NUKLEONIKA 2010;55(2):181–185

ORIGINAL PAPER

A comparison of selected natural radionuclide concentrations in the thermal groundwater of Mszczonów and Cieplice with deep well water from Łódź city, Poland

Paweł Grabowski, Magdalena Długosz, Piotr Szajerski, Henryk Bem

Abstract. A simple procedure using α and γ spectrometry for the determination of natural radionuclides in two Polish geothermal water samples from Mszczonów and Cieplice, as well as in deep well groundwater from the city of Łódź, was described. The ^{222}Rn radionuclide was directly extracted from 10 cm^3 water samples to a scintillator solution placed in scintillation vials and determined by an liquid scintillation (LSC) technique with α/β separation. The activity concentrations of three radium nuclides: ^{228}Ra(^{228}Ac), ^{226}Ra(^{222}Rn), ^{224}Ra, as well as ^{210}Pb and ^{228}Th were measured by γ spectrometry with an HPGe detector after their preconcentration on hydrated MnO_2. ^{210}Po was deposited on a silver disc from dissolved MnO_2 precipitate after γ-spectrometry analysis and measured by α spectrometry. The concentration of ^{210}Pb in the examined samples was below the detection limit of the method (< 6.2 mBq/dm^3), whereas activity of its decay product ^{210}Po was in the range 0.35–1.4 mBq/dm^3. Higher activities of ^{228}Ra (46.7 mBq/dm^3), ^{226}Ra (67.8 mBq/dm^3) and ^{224}Ra (22.4 mBq/dm^3) were observed for the deep well water in Łódź in comparison to those for geothermal water samples from Cieplice and Mszczonów. However, concentrations of all the measured radionuclides were below World Health Organization (WHO) reference activities (0.1 Bq/dm^3 for ^{228}Ra and 1 Bq/dm^3 for ^{226}Ra and ^{226}Ra).

Key words: thermal groundwater • natural radionuclides • ICP-MS • co-precipitation

Introduction

It is expected that due to availability, and economic and environmental issues geothermal energy will play an important role in future worldwide energy budgets. However, because of the relatively high cost of deep drilling, the majority of the medium and low temperature geothermal water fields were in the last decade exploited for bathing, swimming pool heating and, to a lesser extent, for space heating [18]. On the other hand, an observed drinking water shortage or the necessity of arid land farming in many countries has resulted in increasing interest in using geothermal produced fluids for these purposes [13].

Now, in Poland there are several existing geothermal plants, and a few new geothermal installations are planned in the so-called Szczecin-Łódź geothermal district (Fig. 1).

Depending on factors of geothermal waters like their energetic potential (temperature of outcoming water) mineralization and chemical composition, they have been used almost exclusively in Poland for heating purposes, recreation and balneology [8, 14]. There are only three sites in Poland with sufficiently low mineralization thermal groundwater which can be, and in fact are, used as a source of drinking water. These places are Mszczonów, Cieplice and Słomniki. Thermal groundwaters from Mszczonów and Cieplice have a relatively low mineralization (~ 0.5 g/dm^3 and below 1 g/dm^3, respectively) in comparison with waters

P. Grabowski, M. Długosz, P. Szajerski, H. Bem✉
Institute of Applied Radiation Chemistry,
Technical University of Łódź,
116 Żeromskiego Str., 90-924 Łódź, Poland,
Tel.: +48 42 631 3195, Fax: +48 42 636 5008,
E-mail: henrybem@p.lodz.pl

Received: 14 October 2009
Accepted: 27 October 2009

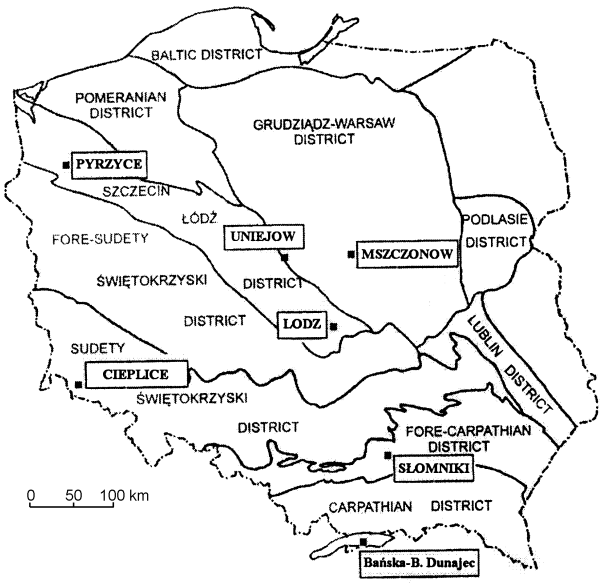

Fig. 1. Localization of the geothermal systems [14].

from other sites in Poland: 3 g/dm^3 in Bańska Biała or 5 g/dm^3 in Uniejow [15, 16]. The thermal water from the Mszczonów wellbore, with its temperature of 42.2°C, comes from 1700 m below ground level, with an average flow rate of 50 m^3/h. In Słomniki water is drawn from 300 m below the surface (flow rate 50–100 m^3/h), thus its temperature is only about 20°C [15, 19].

In the case of utilization of geothermal water for balneological or drinking water purposes, exact chemical studies including the determination of trace elements and radionuclide concentrations must be performed. Thermal groundwater used as drinking water additionally must fulfill very restrictive regulations of radionuclide content. According to the Polish state regulations [25], which are in accordance with EU Council Directive 98/83/EC [12] and WHO recommendations [32], the committed effective dose for members of the public from 1 year's consumption of drinking water ($\sim$ 730 dm^3) should not exceed 0.1 mSv [32]. Consequently, the WHO guidance level values for activity concentrations in drinking water were calculated taking into account their dose conversion factors (mSv/Bq·dm^{-3}) and corresponding activity concentrations, as shown in Table 1. The WHO protocol for radioactivity measurements in drinking water recommends, as the first step, determination of gross α and gross β activity [30, 32]. When gross α or gross β activity exceeds 0.5 and 1 Bq/dm^3, respectively, determination of individual radionuclides must be performed. Water must not be used as drinking water when the measured activity of an individual radionuclide is equal or higher than the guidance level values.

Table 1. WHO guidance levels of natural radionuclides in drinking water [32]

Radionuclide	Activity (Bq/dm^3)
^{238}U	10
^{226}Ra	1
^{222}Rn	100
^{210}Pb	0.1
^{210}Po	0.1
^{228}Ra	0.1
^{228}Th	1
^{224}Ra	1

As is evident from Table 1, the most dangerous natural radionuclides in drinking water are ^{210}Po, ^{210}Pb and ^{228}Ra, whose permissible activities in water must not exceed 0.1 Bq/dm^3. These three nuclides belong to a natural decay series and occur in very low concentrations in surface water. However, the activity of these and other natural radionuclides in underground waters depends on the activity of soil and rocks which surround groundwater resources. In most cases of groundwater samples ^{238}U concentrations are lower than its progeny radionuclides, what is caused by low transfer of this nuclide to water from bedrock [31].

Concentrations of radionuclides in natural water are usually rather low [9] and before their determination a preconcentration step must be applied. In the last decades, for the determination of low activities of uranium, thorium and other long-lived radionuclides, the inductively coupled plasma with mass spectrometry (ICP-MS) method was successfully applied [1–5, 20, 29]. However, because of the high equipment costs for this method, radiometric procedures are still widely used for radionuclide determination in water. An effective and simple method of radionuclide concentration from water samples is their co-precipitation with hydrated manganese dioxide [28]. This method was successfully applied for uranium, thorium and radium radionuclides as well as for ^{210}Po and ^{210}Pb. After preconcentration of radionuclides, they can be measured by γ or α spectrometry methods or also by LSC methods [11, 21, 22, 26, 27].

Although concentrations of radon, uranium and radium isotopes in Polish groundwaters and in bottled mineral waters have been well documented [6, 17, 22–24, 27], until now the activities of some radionuclides were reported for geothermal water from the Uniejow plant only [7].

The aim of these studies was the elaboration of a simple radiochemical procedure for determination of the activity of principal natural radionuclides occurring in thermal groundwater (Mszczonów, Cieplice). For comparison, the activities of the same radionuclides were determined in one of the several deep wells (Lower Cretaceous geological formation) connected to the Łódź city municipal water system with mineralization $\sim$ 0.2 g/dm^3. Additionally, natural radionuclides in Łódź tap water, which is a mixture of the deep well groundwater with surface water from Sulejów reservoir, were also measured.

Experimental

Materials and methods

Sampling

Thermal groundwater samples from Mszczonów were collected from Geotermia Mazowiecka S.A. and in the case of Cieplice directly from the public well situated in the centre of the city. Drinking water samples from Łódź were taken from two locations: deep well water from the Dąbrowa borehole and from the Łódź municipal water network in the centre of the city. All chemicals

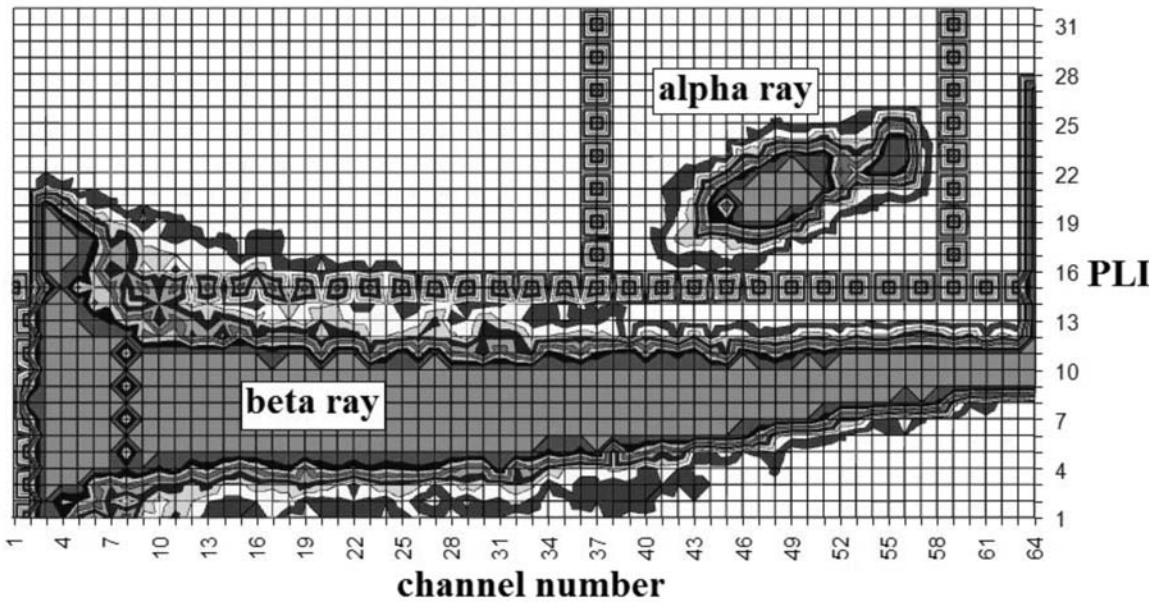

Fig. 2. Energy spectrum of ^{222}Rn as pulse shape discrimination (PSD) plot (2D) *x*-axes × 16 = channel number, *y*-axes × 32 = PLI (pulse length index).

were of analytical grade purity, used as provided. Standard reference material IAEA-327 was supplied by the International Atomic Energy Agency (IAEA).

Sample preparation

For the determination of γ-emitting radionuclides, a preconcentration step on hydrated manganese dioxide from 5 dm^3 of water samples was applied, according to procedure described elsewhere [7].

Radioactivity measurements

^{222}Rn activity was measured by means of a liquid scintillation technique, after its direct extraction in scintillation vials from 10 cm^3 of analysed water using 10 cm^3 of a Ultima Gold F scintillation cocktail. Samples counting were performed for 40,000 s using a BetaScout (PerkinElmer) liquid scintillation counter with α/β separation option, after at least 3 h necessary for establishing radioactive equilibrium of ^{222}Rn and its progeny (^{218}Po and ^{214}Po).

Optimal α/β separation conditions in order to eliminate the overlapping of the β pulses to the α region were chosen for this device after preliminary counting and setting the discrimination levels. Figure 2 shows that complete distinction of α from β pulses is possible for the Ultima Gold F scintillation solution for pulse length index (PLI) equal to 15. The observed background in the chosen α region was very low < 0.2 cpm.

The activity of γ-emitting radionuclides adsorbed on a MnO_2 precipitate was determined using a Canberra spectrometry system with an HPGe detector with a relative efficiency of 25%, according to the procedure described elsewhere [7].

Because of the relatively high detection limit for ^{226}Ra determination from its γ line of 185.6 keV (8.5 mBq/dm^3 according to the Curie criterion [10]) for the Mszczonów thermal groundwater ^{226}Ra was additionally determined by the liquid scintillation method after extraction of the ^{222}Rn from 0.5 dm^3 samples [6].

The samples of manganese dioxide precipitate after γ-spectroscopy measurements were digested with 3% (w/w) solution of hydrogen peroxide in 70 cm^3 of 1 M HCl. The obtained solutions were transferred to a teflon vial, and spontaneous deposition of ^{210}Po on a silver disc was performed for about 8 h at a temperature of about 80°C. ^{210}Po after its deposition on the silver plate was counted using the α-spectrometry system with a passivated implanted planar silicon (PIPS) semiconductor detector (Canberra 7401VR alpha spectrometer) for 2–3 days.

Quality assurance

The accuracy of the analytical procedure was determined in an independent experiment by checking the recovery of ^{210}Po, ^{210}Pb, ^{226}Ra, ^{228}Ra and ^{238}U radionuclides from 1 g of the mineralized standard reference material: SRM-IAEA 327 "Radionuclides in soil". The results are presented in Table 2.

Table 2. Chemical recoveries of the determined radionuclides

Nuclide	Reference value (mBq/g)	Measured value (mBq/g)	Recovery (%)
^{210}Po	49.84	49.33 ± 3.95	99.0
^{210}Pb	49.84	48.08 ± 4.49	96.5
^{226}Ra	33.89	34.04 ± 11.51	100.5
^{228}Ra(^{228}Ac)	38.7	35.21 ± 3.65	91.0
^{238}U(^{234}Th)	32.8	32.95 ± 5.07	100.5

Table 3. Concentration of the main natural radionuclides in water samples

Nuclides	γ line (keV)	$A_{Mszczonow}$ (mBq/dm^3)	$A_{Cieplice}$ (mBq/dm^3)	$A_{Lodz\ tap}$ (mBq/dm^3)	$A_{Lodz\ deep\ well}$ (mBq/dm^3)
^{238}U(^{234}Th)	63.3	< 4.7	≤ 4.7	< 4.7	< 4.7
^{226}Ra	185.6	14.8 ± 4.3	50.0 ± 5.3	< 8.5	67.8 ± 6.5
^{226}Ra(^{222}Rn)	LSC	18.0 ± 0.6	–	–	–
^{222}Rn	LSC	1930 ± 34	9100 ± 560	1093 ± 20	2860 ± 190
^{210}Pb	46.5	≤ 6.2	< 6.2	< 6.2	< 6.2
^{210}Po	α counting	1.4 ± 0.1	0.4 ± 0.1	< 0.2	≤ 0.2
^{228}Ra(^{228}Ac)	911.2	15.3 ± 1.4	10.4 ± 1.5	< 3.3	46.7 ± 2.8
^{228}Th	84.3	29.1 ± 5.9	37.9 ± 6.0	< 12.6	116.4 ± 9.4
^{224}Ra	241.0	≤ 5.7	< 5.7	< 5.7	22.7 ± 4.5

Results

The results of activity concentration of measured radionuclides in different water samples are presented in Table 3.

The measured activities, except for ^{222}Rn, were generally very low. It is interesting that the activity of ^{224}Ra, ^{226}Ra and ^{228}Th in the deep well water samples coming from the Lower Cretaceous geological formation were higher than those for thermal groundwater from Cieplice and Mszczonów, but remarkably lower than the corresponding activities for the previously determined thermal groundwater for Uniejow [7]. The slightly higher temperature of the Mszczonów (42°C) and Cieplice (30°C) thermal groundwater in comparison with deep well water (4°C) does not influence the mobility of these radionuclides from the adjacent geological formations, and the low concentrations of natural radionuclides in these waters are caused by a remarkable input of infiltrated surface water to their underground reservoirs.

The drinking tap water in the Łódź municipal network is a mixture of water coming from several deep wells and surface water pumped from the Sulejow water reservoir. Therefore, concentrations of natural radionuclides in this kind of water (additionally purified in the water supply plants) is extremely low (except for ^{222}Rn) below the detection limits.

Among the radionuclides in all the investigated water samples, the highest activities were observed for ^{222}Rn radionuclide. Depending on the origin of water, the ^{222}Rn activity varied between 1093 mBq/dm^3 and 9100 mBq/dm^3 for the Cieplice samples (Table 3). The last values are in close accord with the data for radon concentration in the groundwaters of the Sudety Mountains where elevated activities of this radionuclide were observed [24].

It is worth underlining that the concentrations of all measured radionuclides were below the recommended WHO values.

Conclusion

1. Co-precipitation of the natural radionuclides with hydrated manganese dioxide from a large volume of water samples can be used for the sample preparation before γ-spectrometry counting.
2. Activities of natural radionuclides from ^{238}U and ^{232}Th decay series in thermal groundwater from Mszczonów and Cieplice, and deep well water in Łódź are below the threshold limit values according to EU and WHO directives for drinking water.
3. The low levels of natural radionuclides in the thermal groundwater from Cieplice and Mszczonów, in contrast to the Uniejow region thermal groundwater, indicate a remarkable input of infiltration of surface waters with a low mineralization to their underground reservoirs.
4. From the radiological points of view both thermal groundwaters from Mszczonów and the Cieplice public well can be used as drinking water.

Acknowledgment. We are grateful to Geotermia Mazowiecka S.A. and Wodociągi Łódź for assistance during samples collection. We gratefully acknowledge the financial support by the European Union from European Public Funds and national budget within the framework of the Operational Integrate Programme of Regional Development and the Protection of the Environment and Water Management Fund in Łódź.

References

1. Becker JS (2002) Inorganic mass spectrometry of radionuclides (invited review). Spectrosc Eur 14;6:8–16
2. Becker JS (2003) Determination of long-lived radionuclides by ICP-MS and LA-ICP-MS (invited review). Spectrochim Acta B 58:1757–1784
3. Becker JS (2005) ICP-MS and LA-ICP-MS for isotope analysis of long-lived radionuclides (invited review). J Mass Spectrom 242:183–195
4. Becker JS (2010) Determination of long-lived radionuclides in nuclear, environmental and clinical samples by ICP-MS and LA-ICP-MS. In: Gross ML (ed) Chapter in: Encyclopedia of mass spectrometry. Vol. 5. Elemental and isotope ratio mass spectrometry. Elsevier, Boston
5. Becker JS, Sela H, Dobrowolska J, Zoriy M (2008) Recent applications of isotope ratio measurements y ICP-MS and LA-ICP-MS on biological samples and single particles. J Mass Spectrom 270:1–7
6. Bem H, Bem EM, Majchrzak I (1998) Comparison of two methods for ^{226}Ra determination in mineral water. Nukleonika 43;4:459–468
7. Bem H, Olszewski M, Kaczmarek A (2004) Concentration of selected natural radionuclides in the thermal groundwater of Uniejów. Nukleonika 49;1:1–5
8. Bujakowski W (1999) Geothermal projects in Poland. Technika Poszukiwań Geologicznych Geosynoptyka i Geotermia 4/5:132–141 (in Polish)
9. Chau ND, Michalec B (2008) Natural radioactivity in bottled natural spring, mineral and therapeutic waters in Poland. J Radioanal Nucl Chem 279;1:121–129

10. Currie LA (1999) Detection and quantification limits: origins and historical overview. Anal Chim Acta 391:127–134
11. Desideri D, Meli MA, Feduzi L, Roselli C, Rongoni A, Saetta D (2007) ^{238}U, ^{234}U, ^{226}Ra, ^{210}Po concentration of bottled mineral waters in Italy and their dose contribution. J Environ Radioact 94:86–97
12. European Union (1998) Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Off J Eur Commum L330, 5 December 1998
13. Gallup DL (2007) Treatment of geothermal waters for production of industrial, agricultural or drinking water. Geothermics 36:473–483
14. Górecki W (2006) Atlas of geothermal resources of mesozoic formations in the Polish lowlands. AGH University of Science and Technology, Kraków
15. Kępińska B (2003) Current geothermal activities and prospects in Poland – an overview. Geotherm 32:397–407
16. Kępińska B (2003) Current state and prospects of geothermal energy implementation in Poland. Appl Energy 74:43–51
17. Kozłowska B, Walencik A, Dorda J, Przylibski TA (2007) Uranium, radium and ^{40}K in bottled mineral waters from Outer Carpathians, Poland. Radiat Meas 42:1380–1386
18. Lund JW, Freeston DH (2001) World-wide direct uses of geothermal energy 2000. Geotherm 30:29–68
19. Nowak W, Stachel AA (2004) Heat-generating geothermal plant in Poland – present and planned state. Czysta Energia 34:50–55 (in Polish)
20. Pawlak Z, Rabiega G (2002) Comparison of inductively coupled plasma-mass spectrometry and radiochemical techniques for total uranium in environmental water samples. Environ Sci Technol 36:5395–5398
21. Pietrzak-Flis Z, Kamińska I, Chrzanowski E (2004) Uranium isotopes in waters and bottom sediments of rivers and lakes in Poland. Nukleonika 49;2:69–76
22. Pietrzak-Flis Z, Suplińska MM, Rosiak L (1997) The dietary intake of ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, ^{228}Th, and ^{226}Ra from food and drinking water by inhabitants of Wałbrzych region. J Radioanal Nucl Chem 222:189–193
23. 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
24. Przylibski TA, Mamont-Cieśla K, Kusyk M, Dorda J, Kozłowska B (2004) Radon concentrations in groundwaters of the Polish part of the Sudety Mountains (SW Poland). J Environ Radioact 75:193–209
25. Regulation of the Polish Minister of Health (2000) Dz U (Law Gazette) no 82, item 937 from 4 October 2000 (in Polish)
26. Rihs S, Condomines M (2002) An improved method for Ra isotope (^{226}Ra, ^{228}Ra, ^{224}Ra) measurements by gamma spectrometry in natural waters: application to CO rich thermal waters from the French Massif Central. Chem Geol 182:409–421
27. Skwarzec B, Strumińska DI, Boryło A (2001) The radionuclides ^{234}U, ^{238}U and ^{210}Po in drinking water in Gdańsk agglomeration (Poland). J Radioanal Nucl Chem 250;2:315–318
28. Skwarzec B, Strumińska DI, Boryło A, Falandysz J (2004) Intake of ^{210}Po, ^{234}U and ^{238}U radionuclides with beer in Poland. J Radioanal Nucl Chem 261;3:661–663
29. US EPA (1994) Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry. Method 200.8, Ohio
30. US EPA (2002) Radionuclides in drinking water: a small entity compliance guide. US Government Publishing Office, Washington
31. Vesterbacka P (2005) ^{238}U-series radionuclides in Finnish groundwater – based drinking water and effective doses. STUK, Helsinki
32. WHO (2006) Guidelines for drinking-water quality. Vol. 1. World Health Organization, Geneva