Malaysian Journal of Analytical Sciences (MJAS)
Published by Malaysian Analytical Sciences Society

^{210}PO DETERMINATION IN URINE SAMPLES AMONG RADIATION WORKERS BY ALPHA SPECTRUM ANALYSIS

(Penentuan ^{210}Po dalam Sampel Urin di Kalangan Pekerja Sinaran Melalui Analisis Spektrum Alpha)

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Received: 26 April 2021; Accepted: 11 June 2021; Published: xx June 2021

Abstract

The radioactivity of ^{210}Po in the urine sample of radiation workers working in radiochemical laboratory, Malaysian Nuclear Agency, was determined. Collected urine samples have to go through the hot acid dissolution process followed by the auto-deposition technique using HCl as the solution. Measurements using the alpha spectrometry system showed good ^{209}Po retrieval, while ^{210}Po determination has no interference by other natural radionuclides. The specific radioactivity of ^{210}Po was determined from 1.33 mBqL^{-1} to 49.84 mBqL^{-1}. This preliminary study was conducted to obtain reference data as part of methods development for further investigations in emergencies. The assessment of the data findings in terms of radiation safety was done. Such radioactivity measurement procedure would also be applying for the routine ^{210}Po analysis in the urine.

Keywords: nium isotopes, Radioactivity, Radiochemical separation, Alpha spectrometry, Bioassay

Abstrak

Radioaktiviti ^{210}Po dalam sampel urin pekerja radiasi yang bekerja di makmal radiokimia, Agensi Nuklear Malaysia telah ditentukan. Sampel urin yang dikumpulkan mesti melalui proses pembubaran asid panas diikuti dengan teknik pemendapan-auto menggunakan HCl sebagai medium larutan. Pengukuran menggunakan sistem spektrometri alpha menunjukkan dapatan semula ^{209}Po yang baik, sementara penentuan ^{210}Po tiada gangguan daripada kehadiran radionuklida semula jadi yang lain. Radioaktiviti spesifik ^{210}Po telah ditentukan dari 1.33 mBqL^{-1} hingga 49.84 mBqL^{-1}. Kajian awal ini dilaksanakan untuk mendapatkan data rujukan sebagai sebahagian dari pengembangan kaedah bagi situasi kecemasan. Penilaian ke atas dapatan data dari segi keselamatan radiasi telah dilakukan. Prosedur pengukuran radioaktif seperti ini juga digunakan untuk aktiviti analisis rutin ^{210}Po dalam sampel urin.

Kata kunci: Isotop polonium, Radioaktiviti, Pemisahan radiokimia, Spektrometri alfa, Bioasai

Introduction

^{210}Pb and ^{210}Po are associated with the ^{238}U decay chain, a naturally occurring radionuclide. ^{210}Pb and its daughter ^{210}Bi are beta sources with a half-life of 22.3 years and 5.0 days, respectively. Meanwhile, ^{210}Po, the granddaughter of ^{210}Pb, is an alpha transmitter. The half-life of ^{210}Po is only 138.4 days, and it is the lengthiest polonium radioisotope. ^{210}Po occurrences have been continually supplied in the environment by ^{210}Pb, which is technologically enhanced from natural radioactive materials (TENORM) [1].

Owing to the natural background radiation, ^{210}Po contributes significantly to human internal dosage when absorbed into the body by inhalation or ingestion and is therefore essential to be monitored [1]. An excessive dose of ^{210}Po may cause acute radiation syndrome (ARS), which includes nausea, vomiting, diarrhea in the prodromal period, and later symptoms, including hair loss and bleeding. A lower dose can cause long-term organ failure, which could lead to death. The medical sequence can be defined when intake of ^{210}Po more than 1 GBq (109 Bq) occurs [2].

Historically, ^{210}Po has also been linked to the death of Mr. Alexande Litvinenko, a former Soviet spy. He died on 23rd November 2006, 22 days after consuming a cup of tea laced with ^{210}Po. The assassins left radioactive traces all over London. Following this attack, London Health officials used alpha spectrometry to track hundreds of urine samples from internally infected individuals [2, 3]. Despite the fact that ^{210}Po can be easily determined by measuring alpha radiation emissions, there is a shortage of reference on ^{210}Po in human tissues and body fluids used as a baseline in determining whether or not the individual would be contaminated [4].

The bioassay technique was used to measure the amount of actinide present in the body based on the rate of excretion of body fluids. In an emergency of high ^{210}Po activity spread, urine samples of individuals dealing specifically with ^{210}Po from open sources should be analysed. It is critical to act rapidly in an emergency to identify radiological threats, particularly to the general public. Urine bioassays are often used to assess internal ^{210}Po exposure [2], which can be separated into two types; spontaneous plating [5] and micro-precipitation technique [6]. However, the pre-concentration approach is tedious and time-consuming, which may not be appropriate in an emergency. Therefore, to measure ^{210}Po in urine samples, new and quick analysis methods are needed.

In this study, sample selection from the radiochemical laboratory of the Malaysian Nuclear Agency was used as a reference group to determine ^{210}Po. This paper defines the procedure used for determining ^{210}Po in urine samples, which involved wet decomposition followed by automated deposition for alpha spectrometry. Furthermore, this research focuses on the factors that affect polonium determination and the need to improve the method. Finally, the study results of ^{210}Po value will be used as the primary baseline reference data, and assessment in terms of radiation safety were done.

Materials and Methods

Materials

^{209}Po was purchased from Perkin Elmer and was diluted to 30Bq. The diluted concentration was calibrated by preparing a set of a known amount of standards and using a calibration curve to create a radioactivity relationship between the amount spiked and an instrument response. Nitric acid (65% purity) and hydrogen peroxide (30% purity) were purchased from MERCK, used for acid dissolution. Hydrochloric acid (37% purity) was supplied by Scharlau, and distilled water was used for acid dilution in preparing final solution of 2M HCl for auto-deposition process. Mixed standard alpha reference sources (^{238}U, ^{234}U, ^{239}Pu and ^{241}Am) were obtained from ANALYTICS used to calibrate the alpha spectrum energy for the alpha spectrometry system.

Sampling and sample analysis

A 24-hour urine specimen obtained from 6 radiochemical workers were used to examine. 50 mL of the obtained urine sample, moved to a 100 mL glass beaker and diluted with 50 mL of distilled water. Each

sample was made in triplicate and heated to just below 90 ºC until almost dry. The known amount (approximately 6 Bq) of ^{209}Po as the tracer was added. In the urine bioassay method, ^{210}Po has often been corrected using a ^{208}Po tracer or ^{209}Po to assess the recovery due to any depletion or cross contamination of ^{210}Po during the sample analysis. In this study, ^{209}Po was used as a tracer due to the advantage in energy isolation from the ^{210}Po peak. The ^{208}Po is not widely used as a tracer since its peak energy is closed to ^{210}Po and can be interference in mistake (Table 1).

Complete dissolution was carried out with 10 mL of 65% nitric acid and 1 mL of 30% hydrogen peroxide until all the organics had been decomposed. The solution was evaporated until almost dry after dissolution, and the digestive residue was converted to chloride form by applying 10 mL 37% hydrochloric acid. Once the evaporation process was completed, 3.5 mL of 37% hydrochloric acid was applied directly to dissolve the residue. The solution was then rendered to 0.5M hydrochloric acid medium by adding 80 mL of distilled water.

Auto plating

In each sample, hydroxylamine chloride and Bi carrier were added, which were then gently heated on a hot plate and dissolved before being placed on the silver disk as seen in
Figure 1. ^{210}Pb and its daughter ^{210}Bi must be entirely separated to maintain the secular equilibrium between ^{210}Bi and ^{210}Po with no interference of ^{210}Pb [3]. 4 hours of plating is needed to achieve optimum recovery [8]. Reducing the plating time (at room temperature) to speed up sample processing throughput could be an alternative, but it will reduce the recovery and increase the MDA. In this case, the volume of tracer used must be adjusted to account for the reduction of recovery.

Active source measurement using alpha spectrometry system

The 450 mm^2 silver discs active surface was then measured using an alpha spectrometry system consisting of Alpha Passivated Implanted Planar Silicon (PIPS) detectors, as shown in
Figure **2**(a). Compared to other radiometric methods, such as γ-ray spectrometry, alpha spectrometry has a distinct advantage: the background is very low. The efficiency of more than 20% was measured based on efficiency measurement of ANALYTICS mixed standard alpha reference sources for a source to the sensor distance less than 1 cm (shelve number 1 in the alpha detector chamber), as shown in
Figure **2**(b). The detector efficiency does not vary with energy (4 MeV to 9 MeV) due to the small distance of α-peak energy. Because of this efficiency's freedom from energy (i.e. the intrinsic efficiency of one), the precise non-standard alpha activity ratio for peak energy's efficiency calibration may be determined [9].

The duration of the active source measurements in this study was 24 hours. Due to its volatility, the polonium atoms readily exit the source disc in the vacuum counting chamber, allowing a significant fraction drift to the detector. Because of the drawback of the long half-life of ^{209}Po, extra care was taken on sample handling to prevent detector contamination. Figure 3. shows the overall ^{210}Po analysis in the urine by wet decomposition for alpha analysis.

The polonium alpha spectrum with ^{209}Po viewed in Alpha Vision software is shown in Figure 4. A particular amount of ^{209}Po was added to the sample to be used as an internal isotope tracer, making it possible to calculate the results of the radiochemical analysis. The result was calculated from the peak area of ^{209}Po using equation (1), while ^{210}Po activity was calculated from equation (2).

$$\eta_{\text{chem}} = \frac{\text{Area}_{209\text{Po}}}{\text{A}_{209\text{Po}} \cdot \text{tm}209_{Po} \cdot \varepsilon_{\text{det}}} \quad (1)$$

$$\text{A}_{210\text{Po}} = \frac{\text{Area}_{210\text{Po}}}{t\eta_{\text{chem}} \cdot \varepsilon_{\text{det}} \cdot m_s} \quad (2)$$

where, A^{210}Po is activity of ^{210}Po in the sample, Bqkg^{-1}, A^{209}Po is activity of ^{209}Po in the sample, Bqkg^{-1}, Area^{210}Po is peak area of ^{210}Po, counts, Area^{209}Po is peak area of ^{209}Po, counts, t is measurement time, s, η_{chem} is yield of ^{209}Po tracer,%, ε_{det} is counting efficiency, %, m^{209}Po is tracer mass, g, and m_s is sample mass, kg.

Table 1. ^{208}Po, ^{209}Po, and ^{210}Po decay data

Radionuclides	**Half-life (t1/2)**	**Disintegration Modes**	**Eα (MeV)**	**Intensity (%)**
^{208}Po	2.898y	α:99.99777%	5.1149	99.9956
			4.220	4.220
^{209}Po	102y	α:99.52%	4.885	19.7
			4.883	79
			4.622	0.551
			4.310	$1.5x10^{-4}$
			4.110	$5.6x10^{-4}$
^{210}Po	138.376	α:100	5.40746	99.99876
			4.60436	$1.24x10^{-3}$

References: [7]

Figure 1. Image of an auto-deposition setup

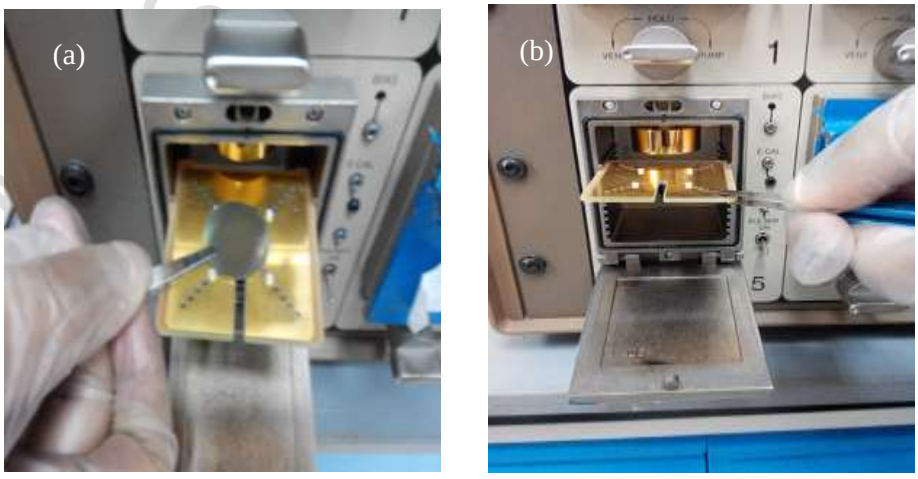

Figure 2. a) Active source placed paralleled to the detector b) Shelve placed at the same calibrated mixed alpha standard ANALYTICS source

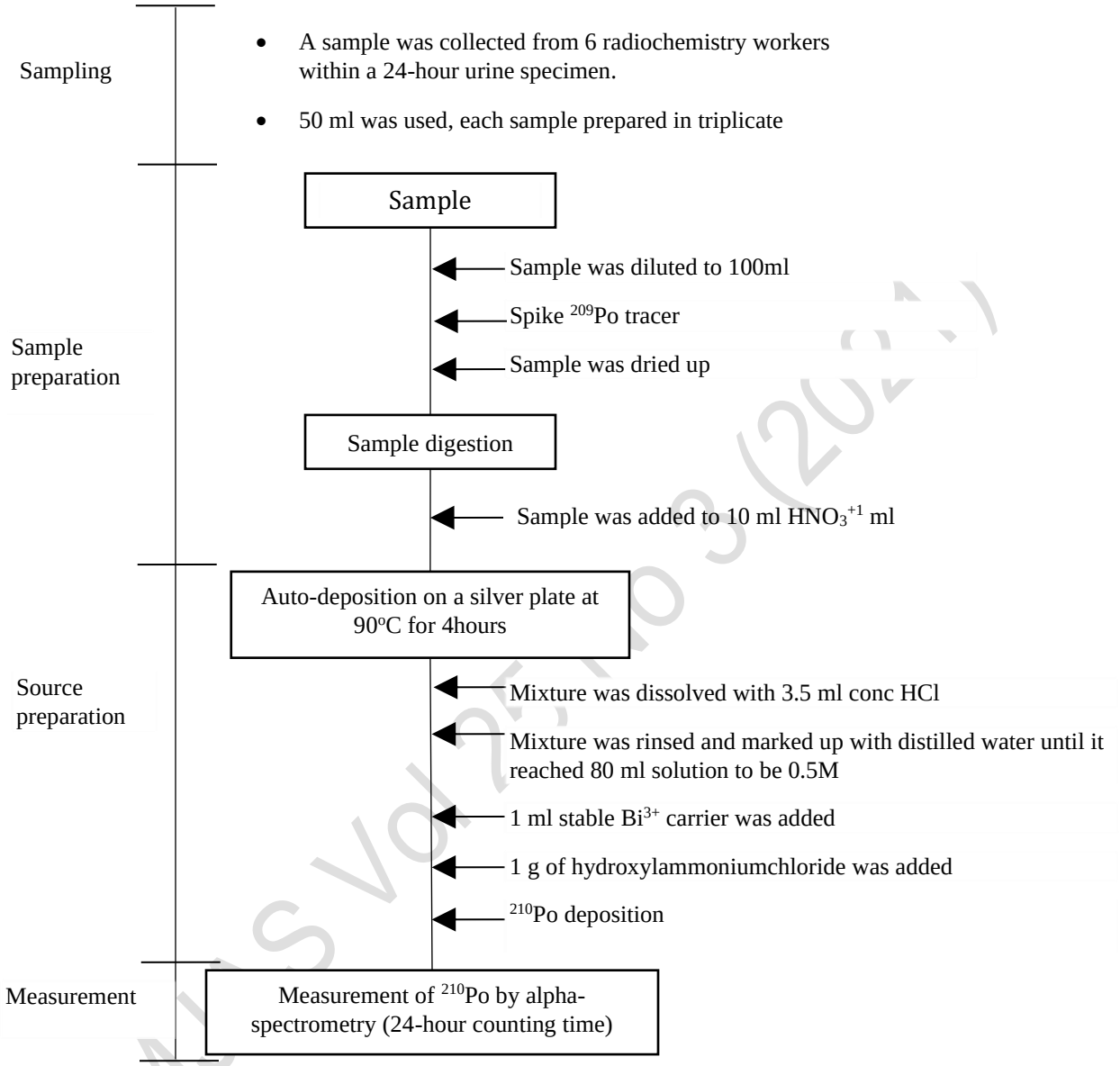

Figure 3. A flow chart for determination of ^{210}Po in urine samples using alpha spectrometry system

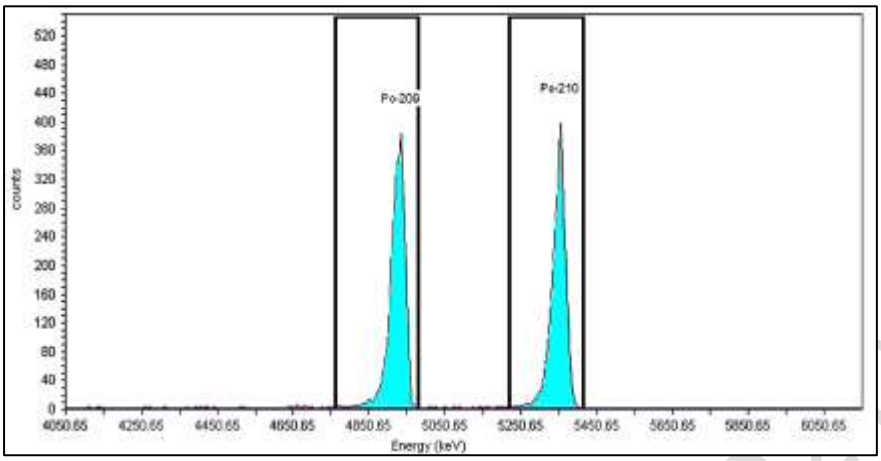

Figure 4. Polonium alpha, ^{210}Po spectrum with ^{209}Po yield tracer from this study

Results and Discussion

Urine samples

Table 2 shows the ^{210}Po concentrations in the urine samples relative to blank samples. The average specific radioactivity measured is 17.93 mBqL^{-1}, with an estimated relative uncertainty of 0.80 mBqL^{-1}. The recovery data is quite good and comparable to other research [6,8]. The varies of ^{210}Po of each individual is greatly dependent upon the daily excretion rates between individuals. Individual variations in urine volume provided to the laboratory for examination may imply that specific urine samples can lead to a collection period of less than or more than 24 hours.

The results of the ^{210}Po bioassay are compared to those of the preceding sample in Table 3. In comparison to previous investigations, the data has showed that the specific radioactivity is slightly greater than other reported research [4, 10]. The variation of ^{210}Po in urine is influenced by the targeted person, with ^{210}Po in urine acquired from radiation workers in this study being more susceptible to internal exposure. Radiation workers who work with TENORM should wear personal protective equipment (PPE) such as a respiratory mask to prevent inhalation or ingestion of the radioactive gas or dust to avoid serious health effects due to external and or internal exposure on workers [12]. Considering the ^{238}U decay series from TENORM activity, workers may internally expose to the radioactive ^{226}Ra gas by inhalation if without applying radiation protection principles. The ^{226}Ra then decays to its granddaughter of ^{210}Po in particulate form and is trapped and accumulated inside the body. The alpha particle will ionize the individual's cell and cause damage to the cell and tissue. The considering pathway may give an acute health risk to the radiation worker. The reported data in this study, however, is still within the background levels of ^{210}Po in urine which has been examined and assessed for almost 550 measurements of the general public [11].

Assessment on the detection level

The ^{210}Po concentration in urine samples from the current study was computed into the daily excretion rate determined in mBq.d^{-1}, as shown in Table 4. Based on the UK Health Protection Agency's experience in assessing ^{210}Po contamination of members of the public in London areas, the maximum committed effective dose to be considered is below 1 mSv.y^{-1}, which is computed by ^{210}Po daily excretion rate determined at or below 30 mBqd^{-1} [4]. It is well known that the ^{210}Po levels in urine differed from person to person based on environmental and lifestyle variables [6]. Studies have indicated that more than 80% of the contribution from ^{210}Po to the total annual background dose is derived from ^{210}Po associated with seafood consumption [14, 15]. The accumulation of ^{210}Po in various environmental products, including fish and shrimp, is

well-reported [16, 17]. Hence, food intake across the district can also affect the data, while uptake through inhalation of air and cigarette smoke gives smaller contributions [18].

According to the category of public, occupational, and emergency, the level of exposure is tabulated in Table 5. According to the findings of the current report, the following screening thresholds were deemed to be of no significance in terms of radiation safety. The required detection level (RDL) for assessing background levels in human urine and chronic exposures is 3mBqd^{-1} for the general public, indicating that the Malaysian Nuclear Agency's Radiochemistry Laboratory has far from the criteria for the assessment of ^{210}Po in urine. Based on this study, we would like to emphasise that the suitability of experimental procedures can be ascertained as ^{210}Po measurements with alpha spectrometry are given in a standardised manner and have been extensively used for various biological samples such as marine samples, body fluids like urine and blood [4, 19].

Table 2. Results of determination ^{209}Po in urine sample

Sample	**^{210}Po Determination (mBqL^{-1}±1SD)**	**Recovery (%)**
Blank	2.85	77.59
P 1	12.67±0.44	72.78
P 2	38.42±0.26	74.93
P 3	41.46±0.51	79.08
P 4	12.48±0.18	76.32
P 5	10.78±0.23	80.61
P 6	17.86±0.57	78.48

Table 3. Comparison of ^{210}Po in urine with the previous study measured using alpha spectrometry system

Concentration (mBqL^{-1})	**Sample**	**References**
Average: 23.27 Min: 1.33 Max: 49.84	Radiochemistry laboratory worker	This study
Min: 0.5 Max: 4.8	Reference group of Portuguese citizens	[4]
	Saudi Arabia Volunteer public	[10]
5.9	• Non-smokers	
8.9	• Smokers	
8.1	• Shisha smokers	
Min: 0.6 Max: 69.6	550 measurements from the general public were examined	[11]

Table 4. ^{210}Po daily excretion rate compared with other studies measured using alpha spectrometry system

Country	**Sample /Country**	**Average Daily Excretion Rate (mBqd^{-1})**	**References**
Malaysia	Radiochemistry laboratory worker	Average:1.16 Min: 0.07 Max: 2.49	This study
Brazil	Monazite plant workers		[13]
	• Non-smokers	5.2	
	• Smokers	9.9	
Italy	Volunteer public		[5]
	• Non-smokers	11.8	
	• Smokers	12	
Portugal	Portuguese citizen potentially exposed to ^{210}Po in London	3.06	[4]
United Kingdom	UK residents acquired internal contamination	30 mBq in 24 hours (when computed to committed effective dose is below 1mSvyr^{-1})	[2]

Table 5. Level of exposure according to category

Category	**Level of Exposure**	**Committed Effective Dose**	**References**
1	Public	0-1 mSvyr-1	
2	Occupational	1-20 mSv yr-1	[6]
3	Emergency	>20mSv	

Conclusion

The proposed method provided an easy way to determine ^{210}Po concentration in a urine sample. The most common method for measuring ^{210}Po in urine is sample digestion, Po isolation, and auto deposition, accompanied by α spectrometric counting. Urine samples are conventionally digested and evaporated in an open beaker on a hotplate in the presence of oxidising agents (acids and hydrogen peroxide). Since radioactive compounds like ^{210}Po are present in nature, they can also be found in the human body. To assess any contaminants, a clearer understanding of the population's baseline level is needed. The ^{210}Po excretion rate can be used to estimate doses resulting from ^{210}Po or a combination of ^{238}U chain radionuclides that comprises ^{210}Po. The ^{210}Po of radiochemistry laboratory's worker in this study were measured between 1.33 mBqL^{-1} to 49.84 mBqL^{-1}. Finally, further research should be conducted to increase the precision and accuracy of ^{210}Po determination on urine samples significantly. The RAS laboratory must always get ready with ^{210}Po and other radionuclides on hand for bioassay research. This method should allow to measure low levels of ^{210}Po and a fast turnaround for screening. In an emergency,

this preliminary study was suggested for further review, considering continuous method development.

Acknowledgments

The authors thank the management of the Waste and Environmental Technology Division for supporting the implementation of this project, and the staff of Alpha Laboratory, Radiochemistry and Environmental Laboratory for their assistance in this work.

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