REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2019

Interlaboratory Proficiency Test 06/2019

Radon in ground water

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

Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2019

Interlaboratory Proficiency Test 06/2019

Radon in ground water

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

[1] Finnish Environment Institute (SYKE), Laboratory Centre, Helsinki, Finland
[2] Raditional and nuclear Safety Authority, STUK, Helsinki, Finland

Proftest SYKE

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

Helsinki 2019
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2019
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 978-952-11-5045-6 (pbk.)
ISBN 978-952-11-5046-3 (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)
Latokartanonkaari 11, FI-00790 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2019

SYKE

ABSTRACT

Interlaboratory Proficiency Test 06 /2019

In April 2019 Proftest SYKE carried out the proficiency test (PT) for analysis of radon in ground water (RAD 06/2019) in cooperation with the Finnish Radiation and Nuclear Safety Authority (STUK) for laboratories conducting radon measurements in ground water. In total, 27 participants took part in the proficiency test. Two ground water samples containing low concentration of radon (<1000 Bq/l) were tested. The robust means of the participants' results were used as the assigned value for radon concentrations. The evaluation of the results was based on z scores. In total 88 % of the results was satisfactory when deviations of 30 % from the assigned value was accepted. The previously observed statistically significant differences between the liquid scintillation method and Radek-gamma spectrometry were not detected in this test.
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 06/2019

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmäärityksestä huhtikuussa 2019. Pätevyyskokeessa oli 27 osallistujaa. Pätevyyskoetta varten osallistujille lähetetään kaksi pohjavesinäytettä, joissa radonpitoisuus oli matala (<1000 Bq/l). Osallistujien robustia keskiarvoa käytettiin radonpitoisuuksien vertailuarvoina ja tulokset arvioitiin z-arvojen avulla. Tuloksista hyväksyttäviä oli 88 %, kun radonpitoisuuden sallittiin poiketa vertailuarvosta 30 %. Aikaisemmissa pätevyyskoekierroksilla todettua eroa nestetuikelaskennan ja Radek-mittausten välillä ei havaittu. Lämmin kiitos kaikille osallistujille!

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

SAMMANDRAG

Provningsjämförelse 06/2019

I april 2019 genomförde Proftest SYKE i samarbete med Strålsäkerhetscentralen (STUK) en provningsjämförelse som omfattade radonmätning i grundvatten. Sammanlagt 27 laboratorier deltog i jämförelsen. Två vattenprov med låg halt av radon (<1000 Bq/l) testades. Som referensvärde användes deltagarnas robusta medelvärden. Totalt 88 % av resultaten var godkända när 30 % variation godkändes. Tidigare skillnader mellan resultat producerade med olika metoder observerades inte här.
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 (RAD 06/2019) 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 is 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 the proficiency test

2.1 Responsibilities

Organizer
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4, 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 27 laboratories participated in this proficiency test (Appendix 1), of which two participants provided two set of results. In total, 20 of the participants reported that they have accredited quality management system based on ISO/IEC 17025, while eight participants did not have accreditation and one did not report its accreditation status. (Appendix 6).

2.3 Samples and delivery

In this proficiency test each participant received two ground water samples, of which both, contrary to the preliminary information, contained low concentration of radon (<1000 Bq/l). The samples were collected on April 1, 2019 and delivered on the following day. The samples arrived to the participants mainly on the following day. Participant 15 received the samples on April 4, 2019 and participant 23 analysed a new sample received on the following week on April 9, 2019. A temperature data logger was included in some of the sample packages (Table 1). Although in some cases the temperatures in the sample packages were high for some time, this was not reflected in the results of the participants.

The samples were requested to be measured latest on April 5, 2019 and the results to be calculated to the reference time April, 1 2019 at noon (Finnish time; GMT/UTC + 3 h). Participants delivered the results accordingly, participant 23 delivered the results on 10 April 2019. The preliminary results were delivered to the participants ProftestWEB and via email on April 17, 2019.

Table 1. Minimum, mean and maximum temperature recorded by the data loggers during the sample transport in RAD 06/2019.

Participant	Min (°C)	Mean (°C)	Max (°C)	Additional info
3	7.4	15.0	24.0	About 20 °C for last 24 hours? Sample arrival form not returned by the participant.
5	6.4	11.2	21.5	Less than 2 h above 20 °C
11	6.5	11.3	21.6	Less than 1 h above 20 °C
12	4.9	10.4	21.6	Less than 1 h above 20 °C
13	8.5	11.7	21.5	Last 20 h above 10 °C
19	9.2	10.5	21.7	
22		ca. 12		Estimation; Logger not swift off after arrival.
23	6.5	8.8	22.4	
25	4.7	7.8	22.0	
29	6.8	9.7	21.8	

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

Sample	Unit	n	Mean	s	s_{pt} (%)	0.5 × s_{pt}	Is s < 0.5 × s_{pt}?
GRn1	Bq/l	10	224	2.6	34 (15 %)	17	Yes
GRn2	Bq/l	10	425	5.6	64 (15 %)	32	Yes

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

Table 3. Results of the radon stability testing of three parallel samples at the temperature +22˚ C. The expanded measurement uncertainties (U_i) of the results are indicated in brackets.

	Mean (U_i) Bq/l					
Sample	On day of delivery (n= 10)	Kept at room temperature for 3 days (n=3)	Difference after keeping (%)	s_{pt} of proficiency test	0.3 x s_{pt}	Is differences in mean ≤ 0.3 ×s_{pt}?
GRn1	224 (11)	219 (11.2)	5 (2 %)	34	10.1	Yes
GRn2	425 (22)	426 (21.6)	-1 (0.2 %)	64	19.1	Yes

n: the number of parallels, $s_{pt:}$ 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 three parallel samples for 72 h in room temperature (+22 °C). The results were compared to concentrations of the samples measured by scintillation count immediately after sampling on Monday the April 1, 2019 at STUK (Table 3). The stability test criteria were met and the samples were considered stable. Therefore 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 (Table 3).

2.5 Feedback from the proficiency test

The comments from the participants mainly dealt concerns about the samples or erroneously reported results (Appendix 2). All the feedback is valuable and is exploited when improving the proficiency scheme. The organizer's feedbacks to the participants are:

- Contrary information before the test, the concentrations of both samples are below 1000 Bg/l. We apologize for any problems this deviation from the original plan may have caused you. In the evaluations we have taken into account the possibility of higher natural variation due to low concentrations and difficult samples.
- 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. Within the optimal measuring range, the expanded measurement uncertainty (*k=2*) should not typically exceed 50 %.

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 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 robust means of the participants' results (Table 4). Because the robust means of the participants' results were used as assigned values, the assigned values also include any variation caused by changes that may have occurred during transportation. The expanded measurement uncertainties of the assigned values (U_{pt}) were below 10 % (*k=2*).

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 4). **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 30 %. Differently from the previous similar proficiency test Rn 05/2017, all different methods used by the participants were combined into the same measurand [5].

Table 4. The assigned values and their uncertainties.

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned values	u_{pt}/s_{pt}
^{222}Rn	GRn1	Bq/l	204	13	6.4	Robust mean	0.21
	GRn2	Bq/l	377	25	6.7	Robust mean	0.22

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

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 both 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 3. The results and the performance of each participant are presented in Appendix 4 and the reported results with their expanded uncertainties (*k*=2) are presented in Appendix 5. The summary of the results are in Table 5. The summary of the z scores is shown in Appendix 6 and z scores in the ascending order in Appendix 7.

The robust standard deviations of the results varied from 13 to 14 % (Table 5). The robust standard deviations were slightly higher than in the previous similar proficiency test Rn 05/2017, where the deviations varied from 8 % to 12 % [5].

3.2 Analytical methods

In total 13 of the participants used the liquid scintillation method, 11 used Radek-gamma spectrometry and four used other methods based on gamma spectrometry (Appendix 8). One participant did not report the analytical method used. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5.

Table 5. The summary of the results in the proficiency test RAD 06/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc z %
^{222}Rn	GRn1	Bq/l	204	205	204	207	27	13.2	30	29	90
	GRn2	Bq/l	377	374	377	385	52	13.7	30	29	86

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{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 number of the participants.

Table 6. Mean values and standard variations (s%) between the different methods used in the proficiency test RAD 06/2019.

	Mean Bq/l (s%)	
Sample	GRn1	GRn2
Rn liquid scintillation count	209 (17)	391 (18)
Rn gamma spectrometry	210 (18)	378 (11)
Rn gamma spectrometry using RADEK	198 (9)	353 (7)

Table 7. 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	5.1-37.13
	GRn2	5-95.36

The previously observed statistically significant differences between the liquid scintillation method and Radek-gamma spectrometry were not detected in this test [5] (Appendix 8). In the turbid and colored sample GRn1 the liquid scintillation count and gamma spectrometry caused higher variation between results than RADEK measurements. In GRn2 the liquid scintillation count caused twice as high variation as both gamma spectrometrical methods (Table 6).

3.3 Uncertainties of the results

All participants except 11 and 12 reported the expanded uncertainties (*k*=2) with their results (Appendix 8). The range of the reported uncertainties varied between the measurands and the sample types, and thus the harmonization of the uncertainties estimation should be continued (Appendix 9).

The range of the reported uncertainties varied between the measurements and the sample types from 5-95 % (Table 7). Within the optimal measuring range, the expanded measurement uncertainty (*k*=2) should not typically exceed 50 %.

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.

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. A comprehensive study on many technical details affecting the uncertainty of radon – in-water analyses has recently been published [6].

Several approaches were used for estimating of measurement uncertainty (Appendix 9). Most commonly data from method validation was used. Three participants used MUkit measurement uncertainty software for the estimation of its uncertainties [7]. 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 9).

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 the performance assessment (Appendix 7). The z score was 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 30 % from the assigned value was accepted (Appendix 6). The summary of the performance evaluation and comparison to the previous performance is presented in Table 8. In the previous similar proficiency test Rn 05/2017, the performance was satisfactory for 78 % of the all participants when the standard deviations for proficiency assessment at the 95 % confidence level were set to 17-25 % [5].

The radon concentration in sample GRn1 was unexpectedly low compared to previous rounds of this proficiency test. One reason for this phenomenon may be that the samples were taken already in April and not later in spring as in previous rounds. It is possible, that the water from the groundwater occurrence has not been used for a long time. Then the radon in the ground water decays and the result is low. Another less likely explanation may be that the water flow in the bedrock had changed and the incoming water originated from a less radon rich area.

Table 8. Summary of the performance evaluation in the proficiency test RAD 06/2019.

Measurand	Sample	2 x s_{pt}%	Satisfactory	Remarks
^{222}Rn	GRn1	30	90	Good performance. In the previous proficiency test Rn 05/2017 the performance was satisfactory for 70-82 % of the results when standard deviation for proficiency assessment was 17 % [5].
^{222}Rn	GRn2	30	86	Good performance. In the previous proficiency test Rn 05/2017 the performance was satisfactory for 81-82 % of the results when standard deviation for proficiency assessment was 17-25 % [5].

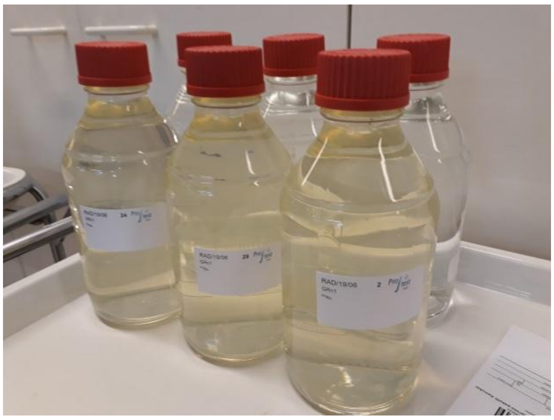


Figure 1. Sample bottles in RAD 06/2019. In the front is the, slightly colored and turbid sample GRn1, and in the back colourless sample GRn2.

According to the analytical experts of this proficiency test, the turbidity observed especially in sample GRn1 is not likely to affect the results obtained by gamma spectrometry. High turbidity of samples may cause quenching in liquid scintillation count methods. The experts consider the turbidity in these samples not high enough to affect the results. The yellow color of the GRn1 samples is not likely to affect the results by any method. The variations between the participants' results were similar in both samples and do therefore not reflect any impact of turbidity or color (Table 6). The results of the participants do not therefore indicate that the turbidity and color of GRn1 increase variation between results.

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 April 2019. In total 27 participants took part in this PT. In total 13 of the participants used liquid scintillation method and 15 used equipment based on gamma spectrometry. One participant did not report the method used.

Two ground water samples containing low concentration of radon (<1000 Bq/l) were tested. The turbidity and color observed in sample GRn1 did not have any observed impact on the results. The robust means of the participants' results were used as the assigned value for radon concentrations. The evaluation of the results was based on z scores. In total 88 % of the results was satisfactory when deviations of 30 % from the assigned value was accepted.

The previously observed statistically significant differences between the liquid scintillation method and Radek-gamma spectrometry were not detected in this test.

6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmäärityksestä huhtikuussa 2019. Pätevyyskokeessa oli 27 osallistujaa, joista 15 määritti radonin gammaspektrometrialla ja 13 nestetuikemenetelmällä. Yksi osallistuja ei ilmoittanut käytettyä analyysimenetelmää.

Pätevyyskoetta varten osallistujille lähetetään kaksi pohjavesinäytettä, joissa radonpitoisuus oli matala (<1000 Bq/l). Näytteessä GRn1 havaittu sameus ja väri ei vaikuttanut tuloksiin. Osallistujien robustia keskiarvoa käytettiin radonpitoisuuksien vertailuarvoina ja tulokset arvioitiin z-arvojen avulla. Tuloksista hyväksyttäviä oli 88 %, kun tulosten sallittiin poiketa vertailuarvosta 30 %.

Aikaisemmissa pätevyyskoekierroksilla todettua eroa nestetuikelaskennan ja Radek-mittausten välillä ei havaittu.

REFERENCES

1. SFS-EN ISO 17043, 2010. Conformity assessment – General requirements for Proficiency Testing.

2. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.

3. Thompson, M., Ellison, S. L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report). Pure Appl. Chem. 78: 145-196, www.iupac.org.

4. Proftest SYKE Guide for laboratories: www.syke.fi/proftest/en → Current proficiency tests www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886.

5. Björklöf, K., Simola, R., Leivuori, M., Tervonen, K., Lanteri, S. and Ilmakunnas, M. (2017). Interlaboratory Proficiency Test 05/2017, Radon in ground water. Reports of the Finnish Environment Institute 22/2017. http://hdl.handle.net/10138/199819.

6. Jobbágy, V., Stroh, H., Marissens and Hult. M. (2019). Comprehensive study on the technical aspects of sampling, transporting and measuring radon-in-water. J. Env. Rad., 197, 30-38.

7. Näykki, T., Virtanen, A. and Leito, I., 2012. Software support for the Nordtest method of measurement uncertainty evaluation. Accred. Qual. Assur. 17: 603-612. MUkit website: www.syke.fi/envical.

8. Magnusson B., Näykki T., Hovind H., Krysell M., Sahlin E., 2017. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. Nordtest Report TR 537 (ed. 4). (http://www.nordtest.info)

9. Ellison, S., L., R. and Williams, A. (Eds). (2012) Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, ISBN 978-0-948926-30-3.

10. ISO/IEC Guide 98-3:2008. Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995).

APPENDIX 1: Participants in the proficiency test

Country	Participant
Belgium	Insitut National des Radio-Eléménts (I.R.E) Joint Research Centre (JRC), JRC-Geel, Unit G.2. Standards for Nuclear Safety, Security and Security and Safeguards
Finland	Eurofins Environment Testing Finland Oy, Lahti KVVY Tutkimus Oy, Tampere Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku MetropoliLab Oy Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta Savo-Karjalan Ympäristötutkimus Oy, Joensuu Savo-Karjalan Ympäristötutkimus Oy, Kajaani Savo-Karjalan Ympäristötutkimus Oy, Kuopio ScanLab Oy SeiLab Oy Seinäjoen toimipiste Vita Laboratoriot Oy ÅMHM laboratoriet, Jomala, Åland
France	Eichrom Laboratoires, Bruz, France IRSN, Le Vesinet, France Laboratoire CARSO LSEHL Laboratoire Phytocontrol PearL, Limoges Cedex, France
Italy	A.R.P.A. Umbria Arpa Lompardia, CRR - Centro Regionale di Radioprotezione
Norway	The Norwegian Radiation Protection Authority
Spain	Unitat de Radioquímica Ambiental i Sanitària, URAIS
Sweden	Eurofins Water Testing Sweden AB
United Kingdom	Scottish Water, UK South West Water Ltd United Utilities Water company

APPENDIX 2: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
11	We have a very simple method for analyzing radon in water and do not have a procedure for calculating the estimation of the expanded measurement uncertainty. We usually report our results by giving the result plus the standard deviation.	We collect the information of the measurement uncertainty in percentage as we compile the info to the final report. You select from dropdown menu “Other procedure” and insert the measurement uncertainty as percentage (expanded). In the latter way you MU will be compared to the others.
19	Samples were overcooled and with large air bubbles.	We are aware that our sampling procedure causes a gas space in the sample bottles. Usually this has not caused problems in performance evaluations, because the variations between the participants’ results have been relatively low. The air bubbles cause a systematic error in relation to the true value that does not relevantly affect performance evaluations. The temperature data logger included in the package, did not indicate significant warming or cooling of the sample packages. This is shown by the fact that the standard deviations for the PT have usually been relatively low.
19	Sample GRn1was yellow brownish and both samples contained suspended materials.	We feel it is important to use real samples in the test, because this gives a better understanding about the real competence of the participants. The color and turbidity of the samples might cause a systematic error in relation to the true value that does not relevantly affect performance evaluations. The turbidity and color observed in sample GRn1 did not have any observed impact on the results compared to sample GRn2 according the results of PT.
19	What can we use to separate decimals? Comma (,) or period (.)?	Both separation signs are possible.
19	Why is more than one significant digit requested in the results?	We ask for more decimals because in some cases the data set might be difficulties to handle statistically without additional decimals.
19	Why do you ask for extra fee for every additional reported result set?	Proftest SYKE is running on commercial basis, and thus extra result handling is not included in the participation fee.
23	The samples supplied were incomplete. In both sample bottles at least 20-30 ml sample were missing. It was checked that no water leakage was visible in the cool box.	New samples were sent to the participant. The new samples were received on Tuesday 9.4.2019. The participant analyzed them on Wednesday 10.4.2019, and the results were included in the database.

Participant	Comments to the results	Action / Proftest SYKE
21	The participant informed that they were calculated their GRn2 result erroneously. The corrected result was 380 Bq/l.	The result was treated as an outlier and thus not included in the calculation of assigned value. If the results had been reported correctly, the result for the sample GRn2 would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].
24	The control sample (milk powder) which was tested after the intercalibration samples were not within the alarm limit (393- 462 Bq/kg), but was within the action limit (376 – 479 Bq/kg).	Thank you for this additional information. Milk powder is a very different matrix compared to water but it seems you quality control measures are functioning well.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
All	Contrary information before the test, the concentrations of both samples are below 1000 Bg/l. We apologize for any problems this deviation from the original plan may have caused you. In the evaluations we have taken into account the possibility of higher natural variation due to low concentrations and difficult samples.
9,13, 18, 19, 30	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.

APPENDIX 3: 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 value attributed to a particular property of a proficiency test item
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
s	Standard deviation
s %	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, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,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 …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 4: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		7.67	204	30	439	207	205	23	11.3	27
	Bq/l	GRn2		-2.25	377	30	250	385	374	52	13.9	26

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.26	204	30	212	207	205	23	11.3	27
	Bq/l	GRn2		0.35	377	30	397	385	374	52	13.9	26

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.29	204	30	195	207	205	23	11.3	27
	Bq/l	GRn2		-0.73	377	30	336	385	374	52	13.9	26

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.85	204	30	230	207	205	23	11.3	27
	Bq/l	GRn2		0.23	377	30	390	385	374	52	13.9	26

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.13	204	30	200	207	205	23	11.3	27
	Bq/l	GRn2		-0.09	377	30	372	385	374	52	13.9	26

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.20	204	30	210	207	205	23	11.3	27
	Bq/l	GRn2		-0.14	377	30	369	385	374	52	13.9	26

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.33	204	30	214	207	205	23	11.3	27
	Bq/l	GRn2		0.58	377	30	410	385	374	52	13.9	26

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.95	204	30	175	207	205	23	11.3	27
	Bq/l	GRn2		1.31	377	30	451	385	374	52	13.9	26

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.98	204	30	174	207	205	23	11.3	27
	Bq/l	GRn2		-1.04	377	30	318	385	374	52	13.9	26

Participant 11													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.11	204	30	170	207	205	23	11.3	27
	Bq/l	GRn2		0.41	377	30	400	385	374	52	13.9	26

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.93	204	30	145	207	205	23	11.3	27
	Bq/l	GRn2		-1.91	377	30	269	385	374	52	13.9	26

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.18	204	30	199	207	205	23	11.3	27
	Bq/l	GRn2		0.24	377	30	391	385	374	52	13.9	26

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.10	204	30	207	207	205	23	11.3	27
	Bq/l	GRn2		-0.58	377	30	344	385	374	52	13.9	26

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.29	204	30	213	207	205	23	11.3	27
	Bq/l	GRn2		0.16	377	30	386	385	374	52	13.9	26

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.33	204	30	214	207	205	23	11.3	27
	Bq/l	GRn2		0.23	377	30	390	385	374	52	13.9	26

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.24	204	30	166	207	205	23	11.3	27
	Bq/l	GRn2		-0.90	377	30	326	385	374	52	13.9	26

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.07	204	30	202	207	205	23	11.3	27
	Bq/l	GRn2		0.11	377	30	383	385	374	52	13.9	26

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.36	204	30	215	207	205	23	11.3	27
	Bq/l	GRn2		0.66	377	30	414	385	374	52	13.9	26

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		1.83	204	30	260	207	205	23	11.3	27
	Bq/l	GRn2		3.94	377	30	600	385	374	52	13.9	26

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		2.45	204	30	279	207	205	23	11.3	27
	Bq/l	GRn2		-2.58	377	30	231	385	374	52	13.9	26

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.75	204	30	227	207	205	23	11.3	27
	Bq/l	GRn2		0.83	377	30	424	385	374	52	13.9	26

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.21	204	30	198	207	205	23	11.3	27
	Bq/l	GRn2		-0.30	377	30	360	385	374	52	13.9	26

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-1.18	204	30	168	207	205	23	11.3	27
	Bq/l	GRn2		-0.83	377	30	330	385	374	52	13.9	26

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-0.75	204	30	181	207	205	23	11.3	27
	Bq/l	GRn2		-1.03	377	30	319	385	374	52	13.9	26

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.10	204	30	207	207	205	23	11.3	27
	Bq/l	GRn2		-0.25	377	30	363	385	374	52	13.9	26

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.39	204	30	216	207	205	23	11.3	27
	Bq/l	GRn2		0.90	377	30	428	385	374	52	13.9	26

Participant 29												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		0.56	204	30	221	207	205	23	11.3	27
	Bq/l	GRn2		1.17	377	30	443	385	374	52	13.9	26

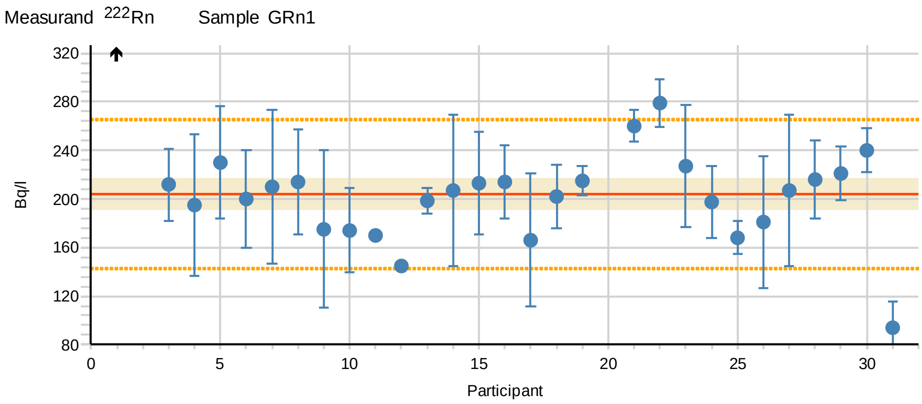
Participant 30												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		1.18	204	30	240	207	205	23	11.3	27
	Bq/l	GRn2		1.38	377	30	455	385	374	52	13.9	26

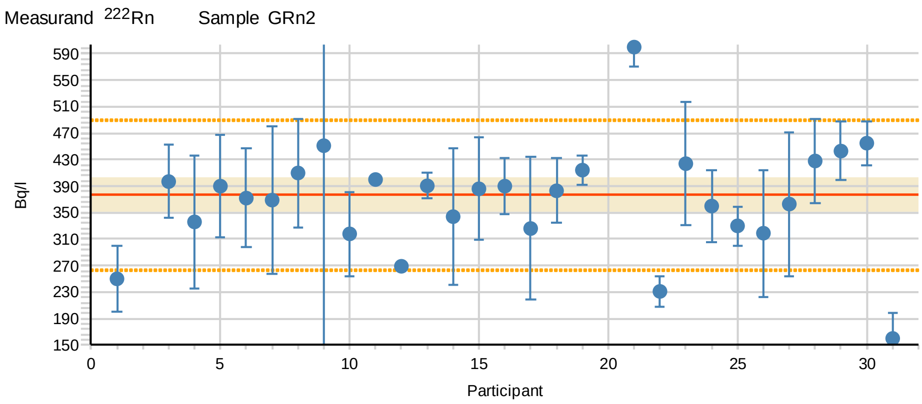
Participant 31												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
^{222}Rn	Bq/l	GRn1		-3.59	204	30	94	207	205	23	11.3	27
	Bq/l	GRn2		-3.84	377	30	160	385	374	52	13.9	26

APPENDIX 5: 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 6: Summary of the z scores

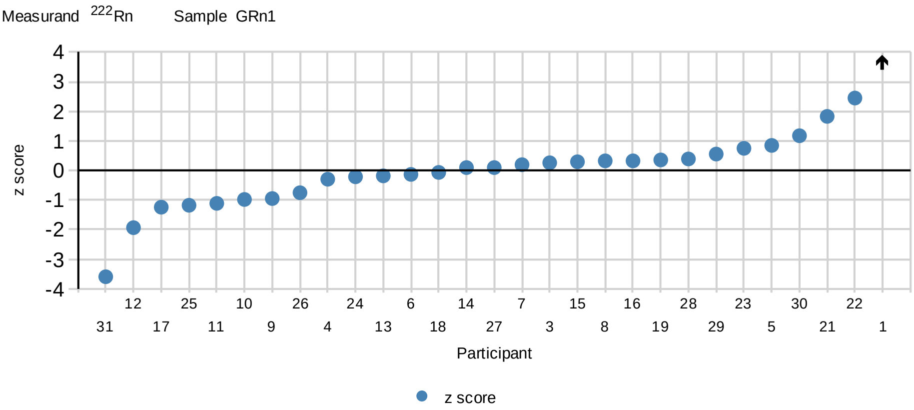
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
^{222}Rn	GRn1	U	.	S	S	S	S	S	S	S	*S*	*S*	S	S	S	*S*	S	*S*	S	*S*	.	S	*Q*	S	89.7
	GRn2	q	.	S	S	S	S	S	S	S	*S*	*S*	S	S	S	*S*	S	*S*	S	*S*	.	U	*q*	S	86.2
%		0		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100		50	0	100	
accredited		2			2	2	2	2	2	2			2	2	2		2		2			2		2	

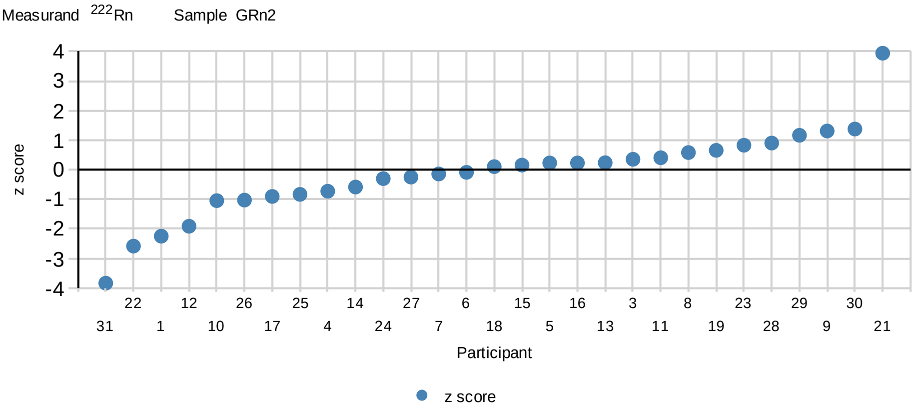
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
	GRn1	S	S	*S*	S	S	*S*	S	u	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	89.7
	GRn2	S	S	*S*	S	S	*S*	S	u	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	86.2
%		100	100	100	100	100	100	100	0																
accredited		2	2		2	2		2	2																

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: 88 % in non-accredited: 88

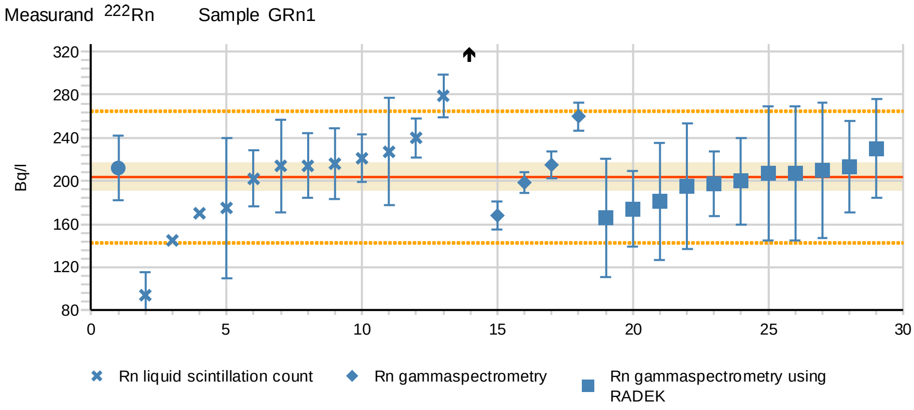
APPENDIX 7: z scores in ascending order

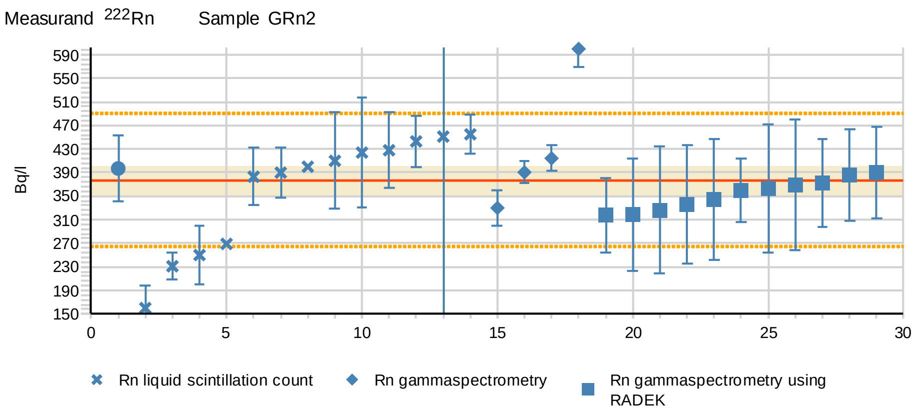




APPENDIX 8: Results grouped according to the methods

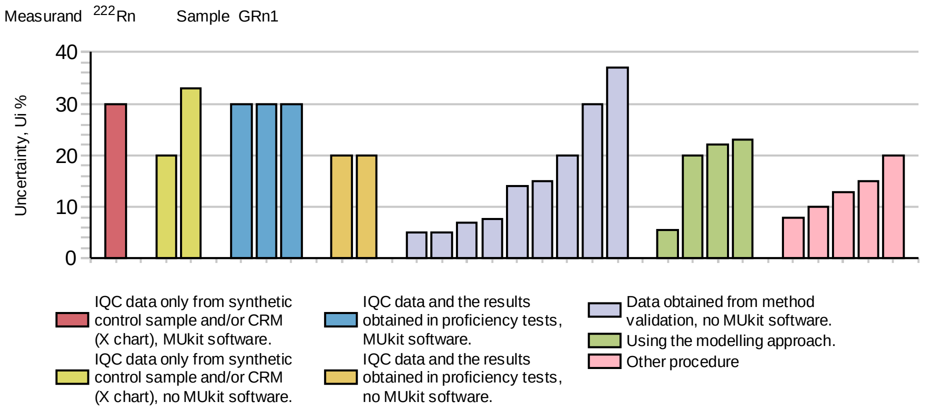
The explanations for the figures are described in the Appendix 5. The results are shown in ascending order.

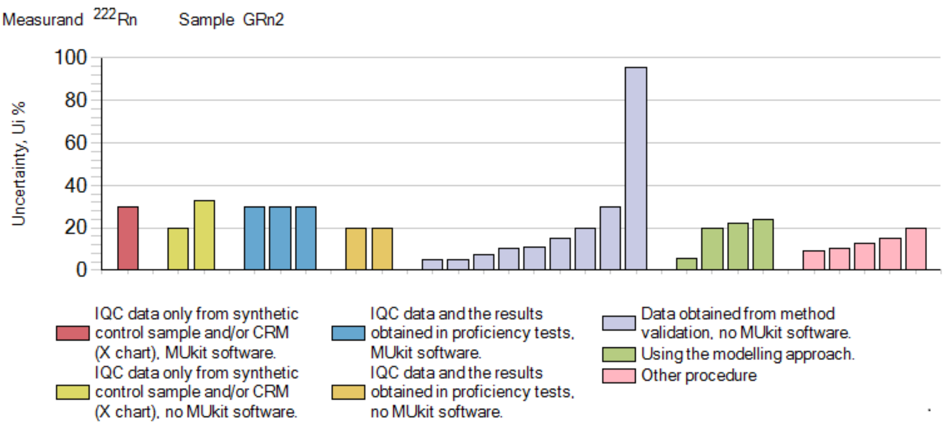




APPENDIX 9: Examples of measurement uncertainties reported by the participants

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 [7, 8] or using a modelling approach based [9, 10].





INTERLABORATORY PROFICIENCY TEST SYKE 06/2019

FINNISH ENVIRONMENT INSTITUTE

SYKE

Proftest SYKE

ISBN 978-952-11-5045-6 (pbk.)
ISBN 978-952-11-5046-3 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)