GROSS ALPHA, GROSS BETA AND GAMMA ACTIVITIES IN BOTTLED NATURAL MINERAL WATER FROM ROMANIA

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The activity concentrations of ^{238}U, ^{226}Ra and ^{232}Th were analysed in eleven natural mineral waters sources, non-carbonated ones from Northern Romania. The samples were collected for a period of three years. The waters originate from a volcanic aquifer containing carbonate rocks. It was found that the concentration of uranium isotope ^{238}U varied in the ranges 0.07-0.48 Bq L^{-1}. The activity ratio between uranium isotope ^{238}U and radium isotope ^{226}Ra was between 0.03 – 1.05. The calculated doses for the analysed samples are in the range 8.84-40.75 µSv/year, with an average value of 20.08 µSv/year, where the reference level of 100µS/year is the committed effective dose recommended by WHO and the EU Council.

Key words: Natural mineral water, Uranium, Dose assessment, Gross alpha-beta activity, Water sample, Water quality.

1. INTRODUCTION

Romania is reach in natural mineral waters. Although it is assumed that these waters are less polluted with organic and inorganic substances, their monitoring is important. Furthermore, their origin needs to be considered and the influence of human activities that can strongly affect their properties. The mineral waters contain natural radionuclides and the rules or directives made and maintained by national and international authorities become more and more important. UNSCEAR and EC [1-3] demand that natural mineral waters consumption is very important regarding the exposure to naturally occurring alpha emitting radionuclides: ^{238}U, ^{226}Ra, ^{232}Th etc. Some of these waters present high natural radionuclide content, which must be monitored.

The bulk of the environmental radioactivity is present in the Earth's crust originating from radionuclides from the ^{232}Th-, ^{238}U-, ^{235}U-series and from ^{40}K. These primordial radionuclides and their progenies are of special interest to us,

because they are α-, β- and γ-ray emitters. As the amount of these radionuclides in materials derived from the Earth's crust like rock, sediments and water depends on the constituting mineral types and provenance 4, a measurement of their α-, β- and γ-ray activity concentrations can give access to geological information.

Long-lived uranium, thorium and radium isotopes from rocks and soils confer natural radioactivity to the natural mineral waters, their decay releasing alpha, beta and gamma radiations (Figure 1).

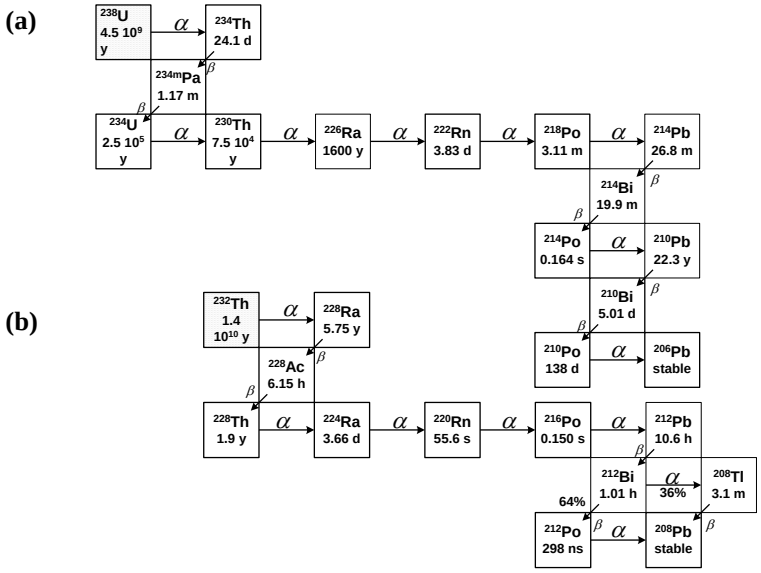

Fig. - 1: Decay series of ^{238}U (a) and ^{232}Th (b) with half-lifes in years (y), months (m), days (d), hours (h) and seconds (s) and the relevant α- and β-ray emitters are indicated with a bold box 5.

Through ^{238}U disintegration in waters, ^{226}Ra appears and the ratio ^{226}U/^{238}U presents variations in mineral waters, depending on the rocks of provenience. Certain amounts of uranium can lead to kidney cancer. While ^{226}Ra is a naturally occurring radioactive isotope present from the ^{238}U series, the ^{228}Ra is present from the ^{232}Th series. Progenies such ^{226}Ra and ^{228}Ra provide a direct evidence that can causes cancers other than lung cancer by ingestion, part of radium enters in the tissues, leading to alpha-particle-induced cancer in humans [6]. Considering the high radiotoxicity of Ra, its presence in water and the associated health risk requires particular attention.

Determination of naturally occurring radionuclides in ground water is useful as a direct input to environmental and public health studies. The authors took also into consideration the legislation on radioactive isotopes for drinking water [7] when calculating the total effective dose. The reference value of the effective dose is 0.1 mSv/yr, given by COUNCIL DIRECTIVE 98/83/EC [8] on the quality of water

intended for human consumption. Although these directives does not refer to natural mineral water, the daily consumption, will lead eventually to an associated dose that sums up to the dose from daily consumption of drinking water.

The effective dose value does not take into consideration the dose received from ^{3}H, ^{40}K and ^{222}Rn decay products.

This study shows some preliminary information about the activity concentrations and effective doses arising from radium, thorium and uranium isotopes in some natural mineral waters from the northern part of Romania. The studied waters were non-carbonated ones (still water), from 5 different producers and 11 sources, rich in Ca and Mg, from volcanic and metamorphic rocks.

2. MATERIALS AND METHODS

2.1 CHEMICAL REAGENTS AND INSTRUMENTATION

The chemical data of ion composition of non-carbonated natural mineral waters were measured on samples from eleven sources, monthly monitored during three years. In the first 24 hours after sampling, electrical conductivity and pH were measured based on (EN 27888:1993-11) and (DIN 38404-5:1984-01, C5). Then the samples were filtered on 0.45 μm cellulose membrane filters, the mineral components being analyzed by ion chromatography standardized methods: SR EN ISO 10304-1: 2009 and SR EN ISO 14911:1999 [9-11].

2.2 INSTRUMENTS FOR RADIOMETRIC MEASUREMENTS

For radiometric measurements 5 L of water samples were slowly evaporated, resulting different amount of residue for each sample. However, fix geometries and specific amount of residue were used for analysis in order to have the appropriate calibration at the instruments used.

Gross alpha–beta measurements were performed using the low background system PROTEAN ORTEC MPC-2000-DP, with a scintillation radiation detector ZnS dual detector phosphor (zinc sulphide and plastic). The calibration of the acquisition system was done using sets of standard radioactive sources manufactured by Radionuclide Metrology Laboratory (LMR IFIN-HH), such as ^{241}Am–alpha source ($T_{1/2}$ = 432.6 ± 0.60 years) and ^{90}(Sr-Y) - beta source ($T_{1/2}$ = 28.80 ± 0.07 years). The working geometry was fixed in metallic trays, inside the lead castle system, directly facing the probe-detector. For the measurement geometry *UP ALPHA + BETA* manual count the metallic tray is at 3 mm below the probe-detector. The calculated efficiencies of the detection were introduced in the system namely $\varepsilon_{up\ alpha-beta}$ = 36.23 ± 0.29 (%) - the alpha efficiency and $\varepsilon_{up\ alpha-beta}$ = 48.53 ± 0.74 (%) - the beta efficiency, with the crosstalk factor X_{talk} = 31.08 ± 0.60 (%) [12]. To ensure accurate measurements, it is necessary to determine both

detector efficiency and crosstalk as a function of sample mass- geometry used. Efficiency determination as a function of sample mass- geometry is equivalent to determining a zero-mass efficiency with an associated self-absorption factor.

The samples were measured in 10 intervals of 100 minutes, the total acquisition time being 16.66 hours. In addition, a measurement with empty metallic tray for used geometries was performed to establish the background count rate.

A low background coaxial p-type HPGe detector (model GEM 25P4, Ortec Inc., Easley, SC, USA) with a relative efficiency of 35% and energy resolution of 1.73 keV at 1332.5 keV for ^{60}Co was used to determine the activity concentrations of the ^{40}K, ^{238}U, ^{232}Th and their progenies. The detector was linked to a DigiDART Ortec data acquisition system and to a Gamma Vision (version 6.01) spectrum analysing software tool. The calibration of the detector for energy, peak shape and efficiency was carried out using certified volume source for ^{60}Co, ^{134}Cs, ^{137}Cs, ^{152}Eu and ^{241}Am, supplied by the institute's radiation metrology laboratory. These radioisotopes cover a relatively wide energy range from 59.54 keV for ^{241}Am to 1408.00 keV for ^{152}Eu [13, 14]. A 10-cm thickness lead shielding and 2 mm of copper lining was built around the detector to diminish the contribution of environmental radioactivity to its background.

For the total annual effective dose calculation, (D_{EFF}) equation 1 was used:

$$D_{EFF} = \sum_i [C_i(\mathrm{Bq/L}) \times K(\mathrm{L/yr}) \times F_i(\mu\mathrm{Sv/Bq})] \quad (1)$$

where: D_{EFF} is the annual effective ingestion dose due to relevant radionuclide in μSv/yr, C_i is radionuclide activity concentration in the water sample in Bq/L, K is the annual consumption rate of 150 L/yr for infants, 350 L/yr for children and 500 L/yr for adults, respectively, according to the IAEA, UNSCEAR and WHO [1, 15, 16], F_i is the dose coefficient (conversion factors: 2.8×10^{-7}, 2.3×10^{-7} and 4.5×10^{-8} Sv/Bq for ^{226}Ra, ^{232}Th and ^{238}U of the relevant radionuclide. However, the present study took into consideration an average consumption of 365L/year of mineral water considering that the rest of 135L/year of water was tap water, for an adult.

3. RESULTS AND DISCUSSIONS

The groundwater composition of the studied natural mineral waters is dominated by HCO_3^-, as well as by Ca^{2+} and Mg^{2+}, and is reflected by the values of the electrical conductivity (Table 1). The studied non-carbonated mineral waters are Ca-Mg-HCO_3^- ones, the correlation between the HCO_3^- (mg/L) versus conductivity for the dataset depicting the contribution of HCO_3^- to groundwater chemistry. The conductivity values are related to total dissolved solid of natural mineral waters.

Table 1

Mean values of electrical conductivity and major ion composition measured for non-carbonated natural mineral water samples, with standard deviation less than 10%

Code Source	C.e.µ (S/cm)	Dry rez. (g/L)	HCO_3 (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
SB1	351.0	0.196	225.7	49.7	16.1
SH2	334.0	0.187	204.4	44.3	15.5
SA3	291.0	0.152	173.8	40.5	11.6
SI1	325,0	0.143	198.3	42.7	14.5
SI4	313.0	0.182	195.2	43.5	16.0
SDA5	352	0.187	213.5	50.9	18.2
SDIA6	359	0.198	-	-	-
SB7	462	0.293	336.4	59.86	30.60
SB8	102	0.350	48.8	9.53	2.63
SPH9	-	0.125	732.0	112.90	40.91
SPC10	-	0.453	-	35.66	19.91

"-" Few values for C.e., HCO_3^-, Ca^{2+} and Mg^{2+} were not determined.

In addition, few elemental concentrations such as Sb, Ni, Cu and Mn have been investigated on the natural mineral water samples. These concentrations were found in the range 0.1-0.5 µg/L, 0.1-20 µg/L, 1-80 µg/L and 1-2 µg/L for the above metals.

3.1 ACTIVITY CONCENTRATIONS OF THE DETERMINED RADIONUCLIDES

The activity concentrations of ^{226}Ra, ^{238}U and ^{232}Th are presented in Table 2. These were determined twice per year for a period of three years. The activity concentration for ^{226}Ra varied from 0.015 Bq/L to 0.12 Bq/L. The activity concentration of uranium isotope varied from 0.065 Bq/L to 0.48 Bq/L, while for ^{232}Th this varied between 0.03 and 0.29 Bq/L.

Table 2

The activity concentrations of ^{238}U, ^{226}Ra and ^{232}Th in the residue of the natural mineral water samples. The gross alpha and gross beta activity concentrations and the annual effective dose

Code Source	^{238}U (Bq/L)	^{226}Ra (Bq/L)	^{232}Th (Bq/L)	Gross α (mBq/L)	Gross β (mBq/L)	^{226}Ra/^{238}U	Annual effective dose, [µSv/year]
SB1	0.105 ± 0.016	0.029 ±0.003	0.050 ± 0.008	3.8 ± 0.7	7.5 ± 1.4	0.28	8.90
SH2	0.135 ± 0.020	0.040 ± 0.005	0.030 ± 0.005	4.1 ± 0.8	4.7 ± 0.9	0.30	8.84
SA3	0.130 ± 0.020	0.031 ± 0.004	0.110 ± 0.017	1.6 ± 0.4	12.9 ± 3.2	0.23	14.50
SI1	0.090 ± 0.014	0.071 ± 0.009	0.030 ± 0.005	5.3 ± 2.6	4.8 ± 1.4	0.79	11.29
SI4	0.065 ± 0.010	0.069 ± 0.008	0.110 ± 0.017	2.4 ± 0.5	16.0 ± 2.2	1.05	17.35
SDA5	0.080 ± 0.012	0.078 ± 0.009	0.115 ± 0.017	4.4 ± 0.8	4.8 ± 1.4	0.98	18.97
SDIA6	0.190 ± 0.029	0.060 ± 0.007	0.120 ±0.018	5.7 ± 1.2	10.3 ± 2.4	0.32	19.34
SB7	0.290 ± 0.044	0.120 ± 0.014	0.210 ± 0.032	7.0 ± 1.8	26.3 ± 7.2	0.41	34.69
SB8	0.400 ± 0.060	0.121 ± 0.014	0.260 ± 0.039	8.0 ± 2.0	35.7 ± 7.1	0.30	40.75
SPH9	0.132 ± 0.020	0.036 ± 0.004	0.080 ± 0.012	3.5 ± 0.5	10.3 ± 3.1	0.27	12.56
SPC10	0.480 ± 0.072	0.015 ± 0.002	0.290 ± 0.044	8.4 ± 2.1	46.5 ± 8.2	0.03	33.73
Mean ± 1σ	**0.191 ± 0.035**	**0.061 ± 0.008**	**0.128 ± 0.023**	**4.9 ± 1.4**	**16.3 ± 4.3**	**0.45**	**20.08**
Range	**0.065 – 0.480**	**0.015 – 0.121**	**0.030 – 0.290**	**1.6 – 8.4**	**4.7 – 46.5**	**0.03 – 1.05**	**8.84 – 40.75**

Strong correlations between activity concentrations of the measured isotopes and amount of dry residue have been observed, R > 0.8 (Figs. 2-6). In general, as the dry mass of the residue increase the activity concentration of ^{238}U, ^{226}Ra and ^{232}Th increases (Figs. 2-4). The same type of relationship can be seen also for gross alpha and gross beta activities and the dry mass of the residue (Figs. 5-6).

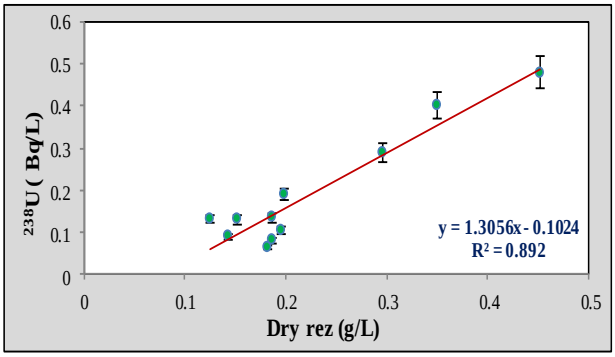

Fig. - 2 Activity concentration of ^{238}U as function of the dry residue

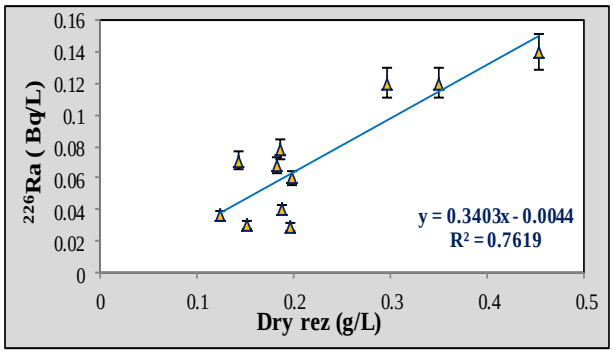

Fig. - 3 Activity concentration of ^{226}Ra as function of the dry residue

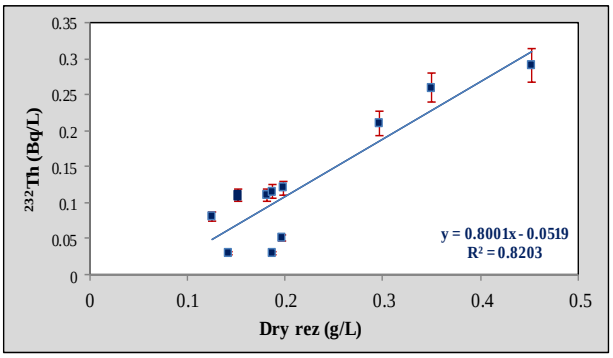

Fig. - 4 Activity concentration of ^{232}Th as function of the dry residue

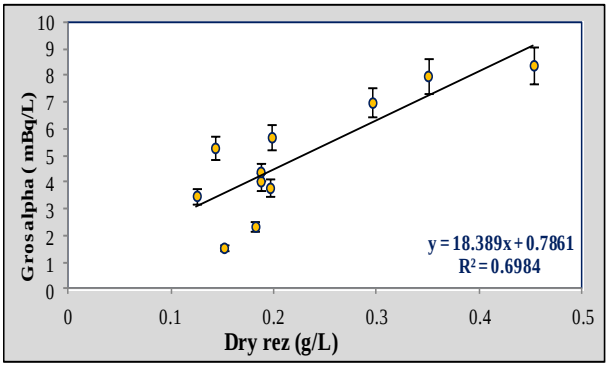

Fig. - 5 The gross alpha activity as function of the dry residue

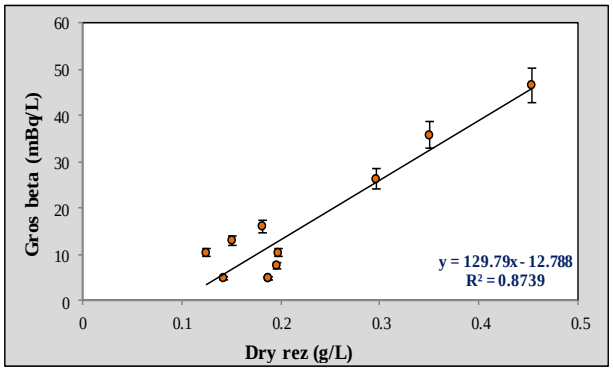

Fig. - 6 The gross beta activity as function of the dry residue

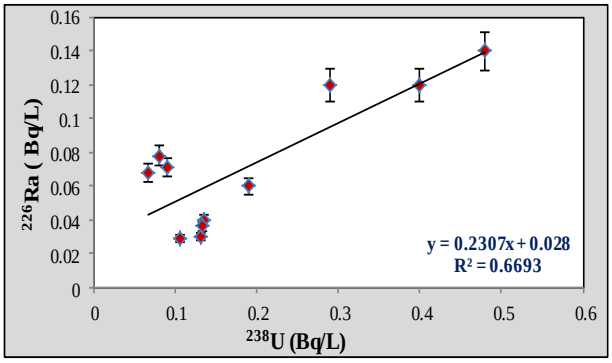

Fig. - 7 The activity concentration of ^{226}Ra as function of the activity concentration of ^{238}U

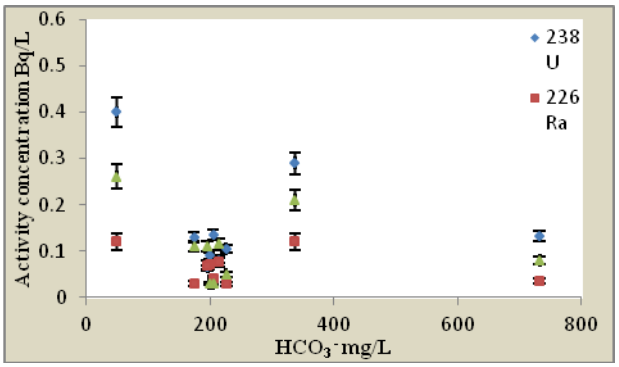

Fig. - 8 Activity concentration of ^{238}U, ^{232}Th and ^{226}Ra as function of HCO_3^- concentration

It can be observed from Figure 7 that correlation exist also between the activity concentration of ^{226}Ra and the activity of ^{238}U increases, as these are part of the same radioactive series. Figure 8 shows that the higher dissolved uranium concentration in natural mineral waters is often associated with carbonate content. Uranium improved its solubility due to its complexation with bicarbonates (resulting uranyl complexes), which confers basicity to the water in comparison with radium which forms precipitates with bicarbonate. In most cases, a poor equilibrium between uranium and radium radionuclides was observed (Fig. 7), the ratio $^{226}Ra/^{238}U$ varying between 0.03 and 1.05, based on the geological origin and on the different chemical compositions of the studied natural mineral waters.

The gross alpha activity concentration of the samples which represents all alpha disintegrating radionuclides from uranium and thorium series is presented in Figure 5 as a function of the dry residue. The data are good correlated.

3.2 DOSE ASSESSMENT

The annual effective dose assessment is presented in Table 2 using the Eq. 1 from section 2.2 for the studied natural mineral water samples. It was assumed a daily consumption of 1 L natural mineral water, corresponding to 365 L/year. According to the Romanian legislation (HG 1020/2005) and WHO guidelines (WHO 2008) – requirements concerning the quality of drinking waters, the annual effective dose from the radionuclides, excepting tritium and radon cannot exceed the value of 100 μSv/yr. It can be noticed from Table 2, last column, that the annual effective dose values do not exceed the reference value.

These results provide preliminary information for consumers and authorities about the radiological risk based on annual intake of ^{238}U, ^{232}Th and ^{226}Ra via natural mineral water consumption [17].

CONCLUSIONS

The samples analysed in this study were non-carbonated natural mineral water from 5 different producers and 11 sources. The analyses were conducted for a period of three years. The studied natural mineral waters belong to sources from carbonate aquifers, from the northern part of Romania.

Alpha emitting radionuclides ^{238}U, ^{232}Th and ^{226}Ra were determined. In these waters the concentrations of uranium radionuclides vary in relatively wide range, correlated with the carbonate concentrations, because of their improved solubility in basic media. The committed effective dose was calculated based on WHO guidelines for drinking water quality, low values being obtained. The results obtained for the annual effective dose, for an adult member of the public in Romania, derived from the intake of naturally occurring radionuclides in water varies between 8.84 μSv/year and 40.75 μSv/year

The present study support, firstly, the natural mineral water consumers and secondly, the health agencies, taking into account the effect of low doses on human health. Moreover, the present study has also considered that the consumption of natural mineral water is a market segment that shows an upward trend, being more 52% of the total volume of water sold. In Bucharest, the consumption of mineral water volume recorded a 66.3% share of total sales of bottled water.

The data on the activity concentrations and effective doses due to intake of natural radionuclides from natural mineral water for Romania are below the WHO and UNSCEAR recommended reference levels.

Acknowledgments:. This study was supported by the PNCDI II Program, Project No. PN 16 42 02 03/2017, by the Romanian Ministry for Education and Research.

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