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Interlaboratory Proficiency Test 06/2021

Radon in ground water

Päivi Grönroos, Tarja Heikkinen, Reko Simola,
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PROF TEST SYKE

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Abstract

Interlaboratory Proficiency Test 06/2021
Proftest SYKE carried out the proficiency test (PT) in cooperation with the Finnish Radiation and Nuclear Safety Authority (STUK) for laboratories conducting radon measurements in ground water in May 2021. In total, 25 participants took part in the PT and three of them provided two sets of results. Two ground water samples were provided, of which one contained lower (GRn1; < 1000 Bq/l) and the other contained higher radon concentration (GRn2; 1000-8000 Bq/l). The median of the participant results was used as the assigned value for radon concentration. The evaluation of the results was based on z scores. In total 88 % of the results were satisfactory when total deviations of 20 % from the assigned value was accepted.

Warm thanks 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 06/2021
Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmäärityksistä toukokuussa 2021. Pätevyyskokeessa oli 25 osallistujaa, joista kolme raportoi kahdet tulokset. Osallistujille toimitettiin kaksi pohjavesinäytettä, joista toisessa radonpitoisuus oli matalampi (GRn1; <1000 Bq/l) ja toisessa korkeampi (GRn2; 1000 - 8000 Bq/l). Vertailuarvoina käytettiin osallistujatulosten mediaaniarvoja ja tulokset arvioitiin z-arvojen avulla. Tuloksista hyväksyttäviä oli 88 %, kun radonpitoisuuden sallittiin poiketa vertailuarvosta 20 %.

Kiitos pätevyyskokeen osallistujille!

Asiasanat: pohjavesianalyysi, talousvesianalyysi, radonmääritys, elintarvike- ja ympäristölaboratoriot, laboratorioiden välinen vertailumittaus, pätevyyskoe

Sammandrag

Provningsjämförelse 06/2021
I maj 2021 genomförde Proftest SYKE i samarbete med Strålsäkerhetscentralen (STUK) en provningsjämförelse som omfattade radonmätning i grundvatten. Sammanlagt 25 laboratorier deltog i jämförelsen, varav tre rapporterade två resultat. Två vattenprov testades varav det ena hade lägre halt av radon (GRn1; <1000 Bq/l) och det andra provet hade högre halt av radon (GRn2; 1000 - 8000 Bq/l). Medianen av deltagarnas resultat användes som referensvärde. Totalt 88 % av resultaten var godkända när 20 % variation godkändes.

Ett varmt tack till alla deltagarna i testet!

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

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1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of radon in ground water (RAD 06/2021) in cooperation with Radiation and Nuclear Safety Authority (STUK) in Finland. The radon ^{222}Rn measurements are required in the Drinking Water Directive (2013/51/EURATOM) [1]. Laboratories that provide these services may prove their competence by taking part in the PT.

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 standard ISO/IEC 17043 [2] and applying ISO 13528 [3] and IUPAC Technical report [4]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer
Proftest SYKE, Finnish Environment Institute SYKE, Laboratory Centre
Mustialankatu 3, FI-00790 Helsinki, Finland
Phone: +358 295 251 000, Email: *proftest@syke.fi*

The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
Päivi Grönroos	substitute for coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Expert laboratory
Radiation and Nuclear Safety Authority (STUK) in Finland (T167, www.finas.fi/sites/en)
Tarja Heikkinen, analytical expert
Reko Simola, technical assistance

Subcontracting
Homogeneity and stability testing of samples**,** STUK

2.2 Participants

In total 25 laboratories participated in this PT and three of them provided two sets of results (Appendix 1). 64 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025, while one participant reported they do not have accreditation. Eight participants did not report their accreditation status. 92 % of the participants used accredited analytical methods at least for a part of the measurements. For this PT, the expert laboratory has code 4 in the result tables.

2.3 Samples and delivery

In this proficiency test each participant received two ground water samples. In one the radon concentration was lower (GRn1; < 1000 Bq/l) and in the other one the radon concentration was higher (GRn2; 1000-8000 Bq/l).

The samples were delivered on 17 May 2021 to the participants abroad and mainly on 18 May 2021 to the national participants. The samples arrived to the participants mainly on 19 May 2021. Three participants received the samples on 20 May 2021 and two participants on 21 May 2021. A new sample was sent to one participant, which arrived on 26 May 2021.

Temperature data loggers were placed in the sample packages of the participants abroad. The loggers measured the temperature inside the cooling bag and the temperature variation during sample transportation was in some cases quite high. During transportation, the highest measured temperatures were about 21 °C. The stability test confirms the stability of the samples at the 20 °C (Appendix 2). Thus, there was no influence on the performance of the participants, which was also confirmed from the participant results.

The samples were requested to be analyzed at the latest on 21 May 2021 and the results to be calculated to the reference time 17 May 2021, 12:00 p.m. (GMT/UTC +3, Helsinki, Finland). The results were requested to be reported at the latest on 24 May 2021. Participants reported the results mainly accordingly, two participants reported the results on 25 May 2021 and one on 27 May 2021. The preliminary results report was delivered to the participants via ProftestWEB and email on 28 May 2021.

2.4 Homogeneity and stability studies

The homogeneity of the samples was determined from ten samples as replicate measurements by liquid scintillation count at STUK. The samples were regarded to be homogenous with the set criteria (Appendix 2).

The stability of the samples was tested by storing three replicate samples at the temperatures of 4 °C and 20 ºC for 48 h. The stability test criteria were met, and the samples were considered stable (Appendix 2). Therefore, in 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 transport and storing.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 3. The comments from the participants focused mainly on sample delivery. The comment from the provider is related to the lacking compliance with the given instructions and to incorrect reporting. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were tested according to Hampel of the Grubbs test before calculating the mean. The results which differed from the data more than $5 \times s_{rob}$ 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 [5].

2.6.2 Assigned values

The assigned values used for evaluation of laboratories performance were the median of the results reported by the participants. The assigned values based on the median are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values.

The reliability of the median as the assigned value was statistically tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value and s_{pt} is the standard deviation for proficiency assessment [3, 4]. The criterion was fulfilled, and the assigned values were considered reliable (Appendix 4). **After reporting the preliminary results report no changes have been done for the assigned values.**

The uncertainties of the assigned values were calculated using the standard deviations [3, 5]. The expanded uncertainties of the assigned values (U_{pt}) were below 5 % (at the 95 % confidence level). Detailed information of the assigned values, their uncertainties and reliability are shown in Appendix 4.

2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated with the z scores.

The standard deviation for proficiency assessment was estimated based on 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 proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set for 20 %. **After reporting the preliminary results report no changes have been done for the standard deviations of the proficiency assessment values.**

The reliability of the standard deviation for proficiency assessment (s_{pt}) and the corresponding z score was estimated by comparing s_{pt} with the standard deviation (s) of the reported results (the uniformity criterion s_{rob} (or s) / $s_{pt} \leq 1.2$) [4]. The criterion was fulfilled in both cases.

3 Results and conclusions

3.1 Results

The summary of the results is presented in Table 1. The terms in the results table are explained in Appendix 5. The results and the performance of each participant are presented in Appendix 6 and the reported results with their expanded uncertainties (k=2) are presented in Appendix 7. The summary of the z scores is shown in Appendix 8 and z scores in the ascending order in Appendix 9.

The robust standard deviations of the results varied from 9 to 10 % and standard deviations were 9.6 % for both samples (Table 1). The robust standard deviations and standard deviations were lower than in the previous similar proficiency test RAD 06/2019, where the robust standard deviations varied from 12 % to 13 % and the standard deviations were 14 % for both samples [6].

Table 1. The summary of the results in the proficiency test RAD 06/2021.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	s	s%	2 x s_{pt} %	n_{all}	Acc z %
^{222}Rn	GRn1	Bq/l	249	246	245	249	24	9.6	24	9.6	20	28	93
	GRn2	Bq/l	5453	5425	5383	5453	491	9.1	521	9.6	20	28	82

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

3.2 Analytical methods

The participants used liquid scintillation count or gamma spectrometry for the measurements in the PT. In total 18 of the result sets were measured with liquid scintillation method and 10 with methods based on gamma spectrometry, of those RADEK gamma spectrometry were used by two participants. Two participating laboratories reported results from both liquid scintillation count and gamma spectrometry techniques and one laboratory reported results from two different liquid scintillation instruments. The used analytical methods and results of the participants grouped by methods are shown in Appendix 10. No statistically significant differences were observed between the used methods. However, gas escape occurs when the sample is transferred from the sample vessel to the measuring vessel. This causes variation to the results especially in gamma spectrometry.

In this proficiency test 64 % of the results were measured with liquid counting technique while in the previous similar proficiency tests RAD 06/2019 and Rn 05/2017 it was 45 % and 35 %, respectively [6, 7]. Further, in this PT 36 % of the results were measured with gamma spectrometry while in the previous similar PTs RAD 06/2019 and Rn 05/2017 it was 52 % and 59 %, respectively. In this PT only 7 % of the results were measured with RADEK gamma spectrometry while in the previous similar PTs it was 38 % and 35 %, respectively [6, 7].

3.3 Uncertainties of the results

Altogether 86 % of the participants reported the expanded uncertainties (k=2) with their results (Appendix 10). The range of the reported uncertainties varied from 4 to 30 % (Table 2). Within the optimal measuring range, the expanded measurement uncertainty (k=2) should typically be 20 – 40 %. Close to the limit of quantification the relative measurement uncertainty is higher. Further, the expanded uncertainties below 5 % could commonly be considered unrealistic. One participant reported very high measurement uncertainties (49 % and 1036 %, not in table 2). It was evident, that these uncertainties had

been reported erroneously as absolute values, not as relative values (%) as the PT organizer had requested. Harmonization of the uncertainties' estimation should be continued.

Several approaches were used for evaluating the measurement uncertainty (Appendix 11). The most commonly used approaches were based on method validation or using the internal quality control data in the estimation. Two participants used MUkit measurement uncertainty software for the estimation of their uncertainties [8]. The free software is available on the webpage: www.syke.fi/envical/en [8, 9]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

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

Measurand	Sample	The range of U_i, %
^{222}Rn	GRn1	6.5-30
	GRn2	3.8-30

4 Evaluation of the results

The performance 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 6). 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, 88 % of the results were satisfactory when total deviation of 20 % from the assigned values were accepted. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar PT, RAD 06/2019, the performance was satisfactory for 88 % of the participant results when total deviation of 30 % from the assigned values were accepted [6]. Altogether 92 % of the participants used accredited analytical methods at least for a part of the measurements and 85 % of those results were satisfactory.

Table 3. Summary of the performance evaluation in the proficiency test RAD 06/2021.

Sample	2 x s_{pt}%	Satisfactory results, %	Remarks
GRn1	20	93	Good performance. In the previous proficiency test RAD 06/2019 90 % of the results were satisfactory when deviation of 30 % from the assigned value was accepted [6].
GRn2	20	82	In the previous proficiency test RAD 06/2019 86 % of the results were satisfactory when deviation of 30 % from the assigned value was accepted [6].

5 Summary

Proftest SYKE carried out the proficiency test (PT) in cooperation with Radiation and Nuclear Safety Authority (STUK) in Finland for the laboratories conducting radon measurements in ground water in May 2021 (RAD 06/2021). Two ground water samples were tested, of which one contained lower (GRn1; < 1000 Bq/l) and the other contained higher radon concentration (GRn2; 1000-8000 Bq/l). In total 25 participants took part in this proficiency test and three of them provided two sets of results. In total 18 of the result sets were measured using liquid scintillation method and 10 using equipments based on gamma spectrometry.

The median of the participant results was used as the assigned value for radon concentration. The performance evaluation was based on the z scores. In total 88 % of the results were satisfactory when deviation of 20 % from the assigned value was accepted. Altogether 92 % of the participants used accredited analytical methods at least for a part of the measurements and 85 % of those results were satisfactory.

No statistically significant differences were observed between the used methods.

6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmäärityksestä toukokuussa 2021. Pätevyyskokeeseen osallistui yhteensä 25 laboratoriota, joista kolme raportoi kahdet tulokset. Tuloksista 18 oli määritetty nestetuikemenetelmällä ja 10 gammaspektrometriaan perustuvalla menetelmällä. Osallistujille toimitettiin kaksi pohjavesinäytettä, joista toisessa radonpitoisuus oli matalampi (GRn1; <1000 Bq/l) ja toisessa korkeampi (GRn2; 1000 - 8000 Bq/l).

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Osallistujien tulosten mediaania käytettiin radonpitoisuuksien vertailuarvoina. Tuloksista hyväksyttäviä oli 88 %, kun radonpitoisuuden sallittiin poiketa vertailuarvosta 20 %. 92 % osallistujista ilmoitti käyttäneensä akkreditoituja analyysimenetelmiä ainakin osassa määrityksiä, ja 85 % ja näistä tuloksista oli hyväksyttäviä.

Nestetuikelaskennalla ja gammaspektrometrialla määritettyjen tulosten välillä ei havaittu tilastollisesti merkitsevää eroa.

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Appendix 1. Participants in the proficiency test

Country	Participant
Belgium	Institute for radioelement, LMR department
Finland	Eurofins Environment Testing Finland Oy, Lahti
	KVVY Tutkimus Oy, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	LUVYLab Oy Ab
	MetropoliLab Oy
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	ScanLab Oy
	STUK, Ympäristön säteilyvalvonta, Mittaus ja Analyysit (MIT)
	Vita Laboratoriot Oy
	ÅMHM laboratoriet, Jomala, Åland
France	Eurofins Eichrom Radioactivite
	Laboratoire CARSO LSEHL
	PearL, Limoges Cedex
Italy	ARPAT
	Environmental Protection Agency of Friuli Venezia Giulia (Arpa FVG)
	Protex Italia Sel
Norway	The Norwegian Radiation Protection Authority
Spain	Unitat de Radioquimica Ambiental i Sanitaria (URAIS)
Sweden	Eurofins Water Testing Sweden AB
	Uppsala Vatten och Avfall AB
United Kingdom	Scottish Water
	South West Water Ltd
United States	Accustar Labs

Appendix 2. Homogeneity and stability of the samples

Homogeneity

Homogeneity was tested from ten samples as replicate measurements by liquid scintillation count at STUK.

Criterion for homogeneity:

$s_{sam}/s_{pt}<0.5$, where

s_{pt} = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

Sample	Concentration Bq/l	n	s_{pt} %	s_{pt}	s_{sam}	s_{saml}/s_{pt}	$s_{sam}/s_{pt}<0.5$?
GRn1	270.9	10	10	27.1	3.80	0.14	Yes
GRn2	5916.7	10	10	591.7	43.5	0.07	Yes

Conclusion: The criterion for homogeneity was fulfilled for both samples and the samples were considered homogenous.

Stability

Stability was tested by analyzing the samples stored at the temperatures 4 °C and 20 °C for 48 hours.

Criterion for stability: $D < 0.3 \times s_{pt}$, where
D = |the difference of results measured from the samples stored at the temperatures 4 °C and 20 °C|
s_{pt} = standard deviation for proficiency assessment

Sample	Result [mg/l]		Sample	Result [mg/l]	
Date	19.5. (4 °C)	19.5. (20 °C)	Date	19.5. (4 °C)	19.5. (20 °C)
GRn1	272.4	265.1	**GRn2**	5837	5765
D	7.03		D	71.4	
$0.3 \times s_{pt}$	7.47		$0.3 \times s_{pt}$	100.4	
D <0.3 × s_{pt}? Yes			**D <0.3 × s_{pt}? Yes**		

Conclusion: The criterion for stability was fulfilled for both samples and the samples were considered stable.

Appendix 3. Feedback from the proficiency test

Feedback from the participants

Participant	Comments on technical excecution	Action / Proftest SYKE
All	The question of the arrival temperature had been accidentally left on the Sample arrival form.	The organizer apologizes this. The sample arrival form was corrected on the website.
2	The participant informed that the samples arrived too late since the analysis should be done before 21.05.2021 and the scheduled data for the arrival was 18.05.2021.	As informed in the information and sample letters, the sample dispatch day was scheduled on 18.05.2021 and the foreseen date of arrival was 19.05.2021. The participant received the samples slightly delayed, on 21.05.2021. The transportation service provider did not deliver the package within the agreed time. The organizer apologizes this.
17	The participant reported that when the sample container was opened, the red light of the electronic temperature data logger did not flash.	As the red light of the temperature data logger was not flashing, the participant could not turn off the temperature data logger. However, the device measured the temperature normally so temperature data was collected and analyzed normally. The organizer checks that the loggers are working properly and will clarify the instructions for using the logger.
21	One sample container had broken during transportation.	A new sample was delivered to the participant. The sample was analysed on 26 May 2021. The delay had no effect on the performance of the participants.

Feedback to the participants

Participant	Comments
All	Some participants received the samples slightly delayed (Chapter 2.3). According to the results the delay had no direct effect on the performance of the participants.
All	After the sample delivery the organizer noticed that the concentration levels of the samples were informed erroneously in the information and sample letters. The informed concentrations referred to wrong samples. Further, the final concentration of the sample GRn2 was higher than foreseen. The correct concentration levels were: GRn1 <1000 Bq/l and GRn2 1000–8000 Bq/l Earlier informed concentration levels were GRn1 1000–5000 Bq/l and GRn2 <1000 Bq/l. The participants were informed, and the updated sample letter was uploaded to ProftestWEB immediately after the issue was noticed. The organizer apologized for any problems or inconvenience this change of the original plan may have caused. The organizer will develop its activities.
1, 15, 16	The participant did not inform the accreditation status of their method for some measurands. The participants should follow the instructions of the organizer.
6	The participant reported absolute measurement uncertainty, but the request from the organizer was to report the relative measurement uncertainty. The participant should follow the instructions of the organizer.
7, 22, 29	The participants did not report the expanded measurement uncertainties for some measurands as required. The measurement uncertainty should be reported with the results obtained with accredited method.

Appendix 4. Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
^{222}Rn	GRn1	Bq/l	249	10	4.0	Median	0.20
	GRn2	Bq/l	5453	224	4.1	Median	0.21

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable.

Appendix 5. Terms in the results tables

The information could be applied according to the PT.

Measurand The tested parameter

Sample The code of the sample

Assigned value The value attributed to a particular property of a proficiency test item

Participant's result The result reported by the participant (when replicate results are reported, the mean value)

2 × s_{pt} % The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level

z score Used for the participant's perfomance evaluation in the PT.
Calculated with formula:

$$z = (x_i - x_{pt})/s_{pt}, \text{ where}$$

x_i = the result of the individual participant
x_{pt} = the assigned value
s_{pt} = the standard deviation for proficiency assessment

Interpretation of the z scores

$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable (warning signal), the result deviates more than 2 × s_{pt} from the assigned value.
$\lvert z \rvert \geq 3$	Unsatisfactory (action signal), the result deviates more than 3 × s_{pt} from the assigned value.

E_n score Error, normalized – Used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. Calculated with formula:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

U_i = the expanded uncertainty of a participant's result
U_{pt} = the expanded uncertainty of the assigned value

Interpretation of the E_n scores

$\lvert E_n \rvert \leq 1.0$	Satisfactory, should be taken as an indicator of successful performance when the uncertainties are valid.
$\lvert E_n \rvert > 1.0$	Unsatisfactory (action signal), could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

Md Median

s Standard deviation

s % Standard deviation, %

n_{stat} Number of results in statistical processing

More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Proftest SYKE Guide for participants [2, 3, 5].

Appendix 6. Results of the participants

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.52	249	20	262	249	246	24	9.6	23
	Bq/l	GRn2		0.32	5453	20	5626	5453	5425	521	9.6	22

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.33	249	20	216	249	246	24	9.6	23
	Bq/l	GRn2		-1.22	5453	20	4790	5453	5425	521	9.6	22

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.48	249	20	237	249	246	24	9.6	23
	Bq/l	GRn2		0.18	5453	20	5550	5453	5425	521	9.6	22

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.56	249	20	263	249	246	24	9.6	23
	Bq/l	GRn2		0.29	5453	20	5613	5453	5425	521	9.6	22

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.41	249	20	214	249	246	24	9.6	23
	Bq/l	GRn2		-1.24	5453	20	4775	5453	5425	521	9.6	22

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.69	249	20	232	249	246	24	9.6	23
	Bq/l	GRn2		-0.97	5453	20	4922	5453	5425	521	9.6	22

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.85	249	20	203	249	246	24	9.6	23
	Bq/l	GRn2		-2.76	5453	20	3950	5453	5425	521	9.6	22

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.05	249	20	248	249	246	24	9.6	23
	Bq/l	GRn2		0.08	5453	20	5496	5453	5425	521	9.6	22

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.84	249	20	270	249	246	24	9.6	23
	Bq/l	GRn2		0.50	5453	20	5727	5453	5425	521	9.6	22

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.29	249	20	217	249	246	24	9.6	23
	Bq/l	GRn2		-1.12	5453	20	4840	5453	5425	521	9.6	22

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.68	249	20	232	249	246	24	9.6	23
	Bq/l	GRn2		-0.68	5453	20	5082	5453	5425	521	9.6	22

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-2.16	249	20	195	249	246	24	9.6	23
	Bq/l	GRn2		-1.84	5453	20	4451	5453	5425	521	9.6	22

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.37	249	20	215	249	246	24	9.6	23
	Bq/l	GRn2		-2.11	5453	20	4300	5453	5425	521	9.6	22

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.20	249	20	254	249	246	24	9.6	23
	Bq/l	GRn2		0.19	5453	20	5555	5453	5425	521	9.6	22

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.16	249	20	253	249	246	24	9.6	23
	Bq/l	GRn2		-0.41	5453	20	5227	5453	5425	521	9.6	22

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.80	249	20	229	249	246	24	9.6	23
	Bq/l	GRn2		-0.78	5453	20	5030	5453	5425	521	9.6	22

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		1.97	249	20	298	249	246	24	9.6	23
	Bq/l	GRn2		2.23	5453	20	6670	5453	5425	521	9.6	22

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.00	249	20	249	249	246	24	9.6	23
	Bq/l	GRn2		-0.64	5453	20	5103	5453	5425	521	9.6	22

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.44	249	20	260	249	246	24	9.6	23
	Bq/l	GRn2		0.32	5453	20	5630	5453	5425	521	9.6	22

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.32	249	20	257	249	246	24	9.6	23
	Bq/l	GRn2		0.99	5453	20	5992	5453	5425	521	9.6	22

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.84	249	20	203	249	246	24	9.6	23
	Bq/l	GRn2		-3.72	5453	20	3424	5453	5425	521	9.6	22

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		1.83	249	20	295	249	246	24	9.6	23
	Bq/l	GRn2		1.91	5453	20	6496	5453	5425	521	9.6	22

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.32	249	20	257	249	246	24	9.6	23
	Bq/l	GRn2		0.67	5453	20	5820	5453	5425	521	9.6	22

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.44	249	20	238	249	246	24	9.6	23
	Bq/l	GRn2		-0.44	5453	20	5211	5453	5425	521	9.6	22

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.00	249	20	249	249	246	24	9.6	23
	Bq/l	GRn2		-0.08	5453	20	5409	5453	5425	521	9.6	22

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.37	249	20	215	249	246	24	9.6	23
	Bq/l	GRn2		-1.22	5453	20	4790	5453	5425	521	9.6	22

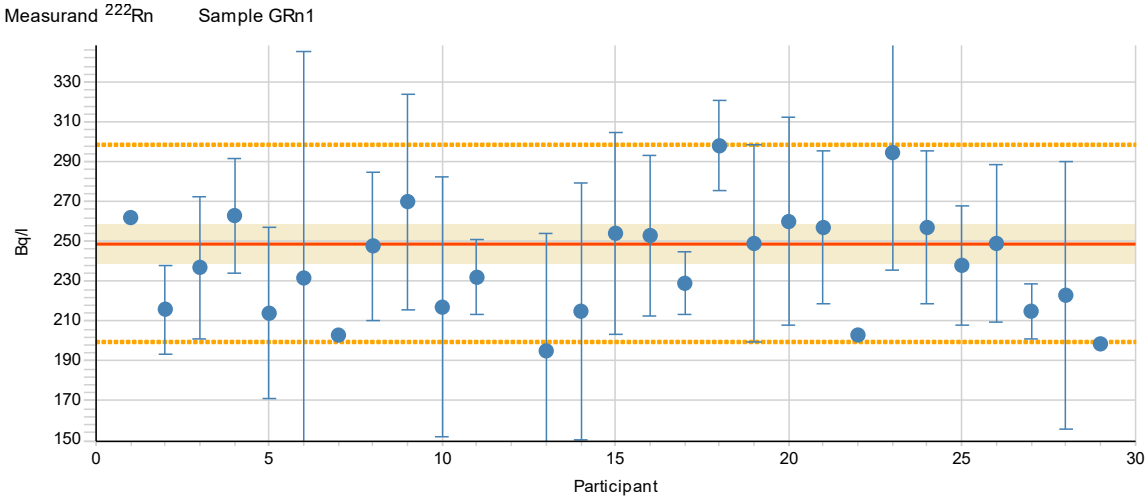
Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.04	249	20	223	249	246	24	9.6	23
	Bq/l	GRn2		-0.54	5453	20	5160	5453	5425	521	9.6	22

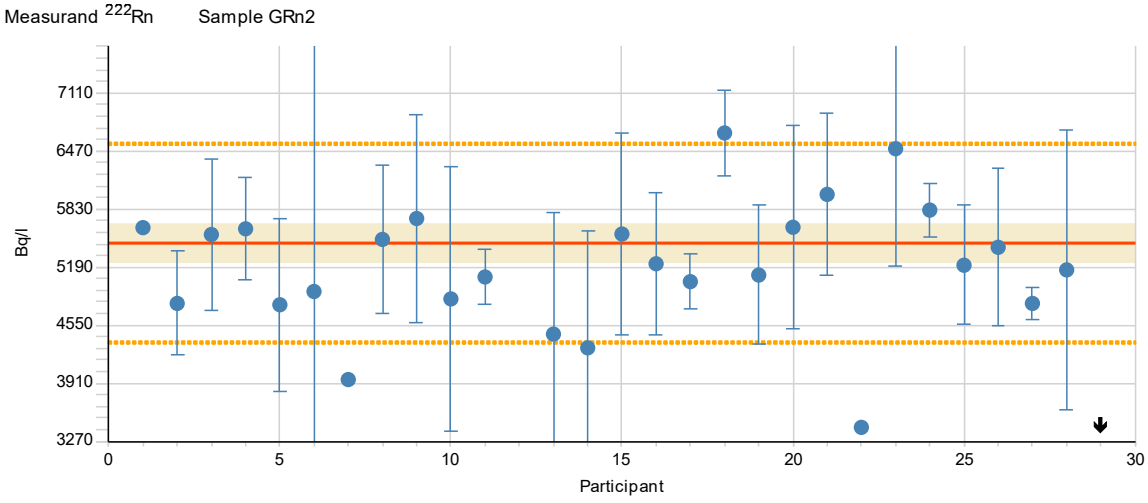
Participant 29												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-2.02	249	20	199	249	246	24	9.6	23
	Bq/l	GRn2		-4.06	5453	20	3238	5453	5425	521	9.6	22

Appendix 7. 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 uncertainty of the assigned value, and the arrow describes the value outside the scale.





Appendix 8. Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	13	14	15	16	17	18	19	20	21	22	23	%
^{222}Rn	GRn1	*S*	**S**	**S**	**S**	*S*	**S**	**S**	**S**	**S**	**S**	**S**	**q**	**S**	**S**	**S**	**S**	**S**	**S**	**S**	**S**	**S**	**S**	92.9
	GRn2	S	**S**	**S**	**S**	*S*	**S**	**q**	**S**	**S**	**S**	**S**	**S**	**q**	S	S	*S*	**Q**	**S**	**S**	**S**	**u**	**S**	82.1
%		100	100	100	100	100	100	50	100	100	100	100	50	50	100	100	100	50	100	100	100	50	100	
accredited			2	2	2		2	2	2	2	2	2	2	2	1	1	1	2	2	2	2	2	2	

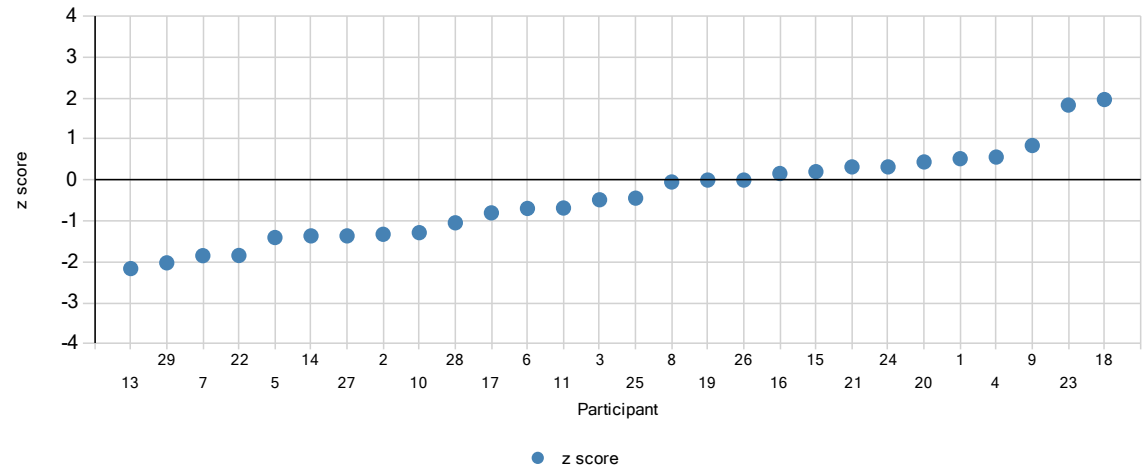
Measurand	Sample	24	25	26	27	28	29	%
^{222}Rn	GRn1	**S**	**S**	**S**	*S*	**S**	**q**	92.9
	GRn2	**S**	**S**	**S**	*S*	**S**	**u**	82.1
%		100	100	100	100	100	0	
accredited		2	2	2		2	2	

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

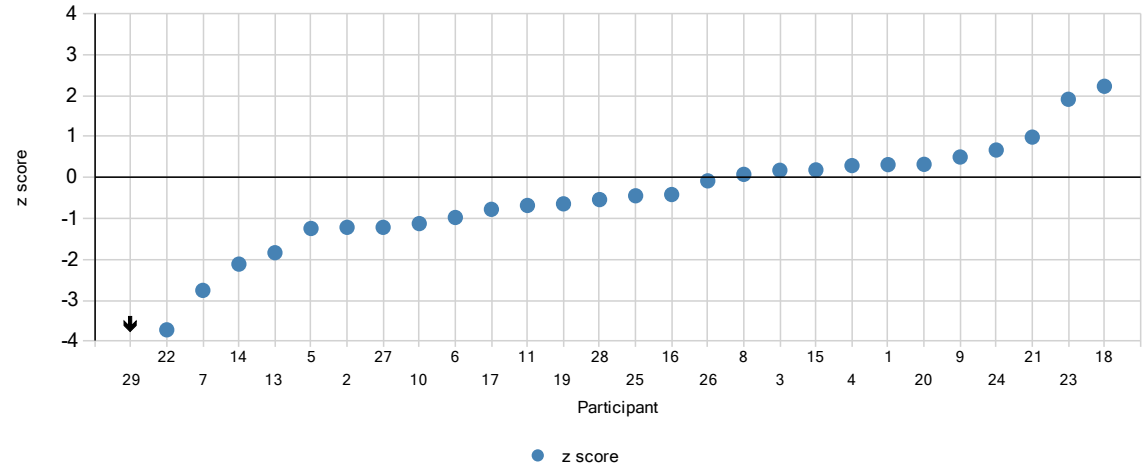
Totally satisfactory, % in all: 88 % in accredited: 85 % in non-accredited: 100

Appendix 9. z scores in ascending order

Measurand ^{222}Rn Sample GRn1

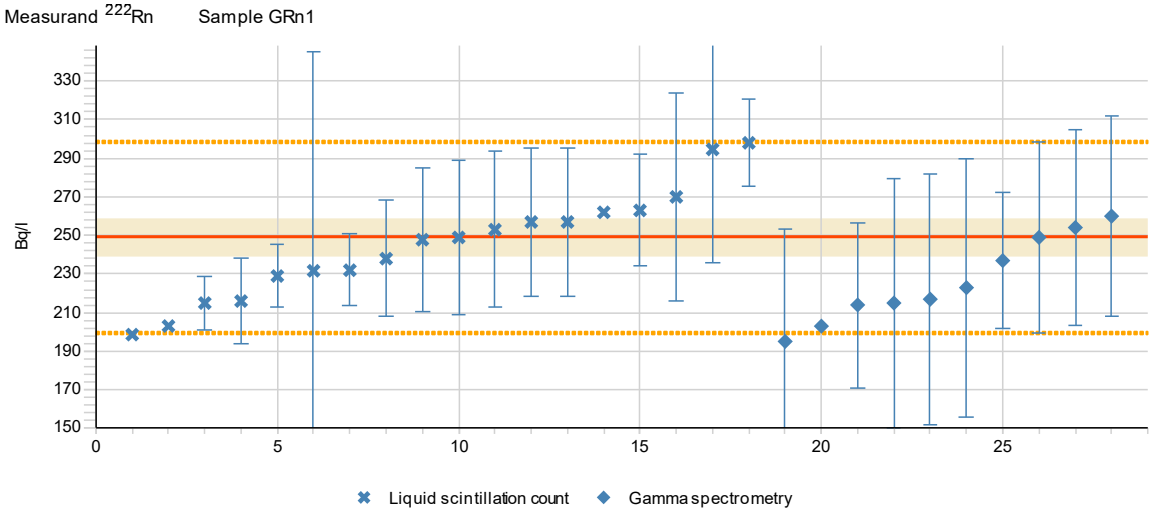


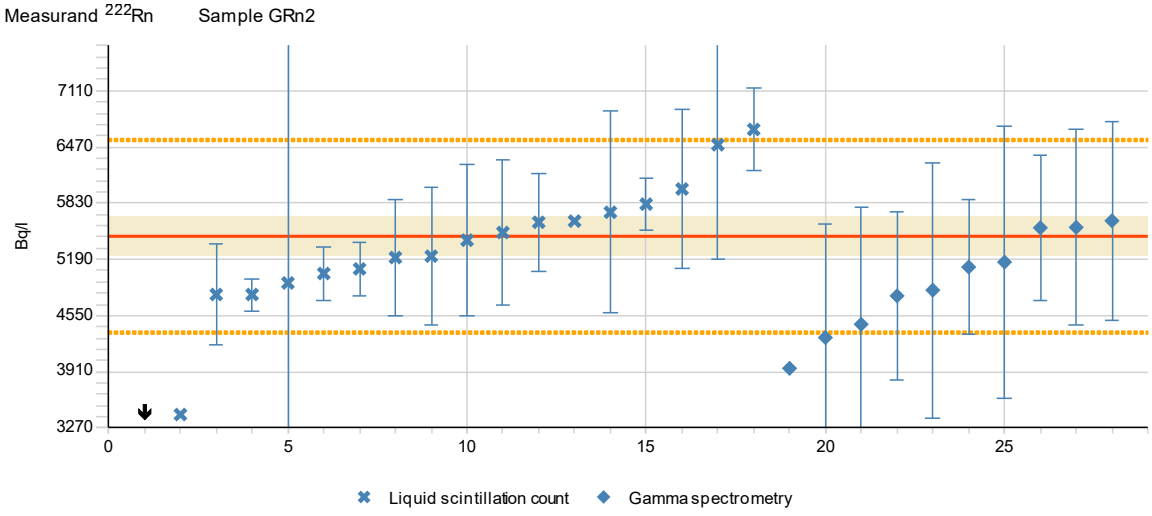
Measurand ^{222}Rn Sample GRn2



Appendix 10. Results grouped according to the methods

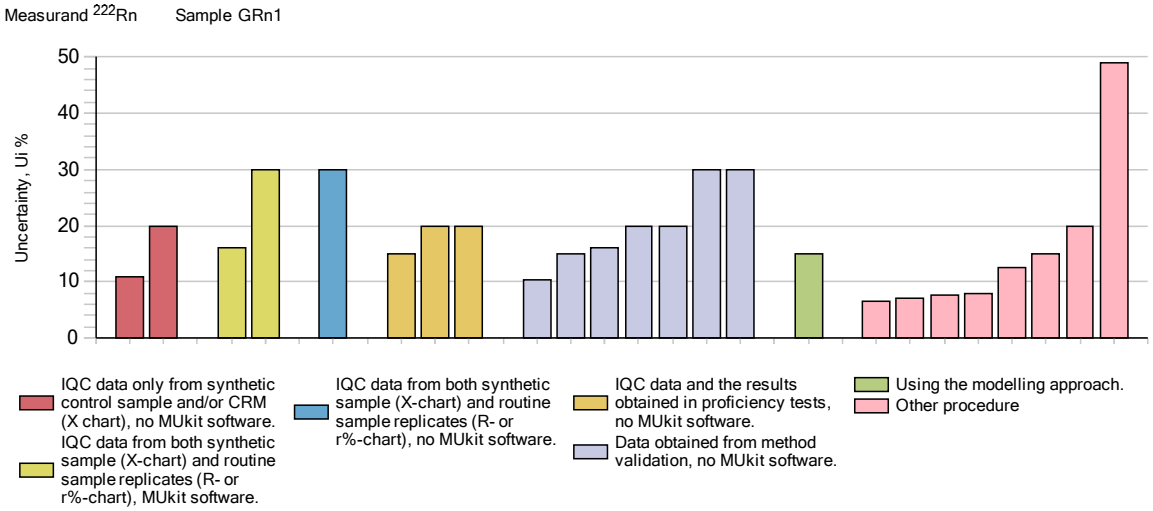
The explanations for the figures are described in the Appendix 7. The results are shown in ascending order.

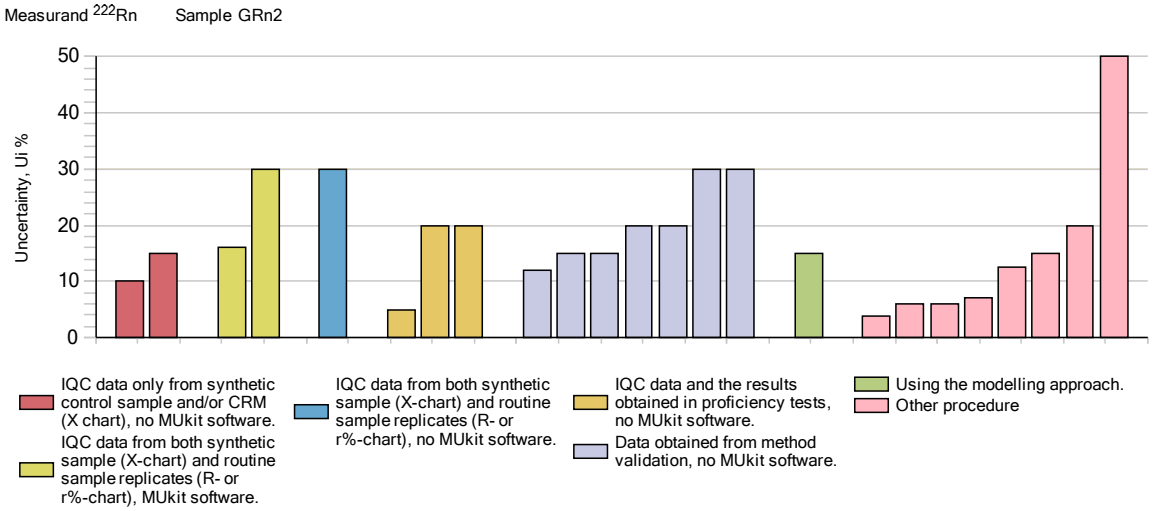




Appendix 11. Examples of measurement uncertainties reported by the participants

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 [8, 9] or using a modelling approach based [10, 11].





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