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RADIOACTIVITY CONCENTRATIONS IN SPA WATERS – DOSE ASSESSMENT

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Abstract. *In this study 6 different spa water samples from Serbia, Hungary and Czech Republic were investigated in order to determine their radioactivity concentrations. These waters have been used on a large scale for medical and bathing purposes; for therapy, rehabilitation and recreation and also used for drinking, which is the most important. The obtained results showed that natural activity concentrations of alpha emitting radionuclides was within World Health Organization recommended levels and Serbian applicable regulations, but the gross beta activity exceed 1 Bq L^{-1} for some of the samples. Considering the fact that gross beta activity in four samples was higher than recommended levels, gamma spectrometric measurements were performed, in order to identify radionuclides which caused increase of the gross beta activity. It was found that ^{40}K was responsible for the elevated gross beta activity. Based on the obtained results the annual effective dose was calculated.*

Key words: spa water, gross alpha, gross beta, gamma spectrometry, dose assessment

1. Introduction

Many thermal and mineral spring waters contain relatively high concentrations of naturally occuring radionuclides, alpha emitters (^{238}U, ^{232}Th, ^{226}Ra) and beta emitters derived from the natural series uranium, thorium and actinium, ^{40}K and artificial isotopes, ^{90}Sr and ^{137}Cs. However, these radioactive substances, even in small accounts, may produce a damaging biological effect, and ingested and inhaled radiation can be a serious health problem [1,2].

Determination of the gross alpha and beta activity is widely used as the first step of the radiological characterization of drinking waters and it makes it possible to screen samples for relative levels of radioactivity [3]. The recommended levels of gross alpha and gross beta radioactivity concentration in drinking water are below 0.5 and 1.0 Bq L^{-1}, respectively [4,5]. If one of the recommended values is exceeded, radionuclides have to be identified by alpha and/or gamma spectrometry, and their individual activity concentrations need to be measured. These guidelines ensure an exposure lower than 0.1 mSv y^{-1} assuming a water consumption rate of 2 L d^{-1}. If the estimated dose is higher than 0.1 mSv y^{-1} the reduction in consumption or radionuclide concentration is necessary [4,5].

Spa Junaković is located in the northwest of Bačka, 4 km away from Apatin of Serbia. Water belongs to alkali-muriatic, bromine iodine waters with temperature of 25 °C. In Spa Junaković it is about well-mineralized water with large amount of sodium, chloride, important amount of iodine, hydro carbonates and hydrogen-sulphide [6].

Vrnjačka Spa is located in central Serbia, 200 km south of Belgrade. Mineral water of Vrnjačka Spa falls into two categories: warm mineral water (36.5 °C) is one of the alkaline carbonic acid homeothermic and cold mineral water (14 °C, 17 °C, 25 °C) belongs to the group of alkaline-earth achrotopegae.

Spa Selters is located in central Serbia, 46 km south of Belgrade. The mineral waters issue from two springs. The older one provides alkaline-muriatic acidic water (31-32 °C), rich with sodium bicarbonate and chlorine. The other spring, in use since 1978, issues the water that belongs to the group of alkaline muriatic carbon-acidic hyper-thermal (50 °C).

Mataruška Spa is located in central Serbia, situated on the right bank of the river Ibar, 160 km from Belgrade. Mineral water from Mataruška Spa is hypothermal (48-52 °C), with the highest concentration of sulfur in the south of Europe (127 mg L^{-1}).

Spa Saint Erzsebet in Morahalom (near Szeged) is located in the south-east of Hungary, 12 km away from the border with Serbia. Alkaline thermal water with hydrocarbon, chlorides and iodine comes from

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depth of 660 m. Water temperature amounts 39.5 °C [7].

Karlovy Vary is a spa city situated in western Bohemia of Czech Republic, on the confluence of the rivers Ohre and Tepla, approximately 130 km west of Prague. It is historically famous for its hot springs. The present healing thermal waters (max. 73.4 °C) are strongly mineralized (above 6 g L^{-1} total dissolved solids (TDS)), of Na-HCO_3^--SO_4^{2-}-Cl type. Barite crystals are commonly in vents of many springs in the town [8,9].

This study is focussed on determination and comparison of the level of gross alpha and beta activity in thermal spa waters from different countries in order to show that the use of these waters may have a radiological hazard to human health. The data obtained can provide an important information to regarding the dose exposure risk if spa water is using as drinking water.

2. EXPERIMENTAL

The spa water samples were collected directly from the springs during April and May 2012. Before measuring of activity concentration in spa waters from Serbia, the samples were first analyzed on pH, temperature and electrical conductivity. The temperature of spa water samples was measured immediately after sampling. Physicochemical parameters of spa water samples are listed in Table 1.

Table 1 Physicochemical parameters of spa water samples from Serbia

Name of spa	pH	T (°C)	Electrical conductivity (μS cm^{-1})
Junaković	7.25	36.5	5100
Vrnjačka	6.50	31.5	2900
Selters	6.77	49.5	2300
Mataruška	6.80	32.1	1700

2.1. Procedure for gross alpha and beta activity

An appropriate amount of spa water sample (about 1 - 1.5 L) was evaporated slowly to a small volume under an infrared lamp and the residue was transferred quantitatively to a stainless-steel planchet [10]. The aliquot concentrate should be quantitatively transffered in small portions (not more than 5 mL at a time) to a planchet, evaporating each portions to dryness. The sample residue is than dried in a drying oven at 105 °C for at least 2 hours, cooled in a desiccator and weighed. For a 5.9 cm diameter of counting planchet, an aliquot containing 130 mg of dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross alpha and beta activity. This mass of solids is important because of self-absorption effect given that only the solid residue on the source surface is measured. In the case of a larger amount than 130 mg, self-absorption corrections must be introduced, because self-absorption effects depend on the mass thickness. Measurements were performed immediately after preparation. The counting time was 7200 s for gross alpha and beta activities.

Gross alpha and beta activity in thermal water samples were determined by α/β low level proportional counter Thermo Eberline FHT 770 T (ESM Eberline Instruments GmbH, Erlangen, Germany). The counting efficiencies for the system are 26 % for alpha and 35 % for beta. Alpha and beta efficiencies of gas proportional counter were checked with ^{241}Am and ^{90}Sr sources, respectively.

The gross alpha and gross beta activity, $A_{\alpha\beta}$ expressed in Bq L^{-1}, was calculated using the following equation:

$$A_{\alpha\beta} = \frac{N - B}{E_f \times V} \quad (1)$$

where N is the count rate for the sample (s^{-1}), B - the background (s^{-1}), E_f - the efficiency of the detectors for alpha and beta measurements and V - volume of the sample (L).

Minimum detectable activity (MDA) was calculated by the equation (2):

$$MDA = \frac{LLD}{V} \quad (2)$$

where LLD is the detection limit (s^{-1}).

2.2. Procedure for gamma spectrometry

Volumes of 1.5 L of samples of spa waters were evaporated to 200 mL under an infrared lamp and then poured into 200 mL cylindrical polyethylene vials. The counting time interval was 60000 s. The samples were stored to reach the radioactive equilibrium between ^{238}U and ^{226}Ra during one month.

Gamma spectrometric measurements were performed using a HPGe Canberra detector (Canberra Industries, Meriden, Connecticut, USA) with a counting efficiency of 20 %. Geometric efficiency for water matrices in the plastic bottle of 200 mL was determined by a reference water material (Czech Metrological Institute, Praha, 9031-OL-116/8, type ERX) spiked with a series of radionuclides (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{88}Y, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{210}Pb). The spectra were analyzed using the program GENIE 2000. The total activity of the calibration source (^{60}Co and ^{133}Ba issued by the Czech Metrological Institute and traceable to BIPM (*Bureau International des Poids et Measures*)) was used to check the efficiency calibration and the general operating parameters of the gamma spectrometry system (source positioning, contamination, library values, and energy calibration).

The specific activity of the radionuclides in the samples was calculated using the equation:

$$A = \frac{N}{t \times P_\gamma \times E_f \times V} \quad (3)$$

Origin	Gross alpha activity	Gross beta activity
Spain (spa water) [11]	0.07 - 2.42	0.1 - 5.8
Turkey (thermal water) [12,13]	0.060 - 3.909	0.12 - 2.097
Hungary (spring water) [3]	0.032 - 1.749	0.033 - 2.02
Brazil (spring water) [14]	0.001 - 0.428	0.12 - 0.86
USA (spring water) [15]	< 0.037 - 31	0.110 - 18.9

where N is the count rate of the sample, P_γ - probability of gamma decay (%), E_f - the efficiency of the detector and V - volume of the sample (L).

Minimum detectable activity was calculated by the equation (4):

$$MDA = \frac{LLD}{V} \qquad (4)$$

where LLD is the detection limit, $LLD = 2.71 + 4.65\sqrt{B}$ and B - background. The combined measurement uncertainty of results was calculated at the 95 % level of confidence (k=2).

3. Results and discussion

The gross alpha and gross beta activity concentrations in thermal spa waters taken from different countries are given in Table 2. It can be seen from Table 2 the gross beta activities are higher than the corresponding the gross alpha activities. For 4 spa water samples the gross alpha activity was lower than the minimum detectable activity (MDA). The activity values of the rest two samples were higher than MDA but below than recommended level of 0.5 Bq L^{-1} for gross alpha activity [4,5]. The gross beta activity ranged between 0.13 and 4.3 Bq L^{-1}. The values of gross beta activity only for 2 spa water samples are lower than recommended upper limit value of 1 Bq L^{-1} [4,5]. On the other hand, if these thermal waters are used for drinking, the criteria of radiological safety have been met only for water samples from Mataruška Spa and Spa Saint Erzsebet.

Table 2 The gross alpha and gross beta activity concentrations of spa waters (Bq L^{-1})

Name of spa	Gross alpha activity	Gross beta activity
Junaković	0.18 ± 0.05	1.8 ± 0.3
Vrnjačka	< 0.13	1.7 ± 0.3
Selters	< 0.41	1.5 ± 0.2
Mataruška	< 0.07	0.50 ± 0.05
Saint Erzsebet	< 0.04	0.13 ± 0.02
Karlovy Vary	0.36 ± 0.09	4.3 ± 0.5

Comparison the results of the gross alpha and gross beta activity concentrations in spa water samples obtained in this study with the values obtained in the other studies is presented in Table 3. The obtained values are in good agreement with those obtained in other studies.

Table 3 Literature data of gross alpha and gross beta activity concentrations (Bq L^{-1})

Due to the fact that the gross beta activity in 4 spa water samples (Junaković, Vrnjačka, Selters and Karlovy Vary) was higher than the recommended level of 1 Bq L^{-1} [4,5], it was necessary to performed gamma spectrometry. Table 4 presents the results of gamma spectrometric measurements. As can be seen from Table 4, the activitiy concentrations of the investigated radionuclides are lower than MDA, except for ^{40}K. Comparison the gross beta activity with the results of gamma spectrometric determination of ^{40}K and the fact that the ^{40}K is included in the gross beta activity (89 %), we can say that the gross beta activity in spa waters is derived only from natural radionuclide ^{40}K.

Table 4 The results of gamma spectrometry for spa water samples (Junaković-1, Vrnjačka-2, Selters-3, Mataruška-4, Saint Erzsebet-5, Karlovy Vary-6) expressed in Bq L^{-1}

Spa	^{226}Ra	^{235}U	^{238}U	^{232}Th	^{40}K	^{137}Cs
1	< 0.5	< 1.8	< 2.9	< 0.3	1.5 ± 0.6	< 0.2
2	< 0.08	< 1.3	< 0.2	<0.06	1.6 ± 0.3	< 0.04
3	< 0.8	< 2.1	< 0.4	< 0.4	1.3 ± 0.2	< 0.03
4	< 0.1	< 0.9	< 0.1	< 0.01	0.5 ± 0.1	< 0.05
5	< 0.8	< 0.3	< 4.7	< 0.7	< 0.5	< 0.2
6	< 0.5	< 2.4	< 2.9	< 0.3	3.2 ± 1.1	< 0.2

If these spa waters are used for drinking, it is necessary to evaluate the annual effective dose. It was assumed that the gross alpha and beta activities originate from ^{226}Ra and ^{228}Ra concentration [16]. The annual effective dose rate (D) can be calculated using the following Equation [17]:

$$D(Sv) = N \times \eta \times W \qquad (5)$$

where N is volume which adults drink (our assumption is 200 mL per day or 73 L per year), W - the concentration of the radioisotope (Bq L^{-1}), η - the age dependent dose conversion factor (Sv Bq^{-1}). For calculation, we used the dose conversion factors [18]: 2.8×10^{-7} Sv Bq^{-1} for ^{226}Ra and 6.9×10^{-7} Sv Bq^{-1} for ^{228}Ra. Results for calculated annual effective doses from ^{226}Ra and ^{228}Ra for adults are given in Table 5.

The annual effective dose values due to the ingestion of ^{226}Ra in the spa waters varied from < 0.82 to < 8.38 μSv and from 6.5 to 217 μSv for ^{228}Ra. The calculated values of the annual effective doses are below the WHO recommended reference level of 0.1 mSv, except for the ingestion of ^{228}Ra for Karlovy Vary spa water.

Table 5 The annual effective doses from ^{226}Ra and ^{228}Ra (μSv) for age group (>17)

Name of spa	Radionuclide	Annual effective dose
Junaković	^{226}Ra	3.68
Vrnjačka		< 2.66
Selters		< 8.38
Mataruška		< 1.43
Saint Erzsebet		< 0.82
Karlovy Vary		7.36
Junaković	^{228}Ra	90.7
Vrnjačka		90.7
Selters		85.6
Mataruška		25.2
Saint Erzsebet		6.5
Karlovy Vary		217

4. Conclusion

The aim of this study was to investigate whether the spa waters (Junaković, Vrnjačka, Selters, Mataruška, Saint Erzsebet and Karlovy Vary) can be hazardous to human health if used for drinking. In investigated samples gross alpha and gross beta activity were analyzed. The gross alpha activities in all samples are below the level allowed by Serbian regulations. The gross beta activities for two samples are below the recommended reference level of 1 Bq L^{-1}, while for four samples exceed the recommended limits and for these spa water samples it is necessary to perform gamma spectrometric measurements. For spa water samples in which the gross beta activity was exceeded 1 Bq L^{-1}, gamma spectrometry was performed and ^{40}K was detected in concentration from 1.3 Bq L^{-1} for Selters to 3.2 Bq L^{-1} for Karlovy Vary while the concentrations of ^{226}Ra, ^{232}Th, ^{235}U, and ^{238}U were below the detection limits. Also, it was shown that the calculated annual effective dose was less than 0.1 mSv for all spa water samples, except for Karlovy Vary where annual effective dose exceed this value. The present study has been carried out to establish baseline data regarding radioactivity levels of radionuclides in spa waters and the corresponding radiation doses. The obtained results allow the determination of the sources of radioactivity and the distribution of the radionuclides in this region and estimation of the potential health risk to the population.

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