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Standardization of sequential separation of naturally occurring radionuclides in drinking water

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ABSTRACT

A procedure for sequential determination of isotopes of polonium, radium, and uranium from the same aliquot of a water sample has been standardized. The important step in the procedure is coprecipitation of radionuclides of interest with calcium phosphate followed by auto deposition of polonium on a silver planchette. Radium is precipitated with barium nitrate under ice cold condition. Uranium isotopes are separated using ion exchange resin. ^{133}Ba was used for estimating the chemical yield of radium assuming that these elements have similar chemical behavior. ^{232}U and ^{209}Po were used for estimating the chemical yield of ^{234} U, ^{238} U, and ^{210} Po, respectively. Seven water samples were analyzed and the average chemical yield for polonium, barium, and uranium were obtained at 71.8, 65, and 51.6%, respectively. The standardized procedure is being used in the analysis of these natural radionuclides in packaged drinking water.

Keywords: Sequential separation; Natural radionuclides; Alpha spectrometry; Tracers; Bottled drinking water

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1. Introduction

Humans are constantly exposed to natural radiation sources both externally and internally. Consumption of drinking water is one of the main route of internal exposure and the potential naturally occurring radioactive isotopes in water are ^{238}U, ^{234}U, ^{226}Ra, ^{210}Po, ^{228}Ra, etc. from uranium and thorium series. ^{226}Ra and ^{228}Ra are two important long-lived isotopes of radium from uranium and thorium series, respectively. These radioisotopes are leached from earth's crust to ground and surface water. Uranium is a widely distributed naturally occurring element usually present in trace quantities, the average crustal abundance being 2–3 mg/kg. Natural uranium is a mixture of three isotopes ^{238}U (99.3%), ^{235}U (0.71%), and ^{234}U (0.0054%). Due to the short half-life (138.4 d), ^{210}Po is one of the radionuclides with very high radio toxicity and is one of the main sources of internal dose received by humans from alpha emitters. The radionuclides of natural uranium and thorium series being alpha/beta emitters, regulatory agencies in

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several countries have guidelines for their safe limiting concentrations. In India, the annual permissible limits for gross alpha and gross beta from natural sources in drinking water have been set at 0.1 and 1 Bq/L, respectively [1]. Uranium, the heaviest of the naturally occurring elements, is more chemically toxic than radiological. It has been identified as a nephrotoxin [2].

In today's world, water has become a traded commodity, particularly as a source of quality water and hence there is a need to determine the contents of radioactivity levels in them. The aim of the present work is the standardization of a method for simultaneous analysis of important naturally occurring radionuclides such as ^{228}Ra, ^{226}Ra, ^{210}Po, ^{238}U, ^{235}U, and ^{234}U in packaged drinking water (PDW). Investigators from several countries, in the process of assessing the radiation exposure through consumption of bottled drinking water have either used discrete quantity of sample for the determination of each element or determined only a few important radionuclides. Desideri et al. have used 150–200 ml of sample each for U, Po, and Ra isotopes [3]. Bonotto and Bueno from Brazil have used 40–45 L of total water and taken sub samples of 10–15 L for gross alpha, gross beta, and individual nuclides [4]. Gharbi et al. from Tunisia [5] and Guogang et al. from Italy [6] have also used sub samples (0.5–2 L) for the determination of natural nuclides and U-isotopes, respectively. The specialized separation techniques have also been used by several investigators for the purpose. Gharbi et al. have used element specific solid chromatograph U-TEVA for U-separation followed by LSA or alpha-particle spectrometry and/or ICPMS measurement techniques [5]. Guogang et al. have used micro-TOPO chromatography columns for the separation of individual nuclides [6]. Considering that concentration of natural radionuclides in water is very low, large volume of sample is required for improving the detection limits. In view of using single aliquot of sample, a sequential procedure for the separation of natural radionuclides using commonly available conventional chemicals has been standardized. As many steps of separations are involved and losses are expected, tracers of ^{232}U, ^{209}Po, and ^{133}Ba were used for the yield determination of ^{234,238}U, ^{210}Po, and ^{226,228}Ra, respectively. ^{209}Po has a longer half-life (102 y) than the other available polonium tracer ^{208}Po (2 y) and also the alpha energy of ^{209}Po (4.88 MeV) is well separated from the energy of ^{210}Po (5.3 MeV) resulting in better separation of the peaks for analysis. Due to non availability of long-lived artificial radioisotopes of Radium, ^{133}Ba was used in our procedure. ^{133}Ba has a half-life of 10.51 y and is a homolog of radium. This method involves various steps like coprecipitation, sequential separation, electrodeposition, autodeposition, and quantifying the activity of each radioisotope using alpha spectrometer, gross alpha, and gross beta counters. This paper describes the method standardization of sequential separation of radionuclides (^{238}U, ^{234}U, ^{226}Ra, ^{210}Po, ^{228}Ra) in water samples with addition of radiotracers for radiochemical yield.

2. Materials and methods

2.1. Tracers

^{209}Po: A working solution with an activity of 8.8 mBq/mL (01.05.2011) was prepared from a calibrated solution, (product code PMP10030), National Physical Laboratory, UK.

^{232}U: A working solution with an activity of 11 mBq/mL was prepared from an activity standard solution of activity 10.37 Bq/g, obtained from NPL, UK (product code UDP 10,050).

^{133}Ba: A working solution with an activity of 22.2063 Bq/mL, prepared from a standard solution of 5,206 Bq/mL from Amersham, UK, was used. (product code: RM 13,969).

2.2. Instruments

A Canberra Model 7401VR alpha-particle spectrometer with PIPS detectors of 450 mm^2 active area and 100 micron depth was used to measure the polonium and uranium radioisotopes. The data acquisition was done through an in-house spectra analysis software. Gamma spectrometry was performed with Baltic Scientific Instrument HPGe detector of 40% relative efficiency. A low background gas flow type beta counter having anti-coincidence mode operation with guard detector, operated in G.M region, was used for β-activity estimation of ^{228}Ac. The background and efficiency were about 1.5 cpm and 30% for ^{40}K standard which was made from analytical grade potassium chloride with visibly similar thickness and dimensions as that of samples.

2.3. Preconcentration

Preconcentration of polonium, radium, and uranium isotope was done using calcium phosphate coprecipitation method. 10 L deionized water sample was taken in a container, acidified with 15 mL conc. HNO_3, and homogenized thoroughly. The radiotracers ^{133}Ba (2.2 Bq), ^{232}U (5.5 mBq), and ^{209}Po (4.4 mBq), 300 mg calcium carrier and 15 ml H_3PO_4 were added. ^{133}Ba is added as a tracer for radium isotopes to obtain the radiochemical recovery of

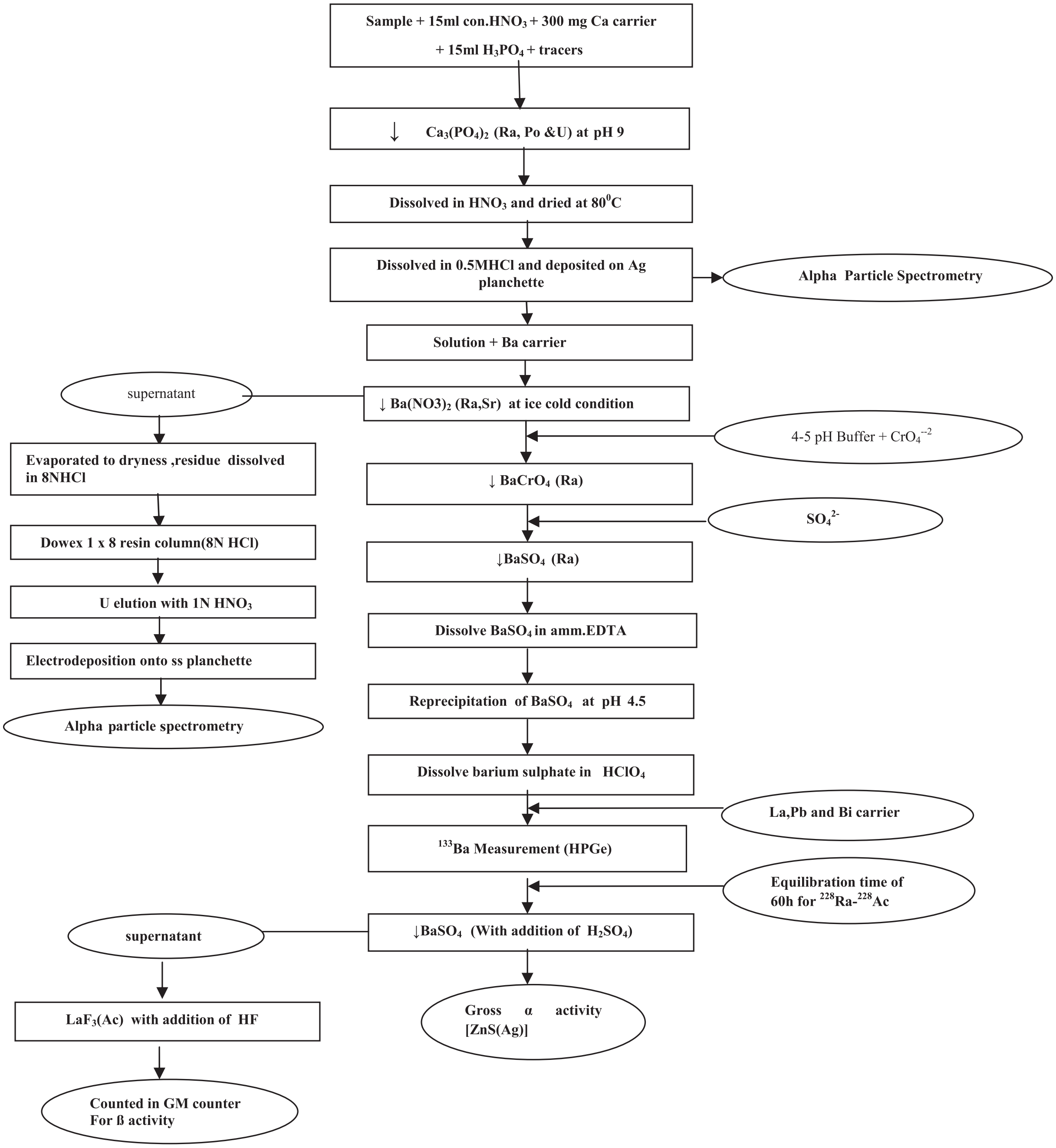

Fig. 1. Outline of sequential radiochemical separation of Po, U, and Ra.

radium in the procedure. The sample was stirred vigorously and left overnight, so as to ensure the chemical equilibrium between tracers and radionuclides is present. Precipitation of $Ca_3(PO_4)_2$ was achieved by adjusting the pH to 9 with ammonia solution. The precipitate was allowed to settle down overnight. The supernatant was discarded, final volume centrifuged, and the precipitate was washed several times with distilled water. The general outline of the sequential separation is given in Fig. 1.

2.4. Sequential separation of ^{226}Ra, ^{228}Ra, ^{210}Po, and U isotopes Separation of polonium

The calcium phosphate precipitate along with the radiotracers was dissolved in nitric acid and evaporated to dryness at temperature not more than 80˚C so that polonium does not volatilize during evaporation. The residue was dissolved in 37% HCl and evaporated to dryness. The residue was redissolved in con. HCl and diluted to 250 ml as the final solution is of 0.5 M HCl. Polonium was auto deposited on silver planchette dipped in 0.5 M HCl by constant stirring at temperature 80˚C for 3 h. The polonium disc was removed from the Teflon holder, washed with distilled water and acetone, and dried. Polonium activity was quantified by alpha-particle spectrometry for a counting duration of 86,400 s.

2.5. Separation of radium and uranium isotopes

The solution, after Po auto-deposition was evaporated to dryness. Further, it was evaporated with 5.0 mg of Ba carrier and conc. HNO_3. Ba carrier is added for the quantitative precipitation of barium nitrate which carries radium along with it leaving uranium and calcium in the supernatant. PDW samples are chemically and physically treated and hence to ensure efficient coprecipitation of radium with barium nitrate, 5 mg of barium carrier is added.

The residue was treated with 30 mL of conc. HNO_3 under ice cold condition to precipitate $Ba(NO_3)_2$ which carries Ra quantitatively. The supernatant and ice cold washings of the nitrate are collected together for subsequent uranium analysis.

2.6. Procedure for ^{226}Ra and ^{228}Ra analysis

The barium nitrate precipitate was dissolved in distilled water and pH was adjusted to 4.5 with addition of ammonium acetate–acetic acid buffer. Barium chromate was precipitated at this pH by adding 10% sodium chromate solution. Barium chromate precipitate was centrifuged and dissolved in dilute HCl. Barium sulfate was precipitated by adding 1:4 H_2SO_4. Barium sulfate precipitate was centrifuged and dissolved in 10% ammoniacal EDTA. Barium sulfate was reprecipitated by adjusting the pH to 4.5 with acetic acid. The $BaSO_4$ precipitate was redissolved in $HClO_4$. Five milligrams each of La, Pb, and Bi carrier were added. Solution was kept for 60 h to obtain equilibrium between ^{228}Ra-^{228}Ac. During this period, the sample was counted in the gamma spectrometer to estimate ^{133}Ba (γ energy- 356.0 keV) recovery, which is used for the evaluation of radium concentration.

Barium lead sulfate which carried the ^{226}Ra was precipitated by adding 1:4 H_2SO_4 to the above solution. The supernatant carried the ^{228}Ac. Barium sulfate precipitate was dissolved in ammoniacal EDTA and reprecipitated at pH 4.5 by adding acetic acid. Barium sulfate precipitate was transferred on to a stainless steel planchette, dried, flamed, and counted in gross alpha counter for ^{226} Ra activity for 86400s after 10 days.

Though ^{232}U decays to ^{224}Ra (half-life 3.66 days) they do not interfere in quantifying ^{226}Ra using gross alpha measurement .Viewing to the short half-life of ^{224}Ra which is also an alpha emitter, they will contribute only during the first few days after radium separation and hence activity measured for ^{226}Ra after 10 days of the precipitation has negligible contribution from ^{224}Ra.

HF: HCl (1:3) mixture was added to the supernatant after separating barium sulfate to precipitate La (Ac)F_3. This precipitate was transferred to aluminium planchettes, dried, and counted for ^{228}Ac beta activity which is in equilibrium with ^{228}Ra. The ^{228}Ac separation and counting was done on the same day to minimize the loss due to decay.

2.7. Procedure for uranium

The supernatant after removing barium nitrate precipitate was used for the analysis of uranium isotopes. Supernatant was evaporated to dryness and dissolved the residue in 8 M HCl (5 ml). This was passed through anion exchange column (Dowex 1 × 8). Thorium which does not form any anionic complex with 8 M HCl does not get exchanged on the column and is washed off when the 8 M HCl is passed through the column while uranium remains on the column. Uranium was eluted with 1 M HNO_3. The eluate was evaporated to dryness. Uranium was electrodeposited on a 25 mm diameter stainless steel disk used as cathode and using platinum wire as anode at a pH of 2.2 and current 0.3A for 2 h. The electrodeposited planchette was dried, flamed red hot, cooled, and counted in alpha-particle spectrometer for alpha energy of ^{232}U (5.3 MeV). In the real water samples, alpha energies of ^{238}U (4.2 MeV), ^{235}U (4.93 MeV), and ^{234}U (4.77 MeV) are used for their quantification. Nuclear data for polonium, uranium, radium, and barium isotopes are given in Table 1 [7].

3. Results and discussion

A method was standardized for sequential separation and analysis of isotopes of polonium, radium, and uranium. In order to evaluate the radiochemical yield of the procedure, seven aliquots of water samples were prepared by adding radiotracers ^{209}Po (4.4 mBq), ^{232}U (5.5 mBq), and ^{133}Ba (2.221 Bq) to 10 L deionized water. The results obtained for the seven samples are given in Table 2.

Table 1
Nuclear data for polonium, uranium, and radium isotopes

Radionuclide	Half-life	Disintegration mode	Energy	Intensity
^{232}U	68.9y	α:100%	5.263 MeV	31.55
			5.320 MeV	68.15
^{238}U	4.468E9y	α:100%	4.151	21
			4.198	79
^{234}U	2.455E+5y	α:100 %	4.722 MeV	28.42
			4.775 MeV	71.38
^{209}Po	102y	α:99.52%	4.885 MeV	20
			4.883 MeV	80
^{210}Po	138.4d	α:100%	5.304	100
^{226}Ra	1,600y	α:100.00%	4.601	6.16
			4.784	93.84
^{133}Ba	10.55y	γ	356.0129	62.05%

Table 2
Radiochemical yield of ^{209}Po, ^{232}U, and ^{133}Ba in drinking water

	^{209}Po/added 4.4 mBq		^{232}U/added 5.5 mBq		^{133}Ba/added 2.221 Bq	
Sample number and analysis date	Measured activity (mBq)	% Recovery	Measured activity (mBq)	% Recovery	Measured activity (Bq)	% Recovery
W-1 21/7/2011	3.7 ± 0.4*	83.9 ± 9.8	2.7 ± 0.1	49.6 ± 2.4	1.4 ± 0.1	61.2 ± 5.4
W-2 10/8/2011	2.6 ± 0.4	57.0 ± 8.0	3.1 ± 0.4	55.6 ± 6.4	1.7 ± 0.2	76.1 ± 7.2
W-3 30/8/2011	2.7 ± 0.4	60.4 ± 8.6	1.9 ± 0.4	34.7 ± 6.6	1.3 ± 0.1	58.1 ± 5.0
W-4 15/9/2011	3.5 ± 0.4	79.5 ± 9.3	2.8 ± 0.1	50.9 ± 2.0	1.2 ± 0.1	54.1 ± 4.5
W-5 10/10/2011	2.9 ± 0.4	64.9 ± 8.6	3.3 ± 0.4	60.0 ± 7.3	1.4 ± 0.1	63.9 ± 5.0
W-6 10/10/2011	2.8 ± 0.6	64.0 ± 13.9	3.0 ± 0.4	54.5 ± 6.9	1.5 ± 0.1	68.4 ± 5.0
W-7 30/12/2011	4.1 ± 0.4	93.0 ± 9.1	3.1 ± 0.4	56.4 ± 7.1	1.6 ± 0.2	73.4 ± 6.8

*The standard deviation expressed at 68% confidence level.

The radiochemical yield of ^{209}Po ranged between 57.0% and 93.0% with an average of 71.8% and standard deviation (SD) of 13.6%. The yield for ^{232}U was in the range of 35.0–60.0% with an average value of 51.7% and SD of 8.2%. The recovery for Ba-133 was in the range of 54.0–76.0% with an average of 65% and SD of 8%. Chemical yield of barium can be applied in the estimation of radium isotopes as they have similar chemical behavior and the experimental ratio of Ba:Ra recovery was reported to be 1.04 [8]. The radiochemical yields obtained in the present sequential experiments were comparable to those obtained by other investigators with discrete aliquots; for instance as 55% for U, 70.9% for Po [3], and 60–91% for ^{226}Ra and ^{228}Ra [9].

The ^{226}Ra was counted several times after the separation, viz. immediately, after 10 days and after 30 days resulting in the same count rate, which shows ^{224}Ra growth was not significant enough to interfere in the ^{226}Ra estimation. Estimation of ^{226}Ra activity was done by the following equation:

$$\text{Activity of } ^{226}\text{Ra (Bq/L)} = \frac{\text{cps}}{E \times R_Q \times 10}$$

where R_Q is the radiochemical recovery of ^{133}Ba and E is the efficiency of gross alpha counter.

A few real PDW samples were analyzed using the developed procedure. The activity concentration was in the range of 0.08–0.78 mBq/L for ^{210}Po, 0.1–0.8 mBq/L for ^{238}U, 0.11–3.3 mBq/L for ^{234}U, BDL to 1.6 mBq/L for ^{226}Ra, and it ranges from BDL to 6.6 mBq/L for ^{228}Ra.

4. Minimum detectable activity

MDA was evaluated with Currie's formula (1968) [10] given below

$$\text{MDA (Bq/L)} = \frac{2.71 + 4.65\sqrt{\text{N}_\text{b}}}{V \times E \times R_Q \times T}$$

where V is the volume of the sample (L), R_Q is the radiochemical yield, T is the sample measurement time (in seconds), and E is the counting efficiency.

For the alpha emitters, using 10 L of sample, with typical counting times of 86,400 s, the MDA values was 0.08 mBq/L for ^{232}U with an average radiochemical yield of 0.52 and 0.05 mBq/L for ^{209}Po with a R_Q value of 0.72. MDA values for ^{226} Ra (counting time 86,400 s) and ^{228} Ra (counting time 3,600 s) are 0.15 mBq/L and 4.9 mBq/L, respectively, R_Q value being 0.65 for radium.

5. Conclusions

- This sequential separation method uses easily available conventional chemicals and consumes lower sample.
- The variation in radiochemical recovery for different isotopes shows the need for yield determination on each sample.
- The standardized procedure was found to be reasonably good for application to packaged water analysis for determining U, Po, and Ra isotopes as the yields are moderate and consistent.
- Though the standardized procedure is tedious and long, it is being successfully used in our laboratory with ease as tracers are added to each sample to determine the radiochemical yield.

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