Radiometric Studies on Carbonated Natural Mineral Waters from the Northern Part of Romania

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As the access to a safe drinking water is essential to human health, a radiometric studywas conducted on a natural mineral carbonated water, located in the northern part of Romania, as a subject to international rules. Activity concentrations of gross alpha and gross beta, of the radionuclides natural decay chains ^{238}U, ^{232}Th and ^{40}K were determined, as well as the associate effective dose for these radionuclides. It was found that the low permeability of the aquifer allows a reduced infiltration of the rain water, seasonal influence showing good chemical stability, oscillating around less than 10%. The results obtained for the effective doses calculated for an adult in Romania, derived from the intake of naturally occurring radionuclides in water varies between: 1.24-2.08(µSv/yr) for ^{40}K; 0.90–3.45 for ^{238}U; 1.00–7.21(µSv/yr) for ^{232}Th and 11.24–46.00 (µSv/yr) for ^{226}Ra.The assessment on natural mineral waters from Bucovina region updates the data on the activity concentrations and effective doses due to intake of natural radionuclides for Romania. The obtained values are below the WHO and UNSCEAR recommended reference levels.

Keywords: mineral water, ground water, radioactivity, gross-α and gross-γ, effective dose

Mineral water, as a microbiologically pure water with a constant chemical and radiochemical composition represents a source of intake of trace elements for human beings, in the European Union being about 1000 recognized brands [1]. Determination of naturally occurring radionuclides in ground water is useful as a direct input to environmental and public health studies. Considering the high radiotoxicity of ^{226}Ra, its presence in water and the associated health risk requires particular attention.

The European Community directives emphasize that bottled mineral water must be groundwater and clearly distinguishable from the drinking one [2-4]. According to EU Directive 80/777/EEC, natural mineral waters are defined as uncontaminated waters from underground aquifers that are bottled without any treatments other than removal of the unstable components (iron, sulfur, manganese, and arsenic) and re-introduction of carbon dioxide [5]. The chemical and radiochemical composition of mineral waters is considered as a result of the chemical processes under natural conditions.

In addition, an estimation of the activity concentration levels for natural radionuclides in drinking water and their corresponding radiation doses has been considered. The paper presents data for the activity concentrations of ^{238}U, ^{232}Th, ^{226}Ra and also for ^{40}K in Romanian natural mineral waters. An assessment of the annual effective doses received from mentioned radionuclides is necessary. Moreover, the gross á and â activities in waters have to be measured for screening purposes. According to WHO guidelines, the recommended screening levels for drinking water below no further action is required, are 0.5 Bq/L for gross alpha activity and 1 Bq/L for gross beta activity.

The radiometric measurements were focused on samples from the same water in Bucovina region (fig. 1). The activity concentrations of various radionuclides were determined annually in samples of water for the mentioned time interval.The purpose of this study is to evaluate the seasonal influence over the chemical and radiochemical composition of the studied mineral water in connection with the aquifer geochemistry.

Experimental part

Materials and methods

Procedure

For each water sample more than 5 L were collected and used for analyses. For the alpha, beta and gamma spectrometry analyses, a fixed quantity of 5 L of water was used, that was subjected to an evaporation process at the temperature of 80°C. The mass of the solid residue obtained after evaporation has values between 0.92 - 1.50 g/L (table 1).

Instruments for radiometric measurem*ents*

Gross alpha–beta measurements were performed using the low background system PROTEAN ORTEC MPC-2000-DP, with the following configuration: scintillation radiation detector ZnS dual detector phosphor (zinc sulphide and plastic), high power voltage; electronic modules for signal processing: preamplifier, amplifier, counter; display module; operation and display control-board equipped with LCD display; mechanical sample feeder; PC interface, specialized software used for transferring acquired data and processing–PIC Communicator–Protean Instrument Corporation. The system was calibrated regarding its efficiency using sets of standard radioactive sources manufactured by Radionuclide Metrology Laboratory (LMR IFIN-HH).^{241}Am–alpha source ($T_{1/2}$ = 432.6 ± 0.60 year) and ^{90}(Sr-Y) - beta source ($T_{1/2}$ = 28.80 ± 0.07 year) were used. The working geometry used 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 being at 3 mm below the probe-detector.

The calculated efficiencies of the detection were subsequently introduced in the system for two working geometries: (1) *measuring geometry* gross alpha-beta

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Table 1
ACTIVITY CONCENTRATION FOR GROSS ALPHA, GROSS BETA AND ANNUAL EFFECTIVE DOSE OF THE NATURAL MINERAL WATER SAMPLES

Sample code/	Residue, [g/L]	Gross α	Gross β [mBq/L]	Annual Effective Dose/ D_{EFF} ([µSv/year])
S1	0.9167	5.50 ± 0.70	21.40 ± 4.80	63.20
S10	1.5022	2.40 ± 1.30	15.90 ± 5.40	53.90
S20	1.1229	1.03 ± 0.16	31.40 ± 3.11	15.45
S30	1.1296	4.56 ± 1.30	28.34 ± 7.70	41.23
Mean*± 1σ**	**1.1678**	**3.37 ± 0.87**	**24.26 ± 5.25**	**43.45**
Range	0.9167 – 1.1296	1.03 ± 0.16-5.50 ± 0.70	15.90 ± 5.40 - 31.40 ± 3.11	15.45 - 63.20

*Mean represents the mean values obtained for each parameter during 30 months
** Standard deviation

with 31.37 ± 0.25 (%) alpha efficiency and 44.94 ± 0.69 (%) beta efficiency and the spillover factor of 25.59 ± 0.50 (%) and (2) *measuring geometry* up alpha – beta with 36.23 ± 0.29 (%) alfa efficiency and 48.53 ± 0.74 (%) beta efficiency and the spillover factor of 31.08 ± 0.60 (%) [6].

The samples were measured in 10 intervals of 100 min., the total acquisition time being 16.66 h. In addition, a measurement with empty metallic tray for this geometry was performed in order 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 the energy resolution of 1.73 keV at 1332.5 keV for ^{60}Co is used for determining the activity concentrations of the ^{40}K, ^{238}U, ^{232}Th and their progenies. The detector used for environmental radiation measurements has a Germanium crystal with a diameter of 59.1 mm and a length of 54.1 mm, corresponding to a volume and mass of active Germanium of 148 cm^3 and 0.8 kg, respectively. The detector is linked to a Digi 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 sources for ^{60}Co, ^{134}Cs, ^{137}Cs, ^{152}Eu and ^{241}Am, supplied by the Institute of Radiation, from the metrology laboratory. These radioisotopes cover a relatively wide energy range (from 59.54 keV for ^{241}Am to 1408.00 keV for ^{152}Eu) and allow the construction of an empirical efficiency curve versus the energy of interest (from 46.54 keV for ^{210}Pb to 2614.53 keV for ^{208}Tl) [7]. 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.

Results and discussions

The surveillance of the natural mineral water and their springs is not a new subject. However, this has to be done continuously to get consistent data with international rules. Analyses done on samples of natural waters are consistent with theDirective2009/54/EC of the European Parliament.

Variations of the concentrations of ^{226}Ra, ^{232}Th and ^{40}K from one site to another for water samples in the Bucovina area indicate that the origins of these waters are the same and that they come from different depths and pass through different geological layers. The application of radiometric spectrometry methods for determination of radionuclide activities give valuable information concerning mutual transportation between surface, subsurface and deeply situated natural mineral water layers.

Fig. 1 Investigated test area on Romania's map

The ^{226}Ra radionuclide, with a half-life of 1630 years, can supply important scientific information concerning mechanisms and rates of water–rock interaction and transport of this element in aquifers. It was also observed that the low permeability of the studied aquifer (fig. 1) allows reduced infiltration of the rain water and a good chemical stability oscillating in range of 10%.

Radiometric analysis results

The activity concentrations for gross-alpha, gross-beta and annual effective doses are presented in table 1. These range between 1.03mBq/L and 5.50mBq/L for gross-alpha and15.9mBq/L and 31.40mBq/L for gross-beta activity. The data obtained can provide basic information for consumers and competent authorities regarding the internal exposure risk due to drinking water intake. It can possibly serve as a comparison when evaluating the dose contribution from artificial radionuclides released to the environment as a result of any human practices and accidents in the studied area. Also, table 1 presents the amount of residue remaining after evaporation (slow evaporation) of 5 L of water.

Regarding the measured radionuclides in the analysed drinking water samples, the total effective doses are in the

Table 2

ACTIVITY CONCENTRATIONS OF ^{40}K, ^{238}U, ^{232}Th AND ^{226}Ra IN THE RESIDUE OF THE WATER SAMPLES

Sample code	^{40}K	^{238}U	^{232}Th	^{226}Ra
S1	0.92 ± 0.11	0.055 ± 0.006	0.028 ± 0.003	0.28 ± 0.03
S10	<0.83 (MDA)	0.084 ± 0.008	<0.28 (MDA)	0.45 ± 0.05
S20	0.55 ± 0.06	0.12 ± 0.02	0.012 ± 0.002	0.11 ± 0.02
S30	0.87 ± 0.08	0.21 ± 0.06	0.086 ± 0.010	0.280 ± 0.006
Mean*± 1σ**	0.79 ± 0.08	0.12 ± 0.02	0.100 ± 0.005	0.28 ± 0.03
Linear Range [Bq/L]	MDA***- 0.92 ± 0.11	0.055 ± 0.006- 0.21 ± 0.06	MDA - 0.086± 0.010	0.11 ± 0.02- 0.45 ± 0.05

*Mean represents the mean values obtained for each parameter during 30 months

** Standard deviation

***MDA represents the mean detected activity, in μS/yr

range of: 15.45 - 63.20 μSv/yr. The mean value forsamples S1-S9 was of 63.20 μSv/yr; the mean value for samples S10-S17 was of 53.90 μSv/yr; the mean value for S18-S25 was of 15.45 μSv/yr and the mean value for samples S26-S30 was of 41.23 μSv/yr (table 1). All values are situated below the reference level of the committed effective dose (100 μSv/yr) recommended by the WHO [8-10]. The doses from some other important alpha and beta emitters, such as radon, for more accurate dose evaluation should also be included.

Table 2 presents the activity concentrations of ^{40}K, ^{238}U, ^{232}Th and ^{226}Ra in the residue of the water samples for the mentioned time interval. The activity concentrations are in the range of a minimum detection activity (MDA) of 0.92±0.11 Bq/Lfor ^{40}K, of 0.055±0.006 and 0.21±0.06 Bq/L for ^{238}U, of 0.086 ± 0.010Bq/L for ^{232}Th and of 0.11±0.02-0.45±0.05 Bq/L for ^{226}Ra (table 2). Reported values of the activity concentrations in drinking water samples were up to 1.37 Bq/L for^{226}Ra [11] and up to 0.103 Bq/L for ^{238}U[12, 13].

Inthe case of the above mentioned radionuclides [14-28], the range of activity concentrations in water starts from few mBq/L, the detection limit is up to 1 Bq/L in case of ^{40}K and ^{226}Ra, while for ^{238}U the activity concentration has very low values of a few mBq/L and detection limit is up to few hundreds of mBq/L. There aren't many reference values reported in the scientific literature in the case of ^{232}Th, so comparative data are not presented. Some of the reported values for ^{232}Th in drinking water are considerably lower than our measured values [29].

As it can be observed from table 2, the measured activity concentrations of ^{232}Th onwater samples are in many cases extremely low, below the minimum detectable activity (MDA) of the system used in the laboratory.

Table 3 shows the total effective doses per each years for an adult member of the public in Romania resulting from the intake of naturally occurring alpha or beta radionuclides (^{40}K, ^{238}U, ^{232}Th and ^{226}Ra) in drinking water. The mean effective doses (table 3) are: 1.24 - 2.08(μSv/yr) for ^{40}K; 0.90 - 3.45(μSv/yr) for ^{238}U; 1.00 - 7.21(μSv/yr) for ^{232}Th and 11.24 - 46.00 (μSv/yr) for ^{226}Ra.

Regarding the variation of activity concentrations (tables 1 and 2) of the analysedwater samples, this is fairly constant over the 30 months sampling period. However, a slight decrease with time can be noticed in the results of gross alpha, gross beta, and gamma spectrometry analyses. The same can be observed in table 3 for the average of total effective doses of adult member of the public. Considering the amount of residue remaining after evaporation it can be observed that the^{226}Ra activity increases with the amount of residue, as expected (tables 1 and 2).

Table 3

TOTAL EFFECTIVE DOSES FOR AN ADULT MEMBER OF THE PUBLIC IN ROMANIA RESULTING FROM THE INTAKE OF NATURALLY OCCURRING ALPHA OR BETA RADIONUCLIDES IN NATURAL MINERAL WATER

Sample code	^{40}K	^{238}U	^{232}Th	^{226}Ra
S1	2.08	0.90	2.35	28.62
S10	nd***	1.38	nd	46.00
S20	1.24	1.97	1.00	11.24
S30	1.96	3.45	7.21	28.61
Mean*± 1σ**	**1.76**	**1.93**	**3.52**	**28.62**
Range [μSv/yr]	1.24-2.08	0.90-3.45	1.00-7.21	11.24-46.00

*Mean represents the mean values obtained for each parameter during 30 months

** Standard deviation

*** nd: not determined

Table 4

ANALYSIS OF THE DOSE CONTRIBUTION FRACTION FROM: POTASSIUM, URANIUM, THORIUM AND RADIUM

Sample code/	Dose fraction from ^{40}K	Dose fraction From ^{238}U	Dose fraction from ^{232}Th	Dose fraction from ^{226}Ra
S1 ÷ S30	3.79	3.23	27.87	65.12

Radiometric dose contribution calculations

As far as measured radionuclides are concerned, the dose contribution fractions for most of the analysed water samples are in the following order: 3.79 % from potassium, 3.23 % from uranium, 27.87 % from thorium and 65.12 % from radium. Table 4 presents the analysis of the dose contribution fractions from potassium, uranium, thorium and radium.

In the calculation of the total effective doses, per member of the public in Romania, resulting from intake of naturally occurring alpha or beta radionuclides in drinking water it has been considered an average consumption of 1 litre per day × 365 days, and the F_i coefficients from [17].For each age group the factors are given in the International Basic Safety Standards for Protection against Ionizing Radiation and for Safety of Radiation Sources. The conversion factors: 2.8×10^{-7}, 2.3×10^{-7}, $4.5\times10^{-8}$and 6.2×10^{-9}Sv/Bq for ^{226}Ra, ^{232}Th, ^{238}U and ^{40}K of the relevant radionuclide.

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

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

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 ICRP, IAEA, WHO and UNSCEAR [29-31], F_i is the dose coefficient for each radionuclide.

In another paper was studied the validation of a RP-HPLC-UV method for the determination of bisphenol A at low levels in natural mineral water [32].

Conclusions

The natural mineral water was investigated with regard to the natural radionuclides: ^{40}K, ^{238}U, ^{232}Th and ^{226}Ra. The natural radioactivity levels in the investigated natural mineral waters vary in a broad range. The ^{226}Ra radionuclide content varies from 0.11Bq/L to about 0.45Bq/L. The ^{232}Th isotopes content varies from 0.028Bq/L to about 0.086Bq/L, ^{40}K between 0.55 – 0.92Bq/L and ^{238}U between 0.055 - 0.21Bq/L. The results obtained are very well in agreement with those reported in many European countries.

Regarding the total effective doses for an adult member of the public in Romania resulting from intake of naturally occurring alpha or beta radionuclides in natural water these are: 1.24-2.08(µSv/yr) for ^{40}K; 0.90–3.45(µSv/yr) for ^{238}U; 1.00–7.21 (µSv/yr) for ^{232}Th and 11.24–46.00 (µSv/yr) for ^{226}Ra.

The mean annual effective doses for all the analysed drinking water samples are in the range of 1.76-28.62 µSv/yr, all being well below the reference level of the committed effective dose (100 µSv/yr) recommended by the WHO.

The obtained data can provide basic information for consumers and competent authorities to be aware of the actual problem of the variation of the chemical composition and of the radiation.

References

1. *** European Union (2005) List of natural mineral waters recognized by member states. Off. J. Eur. Communities 7-32 EEA 2005/C 59/06

2. *** EU Directive 1980/778/EEC, 1980a Council directive 1980/778/EEC on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral water Off. J. Eur. Communities L229, 1-10 30.08.1980

3. *** EU Directive 1996/70/EC of the European Parliament and of the Council of 28 October 1996 amending Council Directive 80/777/EC on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral waters. Off. J. Eur. Communities L299, 26-28 23.11.1996

4. *** EU Directive 2003/40/EC, 2003 Establishing the list, concentration limits and labeling requirements for the constituents of natural mineral waters and the conditions of using ozone-enriched air for the treatment of natural mineral waters and spring waters. Off. J. Eur. Communities L 126, 34-39 22.05.2003

5.ION, A.C., ION,I., ANTONISSE,M.M., SNELLINK-RUEL,B.H.M., REINHOUDT,D.N., Russ. J. General Chem. **71**(2), 2001, p. 159

6.CALIN, M.R., DRUKER, A.E., RADULESCU, I,J.Radioanal. Nucl.Chem.,**295**, 2013, p. 283

7.CALIN, M.R., CALIN, M.A., DONE, L., DRUKER, A.E., CALIN, A.C., J.Radioanal. Nucl.Chem., **288**, 2011, p. 547

8. World Health Organisation WHO. Guidelines for Drinking-Water Quality, Recommendation, Volume 1, Second edition, Geneva, 1998

9. World Health Organisation WHO Guidelines for drinking water quality.Third edition. Geneva, 2004

10. World Health Organisation WHO, Guidelines for drinking water quality. 4thedition. Geneva, 2011

11.JIA, G., TORRI,G., MAGRO,L., J. Environ Radioact.,**100**, 2009, p. 941

12.DESIDERI, D., ROSELLI,C., FEDUZI,L., MELI,M. A., Microchem., J.,**87**, 2007, p. 13

13.GRUBER, V., MARINGER,F. J., LANDSTETTER,C., Appl. Radiat. Isot.,**67**, 2009, p. 913

14.WALLNER, G., JABBAR,T.,J.Radioanal. Nucl.Chem.,**286**, 2010, p. 329

15.CHAU, N.D., MICHALEC, B., J.Radioanal. Nucl.Chem., **279**, 2009, p. 121

16.CALIN, M.R.; ION,A.C., RADULESCU,I., J. Radioanal.Nucl. Chem., **303**, (1), 2015, p. 305

17.PALOMO, M., PENALVER, A., BORRULL,F., AGUILAR, C.,Appl. Radiat. Isot., **65**, 2007, p. 1165

18.YALCIN,P., TASKIN,H., KAM,E., TERZI,M., VARINLIOGLU,A., BOZKURT,A., BASTUG,A., TASDELEN,B., J.Radioanal.Nucl.Chem.,**292**, 2012, p. 999

19.BENEDIK, L., JERAN,Z., Radiat. Prot. Dosimetry, **151**, 2012, p. 306

20.BEYERMANN, M., BÜNGER,T., SCHMIDT,K., OBRIKAT, D., Radiat. Prot. Dosimetry, **141**, 2010, p. 72

21.CHAU, N.D., MICHALEC,N, B.,J.Radioanal. Nucl.Chem.,**279**, 2009, p. 121

22.GRUBER, V., MARINGER,F.J., LANDSTETTER, C., Appl. Radiat. Isot.,**67**, 2009, p. 913

23.JOBBAGY, V., KAVASI,N., SOMLAI,J., MATE,B., KOVACS,T., Microchem. J., **94**, 2010, p. 159

24.KEHAGIA, K., KOUKOULIOU,V., BRATAKOS,S., SEFERLIS,S., TZOUMERKAS,F., POTIRIADIS, C., Desalination,**213**, 2007, p. 98

25.ROZMARIC, M., ROGIC, M., BENEDIK, L., STROK, M., Sci. Total Environment, **437**, 2012, p. 53

26.VESTERBACKA, P., MAKELAINEN, I., ARVELA, H., Radiat. Prot. Dosimetry, **113**, 2005, p. 223

27.ESRAERDEN, P., DIRICAN,A., SEFERINOGLU,M., YELTEPE,E., KEMAL SAHINY,N., J.Radioanal.Nucl.Chem., 301, 2014, p. 159

28.IBRAHIM, A., Abd El-Mageed, Abd El-Hadi El-Kamel, Abd El-BastAbbady, HARB,S., ISSA SALEH, I., Desalination,321, 2013, p. 28

29. *** United Nations Scientific Committee on the Effects of Atomic Radiation UNSCEAR. Report to the General Assembly, with scientific annexes, Vol. 1, Sources and Effects of Ionising Radiation; Vienna, 2000

30. *** IAEA Safety Standards, Radiation Protection and Safety of Radiation Sources International Basic Safety Standards, Interim Edition, General Safety Requirements, Vienna, 2011

31. *** IAEA International Basic Safety Standards for Protection against Ionizing Radiation and for Safety of Radiation Sources, Viena, 1996

32. RADU, E., STOICA, R., CALIN, C., OPRESCU, E.E., BOLOCAN, I., ION, I., ION, A.C., Rev. Chim. (Bucharest), **67**, no. 2, 2016, p. 236

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