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A faster sample preparation method for determination of polonium-210 in fish

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Abstract In order to facilitate Health Canada's study on background radiation levels in country foods, an in-house radio-analytical method has been developed for determination of polonium-210 (^{210}Po) in fish samples. The method was validated by measurement of ^{210}Po in a certified reference material. It was also evaluated by comparing ^{210}Po concentrations in a number of fish samples by another method. The in-house method offers faster sample dissolution using an automated digestion system compared to currently used wet-ashing on a hot plate. It also utilizes pre-packed Sr-resin® cartridges for rapid and reproducible separation of ^{210}Po versus time-consuming manually packed Sr-resin® columns.

Keywords Polonium-210 · Background radioactivity in fish · Alpha spectrometry

Introduction

A large fraction of the natural background radiation experienced by individuals through ingestion of food and water is from the radionuclide polonium-210 (^{210}Po). ^{210}Po delivers about 60 % of the annual effective dose received through the ingestion pathway from all naturally occuring radionuclides expect potassium-40 [1]. Fish products are the major contributor for dietary intake of ^{210}Po when compared to different dietary components and their average annual consumption rates. Based on the reference concentration values of the radionuclides in fish products from the UNSCEAR 2000 report, ^{210}Po constitutes more than 80 % of all long-lived radionuclides in the uranium and thorium series combined [1]. The affinity of ^{210}Po for protein enables it to pass through the food chain, and increased body burdens of ^{210}Po have been found where diets include protein-rich meat and seafood [2]. The radiation protection bureau (RPB) of Health Canada has undertaken a study for the measurement of ^{210}Po in fish samples collected from Canadian lakes, rivers and oceans in order to determine the background concentration for this radionuclide. An accurate knowledge of the background concentration of ^{210}Po in fish is important in order to enrich the existing data gaps to better reflect region-specific dietary intake information. For example, the current UNSCEAR report on the exposure from natural radiation sources contains the measurement data from only the United States for the concentration of ^{210}Po in fish products in North America [1]. Background concentration data is also helpful in establishing guidelines for the threshold level of intake for food safety. Moreover, measurement of ^{210}Po in fish and the associated radiological dose to human provides a perspective to compare and communicate radiological risk from consumption of fish following an accidental release of artificial radionuclides in the aquatic biota.

The most common features of the analytical methods developed and applied for determination of ^{210}Po in environmental and biological samples are (a) dissolution of a representative sub-sample, (b) extraction and separation of ^{210}Po, (c) source preparation and (d) quantitative measurement of ^{210}Po using alpha spectrometry [3]. The purpose of sample dissolution is to mineralise the target radionuclides and render them in a chemical form suitable for subsequent use. For sample dissolution, wet-ashing

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has been shown to be the preferred method of choice over dry-ashing due to substantial loss of ^{210}Po through volatilisation [3–7]. For alpha spectrometic measurement, a source preparation step is necessary in order to deposit polonium in a thin layer on a disk or a filter. Although source preparation can be conveniently carried out directly on a dissolved sample by spontaneous deposition of polonium on a silver disk without any extraction and separation, the presence of interfering ions can make the procedure less reliable both by reducing the deposition yield of polonium and increasing the thickness of the deposited layer. Thus the alpha spectra can be degraded, in extreme cases, even preventing the alpha spectrometric determination of the polonium [3, 8]. Extraction and separation of ^{210}Po has been carried out by ion-exchange chromatography [9], solvent extraction [10–13], and extraction chromatography [8, 14–16]. Optimisation of the source preparation for alpha spectrometric determination of ^{210}Po has been evaluated in a number of studies [17–21].

The RPB did not have a validated method for determination of ^{210}Po in fish samples and contracted out the radiochemical analysis to commercial analytical service laboratories. An in-house method development was thus deemed to be important in terms of long term cost saving as well as having a better control over the quality assurance for the overall study. A review of the existing analytical methods suggested two possible areas for further improvisation, namely faster wet ashing and extraction chromatographic separation that will lead to an improved efficiency for determination of ^{210}Po in fish samples. The details of the method development and validation are presented here.

Experimental

Sample digestion

In order to address the radiological concern from the dietary intake, the edible portion of the fish sample (flesh) was used for the measurement of ^{210}Po. After separating from the skin and bone, the flesh was homogenised in a food processing blender and was kept in a freezer (−20 °C) until further analysis. For sample dissolution, a DigiPREP HT 250-10 digestion system (SCP Science, Baie D'Urfe, QC, Canada) has been used in this work. It consists of a graphite heating block that can accommodate ten tall cylindrical digestion tubes (300 mL, glass). The heating block contains ten built-in cylindrical cavities (5 cm depth) to house the bottom of the digestion tubes to provide a more uniform heating similar to a heating mantle. The digestion system was placed inside a chemical fume hood.

A 20 g aliquot of homogenised fish flesh was placed inside a pre-cleaned digestion tube with a few pre-cleaned boiling chips. A known quantity (50 mBq) of ^{209}Po standard solution (Reference No. 1725-48, Eckert & Ziegler Isotope Products, Valencia, California, USA) was added as a tracer for chemical recovery. A 60 mL aliquot of concentrated nitric (70 %) acid was added to each digestion tube. The sample digestion was carried out in four pre-programmed steps of time-to-temperature and time-at-temperature conditions. In the first step, the temperature of the heating block was raised from ambient to 180 °C (in 30 min) and was held at 180 °C for 1 min. During this heating step, if excessive foaming was observed, the digestion tube was removed from the heating block, gently swirled to subside the foaming and placed back in the heating block. When the frothing subsided, a glass ball condenser (SCP Science, Baie D'Urfe, QC, Canada) was placed on top of the digestion tube to efficiently cool the vapour rising into the glass finger tips of the condenser during the digestion and to allow the condensed acid to flow back into the digestion tube for efficient refluxing. In the second step the temperature was lowered to 140 °C (in 10 min) and was held for 2 h. In the third step, the temperature was raised to 240 °C (in 15 min) and was held for 2 h. In this step, 10 min after the temperature was raised to 240 °C, the scaffold (a Teflon coated aluminum rack that holds the digestion tubes) was raised from the heating block and 12.5 mL of hydrogen peroxide was added (drop wise) to the digestion tube. Once the fizzing subsided, the scaffold was lowered to replace the digestion tube back in the heating block. Addition of hydrogen peroxide was repeated three more times in 20 min time intervals. In the fourth step the temperature was lowered to 140 °C (in 15 min) and was held for 1 h. When the temperature reached 140 °C, the glass ball condenser was removed from the digestion tube, the solution was allowed to evaporate to 5 mL, and the digestion tube was removed from the heating block. The solution of the digested fish sample was transferred to a 50 mL Teflon beaker. The digestion tube was rinsed three times with 10 mL of 2 M hydrochloric acid to quantitatively transfer the content to the Teflon beaker. To carry out the extraction chromatographic separation of ^{210}Po, the digested sample solution was converted from the nitric acid to hydrochloric acid (2 M) medium as described below.

The beaker was placed on a hot plate to evaporate the solution at 90 °C. When the volume of the solution was reduced to about 5 mL, a 5 mL aliquot of concentrated hydrochloric acid was added to the beaker and the heating was continued until approximately 1 mL of the solution was left. This was repeated three times, each time, by addition of a 5 mL aliquot of 2 M hydrochloric acid and evaporation to approximately 1 mL. This solution was transferred to a 50 mL polypropylene tube and the beaker was rinsed thoroughly with 2 M hydrochloric acid; the final volume in the tube was adjusted to 30 mL.

Extraction chromatographic separation

Separation of ^{210}Po from the digested sample matrix containing ^{210}Pb and ^{210}Bi was carried out by extraction chromatography using a Sr-resin® cartridge as described in the Eichrom method for ^{210}Pb and ^{210}Po in water [22] except for stripping of ^{210}Pb. ^{210}Pb was stripped with 20 mL of 0.05 M ammonium citrate.

Measurement of ^{210}Pb-^{210}Bi-^{210}Po by liquid scintillation counting

For the initial chromatographic separation, a liquid scintillation counter (Tri-Carb 3180TR/SL, PerkinElmer Inc., Woodbridge, ON, Canada) was used for the measurement of ^{210}Pb-^{210}Bi-^{210}Po in the load, rinse and the strip fractions. In order to determine the appropriate pulse decay discriminator (PDD) settings for alpha–beta separation in various load, rinse and strip fractions, a PDD settings optimisation was carried out using a alpha emitting radionuclide standard (^{210}Po, 1000 Bq) and a beta emitting radionuclide standard (^{90}Sr/^{90}Y, 1000 Bq) prepared in 2 M HCl, 1 M HNO_3, 0.1 M HNO_3, and 0.05 M ammonium citrate. A 1 mL aliquot of each of the load, rinse, and strip fractions was mixed with 19 mL of liquid scintillation cocktail (OptiPhase HiSafe 3, PerkinElmer Inc., Woodbridge, ON, Canada) and counted for 30 min on the liquid scintillation counter (LSC) with the optimised PDD setting for alpha–beta discrimination.

Deposition of ^{210}Po on silver disk and alpha spectrometric measurement

The stripped solution containing ^{210}Po was transferred to a 50 mL Teflon beaker. The tube was rinsed three times with 5 mL of 2 M HCl to quantitatively transfer the content to the Teflon beaker. The conversion procedure from HNO_3 to HCl medium was repeated as described in the sample digestion section (above) except in the final step a 30 mL aliquot of deionised water was used instead of 2 M HCl and the solution was transferred to a pre-cleaned 50 mL glass beaker containing a magnetic stir bar (Teflon coated). The beaker was placed on a hot plate with stirring (magnetic) capability. 0.33 g of ascorbic acid was added to the beaker and dissolved by magnetic stirring. The pH of the solution was adjusted to 1 using 2 M HCl. For auto deposition of ^{210}Po, preparation of a silver disk and its mounting inside the solution in the beaker was carried out as described in the Eichrom method [22]. The deposition of ^{210}Po on the silver disk was carried out for 3 h at 90 ± 5 °C with moderate stirring. After deposition the silver disk was cleaned with deionised water, rinsed with ethanol (non-painted side) and was dried under an infra-red heat lamp.

The deposited ^{210}Po on the silver disk was measured using a bench top Alpha Analyst system (Canberra Industries Inc., Meriden, CT, USA), where the alpha particles were detected using 25 mm silicon PIPS detectors. The samples were placed on the second shelf, about 2 cm away from the detector, and counted for 24 h using the recoil suppression mode. ^{210}Po activity was then calculated using the APEX-Alpha software using ^{209}Po standard as a yield tracer.

Results and discussion

Sample dissolution by wet ashing

Wet ashing is typically carried out by repetitive digestion on a hot plate in the presence of concentrated acids and hydrogen peroxide in an open beaker (often with a lid to prevent fast evaporation of acids) [3]. Conventional digestion on a hot plate is slow and requires close attention to avoid the risk of cross contamination, formation of insoluble salts, exposure to acid fumes and corrosion and charring during evaporation [23]. Wet ashing carried out on a hot plate can be quite time consuming, taking up to several days to completely dissolve a biological sample such as meat or fish especially if it contains fat [24–26]. Although microwave digestion can be an attractive alternative to open beaker digestion, it can only handle a very small amount of organic sample (typically, 0.5 g dry and 2–3 g for wet sample) per digestion vessel and thus a larger sample (20–25 g, wet weight) may need to be split into a number of digestion vessels to achieve the required sensitivity for the measurement of low levels of ^{210}Po in fish samples [23, 27]. This also leads to an increase in digestion time that will lower the sample throughput capacity. The digestion system (DigiPREP HT 250-10) used in this work was found to efficiently dissolve a fish flesh sample (20 g, wet weight) into a clear liquid solution in less than 7 h without any visible fat residue (up cooling) at the end of the digestion. Tall cylindrical sample digestion tubes, uniform heating inside the built-in ceramic cavities, programmable multi-stage temperature control, and glass ball condensers to cool and condense the acid vapour to flow back in the digestion tubes for efficient refluxing are some of the features of the automated digestion system that enabled a more time efficient dissolution compared to time consuming conventional open beaker digestion for a similar size (20 g, wet weight) sample. Simultaneous digestion of up to 10 samples within a compact system inside the fume hood is also another attractive feature to provide improved sample throughput.

Optimisation of PDD setting for alpha/beta discrimination

For initial optimisation of the extraction chromatographic separation, liquid scintillation counting was used for the

Table 1 Data for the optimisation of PDD settings for alpha/beta discrimination resulting from a pure alpha emitter (^{210}Po, 1000 Bq) and a pure beta emitter (^{90}Sr/^{90}Y, 1000 Bq)

PDD	2 M HCl		1 M HNO_3		0.1 M HNO_3		0.05 M NH_4 citrate	
Settings	Alpha spillover (%)	Beta spillover (%)	Alpha spillover (%)	Beta spillover (%)	Alpha spillover (%)	Beta spillover (%)	Alpha spillover (%)	Beta spillover (%)
145	1.13	3.96	1.90	3.77	0.54	7.34	0.53	8.48
150	2.29	2.69	4.17	2.62	0.86	3.91	0.90	4.45
155	4.97	2.06	8.06	2.05	1.73	2.60	1.57	2.80
160	9.47	1.93	14.45	1.82	3.60	2.13	2.99	2.17
165	16.45	1.65	23.18	1.62	7.02	1.67	6.10	1.91
170	25.52	1.53	33.45	1.48	11.91	1.60	10.67	1.63
175	36.88	1.43	46.01	1.35	19.85	1.52	17.76	1.51
180	48.74	1.33	57.79	1.35	29.61	1.41	26.63	1.48
185	60.59	1.21	68.83	1.25	41.17	1.26	37.23	1.31

measurement of ^{210}Pb, ^{210}Bi, and ^{210}Po in the load, rinse and strip fractions. In liquid scintillation counting, the pulse height spectrum of an alpha particle often overlaps with that of a beta particle. However, the decay time of light produced by an alpha particle in a suitable liquid scintillator is longer than that of the light produced by a beta particle. Discrimination of liquid scintillation signals resulting from alpha and beta emitting radionuclides can be carried out by the difference in the lengths of the pulse decay events [28]. Table 1 shows the data for discrimination of alpha and beta pulses (expressed as % spillover) at various PDD settings.

The ^{210}Po and ^{90}Sr/^{90}Y standards were prepared in 2 M HCl, 1 M HNO_3, 0.1 M HNO_3, and 0.05 M ammonium citrate in order to match the chemical composition of the load, rinse and the strip fractions to account for the quenching effects. A curve of the % spillover versus the PDD settings was constructed for both the ^{210}Po and ^{90}Sr/^{90}Y standards. The optimum PDD setting for α/β discrimination is where the two spillover curves intersect. The optimum PDD settings for α/β discrimination in 2 M HCl, 1 M HNO_3, 0.1 M HNO_3, and 0.05 M ammonium citrate were 151, 148, 157, and 158, respectively. Since the PDD setting for α/β discrimination in 0.1 M NHO_3 and 0.05 M ammonium citrate were close to each other, a PDD setting of 157 was used for the measurement in both conditions.

Extraction chromatographic separation of ^{210}Pb-^{210}Bi-^{210}Po

Sr-Resin® has been widely used for extraction chromatographic separation of ^{210}Po from ^{210}Pb, ^{210}Bi and other interfering radionuclides if present in a sample [8, 29–32]. Typically, a digested sample solution is converted to 2 M HCl before loading on the Sr-Resin®. ^{210}Pb and ^{210}Po is retained on the column while ^{210}Bi and other interfering radionuclides are eluted during the loading (2 M HCl) and rinse (using 2 M HCl) steps [8, 31]. ^{210}Po and ^{210}Pb are stripped from the Sr-Resin® using 6 M HNO_3 and 6 M HCl, respectively. As compared to more concentrated stripping reagents (6 M HMO_3 and 6 M HCl), milder reagents have been previously used for stripping ^{210}Po (1 M HNO_3 and 0.1 M HNO_3) and ^{210}Pb (0.05 M ammonium citrate or water) for determination of these radionuclides in water samples [22, 33]. Since the milder reagents would be less corrosive and would also lead to cost saving, 1 M HNO_3, 0.1 M HNO_3, and 0.05 M ammonium citrate were investigated in this work as stripping reagents for the separation of ^{210}Po and ^{210}Pb from digested fish samples. Figure 1a shows the separation of a standard mixture of ^{210}Pb-^{210}Bi-^{210}Po (4 Bq; radionuclides are in secular equilibrium) prepared in deionised water in the presence of 2 M HCl.

As anticipated, ^{210}Bi was not retained on Sr-Resin® and was eluted during the loading and rinse steps. According to the separation conditions as described in the Eichrom analytical procedure [22], recovery of ^{210}Po (in 5 mL of 1 M HNO_3 and 10 mL of 0.1 M HNO_3) was about 90 % and recovery of ^{210}Pb (in 10 mL of 0.05 M ammonium citrate) was quantitative (~100 %). Also, approximately 10 % of the spiked ^{210}Po was observed in the first 5 mL fraction of 0.05 M ammonium citrate (stripping reagent for ^{210}Pb). To increase the ^{210}Po recovery, the stripping volume of 0.1 M HNO_3 was increased from 10 mL (as described in the Eichrom analytical procedure) to 15 mL. As shown in Fig. 1a, this increased the ^{210}Po recovery (in 5 mL of 1 M HNO_3 and 15 mL of 0.1 M HNO_3) to about 95 % while reducing the concentration of ^{210}Po in 0.05 M ammonium citrate to approximately 5 %. A further increase in volume of 0.1 M HNO_3 did not improve the recovery of ^{210}Po.

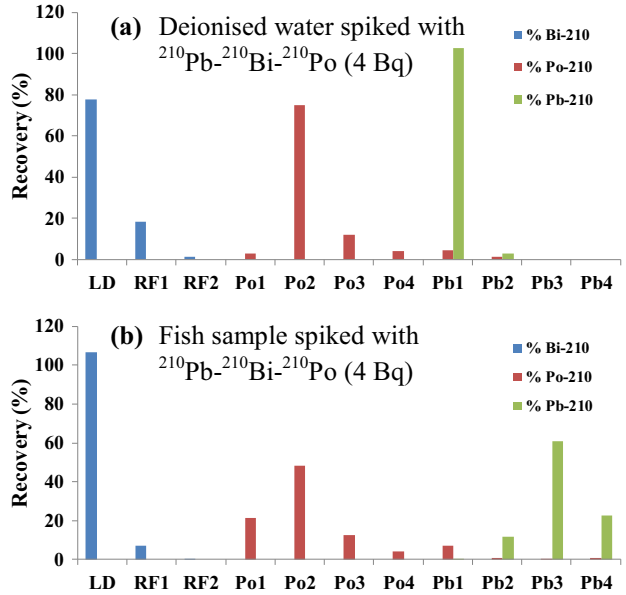

Fig. 1 Extraction chromatographic separation of ^{210}Pb-^{210}Bi-^{210}Po using Sr-Resin® cartridge, **a** deionised water spiked with ^{210}Pb-^{210}Bi-^{210}Po (4 Bq), **b** fish sample spiked with ^{210}Pb-^{210}Bi-^{210}Po (4 Bq); *LD* load (digested sample after chloride conversion, in 2 M HCl), *RF1* and *RF2* rinse fractions (5 mL of 2 M HCl); *Po1* polonium strip solution 1 (5 mL of 1 M HNO_3); *Po2*, *Po3*, and *Po4* polonium strip solutions (5 mL of 0.1 M HNO_3), *Pb1*, *Pb2*, *Pb3*, and *Pb4* lead strip solutions (5 mL of 0.05 M ammonium citrate)

In order to assess the application of the extraction chromatographic separation in the presence of a fish matrix, homogenized flesh samples from three fish (20 g, wet weight each) were spiked with a standard mixture of ^{210}Pb-^{210}Bi-^{210}Po (4 Bq per sample) and digested according to the procedure described above. The elution profile for the extraction chromatographic separation of ^{210}Pb, ^{210}Bi, and ^{210}Po in a digested fish matrix is shown in Fig. 1b. The elution profile of ^{210}Po was similar to that observed in deionised water. The spike recovery of ^{210}Po (in 5 mL of 1 M HNO_3 and 15 mL of 0.1 M HNO_3) in the digested fish samples was found to be 85 ± 5 % (average ± 1-standard deviation, $n = 3$). Lower recovery of spiked ^{210}Po in the digested fish samples (compared to the spiked standard in deionized water) was likely due to the evaporative loss during digestion at elevated temperature. The elution profile of ^{210}Pb for the digested fish sample was significantly different. No ^{210}Pb was observed in the first 5 mL fraction of 0.05 M ammonium citrate and <12 % of the spiked ^{210}Pb was recovered in the second 5 mL fraction (of 0.05 M ammonium citrate). In order to achieve quantitative recovery of ^{210}Pb, the strip volume of 0.05 M ammonium citrate needed to be increased from 10 mL (as described in the Eichrom procedure [22]) to 20 mL (Fig. 1b). After this modification, spike recovery of ^{210}Pb increased to 92 ± 4 %. The change of elution profile for ^{210}Pb is likely due to the matrix effect of the digested fish sample resulting from the residual organic and inorganic components present in the loading solution. Interestingly, in the digested fish samples, the spike recovery of ^{210}Bi in the loading and strip fractions was 111 ± 6 %. The higher (>100 %) recovery could be due to the interference contribution of ^{40}K (present in the fish sample) to the ^{210}Bi liquid scintillation signal.

Determination of ^{210}Po in fish samples: method validation

Although it was used as a convenient radionuclide detection system for the optimisation of extraction chromatographic separation, the liquid scintillation counting could not be used for the measurement of ^{210}Po natively present in the fish samples due to lack of the required detection limit. Alpha spectrometry was used for the determination of ^{210}Po in the fish samples. For the alpha spectrometric determination, the overall chemical recovery of polonium (as determined by the ^{209}Po yield tracer) was 76 ± 3 %. It was lower than the recovery of ^{210}Po (85 ± 5 %) obtained when a number of fish samples were spiked with known quantity (4 Bq) and were determined by liquid scintillation counting after wet digestion and extraction chromatographic separation. The decrease in chemical recovery for alpha spectrometric determination was likely due to the additional evaporative loss during the second chloride conversion step before spontaneous deposition of polonium on silver disk. Shorter auto deposition time (3 h) was also a contributing factor for lower chemical recovery. Lower chemical recovery of polonium (50–70 %) was also reported by Vajda et al. when sample dissolution was carried out by wet ashing through repetitive digestion on a hot plate in the presence of concentrated acids (HNO_3 and HCl) and hydrogen peroxide [8].

A certified reference material (IAEA-414) purchase from the International Atomic Energy Agency (IAEA) for radionuclides in mixed fish from the Irish Sea and North Sea was used to validate the method for determination of ^{210}Po. IAEA-414 provides an information value (2.1 Bq/kg) for ^{210}Po (present in secular equilibrium with ^{210}Pb) with a 95 % confidence interval (1.8–2.5 Bq/kg) for a reference date of January 1, 1997. 5 g (dry weight) of the standard reference material (IAEA-414) was analysed in triplicate. Since the average moisture content of the flesh portion for a fresh fish is about 75 % and the digestion procedure was optimised for a 20 g (wet weight) aliquot of a homogenized fish (flesh portion), 5 g of dry weight for IAEA-414 was a reasonable amount for the method validation. The measured value of ^{210}Po in the IAEA-414 was found to be 1.9 ± 0.4 Bq/kg (average ± 2 standard

deviation). The relative bias between the information value ($value_{IAEA}$) and the measured value ($value_{analyst}$) for ^{210}Po concentration was less than 10 %. For performance evaluation, the *Z*—score and the *U*—score values were calculated according to the IAEA's HELCOM-MORS proficiency test [34]. The HELCOM-MORS proficiency test (PT) was organized by the IAEA's Marine Environmental Laboratory to evaluate the analytical performance for radionuclides on a fish flesh sample (IAEA-414) for the participating laboratories. Normally, the reference value of an analyte in a certified reference material is used for the *Z*—score and *U*—test. However, since there is not any suitable reference material associated with fish matrix and the reference value of ^{210}Po, *Z*—score and *U*—test were carried out using the information value of ^{210}Po from IAEA-414 certificate. The *Z*—score was calculated according to Eq. 1 as shown below:

$$Z - Score = \frac{\text{Value}_{\text{Analyst}} - \text{Value}_{\text{IAEA}}}{\sigma} \quad (1)$$

As outlined in the PT guidance, on the basis of the "fitness for purpose" principle, the target value of the standard deviation (σ) is: $\sigma = 0.1 \times \text{value}_{\text{IAEA}}$.

A laboratory performance is evaluated as satisfactory if $|Z - \text{score}| \leq 2$; questionable for $2 \leq |Z - \text{score}| \leq 3$, and unsatisfactory for $|Z - \text{score}| \geq 3$.

The value of the *U*—score, expressed as, U_{test} was calculated according to (Eq. 2) as follows:

$$U_{\text{test}} = \frac{|\text{value}_{\text{IAEA}} - \text{value}_{\text{analyst}}|}{\sqrt{\text{Unc}^2_{\text{IAEA}} + \text{Unc}^2_{\text{analyst}}}} \quad (2)$$

where Unc_{IAEA} and $\text{Unc}_{\text{Analyst}}$ are expanded uncertainties (2σ), which cover 95 % confidence interval. The limiting value of the *U*—score for the PT was set to be 2.58, so that a laboratory passes the test if $U_{\text{test}} < 2.58$.

The values for the *Z*—score and *U*—score for the current method were 0.95 and 0.24, respectively. Thus, the method presented here, passes the performance criteria for both *Z*—score and *U*—score according to the IAEA's HELCOM-MORS proficiency test.

Determination of ^{210}Po in fish samples: method intercomparison

Prior to the development of this method, RPB used to contract out the measurement for ^{210}Po to Saskatoon Research Council (SRC), a commercial analytical service laboratory. A method intercomparison was undertaken to further evaluate the method performance on wet fish flesh samples. A number of homogenized fish flesh samples were split into two aliquots. One set of these samples was analyzed by the SRC and the second set was analyzed by the method described in this paper. The results for the ^{210}Po concentration in these fish samples analyzed by the two laboratories are shown in Table 2. For the measurements carried out in RPB, concentration of ^{210}Po in a fish sample and the associated combined standard uncertainty were calculated according to the procedure described in the MARLAP manual [35].

Comparison of the two methods was carried out by means of *Z*—score and Chi squared (χ^2) test as described by Saidou et al. [36]. Since the concentration of ^{210}Po in a fish sample is not known, Saido et al. [36] used following equation (Eq. 3) to calculate the *Z*—score value:

$$Z - \text{score} = \frac{\text{value}_{\text{method1}} - \text{value}_{\text{method2}}}{\sqrt{\sigma^2_{\text{method1}} + \sigma^2_{\text{method2}}}} \quad (3)$$

Table 2 Intercomparison results for ^{210}Po concentrations in the fish flesh samples by the RPB method and the method used by the Saskatoon Research Council (SRC)

Sample no.	^{210}Po-RPB value (Bq/kg)	^{210}Po-SRC value (Bq/kg)	*Z*–score
1	0.93 ± 0.27	1.20 ± 0.50	−0.94
2	0.60 ± 0.41	0.50 ± 0.30	0.40
3	0.68 ± 0.21	1.00 ± 0.40	−1.39
4	1.50 ± 0.26	1.20 ± 0.50	1.06
5	0.57 ± 0.22	0.70 ± 0.40	−0.58
6	0.56 ± 0.18	0.70 ± 0.40	−0.64
7	0.76 ± 0.25	0.80 ± 0.40	−0.15
8	0.94 ± 0.36	0.60 ± 0.30	1.45
9	1.09 ± 0.15	1.40 ± 0.60	−1.01
10	0.40 ± 0.15	0.30 ± 0.20	0.80
11	0.76 ± 0.14	1.20 ± 0.50	−1.69
12	0.69 ± 0.16	1.20 ± 0.50	−1.94
Chi squared (χ^2) value = 15.28			

Uncertainty is expressed as 2 standard deviations to cover 95 % confidence interval

The Chi squared (χ^2) value was calculated using the equation (Eq. 4) as shown below:

$$\chi^2 = \sum_{i=1}^{n} Z_i^2 \quad (4)$$

The $|Z - \text{score}|$ values for each pair of measurement by the two methods were <2. A $|Z - \text{score}|$ value of <2 indicates that there is no significant difference between the two measured values of ^{210}Po for a fish sample within 95 % confidence interval. The concordance of the two methods was evaluated by a χ^2 test for measurements of multiple samples [36]. For measurement of 12 fish samples by the two methods, the result of the χ^2 test on the *Z*—score values was 15.3. It is lower than the critical value (21.0) for 95 % confidence interval ($\alpha = 0.05$) and 12 measurements ($n = 12$). This indicates that there is no significant difference between the two methods within a 95 % confidence interval.

Minimum detectable concentration and sample throughput

Minimum detectable concentration (MDC) was calculated according to the MARLAP recommendations [35] using the Poisson-Normal approximation with Type I (false positive) and Type II (false negative) error rates at 5 % ($\alpha = \beta = 0.05$). The MDC for ^{210}Po was 0.1 Bq/kg for the measurement of a 20 g aliquot of a fish flesh sample with a counting time of 24 h using an alpha spectrometer. The SRC reported a sample specific MDC that ranged from 0.2 to 0.3 Bq/kg. Data available from the UNSCEAR 2000 report for the measured concentration of ^{210}Po in fish products from the United States range from 0.15 to 55 Bq/kg [1]. The MDC for the in-house method was, thus, considered to be adequate in terms of the required sensitivity for measurement of the background level of ^{210}Po in Canadian fish samples. The current sample throughput of the in-house method is eight fish samples in a week (37.5 working hours) by one laboratory personnel using two chemical fume hoods and one alpha spectrometer with eight detector chambers.

Conclusions

An in-house radio-analytical method has been developed for the determination of ^{210}Po in fish samples to facilitate Health Canada's study on background radiation levels in country foods. Over the existing analytical methods for determination of ^{210}Po in fish samples, this the new method offers improvisations in two different aspects: (1) faster sample dissolution (in <7 h) using an automated digestion system compared to wet ashing on a hot plate (in several days), and (2) rapid and reproducible extraction chromatographic separation of ^{210}Po using a standardized (2 mL) pre-packed Sr-resin® cartridge over a manually packed Sr-resin® column that requires additional packing time. A certified reference material (IAEA-414) for radionuclides in a mixed fish sample was used to validate the method for determination of ^{210}Po. The relative bias between the measured concentration and IAEA's information value was less than 10 %. The method also passed the performance criteria for both *Z*—score and *U*—score for determination of ^{210}Po in the certified reference material according to the IAEA's HELCOM-MORS proficiency test. Further, an intercomparison study on 12 fish flesh samples between the in-house method and a method used by the SRC demonstrated no significant difference on the measurement results for ^{210}Po concentration within the 95 % confidence interval on the basis of *Z*—score values and a Chi squared (χ^2) test. The MDC (0.1 Bq/kg) of the in-house method is adequate in terms of the required sensitivity for measurement of the background level of ^{210}Po in Canadian fish samples. Since the completion of the method development, over 100 fish samples have been analysed for ^{210}Po for the Canadian background radioactivity measurement study and will be presented in a separate publication.

References

1. UNSCEAR (2000) sources and effects of ionizing radiation. United Nations Scientific Committee on the Effects of Atomic Radiation UNSCEAR 2000, report to the general assembly with scientific annexe, United Nations, New York
2. Alam A, Mohamed CAR (2011) Int Food Res J 18:1–10
3. Matthews KM, Kim CK, Martin P (2007) Appl Radiat Isot 65:267–279
4. Seiner BN, Morley SM, Beacham TA, Hanley MM, Gregory S, Metz L (2014) J Radioanal Nucl Chem 302:673–678
5. Martin A, Blanchard RL (1969) Analyst 94:441–446
6. Cleary JJ, Hamilton EI (1968) Analyst 93:235–236
7. Mabuchi HJ (1963) Inorg Nucl Chem 25:657–660
8. Vajda N, LaRosa J, Zeisler R, Danesi P, Kis-Benedek GY (1997) J Environ Radioact 37:355–372
9. Pacer RA (1983) J Radioanal Chem 77:19–28
10. Uesugi M, Noguchi M, Yokoyama A, Nakanishi T (2010) J Radioanal Nucl Chem 283:577–584
11. Kim C-K, Lee MH, Martin P (2009) J Radioanal Nucl Chem 279:639–646
12. Chen Q, Hou X, Dahlgaard H, Nielsen SP, Aarkrog A (2001) J Radioanal Nucl Chem 249:587–593
13. Veronneau C, Aupiais J, Dacheux N (2000) Anal Chim Acta 415:229–238
14. Maxwell SL, Culligan BK, Hutchison JB, Utsey RC, McAlister DR (2013) J Radioanal Nucl Chem 298:1977–1989
15. Reischmann FJ, Trautmann N, Herrmann G (1984) Radiochim Acta 36:139–143

16. Ordonez-Regil E, Iturbe JL (1993) J Radioanal Nucl Chem 17:47–53
17. Lee HM, Hong GH, Baskaran M, Kim SH, Kim YI (2014) Appl Radiat Isot 90:170–176
18. Porntepkasemsan B, Srisuksawad K, O-manee A TIChE International Conference 2011, Hatyai, Songkhla Thailand. http://www.chem.eng.psu.ac.th/tiche2011/TCHE/data/paper/international/ms/poster/ms006.pdf. Accessed 07 May 2015
19. Lee MH, Lee CH, Song K, Kim CK, Martin P (2010) Bull Korean Chem Soc 31:2488–2492
20. Henricsson F, Ranebo Y, Holm E, Roos P (2011) J Environ Radioact 102:415–419
21. Vesterbacka P, Ikaheimonen TK (2005) Anal Chim Acta 545:252–261
22. Lead-210 and polonium-210 in water. Analytical procedures. Eichrom Technologies LLC: Rev. 2.0. (OTW01). http://www.eichrom.com/docs/methods/pdf/otw01-20_pb-po-water.pdf. Accessed 15 April 2015
23. Louw I, Faanhot A, Kotze D (2009) Radioprotection 44:89–95
24. Clayton RF, Bradley EJ (1995) Sci Total Environ 173(174):23–28
25. Ham GJ, Ewers LW, Clayton RF (1997) J Radioanal Nucl Chem 226:61–65
26. Samad OE, Baydoun R, Jeaid HE (2010) Leban Sci J 11:39–45
27. Gjelsvik R, Brown J, Holm E, Roos P, Saxen R, Outola I (2012) Results from the NKS project GAPRAD (Filling knowledge gaps in radiation protection methodologies for non-human biota), Sralevern Rapport 2012:3. Østerås: Norwegian Radiation Protection Authority. http://www.nrpa.no/dav/a7950bbba1.pdf. Accessed 07 May 2015
28. L'Annunziata MF, Kessler MJ (2003) In: L'Annunziata MF (ed) Handbook of radioactivity analysis, 2nd edn. Academic Press, California
29. Miura T, Hayano K, Nakayama K (1999) Anal Sci 15:23–28
30. Biggin CD, Cook GT, MacKenzie AB, Pates JM (2002) Anal Chem 74:671–677
31. Vrecek P, Benedik L, Pihlar B (2004) Appl Radiat Isot 60:717–723
32. Lin Z, Wu Z (2009) Appl Radiat Isot 67:907–912
33. Johansson LY (2008) Determination of Pb-210 and Po-210 in aqueous environmental samples. Ph. D. Thesis. http://pbadupws.nrc.gov/docs/ML1105/ML110560301.pdf. Accessed 15 April 2015
34. HELCOM-MORS Proficiency Test, Determination of Radionuclides in Fish Flesh Sample, IAEA Analytical Quality in Nuclear Application No. IAEA/AQ/13, International Atomic Energy, Vienna, 2010
35. Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual, NUREG-1576, EPA 402-B-04-001C, NTIS PB2004-105421, July, 2004
36. Saidou, Bochud F, Laedermann J-P, Njock MGK, Froidevaux P (2008) Appl Radiat Isot 66:215–222