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Determination of a Supported Radon Activity Concentration in Bottled Mineral Waters★

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Results of determination of supported radon concentration in bottled mineral waters purchased at markets in Lublin city were presented. Procedure of determination consists in radon extraction from water using the scintillation cocktail (Permablend III in toluene) followed by measurement with the ultra low-level spectrometer Quantulus with the alpha/beta separation option. It was found that activity concentration of supported radon in water samples ranged from 8.70 to 388 mBq dm^{-3}. Annual effective dose calculated for maximum Rn activity value determined and total annual water consumption was equal only to about 0.2% of effective annual dose causing by atmospheric gaseous radon.

W pracy przedstawiono wyniki oznaczeń stężenia radonu (będącego w równowadze z ^{226}Ra) w butelkowanych, niegazowanych wodach mineralnych pochodzących z sieci handlowych Lublina. Procedura oznaczania polegała na bezpośredniej ekstrakcji radonu z wody przy użyciu koktajlu scyntylacyjnego (roztwór toluenowy scyntylatora Permablend III, Packard) i pomiarze aktywności fazy organicznej przy użyciu ultra niskotłowego spektrometru Quantulus. Stwierdzono, że aktywności właściwe radonu zawierają się w granicach 8,70–388 mBq dm^{-3}. Roczna skuteczna dawka, obliczona dla maksymalnego stężenia radonu i całkowitego rocznego spożycia wody, stanowi jedynie 0,2% dawki otrzymywanej od gazowego radonu.

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★ Dedicated to Professor Rajmund Dybczyński on the occasion of his 75th birthday.

Mineral waters can contain natural radionuclides as ^{40}K, and ^{238}U, ^{232}Th and their decay products, including radium isotopes. Presence of ^{226}Ra and ^{228}Ra involves appearance their daughters, radon isotopes – the most important ones – ^{222}Rn and ^{220}Rn, respectively. All these isotopes presence in water can reveal a certain hazard for human health, if their activity levels are high. From time to time a public opinion is perturbed to learn from the media about a risk connected with presence of radioactivity in drinking water [1].

Requirements for quality of drinking water and mineral waters are based on Drinking Water Directive 98/93/EC [2]. The Directive states that tritium radioactivity should not exceed a value 100 Bq dm^{-3} and a total indicative dose – 0.1 mSv $year^{-1}$. Simultaneously, from the indicative dose value a tritium, ^{40}K, radon and radon decay products are excluded [2].

Polish regulations being until recently in force (Regulation of Polish Ministry of Health) have specified a gross alpha and beta activity in water, respectively at a level of 0.1 and 1 Bq dm^{-3}. At present, this regulation is not applied. What is more, the Regulation of Ministry of Environment, being in force, concerned the tap and drinking waters, does not refer to radionuclides at all [3].

In spite of the fact that concentration of radionuclides in mineral and drinking water (including radium and radon) is not regulated by law, a knowledge about their levels appears to be important from a human health point of view. Study on radium and radon concentration in waters was developed relatively intensive. Usually it focuses on drinking waters [4–8], groundwaters [9–12, 17–20], and also mineral waters [13–15, 21]. Various approaches to determination methods are known including direct measurement of water sample mixed with mineral-oil scintillation cocktails [4, 5, 9–13, 17, 18, 20], extraction of radon with scintillation cocktail from larger volume of water [6, 7, 15] co-precipitation of radium [7, 15, 19, 21], or using radium selective filters [7].

Most frequently a liquid scintillation spectrometry was used for radioactivity measurements. Ultra low-level spectrometers with liquid scintillator ensure good measurement conditions for direct radon determination. The method, proposed by Schönhofer [6] is simple and precise thanks to high selectivity of radon extraction to organic phase by scintillation cocktail. In 80% of the papers cited in the References this method was used. There are two ways of the method realization. First one relays on mixing a water sample with the same volume of scintillation cocktail, the second – on radon extraction from a large volume of water.

In Poland it was found that ^{226}Ra activity concentration in groundwaters in the region of Sudeten Mountains [18–20] was about several dozen of mBq dm^{-3} [18, 19], however radon concentration was significantly higher, even up to 1600 Bq dm^{-3} with median equal to 125 Bq dm^{-3} [20]. These data relate to samples taken directly from sources, which contained high concentration of dissolved unsupported radon. Ther-

mal groundwaters coming from sources of central Poland revealed low concentrations of radium and radon, *i.e.* below 1 Bq dm^{-3}, and several Bq dm^{-3}, respectively [17]. It was found that bottled mineral waters revealed relatively small concentrations of ^{226}Ra, ranged from several mBq dm^{-3} to more than ten. Simultaneously, there were single samples with a little higher concentration as 800 mBq dm^{-3} [15], 600 mBq dm^{-3} [1], or 300 mBq dm^{-3} [21].

The aim of our study was determining of supported ^{222}Rn, *i.e.* radon in equilibrium with its parent, ^{226}Ra, in bottled mineral waters, available in markets of Lublin city. Taking into account half-life of ^{226}Ra (1600 y) and ^{222}Rn (3.83 d) one can calculate that practically stable radioactive equilibrium (secular) can be reached after about 25 days [22]. Therefore, a supported radon determination is equivalent with determination of radium itself.

EXPERIMENTAL

Twenty bottled, non-carbonated mineral waters of various origin, purchased in markets of Lublin city area was taken for investigation. After buying bottles with water were kept in darkness by about one month to ensure a radioactive equilibrium achievement and unsupported radon decay.

To determine supported radon concentration a standard method was used [4] in which accumulated radon was extracted to organic phase. As an extractant a scintillation cocktail composed of Permablend III (Packard) dissolved in a scintillator grade toluene (Fluka) of concentration 7 g dm^{-3} was used. Detailed procedure was as follows: 0.45 dm^3 of water sample was introduced to separatory funnel, 12 cm^3 of scintillation cocktail was added and shacked by 5 min (at laboratory temperature of 22 ± 2°C). Next, after phase separation, 10 cm^3 of organic phase was transferred to a low-diffusion (Teflon coated) scintillation vial (Packard). To improve alpha/beta separation 4 cm^3 of Ultima Gold AB cocktail (Packard) was added, according to information presented by Bem *et al.* [15]. Sample was placed in Quantulus spectrometer and measured after 3 h of equilibration. Measurement was performed within 180 min using alpha/beta option. Count rate of measured sample was calculated back to the time of start of measurement, taking into account half-life of radon. In the same way the count rate of standard solution was measured and a blank sample (this latter was measured within 300 min). Standard solution obtained from Central Mining Institute contained 5.6 ± 0.1 Bq dm^{-3} of ^{226}Ra [23]. Procedure for standard solution preparation and measurement was the same as mineral water samples. Attention was paid to maintain the same volume of solutions because the amounts of radon distributed between suitable phases (air, water and scintillation cocktail) depend on the phase volume. If all conditions of sample and standard handling are the same this correction can be avoided. For measurements the ultra low-level spectrometer Quantulus (Wallac, Perkin–Elmer) was used with alpha/beta separation option set at value of 100, according to data presented in papers [9, 29].

RESULTS AND DISCUSSION

The known data about bottled mineral waters studied include value of mineralization and location of springs from where the water was taken. Table 1 presents these data as shown by producers.

Table 1. Names of mineral waters, location of springs and total mineralization as stated by producers on bottle labels

Name	Place of water intake	Total mineralization, g dm^{-3}
Alvin	Stępin	0.457
Aqua Minerale	Michrów	0.570
Cisowianka	(Cisy) Drzewce	0.714
Deep	Koziegłowy	0.410
Eco Plus	(S-1a, Amita) Włoszakowice	0.445
Kazimierska	Kazimierz Dolny	0.589
Kropla Beskidu	Tylicz	0.364
Nałęczowianka	Nałęczów	0.624
Rogowiec	Rogowiec	0.294
Saguaro	(S-3) Koziegłowy	0.410
Silverado	(Janowiec) Oblasy	0.362
Słowianka	(S-3) Domnica	0.245
Staropolanka HM*	Polanica Zdrój	2.088
Staropolanka MM*	Polanica Zdrój	0.915
Świtezianka	Michrów	0.400
Ustronianka	Ustroń	0.509
Vita	Krynica Zdrój	0.755
Wielka Pieniawa	Polanica Zdrój	1.467
Źródło Tymbark	Tymbark	0.585
Żywiec Zdrój	(Pilsko) Jeleśnia	0.232

* HM – highly mineralized, MM – moderately mineralized.

According to Polish regulations, among mineral waters presented in Table 1 nine of them belongs to low mineralized (< 500 mg dm^{-3}), five to moderately mineralized (< 1500 mg dm^{-3}) and one to highly mineralized (> 1500 mg dm^{-3}) [24].

Figure 1 presents a spectrum of alpha and beta radiation emitted from the sample of standard water. As it is seen, on alpha spectrum three peaks are present, which correspond to ^{222}Rn (5.49 MeV), ^{218}Po (6.00 MeV) and ^{214}Po (7.69 MeV). In beta range a continuum is observed, in which beta emitting radon daughters (^{214}Bi and ^{210}Bi), ^{40}K and other natural radionuclides have its contribution.

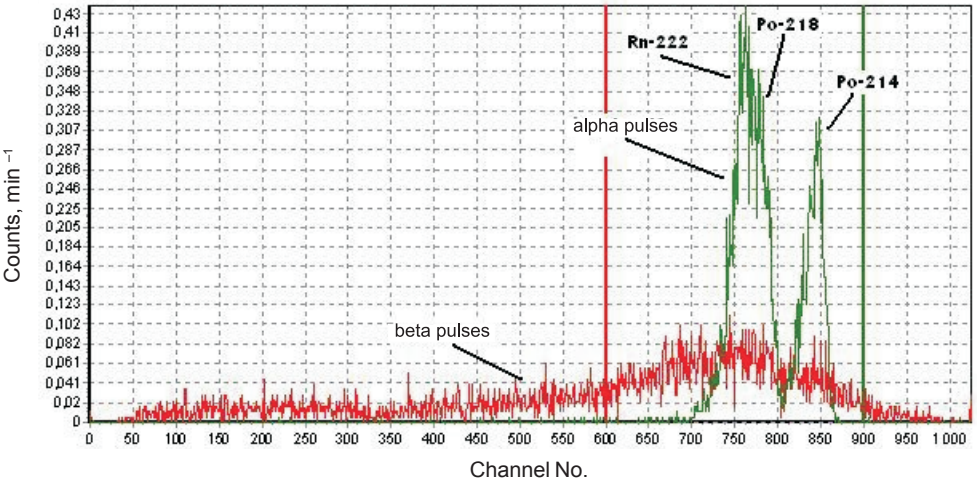

Figure 1. Spectrum of radon and its alpha emitting daughters extracted from the standard water sample containing 5.6 Bq dm^{-3} of ^{226}Ra

Measured count rate after background correction was directly calculated to activity concentration by comparison with the results of standard water measurement. Time between extraction and the measurement was also taken into account. Mean value of quenching parameter SQP was about 850. Minimum detectable amount was calculated according to Currie equation [25]. Results of measured activity concentration of supported radon in mineral waters are presented in Table 2.

Table 2. Results of supported radon activity concentration determined in mineral water samples [mBq dm^{-3}]

Name	Radon concentration ± 1σ mBq dm^{-3}
Alvin	52.8 ± 6.80
Aqua Minerale	72.1 ± 7.60
Cisowianka	52.8 ± 6.80
Deep	172 ± 11.1
Eco Plus	74.9 ± 7.70
Kazimierska	40.4 ± 6.40
Kropla Beskidu	31.3 ± 5.90
Nałęczowianka	17.9 ± 5.10
Rogowiec	8.70 ± 4.70
Saguaro	101 ± 8.80
Silverado	36.2 ± 6.10
Słowianka	35.0 ± 6.00
Staropolanka HM*	388 ± 16.6
Staropolanka MM*	354 ± 50.5
Świtezianka	68.1 ± 7.60
Tymbark	34.2 ± 6.10
Ustronianka	71.5 ± 7.70
Vita	64.9 ± 7.30
Wielka Pieniawa	260 ± 13.4
Żywiec Zdrój	59.6 ± 7.20

* HM – highly mineralized, MM – moderately mineralized.

Analyzing presented data one can state that in spite of rather high variability of activity the values of supported radon concentrations are very low. They are comparable with the results for other bottled mineral waters [1, 15, 21].

In Table 3 collective data are given. It was also observed a high correlation between the total mineralization value and the radon activity concentration, shown as Pearson's correlation coefficient.

Table 3. Collective data of the results

Number of samples	20
Arithmetic mean	99.4 [mBq dm^{-3}]
Standard deviation	108 [mBq dm^{-3}]
Geometric mean	64.3 [mBq dm^{-3}]
Median	62.3 [mBq dm^{-3}]
Minimum value	8.70 [mBq dm^{-3}]
Maximum value	388 [mBq dm^{-3}]
Blank	0.178 ± 0.0260 CPM
MDA	6.0 ± 2.6 [mBq dm^{-3}]
Pearson's correlation coefficient between mineralization and activity	0.81

Risk for human health connected with drinking mineral waters can be described by effective dose, what depends on water consumption by individual person. In 2007 annual consumption of bottled mineral waters by people in Poland was equal to about 80 dm^3 per person [26], whereas total drinking water consumption by adults is 500 dm^3 per year per person [27]. Considering the dose conversion factor of ^{222}Rn given by UNSCEAR, amounted for adults 10^{-8} Sv Bq^{-1}, and for ^{226}Ra 2.8×10^{-7} Sv Bq^{-1} [28] and maximum measured radon activity concentration (388 ± 16.6 mBq dm^{-3}), the effective dose connected with water consumption was calculated. The results are shown in Table 4.

Table 4. Annual effective dose [μSv] for adults from ingestion of water of maximum supported radon concentration measured, calculated for two levels of water consumption

Water consumption, dm^3	Activity intake, Bq	Effective dose of ^{222}Rn, μSv	Effective dose of ^{226}Ra, μSv
80	31 ± 1.3	0.30 ± 0.01	8.7 ± 0.37
500	194 ± 8.30	1.9 ± 0.083	54 ± 2.3

Presented data show that even all annually consumed water is the bottled mineral water, having maximum activity found by us; the combined annual effective dose will be as low as 0.2% of annual effective dose from gaseous radon present in the atmosphere (amounted 1.36 mSv [30]). Therefore, it can be concluded that presence of such negligible concentration of radium and radon has no effect on human health at all.

CONCLUSIONS

Twenty samples of bottled mineral waters purchased in markets of Lublin city were taken for analysis. Using extraction method the supported radon was transferred to organic phase by the scintillating cocktail. Measurements using Quantulus with alpha/beta option reveal that mean activity concentration of radon was 64.3 mBq dm^{-3} (range 8.70–388 mBq dm^{-3}). Calculated effective dose value is negligible in comparison with that obtained from atmospheric radon.

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