Concentration of selected natural radionuclides in the thermal groundwater of Uniejów, Poland

Henryk Bem,
Marcin Olszewski,
Aneta Kaczmarek

Abstract Activities of the main radionuclides from the ^{238}U and ^{232}Th series in the Uniejów geothermal water were determined by combining liquid scintillation counting with α/β separation and γ-spectrometry methods. The ^{222}Rn and ^{226}Ra activities were measured after extraction of radon from 10 ml water samples to 10 ml of an Ultima Gold F scintillation cocktail directly in 22 ml scintillation vials. The samples were counted in a new generation portable liquid scintillation counter, Betascout, without separation of the phases over the period of 30 days after extraction. The average values of the specific activities were equal to 2.95 and 0.64 Bq/dm^3 for ^{222}Rn and ^{226}Ra, respectively. The ^{210}Po radionuclide before counting was preconcentrated from 1 dm^3 water samples on hydrated manganese oxide and deposited on silver discs. The discs were immersed in 10 ml of the scintillator and their activity was measured also by the same method. The average ^{210}Po concentration was 0.052 Bq/dm^3. Activity of the remaining radionuclides was determined by γ-spectrometry after their preconcentration on hydrated manganese oxides from 10 dm^3 samples. The activities of two radium radionuclides, ^{224}Ra and ^{226}Ra, can be calculated from their basic γ-lines, whereas ^{228}Ra can be determined from its decay product – ^{228}Ac, and were equal to 0.40, 0.65 and 0.58 Bq/dm^3, respectively. The activities of ^{210}Pb and ^{238}U (^{234}Th) were below the detection limit of the method equal to 0.03 Bq/dm^3. Based upon the obtained results, it can be concluded that there are not any radiological restrictions for using this water as a heat source or for balneological purposes. However, it cannot be used as drinking water, because the calculated committed effective dose from its one year consumption exceeds the WHO recommended value of 0.1 mSv.

Key words natural radionuclides • α/β liquid scintillation counting • thermal groundwater

H. Bem✉, M. Olszewski, A. Kaczmarek
Institute of Applied Radiation Chemistry,
Technical University of Łódź,
116 Żeromskiego Str., 90-924 Łódź, Poland,
Tel.: +48 42/ 631 31 95, Fax: +48 42/ 636 50 08,
e-mail: henrybem@mail.p.lodz.pl

Introduction

Low enthalpy geothermal energy resources beneath the area of Poland are relatively significant and they should cover in the near future not only a substantial part of the country's needs for heat energy but also should contribute to further development of balneological and recreation centres [10, 13]. The important underground water reservoir, with almost half of the total Polish geothermal heat energy, the so called Szczecin–Łódź geothermal district is located in the sedimentary basins of the Polish Lowland [19]. In this district, one of the most important geothermal aquifers is that close to the Poddębice and Uniejów areas in the Central Poland [4]. The geothermal water in this region is characterised by relatively high temperatures, 70 to 80°C and low salinity with TDS up to 60 mg/dm^3 [1].

In the Uniejów site during 1986–1991 period three 2000 m deep geothermal wells were drilled and now water from these wells is used for heating purposes, replacing 9 coal fired local units. Very recently, in co-operation with the Medical University of Łódź, the new balneological centre has also been opened on this site. Taking advantage of high water efficiency from the wells (up to 90 m^3/h) and good curative quality of the geothermal water, further development of this balneo-therapeutical centre is planned.

The distribution and behaviour of natural radionuclides, particularly radon and radium isotopes, in such water are

subjects of both scientific and practical importance. From a scientific point of view, understanding of the factors controlling water quality can be done by isotope tracing the mechanisms and rates of the nuclide transport from rocks [5, 6, 20]. The practical importance arises from the human health risk associated with ingestion of radionuclides with drinking water and inhalation of radon during technical and balneological activities. According to the new Polish state recommendation, the total dose from consumption public drinking water should not exceed 0.1 mSv/year [17]. However, in relation to the older regulation, the radium and radon radionuclides as well as the gross α and β activities were almost exclusively determined in the domestic underground and spring waters [11, 14, 15, 21]. In accordance with the World Health Organization (WHO) recommendations [8] the reference level of committed effective dose from 1 year's consumption of drinking water is 0.1 mSv. Therefore, if either the gross α activity concentration of 0.1 Bq/dm^3 or the gross β activity concentrate of 1 Bq/dm^3 is exceeded, then the activity of individual radionuclides should be measured. Particularly, it concerns to some ^{232}Th and ^{238}U series radionuclides: ^{232}Th, ^{210}Pb and ^{210}Po, for which dose conversion factors (DCF) are equal or even higher than that for ^{226}Ra nuclide. The rounded up guideline levels for radionuclides in drinking water are given in the recent WHO draft publication available on internet [9].

The first aim of the present work was to elaborate a simple but complete procedure for the determination of the main natural radionuclides in ground waters. For α-emitting radionuclides a new generation portable liquid scintillation counter with separation of α/β-pulses – Betascout (Perkin Elmer) has been used. In such a device, with very low background in the α region, the radon concentration can be measured after its direct extraction in scintillation vials from 10 ml water samples to 10 ml of immiscible with water scintillation cocktails. For the other γ-emitting radionuclides, a preconcentration step on hydrated manganese oxides, before γ-spectrometry finishing has been applied [18].

The second aim of these studies was to appraise from a radiological point of view, the utility of these waters as potential mineral drinking waters.

Experimental

Materials and methods

Sampling

Thermal groundwater samples were collected from the main water well in the Uniejów site into 1 and 10 dm^3 drained plastic containers and immediately acidified with 1 ml of 65% HNO$_3$ per 1 dm^3 of water. From the plastic bottles a set of 10 ml water samples were directly transferred into a scintillation vial containing 10 ml of the scintillation cocktail Ultima Gold F. The scintillation vials were closed hermetically and shaken to extract ^{222}Rn to the organic phase. Such fixed samples together with those in plastic containers were taken to the laboratory for radioactivity counting.

Preconcentration of radionuclides

For the determination of ^{210}Po as well as for γ-emitting radionuclides a preconcentration step on hydrated manganese dioxide was applied [18]. For preconcentration of ^{210}Po nuclide 1 dm^3 of water samples were sufficient. Prior to preconcentration, the thermal groundwater samples were again acidified to pH = 1 with 65% HNO$_3$ and 5 ml of 0.2 mol/dm^3 KMnO$_4$ were added. The solution was mixed for 1 h and then brought to pH = 9 with concentrated ammonia, followed by the addition of 5 ml of 0.3 mol/dm^3 MnCl$_2$ and heated for another 1 h. The precipitated hydrated MnO$_2$ was allowed to settle overnight. The liquid phase was sucked off and the remaining mixture was transferred to the tubes and centrifuged. The liquid phase over MnO$_2$ was again removed and the remaining sediment was dissolved with 15 ml 1% H$_2$O$_2$ solution in 1 mol/dm^3 HCl. After adding about 0.2 g of hydroxylamine (reduction Fe^{3+} to Fe^{2+}) the solution was diluted to 30 ml and transferred to PTFE vessels equipped with a silver sheet bottom. The ^{210}Po was spontaneously deposited for 12 h at 70°C.

A similar preconcentration procedure was applied for 10 dm^3 geothermal water samples, but the MnO$_2$ sediment was collected on a paper filter and dried at 105°C and the filter was put into standard plastic dishes before γ-spectrometry measurements.

Liquid scintillation counting

A new generation liquid scintillation counter with α- and β-pulses separation option Betascout (Perkin-Elmer) was used for α activity determination of the ^{226}Ra, ^{222}Rn and ^{210}Po radionuclides.

For ^{222}Rn determination, the samples prepared directly in scintillation vials were cooled to ambient temperature and kept for at least 3 h to achieve the transient radioactive equilibrium between ^{222}Rn and its daughters. Samples were counted in α-mode for 3600 s, after adjusting optimal Pulse Length Index (PLI = 440 a.u.) and alpha counting window settings. The samples were recounted several times over one-month periods in order to check the availability of this method for ^{226}Ra determination, too.

For ^{210}Po activity measurements, the silver disks after deposition were put directly on the bottom of the scintillation vials and 10 ml of the Ultima Gold F scintillation cocktail was added. After adjusting the new optimal separation conditions the activity of this nuclide was measured over 40,000 s.

The ^{226}Ra activities in geothermal water, collected in 1 dm^3 plastic bottles, were measured for comparison by an independent method described by us elsewhere [3].

γ-Spectrometry

Activities of γ-emitting radionuclides (listed in Table 1) from the uranium and thorium series were determined using the Canberra spectrometric system with a REGe detector. The filter containing traces of natural radioisotopes separated on MnO$_2$ in plastic dishes were put directly on the detector and counted for 320,000 s. The system had been previously calibrated for detection efficiency for the whole γ-energy region by preparing an identical filter sample containing known activity of coprecipi-

Table 1. Results of concentration measurement of ^{222}Rn in the thermal groundwater by its direct extraction from water to scintillation cocktail Ultima Gold F.

Date of sampling	Concentration of ^{222}Rn (Bq/dm^3)	Date of sampling	Concentration of ^{222}Rn (Bq/dm^3)
Autumn 16 October 2002	4.45 ± 0.20	Winter 26 February 2003	3.43 ± 0.18
	2.94 ± 0.17		3.56 ± 0.18
	2.92 ± 0.17		3.52 ± 0.18
	mean 3.44 ± 0.88		mean 3.50 ± 0.07
Autumn 27 November 2002	2.90 ± 0.17	Spring 25 April 2003	2.18 ± 0.14
	2.75 ± 0.16		1.81 ± 0.13
	2.57 ± 0.16		1.81 ± 0.13
	mean 2.74 ± 0.16		mean 1.93 ± 0.21

Mean value for autumn–winter = 3.23 Bq/dm^3.

tated ^{152}Eu standard (SREu-4, POLATOM). The data were processed by means of the InSpector spectroscopy system. The activity concentration of ^{210}Pb, ^{228}Th, ^{224}Ra and ^{226}Ra was calculated directly from their basic γ-lines, taking into account the possible interference of ^{214}Pb and ^{235}U for the two latest nuclides. For calculation of ^{228}Ra and ^{238}U nuclides, the activities of their daughters, ^{228}Ac and ^{234}Th, were taken into account, respectively.

Quality assurance

The accuracy of the analytical procedure was determined in an independent experiment by checking the recovery of added to 1 dm^3 and 10 dm^3 thermal groundwater samples the following standard solutions: ^{210}Pb–^{210}Po (RBZ-44, Amersham), ^{152}Eu (SREu-4, POLATOM) and ^{226}Ra (Isotope Product Laboratory, USA).

Uranium and thorium recovery was checked by the addition of 1 mg of uranyl nitrate (Chemapol) to 10 dm^3 of the thermal groundwater. The obtained recoveries were above 95%.

Results

The results of ^{222}Rn determination in different sampling periods are presented in Table 1. The spring activities (April 2003) of ^{222}Rn are considerably lower, with an average value of 1.93 Bq/dm^3, in comparison to an autumn–winter (2002/2003) value equal to 3.23 Bq/dm^3.

As was mentioned before, the sealed scintillation vials with 10 ml of the geothermal water and 10 ml of the Ultima Gold cocktail were recounted several times over at least one-month period. Typical ^{222}Rn activity decay with time is shown in Fig. 1.

As is evident from Fig. 1, the ^{222}Rn activity A is not decreasing exactly with the first order kinetics, according to equation $A = A_0 \cdot e^{-\lambda t}$, where A_0 – denotes initial Rn activity and λ its decay constant. In order to get the best fitting curve, it is necessary to add, time independent, coefficient C. In this manner, after almost complete decay of unsupported ^{222}Rn, C coefficient could be assigned as equilibrium ^{222}Rn activity resulting from the presence of ^{226}Ra in the water phase. In this counting system, besides ^{222}Rn, only ^{210}Po and ^{220}Rn could be partly extracted to the organic phase. Usually, in typical water samples average concentrations of ^{210}Po are at least three orders of magni-

tude lower, and its contribution is negligible [7, 12]. In fact, ^{220}Rn nuclide, as a product of ^{224}Ra decay can be sometimes present in water samples at levels comparable to those of ^{222}Rn, but because of a very short half-life of ^{220}Rn ($T_{1/2}$ = 55 s), only a relatively small part of its total amount can diffuse from water to an organic scintillation phase. Therefore, its contribution to the total alpha activity in the organic phase can be usually also neglected. Assuming that the average equilibrium activity C = 1.12 cpm corresponds to the activity ^{222}Rn generated from ^{226}Ra, it is possible to calculate ^{226}Ra concentration from Equation (1):

$$(1) \qquad A = \frac{C}{3 \cdot 0.97 \cdot V_p \cdot 60} \quad (Bq/dm^3)$$

where: A – calculated ^{226}Ra activity; C – measured ^{222}Rn equilibrium activity in cpm; V_p – volume of water phase in a scintillation vial (0.01 dm^3); 3 – total detection efficiency for ^{222}Rn and its daughters (^{218}Po and ^{214}Po) counted in α-mode of the device; 0.97 – Rn extraction efficiency for 10 ml of organic (Ultima Gold F) and water phase system determined in independent experiments.

Calculated in this way, the average ^{226}Ra activity, equal to 0.64 Bq/dm^3 was slightly higher than the average ^{226}Ra activity of 0.51 Bq/dm^3 determined by the previously elaborated extraction method from 0.5 dm^3 [3].
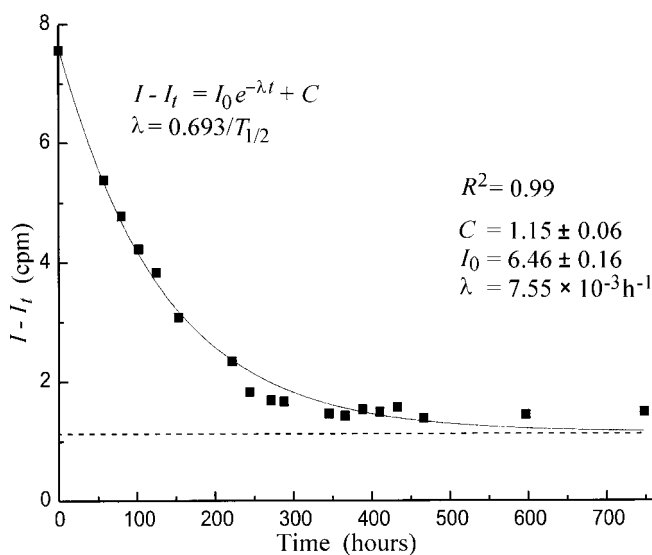
Fig. 1. Decay of ^{222}Rn activity in the thermal groundwater samples.

Table 2. Concentration of the main natural radionuclides in the Uniejów thermal groundwater.

Radionuclides	γ-lines (keV)	Concentration, A_i (Bq/dm^3)	Reference concentration, A_{ri}, corresponding to 0.1 mSv effective dose (Bq/dm^3)
^{210}Pb	46.5	<0.02	0.1
^{210}Po	α-counting	0.052 ± 0.01	0.1
^{222}Rn	α-counting	2.90 ± 0.77	–
^{224}Ra	241.0	0.40 ± 0.05	1
^{228}Th	84.3	0.47 ± 0.09	1
^{226}Rn(^{222}Rn)	α-counting	0.51 ± 0.01	1
^{226}Ra	185.6	0.65 ± 0.07	1
^{228}Ra(^{228}Ac)	911.2	0.58 ± 0.05	0.1
^{238}U(^{234}Th)	63.3	<0.03	10

Concentration of all determined radionuclides in geothermal samples is shown in Table 2.

The average values from at least three determinations are given together with appropriate standard deviation. In the case of very low uranium concentration and lack of ^{235}U contribution to 185.6 keV γ-line, the total intensity of this line can be attributed to ^{226}Ra. The value of 0.65 Bq/dm^3 obtained by this method is very close to that calculated from ^{222}Rn decay experiments.

The WHO reference activities corresponding to the annual effective dose of 0.1 mSv resulting from drinking two litres water per day are given in Table 2 (last column). The value for ^{222}Rn is not listed in original WHO guidelines, but its contribution to the total dose from ingestion is negligible.

Discussion

A new simple protocol combining preconcentration on hydrated manganese dioxide with γ-spectrometry and state-of-the-art for liquid scintillation α-counting for natural radionuclides in water has been elaborated. A new generation portable LSC counter, Betascout, proved its usefulness for the direct, in-site measurement of radon concentration in a small (10 ml) water sample. This simple method can be applied for routine radon determination since the determination level with 10% accuracy, according to the Curie criterion, is below 1 Bq/dm^3 for 1 h counting time. Concentration of ^{226}Ra can be also appraised for dosimetric purposes by recounting for 80,000 s the same sample after one month waiting time, necessary for decay of the unsupported ^{222}Rn. However, in this method one can expect slightly higher results caused by the possible interference from ^{224}Ra, because its short-lived decay product ^{220}Rn ($T_{1/2}$ = 55 s) can also partially move from water to the organic phase.

The silver disks with deposited Po can be also efficiently counted by this method. After preconcentration of ^{210}Po from 1 dm^3 water, the calculated determination limit for 10^4 s counting is equal to 0.01 Bq/dm^3.

Almost all γ-emitting radionuclides (except for ^{40}K) present in thermal groundwater can be quantitatively preconcentrated from 10 dm^3 water samples with hydrated manganese dioxides. After filtration of the obtained precipitate, a suitable source for γ-spectrometry measurements can be simply prepared. This procedure can be applied for determination of the main natural radionuclides in thermal groundwater.

The observed values for radionuclide concentration in the Uniejów thermal groundwater are close to those reported for this type of water in Europe, particularly in Hungary [2] and French Massive Central [16]. The Uniejów thermal groundwater is Mg-Ca-Cl type with relatively high concentrations of these elements (25, 130 and 3600 mg/dm^3, respectively). In such water favourable conditions for mobilization of radium nuclides from the background occur [7]. Therefore, enhanced radium concentrations in groundwater, even in the region with a moderate natural radioactivity such as in the Uniejów–Poddębice area can be expected. The obtained results showing a strong disequilibrium between uranium and radium confirm it. The determined activities of ^{226}Ra and two other radium isotopes from the thorium series: ^{228}Ra and ^{224}Ra, are much higher than for dissolved uranium. For example, as it is evident from Table 2, the ^{228}Ra specific activity exceeds almost six times the WHO reference level, corresponding to 0.1 mSv effective dose from one year consumption of such water, whereas for few other nuclides, their activities are close to the recommended value for a single radionuclide. Therefore, from a radiological point of view, this water, without some action to reduce the radioactivity (particularly caused by radium isotopes), cannot be supplied as drinking water. However, as far as we know, there are no such plans. On the other hand, relatively low Rn concentration and good curative and healing properties allow a wide use of this water for recreation, therapeutic and domestic heating purposes.

References

1. Atlas of geothermal energy resources in the Polish Lowland (1995) Górecki W (ed.) ZSE AGH, Towarzystwo Geosynoptyków GEOS, Kraków (in Polish)

2. Baradacs E, Hunyadi I, Dezso Z, Csige I, Szerbin P (2001) [226]Ra in geothermal and bottled mineral waters of Hungary. Radiat Meas 34:385–390
3. Bem H, Bem EM, Majchrzak I (1998) Comparison of two methods for [226]Ra determination in mineral water. Nukleonika 43;4:459–468
4. Bujakowski W (1999) Geothermal projects in Poland. Technika Poszukiwań Geologicznych Geosynoptyka i Geotermia 4/5:132–141
5. De Oliveira J, Mazzilli B, De Oliveira Sampa MH, Silva B (1998) Seasonal variations of [226]Ra and [222]Rn in mineral spring waters of Aquas da Prata, Brazil. Appl Radiat Isot 49;4:423–427
6. Dickson BL (1990) Radium in ground water. In: The environmental behaviour of radium. Vol. 1. IAEA, Vienna, pp 335–372
7. Gellermann R, Wiegand J, Funke L, Gerler J (2000) Mineral water with anomalous radium concentration from the northern Harz Mountain region. In: Proc of the 5th Int Conf on High Levels of Natural Radiation and Radon Areas held in Münich, 4–7 September 2000, Germany. Bundesamt für Strahlenschutz, Salzgitter, vol. 2, pp 83–86
8. Guidelines for drinking-water quality (1993) Vol. 1. Recommendations, 2nd ed. WHO, Geneva
9. Guidelines for drinking-water quality (2003) 3rd ed. http://www.who.int/docstore/water_sanitation_health/GDWQ/Updating/draftguidel/draftchap9.htm
10. Kępińska B (2002) Thermal springs and spas in Poland. Geo-Heat Center Bulletin 3:10–17
11. Kozłowska B, Hetman A, Dorda J, Zipper W (2001) Radon-enriched spring waters in the South of Poland. Radiat Phys Chem 61;3/6:677–678
12. Nieri NA, Mazzilli B (1998) Evaluation of [210]Po and ^{210}Pb in some mineral spring waters in Brazil. J Environ Radioact 41:11–18
13. Pietruszko SM, Wiśniewski G, Chwieduk D, Wnuk R (1996) Potential of renewable energies in Poland. Renewable Energy 9:1124–1126
14. Przylibski TA, Dorda J, Kozłowska B (2002) The occurrence of [226]Ra and [228]Ra in groundwaters of the Polish Sudety Mountains. Nukleonika 47;2:59–64
15. Przylibski TA, Kozłowska B, Dorda J, Kiełczawa B (2002) [222]Rn and [226]Ra concentrations in mineralized groundwaters of Gorzanow (Klodzko Basin, Sudeten Mountains, SW Poland). J Radional Nucl Chem 253:1–19
16. Rihs S, Condomines M (2002) An improved method for Ra isotope ([224]Ra, [226]Ra, [228]Ra) measurements by gamma spectrometry in natural water. Chem Geol 182:409–421
17. Regulation of Polish Minister of Health (2002) Dziennik Ustaw of 5th December 2002, 02.203.1718
18. Skwarzec B (1997) Radiochemical method for the determination of polonium, radiolead, uranium and plutonium in environmental samples. Chem Anal 42:117–122
19. Sokołowski J (1993) Geothermal resources of Poland and possibility of their utilisation in environmental protection. Technika Poszukiwań Geologicznych Geosynoptyka i Geotermia 5/6:67–80
20. Sturchio NC, Banner JL, Binz CM, Heraty LB, Musgrove M (2001) Radium geochemistry of ground waters in Paleozoic carbonate aquifers, mid-continent, USA. Appl Geochem 16:109–122
21. Żak A, Jankowski J, Brzozowski R (1999) Natural radio-activity of underground water. Medycyna Pracy 1:51–60 (in Polish)