REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 22 | 2017

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Katarina Björklöf[1], Reko Simola[2], Mirja Leivuori[1], Keijo Tervonen[1], Sari Lanteri[1] and Markku Ilmakunnas[1]

[1])Finnish Environment Institute, Laboratory centre, Helsinki, Finland

[2])Radiation and Nuclear Safety Authority, STUK, Helsinki, Finland

Proftest SYKE

FINAS
Finnish Accreditation Service
PT01 (EN ISO/IEC 17043)

Helsinki 2017
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 22 | 2017
Finnish Environment Institute SYKE
Proftest SYKE

Layout: Markku Ilmakunnas

The publication is also available in the Internet: www.syke.fi/publication | helda.helsinki.fi/syke

ISBN 978-952-11-4651-4 (pbk.)
ISBN 978-952-11-4852-1 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)

Author(s): Katarina Björklöf, Reko Simola, Mirja Leivuori, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas

Publisher and financier of publication: Finnish Environment Institute (SYKE)
P.O. Box 140, FI-00251 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2017

SYKE

ABSTRACT

Interlaboratory Proficiency Test 05/2017

In May 2017 Proftest SYKE carried out the proficiency test (PT) for analysis of radon in ground water (Rn 05/2017) in cooperation with the Finnish Radiation and Nuclear Safety Authority (STUK) for laboratories conducting radon-222 measurements in ground water. In total, 29 participants took part in the proficiency test.

Two ground water samples were tested, in which one contained high radon concentration (1000–5000 Bq/l) and the other contained lower concentration of radon (<1000 Bq/l). Eleven of the participating laboratories used the liquid scintillation method and 21 used equipment based on gamma spectrometry. The mean of the results measured by STUK with the liquid scintillation counting was used as the assigned value for radon concentration. The evaluation of the results was based on z scores. In total 78 % of the results were satisfactory when allowing for 17-25 % variation. This is slightly poorer performance than in the previous round in 2015.
A warm thank you to all the participants of this proficiency test.

Keywords: ground water analysis, drinking water analysis, measurement of radon, food and environmental laboratories, interlaboratory comparison, proficiency test

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 05/2017

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen (STUK) kanssa pätevyyskokeen pohjaveden radonmäärityksestä toukokuussa 2017. Näytteet olivat kaksi pohjavesinäytettä, joissa radonpitoisuus on toisessa korkea (1000–5000 Bq/l) ja toisessa matalampi (<1000 Bq/l). Pätevyyskokeeseen oli 29 osallistujaa. Kaksikymmentäyksi osallistujaa määritti radonin gamma-spektrometrisesti ja 11 nestetuikemenetelmällä. STUKin nestetuikemenetelmällä mitattujen tulosten keskiarvoa käytettiin radonpitoisuuden vertailuarvona. Tulokset arvioitiin z-arvon avulla. Hyväksyttäviä tuloksia oli 78 %, kun sallittiin tuloksien poiketa vertailuarvosta 17-25 %. Tulos on hieman huonompi kuin edellisellä kierroksella vuonna 2015.
Lämmin kiitos kaikille osallistujille!

Avainsanat: pohjavesianalyysi, talousvesianalyysi, radonmääritys, elintarvike- ja ympäristölaboratoriot, vertailumittaus, pätevyyskoe

SAMMANDRAG

Provningsjämförelse 05/2017

I maj 2017 genomförde Proftest SYKE i samarbete med Strålsäkerhetscentralen (STUK) en provningsjämförelse som omfattade radonmätning i grundvatten. Sammanlagt 29 laboratorier deltog i jämförelsen. Totalt 21 av deltagarna bestämde radon med gammaspektrometri och 11 av deltagarna använde vätskeskintillationsräknare. Två vattenprov testades varav det ena hade hög radonhalt (1000–5000 Bq/l) och det andra provet hade lägre halt av radon (<1000 Bq/l). Som referensvärde användes medelvärdet av resultaten mätt av STUK med vätskeskintillationsräknare. Totalt 78 % av resultaten var godkända när 17-25 % variation godkändes, vilken var lite färre än i den förra provningsjämförelsen 2015.

Ett varmt tack till alla deltagarna!

Nyckelord: vattenanalyser, grundvatten, radon analys, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of radon in ground water (Rn 05/2017) in cooperation with the Finnish Radiation and Nuclear Safety Authority (STUK). The Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). This proficiency test has been carried out under the accreditation scope of the Proftest SYKE.

2 Organizing of the proficiency test

2.1 Responsibilities

Organizer
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, FI-00430 Helsinki, Finland
Phone: +358 295 251 000
Email: proftest@environment.fi

The responsibilities in organizing the proficiency test

Katarina Björklöf	coordinator
Mirja Leivuori	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Co-operation partner and analytical expert: Reko Simola, Radiation and Nuclear Safety Authority (STUK) (T167, EN ISO/IEC 17025, www.finas.fi/sites/en)

2.2 Participants

In total 29 laboratories participated in this proficiency test (Appendix 1). In total, 12 participants were from Finland and 17 from other European countries.

2.3 Samples and delivery

In this proficiency test each participant received two ground water samples, one of which contained high radon concentration (1000–5000 Bq/l) and the other contained lower concentration of radon (<1000 Bq/l). The samples were collected on Monday 8 May 2017 and delivered on the following day. The samples arrived to the participants mainly within the two following days but some received the samples on the following week (Table 1). Participants were requested to report the temperature of an extra water sample that was included in the parcel (Table 1).

The samples were requested to be measured latest on 12 May 17, 2017 and the results to be calculated to the reference time 8 May 2017 at noon (Finnish time; GMT/UTC + 3 h). The preliminary results were delivered to the participants ProftestWEB and via email on 24 May 2017.

Table 1. The time point for samples arrival, approximate temperatures of the samples and preliminary success in the proficiency test.

Samples received date (time)	Temperature of samples (°C)	Participant code	Amount of accepted results / reported results
17.5.2017 (10:30)	15.0	16	0/2
15.5.2017 (09:30)	21.3	17	0/2
12.5.2017 (10:00)	15.0	9	2/2
12.5.2017 (10:00)	15.3	10	2/2
12.5.2017 (10:05)	15.2	29	2/2
12.5.2017 (14:08)	9.2	19	1/2
12.5.2017 (18:00)	9.8	22	2/2
11.5.2017 (14:20)	7.5	6	2/2
11.5.2017 (13:00)	11.7	7	2/2
11.5.2017 (13:00)	15.9	23	2/2
11.5.2017 (11:45)	15.0	20	0/1
11.5.2017 (11:00)	16.5	14	2/2
11.5.2017 (11:00)	10.0	2	2/2
10.5.2017 (08:30)	11.0	3	2/2
10.5.2017 (08:00)	14	4	2/2
10.5.2017 (08:50)	13.3	8	2/4
10.5.2017 (08:50)	7.0	15	2/2
10.5.2017 (09:00)	6.8	13	1/2
10.5.2017 (08:30)	10.8	24	0/2
10.5.2017 (10:30)	9.2	25	4/4
10.5.2017 (08:05)	9.5	26	0/2
10.5.2017 (08:00)	NR	21	2/2
10.5.2017 (09:00)	7.7	28	2/2
9.5.2017 (11:42)	5.0	1	4/4
NR	15.0	5	2/2
NR	NR	11	2/2
NR	NR	12	1/2
NR	NR	18	2/2
NR	NR	27	2/2

NR* = not reported

Table 2. Results of the homogeneity testing of the samples.

Sample	Unit	n	Mean	SD	s_{pt} (%)	0.5 × s_{pt}	Is SD < 0,5 x s_{pt}?
G1L	Bq/l	10	2732	16	232 (8.5 %)	116	Yes
G2R	Bq/l	10	399	2	34 (8.5 %)	17	Yes

n: the number of parallels, SD: the standard deviation, s_{pt}: the standard deviation for proficiency assessment.

2.4 Homogeneity and stability studies

The homogeneities of the samples were determined from ten samples measured by liquid scintillation samples at STUK. The samples were regarded to be homogenous with the set criteria (Table 2).

The stability of the samples was tested by storing two parallel samples for 48 h in room temperature (+22 ºC) and by storing four samples in the refrigerator for eight days. The results were compared to concentrations of the samples measured by scintillation count immediately after sampling on Monday the 8 May 2017 at STUK (Table 3). According to the stability testing criteria the standard deviation for the proficiency assessment (s_{pt}) included also variation caused by possible instabilities of the samples caused by storing (Table 3). The stability test criteria were met and the samples were considered stable for one week.

2.5 Feedback from the proficiency test

The comments from the participants mainly dealt with the delay of samples to international participants or erroneously reported results (Tables 4 and 5). The comments from the provider were a recommendation for sampling and a comment related to sending of the samples abroad (Table 6). All the feedback is valuable and is exploited when improving the proficiency scheme.

Table 3. Results of the stability testing of three parallel samples at +4 ° C and +22 ° C. The measurement uncertainties (U_i) of the results are indicated in brackets.

Sample	MEAN (U_i) Bq/l			Differences after keeping (%)		Is differences in mean ≤ 0.3 ×s_{pt}?	
	On day of delivery (n= 10)	Kept at room temperature for 2 days (n=2)	Kept in refrigerator (+4°C) for 8 days (n=4)	Kept at room temperature for 2 days (n=2)	Kept in refrigerator (+4°C) for 8 days (n=4)	Kept at room temperature for 2 days (n=2)	Kept in refrigerator (+4°C) for 8 days (n=4)
G1L	2732 (140)	2716 (137)	2695 (136)	16 (0.6 %)	37 (1.4 %)	Yes	Yes
G2L	399 (20.8)	407 (21)	406 (21)	-8 (2.0 %)	-7 (1.7 %)	Yes	Yes

n: the number of parallels, $s_{pt:}$ the standard deviation for proficiency assessment (see s_{pt} values in Table 2).

Table 4. Feedback from the participants on the technical execution.

Participant	Comments on technical execution	Action / Proftest
1	Making LSC sample was not possible without opening the bottle (loss of radon can happen). Bottle caps with septum could be a solution to transfer the sample to measuring LSC bottles using gas-tight syringe through the septum. We propose considering gamma-ray spectrometry (HPGe) as reference method, because direct measurement is possible, there is no need for any kind of sample preparation and decay can be followed from the spectra.	We will consider your proposals in the preparation of future PT rounds.
1, 14, 28	The participants reported some air bubbles in the samples.	The air bubbles are formed due to the temperature differences between the sample transport and storage and cannot totally be avoided. This may be a reason for lower results than the assigned value. The effect however will be marginal if the volumes of air bubbles are significantly smaller than the volume of water.
9	Sample reconditioned in a 1.2 l aluminum bottle (accredited method). Sample G1R n°5: 2270 Bq/l. Sample reconditioned in a 1.2l aluminum bottle (accredited method). Same result for bottle G2R n°1.	Both reported results were satisfactory.
10	Participant received the samples after 95 hours of sampling. The temperature of the samples was 15.3˚C.	Both reported results were satisfactory.
13, 15, 21	Sample (G1R or G2R) was broken during the tempering.	The new samples were sent to the participants. The delay in measurement may be the reason for lower results than the assigned value. The uncertainty of the results increase due to the half-life of radon. This may affect the results especially in lower concentrations.
16	Participants received samples within six days after the target delivery day.	The new samples had already been sent to the participant. The delay in measurement may be the reason for lower results than the assigned value. The uncertainty of the results increase due to the half-life of radon. This may affect the results especially in lower concentrations.
17	Participants received samples within five days after the target delivery day.	The delay in measurement may be the reason for lower results than the assigned value The uncertainty of the results increase due to the half-life of radon. This may affect the results especially in lower concentrations.
19, 22, 29	Participants received samples within one day after the target delivery day. The temperature of the samples was between 9.2 ˚C and 15.2 ˚C.	This may be the reason for lower results than the assigned value The uncertainty of the results increase due to the half-life of radon. This may affect the results especially in lower concentrations.
20	The participant needed help with calculating z score.	Help was provided.
24	The Sample arrival form is too difficult to forward.	Thank you for your feedback. We will do our best to improve the system.

Table 5. Feedback from the participants on the results.

Participant	Comments to the results	Action / Proftest
1	The decay correction maybe a problem for some participants and an interesting observation is if we use UTC – 3 hours instead of +3 hours the results are very compatible.	The correction calculation may be a source of error, but the calculation was guided for the Finnish time.
24	The participant reported the results for radon erroneously. The right results were: Sample G1R: 2220 Bq/l Sample G2R: 341 Bq/l	If the results had been reported correctly, the result for the sample G1R would have been questionable and the result for the sample G2R would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].

Table 6. Feedback from the organizer to the participants.

Participant	Comments
All	As some of the participants pointed out, a big source of error in this proficiency test is due to the fact that the sample has to be transferred to the measuring vial in the proficiency test. In a real situation this error may be decreased by taking the sample directly into the measuring vial. This is the standard procedure in some laboratories and is highly recommended.
All	We are sorry for all the extra trouble the delay of the samples caused international participants. In future proficiency test of radon we will improve the delivery process.
1, 7, 9, 10, 17, 19, 22, 23, 29	Some participants reported the expanded uncertainties with the precision of one or two decimals. Measurement uncertainties always are estimations. The values of the expanded measurement uncertainties (U_i) should be related to the accuracy of the reported results. Most commonly U_i is expressed as whole numbers without decimals.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. Results, which differed more than 5 times from the robust standard deviation or 50 % from the robust mean, were rejected before the statistical results handling.

More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

The assigned values used for evaluation of a laboratory performance were the mean radon concentrations from ten samples measured by scintillation counting at STUK and the expanded measurement uncertainties reported by STUK were used as the expanded measurement uncertainties of the assigned values (U_{pt}). U_{pt}:s were 5 % (k=2) (Table 7).

There seems to be a systematic error between the results of the expert laboratory and the results of the participants (Appendix 4). This could be due to the participants' calculations to the reference time or due to the possible changes during the transportation. However, the sample

Table 7. The assigned values and their uncertainties.

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value
$^{222}Rn_{lsc}$	G1L	Bq/l	2732	139	5.1	Expert laboratory STUK
	G2L	Bq/l	399	21	5.2	Expert laboratory STUK
$^{222}Rn_{RADEK}$	G1R	Bq/l	2732	139	5.1	Expert laboratory STUK
	G2R	Bq/l	399	21	5.2	Expert laboratory STUK

U_{pt}: the expanded uncertainty of the assigned value.

stability was followed until the last package arrived to the participants and no clear evidence of any change was noticed (Table 1). If needed participant may recalculate z scores using the mean values as assigned values [4].

The reliability of assigned values was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [3]. This criterion was fulfilled and the assigned values were considered reliable (Table 7).

After reporting the preliminary results no changes have been done for the assigned values.

2.6.3 Standard deviation for proficiency assessment and z score

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for the proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set to 17–25 % depending on the measurement.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation of the reported results (s_{rob}) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was fulfilled in all cases. **After reporting of the preliminary results no changes have been done for the standard deviations for proficiency assessment.**

3 Results and conclusions

3.1 Results

The terms used in the results tables are shown in Appendix 2. The results and the performance of each participant are presented in Appendix 3 and the summary of the results in Table 8. The reported results with their expanded uncertainties (*k*=2) are presented in Appendix 4. The summary of the z scores is shown in Appendix 5 and z scores in the ascending order in Appendix 6.

Table 8. The summary of the results in the proficiency test Rn 05/2017.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
$^{222}Rn_{lsc}$	G1L	Bq/l	2732	2526	2447	2530	237	9.7	17	11	82
	G2L	Bq/l	399	363	363	364	36	10.0	17	11	82
$^{222}Rn_{RADEK}$	G1R	Bq/l	2732	2429	2413	2344	201	8.3	17	20	70
	G2R	Bq/l	399	348	356	343	43	12.1	25	21	81

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

The robust standard deviations of the results varied from 8.3 to 12.1 % (Table 8). This is the same level as in the previous proficiency test in Rn 05/2015 [5], where the deviations varied from 6.5 % to 11.2 %.

3.2 Analytical methods

Eleven of the participating laboratories used the liquid scintillation method and 21 used equipment based on gamma spectrometry. The participants were allowed to use different analytical methods for the measurements of the 1 liter sample intended for RADEK- or other gamma spectrometry. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. The statistically significant differences between the results are shown in Appendix 7. The used analytical methods and results of the participants grouped by methods are shown in Appendix 8.

The results measured by RADEK-technology were significantly lower than the results measured with other gamma spectrometry (Appendix 7). Lower RADEK results have been observed compared to liquid scintillation counts and other gamma spectrometry-based methods in all the proficiency tests performed by Proftest SYKE since 2006. The reason for this observation may be due to many reasons. The RADEK measurement is highly dependent on temperature and moisture. Also a delay in starting the RADEK measurement after transferring the sample causes smaller results. In addition, the energy calibration affects the results.

3.3 Uncertainties of the results

The reported results with their expanded uncertainties (k=2) are presented graphically in Appendix 4 and examples of uncertainties reported by the participants in Appendix 9.

All participant except one reported the expanded uncertainties with their results (Appendix 4). The range of the reported uncertainties varied between the measurements and the sample types from 3.5-33 % (Table 9). Some participants reported the expanded uncertainties with the precision of one or two decimals. Measurement uncertainties always are estimations. The values of the expanded uncertainties (U_i) should be related to the accuracy of the reported results. Most commonly U_i is expressed as whole numbers without decimals.

Uncertainty for radon measurements is composed of sample taking, transfer of the sample to measuring vessel, accuracy of calibration of the equipment and correctness of counting of the uncertainty.

Table 9. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Analyte	Sample	The range of the reported expanded measurement uncertainties, %
$^{222}Rn_{lsc}$	G1L	3.5-20
	G2L	5.1-20
$^{222}Rn_{RADEK}$	G1R	6-33
	G2R	6.5-33

Several approaches were used for estimating of measurement uncertainty (Appendix 9). For liquid scintillation counts, most commonly data from method validation was used. For RADEK or other gamma spectrometry, mostly other procedures than given were used. One participant used MUkit measurement uncertainty software for the estimation of its uncertainties [6]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates (Appendix 8).

4 Evaluation of the results

The evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for performance assessment (Appendix 2). The z scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 78 % of the results were satisfactory when total deviation of 17–25 % from the assigned value was accepted (Appendix 5). Altogether 69 % of the participants used accredited analytical methods at least for a part of the measurements and 84 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 10. In the previous similar proficiency test Rn 05/2015 [5], the performance was satisfactory for 88 % of the all participants.

Table 10. Summary of the performance evaluation in the proficiency test Rn 05/2017.

Measurand	Sample	2 × s_{pt}, %	Satisfactory results, %	Assessment
$^{222}Rn_{lsc}$	G1L	17	82	Satisfactory performance. In the previous proficiency test Rn 05/2015 the performance was satisfactory for 79 % of the results when standard deviation for proficiency assessment was 10 % [5].
	G2L	17	82	Satisfactory performance. In the previous proficiency test Rn 05/2015 the performance was satisfactory for 100 % of the results when standard deviation for proficiency assessment was 15 % [5].
$^{222}Rn_{RADEK}$	G1R	17	70	Satisfactory performance. In the previous proficiency test Rn 05/2015 the performance was satisfactory for 83 % of the results when standard deviation for proficiency assessment was 20 % [5].
	G2R	25	81	Satisfactory performance. In the previous proficiency test Rn 05/2015 the performance was satisfactory for 91 % of the results [5].

5 Summary

Proftest SYKE in co-operation with the Radiation and Nuclear Safety Authority (STUK) carried out the proficiency test (PT) for the measurement of radon in groundwater in May 2017. In total 29 participants took part in this PT. Eleven of the participating laboratories used the liquid scintillation method and 21 used equipment based on gamma spectrometry.

In this proficiency test two ground water samples were tested, in which one contained high radon concentration (1000–5000 Bq/l) and the other contained lower concentration of radon (<1000 Bq/l). The mean of the results measured by STUK with the liquid scintillation counting was used as the assigned value for radon concentrations. The evaluation of the results was based on z scores. In total 76 % of the results was satisfactory using gamma spectrometry and deviations of 17 % and 25 % from the assigned value was accepted. A total of 82 % of the liquid scintillation counting results were accepted when deviation of 17 % from the assigned value was accepted.

6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmäärityksestä toukokuussa 2017. Pätevyyskokeessa oli 29 osallistujaa, joista 21 määritti radonin gammaspektrometrialla ja 11 nestetuikemenetelmällä.

Pätevyyskoetta varten osallistujille lähetetään kaksi pohjavesinäytettä, joissa radonpitoisuus on toisessa korkea (1000–5000 Bq/l) ja toisessa matalampi (<1000 Bq/l). STUKin nestetuikemenetelmällä mitattujen tulosten keskiarvoa käytettiin radonpitoisuuden vertailuarvona. Tulokset arvioitiin z-arvon avulla. Gammaspektrometrialla mitatuista tuloksista hyväksyttäviä tuloksia oli 75 %, kun radonpitoisuuden sallittiin poiketa vertailuarvosta 17 % ja 25 %. Nestetuikemenetelmällä 82 % tuloksista oli hyväksyttäviä, kun sallittiin 17 % poikkeama vertailuarvosta.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Austria	Seidersdorf Labor GmbH
Belgium	Joint Research Centre (JRC), JRC-Geel, Unit G.2. Standards for Nuclear Safety, Security and Safeguards
	SCK-CEN , Low-level Radioactivity Measurement (LRM)
Finland	BotniaLab Oy Vaasa
	Eurofins Environment Testing Finland Oy, Lahti
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Metropolilab Oy
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	ScanLab Oy
	SeiLab Oy
	VITA-Terveyspalvelut Oy, VITA Laboratorio
	ÅMHM laboratoriet, Jomala, Åland
France	Eichrom Laboratoires, Bruz
	Eurofins Expertises Environnementales, Maxeville
	Eurofins Hydrologie
	ISRN, Le Vesinet
	Laboratoire CARSO LSEHL
	PearL, Limones Cedex
	Responsable technique, ALGADE, Laboratoire LED/UE
Hungary	National Public Health Institute, Public Health Directorate, Division of Environmental and Residential Radiohygiene
Norway	The Norwegian Radiation Protection Authority
Portugal	Instituto Superior Técnico Portugal, Laboratório de Protecao e Seguranca Radiológica
Sweden	Eurofins Environment testing Sweden AB, Lidköping
United Kingdom	Scottish Water
	LGC Ltd, Middlesex
	United Utilities Water company

APPENDIX 2: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The reference value
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:

x^* = median of x_i ($i = 1, 2, \ldots, p$)

s^* = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i ($i = 1, 2 \ldots p$):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 3: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{lsc}$	Bq/l	G1L		-1.12	2732	17	2473	2530	2526	126	5.0	9
	Bq/l	G2L		-1.33	399	17	354	364	363	32	8.9	11
$^{222}Rn_{RADEK}$	Bq/l	G1R		-1.00	2732	17	2500	2344	2429	213	8.8	17
	Bq/l	G2R		-0.56	399	25	371	343	348	32	9.1	16

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{lsc}$	Bq/l	G1L		-0.87	2732	17	2531	2530	2526	126	5.0	9
	Bq/l	G2L		-0.12	399	17	395	364	363	32	8.9	11

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{RADEK}$	Bq/l	G1R		-1.99	2732	17	2270	2344	2429	213	8.8	17
	Bq/l	G2R		-1.02	399	25	348	343	348	32	9.1	16

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{lsc}$	Bq/l	G1L		-0.05	2732	17	2720	2530	2526	126	5.0	9
	Bq/l	G2L		0.47	399	17	415	364	363	32	8.9	11

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{RADEK}$	Bq/l	G1R		0.92	2732	17	2945	2344	2429	213	8.8	17
	Bq/l	G2R		1.42	399	25	470	343	348	32	9.1	16

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{RADEK}$	Bq/l	G1R		-0.22	2732	17	2680	2344	2429	213	8.8	17
	Bq/l	G2R		-0.10	399	25	394	343	348	32	9.1	16

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{lsc}$	Bq/l	G1L		-1.84	2732	17	2304	2530	2526	126	5.0	9
	Bq/l	G2L		-1.69	399	17	342	364	363	32	8.9	11

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{lsc}$	Bq/l	G1L		-0.18	2732	17	2690	2530	2526	126	5.0	9
	Bq/l	G2L		-0.35	399	17	387	364	363	32	8.9	11
$^{222}Rn_{RADEK}$	Bq/l	G1R		-3.22	2732	17	1985	2344	2429	213	8.8	17
	Bq/l	G2R		-2.07	399	25	296	343	348	32	9.1	16

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-1.30	2732	17	2430	2344	2429	213	8.8	17
	Bq/l	G2R		-0.62	399	25	368	343	348	32	9.1	16

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn lsc	Bq/l	G1L		-1.01	2732	17	2497	2530	2526	126	5.0	9
	Bq/l	G2L		-1.03	399	17	364	364	363	32	8.9	11

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-1.67	2732	17	2344	2344	2429	213	8.8	17
	Bq/l	G2R		-1.78	399	25	310	343	348	32	9.1	16

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-2.29	2732	17	2200	2344	2429	213	8.8	17
	Bq/l	G2R		-1.78	399	25	310	343	348	32	9.1	16

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-2.08	2732	17	2250	2344	2429	213	8.8	17
	Bq/l	G2R		-1.39	399	25	330	343	348	32	9.1	16

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-1.43	2732	17	2400	2344	2429	213	8.8	17
	Bq/l	G2R		-0.78	399	25	360	343	348	32	9.1	16

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-0.91	2732	17	2520	2344	2429	213	8.8	17
	Bq/l	G2R		-1.28	399	25	335	343	348	32	9.1	16

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn lsc	Bq/l	G1L		-3.53	2732	17	1913	2530	2526	126	5.0	9
	Bq/l	G2L		-2.54	399	17	313	364	363	32	8.9	11

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn lsc	Bq/l	G1L		-2.81	2732	17	2080	2530	2526	126	5.0	9
	Bq/l	G2L		-2.54	399	17	313	364	363	32	8.9	11

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-1.99	2732	17	2269	2344	2429	213	8.8	17
	Bq/l	G2R		-1.42	399	25	328	343	348	32	9.1	16

Participant 19

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-2.36	2732	17	2184	2344	2429	213	8.8	17
	Bq/l	G2R		1.40	399	25	469	343	348	32	9.1	16

Participant 20

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G2R		-4.72	399	25	164	343	348	32	9.1	16

Participant 21

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-1.69	2732	17	2340	2344	2429	213	8.8	17
	Bq/l	G2R		-1.34	399	25	332	343	348	32	9.1	16

Participant 22

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		0.15	2732	17	2768	2344	2429	213	8.8	17
	Bq/l	G2R		0.23	399	25	410	343	348	32	9.1	16

Participant 23

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-0.61	2732	17	2590	2344	2429	213	8.8	17
	Bq/l	G2R		-0.32	399	25	383	343	348	32	9.1	16

Participant 24

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-10.30	2732	17	341	2344	2429	213	8.8	17
	Bq/l	G2R		36.51	399	25	2220	343	348	32	9.1	16

Participant 25

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn lsc	Bq/l	G1L		-1.30	2732	17	2430	2530	2526	126	5.0	9
	Bq/l	G2L		-1.15	399	17	360	364	363	32	8.9	11
^{222}Rn RADEK	Bq/l	G1R		-1.82	2732	17	2310	2344	2429	213	8.8	17
	Bq/l	G2R		-0.98	399	25	350	343	348	32	9.1	16

Participant 26

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-4.57	2732	17	1670	2344	2429	213	8.8	17
	Bq/l	G2R		-2.97	399	25	251	343	348	32	9.1	16

Participant 27

Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn RADEK	Bq/l	G1R		-1.86	2732	17	2300	2344	2429	213	8.8	17
	Bq/l	G2R		-1.22	399	25	338	343	348	32	9.1	16

Participant 28

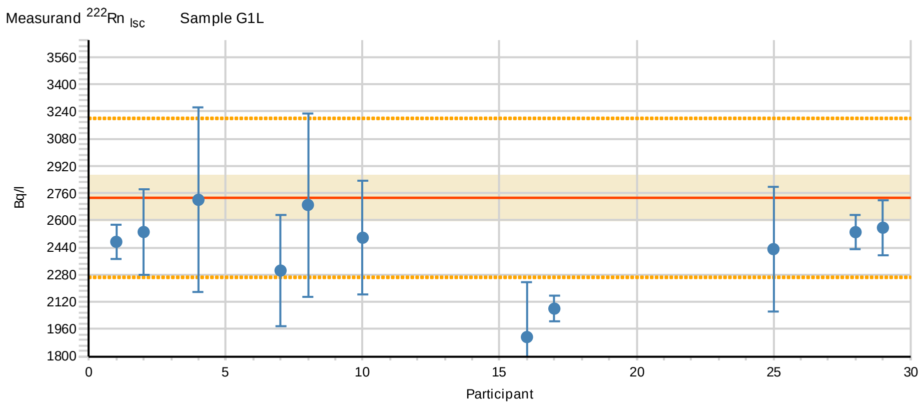
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
^{222}Rn lsc	Bq/l	G1L		-0.87	2732	17	2530	2530	2526	126	5.0	9
	Bq/l	G2L		-0.44	399	17	384	364	363	32	8.9	11

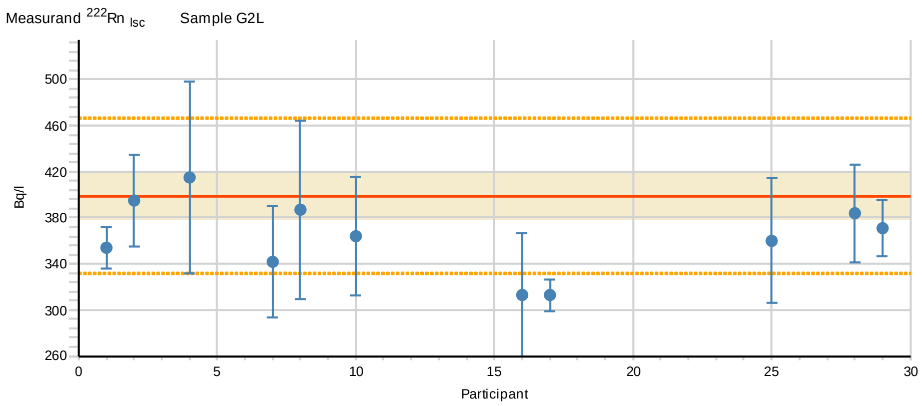
Participant 29													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	SD	SD%	n (stat)
$^{222}Rn_{lsc}$	Bq/l	G1L		-0.76	2732	17	2556	2530	2526	126	5.0	9
	Bq/l	G2L		-0.83	399	17	371	364	363	32	8.9	11

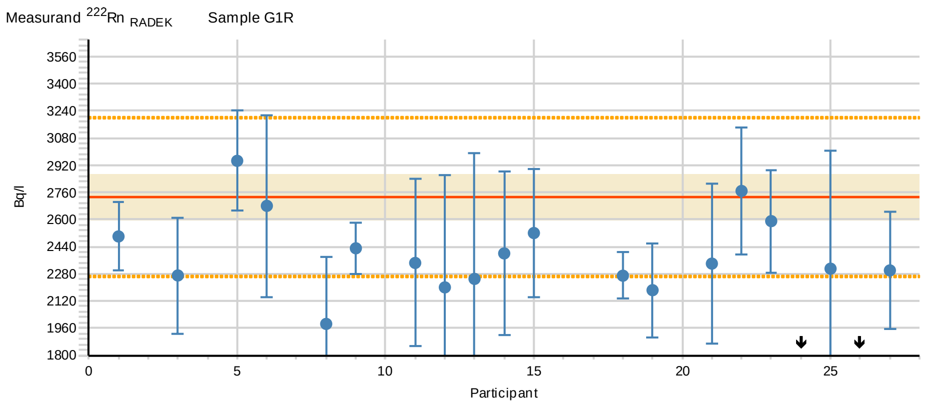
APPENDIX 4: Results of participants and their uncertainties

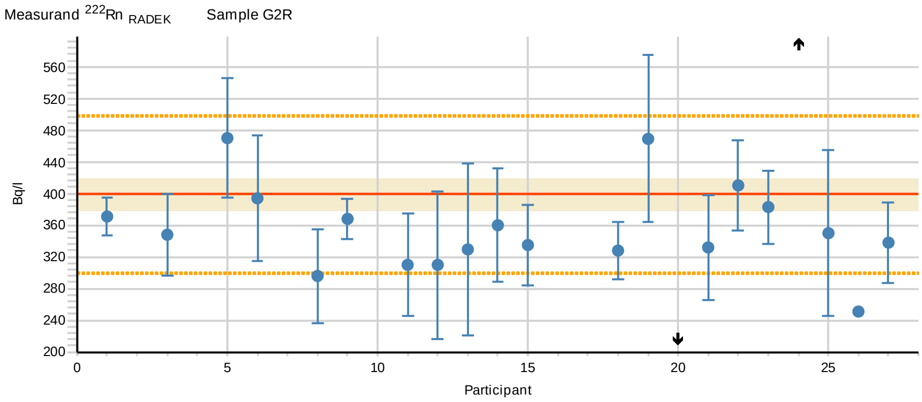
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.








Measurand $^{222}Rn_{RADEK}$ Sample G2R
Bq/l
560
520
480
440
400
360
320
280
240
200
0
5
10
15
20
25
Participant

APPENDIX 5: Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
$^{222}Rn_{lsc}$	G1L	*S*	*S*	.	S	.	.	S	S	.	S	.	.	.	.	.	u	*q*	.	.	.	.	.	.	82
	G2L	*S*	*S*	.	S	.	.	S	S	.	S	.	.	.	.	.	q	*q*	.	.	.	.	.	.	82
$^{222}Rn_{RADEK}$	G1R	*S*	.	*S*	.	S	S	.	*u*	S	.	S	q	*q*	S	*S*	.	.	S	q	.	S	*S*	S	70
	G2R	*S*	.	*S*	.	S	S	.	*q*	S	.	S	S	*S*	S	*S*	.	.	S	S	u	S	*S*	S	81
%		100	100	100	100	100	100	100	50	100	100	100	50	50	100	100	0	0	100	50	0	100	100	100	
accredited					2	2	2	2	2	2	2	2	2		2		2		2	2	1	2		2	

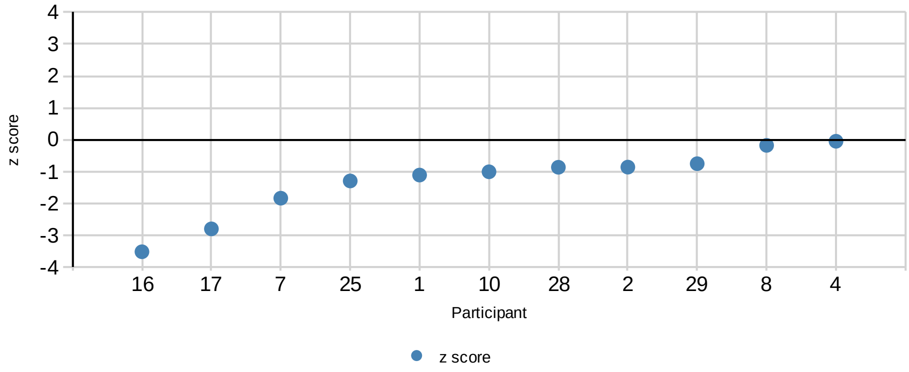
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
$^{222}Rn_{lsc}$	G1L	.	S	.	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	82
	G2L	.	S	.	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	82
$^{222}Rn_{RADEK}$	G1R	u	S	*u*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	70
	G2R	U	S	*q*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	81
%		0	100	0	100	100	100																		
accredited		2	4		2	2	2																		

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

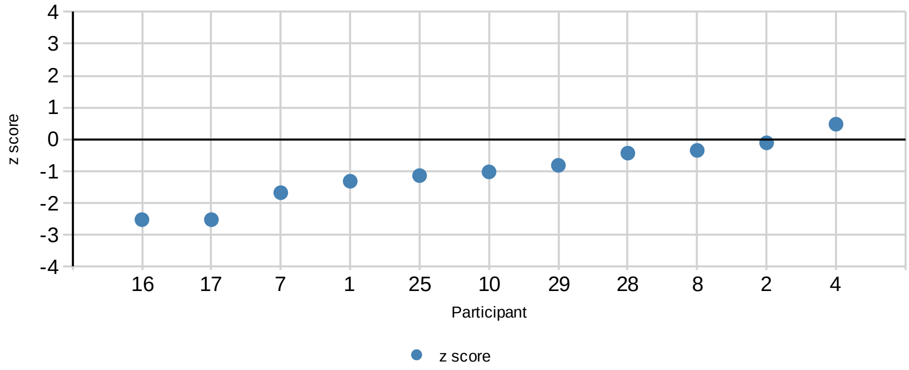
Totally satisfactory, % in all: 78 % in accredited: 84 % in non-accredited: 65

APPENDIX 6: z scores in ascending order

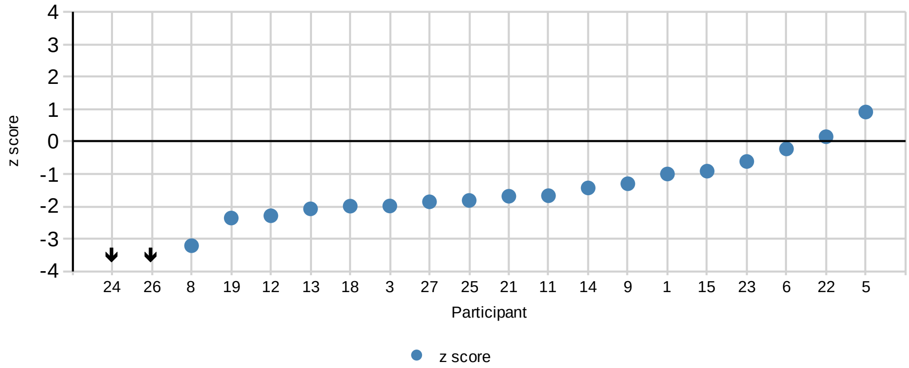
Measurand $^{222}Rn_{Isc}$ Sample G1L



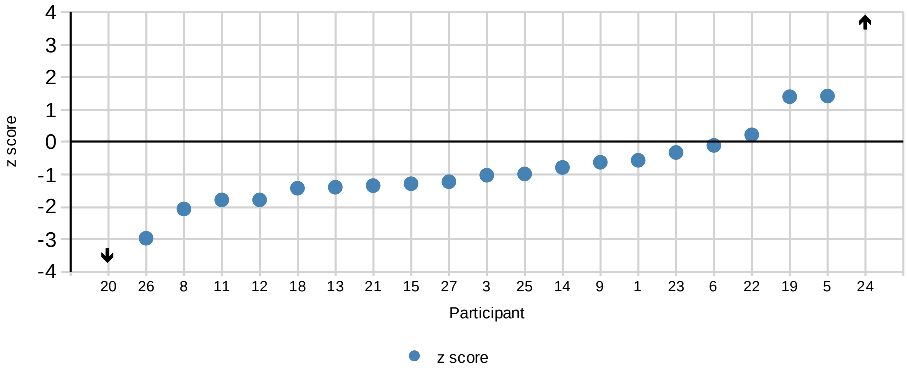
Measurand $^{222}Rn_{Isc}$ Sample G2L



Measurand $^{222}Rn_{RADEK}$ Sample G1R

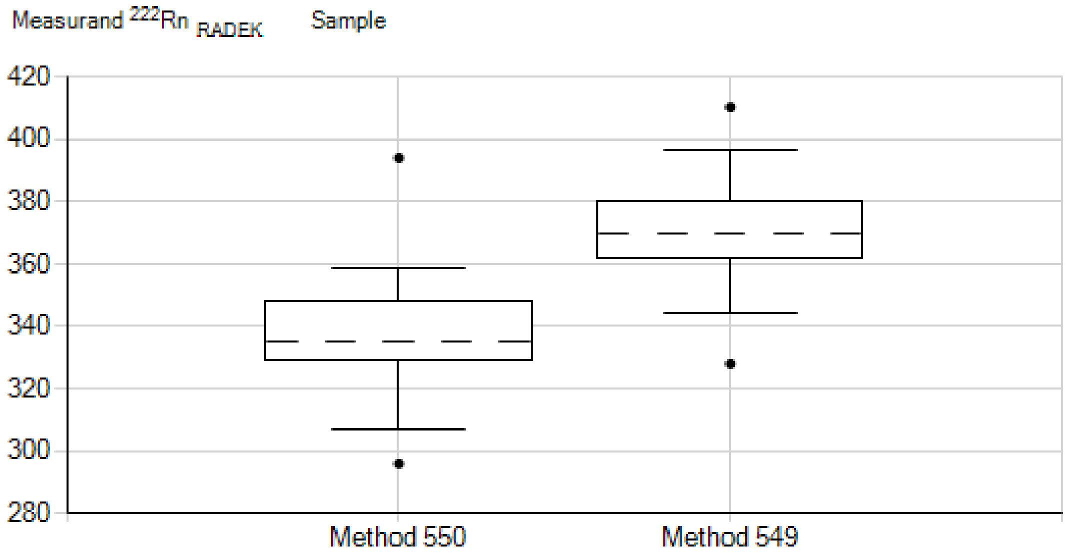


Measurand $^{222}Rn_{RADEK}$ Sample G2R



APPENDIX 7: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.

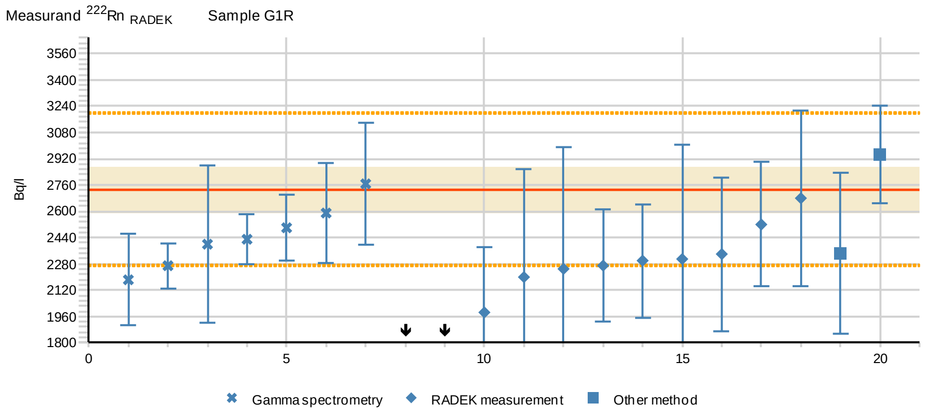


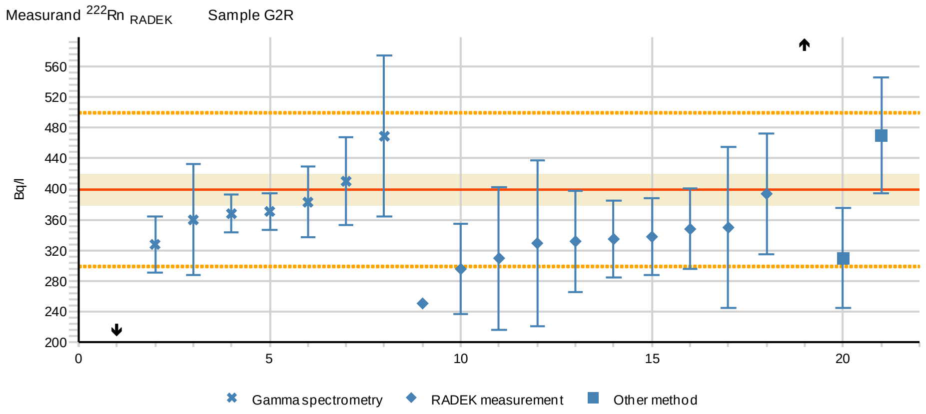
Method	n	Mean (Bq/l)	SD (Bq/l)
Method 550: Radek measurement	9	337	27
Method 549: Gamma spectrometry	6	370	27
Method 99: Other method	1	310	0

n = number of results; SD = standard deviation

APPENDIX 8: Results grouped according to the methods

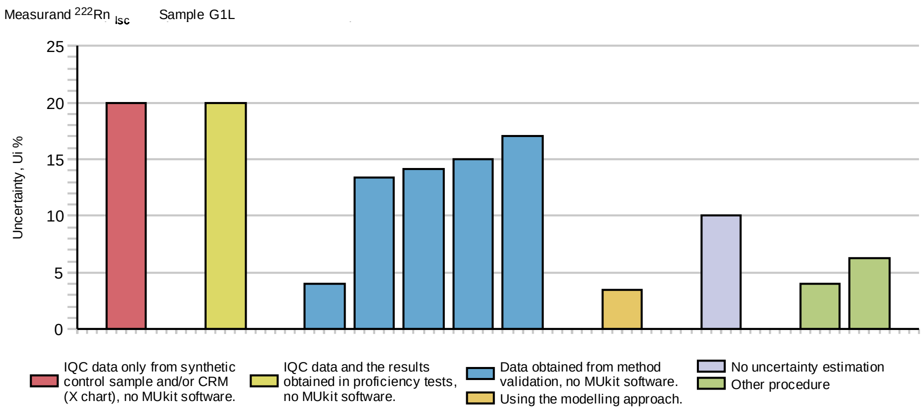
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.

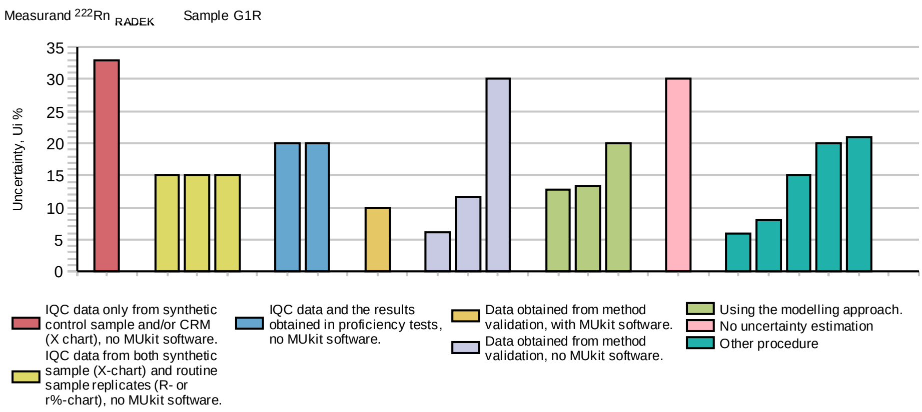




APPENDIX 9: Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (*k*=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [6, 7] or using a modelling approach based [8, 9].





PROFICIENCY TEST SYKE 05/2017

FINNISH ENVIRONMENT INSTITUTE

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ISBN 978-952-11-4851-4 (pbk.)
ISBN 978-952-11-4852-1 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)