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Determination of gross alpha and beta activity and uranium isotope content in commercially available, bottled, natural spring waters

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Abstract: Determination of content (active concentration) of radio-nuclides has recently become an indispensable part of the study dealing with the protection of the environment. Uranium concentration levels in aquatic environment are of great importance for environmental and safety assessment and for the protection of public health. Achieving this purpose, monitoring program for this radio-nuclide, radium and thorium, as well as gross alpha and beta activities, seems necessary and it is applied in many countries. This study determined the activity concentration of uranium isotopes in 10 samples of drinking water, natural spring and mineral water (bottled, commercially available water). Also, gross alpha and beta activity has been determined for all samples. Activity concentration of uranium isotopes was measured with alpha-spectrometry, while gross alpha-beta activity was measured by low level gas-flow proportional alpha-beta counter. Results of the research show that the concentration of isotopic uranium activities in the tested samples of drinking water varies from 10-8 to 10-2 Bq/L, while gross alpha-beta activity is between 10-3 and 10-1 Bq/g. The results show that the analyzed brands of spring, commercially available bottled waters meet the defined criteria of radiological safety.

INTRODUCTION

Throughout the world, tap water is being replaced by commercially available natural spring and mineral waters used in households and industry, as well as in the production of various soft drinks. This increased consumption and the fact that exposure to natural radiation sources contributes more than 98% of the total irradiation of population call for determination of total effective dose received from consumption of these products and for determination of contributions of particular natural radio-nuclides to the total effective dose. A major contribution comes from uranium and thorium series radio-nuclides in the following order:

^{210}Po > ^{228}Ra > ^{210}Pb > ^{226}Ra > ^{234}U > ^{238}U > ^{224}Ra > ^{235}U.

Radiological control of water is necessary due to its importance for human life and the need for minimum exposure to radiation. Therefore, maximum permissible concentration limits of radio-nuclide activity in drinking water have been prescribed by the World Health Organization (Mačefat *et al*., 2011).
Water plays a big and diverse role in the world. Processed or not, water is used in industry and commercial sector, for irrigation, sanitation and primarily for supplying the population with drinking water and water for household needs.

Uranium is a naturally occurring radioactive element, widely distributed in nature, consists of the isotopes ^{234}U, ^{235}U and^{238}U,with a mass ratio of 0.0054 : 0.711 : 99.2836%.

All of these three nuclides are alpha emitters, which have a particular biological effectiveness (Pimpl *et al.*,1992). Natural uranium can be detected in low concentrations in almost all materials from the environment. Long half-lives of uranium and transuranic isotopes make these elements long-term hazardous. Considering toxicity and radio-toxicity of uranium (Becker *et al*., 1997), its determination at trace and ultra-trace levels with high accuracy is very important. The average concentration of uranium in the Earth's crust is 3 mg/kg (Bleise *et al.*, 2003). Uranium concentration in ground and surface waters is three orders of magnitude lower, approximately 1 mg/L, although it can range from 0.001 to 1000 mg/L (Osmond *et al.,* 1983). Uranium isotopes and its decay series radio-nuclides, enter the human body mainly through food and drinking water (Bansal *et al.*, 1992). Water comes into contact with several minerals under the earth's surface, and uranium is transferred to water by its leaching action. Also, human activity, such as the use of depleted uranium ammunition, which is the case in some areas in BiH, inappropriately stored radioactive waste and other activities, can affect the radio-nuclide content in drinking water. $^{234}U/^{238}U$ activity ratio in natural water is an important indicator of the origin of the uranium in the studied sample. Typically, the $^{234}U/^{238}U$ activity ratio in natural water varies from 1 to 2, but it can range up to 30 in extreme cases (Osmond *et al.,* 1983). Commonly observed fractionation and disequilibrium between ^{234}U and ^{238}U in water is a result of nuclear recoil effects (Fleischer and Raabe, 1978; Osmond *et al.*, 1983) and extensive rock/water interactions.

The aim of this study is to determine uranium isotopes activity concentration, $^{234}U/^{238}U$ activity ratio in the spring waters (bottled, non-mineral and mineral, and crude spring water), and gross alpha beta activity of the supra samples. According to the available literature, drinking water quality monitoring in BiH mainly comes down to chemical and microbiological analyses. Given the use of depleted uranium ammunition in the war in the 90 s and a highly varied geo-structure of soil, among many other parameters (microbiological, chemical), radium and uranium isotopes have to be regularly monitored in drinking waters (Vasile *et al.,* 2008) (Council Directive 98/83/EC,1998). We analyzed ten bottled samples of drinking water, the most commonly used on the BiH market, in order to obtain some detailed information about content of uranium, and gross alpha beta activity in spring drinking water.

EXPERIMENTAL

This study analyzed mineral and natural commercially available spring waters, ten randomly selected brands of well-known producers, in order to determine uranium isotopes and gross alpha-beta activity.

Gross alpha-beta activity was determined by standard methods from ISO 9696 or ISO 9697.

1 mL of concentrated H_2SO_4 was added to each 1 L sample aliquot. The aliquots were then evaporated to dryness. The obtained dry residue was transferred to pre-weighed crucibles. These samples were calcinated in the calcinator at the temperature of 350°C. The calcinated residue was homogenized and 100 mg was transferred to a 5-cm-diameter planchet for measurement. Gross alpha-beta activity was measured by the gas-flow proportional counter MPC-9604, Protean Instruments Corporation, for 84600 seconds. Efficiency for gross alpha activity was 7.6% and 38.6% for gross beta activity.

Activity concentration of uranium isotopes was determined by alpha spectrometry. Approximately 1 L of each water sample was taken and the liquid was weighed in glasses of known mass.

Each sample was acidified with 1 mL concentrated HNO_3 and known mass of U-232 tracer was added. Uranium was precipitated with $CaCl_2$ and $(NH_4)_2HPO_4$ according to the Eichrom procedure (Eichrom Technologies Inc., 2001).

Several mL of $NH_{3(aq)}$ were then added to each sample and heated for 20 minutes until deposition formed, which was obvious from the white turbidity of the sample. The liquid above the deposition was decanted, and several mL of 8 mol/L HCl were added to the deposition to dissolve it. Uranium was separated from interfering elements by passing it through an anion exchange column, DOWEX 1x8, Cl^- form, 100-200. After thorium isotopes were removed with 45 mL 8 mol/L HCl, uranium was eluted with 15 mL 0.5 mol/L HCl. The samples were prepared for measurement by electro-deposition and were measured for 2 hours at 1.2 A amperage according to HASL-300 procedure (DOE EML, 1997). The measurement was performed by alpha spectrometer Alpha Analyst, Canberra, equipped with silicon detector (PIPS) with 450 mm^2 active surface. Sample counting time was 172800 s, and the chemical yield was 15-96%. Lower limit of detection was 0.717-3.69 mBq/L ^{238}U, 0.0897-0.222 mBq/L ^{235}U, and 0.269-5.45 mBq/L for ^{234}U. The results are reported with combined standard uncertainty with coverage factor 1.

RESULTS AND DISCUSSION

The tested samples of the above mentioned water were analyzed for gross alpha and beta activity, including an isotopic analysis of uranium. Results of the analyses of tested samples are shown in Tables 1, 2, 3, 4, 5 and 6.

Table 1. Gross alpha and beta activity of analyzed samples of mineral commercially available water

Water samples	Gross alpha activity (Bq/g)	Gross beta activity (Bq/g)
1	0.019	0.00318
2	0.00115	0.177
3	0.0112	0.0584
4	0.034	0.0123
5	0.00439	0.105

Table 2. Gross alpha and beta activity of analyzed samples of mineral commercially available natural spring water

Water samples	Gross alpha activity (Bq/g)	Gross beta activity (Bq/g)
1	0.0190	0.0266
2	0.0389	0.0626
3	0.00240	0.0364
4	0.0241	0.0423
5	0.038	0.0772

According to the Rulebook on Sanitary Quality of Drinking Water (Official Gazette of BIH, No.40/10) and recommendations of the World Health Organization *(WHO*, 2011), permissible level of gross α-activity is 0.5 Bq/g, and permissible level of gross β-activity is 1 Bq/g. Order of magnitude of the results of all processed samples is between 10^{-2} and 10^{-4} Bq/g, which shows that the gross alpha and beta activity of all ten analyzed samples does not exceed the permissible level of activity.

The highest gross alpha activity was registered in sample No. 4, while the lowest alpha activity was registered in sample No. 2. The highest gross beta activity was registered in sample No. 2, while the lowest activity was registered in sample No.1

Table 3. Results of uranium radioisotopes activity concentration obtained through Alpha-spectrometric analysis of commercially available mineral spring water samples

Water samples	A(^{238}U) (Bq/L)	A(^{235}U) (Bq/L)	A(^{234}U) (Bq/L)	Activity ratio ^{234}U/^{238}U
1	$6.07\cdot10^{-3}$	$4.78\cdot10^{-4}$	$4.04\cdot10^{-2}$	6.6557
2	$1.08\cdot10^{-3}$	$5.40\cdot10^{-5}$	$7.07\cdot10^{-3}$	6.5463
3	$2.80\cdot10^{-3}$	$2.77\cdot10^{-5}$	3.6310^{-3}	1.2964
4	$2.21\cdot10^{-3}$	$1.03\cdot10^{-4}$	$2.00\cdot10^{-3}$	0.9049
5	$4.14\cdot10^{-4}$	$3.45\cdot10^{-5}$	$1.73\cdot10^{-4}$	0.4179

Table 4. Results of uranium radioisotopes activity concentration obtained through Alpha-spectrometric analysis of commercially available natural spring water samples

Water samples	A(^{238}U) (Bq/L)	A(^{235}U) (Bq/L)	A(^{234}U) (Bq/L)	Activity ratio ^{234}U/^{238}U
1	$3.27\cdot10^{-7}$	$1.87\cdot10^{-7}$	$2.86\cdot10^{-6}$	0.8746
2	$1.17\cdot10^{-6}$	$2.97\cdot10^{-8}$	$1.31\cdot10^{-6}$	1.1197
3	$1.72\cdot10^{-5}$	$6.72\cdot10^{-7}$	$2.54\cdot10^{-5}$	1.4767
4	$2.14\cdot10^{-6}$	$2.93\cdot10^{-8}$	$6.55\cdot10^{-6}$	3.0607
5	$1.17\cdot10^{-7}$	$3.38\cdot10^{-8}$	$6.82\cdot10^{-7}$	5.8291

According to the World Health Organization (WHO), (Water Sanitation Health, Chapter 9), permissible level of activity concentration (content) of uranium isotopes is as follows: For ^{238}U 10 Bq/kg, for ^{235}U 1 Bq/kg and for ^{234}U 1 Bq/kg.

Therefore, all ten analyzed samples of known brands of commercially available mineral and natural spring water contain a permissible concentration of uranium isotopes, within the limits prescribed by the World Health Organization.

The analysis of commercially available mineral waters shows the highest concentration of uranium isotopes in sample No. 1, while the lowest concentration was registered in sample No. 3. The analysis of commercially available natural spring waters shows the highest concentration of uranium isotopes in sample No. 3, while the lowest concentration was registered in sample No. 5.

^{234}U/^{238}U ratio in natural waters is within the limit of 0.5-1.2. Activity ratio in this study varies between 0.4179-6.6557. ^{234}U/^{238}U activity ratio value larger than 2 indicates a more intensive solid to liquid phase transition than normal and/or transition to liquid phase in slow moving waters, while the value lower than 1 indicates less intensive dissolution or contact with fast moving waters (Vidic, 2010).

Table 5. Results for dry residue and conductivity of commercially available mineral water samples

Water samples	V (mL of sample)	m (g) dry residue before drying)	m (g) dry residue after drying, 350°C)	Conductivity (μS/cm)
1	1000	2.859	2.5029	1300
2	1000	2.755	2.1471	1840
3	1000	1.5568	0.8829	1260
4	1000	2.3028	1.6966	2570
5	1000	2.901	1.7948	2130

Table 6. Results for dry residue and conductivity of commercially available natural spring water samples

Water samples	V (mL of sample)	m (g) dry residue before drying)	m (g) dry residue after drying, 350°C)	Conductivity (μS/cm)
1	1000	0.3916	0.3000	412
2	1000	0.4621	0.4100	462
3	1000	0.4682	0.3600	434
4	1000	0.4862	0.3800	611
5	1000	0.5999	0.5800	471

The analyzed waters have relatively high values for dry residue and specific conductivity which indicates that they are very hard waters with high ion content, which was expected since we are talking about mineral waters. Lack of correlation is usually connected with different origin and different chemical composition of waters.

CONCLUSIONS

After described processing and preparation of samples, the obtained data were calculated and concentration values of all three uranium isotopes present in the samples were obtained, as well as gross alpha-beta activity. According to the Rulebook on Sanitary Quality of Drinking Water (Official Gazette of BIH, No. 40/10) and recommendations of the World Health Organization (WHO, 2011), permissible level of gross α-activity is 0.5 Bq/g, and permissible level of gross β-activity is 1 Bq/g. Order of magnitude of the results of all processed samples is between 10^{-3} and 10^{-1} Bq/g, which shows that the gross alpha and beta activity of all five analyzed samples does not exceed the permissible level of activity. According to the World Health Organization (WHO), (Water Sanitation Health, Chapter 9), permissible level of activity concentration (content) of uranium isotopes is as follows: 10 Bq/kg for ^{38}U, 1 Bq/kg for ^{235}U and 1 Bq/kg for ^{234}U. All ten analyzed samples contain a permissible concentration of uranium isotopes and are very well-correlated with the quantity of total water mineralization. The analysis showed that the water samples are fully radiologically safe and not harmful to human health and environment.

REFERENCES

Bansal, K.C., Viret, J.F., Haley, J., Khan, B.M., Schantz, R., Bogorad, L. (1992). Transient expression from cab-ml and rbcS-m3 promoter sequences is different in mesophyll and bundle sheath cells in maize leaves. *Proceding of the National Academy of Sciences*. 89(8), 3654-3658.

Becker, G.S., and Mulligan, C.B. (1997). The endogenous determination of time preference. *The Quarterly Journal of Economics*, 729-758.

Bleise, A., Danesi, P.R., Burkart, W. (2003). Properties, use and health effects of depleted uranium (DU): a general overview, *Journal of Environmental Radioactivity*, 64(2),93-112.

DOE EML Procedures Manual HASL-300, (1997). 1(28).

Eichrom Technologies Inc. (2001). Analytical Procedures-Uranium and Thorium in Water-ACW03 Version 1.7.

EU (1998). Council Directive 98/83/EC of 3 November 1998 on The Water Intended for Human Consumption. European Uninion *Official Journal L* 330 (05/12/98).

Fleischer, R.L., Raabe, O.G. (1978). Recoiling alpha-emitting nuclei. Mechanisms for uranium-series disequilibrium. *Geochimica et Cosmochimica Acta*, 42(7), 973-978.

ISO 9696 (2007). Water quality - Measurement of gross alpha activity in non-saline water Thick source method. International Standardization Organization, Geneva, Switzerland.

ISO 9697 (2008). Water quality - Measurement of gross beta activity in non-saline water - Thick source method. International Standardization Organization, Geneva, Switzerland.

Mačefat, M., Krmpotić, M., Barišić, D. (2011). Determination of natural alpha emitting radio-nuclides in bottled drinking and mineral water. In *Eight symposium of the Croatian Radiation Protection Association with international participation*, Croatian Scientific Bibliography and Ministry of Science, Education and Sports -Svibor.

Osmond, J.K., Cowart, J.B., Ivanovich, M. (1983). Uranium isotopic disequilibrium in ground water as an indicator of anomalies. *The International Journal of Applied Radiation and Isotopes*, 34(1), 283-308.

Pimpl, M., Yoo, B., Yordanova, I. (1992). Optimization of a radioanalytical procedure for the determination of uranium isotopes in environmental samples. *Journal of radioanalytical and nuclear chemistry*, 161(2), 437-441.

Rulebook on Sanitary Quality of Drinking Water (*Official Gazette of BIH, No.40/10*). Public Health Institute.

Vasile, M., Altzitzoglou, T., Benedik, L., Spasova, Y., Wätjen, U. (2008). Radiochemical separation and determination of 228Ra in mineral waters by low-level liquid scintillation counting. *LSC*, 375-380.

Vidic, A. (2010). *Radiohemijska separacija i alfaspektrometrijsko određivanje uranovih izotopa u rejonu TRZ Hadžići,* Magistarski rad, Prirodno-matematički fakultet, Univerzitet u Tuzli.

World Health Organization (WHO). (2008). Guidelines for drinking-water quality, 1st Ed.

World Health Organization (WHO). (2011). Guidelines for drinking-water quality, 4st Ed.

Summary/Sažetak

Određivanje sadržaja (aktivne koncentracije ili koncentracije aktivnosti) radionuklida u posljednje vrijeme postaje neizostavni dio studija koje se bave zaštitom okoliša. Sadržaj urana u vodenom okruženju je od velike važnosti za okoliš i sigurnosne procjene istog, a u svrhu zaštite zdravlja. Shodno navedenom, praćenje sadržaja ovog radionuklida, radija, torija, kao i ukupne alfa i beta aktivnosti u okolišu, se nameće kao neophodno i primjenjuje se u mnogim zemljama u svijetu. U ovom radu određena je koncentracija aktivnosti uranovih izotopa u deset uzoraka vode za piće, prirodne izvorske i mineralne vode (flaširane, komercijalno dostupne vode). Također, za sve navedene uzorke vode određena je ukupna alfa i beta aktivnost. Koncentracija aktivnosti uranovih izotopa mjerena je alfa-spektrometrijski, a ukupna alfa-beta aktivnost je mjerena na niskofonskom, gas-proporcionalnom alfa-beta brojaču. Rezultati istraživanja su pokazali da se koncentracija aktivnosti uranovih izotopa ispitivanih uzoraka vode za piće kreće od 10^{-8} do 10^{-2} Bq/L, a ukupna alfa-beta aktivnost od 10^{-3} do 10^{-1} Bq/g. Dobijeni rezultati su pokazali da su analizirani brendovi izvorskih, komercijalno dostupnih, flaširanih voda, radiološki ispravni.