

Interlaboratory Proficiency Test

05/2015

Radon in ground water

**Katarina Björklöf, Reko Simola, Mirja Leivuori,
Keijo Tervonen, Sari Lanteri, Markku Ilmakunnas
and Ritva Väisänen**

**REPORTS OF THE FINNISH ENVIRONMENT
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S Y K E

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1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of radon in ground water in May 2015 (RAD 05/15). The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3].

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 Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/scope/PT01/uk). This proficiency test is not included in scope of the accreditation scope but the testing procedures are the same.

A warm thank you to all the participants of this proficiency test.

2 Organizing the proficiency test

2.1 Responsibilities

Organizing laboratory:

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, FI-00430 Helsinki, Finland
Phone: +358 295 251 000, Fax. +358 9 448 320

The responsibilities in organizing the proficiency test were as follows:

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

Co-operation partner and analytical expert:

Reko Simola Finnish Radiation and Nuclear Safety Authority (STUK). The analytical method used by STUK is accredited by the Finnish Accreditation Service (T167, SFS-EN ISO/IEC 17025:2005, www.finas.fi/scope/T167/uk).

2.2 Participants

In total 34 participants took part in this proficiency test (Appendix 1), 19 from Finland and 15 from other EU countries. One registered participant failed to send any results due to broken equipment. Altogether 16 % of the participants used accredited analytical methods for the measurements.

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 first delivery on the 5 May failed because many sample bottles were frozen and broken during the delivery. New samples were collected from the same sampling sites and delivered on 18 May 2015. The samples arrived to the participants mainly on the following day. Participants 5 and 17 received the samples on 20 May 2015 and participant 27 received the samples on 21 May 2015.

The samples were requested to be measured latest on 22 May 2015 and the results to be calculated to the reference time 19 May 2015 at noon (Finnish time; GMT/UTC + 3 h). The preliminary results were delivered to the participants by email on 12 June 2015.

2.4 Homogeneity and stability studies

Homogeneity of the samples was tested by scintillation counting from 10 parallel samples by STUK. For both samples the homogeneity criteria were met and the samples were considered homogeneous (Table 1).

Table 1. Results of the homogeneity testing of the samples.

Sample	Unit	n	Mean	SD	s _p of proficiency test (%)	0,5*s _p	Is SD <0,5*s _p ?
G1	Bq/l	10	296	9.5	22.3 (7,5 %)	11.1	Yes
G2	Bq/l	10	2087	33.7	104.3 (5 %)	52.2	Yes

n: the number of parallels, SD: the standard deviation, s_p: the total standard deviation for proficiency assessment at the 95 % confidence interval.

The stability of the samples were tested on Friday the 22 of May 2015 by storing three parallel samples for 48 h in room temperature (+22 °C) and three samples for the same time in a refrigerator (+ 4 °C). The results were compared to concentrations of the samples measured by scintillation count immediately after sampling on Monday the 18 May 2015. According to the stability testing criteria the standard deviation for the proficiency assessment (s_p) included also in differences caused by possible instabilities of the samples caused by storing (Table 2). The stability test was not passed for sample G1 kept in the refrigerator. The expanded measuring uncertainty of the assigned value (5%) is higher than the observed change during storage and therefore also this sample is considered stable.

Table 2. Results of the stability testing of three parallel samples at +4 °C and +22 °C.

			Mean of n parallels (SD)			Difference in mean after 2 days		Is difference in mean $\leq 0,3 \cdot s_p$?	
Sample	Unit	$0,3 \cdot s_p$	0 days storage (n= 10)	2 days in +4 °C (n=3)	2 days in +22 °C (n=3)	+4 °C	+22 °C	+4 °C	+22 °C
G1	Bq/l	6,7	296 (8,6)	307 (16,4)	302 (16,2)	11	6	No*	Yes
G2	Bq/l	31,3	2087 (33,7)	2084 (106,8)	2076 (106,4)	3	11	Yes	Yes

n: the number of parallels, SD: the standard deviation, s_p : the total standard deviation for proficiency assessment at the 95 % confidence interval (see s_p values in Table 1).

* The observed difference is within the expanded measuring uncertainty of the assigned value (5% of 296, 14,8).

2.5 Feedback from the proficiency test

The comments from the participants mainly dealt with their reporting errors. The comments from the provider to the participants are mainly clarifying notes on the given information provided with the samples (see below). Proftest SYKE is currently developing an electronic interface for customer service and result handling. All the feedback is valuable and is exploited when improving the activities.

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments	Action / Proftest
All	The first delivery on the 5 May failed because some sample bottles were frozen and broken during the delivery.	The used freezing blocks were too effective for cooling during the transportation. In the future test only cooling blocks will be used in the transportation boxes.
30	Too many sample bottles were sent to the participant due to unclarities in the registration form.	The registration and sample ordering form will be improved for the next round of proficiency test.
9, 26	Results were reported to wrong samples.	Proftest generally do not accept changes in the results after the preliminary results have been sent. In this case we made an exception, because the datasets would have been too small for the statistical testing without the results.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
9, 30	In the column UC% in the results scheme the expanded uncertainty (k=2) of the results should be reported. The uncertainty is a larger component than the SD, consisting of several parameters.
20	Zeta-scores were not provided in Appendix 7, because no estimate for measurement uncertainty was provided.
20	Correction factors for RADEK-measurements can be used by laboratories. A correction factor is always laboratory –specific and shall be determined on sufficient data to validate the factor.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

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

2.6.2 Assigned values

The assigned values used for evaluation of participant's performance were the mean radon concentrations from ten samples measured by STUK by scintillation counting using the accredited method of STUK. The expanded measurement uncertainties of the assigned values are 5 % ($k=2$).

According to standard procedures [4] the assigned value is considered reliable when the expanded measurement uncertainty (u) of the assigned value is smaller than $s_p * 0.3$, or $u/s_p \leq 0.3$. This was the case except for sample G2 using liquid scintillation counting where there the criterion was not met (Table 3). Therefore the evaluation of this analyte may be stricter than recommended the guidelines [4].

Table 3. The assigned values and their uncertainties.

Analyte	Sample	Unit	Assigned value	U_{pt}	$U_{pt, \%}$	Evaluation method of assigned value	u_{pt}/s_p
Rn_LSC	G1	Bq/l	296	15	5,0	Expert laboratory	0,33
	G2	Bq/l	2087	104	5,0	Expert laboratory	0,50
Rn_RAD	G1	Bq/l	296	15	5,0	Expert laboratory	0,20
	G2	Bq/l	2087	104	5,0	Expert laboratory	0,25

U_{pt} : the expanded uncertainty of the assigned value, s_p : the total standard deviation for proficiency assessment at the 95 % confidence interval (see s_p values in Table 1).

2.6.3 Standard deviation for proficiency assessment and z score

The performance of laboratories was evaluated by calculating z scores using standard deviations for proficiency assessment (s_p). The standard deviation for proficiency assessment was estimated on the basis of the analyte 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 target value for the standard deviation for the proficiency assessment ($2 \times s_p$ at the 95 % confidence interval) was set to 10– 25 % depending on the measurements. The same values have been used in the previous proficiency test [5].

After reporting the preliminary results no changes have been done to the standard deviations of the proficiency assessment values.

3 Results and conclusions

3.1 Results

The summary of the results of the proficiency test is shown in Table 4. The terms in the results table are explained in the Appendix 2, the results of each participant are given in the Appendix 3, results of participants and their uncertainties presented graphically in the Appendix 4, the summary of the z scores is in the Appendix 5, the summary of the z scores is presented in Appendix 5 and z scores in the ascending order are presented graphically in Appendix 6. Summary of the z and zeta scores are shown in Appendix 7. The zeta scores (Appendix 7) were possible to calculate only for the results for which the uncertainty was reported.

The robust standard deviations of the results varied from 6.6 to 11.2 % (Table 4). This is the same level as in the previous proficiency test in 2013 [5], where the deviations varied from 6.3 % to 10.9 %.

Table 4. The summary of the results in the proficiency test 05/2015.

Analyte	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2*s _p %	n (all)	Acc z %
Rn_LSC	G1	Bq/l	296	303	303	301	20	6,5	15	14	100
	G2	Bq/l	2087	2114	2112	2084	166	7,9	10	14	79
Rn_RAD	G1	Bq/l	296	257	254	247	29	11,2	25	23	91
	G2	Bq/l	2087	1808	1796	1800	176	9,8	20	23	83

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, 2*s_p %: the total standard deviation for proficiency assessment at the 95 % confidence interval, Acc z %: the results (%), where |z| ≤ 2, n(all): the total number of the participants.

3.2 Uncertainties of the results

The reported results with their expanded uncertainties ($k=2$) are presented graphically in Appendix 4. The summaries of z and zeta scores are presented in Appendix 7 and examples of uncertainties reported by the participants in Appendix 8.

Two of the participants did not report the expanded uncertainties ($k=2$) with their results (Appendix 4). The range of the reported uncertainties varied between the measurements and the sample types from 2-33 % (Table 5).

The counting uncertainty is higher for lower concentrations. Therefore uncertainty for lower concentrations is usually higher than uncertainty for samples with higher concentrations. Participants 17, 27, 29 and 30 reported lower uncertainty for a higher concentration.

Uncertainty for radon measurements with RADEK MKGB-01 (Rn_RAD) is composed of sample taking, transfer of the sample to measuring vessel, counting uncertainty and calibration of RADEK MKGB-01. In this case sample taking can be ignored, but with customer samples uncertainty for sample taking is usually at least 10% and should be included to the results.

Table 5. The range of the expanded measurement uncertainties ($k=2$, U%) reported by the participants.

Analyte	Sample	The range of the reported expanded measurement uncertainties, %
Rn_LSC	G1	2-24
	G2	2-24
Rn_RAD	G1	6-33
	G2	6-33

Several approaches were used for estimating of measurement uncertainty (Appendix 8). For liquid scintillation counts, most commonly data from method validation was used or using the Eurachem modeling approach. For RADEK technology, most commonly information from method validation was used or information from internal quality control data and replicates were used. No participant used MUkit measurement uncertainty software for the estimation of their 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 proficiency assessment (Appendix 2). The z scores were interpreted as follows:

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

In total, 88 % of the results were satisfactory when total deviations of 10 – 25 % from the assigned values were accepted (Appendix 5).

Altogether 43 % of the participants used accredited analytical methods and 97 % of their results were satisfactory. In non-accredited laboratories 81 % of the results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 6. The standard deviations used for performance evaluation are the same as in the previous proficiency test, SYKE 8/2013 [5], where the performance was satisfactory for 86 % of the all participants.

The mean values of the scintillation count results were 1-2 % higher than the assigned value and the mean values of RADEK technology or equivalent gamma spectrometry 11-13 % lower than the assigned values. Lower RADEK results have been observed in all the proficiency tests

performed by Proftest SYKE since 2006. The reason for this observation may be due to many reasons. One important factor is that the sample must be transferred to the RADEK measuring vessel before measurement. During transfer some evaporation occurs. The way the sample is transferred affects the amount of evaporation; by pouring carefully about 10 % of the sample is lost. Also a delay in starting the RADEK measurement after transferring the sample causes smaller results. In addition, the energy calibration affects the results. The RADEK measurement is highly dependent on temperature and moisture.

At least two participants used other gamma spectroscopy technology than RADEK (participant 27 used high resolution gamma spectroscopy and participant 33 used gamma-ray spectrometry). The results from these participants were not lower compare to scintillation count results (see Appendix 4).

Table 6. Summary of the performance evaluation in the proficiency test 05/2015.

Analyte	Sample	$2 * s_p$, %	Satisfactory results, %	Assessment
Rn_LSC	G1	15	100	Good performance. In the PT SYKE 8/2013 the performance was satisfactory for 83 % of the results [5].
	G2	10	79	Satisfactory performance. In the PT SYKE 8/2013 the performance was satisfactory for 67 % of the results [5]. The s_p is slightly tighter than recommended in guidelines.
Rn_RAD	G1	25	91	Good performance. In the PT SYKE 8/2013 the performance was satisfactory for 89 % of the results [5].
	G2	20	83	The evaluation is only approximate since the stability test criteria were not met. In the PT SYKE 8/2013 the performance was satisfactory for 89 % 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 2015. In total 34 participants took part in this PT. Fourteen of the participating laboratories used the liquid scintillation method and 23 used equipment based on gamma spectrometry (Radek MKGB-01).

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 87 % of the results was satisfactory when the result measured with Radek equipment was accepted when deviation of 20 % and 25 % from the assigned value was accepted. A total of 90 % of the liquid scintillation counting results were accepted when deviation of 10 % and 15 % from the assigned value was accepted. The results obtained with Radek equipment was systematically about 10 % smaller than results obtained with liquid scintillation technology.

6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmääritystä toukokuussa 2015. Pätevyyskokeessa oli 34 osallistujaa, joista 23 määritti radonin Radek-laitteella ja 14 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. Hyväksyttäviä tuloksia oli 87 %, kun Radek-laitteella mitatun radonpitoisuuden sallittiin poiketa vertailuarvosta 20 % ja 25 %. Nestetuikemenetelmällä 90 % tuloksista oli hyväksyttäviä, kun sallittiin 10 % ja 15 % vaihelevuus vertailuarvosta. Radek-laitteella saadut tulokset olivat systemaattisesti noin 10 % pienempiä kuin nestetuikelaskennalla saadut tulokset.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Austria	Seidersdorf Labor GmbH, Austria
Belgium	IRE-ELIT_Service LMR, Institut National des Radio-Eléménts (I.R.E) Belgium
	LRM, SCK-CEN, Belgium
Denmark	DTU Nutech, Technical University of Denmark, Center for nuclear Technologies
Finland	Alcontrol Laboratories, LINKÖPING, Sweden
	BotniaLab Oy
	HaKaLab Oy
	KCL Kymen Laboratorio Oy
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Hämeenlinna
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Pori
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Rauma
	Lounais-Suomen vesi- ja ympäristötukimus Oy, Turku
	Länsi-Uudenmaan vesi ja ympäristö ry, Lohja
	Nab Labs Oy Jyväskylä
	Oulun seudun elintarvike- ja ympäristölaboratorio, Oulu
	Ramboll Finland Oy, Ramboll Analytics, Lahti
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kajaani
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	Seilab Oy
	VITA-Terveyspalvelut Oy, VITA Laboratorio
	ÅMHM laboratoriet, Jomala, Åland
France	ISRN, Le Vesinet, France
Latvia	Laboratory of the Latvian Environment , Meteorology and Geology Centre
Norway	Norwegian Radiation Protection Authority (NRPA), Osterås
Portugal	Instituto Superior Técnico Portugal , Laborat�o de Protec�o�e Seguran�a Radiol�a
Spain	LaRUC, Santander, Facultad de Medicina, Dpto. Ciencias Medicas y Quirurgicas
	Unitat de Radioquimica Ambiental i Sanitaria (URAIS), Spain
Sweden	Eurofins Environment testing Sweden AB, Lidköping
	Studsvik Nuclear AB Nyk�oping Sweden
	Swedish Radiation Safety Authority, Solna
United Kingdom	LGC Ltd, Middlesex, UK
	Scottish Water, UK

APPENDIX 2: Terms in the results tables

Results of each participant

Analyte	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - X)/s_p$, where x_i = the result of the individual participant X = Assigned value s_p = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
$2 \cdot s_p$ %	The total standard deviation for proficiency assessment (s_p) at the 95 % confidence level
Lab's result	The result reported by the participant (the mean value of the replicates)
Md	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)

Q – questionable ($2 < z < 3$), positive error, the result deviates more than $2 \cdot s_p$ from the assigned value

q – questionable ($-3 < z < -2$), negative error, the result deviates more than $2 \cdot s_p$ from the assigned value

U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 \cdot s_p$ from the assigned value

u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 \cdot s_p$ from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_3, \dots, x_p$.

Initial values for \bar{x}^* and s^* are calculated as:

$$\bar{x}^* = \text{median of } x_i \quad (i = 1, 2, \dots, p)$$

$$s^* = 1,483 \cdot \text{median of } |x_i - \bar{x}^*| \quad (i = 1, 2, \dots, p)$$

The mean \bar{x}^* and s^* are updated as follows:

Calculate $\varphi = 1.5 \cdot s^*$. A new value is then calculated for each result x_i ($i = 1, 2 \dots p$):

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

The new values of \bar{x}^* and s^* are calculated from:

$$\bar{x}^* = \sum x_i^* / p$$

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

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

APPENDIX 3: Results of each participant

Participant 1													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1		0,270	296	15	302	301	303	17,4	5,8	14	
	Bq/l	G2		0,000	2087	10	2087	2084	2114	151,9	7,2	14	
Participant 2													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1		-0,721	296	15	280	301	303	17,4	5,8	14	
	Bq/l	G2		-1,246	2087	10	1957	2084	2114	151,9	7,2	14	
Participant 3													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1		-1,649	296	25	235	247	257	29,9	11,7	23	
	Bq/l	G2		-1,663	2087	20	1740	1800	1808	186,5	10,3	23	
Participant 4													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1		-2,027	296	25	221	247	257	29,9	11,7	23	
	Bq/l	G2		-2,381	2087	20	1590	1800	1808	186,5	10,3	23	
Participant 5													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1		-0,243	296	25	287	247	257	29,9	11,7	23	
	Bq/l	G2		-0,561	2087	20	1970	1800	1808	186,5	10,3	23	
Participant 6													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1		-1,892	296	25	226	247	257	29,9	11,7	23	
	Bq/l	G2		-2,837	2087	20	1495	1800	1808	186,5	10,3	23	
Participant 7													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1		-1,514	296	25	240	247	257	29,9	11,7	23	
	Bq/l	G2		-1,854	2087	20	1700	1800	1808	186,5	10,3	23	
Participant 8													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1		0,000	296	15	296	301	303	17,4	5,8	14	
	Bq/l	G2		-0,163	2087	10	2070	2084	2114	151,9	7,2	14	
Participant 9													
Analyte	Unit	Sample	-3 .. 0 .. 3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1		-0,721	296	15	280	301	303	17,4	5,8	14	
	Bq/l	G2		-1,792	2087	10	1900	2084	2114	151,9	7,2	14	

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Participant 10														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,514	296	25	240	247	257	29,9	11,7	23
		G2				-1,375	2087	20	1800	1800	1808	186,5	10,3	23
Participant 11														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,730	296	25	232	247	257	29,9	11,7	23
		G2				-1,950	2087	20	1680	1800	1808	186,5	10,3	23
Participant 12														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,568	296	25	238	247	257	29,9	11,7	23
		G2				-1,854	2087	20	1700	1800	1808	186,5	10,3	23
Participant 13														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,324	296	25	247	247	257	29,9	11,7	23
		G2				-1,567	2087	20	1760	1800	1808	186,5	10,3	23
Participant 14														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-0,432	296	25	280	247	257	29,9	11,7	23
		G2				-0,369	2087	20	2010	1800	1808	186,5	10,3	23
Participant 15														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-0,973	296	25	260	247	257	29,9	11,7	23
		G2				-0,896	2087	20	1900	1800	1808	186,5	10,3	23
Participant 16														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-0,973	296	25	260	247	257	29,9	11,7	23
		G2				-1,375	2087	20	1800	1800	1808	186,5	10,3	23
Participant 17														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_LSC	Bq/l	G1				0,689	296	15	311	301	303	17,4	5,8	14
		G2				2,083	2087	10	2304	2084	2114	151,9	7,2	14
Participant 18														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-0,703	296	25	270	247	257	29,9	11,7	23
		G2				-1,184	2087	20	1840	1800	1808	186,5	10,3	23
Participant 19														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,919	296	25	225	247	257	29,9	11,7	23
		G2				-2,573	2087	20	1550	1800	1808	186,5	10,3	23

Participant 20														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,243	296	25	250	247	257	29,9	11,7	23
	Bq/l	G2				-1,327	2087	20	1810	1800	1808	186,5	10,3	23
Participant 21														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-0,243	296	25	287	247	257	29,9	11,7	23
	Bq/l	G2				-1,184	2087	20	1840	1800	1808	186,5	10,3	23
Participant 23														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,324	296	25	247	247	257	29,9	11,7	23
	Bq/l	G2				-1,179	2087	20	1841	1800	1808	186,5	10,3	23
Participant 24														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_RAD	Bq/l	G1				-1,486	296	25	241	247	257	29,9	11,7	23
	Bq/l	G2				-1,519	2087	20	1770	1800	1808	186,5	10,3	23
Participant 25														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_LSC	Bq/l	G1				-0,410	296	15	287	301	303	17,4	5,8	14
	Bq/l	G2				-0,077	2087	10	2079	2084	2114	151,9	7,2	14
Participant 26														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_LSC	Bq/l	G1				0,090	296	15	298	301	303	17,4	5,8	14
	Bq/l	G2				-0,067	2087	10	2080	2084	2114	151,9	7,2	14
Participant 27														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_LSC	Bq/l	G1				-0,631	296	15	282	301	303	17,4	5,8	14
	Bq/l	G2				-1,284	2087	10	1953	2084	2114	151,9	7,2	14
Rn_RAD	Bq/l	G1				0,689	296	25	322	247	257	29,9	11,7	23
	Bq/l	G2				0,793	2087	20	2253	1800	1808	186,5	10,3	23
Participant 28														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_LSC	Bq/l	G1				0,405	296	15	305	301	303	17,4	5,8	14
	Bq/l	G2				0,125	2087	10	2100	2084	2114	151,9	7,2	14
Rn_RAD	Bq/l	G1				-2,081	296	25	219	247	257	29,9	11,7	23
	Bq/l	G2				-2,621	2087	20	1540	1800	1808	186,5	10,3	23
Participant 29														
Analyte	Unit	Sample	-3	0	3	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)
Rn_LSC	Bq/l	G1				1,261	296	15	324	301	303	17,4	5,8	14
	Bq/l	G2				3,000	2087	10	2400	2084	2114	151,9	7,2	14

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Participant 30												
Analyte	Unit	Sample	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1	-1,322	296	15	325	301	303	17,4	5,8	14	
	Bq/l	G2	1,116	2087	10	2204	2084	2114	151,9	7,2	14	

Participant 31												
Analyte	Unit	Sample	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1	0,180	296	15	300	301	303	17,4	5,8	14	
	Bq/l	G2	-1,313	2087	10	1950	2084	2114	151,9	7,2	14	

Participant 32												
Analyte	Unit	Sample	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1	-1,000	296	25	259	247	257	29,9	11,7	23	
	Bq/l	G2	-0,848	2087	20	1910	1800	1808	186,5	10,3	23	

Participant 33												
Analyte	Unit	Sample	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1	1,667	296	15	333	301	303	17,4	5,8	14	
	Bq/l	G2	2,051	2087	10	2301	2084	2114	151,9	7,2	14	
Rn_RAD	Bq/l	G1	0,784	296	25	325	247	257	29,9	11,7	23	
	Bq/l	G2	0,446	2087	20	2180	1800	1808	186,5	10,3	23	

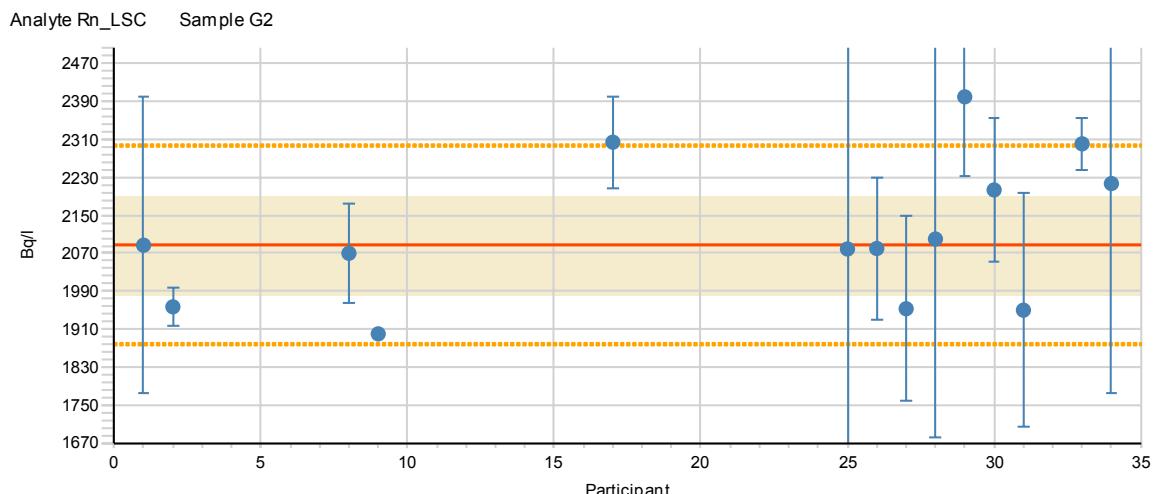
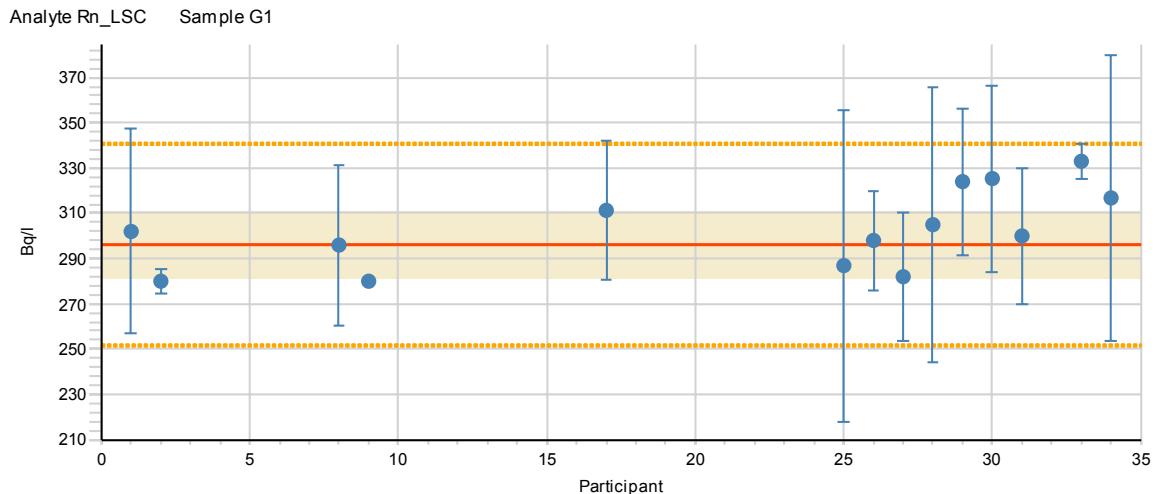
Participant 34												
Analyte	Unit	Sample	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_LSC	Bq/l	G1	0,937	296	15	317	301	303	17,4	5,8	14	
	Bq/l	G2	1,246	2087	10	2217	2084	2114	151,9	7,2	14	

Participant 35												
Analyte	Unit	Sample	z score	Assigned value	2*s _p , %	Lab's result	Md	Mean	SD	SD%	n (stat)	
Rn_RAD	Bq/l	G1	-0,162	296	25	290	247	257	29,9	11,7	23	
	Bq/l	G2	-0,896	2087	20	1900	1800	1808	186,5	10,3	23	

APPENDIX 4: Results of participants and their uncertainties

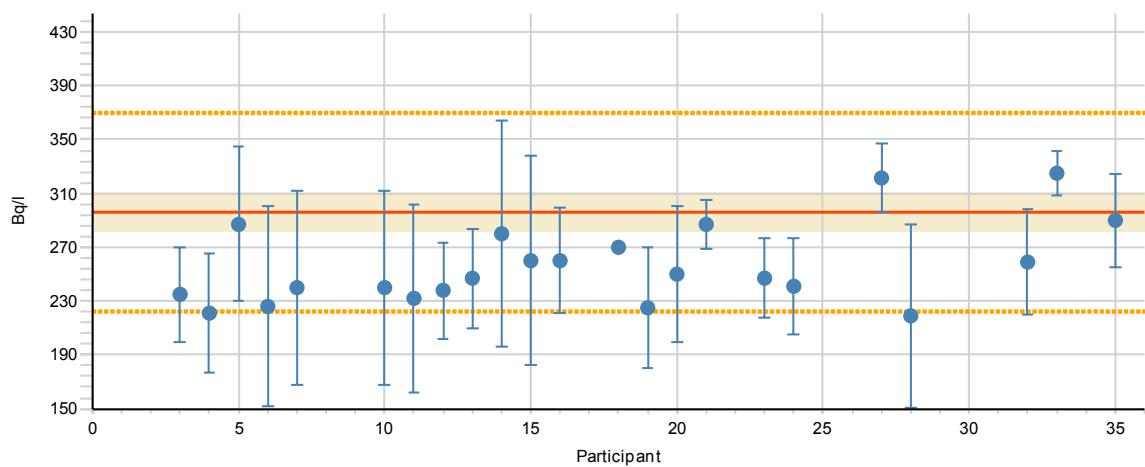
In figures:

- 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.

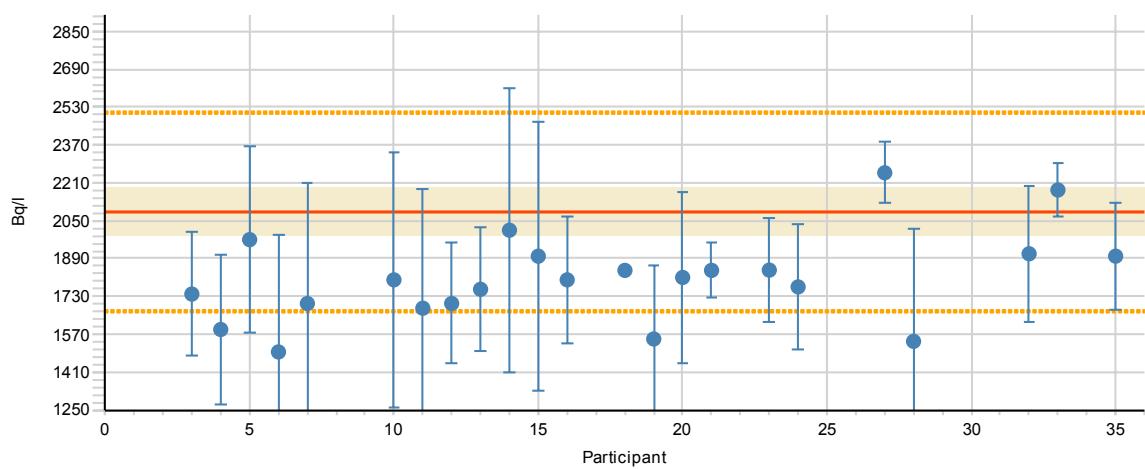


APPENDIX 4 (2/2)

Analyte Rn_RAD Sample G1



Analyte Rn_RAD Sample G2



APPENDIX 5: Summary of the z scores

Analyte	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Rn_LSC	G1	S	S	S	S	S	100
	G2	S	S	S	S	Q	78,6
Rn_RAD	G1	.	.	S	q	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	91,3	
	G2	.	.	S	q	S	q	S	.	S	S	S	S	S	S	S	S	S	q	S	S	S	S	82,6	
%		100	100	100	0	100	50	100	100	100	100	100	100	100	100	100	100	50	100	50	100	100	100	100	100
accredited		2			2			2		2		2		2		2		2		2		2		2	
Analyte	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
Rn_LSC	G1	.	S	S	S	S	S	S	S	.	S	S	100
	G2	.	S	S	S	S	Q	S	S	.	Q	S	78,6
Rn_RAD	G1	S	.	.	S	q	.	.	S	S	.	S	91,3
	G2	S	.	.	S	q	.	.	S	S	.	S	82,6
%		100	100	100	100	50	50	100	100	100	100	75	100	100											
accredited		2			2			2		2		2		2											

S - satisfactory ($-2 \leq z \leq 2$), **Q** - questionable ($2 < z < 3$), **q** - questionable ($-3 < z < -2$),

U - unsatisfactory ($z \geq 3$), **u** - unsatisfactory ($z \leq -3$)

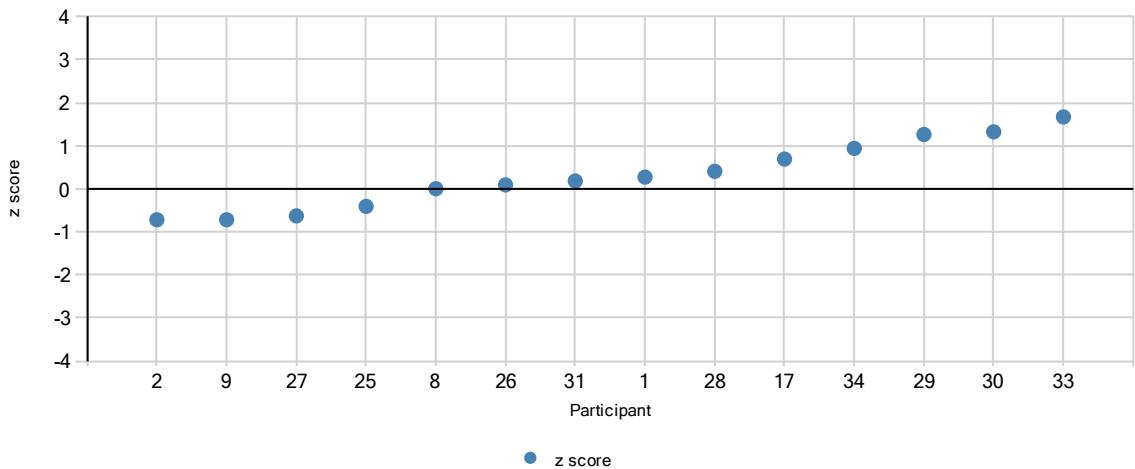
bold - accredited, **italics** - non-accredited, **normal** - other

% - percentage of satisfactory results

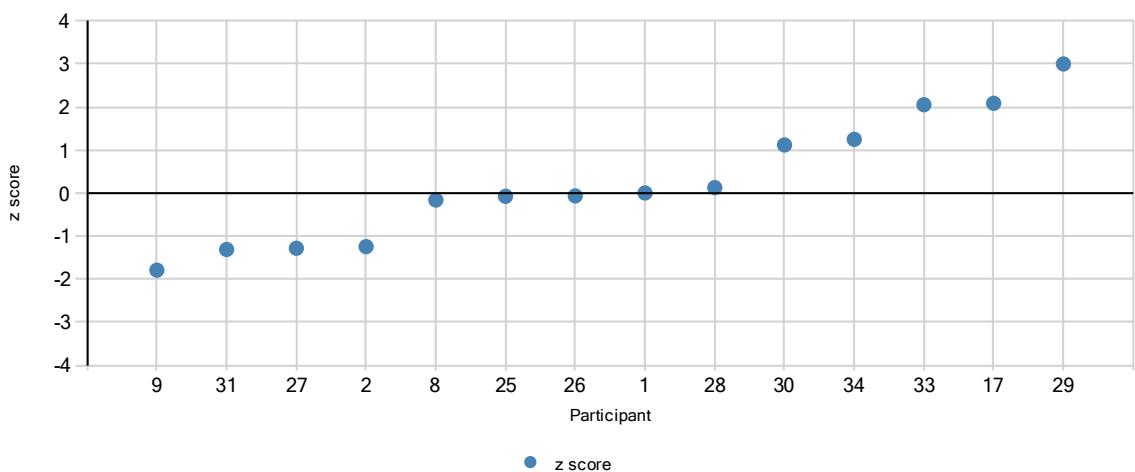
Totally satisfactory, % in all: 88 % in accredited: 97 % in non-accredited: 81

APPENDIX 6: z scores in ascending order

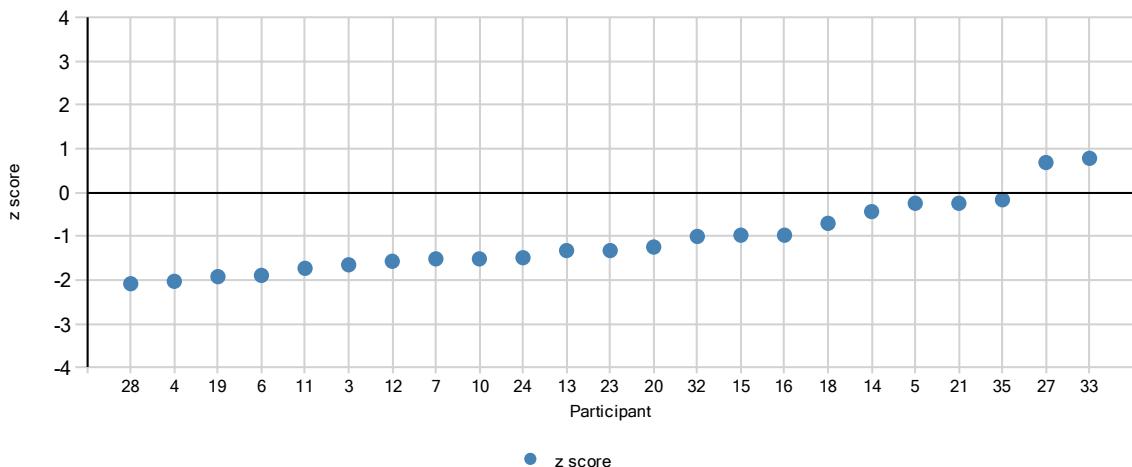
Analyte Rn_LSC Sample G1



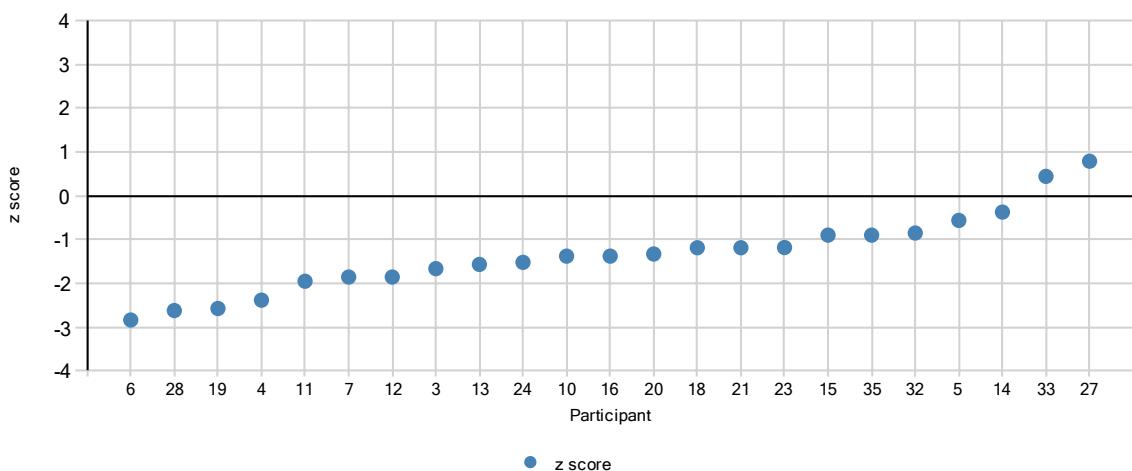
Analyte Rn_LSC Sample G2



Analyte Rn_RAD Sample G1

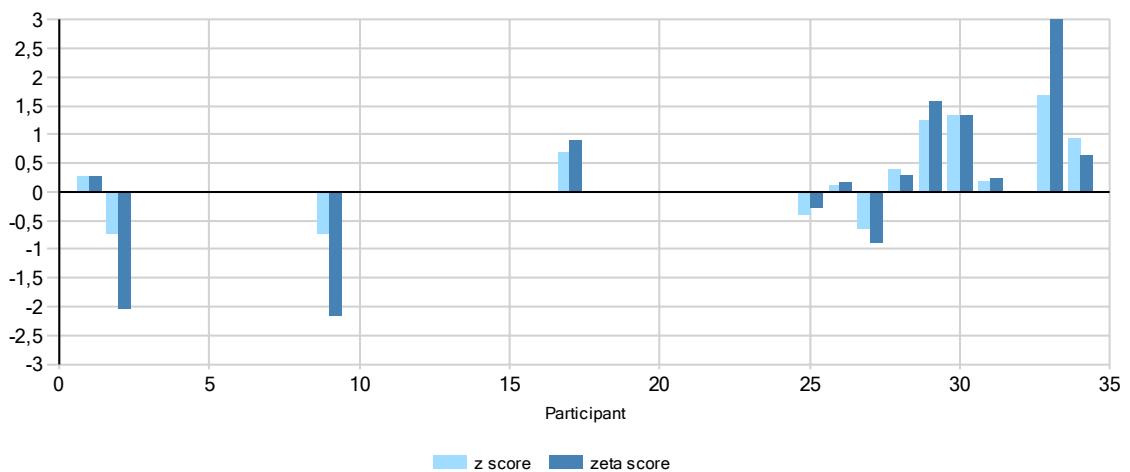


Analyte Rn_RAD Sample G2



APPENDIX 7: Summary of the z and zeta scores

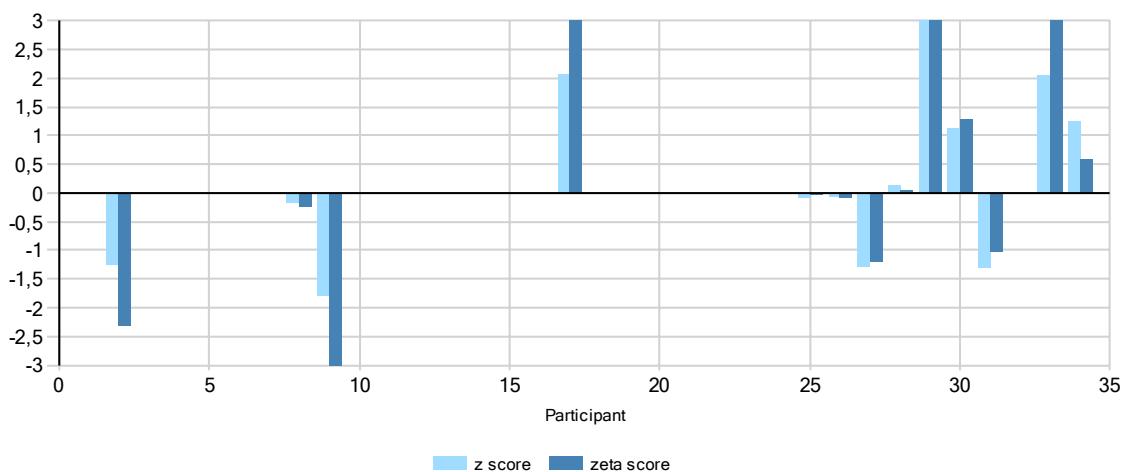
Analyte Rn_LSC Sample G1



Assigned value $2\bar{u}_c 2s_p \%$		
296	5,0	15,0

Participant	Mean U_{lab} , %	z	zeta
1	302	15,0	0,27
2	280	2,0	-0,72
8	296	12,0	0,00
9	280	0,0	-0,72
17	311	9,9	0,69
25	287	24,0	-0,41
26	298	7,4	0,09
27	282	10,0	-0,63
28	305	20,0	0,41
29	324	10,0	1,26
30	325	12,7	1,32
31	300	10,0	0,18
33	333	2,4	1,67
34	317	20,0	0,94

Analyte Rn_LSC Sample G2

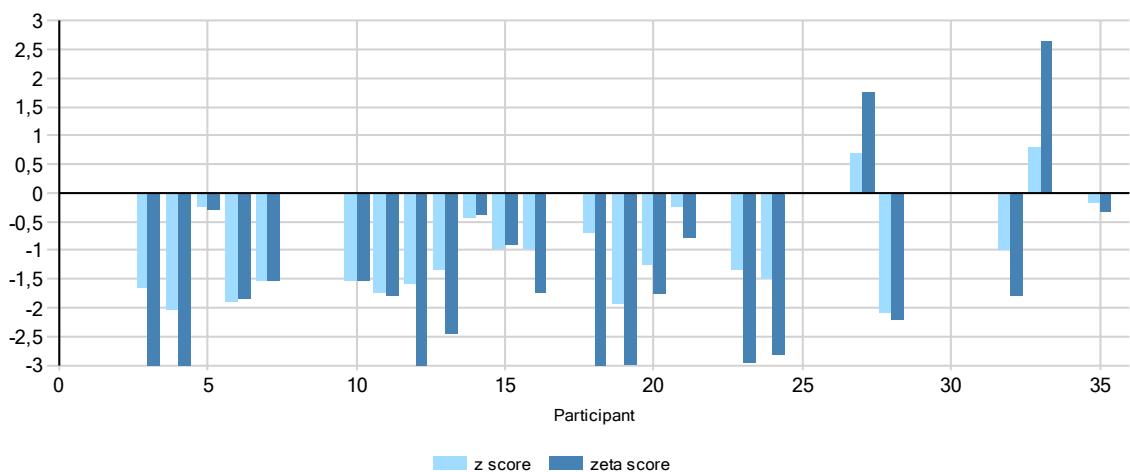


Assigned value 2 <u>U</u> c 2s _p %		
2087	5,0	10,0

Participant	Mean U _{lab} , %	z	zeta
1	2087	15,0	0,00
2	1957	2,0	-1,25
8	2070	5,0	-0,16
9	1900	0,0	-1,79
17	2304	4,2	2,08
25	2079	24,0	-0,08
26	2080	7,2	-0,07
27	1953	10,0	-1,28
28	2100	20,0	0,12
29	2400	7,0	3,00
30	2204	6,9	1,12
31	1950	12,6	-1,31
33	2301	2,4	2,05
34	2217	20,0	1,25

APPENDIX 7 (3/4)

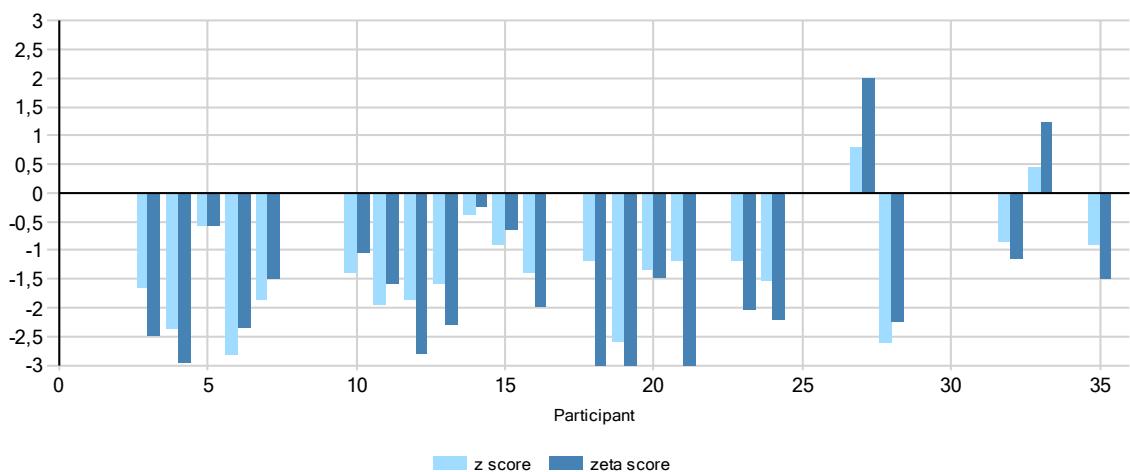
Analyte Rn_RAD Sample G1



Assigned value 2 <u>U</u> c 2s _p %		
296	5,0	25,0

Participant	Mean U _{lab} , %	z	zeta
3	235	15,0	-1,65
4	221	20,0	-2,03
5	287	20,0	-0,24
6	226	33,0	-1,89
7	240	30,0	-1,51
10	240	30,0	-1,51
11	232	30,0	-1,73
12	238	15,0	-1,57
13	247	15,0	-1,32
14	280	30,0	-0,43
15	260	30,0	-0,97
16	260	15,0	-0,97
18	270	0,0	-0,70
19	225	20,0	-1,92
20	250	20,0	-1,24
21	287	6,3	-0,24
23	247	12,0	-1,32
24	241	15,0	-1,49
27	322	7,8	0,69
28	219	31,0	-2,08
32	259	15,0	-1,00
33	325	5,0	0,78
35	290	12,0	-0,16

Analyte Rn_RAD Sample G2



Assigned value 2 <u>U</u> c 2s _p %		
2087	5,0	20,0

Participant	Mean U _{lab} , %	z	zeta
3	1740	15,0	-1,66
4	1590	20,0	-2,38
5	1970	20,0	-0,56
6	1495	33,0	-2,84
7	1700	30,0	-1,85
10	1800	30,0	-1,38
11	1680	30,0	-1,95
12	1700	15,0	-1,85
13	1760	15,0	-1,57
14	2010	30,0	-0,37
15	1900	30,0	-0,90
16	1800	15,0	-1,38
18	1840	0,0	-1,18
19	1550	20,0	-2,57
20	1810	20,0	-1,33
21	1840	6,3	-1,18
23	1841	12,0	-1,18
24	1770	15,0	-1,52
27	2253	5,7	0,79
28	1540	31,0	-2,62
32	1910	15,0	-0,85
33	2180	5,1	0,45
35	1900	12,0	-0,90

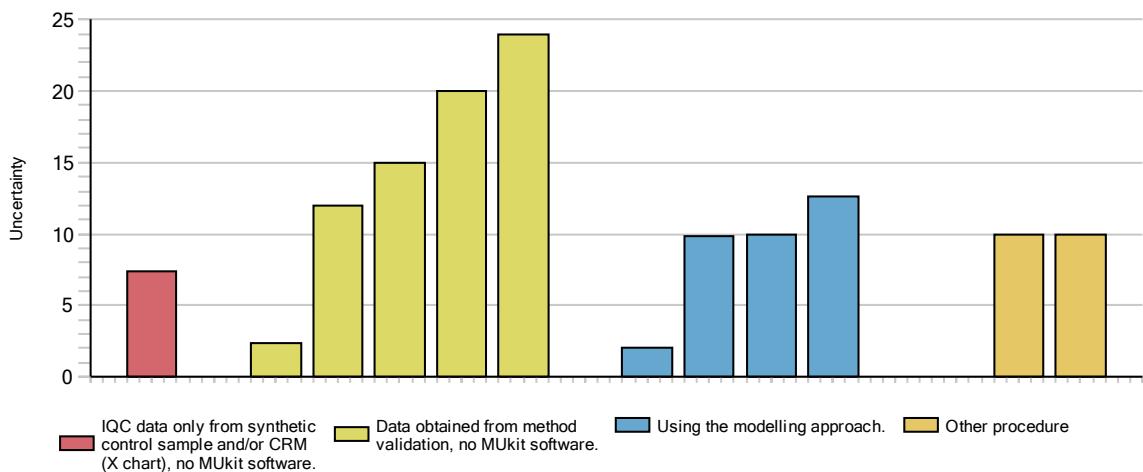
APPENDIX 8: Examples of measurement uncertainties reported by the participants

In figures, the presented measurement uncertainties are grouped according to the method of calculation. The following procedures are used for the estimation of the expanded measurement uncertainty at 95 % confidence level ($k=2$). In figures, the corresponding method numbers are used.

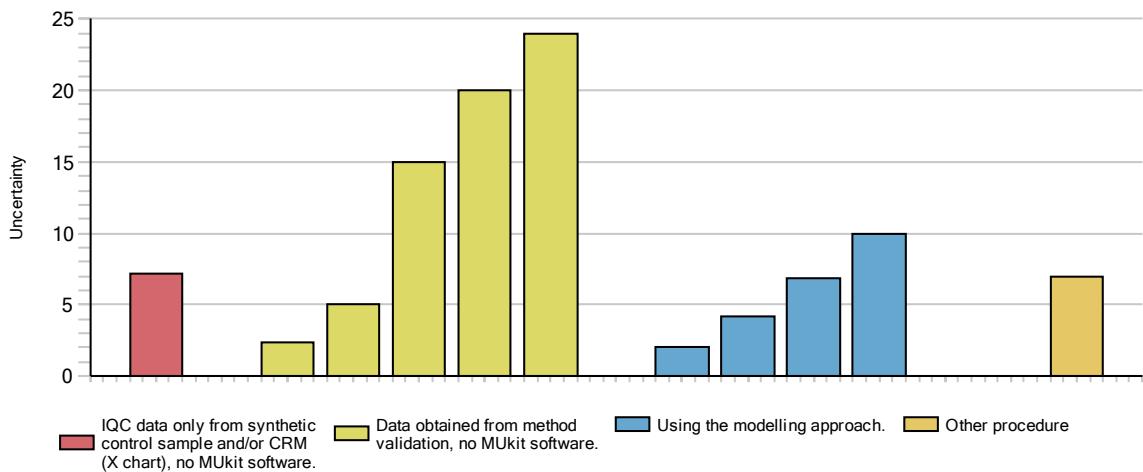
1. Using the IQC data only from synthetic control sample and/or CRM (X-chart). **Using MUkit measurement uncertainty software.** [6, 7]
2. Using the IQC data only from synthetic control sample and/or CRM (X-chart). **Without MUkit measurement uncertainty software.** [7]
3. Using the IQC data from synthetic sample (X-chart) together with the IQC data from routine sample replicates (R-chart or r%-chart). **Using MUkit software.** [6, 7]
4. Using the IQC data from synthetic sample (X-chart) together with the IQC data from routine sample replicates (R-chart or r%-chart). **Without MUkit software.** [7]
5. Using the IQC data and the results obtained in proficiency tests. **Using MUkit software.** [6, 7]
6. Using the IQC data and the results obtained in proficiency tests. **Without MUkit software.** [7]
7. Using the data obtained in method validation. **Using MUkit software.** [6]
8. Using the data obtained in method validation. **Without MUkit software.** [7]
9. Using the "modeling approach". [8, 9]
10. Other procedure, please specify
11. No uncertainty estimation

IQC = internal quality control

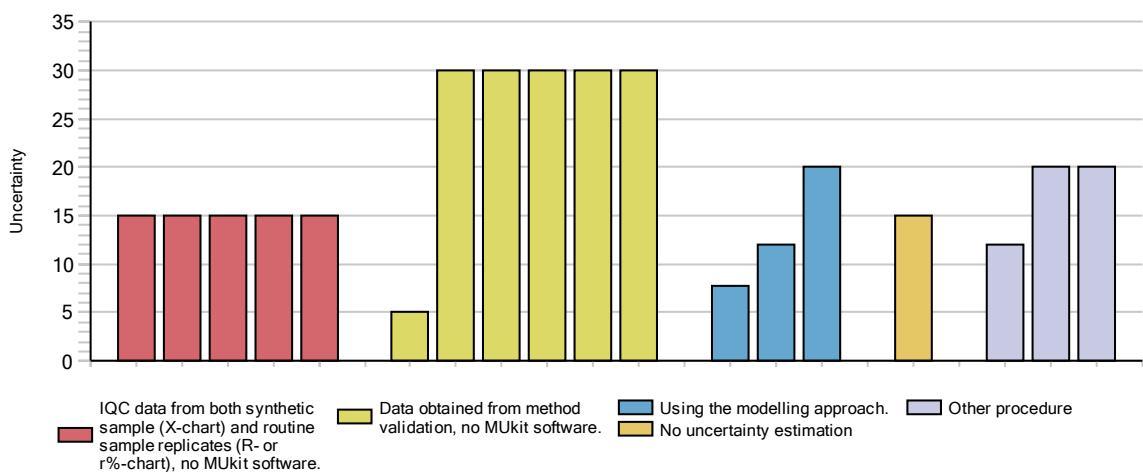
Analyte Rn_LSC Sample G1



Analyte Rn_LSC Sample G2



Analyte Rn_RAD Sample G1



DOCUMENTATION PAGE

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Publication series and number	Reports of the Finnish Environment Institute 33/2015	
Theme of publication		
Parts of publication/other project publications	The publication is available in the internet: www.syke.fi/publications helda.helsinki.fi/syke	
Abstract	<p>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 2015. 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). In total 34 participants took part in this PT. Fourteen of the participating laboratories used the liquid scintillation method and 23 used equipment based on gamma spectrometry (Radek MKGB-01). In total 88 % of the results were satisfactory when allowing for 10-25 % variation. This is the same level as in previous round in 2013.</p> <p>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. The results obtained with Radek equipment was systematically about 10 % smaller than results obtained with liquid scintillation technology.</p>	
Keywords	ground water analysis, drinking water analysis, measurement of radon, food and environmental laboratories, interlaboratory comparison, proficiency test	
Financier/commissioner		
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Julkaisun nimi	Interlaboratory Proficiency Test 05/2015. Radon in ground water	
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Tiivistelmä	<p>Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmääritystä toukokuussa 2015. Näytteet olivat kaksi pohjavesinäytettä, joissa radonpitoisuus on toisessa korkea (1000–5000 Bq/l) ja toisessa matalampi (<1000 Bq/l). Pätevyyskokeeseen oli 34 osallistujaa, joista 23 määritti radonin Radek-laitteella tai gammaspektrometrisesti ja 14 nestetuikemenetelmällä. Hyväksyttyviä tuloksia oli 88 %, kun sallittiin tuloksiin poiketa vertailuarvosta 10-25 %. Tämä on samaa tasoa kuin edellisellä kierroksella vuonna 2013.</p> <p>STUKin nestetuikemenetelmällä mitattujen tulosten keskiarvoa käytettiin radonpitoisuuden vertailuarvona. Tulokset arvioitiin z-arvon avulla. Radek-laitteella saadut tulokset olivat systemaattisesti noin 10 % pienempiä kuin nestetuikelaskennalla saadut tulokset.</p>	
Asiasanat	pohjavesianalyysi, talousvesianalyysi, radonmääritys, elintarvike- ja ympäristölaboratoriot, vertailumittaus, pätevyyskoe	
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Sammandrag	I maj 2015 genomförde Proftest SYKE i samarbete med Strålsäkerhetscentralen (STUK) en provningsjämförelse som omfattade radonmätning i grundvatten. Sammanlagt 34 laboratorier deltog i jämförelsen. Totalt 23 av deltagarna bestämde radon med gammaskintillationsräknare (RADEK) och 14 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). Total 88 % av resultaten var godkända när 10-25 % variation godkändes, vilken var resultaten också i den förra provningsjämförelsen 2013. Som referensvärde användes medelvärdet av resultaten mätt av STUK med vätskeskintillationsräknare. Resultat mätta med RADEK-mätare var systematiskt ca 10 % mindre än resultat mätta med vätseskintillationsräknare.	
Nyckelord	vattenanalyser, grundvatten, radon analys, provningsjämförelse, vatten- och miljölaboratorier	
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