of polonium with Sr-resin, polonium self-deposition, and finally its determination by α-particle spectrometry.

2 Materials and methods

2.1 Instrumentation

An α-spectrometry instrument (Alpha Analyst, Canberra) was used for the measurement of polonium planchets. Each measurement chamber contained a Passivated Implanted Planar Silicon (PIPS) detector with an 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 placed at 1.5 mm from the PIPS detector. Alpha Analyst software were used for α spectrum analysis [17].

2.2 Reagents and analytical solutions

Deionised water (DI water, Millipore) with 18.0 MΩ cm^{-1} resistivity, and suprapure grade chemicals (HCl, H_2O_2,

HNO_3, ascorbic acid, and oxalic acid from Merck) were utilized where needed. Chromatographic extraction of ^{210}Po was carried out using 2 mL Sr-resin cartridges (TRISKEM, France) placed on a vacuum box with a pressure valve.

^{210}Po activity concentration and radiochemical yield were calculated using a ^{209}Po standard solution (Eckert & Ziegler) of 0.2404 ± 0.0024 Bq g^{-1}.

Finally, the counting efficiency calibration of the α-particle spectrometer was performed with a ^{241}Am standard electroplated source from PTB (Germany) containing 93.3 ± 1.9 Bq. The obtained values for the measurement chambers range from 0.245 to 0.263 and the uncertainty was less than 3 % within a confidence probability of 95 %.

2.3 Samples

As described in previous papers [18] bilberry samples were collected near Chernobyl reactor site in the summer of 2005. The material was oven-dried, cryo-milled, sieved, homogenised before being bottled [19]. Homogeneity and an isochronous long-term stability studies were carried out. Given the time elapsed since sample collection and isolation, and bearing in mind the comparatively short half-life of ^{210}Po (134.4 d) with respect to that of its father ^{210}Pb, it can be established that both nuclides are in radioactive equilibrium, hence the ^{210}Po radioactive concentration accounts for that of ^{210}Pb.

In this work, each sample was dried to constant weight at 60 °C and stored in plastic bags prior to performing the analysis.

3 Experimental

3.1 Radiochemical method

The radiochemical method was adapted and simplified from a previous study [16] and it is shown in Figure 1. Firstly, a dry weight of 1–5 g of wild bilberry sample (five aliquots for the sake of reproducibility of results) was put into a Teflon beaker and ^{209}Po internal standard (0.1 Bq) was added in order to evaluate ^{210}Po chemical recovery. At a first stage the sample was digested at low temperature (<25 °C) with concentrated HNO_3 and H_2O_2 during 24 h in order to avoid foam formation. Then the sample aliquot was wet digested following EPA 3050B method [20] with several additions of HNO_3 and H_2O_2. Next, the solution was filtered through a 0.45 µm filter (Millipore), and evaporated to dryness keeping the temperature below 100 °C to avoid losses due to polonium volatilisation [21]. Afterwards, the residue was dissolved with 10 mL of 8 M HNO_3.

Previously the resin cartridge was preconditioned with 5 mL 8 M HNO_3, and then the sample solution was passed through the resin. The resin cartridge was successively loaded with 5 mL of 8 M HNO_3, 5 mL of 3 M HNO_3

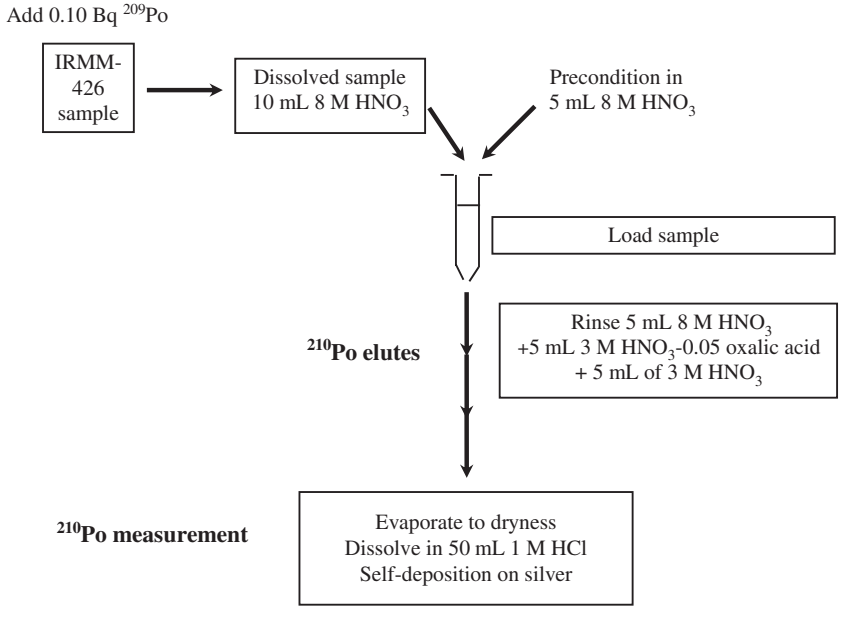

Figure 1: Radiochemical procedure for ^{210}Po isolation using prepacked Sr resin columns.

Table 1: Validation results including $^{210}Po_{(LAB)}$ obtained in five aliquots (n = 5) and $^{210}Po_{(REF)}$ certified in IAEA reference materials.

Sample	$^{210}Po_{(LAB)}$ (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	$^{210}Po_{(REF)}$ (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	z-Score	u	Trueness	Precision P (%)
IAEA-437 (mussel)	4.3	0.4	4.2	0.7	0.14	0.12	Acceptable	19
IAEA-414 (fish)	2.2	0.4	2.1	0.3	0.33	0.20	Acceptable	23

Uncertainties (σ) are expressed at k = 1.

– 0.05 oxalic acid, and 5 mL of 3 M HNO_3, in order to extract polonium.

The solution containing polonium was evaporated to dryness and then re-dissolved in 1 mL of concentrated HCl acid. This evaporation step was repeated three times and finally dissolved in 50 mL 1 M HCl. In order to avoid iron plating, few milligrams of ascorbic acid were added to the solution. Polonium self-deposition was carried out on silver discs during 6 h in 1 M HCl at about 80 °C [22, 23], and then measured using the α-particle spectrometer.

3.2 Method validation

IUPAC [24] and ISO [25] recommendations for assessment of performance of laboratories include z-score test, u-test, and trueness and precision tests. The proposed radiochemical methods were performed in two IAEA CRM. Five aliquots of 1 g were analysed for each IAEA CRM (n = 5) and results are shown in Table 1. The z-score and u values obtained are within the acceptable range for trueness, so an "Acceptable" status referring to precision and trueness was achieved. The analysis of the IAEA-437 sample gave a ^{210}Po activity of 4.3 Bq kg^{-1}, very close to the reference material reported value and within the 95 % confidence interval. The median value obtained for IAEA-414 sample was within the reported 95 % confidence interval.

The observed deviations are in the order of the precision values associated with environmental materials, and overall, we conclude that the proposed method is adequate to analyse 210Po in environmental samples.

4 Results and discussion

The ratio of the net count rates of the ^{210}Po (n) and ^{209}Po α peaks (n_{std}), was used to calculate the activity concentration of ^{210}Po ($C_{Po\text{-}210}$) in the wild bilberry samples on the date of radiochemical separation. The activity concentration of the ^{209}Po standard solution (C_{std}) and the mass of the standard solution used (m_{std}), the sample mass (m_{sample}), the decay of ^{209}Po (with standard half-life T) between its calibration date and counting (t), and standard gross count rate (N_{std}), background count rate (B), and sample count rate (N), were taken into account.

$$C_{Po\text{-}210} = \frac{n}{n_{std}} \times \frac{m_{std}}{m_{sample}} \times C_{std} \times f_t \quad (1)$$

$$n = N - B \quad (2)$$

$$n_{std} = N_{std} - B \quad (3)$$

Table 2: Activity concentration for ^{210}Po measured in five IRMM-426 samples and its associated mean.

Sample	Weight (g)	^{210}Po (Bq kg^{-1})	Uncertainty (Bq kg^{-1})	Chemical recovery (%)	MDA (Bq kg^{-1})
IRMM-426-1	2.248	0.631	0.053	51	0.05
IRMM-426-2	3.419	0.643	0.080	84	0.04
IRMM-426-3	1.505	0.641	0.060	77	0.09
IRMM-426-4	2.622	0.641	0.077	54	0.08
IRMM-426-5	5.099	0.582	0.058	53	0.03
Mean		0.628	0.026		

The reference date is 2018-07-20 0:00 UTC. The uncertainties are expanded uncertainties (k = 1). The chemical recovery and the Minimum Detectable Activity (MDA) was also shown for each sample.

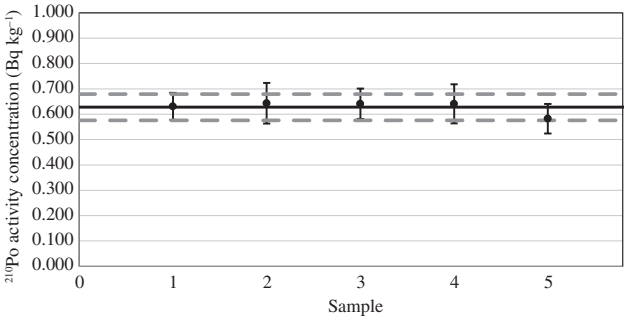

Figure 2: Plot of the activity concentration results of ^{210}Po in the IRMM-426 wild bilberries.
All uncertainties are combined uncertainties at k = 1. The solid horizontal line indicates the weighted mean and the dashed lines the expanded uncertainty from the standard deviation (k = 2).

Table 3: Summary of the uncertainty budget for ^{210}Po using GUM Workbench software.

Parameter	Value	Standard uncertainty	Distribution	Uncertainty contribution	Index
C_{std}	240.40 Bq kg^{-1}	2.4 Bq kg^{-1}	Normal	$6.4 \cdot 10^{-3}$ Bq kg^{-1}	1.2 %
t	3.9232 a	–	–	–	–
T	124.00 a	1.73 a	Rectangular	$200 \cdot 10^{-6}$ Bq kg^{-1}	0.0 %
m_{std}	$2.099200 \cdot 10^{-3}$ kg	$100 \cdot 10^{-9}$ kg	Normal	$31 \cdot 10^{-6}$ Bq kg^{-1}	0.0 %
N	$192.2 \cdot 10^{-6}$ cps	$14.4 \cdot 10^{-6}$ cps	Normal	0.055 Bq kg^{-1}	90.6 %
B	$25.30 \cdot 10^{-6}$ cps	$4.28 \cdot 10^{-6}$ cps	Normal	–0.016 Bq kg^{-1}	8.0 %
N_{std}	0.057318 cps	$248 \cdot 10^{-6}$ cps	Normal	$-2.8 \cdot 10^{-3}$ Bq kg^{-1}	0.2 %
m_{sample}	$2.248000 \cdot 10^{-3}$ kg	$1.00 \cdot 10^{-6}$ kg	Normal	$-290 \cdot 10^{-6}$ Bq kg^{-1}	0.0 %

The parameters used in uncertainty budget calculation of the activity concentration are standard activity concentration (C_{std}), standard mass (m_{std}), ^{209}Po half-life (T), standard gross count rate (N_{std}), background count rate (B), sample count rate (N), and sample mass (m_{sample}).

The decay correction factor (f_t) was calculated using the elapsed time between the separation time and the start of measurement (t) as follows:

$$f_t = e^{\frac{\ln(2)}{T} \times t} \tag{4}$$

According to the Guide for the expression of Uncertainty in Measurement GUM [26] the combined uncertainty corresponding to the ^{210}Po activity concentration on the separation date ($u(C_{Po\text{-}210})$) was calculated according to the following equations:

$$u(C_{Po\text{-}210}) = C_{Po\text{-}210} \sqrt{\frac{u^2(n)}{n^2} + \frac{u^2(n_{std})}{n_{std}^2} + \frac{u^2(m_{sample})}{m_{sample}^2} + \frac{u^2(m_{std})}{m_{std}^2} + \frac{u^2(C_{std})}{C_{std}^2} + \frac{u^2(f_t)}{f_t^2}} \tag{5}$$

$$u(n) = \sqrt{N^2 + B^2} \tag{6}$$

$$u(n_{std}) = \sqrt{N_{std}^2 + B^2} \tag{7}$$

$$u(f_t) = f_t \times t \times u(T) \tag{8}$$

The activity concentration results and the uncertainties obtained for ^{210}Po measured in the IRMM-426 CRM are summarized in Table 2. The analytical procedure was applied to five aliquots of the CRM. High chemical yields (>50 %) were obtained in the analysis carried out by α-particle spectrometry. The reference date was 2018-07-20 0:00 UTC. The uncertainties in Table 2 are expanded uncertainties with k = 1. The mean activity concentration of ^{210}Po in IRMM-426 CRM was 0.628 ± 0.026 Bq kg^{-1}.

In Figure 2, the results for ^{210}Po are plotted and in Table 3 the uncertainty budget for a typical measurement is given. The final combined uncertainty was calculated with a coverage factor of k = 1. The uncertainty analysis for the obtained results was performed using GUM Workbench software [27] recommended from BIPM [28]. The main contributor to the uncertainty of the activity concentration of the measured sample is the gross count rate (N) of the sample (90.7 %). Minor contributions to the overall uncertainty are the background count rate (B) with 8.0 %, and gross count rate (N_{std}) of the ^{209}Po standard (0.2 %). This may be due to the fact that IRMM-426 has a low ^{210}Po activity concentration, and the measurement time had to be extended up to $1 \cdot 10^6$ s.

5 Conclusions

The IRMM-426 wild bilberry CRM can be used for quality assurance and quality control of low-level ^{210}Po analysis of radionuclides in biota for taking decisions on radiological protection, as well as for development and validation of radioanalytical methods, and for training of laboratory analysts.

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