DETERMINATION OF ^{226}Ra CONCENTRATION IN MINERAL WATERS FROM BULGARIA

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Abstract

In the last years the interest in drinking and mineral water radioactivity has grown. Due to the importance of water for human life, its quality must be strictly controlled. For this reason, studies of mineral water must be performed in order to guarantee that they have a low level of radioactivity.

Recently national and EU regulations decrease the drinking water norms with the aim to strengthen consumer's security concerning drinking water quality.

This study presents the results of ^{226}Ra content and physical and chemical indices in mineral waters from different areas of Bulgaria.

^{226}Ra is a naturally occurring radioisotope with a period of half live equal to 1 600 years, which specific activity in water has been determined through analysis of the daughter ^{222}Rn. The measurements were carried out by us using low-level liquid scintillation counting. The results show that the concentration of ^{226}Ra range from ≤0.018 to 0.210 Bq/l. Due to differences in the geological structure of the aquifer, a large difference in values of the ^{226}Ra concentration was observed.

The total indicative doses (TID), originating from mineral water, were estimated.

For the determination of physical and chemical indices (pH and total dissolved solids, TDS), a portable pH meter Sension 156 was used.

Key words: *^{226}Ra, mineral water, liquid scintillation counting, total indicative doses.*

Introduction.

Waters as one of the most important components of the environment are part of all food chains and a major route for the entry of radioactive substances into the human body.

The studies of the radioactivity of natural waters, including mineral waters has become extremely important for the Bulgarian society after detecting elevated levels of alpha radioactivity in some of the drinking water sources in the country in 2017.

The mineral waters are one of the most precious natural resources in Bulgaria. There are more than 240 hydrothermal sources, with over 800 springs and drilling mineral waters. Only in the territory of its capital Sofia, there are 75 mineral water supplies [1]. Bulgaria is one of the five countries with the largest number of radioactive mineral sources [15]. Most of the Bulgarian mineral waters are low mineralized and are suitable for daily consumption, balneology (drinking balneology), recreation and others.

The most commonly applied approach for protecting human health from the adverse effects of radioactive water pollution is conducting systematic studies of quality indicators of drinking water. Continuous measurement of water radioactivity allows the levels of radioactivity to be below the normative limits for drinking water because these waters are an important factor for increasing the total population exposure as a result of ingestion of natural radionuclides with them [10].

Water radioactivity depends on its origin and chemical composition. Radionuclides can penetrate into ground water by processes of erosion and dissolution from rocks and minerals which form the aquifer or infiltration of rain water [2, 14].

One of the most significant sources of radiation from drinking water is ^{226}Ra due to its high radiotoxicity and a long half-life. Contribution of ^{226}Ra to the total indicative dose due to ingestion is estimated to be 90 %. The great health risk is due to the fact that the dissolved radium, and in particular its cationic form, is deposited directly and permanently in the bone like calcium. Continues drinking of the water containing ^{226}Ra with a concentration higher than the maximum allowed may cause adverse health effects.

^{226}Ra may be contained in groundwater as a result of its interaction with various natural materials containing radium, such as rocks, soils, minerals, etc. It is known that Ra is easily absorbed by clays and oxidized minerals present in the soil. It is always in second valence and can easily be extracted from the solid matrix. All these parameters vary considerably and determine variations in the Ra concentration in groundwater [5].

The objective of this study is to measure ^{226}Ra concentration in mineral waters. These results can be used as a baseline for future studies, and to find their relations to the water quality index. This paper also focus on the estimating the total indicative dose in water at the sampling points.

Material and methods.

The object of the research is mineral water for drinking from different areas of Bulgaria. The samples of mineral water were directly collected from natural mineral water springs. Water samples were collected using 2 L polyethylene bottles. Two samples were collected at every sampling point.

^{226}Ra was determined in 40 Bulgarian drinking mineral water sources (Table 1)

Table 1. Location of the investigated mineral water sources in Bulgaria

Number of point	Name of mineral source	Location
1	Medovo, well number B-72	Village of Medovo, Burgas District
2	Stefan Karadjovo, well number 32a	Village of Stefan Karadjovo, Yambol District
3	Devin, well number 3	Town of Devin**,** Smolyan District
4	Devin, well number 5	
5	Mihalkovo, well 1aVP	Village of Mihalkovo, Smolyan District
6	Mihalkovo, well VKP	
7	Hissar, Choban Cheshma well	Town of Hissar, Plovdiv District
8	Hissar, well number 1	
9	Hissar, well number 7	
10	Staro Zhelezare, well number 2	Village of Staro Zhelezare, Plovdiv District
11	Staro Zhelezare, well number 4	
12	Klisura, well number 1	Town of Klisura, Plovdiv District
13	Kliment, well number 12	Village of Kliment, Plovdiv District
14	Lenovo, well number 12	Village of Lenovo, Plovdiv District
15	Dragoynovo, well number 9	Village of Dragoynovo, Plovdiv District
16	Belovo, well number Ch-3	Town of Belovo, Pazardjik District
17	Strelcha, well number 1hg	Town of Strelcha, Pazardjik District
18	Rakitovo-Kostandovo, well number 5	Town of Rakitovo, Pazardjik District
19	Bratsigovo, well number 2	Town of Bratsigovo, Pazardjik District
20	Velingrad, well number 2	Town of Velingrad, Pazardjik District
21	Velingrad, well number 5	
22	Banichan, well number 273	Village of Banichan, Blagoevgrad District
23	Katuntsi, well number 236 “Razsadnika”	Village of Katuntsi, Blagoevgrad District
24	Nevestino	Village of Nevestino, Kyustendil District

25	Belchin	Village of Belchin, Sofia District
26	Dolna Banya, well number 141	Town of Dolna banya, Sofia District
27	Kostenets, well number 2hg	Town of Kostenets, Sofia District
28	Gorna Banya, Domus Dere well	Town of Sofia, Sofia-city District
29	Gorna Banya, Haznata well	
30	Gorna Banya, well 4	
31	Sofia-Kniazhevo, Knizhna Fabrika well	
32	Sofia-Kniazhevo, well number 1hg	
33	Sofia city-centre mineral water spring	
34	Bankya, well number 1hg	Town of Bankya, Sofia-city District
35	Transka Bankya	Village of Bankya, Pernik District
36	Shipkovo, well number L-37	Village of Shipkovo, Lovech District
37	Barzia, well number 1	Village of Barzia, Montana District
38	Shivachevo, Hadzhi Dimitar well	Town of Shivachevo, Sliven District
39	Targovishte, well number R-77h	Town of Targovishte, Targovishte District
40	Voditsa, well number R-2	Village of Voditsa, Varna District

Analytical procedure for ^{226}Ra. It was based on a radon extraction by a scintillation cocktail immiscible with water, followed by a measurement with a liquid scintillation counter of the alpha-emission of radon and of its decay products in radioactive equilibrium with the parent. Radon, being a noble gas, is easily and selectively extracted by the organic phase, whereas all the other radionuclides present in ionic form are not extracted.

Water of each 1.0 L sample was placed in a tightly closed glass bottle, containing 25 cm^3 scintillation cocktail (**Rotiscint eco** from Roth/Karlsrue with 20 % of cyclohexane). The samples were kept in a dark and cool place until ^{226}Ra/^{222}Rn equilibrium was reached after more than 40 days. Organic phase of 20 cm^3 was transfered into polyethylene vials coated inside with teflon [3, 9, 11, 17].

The activity measurement was performed by means of a low-level LSC in a Packard Tri-Carb 2770 TR/SL liquid scintillation system, which uses pulse shape discrimination (PSD) to separate α and β events into different multi-channel analysers (MCAs).

The detector is connected with a multi-channel analyzer (MCA) and a software that separates the signals produced by chemiluminescence in different spectra [13].

Calibration of the system consisted of determination of the detector efficiency and the background value for ^{226}Ra.The counting efficiency was evaluated with using a ^{226}Ra reference solution with activity 556.1 mBq and oscillates around 95 %. As a blank sample, de-ionised (DI) water was used.

TID was estimated using the hypothesis that any person from the public would drink at most 730 l/year from any given spring.

Physical and chemical indices. Portable pH meter Sension 156 was used for the measurements of the indices: chemical reaction (pH) and total dissolved solids (TDS).

Results and discussion.

^{226}Ra concentration. Experimental results obtained from liquid scintillation determination of ^{226}Ra concentration in water samples from mineral springs are shown in Fig. 1. The concentration of ^{226}Ra in mineral waters for drinking purposes ranged from values lower than 0.018 Bq.L^{-1} (minimum detectable activity) to 0.210 Bq.L^{-1} with an average value of 0.073 Bq.L^{-1}. This wide range of ^{226}Ra concentration can be connected with the different local, geological and hydrological conditions of the areas of the investigated mineral waters. The highest concentrations were measured in samples 6 (Nevestino, well number 2hg), 26 (Mihalkovo, well VKP) and 38 (Shipkovo, well number L-37) that originated from sources situated in the Southern Bulgaria and in the North-Western Bulgaria, respectively.

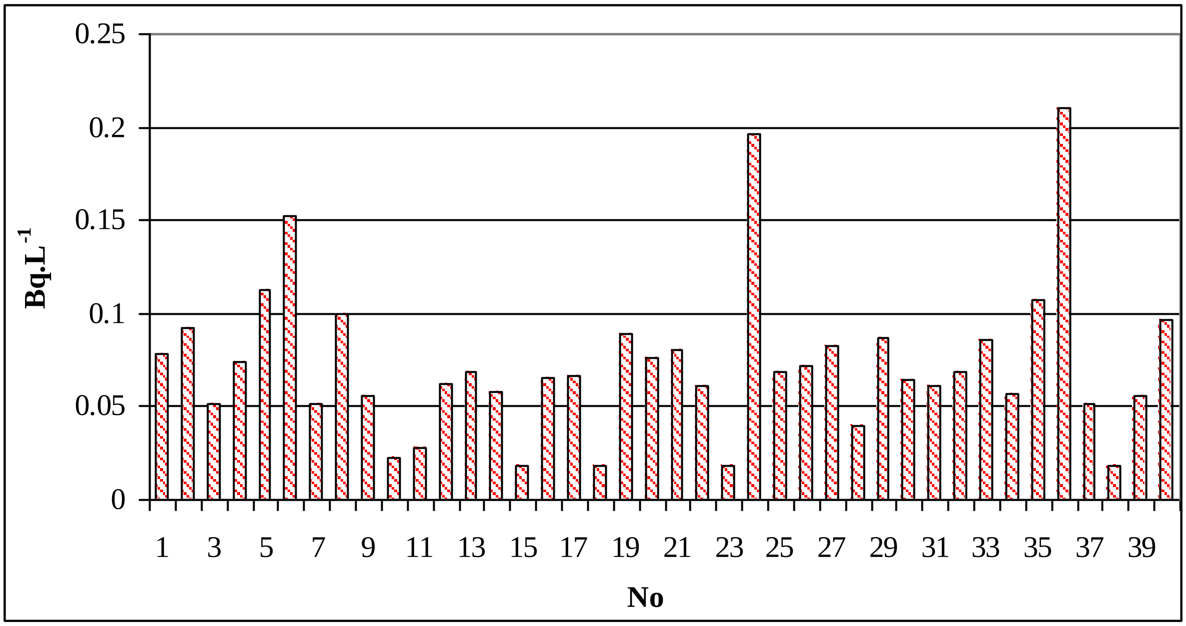

Fig. 1 ^{226}Ra concentration in mineral waters for drinking

The reason for the high value of ^{226}Ra concentration of water from Mihalkovo is due to the high mineralization. The natural radioactivity levels generally increase with increasing mineralization [4]. Water with high levels of carbonate and sulfate salts, like Nevestino and Shipkovo, showed maximum values for ^{226}Ra [2].

Total indicative dose (TID). The calculated TID coming from the ^{226}Ra for adults (older than 17 years), assuming a yearly average consumption of 730 liters (around 2.L day^{-1} water consumption) of mineral water are presented in Fig. 2. The dose conversion coefficient of 2.8 x 10^{-4} mSv.Bq^{-1} for the ingestion of ^{226}Ra by adults were used [6, 8]. For radionuclide concentrations below the detection limit, the minimum detectable activity (MDA) was considered.

We established that, in the water of mineral springs, TID ranged from 0.0037 mSv.y^{-1} (Dragoynovo, well number 9; Rakitovo-Kostandovo, well number 5; Katuntsi, well number 236) to 0.0429 mSv.y^{-1} (Shipkovo, well number L-37). According to the WHO (2017) and Bulgarian standard for drinking water, the recommended value for total indicative dose is 1 0.1 mSv.y^{-1} [16, 12]. In the case of the maximum determined ^{226}Ra activity, a TID of 0.0429 mSv.y^{-1} was determined which is more than 2 times lower than the maximum permissive level. The results showed that 85 % of the calculated doses were below 0.02 mSv.y^{-1}. The estimated TID from ^{226}Ra were many times below than the allowed level. Consequently, the health hazards related to ^{226}Ra in drinking mineral water are expected to be negligible in the areas studied.

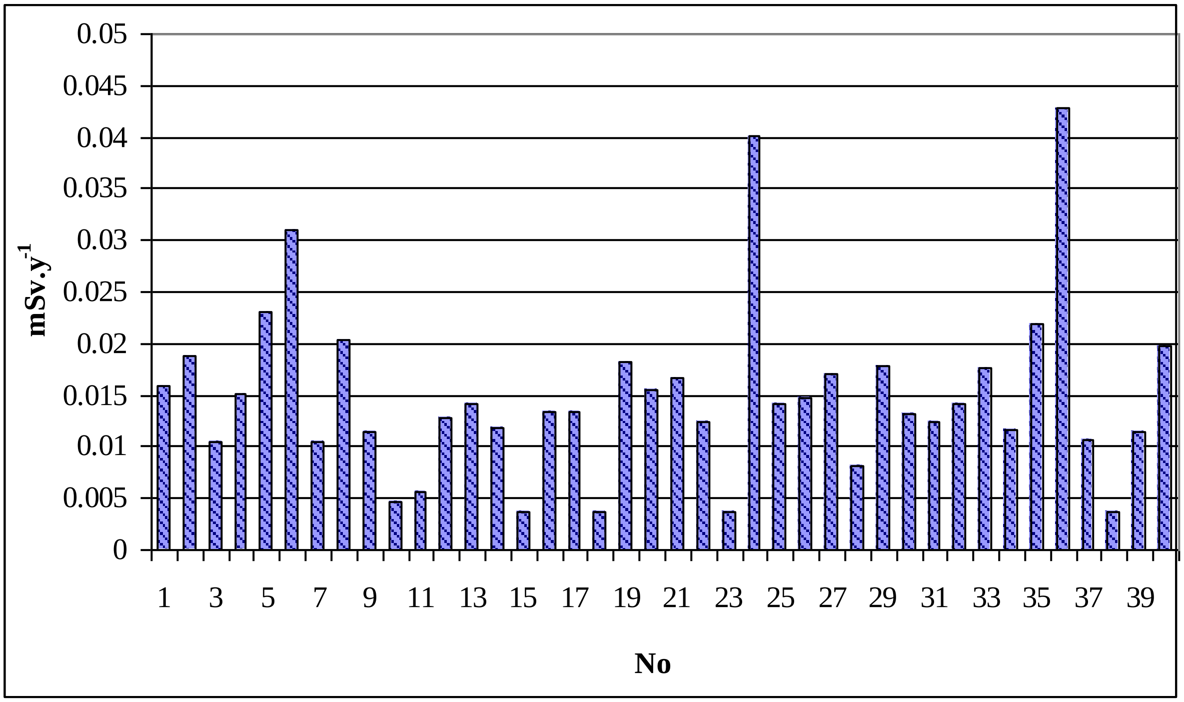

Fig. 2. Total indicative dose (TID) of mineral waters for drinking

Chemical reaction (pH). Different kinds of mineral water have a neutral to mild alkaline reaction with pH of 7.04-9.92. Only one of the samples is slightly acidic.

The pH value varies according to the mineral content of water. This is affected by the type of Earth layers, from which the water is drawn. Water, percolating through a hard rock like granite, will have a higher mineral content, and will thus tend to be more acidic.

Total dissolved solids (TDS). TDS is the term used to describe the inorganic salts and small amount of organic matter present in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations, chloride, sulfate and nitrate anions [7]. The TDS content of mineral water for drinking ranged from 141 to 3193 mg.L^{-1}. 87.5 % of the different kinds of mineral water are slightly mineralized (TDS ≤ 500 mg/l) and suitable for everyday use.

Conclusions.

A investigation of ^{226}Ra concentration and physical and chemical indices of mineral waters from different areas of Bulgaria, was carried out.

The results show that the concentration of ^{226}Ra range from values lower than 0.018 Bq.L^{-1} (minimum detectable activity) to 0.210 Bq.L^{-1}. This wide range of ^{226}Ra concentration is in relation to the temperature of water, the dissolved inorganic salts, pH and to the geological structure of the areas.

The estimated TID from ^{226}Ra for drinking mineral water varies between 0.0037 and 0.0429 mSv.y^{-1} and are many times below than permissible level of 0.1mSv.y^{-1}.

The waters are neutral to mild alkaline reaction with values of pH from 7.04 to 9.926.8 to 7.4. The values for TDS vary between 141 and 3193 mg.L^{-1}.

All performed analyses conclude that the investigated mineral waters are suitable for human consumption without any radiological hazard.

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