Microchemical Journal 110 (2013) 675–680

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Radiochemical characterization of mineral waters for a European interlaboratory comparison

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ARTICLE INFO

Article history:
Received 15 July 2013
Accepted 14 August 2013
Available online 24 August 2013

Keywords:
^{226}Ra
Uranium
^{210}Po
Alpha spectrometry
Drinking water
Dose assessment

ABSTRACT

The objective of this work was to select waters as realistic test items for an interlaboratory comparison on gross alpha/beta measurement in drinking waters. For this reason, a preliminary radioanalytical survey studying the naturally occurring alpha emitting radionuclides was carried out in 11 popular and regularly consumed mineral waters from the European market. The activity concentrations of the main naturally occurring alpha-emitting radionuclides (^{226}Ra, ^{210}Po, ^{234}U, ^{235}U, ^{238}U and ^{228}Th) were determined by using alpha spectrometry after separation from the matrix elements. Additionally, the committed effective dose was also estimated from the water consumption. Average activity concentrations of radionuclides in the mineral waters were in the following order: ^{226}Ra > ^{234}U > ^{238}U > ^{210}Po > ^{228}Th > ^{235}U. The estimated committed effective doses for the analyzed mineral water samples are in the range 2.5–134.2 μSv a^{-1} with an average 41.5 μSv a^{-1}, which is well below 100 μSv a^{-1}, the total indicative dose recommended by EC/WHO for drinking water (excluding mineral waters). Only one mineral water sample did not meet this requirement, its constant consumption would result in a dose higher than 100 μSv a^{-1}, mainly due to the contribution of ^{226}Ra and ^{210}Po. Apart from the main radiological characteristics of the analyzed waters, this study provides additional information for consumers and authorities about the potential internal exposure risk from mineral water intake. Based on the radionuclide composition and the total dissolved solids of the mineral waters two candidates were selected as potential test items for an interlaboratory comparison exercise.

1. Introduction

On the basis of the EURATOM treaty (Article 35–36) [1] monitoring and reporting of environmental radioactivity is one of the EU member states' obligations. To check quality and comparability of these measurement results the Institute for Reference Materials and Measurements (IRMM) was requested to organize interlaboratory comparisons (ILCs) by the European Commission's Directorate - General for Energy (Fig. 1).

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies and directives. The realizations of this policy support in practice are development of rapid and accurate measurement methods, provision of reference data, production and characterization of certified reference materials (CRMs) and organization of ILCs. With regard to this latest task, IRMM is responsible for the coordination of ILCs in environmental radioactivity measurements since 2003. ILCs have been already organized in different matrixes: air filter, soil, organic material and water. The next ILC focuses on one of the most widespread radioanalytical monitoring methods, gross alpha/beta activity measurement in drinking water samples [2].

One of the main purposes of such an interlaboratory exercise is to obtain a realistic estimate of accuracy under routine conditions. With this tool one can verify the quality of laboratory work, whether the reported results are reliable and comparable. Furthermore, an ILC plays another important role. It is a feedback for laboratories about their performance. If any problems exist during the laboratory work (method validation, calibration, settings, data analysis, staff expertise), an ILC helps to identify them. Last but not least, proficiency test participation is recommended in ISO 17025 [3] and necessary for laboratory accreditation.

To run a representative ILC, the selection of test items is a crucial step. In order to find representative natural origin water samples for the gross alpha/beta ILC, numerous important parameters had to be taken into account during the material selection (e.g.: activity concentration of the alpha emitting radionuclides, salinity, chemical composition, international drinking water directives and recommendations) [4,5].

After a literature study on radioactivity and chemical composition of mineral waters, 11 commercially available mineral water samples were pre-selected for radionuclide specific analysis for our ILC. The activity concentrations of ^{226}Ra, ^{210}Po and U isotopes were determined in each sample. On the basis of the alpha spectrometry results and the salinity, two candidates were selected as ILC materials. To complete the radiochemical analysis of the naturally occurring alpha emitting

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http://dx.doi.org/10.1016/j.microc.2013.08.008

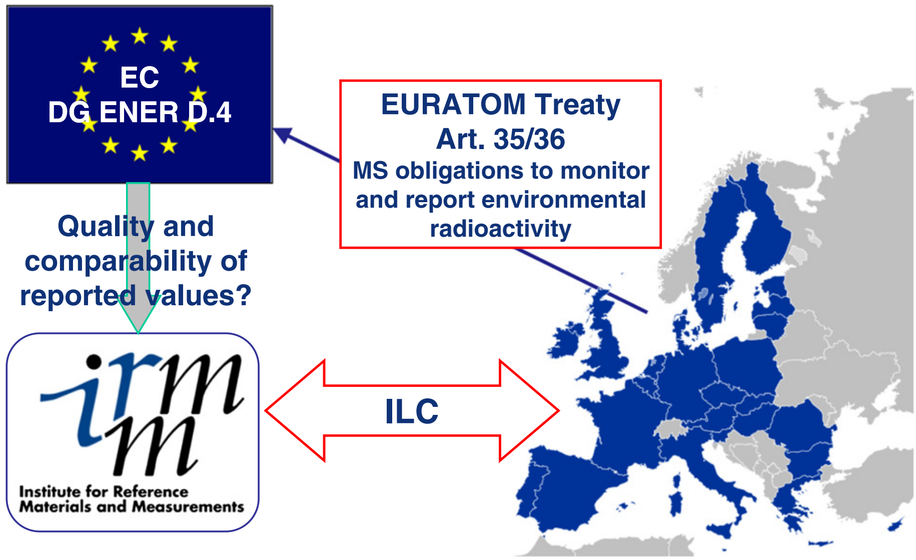

Fig. 1. The scheme of the interlaboratory comparisons organized by JRC-IRMM.

radionuclides in these two ILC candidates, the thorium activity concentration was also measured. Besides these two natural waters, additionally one spiked sample was prepared at IRMM (not discussed in this paper), thus three ILC samples were prepared in total.

From dose exposure point of view, more and more attention is being paid to the importance of restricting radiation from natural isotope origins. Water is an essential part of human diet with an average of 2 L d^{-1} consumption rate [5]. Besides its main inorganic constituents, water contains natural origin contaminants (e.g. radionuclides) with different concentration. Radionuclides — especially alpha emitting nuclides such as ^{226}Ra, $^{234/238}$U, ^{210}Po — can be found in some drinking waters in concentrations that may be of health concern [6]. In order to protect public health from internal radiation from water intake, the WHO established guidelines for drinking water quality on screening levels for gross alpha (0.5 Bq L^{-1}) and gross beta activities (1 Bq L^{-1}) [5]. Below these screening levels of gross activity, drinking water is acceptable for human consumption and actions to reduce radioactivity are unnecessary. Otherwise, nuclide specific analysis is required to determine the radionuclide content and assess the dose exposure.

Furthermore, the EU Council [4] and the WHO [5] recommend a reference level of effective dose received from drinking water consumption at 100 μSv a^{-1}. It must be noted that this value excludes the dose received from ^{3}H, ^{40}K, ^{222}Rn and radon decay products and these recommendations do not apply to natural mineral waters and to waters that are classified as of medicinal benefit. Because of the potential health hazard, it is important to check the radioactivity of drinking waters regularly with accurate methods in competent laboratories. In this respect, we assessed in our work the expected dose contribution attributable to the water consumption of the adult population, if it were exclusively covered by mineral water.

Our paper discusses the preparation of the interlaboratory comparison (ILC) on gross alpha/beta activity measurements in drinking waters focusing on the radionuclide specific analysis and provides information on the potential dose exposure due to exclusive mineral water consumption.

2. Materials and methods

2.1. Sampling

Eleven commercially available mineral waters were purchased from different supermarkets in Europe. Most of the samples — seven brands — were purchased in supermarkets in Belgium (in June, July 2011) while four Polish mineral waters were taken from supermarkets in Poland in May 2011. All the mineral water samples were bottled in polyethylene terephtalate (PET) bottles with volume of 0.5 – 2 L. Before the analysis, the collected waters were acidified ($pH < 2$) with concentrated nitric acid to avoid loss of radionuclide fractions by adsorption onto the wall of the can and prevent any biological activities.

2.2. Gross alpha activity determination

The gross alpha/beta analysis is based on a standard method which consists of a co-precipitation pre-concentration step, filtration and measurement step [7]. The pH of the filtered water sample is set with sulfuric acid and is heated to purge radon and CO_2. Then the radium isotopes are co-precipitated with barium as $Ba(Ra)SO_4$, whereas uranium, thorium and polonium isotopes can be co-precipitated with $Fe(OH)_3$ by adding Fe^{3+} carrier while NH_4OH is used to adjust the pH ≈ 7–8. In the next step the co-precipitates are filtered through a membrane filter and the filters with the precipitate are dried.

Gross alpha measurements were carried out with a 10-detector, low-background gas-flow proportional counting system (Berthold, model LB790). The high voltage was set to 1450 V and the counting gas (Ar/CH_4, 90/10) flow was kept stable with a flow rate of ~25 mL min^{-1}. The gross alpha activity of the filtered–dried precipitate was measured for 3 × 300 min. Alpha counting efficiency was determined by checking the degree of self absorption for this geometry. Sources for self absorption were prepared by using ^{241}Am standard solution, deionized water and the ISO standard was followed as for the routine water analysis. The alpha counting efficiency of the non attenuated source was 21.0%.

2.3. ^{226}Ra determination

The ^{226}Ra determination is based on the analytical scheme adapted by Vasile et al. [8] using micro co-precipitation alpha source preparation [9]. An aliquot of water sample (1 L) was spiked gravimetrically with ^{133}Ba tracer (~30 Bq) followed by adding concentrated H_2SO_4 10 mL L^{-1} water. Precipitate was formed by adding 1 mL of 30 mg Pb^{2+} mL^{-1} drop wise while it was kept stirred for 2 h and it was left to settle overnight. After decanting the supernatant the precipitate was transferred into a centrifuge tube and centrifuged at 3500 rpm for