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Sequential determination of ^{210}Po and uranium radioisotopes in drinking water by alpha-particle spectrometry

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ABSTRACT

Procedures for the sequential determination of low level ^{210}Po and uranium radioisotopes in drinking water by alpha-particle spectrometry are presented. After addition of ^{208}Po and ^{232}U tracers, the radionuclides were preconcentrated from water samples by co-precipitation on $Fe(OH)_3$ or MnO_2 at pH 9 using ammonia solution. The ^{210}Po source was prepared by spontaneous deposition onto a copper disc either before or after uranium separation. The uranium source for alpha-particle counting was prepared by micro co-precipitation with CeF_3. The procedures were tested on mineral water and the results obtained are compared.

1. Introduction

The geological setting strongly influences the occurrence of natural radionuclides in drinking water. Their concentrations are variable and depend on the nature of the aquifer rock types and the prevailing lithology. Most radionuclides are at levels that are low enough to not be considered a public health concern. But there are, however, areas where higher levels of naturally occurring radionuclides are found or contamination of drinking water sources from man-made nuclear materials occurred. Measurements of their levels in drinking water are therefore important to reduce the potential exposure of the public. Quantitative information about the concentration of critical alpha-particle emitting nuclides in food and drink is important in the study of cumulative radiation effect on human health. The dose coefficient is always related to the specific radionuclide. Concern about the radioactivity content of water intended for human consumption has been taken into account in international regulations.

In 1998, the European Community issued Directive 98/83/EC on the quality of water intended for human consumption (EC, 1998) which replaced the old drinking water regulation of 1980 (EC, 1980). Directive 98/83/EC deals with microbiological, chemical and radioactive requirements and asks public authorities to organize drinking water surveys. With respect to radioactivity measurements, parameter values have been fixed for tritium and for total indicative dose. The Directive 98/83/EC points out that the total indicative dose must be evaluated excluding tritium, ^{40}K, ^{14}C, radon and its decay products, but including all the other radionuclides of the natural decay series. Maximum values for radon and long-lived radon decay products such as ^{210}Pb and ^{210}Po are separately proposed in a European Commission Recommendation (EURATOM 2001). The recommendation gives a maximum concentration of 0.2 and 0.1 Bq/L for ^{210}Pb and ^{210}Po, respectively. The future refinement of the European regulation on the quality of drinking water will define reference values for more individual radionuclides than at present and required parameters to be monitored. Laboratories should accordingly measure the most common natural (^{226}Ra, ^{228}Ra, ^{234}U and ^{238}U) as well as artificial radionuclides in the drinking water. In the Council Regulation (EURATOM) No 2218/89, the European Union fixed maximum permitted levels of radioactive contamination of foodstuffs in the case of radiological emergency (EURATOM, 1989).

The World Health Organization (WHO) produces international requirements on water quality and human health in the form of guidelines that are used as the basis for regulation and standard setting in developing and developed countries world-wide. In the "Guidelines for Drinking Water Quality" second edition, 1993 (WHO, 1993), the measurement of gross alpha and beta activities was recommended. These values were fixed to 0.1 and 1.0 Bq/L for alpha and for beta activity, respectively. In the third (current) edition (WHO, 2006), the guidance levels for the radionuclides originating from natural sources or discharged into the environment as the result of current or past activities were presented. However, for the first year immediately after an accident, not these levels but generic action levels for foodstuffs apply. In the WHO Guidelines the guidance levels for the individual natural and artificial radionuclides in drinking water are defined.

Recently, the Institute for Reference Materials and Measurements (IRMM) of the EC Directorate General Joint Research Centre (JRC) organized an international comparison exercise on determination of ^{226}Ra, ^{228}Ra, ^{234}U and ^{238}U in drinking water.

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The determination of the reference values for ^{226}Ra, ^{234}U and ^{238}U in drinking water, obtained by alpha-particle spectrometry with emphasis on the radiochemical separation procedures, was described in detail elsewhere (Benedik et al., 2008).

Due to its short half life of 138.4 days, ^{210}Po is one of the radionuclides with the highest radiotoxicity and one of the important sources of the internal dose received by humans from alpha emitters. Therefore, the aim of the work presented in this paper was to investigate two different approaches for the sequential determination of low-levels of ^{210}Po and uranium radioisotopes in bottled drinking water by alpha-particle spectrometry. Two different preconcentration methods for polonium and uranium were used by co-precipitation with $Fe(OH)_3$ and MnO_2 at pH 9 using an ammonia solution. The ^{210}Po source for alpha counting was prepared by spontaneous deposition onto a copper disc before and after uranium separation using a UTEVA column. The uranium source for alpha counting was prepared by micro co-precipitation with CeF_3.

2. Experimental

2.1. Samples

For this study, we used three water samples from the same batches which were used for the international comparison exercise on the determination of ^{234}U and ^{238}U. The water was bought from different companies in Hungary and it was bottled in 1.5 L PET bottles.

2.2. Tracers

^{208}Po: A calibrated solution, product code PMP10030, was purchased from AEA technology, UK. The tracer contained 0.8% impurities of ^{209}Po at the date of purchase. A working solution with an activity (1.172 ± 0.015) Bq/g on reference date 15.04.2008 was used.

^{232}U: A working solution with an activity of (1.158 ± 0.016) Bq/g on 19.06.2007 was prepared from an activity standard solution with an activity 0.734 kBq/g, standardized at IRMM (Sibbens et al., 2004).

2.3. High-efficiency alpha-particle spectrometry

A Canberra Model 7401 VR (Canberra, Meriden, CT, USA) alpha-particle spectrometer and PIPS detectors with 450 mm^2 sensitive areas were used to measure the polonium and uranium radioisotopes. The data acquisition was done using the Canberra Genie-2000 software. The counting times varied from 4 to 8 days, depending on the volume of the sample.

2.4. Separation techniques

2.4.1. Preconcentration

The preconcentration of polonium and uranium from the water samples (1.5–4.5 L) was done applying the two most frequently used methods, co-precipitation with $Fe(OH)_3$ and MnO_2, respectively. All the samples were treated in the same way. After pouring the sample into a beaker, the water was acidified and homogenized by mixing. ^{208}Po ($\sim$0.05 Bq) and ^{232}U tracers ($\sim$0.05 Bq) were added and the solution was stirred in order to allow establishing of a chemical equilibrium between the tracers and the radionuclides in the sample. Due to the low level activity concentrations of ^{210}Po and the uranium radioisotopes in the water, the sample was—after addition of the reagents for preconcentration—vigorously mixed for 6 hours. Finally, the precipitate was allowed to settle down overnight.

2.4.1.1. Precipitation with iron (III) hydroxide. After sample acidification with concentrated HNO_3 (3 mL of acid per 1 L of the sample), a known amount of ^{208}Po and ^{232}U tracers were added. The $Fe(OH)_3$ was produced by a reaction of added $FeCl_3$ solution with ammonia solution. The precipitate was allowed to settle down for several hours. The supernatant was discarded, the final volume was centrifuged and the precipitate was washed several times with distilled water.

2.4.1.2. Precipitation with manganese dioxide. After sample acidification with concentrated HCl (2 mL of acid per 1 L of the sample), known amounts of ^{208}Po and ^{232}U tracers were added. Precipitation of MnO_2 was achieved by adding $KMnO_4$ and $MnCl_2$ and adjusting the pH to 9 with ammonia solution. The precipitate was allowed to settle down for several hours. The supernatant was discarded, the final volume was centrifuged and the precipitate was washed several times with distilled water.

2.4.2. Radiochemical separation

For the sequential determination of polonium and uranium radioisotopes in water we used two different approaches. After dissolution of the $Fe(OH)_3$ or the MnO_2 precipitates, Procedure 1 achieved the uranium separation by a UTEVA column and a spontaneous deposition of the polonium after the uranium separation. In Procedure 2, a spontaneous deposition of polonium was done at first and the radiochemical separation of uranium using UTEVA resin was included in the last step.

2.4.2.1. Procedure 1. Procedure 1 is schematically shown in Fig. 1.

1st step: separation of uranium by using a UTEVA column.

2nd step: spontaneous deposition of polonium.

The $Fe(OH)_3$ or MnO_2 precipitate was dissolved directly in the centrifuge tube with concentrated nitric acid (for $Fe(OH)_3$) or with a mixture of concentrated nitric acid and hydrogen peroxide (for MnO_2), respectively. The solution was adjusted to 3 M HNO_3 and loaded onto a 2 mL prepacked UTEVA column, pre-conditioned with 3 M HNO_3. The column was then rinsed with 3 M HNO_3 (Horwitz et al., 1993). The 3 M HNO_3 fraction was collected into a clear beaker for further polonium analysis. The column was washed with 9 M and 5 M HCl to remove the thorium and finally the uranium radioisotopes were eluted with 15 mL of 1 M HCl. The micro co-precipitation method with cerium fluoride was used for thin source preparation and alpha spectrometric determination (Hindman, 1983; Sill and Williams, 1981). The cerium fluoride suspension was filtered through polypropylene Resolve™ Filter (Eichrom Industries Inc.) with 25 mm in diameter and a pore size of 0.1 μm. The dried filter was mounted onto a stainless steel disc and covered with 6% VYNS foil in order to prevent recoil ion contamination of the detector. The activities of the uranium radioisotopes were measured by alpha-particle spectrometry.

Depending on the preconcentration of radioisotopes from the water, the collected 3 M HNO_3 solution was slowly evaporated to dryness, the resulting residue was dissolved with concentrated hydrochloric acid and with a mixture of concentrated hydrochloric acid and hydrogen peroxide. The solution was adjusted with distilled water to pH 1. To prevent co-plating of other potentially interfering ions (Fe^{3+}, Mn^{6+}), 0.5 g of ascorbic acid was added. A spontaneous deposition of polonium on a 19 mm diameter, thoroughly cleaned Cu disc was carried out at 90 °C for 4 hours. The Cu disc covered on one side was fixed in a holder and immersed into the solution (Benedik and Vreček, 2001). After deposition, the disc was removed, washed with distilled water