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RADIOACTIVITY OF MINERAL AND SPRING WATERS FROM BULGARIA

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Abstract. *Radiological analysis of mineral waters sampled from springs in the region of Sofia and Velingrad spa resort, and of bottled mineral, spring and table waters from other regions in Bulgaria was carried out as part of the overall monitoring of drinking waters in the country. Content of natural uranium was from 0.003±0.001 to 0.023±0.005 mg/l, gross alpha activity from ≤0.01 to 0.50±0.05 Bq/l and beta activity from ≤ 0.02 to 0.30±0.06 Bq/l. Concentration of indicators in all studied waters met the requirements, provided for in the Regulation for mineral, spring and bottled waters in Bulgaria (U ≤ 0.06 mg/l; gross alpha activity ≤ 0.5 Bq/l; gross beta activity ≤ 1 Bq/l). However alpha activity higher than 0.1 Bq/l, specified in the Regulation for drinking waters, was determined in the mineral water from Ovcha Kupel in Sofia (0.34 Bq/l) and in the bottled mineral water from Devin in the Rhodopes (0.49 Bq/l). Both water samples were further tested for Po-210. Content of Po-210 was under the derived concentration of 0.1 Bq/l laid down in the Regulation on drinking waters. In result of analyses carried out it was concluded the studied waters were not hazardous for human consumption in terms of radiology.*

Keywords: *radioactivity of mineral waters, U, ^{222}Rn, ^{210}Po, gross alpha and beta activity*

1. Introduction

Bulgaria is distinguished by a wide variety of mineral waters. The amount of total dissolved solids (TDS) in most of them is less than 1 g/l, making them suitable for daily consumption.

Radioactivity of waters is determined by the normal presence of traces of natural radionuclides from uranium-radium and thorium series. However, activity concentrations of radioactive elements higher than permissible, may lead to risk for human health. In this regard, the monitoring of radiological characteristics of mineral waters, along with that of drinking waters, is essential, since the main amount of absorbed dose of radioactive radiation in humans is formed by the water consumption.

Radiological monitoring of drinking waters is based on determining the contents of natural and man-made radionuclides. These indicators are dynamic and depend on a number of factors such as erosion processes, amount of precipitation, dissolution processes from aquifers, etc., and require constant and regular monitoring.

The monitoring of drinking waters in Bulgaria is regulated by Regulation 9 on the quality of water intended for drinking and domestic purposes [1] based on the EU recommendations from 1998 and the Regulation on the requirements for bottled natural mineral, table and spring waters intended for drinking purposes [2].

Radiological characteristics of mineral waters sampled from springs in the region of Sofia and Velingrad in the Rhodopes, as well of the most widely sold bottled mineral and spring waters in Bulgaria, were studied to assess the risk of additional radioactive dose load on the population.

2. Materials and methods

2.1. Sampling

2.1.1. Mineral waters sampled from the region of Sofia city

The mineral waters were sampled from the fountains most widely used by the population of the city for drinking purposes and balneology. Some general characteristics of the mineral waters are described below according to the Registry of certificates of mineral waters of the Ministry of Health in Bulgaria [3].

Rudartsy. The total mineralization of water is 270 mg/l. It is characterized as hypothermal (28°), sulfate-hydrocarbonate sodium water without sanitary chemical and microbiological signs of contamination.

Knyazhevo. The water is hypothermal (31°C), pH 9.5 with TDS of 138 mg/l, containing hydrocarbonate, sulfate and sodium ions and metasilicic acid in a colloidal state.

Gorna Banya - hyperthermal (42°C), TDS are 150 mg/l, containing hydrocarbonate, sulfate and sodium ions, metasilicic acid in a colloidal state.

Bankya - hypothermal (36°C), pH 9.6 and total mineralization of 280 mg/l, containing hydrocarbonate, sulfate, calcium and sodium ions, and metasilicic acid in a colloidal state.

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Central Bath - hyperthermal (45⁰C), pH 9.3, TDS – 280 mg/l, containing hydrocarbonate, sulfate and sodium ions and metasilicic acid in a colloidal state.

Pancharevo. The total mineralization of the water is 470 mg/l. It is characterized as hyperthermal (48⁰C), hydrocarbonate calcium magnesium water.

Ovcha Kupel. Content of TDS in the water is 210 mg/l. It is characterized as hypothermal, mineralized, sulfated calcium-sodium, calcium-sodium water containing fluoride.

2.1.2. Mineral waters from spa resort Velingarad

The mineral waters from Velingrad were sampled from two main deposits - the first is from the "Velingrad-Chepino" deposit, and the other three are from "Velingrad-Ladjene" deposit.

"Velingrad-Chepino". The water is characterized as hyperthermal, with low mineralization, hydrocarbonate-sulfate sodium and silicon water, containing fluoride, without sanitary chemical and microbiological signs of contamination [3].

"Velingrad-Ladzhene" - hyperthermal, with low-mineralization, sulfate-hydrocarbonate, sodium and silicon water, containing fluoride, without sanitary chemical and microbiological signs of contamination [3].

2.1.3. Bottled mineral and spring waters

The studied bottled mineral and spring waters were purchased from the commercial network representing the most frequently consumed waters.

2.2. Radiological analysis

The laboratory of radioecology and radioisotope research at ISSAPP "N. Pushkarov" is accredited for determining the content of radioactive elements in waters, soils, plants, food and food products in accordance with the BSS EN ISO/IEC 17025:2018 standard [4].

The content of natural uranium in mineral waters was determined according to a method developed and validated in the Laboratory, based on the principle of forming a complex of tetravalent uranium with arsenazo III and measuring the extinction of the resulting colored solutions at 655 nm wavelength by a spectrophotometer.

The concentration of Rn-222 was measured by gamma-spectrometry by the line of the daughter product Bi-214 at 609 keV in accordance with BSS EN ISO 13164-2:2020 [5]. The gamma-spectrometric system product of Canberra, USA, includes: a coaxial detector of ultrapure germanium with relative efficiency of 30% and energy resolution of 1.8 keV at the 1332 keV of ^{60}Co, a multichannel analyzer (MSA) (Canberra) and a low-background protection camera.

Gross alpha and beta activity in waters were determined according BSS EN ISO 9696/2017 [6] and BSS ISO 9697/2019 [7] respectively preparing a dry residue planchet from an aliquot of the water sample and measuring it on a low background MPC 9300 gas flow alpha/beta counter product of Protean Instrument Corporation.

The content of Po-210 in waters was determined according to standard BSS EN ISO 13161:2020 Water quality - Polonium 210 - Test method using alpha spectrometry [8]. An alpha spectrometer (Alpha Analyst, Canberra, USA) with passivated implanted planar silicon (PIPS) semiconductor detectors and 25% efficiency was used for measuring ^{210}Po activity. The counting time was 120000 s.

3. RESULTS AND DISCUSSION

The results of the water samples study carried out are presented in Table 1.

3.1. Radon

Parametric values for ^{222}Rn are not specified in the Regulation on mineral waters. The concentration of the radionuclide in bottled waters is usually low, since the half-life of radon (3.8 days) is much shorter than the time from the moment of bottling until the water reaches consumers. In addition, radon losses may also occur during the bottling process. However, this is not the case with the direct pouring of mineral water from the source and its subsequent consumption by the population [9]. Therefore, in the present study, the concentration of radon in the waters sampled from fountains was analyzed according to the provisions of the Regulation on drinking waters.

Radon activity concentration in the waters from Sofia region was between ≤ 10 and 25 Bq/l, and in all waters it is lower than the parametric value of 100 Bq/l. In three of the waters it was below the minimum detectable activity (MDA) of 10 Bq/l.

Comparison of results with values obtained for other regions of the country, such as Momin Prohod (1595 Bq/l) [10], Narechenski Bani (613 Bq/l), Pavel Banya (428 Bq/l) [11], shows radon content in the mineral waters in the region of Sofia city is low.

Radon content in the mineral waters, sampled from Velingrad, was relatively higher. The average value was 62 Bq/l compared to 16 Bq/l for the waters from Sofia region. The water from Velingarad-Chepino, showed an activity even higher than the parametric value of 100 Bq/l. Velingrad is located in the Rhodope Mountains, and the higher radon content could be explained with the circulation of the water from Chepino in a bed formed by Proterozoic gneisses and Paleozoic granites and granitoids [3], generally characterized by higher uranium content [12]. The value obtained for the water from Velingarad-Chepino spring is comparable to the results obtained for a natural water from Catalonia, Spain (104.9 Bq/l) sampled from spring characterized by predominantly granite lithology [13] and to the spring-water from the Balaton Highland in Hungary (120 Bq/l) [14].

Bottled waters were not tested for radon, due to the above-mentioned factors concerning the relatively short half-life of the radionuclide and its possible volatilization.

Table 1. Radiological characteristics of studied waters

No.	Sampling location	^{222}Rn	U	Gross alpha activity	Gross beta activity
		Bq/l	mg/l	Bq/l	Bq/l
Mineral waters sampled from Sofia city region					
1	Rudartsy	25 ± 5	0.005 ± 0.001	0.031 ± 0.006	≤ 0.02
2	Knyazhevo	10 ± 3	0.003 ± 0.001	≤ 0.01	≤ 0.02
3	Gorna Banya (fountain in front of the Bath)	≤ 10	0.004 ± 0.001	≤ 0.01	≤ 0.2
4	Gorna Banya (fountain next to the Ring Road)	18 ± 4	0.003 ± 0.001	≤ 0.01	≤ 0.02
5	Bankya (fountain next to the Bath)	≤ 10	0.005 ± 0.001	≤ 0.01	0.03 ± 0.01
6	Bankya (fountain next to Bottling center)	≤ 10	0.003 ± 0.001	≤ 0.01	≤ 0.02
7	Central Bath (Sofia city Center)	25 ± 5	0.005 ± 0.001	≤ 0.01	≤ 0.02
8	Pancherevo	20 ± 4	0.007 ± 0.001	0.048 ± 0.009	0.09 ± 0.02
9	Ovcha Kupel	12 ± 3	0.006 ± 0.001	0.344 ± 0.069	0.28 ± 0.06
Mineral waters sampled from spa resort Velingrad					
9	Velingrad - Chepino (fountain at the Park)	120 ±10	0.008 ± 0.002	0.036±0.007	≤ 0.02
10	Velingrad - Ladzhene (fountain - Recreation Center)	51±5	0.006 ± 0.001	≤ 0.01	≤ 0.02
11	Velingrad – Ladzhene (fountain - Park)	29±3	0.005 ± 0.001	≤ 0.01	≤ 0.02
12	Velingrad - Ladzhene (fountain – Mineral Beach)	47±4	0.004 ± 0.001	≤ 0.01	≤ 0.02
Commercial bottled waters					
13	Mineral water *Bankya*	-	0.005 ±0.001	0.023±0.005	0.05±0.01
14	Mineral water *Velingrad*	-	0.004±0.001	≤0.01	≤0.02
15	Mineral water *Gorna Banya*	-	0.004±0.001	≤0.01	≤0.02
16	Mineral water *Devin*	-	0.023±0.005	0.49 ± 0.05	0.30±0.06
17	Mineral water *Pirin*	-	0.007±0.001	0.051±0.02	0.09±0.03
18	Spring water *Bachkovo*	-	0.002±0.001	≤0.01	0.02±0.01
19	Spring water *Rhodopes*	-	0.004±0.001	≤0.01	0.08±0.02
20	Spring water *Bratsigovo*	-	0.002±0.001	≤0.01	0.04±0.01
21	Spring water *Rila*	-	0.005±0.001	0.024±0.005	≤0.02
22	Table water *Serdika*	-	0.003±0.001	≤0.01	≤0.02

3.2. Natural uranium, gross alpha and beta activity

The maximum permissible concentration of natural uranium specified in the Regulation on mineral waters is 0.06 mg/l. The reference levels of gross alpha and beta activity are 0.5 and 1 Bq/l, respectively. In the Regulation on drinking water, where a consumption of 730 l of water per year is assumed, the maximum concentration of uranium is 0.03 mg/l, and the control levels for gross alpha and beta activity are 0.1 and 1 Bq/l, respectively.

In all tested waters, the concentration of uranium was not exceeding the maximum permissible value, both according to the Regulation on mineral waters and according to that for drinking water. The values ranged from 0.003±0.001 to 0.023±0.005.

The content of alpha activity was between ≤ 0.01 (MDA) and 0.49 Bq/l, and of beta activity between ≤ 0.02 and 0.30 Bq/l, which was within the reference values, provided for in the Regulation on mineral waters.

The comparison between the mineral waters sampled directly from fountains and commercially available bottled waters from the same locations (Bankya, Gorna Banya and Velingrad) showed good correspondence between the values of radiological indicators studied.

Gross alpha activity higher than the control level for drinking water 0.1 Bq/l was determined in the mineral water from Ovcha Kupel (Sofia Region) and bottled mineral water *Devin*. These relatively higher values could be explained in first place by the higher mineralization and absorption of radionuclides in mineral waters, compared to surface waters [15]. According to hydrogeologic characterization of the deposit the circulation of the mineral water from Ovcha Kupel in the aquifer is deeper and longer compared to the rest waters from Sofia region, which probably leads to the higher mineralization. The amount of solids measured in the water was 1.306 g/l, while for the other waters it varied between 0.156 and 0.391 g/l. The dependence between the amount of solids in the dry residue and the content of alpha activity in mineral waters has been reported by other authors too [16] the correlation being stronger with high activity samples and weaker with low activity ones.

The water deposit of *Devin* mineral water is located in the Rhodope Mountains. The water bed is formed by breccias, breccia conglomerates and conglomerates of granite and metamorphic clasts [3]. The higher content of uranium and hence alpha activity in the water can probably be explained by the higher concentration of U in these rocks typical for the Rhodope massif.

If gross alpha and beta activity are below the parametric value, the indicative dose is assumed to be lower than 0.1 mSv/year and no further radiological investigation is required. In all waters, with the exception of Ovcha Kupel from Sofia region and Devin in the Rhodopes, the total indicative dose was lower than the parametric value.

Additional analysis was carried out and it was found the gross alpha activity in the water sample from Ovcha Kupel was entirely due to the amount of uranium in it. Then according to the Regulation on drinking water if the following formula is satisfied, no further action is required.

$$\sum C_{(obs)}/C_{(der)} \leq 1 \qquad (1)$$

Using the derived concentration for uranium provided for in the Regulation it was found the effective dose of 0.1 mSv/year would not be exceeded. Traditionally, the water from Ovcha Kupel is mainly used for external balneology. Daily use of the water for drinking purposes is not recommended, both due to the higher mineralization as well to the established higher alpha activity.

In *Devin* water, the calculated amount of alpha activity above that caused by uranium was 0.26 Bq/l.

Both waters were tested for Po-210, due to the highest radiotoxicity of this radionuclide compared to the other natural alpha emitters. Activity concentration of Po-210 in the water sample from Ovcha Kupel was 0.00085 Bq/l ± 0.00013, and in the water from Devin 0.0026 ±0.0005 Bq/l. These values are comparable with the radionuclide activity concentrations obtained in other countries. Rožmarić et al. report Po-210 content in Croatian bottled mineral and spring waters between 0.25 and 3.0 mBq/l [17], Desideri et al. – between <0.04 to 21.01 mBq/l in bottled mineral waters from Italy [18] and the mean values found in natural spring waters in the province of Granada, Spain cited by Milena-Pérez et al. are 1.74 ± 0.15 mBq/l [19].

In both cases Po-210 was under the derived concentration of 0.1 Bq/l, calculated for a dose of 0.1 mSv, for an annual intake of 730 liters. However, the use of water from Devin on a daily basis is not recommended. As a result of analyses carried out it was found the total indicative dose would not exceed 0.1 mSv in all water samples tested.

4. Conclusion

Radiological indicators in all waters under study were below the respective maximum permissible values and reference levels specified in the Regulation on mineral waters. The radon content in waters was not exceeding the parametric value provided for in the Regulation on drinking waters, being relatively higher only in the water from the Chepino area in the city of Velingrad, which is mainly used for outdoor balneology.

The content of alpha activity in the waters from Ovcha Kupel from the Sofia region and Devin from the Rhodopes was higher than the parametric value for drinking water. The analyses of possible reasons and the tests for determining Po-210 content showed the waters did not pose a risk on human health from radiological point of view, although their daily use for drinking purposes is not recommended.

In all waters under study the total indicative dose did not exceed the screening level of 0.1 mSv/year.

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