REPORTS OF FINNISH ENVIRONMENT
INSTITUTE 4| 2014

Proficiency Test SYKE 8/2013

Radon in ground water

Katarina Björklöf, Reko Simola, Kaija Korhonen-Ylönen,
Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas

Finnish Environment Institute

SUOMEN YMPÄRISTÖKESKUKSEN RAPORTTEJA
4 | 2014

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Helsinki 2014
Suomen ympäristökeskus

REPORTS OF FINNISH ENVIRONMENT INSTITUTE 4|2014
Finnish Environment Institute SYKE

The proficiency test provider:

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, 00430 Helsinki

Publication is available only on the internet :
www.syke.fi/publications / helda.helsinki.fi/syke

ISBN 978-952-11-4259-8 (PDF)
ISSN 1796-1726 (Online)

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ALKUSANAT

Suomen ympäristökeskus (SYKE) on toiminut ympäristöalan kansallisena vertailulaboratoriona vuodesta 2001 lähtien. Toiminta perustuu ympäristöministeriön määräykseen, mikä on annettu ympäristönsuojelulain (86/2000) nojalla. Vertailulaboratorion tarjoamista palveluista yksi tärkeimmistä on pätevyyskokeiden ja muiden vertailumittausten järjestäminen. SYKEn laboratoriot on FINAS-akkreditointipalvelun akkreditoima testauslaboratorio T003 ja kalibrointilaboratorio K054 (SFS-EN ISO/IEC 17025) sekä vertailumittausten järjestäjä Proftest SYKE PT01 (SFS-EN ISO/IEC 17043, www.finas.fi).

Tämä pätevyyskoe on toteutettu SYKEn vertailulaboratorion pätevyysalueella ja se antaa tietoa osallistujien pätevyyden lisäksi tulosten vertailukelpoisuudesta myös yleisemmällä tasolla. Pätevyyskokeen onnistumisen edellytys on järjestäjän ja osallistujien välinen luottamuksellinen yhteistyö.

Parhaat kiitokset yhteistyöstä kaikille osallistujille!

PREFACE

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector by the Ministry of the Environment according to section 24 of the Environment Protection Act (86/2000) since 2001. The duties of the reference laboratory service include providing proficiency tests and other interlaboratory comparisons for analytical laboratories and other producers of environmental information. SYKE laboratories has been accredited by the Finnish Accreditation service as the testing laboratory T003 and the calibration laboratory K054 (EN ISO/IEC 17025) and as the proficiency testing provider Proftest SYKE PT01 (EN ISO/IEC 17043, www.finas.fi).

This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides information about performance of the participants as well as comparability of the results at a more general level. The success of the proficiency test requires confidential co-operation between the provider and participants.

Thank you for your co-operation!

Helsingissä 13. tammikuuta 2014 / Helsinki 13 January 2014

Marja Luotola

Laboratorionjohtaja / Director of Laboratory

1 INTRODUCTION

Proftest SYKE carried out this proficiency test for the analysis radon in ground water in October 2013. 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). For liquid scintillation counting, the samples were distributed in 250 ml glass bottles and for measurements on RADEK equipment in one litre glass bottles.

The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi). This proficiency test is not included in scope of the accreditation.

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, 00430 Helsinki
tel. +358 0295 251 000, fax +358 9 448 320

The responsibilities in organizing the proficiency test were as follows:
Katarina Björklöf, coordinator
Kaija Korhonen-Ylönen, substitute of coordinator
Keijo Tervonen, technical assistance
Sari Lanteri, technical assistance
Markku Ilmakunnas, technical assistance and layout of the report.

The co-operation partner and analytical expert was:
Reko Simola, Radiation and Nuclear Safety Authority (STUK), Helsinki, Finland

2.2 Participants

In this proficiency test (PT) in total 24 laboratories participated, from which 20 were from Finland and 4 from other countries (Table 1). Six of the participating laboratories used the liquid scintallation method and 19 used equipment based on gamma spectrometry (Radek MKGB-01).

2.3 Samples and delivery

The two ground water samples were collected from drinking water wells in Southern Finland on Monday the 21 of October 2013. Well water was drained for 15 minutes before collecting of water into 50 l jars. In the laboratory the water was transferred into glass bottles using a tube to avoid excess contact of the water with air and evaporation of radon during the procedure. Samples were sent by courier on Tuesday the 22 of October 2013 and the samples were received the next day. The analyses were asked to be carried out according to normal laboratory procedures not later than on 25 October 2013. The results were asked to be calculated to the reference time of 21 October 2013 at noon. The participating laboratories sent their results no later than the 4 of November. The preliminary results were sent to the participants on 7 of November 2013.

Table 1. Paricipants in the radon in groundwater proficiency test in 2013.

Country	Organisation
Finland	Biopap Oy, Fiskari
	Haapaveden Kaupungin Ympäristölaboratorio, Haapavesi
	Jyväskylän Ympäristölaboratorio, Jyväskylä
	Kainuun elintarvike- ja ympäristölaboratorio, Kajaani
	KCL Kymen laboratoriot, Kuusankoski
	Kokemäenjoen Vesistön Vesiensuojeluyhdistys ry, Hämeenlinna
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Länsi-Uudenmaan vesi ja ympäristö ry, Lohja
	Oulun seudun elintarvike- ja ympäristölaboratorio, Oulu
	Porilab, Pori
	Porvoon elintarvikelaboratorio, Porvoo
	Ramboll Analytics, Lahti
	Rauman ympäristölaboratorio, Rauma
	Riihimäen seudun terveyskeskus ky, elintarvike- ja vesilaboratorio, Riihimäki
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan ympäristötutkimus Oy, Joensuu
	Savo-Karjalan ympäristötutkimus Oy, Kuopio
	Snellmans köttförädling, Laboratorium, Pietarsaari
	Säteilyturvakeskus STUK, Pohjois-Suomen aluelaboratorio, Rovaniemi
	Vaasan kaupungin ympäristölaboratorio, Vaasa
Norway	Norwegian Radiation Protection Authority, Oesteraas, Norway
Sweden	Eurofins Environment Testing Sweden Ab, Lidköping, Sweden
	SSM Radioanalytical Laboratory, Solna, Sweden
United Kingdom	South West Water Ltd., Devon, England

2.3.1 Homogeneity and stability testing of the samples

Homogeneity of the samples was tested by scintillation counting from 10 parallel samples by STUK. For both samples the homogeneity criteria (Table 2) was met and the samples were considered homogeneous.

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

Sample	Concen-tration	Standard deviation of test allowed (s_p)	0.5 x s_p	SD*	Is sd < 0.5x s_p?
G1R	2194	110	55	21	Yes
G2R	197	14	7	5	Yes

*SD = standard deviation of the mean concentration.

The stability of the samples were tested on Friday the 25 of October by storing four parallel samples for 24 h at room temperature and compare the concentrations measured by scintillation count to samples kept in cold for the whole time. According to the stability testing criteria the samples were stable using the standard deviation for the test (s_p) used (Table 3).

Table 3. Results of the stability testing of the samples.

Sample	Concentration (Bq/l)			s_p (%)	0.3 x s_p	Is D<0.3 x s_p?
	in cold whole time	in 21 C for 24 h	difference (D)			
G1R	2179	2204	25	109 (5 %)	33	Yes
G2R	194	195	1	15 (7%)	4	Yes

2.4 Feedback from the proficiency test

We received two comments concerning this proficiency test and one laboratory registered late (Table 4).

The main feedback from the proficiency test provider to the participating laboratories is that the success of energy calibration of the instrument has great impact on radon measurements. The function of the instruments should be monitored regularly using control samples. The results of the control samples should be registered on X-charts including action- and alarm limits, to be able to follow trends in the functioning of the instruments. A systematic change in the results is an indication of changes in the method. Although radon is technically easily measured, the principle for the analytics differs considerately from basic chemical analytics. Therefore it is very important that new personnel are properly trained in using best considered procedures.

Table 4. Feedback from the proficiency test.

Lab	Comment	Action/Proftest
22	The uncertainties of the results were reported as absolute numbers not per cent.	The error does not affect the performance of this laboratory. Therefore the uncertainties were changed to per cent in this report. We point out that good customer service includes providing the data in the format agreed with the customer.
23	The results of the samples G1R and G2R are mixed up.	The results reported by the participants cannot be corrected after the preliminary results have been sent. The results were treated as outliers. The z-values would have been satisfactory (G1R: z = 1.9 and G2R: z = 1.3) if the results would have been reported right.
24	Laboratory registered late and analysed their samples on Wednesday the 30 of October.	The results were slightly lower compared to the mean values: this may be due to the later time for analysing the samples. Analyses were made 9 days after sampling. In 9 days radon decays two times. In that case the counting uncertainty is higher. Also a small amount of radon could have escaped during that time. The z-scores are however acceptable.

2.5 Processing of the data

2.5.1 Pretesting of the data

Before the statistical treatment, the data was tested according to the Kolmogorov-Smirnov normality test and the outliers were rejected according to the Hampel test for calculation of the mean value (H in the results sheets). The results of laboratory 23 was also rejected before the robust calculation because the result were reported erroneously

2.5.2 Assigned values and their uncertainties

The mean radon concentration from ten samples measured by STUK by scintillation counting was used as the assigned value. The standard deviations for these measurements were 1 % (G1R) and 2.5 % (G2R). The uncertainties of the assigned values were calculated using the homogeneity results. The reliability of the assigned value was statistically tested according to the IUPAC Technical report [3]. The assigned values could be considered reliable (Table 5).

Table 5. The uncertainties and reliabilities of the assigned values.

Sample	Assigned value	U %	u/s_p	Is $u/s_p < 0.3$?
G1R	2190	2	0,2	Yes
G2R	197	2	0,1	Yes

2.5.3 Standard deviation for proficiency assessment and z score

The target values for the total standard deviation for this proficiency assessment was decided based the results of the participants and the homogeneity of the samples.

The reliability of the target value for the total deviation and the reliability of the corresponding z score were estimated by comparing the deviation for proficiency assessment (s_p) with the robust standard deviation of the reported results (s_{rob}). The criterion $s_{rob} < 1.2 * s_p$ was fulfilled and the evaluation of performance is reliable for this proficiency test (Table 6).

After reporting the preliminary results in November 2013 no changes has been done to the standard deviations for the proficiency assessment.

Table 6. The reliability of the target values for the total standard deviation for this proficiency assessment.

Analyte	Sample	s_{rob}	Target standard deviation % (s_p)	1.2 x s_p	Is $u/s_p < 0.3$?
Liquid scintillation counting	G1R	116	5	131	Yes
	G2R	15	7,5	18	Yes
Radek	G1R	134	10	263	Yes
	G2R	19	12,5	24	Yes

3 RESULTS AND CONCLUSIONS

3.1 Results

The summary of the results is presented in Table 7. Explanations to terms used in the result tables are presented in Appendix 1. The results and the performance of each laboratory are presented in Appendix 2. The results of participants and their uncertainties are presented graphically in Appendix 3. The summary of z scores is shown in Appendix 4.

The robust standard deviations of results were below 11 % for all the analytes (Table 7) which is slightly higher than in the previous proficiency test [4] where the robust standard deviations were 0.4 % for liquid scintillation counts and 8.5 % for Radek measurements. In this proficiency test the concentrations were lower, which increase the variations.

Table 7. Summary of the result in the proficiency test 8/2013.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Ac-cepted z-val%
Rn_LSC	G1R	Bq/l	2190	1998.32	1998.32	2025.00	131.91	6,6	6	10	67
	G2R	Bq/l	197	188.15	184.34	182.00	15.18	8,2	6	15	83
Rn_RAD	G1R	Bq/l	2190	1896.67	1891.27	1860.00	119.40	6,3	19	20	89
	G2R	Bq/l	197	168.37	167.97	166.00	18.23	10,9	19	25	89

Ass. Val.- the assigned value, Mean- the mean value, Mean rob- robust mean, Md - the median value, SD %-the standard deviation as percent, SD rob - the robust standard deviation, SD rob % - the robust standard deviation as percents, Num of Labs - the number of participants, 2*Targ. SD% - the total standard deviation for proficiency assessment at 95 % confidence level ($2*s_p$), Accepted z-val% - the satisfactory z scores: the results (%), where $|z| \leq 2$.

3.2 Analytical methods and quality assurance

Table 8. Quality assurance procedures used by the participants.

Lab	Quality of reference sample	Theoretical value of quality sample (measured result)	Detection limit (Bq/l)	Method for transfer of sample	Sample	Time for opening the sample	Time for closing the Marinelli lid (measurement started)	Length of measurement (s)
RADEK								
2	2 point calibration, background calibration using destilled water, efficiency test using STUK internal standard		50	Careful pouring into the Marinelli	G1R	20131023 14:55	14:57 (15:00)	1000
					G2R	20131023 14:21	14:23 (14:26)	1000
3	Milk powder	293Bq/kg (305 Bq/kg)	40	Pouring	G1R / G2R	20131023 15:15	15:16 (15:16)	1000
7	STUK milk powder Cs-concentration is measured regularly. Last time measured 17.10.2013.	293Bq/kg (282 Bq/kg)	30	Pouring	G1R / G2R	20131023 13:15	13:16 (15:16:29)	1000
8	137 Cs / Quartz sand 1.3.2003 (420 g)	1.80 kBq / Ra-226 (725 Bq/kg)	30	Pouring	G1R	20131023 11:56	11:56 (11:57)	1000
					G2R	20131023 13:40	13:40 (13:41)	1000
9	Milk powder (30.12.1992)	293 Bq/kg (271 Bq/kg)	30	Careful pouring against the edge of the jar	G1R	20131023 12:43	12:45 (12:48)	1000
					G2R	20131023 13:29	13:31 (13:34)	1000
11	Milk Powder	293 Bq/kg (268 Bq/kg), control limits 234-352 Bq/kg	30	Using tube.	G1R / G2R	20131023 13:15	13:15 (15:21)	1000

12	Milk Powder	293 Bq/kg (303 Bq/kg and 290 Bq/kg)	50	Careful pouring against the edge of the jar	G1R	12:09	12:10 (12:10)	1800
					G2R	13:37	13:38 (13:38)	1800
13	STUK milk Powder 0,32 l, 0.2140 kg, 17.11.1986	409 Bq/kg (386 Bq/kg)		Pouring	G1R	20131024 9:00	9:00 (9:02)	1000
					G2R	20131024 9:40	9:40 (9:42)	1000
14	Milk Powder 30.12.1992	293 Bq/kg		Slow pouring	G1R	20131023 12:25	12:26 (12:31)	1000
					G2R	20131023 13:55	13:56 (14:01)	1000
16				Pouring	G1R	20131025 10:58	10:59 (10:59)	1000
					G2R	20131025 12:08	12:09 (12:09)	1000
17	Milk Powder 30.12.1992	293 Bq/kg (310 Bq/kg)	30	Careful pouring against the edge of the jar	G1R	20131024 13:55	13:59 (14:00)	1000
					G2R	20131024 14:36	14:38 (14:38)	1000
18	STUK milk Powder 17.11.1986	409 Bq/kg (423 Bq/kg)	30	Pouring	G1R	20131023 13:30	13:30 (13:30)	1000
					G2R	20131023 14:12	14:12 (14:12)	1000
19	Milk Powder	293 Bq/kg (297 Bq/kg)	20	Pouring	G1R	20131023 11:58	11:58 (11:59)	1000
					G2R	20131023 12:20	12:20 (12:21)	1000
20	Milk Powder and own tap water	Tap water 8.7 Bq/kg (18 Bq/kg). Monitoring on X-chart	30	Careful pouring against the edge of the jar	G1R	20131025 11:28	11:28 (11:29)	1000
					G2R	20131025 12:42	12:43 (12:44)	1000
23*			25		G1R / G2R		20131024 (9:45)	1800
24	Milk Powder 30.12.1992	330 Bq/kg (306 Bq/kg)	30	Careful pouring against the edge of the jar	G1R	20131030 13:02	13:03 (13:04)	1000
					G2R	20131030 14:00	14:01 (14:01)	1000

LIQUID SCINTALLATION COUNTS								
1			10		G1R	20131025 09:08	09:09 (13:48)	150 s
					G2R	20131025 09:09	09:10 (13:53)	1140 s
4	Ultrapure water	0 Bq/l (4 Bq/l)	3	Pipetting using Biohit micropipette	G1R / G2R			
6	NIST 4966A Radium ss6 solution	(112 bq/l)	30	Pipetting by submerging the pipette into the sample until the pipette contains 10 ml of sample. Sample is transferred into scintillation vial containing scintillation liquid. Volume is weighted.	G1R / G2R			
21	Background sample containing 10 ml of scintillation solution and 10 ml of distilled water			Direct liquid scintillation (LS) method, standard ASTM method (ASTM 1998). 10 ml of liquid scintillation solution Optiphase Supermix mixed with 10 ml of water sample. The sample is stored for minimum 3 hours before measurement.	G1R / G2R	20131024 15:00	20131025 (08:35)	1800
22	Perkin Elmer LSC standard 194800 dpm tritium, 1.6.2003	194800 (195792.68)	0.05	Toluene extraction	G1R / G2R	20131024 16:15	(19:00)	5000

* Lab 23 do not have the RADEK instrument. The measurement method was high resolution gamma spectrometry. The samples could directly be measured since a calibration exists for the same type of glass bottles received.

In the Radek measurement the samples were correctly measured immediately after they had been placed into the marinelli. The Radek instrument measures radon concentrations from radon daughter nuclides. The effect of escaped radon during the transfer of the samples to the marinelli is lower if radon is measured immediately after the transfer because the daughter nuclides have not had time to decay.

3.3 Uncertainties of the results

The reported uncertainties of the results of the participants were 10-30 % for sample G1R and 10-30 % and 6-30 % for scintillation counts and Radek measurements, respectively, for sample G2R. Several approaches were used for estimating of measurement uncertainty (Table 9). Most commonly data from parallel measurements and control samples were used.

The counting uncertainty is higher for lower concentrations. Therefore also total uncertainty for lower concentrations is usually higher than uncertainty for samples with higher concentrations. Only one laboratory (Lab 23) reported lower uncertainty for a higher concentration.

Uncertainty for radon measurements with RADEK MKGB-01 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 results.

Table 9. Measurement uncertainties of the participants.

Analyte	Method for estimating measurement uncertainty
Radek	Based on validation results (Lab 2, 8) Based on controls and parallel samples (Lab 3, 13, 19) Based on controls and parallel samples according to Nordtest (Lab 9, 17) Using uncertainty provided by STUK (Lab 7, 11, 18) Based on validation and control material (Lab 20) GUM: The uncertainty sources taken into account are the sample weight/volume, counting uncertainty, blank background correction, activity of the reference standard, calibration procedure (Lab 23). Based on controls, parallel samples and results from previous proficiency tests (Lab 24)
Scintillation count	Own estimation, new equipment (Lab 4) 95% confidence level (Lab 21) Uncertainty on the count 0 0.005625 * error on toluene dispenser = 5 % (Lab 22)

4 EVALUATION OF PERFORMANCE

The evaluation of the participants was based on z scores, which were calculated using the estimated target values for the total deviation. 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, 86 % from the results were satisfactory when deviations of 10–25 % from the assigned values were accepted. Slightly more results were acceptable in accredited laboratories (88 %) compared to non-accredited laboratories (85 %). In the previous proficiency test arranged by SYKE in 2011 only 70 % of the results were satisfactory [4].

Radon is a volatile gas, which easily evaporate during sample handling and analysis. The main sources of error in radon measurements are human errors, preparation of samples and function of the instrument used. The success of energy calibration of the instrument has great impact on radon measurements. The function of the instruments should be monitored regularly using control samples. The results of the control samples should be registered on X-charts including action- and alarm limits, to be able to follow trends in the functioning of the instruments. A systematic change in the results is an indication of changes in the method. Although radon is technically easily measured, the principle for the analytics differs considerately from basic chemical analytics. Therefore it is very important that new personnel are properly trained in using best considered procedures.

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 October 2013. In total 24 laboratories participated in this PT. Six of the participating laboratories used the liquid scintallation method and 19 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 concentration. The evaluation of the results was based on z scores. In total 86 % of the results was satisfactory when the result measured with Radek equipment was accepted to deviate 20 % and 25 % from the assigned value and the result measured with the liquid scintillation counting was accepted to deviate 10 % and 15 % from the assigned value.

6 YHTEENVETO

Proftest SYKE järjesti yhteistyössä Säteilyturvakeskuksen kanssa pätevyyskokeen pohjaveden radonmäärityksestä lokakuussa 2013. Pätevyyskokeeseen osallistui 24 laboratoriota, joista 19 määritti radonin Radek-laitteella ja kuusi 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. Tulosten hajontaa käytettiin homogeenisuustestissä, jonka tulosten perusteella osanäytteet olivat homogeenisia. Tulokset arvioitiin z-arvon avulla. Hyväksyttäviä tuloksia oli 86 %, kun Radek-laitteella mitatun radonpitoisuuden sallittiin poiketa vertailuarvosta 20 % ja 25 % ja nestetuikemenetelmällä 10 % ja 15 %.

7 REFERENCES

1. ISO/IEC 17043, 2010. Conformity assessment – General requirements for proficiency testing.

2. ISO 13528, 2005. 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 (http://www.iupac.org/publications/pac/2006/pdf/7801x0145.pdf).

4. Korhonen-Ylönen, K., Hanste, U.-M., Leivuori, M., Ilmakunnas, M. 2012. Laboratorioiden välinen pätevyyskoe 6/2011, radon pohjavedestä. Suomen ympäristökeskuksen raportteja, 1, 23 pp. http://hdl.handle.net/10138/39764

TERMS IN THE RESULT TABLES

Results of each participants

Sample	the code of the sample
z-Graphics	z score - the graphical presentation
z value	calculated as follows: $z = (x_i - X)/s_p$, where x_i = the result of the individual laboratory X = the reference value (*the assigned value*) s_p = the target value of the standard deviation for proficiency assessment
Outl test OK	yes - the result passed the outlier test H = Hampel test (a test for the mean value) In addition, in robust statistics some results deviating from the original robust mean have been rejected
Assigned value	the reference value
2* Targ SD %	the target value of total standard deviation for proficiency assessment (s_p) at the 95 % confidence level, equal 2 * s_p
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, %
Passed	The results passed the outlier test
Outl. failed	The results not passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

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 * s_p from the assigned value
q – questionable ($-3 > z < -2$), negative error, the result deviates more than 2 * s_p from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 * s_p from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 * s_p from the assigned value

Robust analysis:

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:*

The items of data is sorted into increasing order, x_1, x_2, x_i,…,x_p.
Initial values for x^* and s^* are calculated as:
$\varphi = 1.5$

$x_i^* = x^* - \varphi$	if $x_i < x^* - \varphi$
$x_i^* = x^* + \varphi$	if $x_i > x^* + \varphi$
$x_i^* = x_i$	otherwise

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.
Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons, Annex C [3].

LIITE 2. RESULTS OF EACH PARTICIPANT

APPENDIX 2.

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
Rn_LSC	Bq/l	G1R		-0,639	yes	2190	10	2120	2025	1998	116,3	5,8	6	0	0	6
	Bq/l	G2R		-0,880	yes	197	15	184	182	188,2	21,79	11,5	6	0	0	6
Laboratory 2																
Rn_RAD	Bq/l	G1R		-0,411	yes	2190	20	2100	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-0,284	yes	197	25	190	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 3																
Rn_RAD	Bq/l	G1R		-1,279	yes	2190	20	1910	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,665	yes	197	25	156	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 4																
Rn_LSC	Bq/l	G1R		-0,849	yes	2190	10	2097	2025	1998	116,3	5,8	6	0	0	6
	Bq/l	G2R		2,234	yes	197	15	230	182	188,2	21,79	11,5	6	0	0	6
Laboratory 5																
Rn_RAD	Bq/l	G1R		-1,507	yes	2190	20	1860	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,299	yes	197	25	165	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 6																
Rn_LSC	Bq/l	G1R		-1,279	yes	2190	10	2050	2025	1998	116,3	5,8	6	0	0	6
	Bq/l	G2R		-0,406	yes	197	15	191	182	188,2	21,79	11,5	6	0	0	6
Laboratory 7																
Rn_RAD	Bq/l	G1R		-1,142	yes	2190	20	1940	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,096	yes	197	25	170	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 8																
Rn_RAD	Bq/l	G1R		0,046	yes	2190	20	2200	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-0,325	yes	197	25	189	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 9																
Rn_RAD	Bq/l	G1R		-1,507	yes	2190	20	1860	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,624	yes	197	25	157	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 10																
Rn_RAD	Bq/l	G1R		-2,466	yes	2190	20	1650	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-2,680	yes	197	25	131	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 11																
Rn_RAD	Bq/l	G1R		-1,781	yes	2190	20	1800	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,909	yes	197	25	150	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 12																
Rn_RAD	Bq/l	G1R		-1,918	yes	2190	20	1770	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,665	yes	197	25	156	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 13																
Rn_RAD	Bq/l	G1R		-1,689	yes	2190	20	1820	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		0,609	yes	197	25	212	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 14																
Rn_RAD	Bq/l	G1R		-0,685	yes	2190	20	2040	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-0,731	yes	197	25	179	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 15																
Rn_LSC	Bq/l	G1R		-1,735	yes	2190	10	2000	2025	1998	116,3	5,8	6	0	0	6
	Bq/l	G2R		-1,827	yes	197	15	170	182	188,2	21,79	11,5	6	0	0	6
Rn_RAD	Bq/l	G1R		-0,868	yes	2190	20	2000	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-0,690	yes	197	25	180	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 16																
Rn_RAD	Bq/l	G1R		-1,689	yes	2190	20	1820	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,673	yes	197	25	155,8	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 17																
Rn_RAD	Bq/l	G1R		-1,187	yes	2190	20	1930	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-0,650	yes	197	25	181	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 18																
Rn_RAD	Bq/l	G1R		-1,050	yes	2190	20	1960	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,259	yes	197	25	166	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 19																
Rn_RAD	Bq/l	G1R		-1,735	yes	2190	20	1810	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,836	yes	197	25	151,8	165,5	168,4	19,1	11,3	18	1	0	19

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

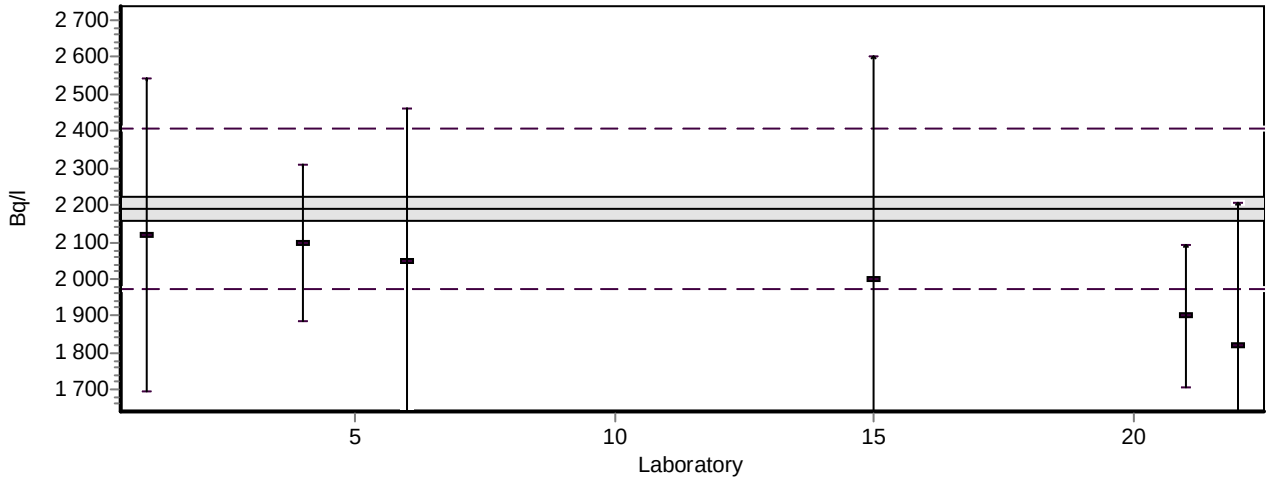
Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 20																
Rn_RAD	Bq/l	G1R		-1,735	yes	2190	20	1810	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-1,624	yes	197	25	157	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 21																
Rn_LSC	Bq/l	G1R		-2,648	yes	2190	10	1900	2025	1998	116,3	5,8	6	0	0	6
	Bq/l	G2R		-1,151	yes	197	15	180	182	188,2	21,79	11,5	6	0	0	6
Laboratory 22																
Rn_LSC	Bq/l	G1R		-3,353	yes	2190	10	1822,89	2025	1998	116,3	5,8	6	0	0	6
	Bq/l	G2R		-1,562	yes	197	15	173,922	182	188,2	21,79	11,5	6	0	0	6
Laboratory 23																
Rn_RAD	Bq/l	G1R		-9,009	H	2190	20	217	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		89,460	H	197	25	2400	165,5	168,4	19,1	11,3	18	1	0	19
Laboratory 24																
Rn_RAD	Bq/l	G1R		-1,507	yes	2190	20	1860	1860	1897	130,3	6,9	18	1	0	19
	Bq/l	G2R		-0,528	yes	197	25	184	165,5	168,4	19,1	11,3	18	1	0	19

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

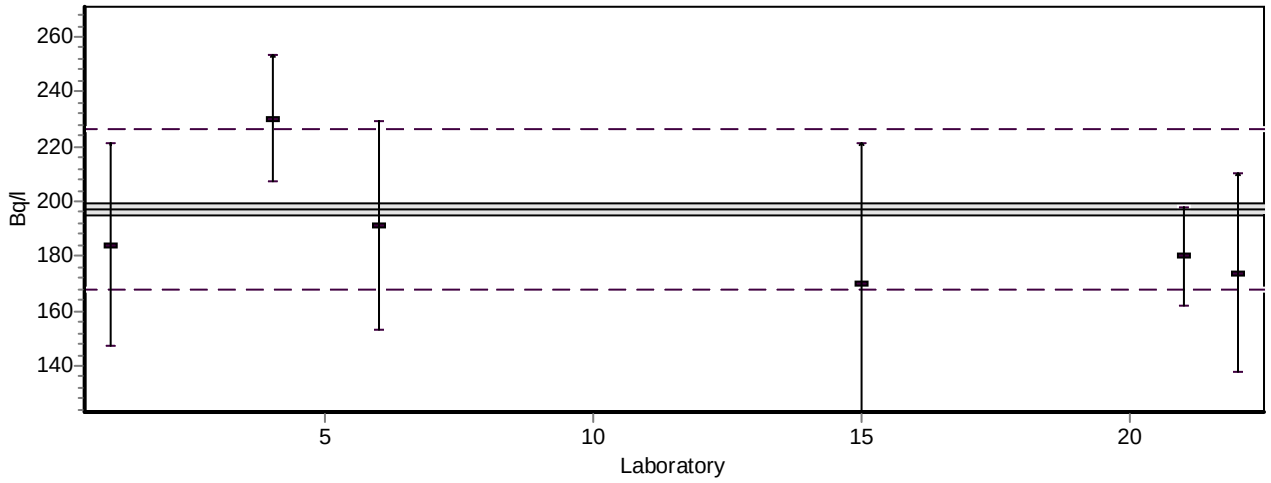
LIITE 3. RESULTS AND THEIR UNCERTAINTY ESTIMATES

APPENDIX 3.

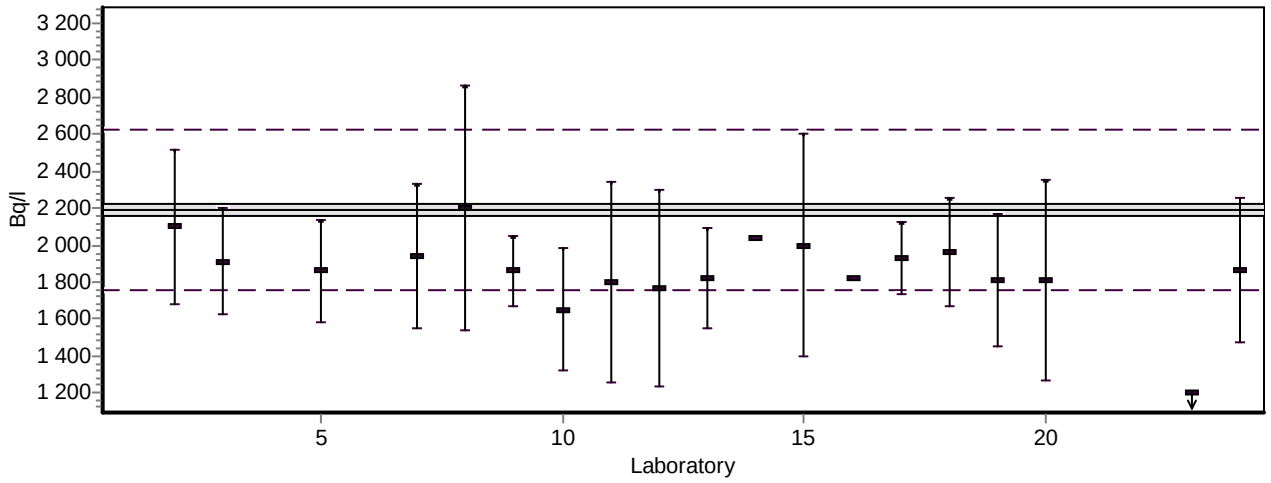
Analyytti *(Analyte)* **Rn_LSC** Näyte *(Sample)* G1R



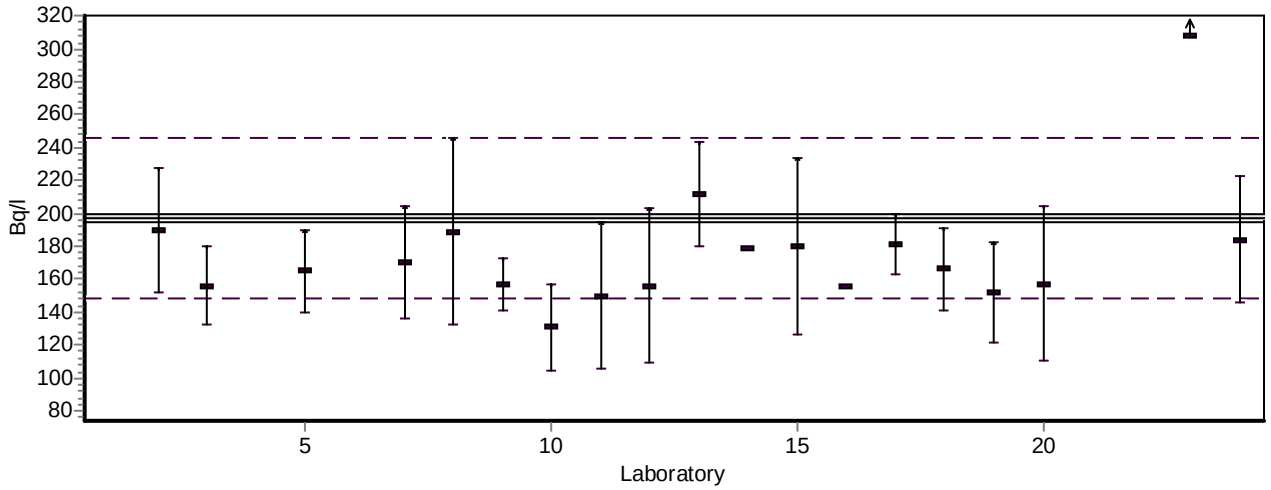
Analyytti *(Analyte)* **Rn_LSC** Näyte *(Sample)* G2R



Analyytti *(Analyte)* **Rn_RAD** Näyte *(Sample)* G1R



Analyytti *(Analyte)* **Rn_RAD** Näyte *(Sample)* G2R



LIITE 4. SUMMARY OF THE z SCORES

APPENDIX 4.

Analyte	Sample\Lab	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	G1R	S	.	.	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	q	u	.
	G2R	S	.	.	Q	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	S	S	.
Rn_RAD	G1R	.	S	S	.	S	.	S	S	S	q	S	S	S	S	S	S	S	S	S	S	.	.	u
	G2R	.	S	S	.	S	.	S	S	S	q	S	S	S	S	S	S	S	S	S	S	.	.	U
%		100	100	100	50	100	100	100	100	100	0	100	100	100	100	100	100	100	100	100	100	50	50	0
Accredited		yes	yes	yes					yes		yes		yes			yes				yes	yes		yes	

Analyte	Sample\Lab	24	%
Rn_LSC	G1R	.	67
	G2R	.	83
Rn_RAD	G1R	S	89
	G2R	S	89
%		100	
Accredited		yes	

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), u - unsatisfactory ($z \leq -3$)

%* - percentage of satisfactory results

Totally satisfactory, % In all: 86 In accredited: 88 In non-accredited: 85

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date January 2014
Author(s)	Katarina Björklöf, Reko Simola, Kaija Korhonen-Ylönen, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas	
Title of publication	SYKE Proficiency Test 8/2013 Radon in ground water	
Parts of publication/ other project publications		
Abstract	Proftest SYKE in co-operation with the Radiation and Nuclear Safety Authority (STUK) carried out the proficiency test for measurement of radon in ground water in October 2013. In total, 26 laboratories participated in the proficiency test. Most laboratories (19) used the equipment based on gamma spectrometry (RADEK MKGB-01) for measurement of radon. Six laboratories measured radon with liquid scintillation counting. 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 liquid scintillation counting were used as the assigned value. The evaluation of the results was based on z scores. In total 86 % of the results was satisfactory when the result measured with Radek equipment was accepted to deviate 20 % and 25 % from the assigned value and the result measured with the liquid scintillation counting was accepted to deviate 10 % and 15 %from the assigned value.	
Keywords	ground water analysis, drinking water analysis, measurement of radon, food and environmental laboratories, interlaboratory comparison, proficiency test	
Publication series and number	Suomen ympäristökeskuksen raportteja 4/2014	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
	ISSN 1796-1726 (online)	ISBN 978-952-11-4259-8 (PDF)
	No. of pages 24	Language English
	Restrictions Public	Price
For sale at/ distributor	The publication is available only on the internet helda.helsinki.fi/syke.	
Financier of publication	Finnish Environment Institute, P.O.Box 140, FI-00251 Helsinki, Finland	
Printing place and year	Helsinki 2014	
Other information		

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Tammikuu 2014
Tekijä(t)	Katarina Björklöf, Reko Simola, Kaija Korhonen-Ylönen, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas	
Julkaisun nimi	SYKE Proficiency Test 8/2013 Radon in ground water	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Proftest SYKE laboratorio järjesti yhdessä Säteilyturvakeskuksen (STUK) kanssa viidennen kerran pätevyyskokeen radonmittauksista pohjavedestä lokakuussa 2013. Pätevyyskokeeseen osallistui yhteensä 24 laboratoriota, joista 19 käytti gammaspektrometriaan perustuvia RADEK MKGB-01-mittareita ja kuusi käytti nestetuikemenetelmää. Osallistujille toimitettiin kaksi porakaivosta otettua pohjavesinäytettä, joista toisessa oli korkea radon pitoisuus (1000–5000 Bq/l) ja toisessa pienempi pitoisuus (<1000 Bq/l). Radonpitoisuuden vertailuarvona käytettiin STUKin nestetuikemenetelmällä mitattujen tulosten keskiarvoa. Pätevyyden arviointi tehtiin z-arvon avulla. Hyväksyttäviä tuloksia oli 86 %, kun Radek-laitteella mitatun radonpitoisuuden sallittiin poiketa vertailuarvosta 20 % sekä 25 % ja nestetuikemenetelmällä 10 % sekä 15 %.	
Asiasanat	pohjavesianalyysi, talousvesianalyysi, radonmääritys, elintarvike- ja ympäristölaboratoriot, vertailumittaus, pätevyyskoe	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 4/2014	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
	ISSN 1796-1726 (verkkoj.)	ISBN 978-952-11-4259-8 (PDF)
	Sivuja 24	Kieli suomi
	Luottamuksellisuus Julkinen	Hinta
Julkaisun myynti/ jakaja	Julkaisu on saatavana vain internetistä. helda.helsinki.fi/syke	
Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2014	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Januari 2014
Författare	Katarina Björklöf, Reko Simola, Kaija Korhonen-Ylönen, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas	
Publikationens titel	SYKE Proficiency Test 8/2013 Radon in ground water	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	Under oktober 2013 genomförde Proftest SYKE i samarbete med Strålsäkerhetscentralen (STUK) en provningsjämförelse, som omfattade radonmätning i grundvatten. Sammanlagt 26 laboratorier deltog i jämförelsen. Totalt 19 av deltagarna bestämde radon med gammaspektrometri (RADEK MKGB-01 meter) och sex av deltagarna använde vätskeskintillationsräknare. Två vattenprov testades i denna kompetensprovning varav det ena hade hög radonhalt (1000–5000 Bq/l) och det andra provet hade lägre halt av radon (<1000 Bq/l). Som referensvärde användes medelvärdet av resultaten mätt av STUK med vätskeskintillationsräknare. Deltagarnas kompetens bestämdes med hjälp av z-värden. Totalt var 86 % av alla resultaten tillfredsställande med Radek instrumenten, när den tillåtna totalavvikelsen från referensvärdet i var 20 % och 25 % samt 10 % och 15 % för vätskeskintillationsräkning.	
Nyckelord	vattenanalyser, alkalinitet, näringsämnen, pH, ledningsförmåga, provningsjämförelse, vatten- och miljölaboratorier	
Publikationsserie och nummer	Suomen ympäristökeskuksen raportteja 4/2013	
Publikationens tema		
Projektets namn och nummer		
Finansiär/ uppdragsgivare		
Organisationer i projektgruppen		
	ISSN 1796-1726 (online)	ISBN 978-952-11-4259-8 (PDF)
	Sidantal 24	Språk Engelska
	Offentlighet Offentlig	Pris
Beställningar/ distribution	Publikationen finns tillgänglig på internet helda.helsinki.fi/syke	
Förläggare	Finlands Miljöcentral, PB 140, 00251 Helsingfors	
Tryckeri/ tryckningsort och –år	Helsingfors 2014	
Övriga uppgifter		

PROFICIENCY TEST SYKE 8/2013

FINNISH ENVIRONMENT INSTITUTE

ISBN 978-952-11-4259-8 (PDF)
ISSN 1796-1726 (online)