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National comparison of methods for determination of radon in water

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Abstract. The article describes three interlaboratory experiments concerning ^{222}Rn determination in water samples. The first two experiments were carried out with the use of artificial radon waters prepared by the Laboratory of Radiometric Expertise (LER), Institute of Nuclear Physics, Polish Academy of Sciences in Kraków in 2014 and 2018. The third experiment was performed using natural environment waters collected in the vicinity of the former uranium mine in Kowary in 2016. Most of the institutions performing radon in water measurements in Poland were gathered in the Polish Radon Centre Network, and they participated in the experiments. The goal of these exercises was to evaluate different measurement techniques used routinely in Polish laboratories and the laboratories' proficiency of radon in water measurements. In the experiment performed in 2018, the reference values of ^{222}Rn concentration in water were calculated based on the method developed at LER. The participants' results appeared to be worse for low radon concentration than for high radon concentrations. The conclusions drawn on that base indicated the weaknesses of the used methods and probably the sampling. The interlaboratory experiments, in term, can help to improve the participants' skills and reliability of their results.

Keywords: AlphaGUARD monitor • Interlaboratory comparison • LSC method • Radon in water • *Z*-score value

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Introduction

Radon is a noble gas and well soluble in water. Among all radon isotopes, only ^{222}Rn is radiologically important due to the longest half-life, i.e., $t_{1/2}$ = 3.8232 days (Decay Data Evaluation Project). The literature data indicate that water from springs, wells, and boreholes usually contains higher radon concentration than surface water. It is known that exposure to high radon concentration may lead to lung cancer [1]. Therefore, controlling the radon concentration in drinking water is important from radiological and dosimetric point of view. Radon-in-water analyses are very often used for radiological monitoring. The measurement techniques are rather simple; however, the sampling is very important for reliability of results because of radon's easy escape from a sample [2]. Quality and comparability of the measurements results can be checked and proved by the interlaboratory comparisons (ILC). Such experiment was organized by the Institute for Reference Materials and Measurements (JRC-IRMM/JRC-Geel) in 2018 [3].

The institutions gathered in the Polish Radon Centre took part in the intercalibration experiments for ^{222}Rn in water samples determination covering a wide range of concentrations. Participation in such experiments, and thus evaluation of the methods used, is very important for laboratories in order to have valid and reliable results as well as to be professionals for water routine measurements. Moreover, Poland is currently in the process of implementing the latest European Water Directive 2013/51/Euratom [4], which establishes the requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption. In particular, the directive specifies that the 2001 Euratom recommendation 928 relative to radon in drinking water only now applies to "water intended for human consumption", meaning all water used for domestic purposes.

Having this in mind, three intercomparison experiments were proposed. Two of them were carried out in 2014 and 2018 and were based on the "artificial water samples", i.e., on different radon concentrations in waters prepared in the laboratory. The third experiment was organized *in situ* in the Sudety Mountains (south-western part of Poland) where radon in natural water was measured.

This paper presents the overview of the organization of experiments and the evaluation of the results obtained by the participants.

Participants and methods

Experiments with "artificial waters" – samples prepared in laboratory conditions

Two experiments were performed with "artificial waters", i.e., different radon concentrations were prepared in waters in the laboratory conditions. The Laboratory of Radiometric Expertise, Institute of Nuclear Physics PAN (LER IFJ PAN) in Kraków, the organizer of the experiments, prepared the samples. The laboratories participating in both experiments are listed in Table 1.

The first experiment was performed in March 2014 in which six laboratories were participated. All laboratories used the liquid scintillation counting (LSC) method but with different instrumentations. Two of them also used the AlphaGUARD ionization chambers based on alpha spectrometry. One laboratory, LER IFJ PAN, has the accreditation of the method. The participants sent their reports containing the description of the methods used and the results with the uncertainties. The preparation of water samples with different radon concentrations consisted of pumping radon gas from the certified radon source (Pylon) to a known volume of water in a tight container, from which the participants collected samples according to their procedures. The reference values of two radon concentrations in water were determined as the respective averages of all participants' results after rejecting the doubtful result according to the Dixon's test. In this experiment, the reference values were equal to 69.5 Bq/L (concentration C_1) and 12.3 Bq/L (concentration C_2).

The second experiment with "artificial waters" was performed in March 2018 in which nine laboratories were participated. All laboratories once again examined different types of LSC and AlphaGUARD ionization chambers. As mentioned earlier, LER IFJ PAN provided two different radon activity concentrations in water samples. The preparation of water samples followed the method developed at LER IFJ PAN and presented by Mazur *et al.* [5]. The known activity of radon gas was first pumped from the source to a large radon chamber A (volume of 608 L). Then, radon gas was bubbled from the chamber through the known volume of distilled water (5 L), which was much smaller than the chamber volume. When equilibrium is reached between radon in water and air phases, the concentration of radon in water C_W can be expressed by the following formula [5]:

$$C \quad = k \cdot \frac{}{V_A + V_W \cdot k} \qquad (1)$$

where k is the Ostwald coefficient, R is total radon activity in the entire system, V_A is volume of the air phase (V_A = 614 L) and V_W is volume of the water phase (V_W = 4 L).

The values of C_W calculated in this way were the reference values for the second experiment and they were equal to 4.56 Bq/L (concentration C_3) and 24.35 Bq/L (concentration C_4). Concentration C_3 was chosen to be close to the level of low limit of detection (LLD) due to special requirements of participants. It is known that very low concentra-

Table 1. Participants of ILC experiments with water samples prepared in laboratory ("artificial waters") and technique used

No.	Participants	Technique
1.	University of Silesia in Katowice, Institute of Physics, Katowice	LSC, Wallac 1414; WinSpectral α/β
2.	Institute of Nuclear Physics PAN, Laboratory of Radiometric Expertise, Kraków	AlphaGUARD + AquaKIT LSC, Triathler Beta Scout
3.	Central Laboratory of Radiological Protection, Warszawa	LSC, TriCARB; AlphaGUARD + AquaKIT
4.	Central Mining Institute, Silesian Centre for Environmental Radioactivity, Katowice	LSC α/β Quantulus 1220
5.	AGH University of Science and Technology, Kraków	LSC Guardian Wallac 1414
6.	Wroclaw University of Science and Technology, Wrocław	LSC α/β Quantulus 1220
7.	Łódź University of Technology, Łódź	LSC (BetaScout + Rackbeta)
8.	National Centre for Nuclear Research, Otwock-Świerk	AlphaGUARD + AquaKIT; LSC, TriCARB
9.	The President Stanisław Wojciechowski State College, Kalisz	LSC, Beckman 3801

tions are always the hardest to evaluate. The LLD values reported by the participants ranged from 0.05 Bq/L to 5.0 Bq/L, depending on the technique used.

The participants applying LSC technique [6] collected the samples with disposable syringes from the tap located at the bottom of the water container and then injected them into the 20-mL glass vial filled with scintillation cocktails. Then the participants followed their own procedures. The measurements were made with their liquid scintillation counters, and the most common were α/β Quantulus and Guardian Wallac 1414. For all counter types, the spectra were collected for the samples using the calibrated window for alpha counting over a period of 10 days, with 1800 counting time. The backgrounds were determined by counting "blank" vials with 10 mL of liquid scintillation cocktails (Insta Fluor Plus) and 10 mL of distilled water. Two laboratories also used alpha spectrometry method with the radon monitor AlphaGUARD and the AquaKIT setup [7]. After collection, the samples were bubbled in the close systems, and thus radon escaped from water to air was registered by the ionization chamber in the AlphaGUARD monitor. All participants collected at least three samples for each radon concentration. The result was given as an average of results for a given radon concentration, and it was calculated for the moment of sample collection.

Experiment with natural waters – samples collected in the Sudety Mts.

The experiment was performed *in situ* in 2016. Natural water samples were taken directly from two sources: Kowary adit (concentration C_5) and source no. 26 from free intake in Kowary (concentration C_6). In this experiment, only four laboratories took part. The techniques used by the participants were same as in the experiments with "artificial waters".

Results and evaluation

Table 2 presents the results obtained by the participants involved in the experiments with "artificial waters" and natural waters. The participants' codes are known to each institution involved in the measurements. Each laboratory is known only by its own code.

The criterion for assessing the results of each participant was based on the analysis of the Z-score value calculated in accordance with the formula:

$$Z_{\text{score}} = \frac{(x_i - x_{\text{ref}})}{\sigma} \tag{2}$$

where x_i is participant's result, x_{ref} is reference concentration value for each exposure – it is the mean value from all participants' results (ILC 2014) or the value calculated according to formula (1) in case of ILC 2018, and σ is standard deviation of obtained results, after the rejection of outliers. The values of σ ranged from 0.8 (for concentration C_3) to 8.2 (for concentration C_1).

The absolute value of the Z-score parameter determines whether the result of a particular participant is acceptable:

$|Z\text{-score}| \le 2$ acceptable performance,
$2 < |Z\text{-score}| < 3$ warning signal, and
$|Z\text{-score}| \ge 3$ unacceptable performance.

The evaluation of the results obtained by the participants for "artificial waters" is presented in Table 3. This evaluation was not made for natural radon waters because of the small number of participants and thus too few results.

As mentioned in Table 3, based on the Z-score test, there is no reason for rejecting any result as unacceptable in case of concentrations C_1, C_2, and C_4.

In case of concentrations C_3, the results are much worse. Five results are warning signal and two ones are unacceptable. Concentration C_3 is the lowest of all (4.56 Bq·dm^{-3}), almost on the level of LLD pointed out by the participants using AquaKIT technique (1–5 Bq·dm^{-3}). In this situation, the crucial point is

Table 2. Results of radon concentration measurements obtained by the participants in evaluating the "artificial waters" and natural waters

Laboratory code	"Artificial waters"				Natural waters	
	2014		2018		2016	
	C_1	C_2	C_3	C_4	C_5	C_6
	[Bq/L]					
A1	67.5 ± 4.9	10.8 ± 2.2	4.0 ± 2.7	30.3 ± 11.6		
A2	71.1 ± 2.0	12.3 ± 0.4	4.0 ± 0.3	29.6 ± 0.7		
B1	63.1 ± 6.8	10.1 ± 2.0	5.6 ± 1.7	25.0 ± 3.1		451.0 ± 19.0
B2	47.3 ± 8.0	8.9 ± 1.5	4.1 ± 0.4	28.8 ± 1.8		446.0 ± 16.0
C	71.8 ± 2.4	13.1 ± 0.5	3.7 ± 0.4	27.7 ± 1.6	315.2 ± 1.3	512.6 ± 1.9
D	–	–	4.6 ± 1.6	27.0 ± 1.8	160.9 ± 3.7	403.4 ± 14.0
E	72.4 ± 2.5	14.0 ± 0.6	3.4 ± 0.2	27.6 ± 1.4	300.0 ± 1.0	486.0 ± 2.0
F	69.1 ± 5.2	13.5 ± 1.0	5.5 ± 1.2	20.2 ± 4.3		
G	66.3 ± 3.1	13.9 ± 0.6	3.1 ± 0.4	28.2 ± 3.0		
H1	–	–	3.2 ± 0.1	23.9 ± 4.2		
H2	–	–	3.5 ± 0.9	26.6 ± 4.0		
I	–	–	4.3 ± 1.2	29.7 ± 3.0		
Reference value	69.5	12.3	4.56	24.35	–	–

Table 3. Evaluation of the results of comparative measurements of radon concentration in "artificial waters"

Laboratory code	2014		2018	
	Z-score value (evaluation of result)			
	C_1	C_2	C_3	C_4
A1	0.53 (+)	0.78 (+)	–1.40 (+)	1.91 (+)
A2	0.43 (+)	0.01 (+)	–1.40 (+)	1.68 (+)
B1	1.71 (+)	1.15 (+)	2.60 (±)	0.21 (+)
B2	No data	1.77 (+)	–1.15 (+)	1.43 (+)
C	0.61 (+)	0.41 (+)	–2.15 (±)	1.07 (+)
D	No data	No data	0.10 (+)	0.85 (+)
E	0.77 (+)	0.88 (+)	–2.90 (±)	1.04 (+)
F	0.11 (+)	0.62 (+)	2.35 (±)	–1.33 (+)
G	0.85 (+)	0.82 (+)	–3.65 (–)	1.23 (+)
H1	No data	No data	–3.40 (–)	–0.14 (+)
H2	No data	No data	–2.65 (±)	0.72 (+)
I	No data	No data	–0.65 (+)	1.71 (+)

Evaluation of results: + result is acceptable, ± result is warning signal, and – result is unacceptable.

proper sampling. The possible explanation of bad results for concentration C_3 is radon escape from a sample during its collection. Nevertheless, it should be emphasized that very low concentrations evaluated with up to 100% uncertainty should still be acceptable.

In case of natural Sudety Mts. waters, no mean value was presented due to the lack of adequate number of results. The results obtained by the participants during the experiment were consistent in case of source no. 26. The measured concentrations ranged from 403 Bq/L to 512 Bq/L. For the samples from Kowary adit, laboratory D measured approximately two times lower concentration than other participants, i.e., 160 Bq/L whereas the rest of results amounted to 300–315 Bq/L. More field experiments are planned in 2020 since all participants learned about certain difficulties arising in these kinds of exercises.

Summary and conclusions

In this paper, the results of ILC measurements concerning radon concentration in water are presented. Nine radon laboratories from Poland took part in comparative measurements of radon concentration in different types of waters. The participants used different measurement methods, mainly LSC technique.

In over 80% of cases, participants obtained positive results for "artificial waters" for all measurement techniques. It is worth mentioning that the first ILCs (within the activities of Polish Radon Centre) were organized during 2001–2003 and the results were presented by Kozak *et al*. [8]. In 2001, about 50% of the participants obtained acceptable results, while in 2003 all laboratories practically measured radon concentrations comparable within uncertainty limit and close to the estimated reference values.

The main observation after analysis of the results of all experiments is that the reliable measurement of low radon concentration in water is not easy, and such concentrations are very often found in environmental waters. Thus, the most important advice to all laboratories from the presented experiments is the improvement of sampling. In case of LSC method, it is also worth checking and correcting whether the assumed values of radon extraction coefficient from water to scintillator are correct.

The main conclusions obtained from the presented experiments concern the choice of the best measurement method (1) and the tests and improvement of the set-up for preparation of different radon concentrations in water which were built by LER IFJ PAN (2):

1) The results show that with LSC instruments one can obtain low detection limits, good accuracy, and precision for determining radon.
2) This set-up was developed because the ILC experiments based on natural waters are generally more difficult to perform and the reference value is not exactly known, so the evaluation of participants' results cannot be done very precisely. The accurate knowledge of radon concentration in water samples is crucial in ILC experiments.

It can be stated that most of the laboratories improved their procedures during these years when ILC experiments were organized in Poland. This indicates the high value of such experiments. The advantages of participation in such experiments are not to be overestimated.

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References

1. World Health Organization. (2017). *Guidelines for drinking-water quality: fourth edition incorporating the first addendum*. Geneva: WHO.
2. Jobbágy, V., Altzitzoglou, T., Malo, P., Tanner, V., & Hult, M. (2017). A brief overview on radon measurements in drinking water. *J. Environ. Radioact. 173,* 18–24.
3. Jobbágy, V., & Hult, M. (2019). *Performance evaluation report of the REM 2018 radon-in-water proficiency test*. Geel: European Commission. (JRC116812).

4. European Union. (2013). Council Directive 2013/51/ Euratom of 22 October 2013 laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption. *Official Journal of the European Union*, 7.11.2013, L 296/12. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013L0051&rid=7.
5. Mazur, J., Guguła, S., Danyłec, K., Kozak, K., & Grządziel, D. (2017). Radon in water standards samples for intercomparison experiments. *Radiat. Meas.*, *107*, 80–86.
6. Suomela, J. (1993). Method for determination of Radon-222 in water by liquid scintillation counting. ISO Standard: ISO/TC147/SC3/WG6.
7. Bertin Instruments. (2017). *AlphaGUARD Professional Radon Monitor, User manual 01/2017*. France: Bertin Technologies.
8. Kozak, K., Kozłowska, B., Przylibski, T. A., Mazur, J., Adamczyk-Lorenc, A., Mamont-Cieśla, K., Stawarz, O., Dorda, J., Kłos, B., Janik, M., & Kochowska, E. (2012). Intercomparison measurements of Rn-222 concentration in water samples in Poland. *Radiat. Meas.*, *47*, 89–95.