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Improved urine analysis for polonium, natural uranium, and thorium isotopes and background survey in collected samples of normal people

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Abstract
A sequential analysis procedure for urine samples was developed and validated focusing on ^{210}Po, natural uranium, and thorium radioisotopes. The amount of sample for analysis and counting time were estimated to meet the criteria of minimum detectable activity, which was referenced from the ICRP. The analysis procedure was modified via sequential extraction and was validated using certified reference samples. The time required for sample preparation by this method was compared with those by other methods. Forty-four urine samples collected from participants were analyzed, and the results were compared with those obtained in other studies.

Keywords Sequential extraction · Thorium · Natural uranium · Polonium · Background survey · Urine analysis

Introduction

Internal dosimetry of victims can be used as critical information for medical treatments pertaining to radiation emergency. Many international organizations recommend performing radiobioassays for an efficient medical treatment. In vitro techniques and analytical methods, especially using excreta samples, is an effective way of conducting the radiobioassays [1]. In case of artificial radionuclides such as plutonium and americium, the background radioactivity level in the urine samples is hardly measurable if there is no internal exposure to the radionuclides, while the uptake of naturally occurring radionuclides may occur through air and food intake [2]. The background level in these natural contaminants should be corrected in response to the radiation emergency, and this has also been suggested in previous studies [3].

Generally, alpha-emitting radionuclides such as polonium, uranium, and thorium isotopes should be extracted from raw samples by chemical treatment because of their physical characteristics [4]. Many studies have focused on enhancing the efficiency of the sample preparation time, and several analysis procedures for polonium, uranium, and thorium isotopes have been reported [5–11]. The conventional methods mainly focus on the single extraction technique or other types of matrix such as environmental samples. However, the pretreatment step is time-consuming, and urinalysis, in particular, has a limit on the total amount of sample owing to the difficulties in sampling from the victims.

In this study, the conventional method was improved for sequential extraction using the limited amount of urine sample, and the overall analysis procedure was reviewed and verified by focusing on ^{210}Po, natural uranium, and thorium radioisotopes. The amount of sample and counting time were estimated following the criteria of minimum detectable activity (MDA). The analysis procedure was validated using the synthetic urine spiked with certified reference materials provided by U.S. NIST (National Institute of Standards and Technology) intercomparison program. The chemical recovery of each radionuclide was estimated to verify the effectiveness of this method. Forty-four urine samples collected from participants were analyzed. The participants were from local areas where there was no radiation work. Also, the results were compared with those obtained in other studies [16].

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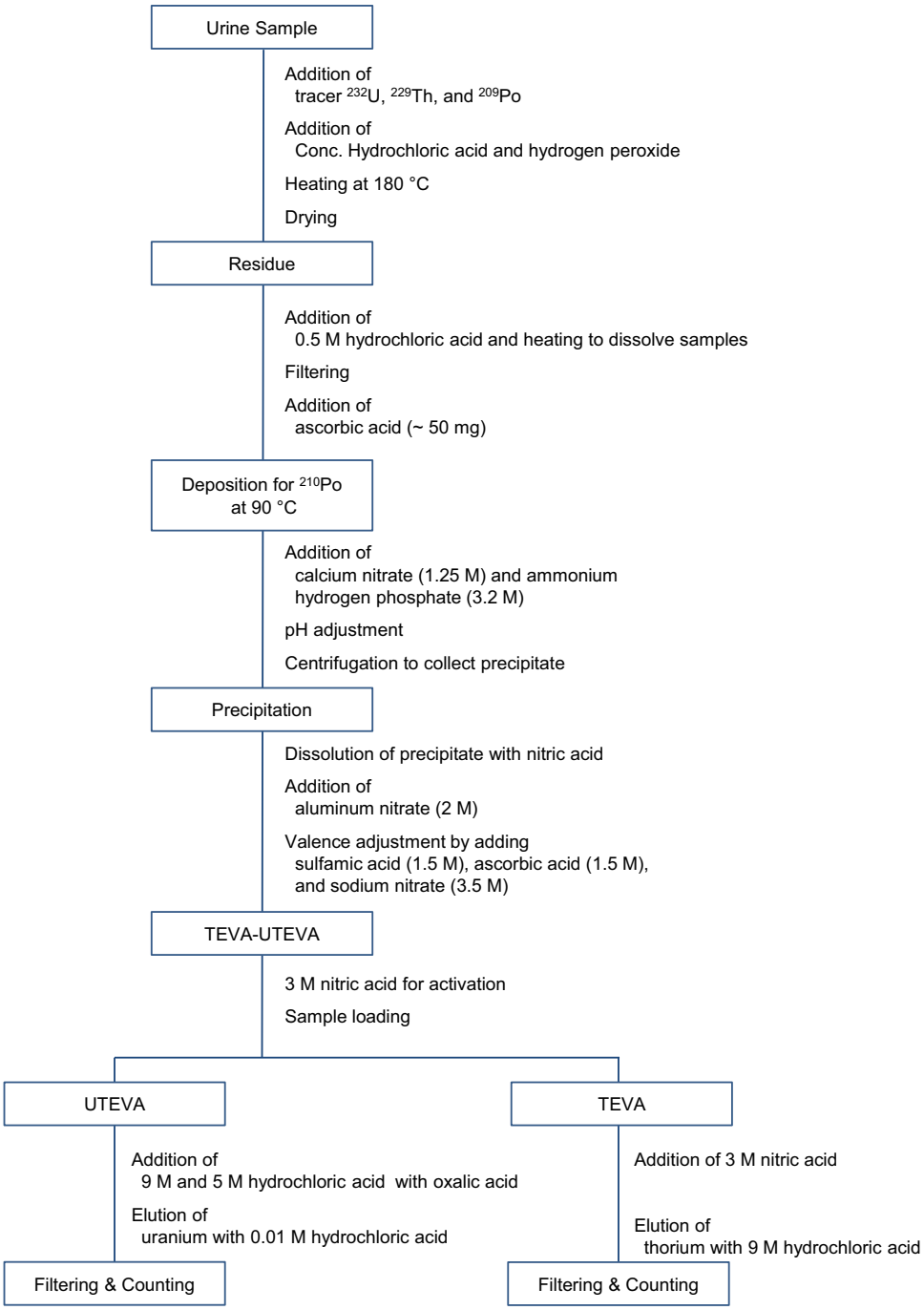

Fig. 1 Protocol for the preparation of urine samples for analysis

Experimental

Sample preparation

Urine samples were acidified with 6 M nitric acid below pH 3 for preservation, and the collected samples were concentrated by evaporation method using a hot-plate. Nitric acid and hydrogen peroxide were used to eliminate the organic matter [12]. The ^{210}Po counting source was prepared by auto-deposition using silver disks (diameter 17.2 mm). The disk was immersed into the sample solution, and the deposition was carried out for 180 min at 90 °C [13, 14].

The sample solution is directly used for making calcium phosphate precipitation step after removing the disk. The thorium and uranium isotopes were separated by sequential extraction using TEVA (TEVA Resin, AliquatTM 336) and UTEVA (UTEVA Resin, dipentyl pentylphosphonate) (Fig. 1) The chemical recoveries of ^{230}Th and natural uranium were corrected by the addition of ^{228}Th and ^{232}U, respectively [15].

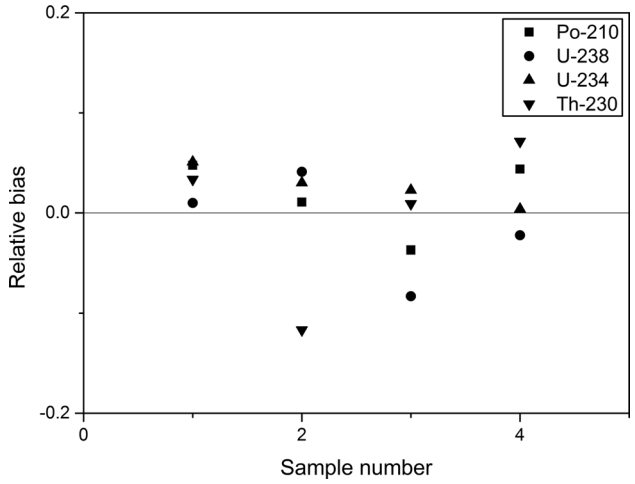

Fig. 2 Validation of spiked urine samples

The column separation was conducted using a vacuum manifold system. To obtain the counting source probes, cerium fluoride co-precipitate was deposited on a polypropylene filter (pore size 0.1 µm, diameter 25 mm). The filter was dried under an infrared lamp for 30 min and attached to a sticky plate, and subsequent radioactivity measurements were conducted for 200,000 s using alpha spectrometry (Alpha Analyst, Canberra Inc.).

Criterion for minimum detectable activity

Many expert groups have recommended the MDA derived from the reference dose as a criterion for reasonably establishing bioassays for radiation protection [16, 17]. Urine samples collected from a normal patient can be stored up to 24 h. In this study, the normalization method proposed by ICRP was adopted, using the creatinine content within 10 h of sample collection [18]. The minimum counting time was 23 h per sample, when using alpha spectrometer. The MDAs were derived based on the simplified MDA equation proposed by ANSI N13.30 [19] (1). The s_b is the standard deviation of a total blank count, and t and V are counting time and sample volume, respectively.

$$\mathrm{MDA} = \frac{(4.65 s_b + 3)}{tV} \quad (1)$$

Results and discussion

Validation

Four reference urine samples spiked with certified reference materials (CRMs) were used for validation. Urine samples were collected from normal people regardless of their exposure to radiation. The overall chemical yield ranged from 60.5 to 96.4%, and the result was in good agreement with the reference values ($< \pm 10\%$) according to ANSI N13.30 criteria [19] (Fig. 2).

Validation was performed using five reference urine samples spiked with NIST CRMs as test samples of Radiochemistry Intercomparison Program hosted by the U.S. NIST. Each synthetic urine sample was spiked with 13 alpha-emitting radionuclides (^{210,214,218}Po, ^{222}Rn, ^{226}Ra, ^{230}Th, ^{234,235,238}U, ^{238,240}Pu, ^{241}Am, and ^{243}Cm) and 12 beta- and

Table 1 Validation of reference samples

Radionuclide	Traceability test		Performance test		
	Traceable	Traceability (%)	Relative bias (%)	Relative precision (%)	Acceptance
^{238}U	Yes	43	−4.5	8.3	Pass
^{234}U	Yes	45	−0.4	7.0	Pass
^{230}Th	Yes	50	3.9	9.4	Pass
^{210}Po	Yes	99	−10	11	Pass

Table 2 Nature of sampling site and details of participants

Sampling site	Nature of sampling site	Number of participants (female)	Age	Number of smokers
A	Metropolis	5 (4)	24–56	2
B	Inland area	10 (5)	57–76	1
C		10 (5)	32–56	1
D	Coastal area	10 (3)	35–75	2
E	Mountainous area	9 (4)	23–69	1

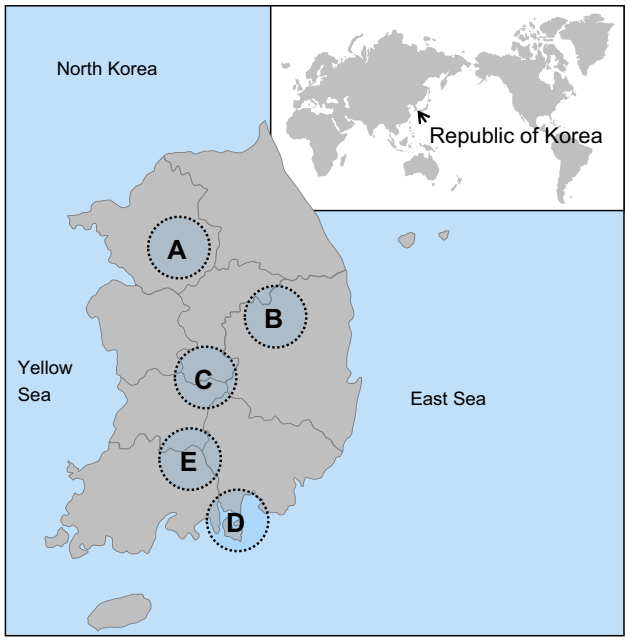

Fig. 3 Map of the sampling sites in Korea

Table 3 Background radioactivity level of natural uranium [16]

Country	^{234}U (mBq/d)	^{238}U (mBq/d)	Comments
U.S.	1.42	1.30	Control subjects, US
Jordan	–	3.95	Unexposed subjects, JO
Germany	–	0.17	Unexposed subjects from south of DE
This study	10.8	8.34	Normal people

Table 4 Background radioactivity level of ^{210}Po and ^{230}Th [16]

Country	^{210}Po (mBq/d)	^{230}Th (mBq/d)	Comments
U.S.	9.30	–	–
Germany	2(LD)-9.9	–	People in Berlin
Belgium	–	0.53 (Urine) 7.7 (Feces)	Workers not exposed to Th
Japan	25 66	–	Non-smoker Smoker
This study	22.5	6.06 (Urine)	Normal people

gamma-emitting radionuclides (^{57,60}Co, ^{90}Sr, ^{90}Y, ^{137}Cs, ^{210,214}Pb, ^{210,214}Bi, ^{231,234}Th, and ^{234m}Pa), and five samples were repeatedly analyzed to confirm the reproducibility of the data. The traceability and relative bias and precisions were examined as the performance criteria following ANSI N42.22 and N13.30 [19, 20]. The results for natural uranium, ^{230}Th, and ^{210}Po were within the range of reference values (Table 1).

Study of the background level

Previous studies have reported that the background level of several radionuclides in the human body was dependent on the exposure to terrestrial radiation by naturally occurring radionuclides [5–11]. To investigate this, some projects were carried out to survey the background level in urine samples. In this study, forty-four urine samples collected from normal people dwelling in five local areas were analyzed. Each sampling site was specifically selected considering the lifestyles and environment, such as metropolis with over million residents, inland cities, mountainous districts, and coastal areas (Table 2 and Fig. 3).

The radioactivities of ^{238}U, ^{234}U, ^{230}Th, and ^{210}Po were 8.34, 10.8, 6.06, and 22.5 mBq/d, respectively. The ratio of ^{238}U and ^{234}U were relatively different from the general natural uranium ratio due to the variaction of total values. The coefficients of variation for ^{238}U and ^{234}U were 17% and 24%, respectively. The overall data were similar to those of the previous studies reported from other countries. Moreover, the background levels did not differ significantly with the sampling site, suggesting that Koreans normally consume processed foodstuffs and agricultural and marine products distributed by well-organized logistics. The lifestyle and dwelling condition of the participants were also similar despite the different sampling area following questionnaires. The radioactivity of ^{210}Po was slightly higher than the other radionuclides, and this observation was similar to that in other studies [8, 21, 22] (Tables 3 and 4).

The comparison of the radioactivities of ^{238}U and ^{210}Po showed slightly different trends, which was not affected by the decay series. The results showed that the background levels of naturally occurring radionuclides in the human body were not dominated by the decay series but mainly originated from the inhabiting environment [10] (Fig. 4).

Conclusions

In this study, a sequential method for the analysis of ^{210}Po, natural uranium, and thorium radioisotopes in urine samples is developed and validated. The procedure was applied to measure the background levels in urine samples collected from normal people. The total counting time was assessed to meet the MDA criteria. In the future, trace element detection techniques need to be applied to the sequential procedure to reduce the measurement time.

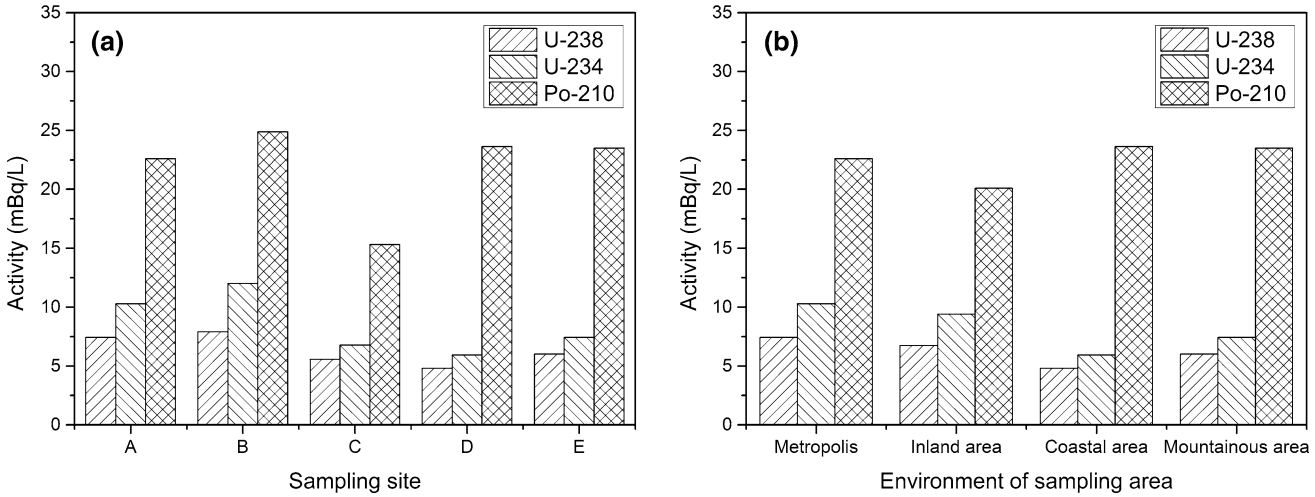

Fig. 4 Measurement by sampling sites (**a**) and environment (**b**)

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