REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 28 | 2018

Interlaboratory Proficiency Test 07/2018

Gross and net calorific values in fuels

Mirja Leivuori, Minna Rantanen, Eliisa Hatanpää, Riitta Koivikko, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas

Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 28 | 2018

Interlaboratory Proficiency Test 07/2018

Gross and net calorific values in fuels

Mirja Leivuori, Minna Rantanen, Eliisa Hatanpää, Riitta Koivikko, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas

Proftest SYKE

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

Helsinki 2018
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 28 | 2018
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 978-952-11-4975-7 (pbk.)
ISBN 978-952-11-4976-4 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)

Author(s): Mirja Leivuori, Minna Rantanen, Eliisa Hatanpää, Riitta Koivikko, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas

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

Year of issue: 2018

SYKE

ABSTRACT

Interlaboratory Proficiency Test 07/2018

Proftest SYKE arranged the proficiency test (PT) for measurement the gross and the net calorific value, the content of ash, carbon, nitrogen, hydrogen, moisture, sulphur, and volatile matter in peat, wood pellet (not sulphur) and coal samples in September 2018. In total, there were 26 participants in the PT. The participants could also calculate the emission factor for the peat and coal samples.

The robust mean, median or mean of the reported results by the participants was used as the assigned value for measurements. The evaluation of performance was based on the z and E_n scores. In total, 89 % of the reported results were satisfactory based on z scores when the deviations of 1–30 % from the assigned values were accepted. In measurement of the gross calorific value from the peat sample 92 %, from the wood pellet sample 83 % and from the coal sample 88 % of the results were satisfactory. In measurement of the net calorific value from the peat sample 82 %, from the wood pellet 73 % and from the coal sample 79 % of the results were satisfactory. All results evaluated based on E_n scores were satisfactory. The evaluation of performance was not done for the measurement of M_{ad} in all samples and N_d in the wood pellet sample.
Warm thanks to all the participants of this proficiency test!

Keywords: Proficiency test, interlaboratory comparison, coal, peat, wood pellet, calorific value, emission factor, ash, moisture, carbon, sulphur, nitrogen, hydrogen, volatile matter, environmental laboratories

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 07/2018

Proftest SYKE järjesti syyskuussa 2018 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, hiilen, typen, rikin, haihtuvien yhdisteiden ja kosteuden määrittämiseksi turpeesta, puupelletistä (ei rikkiä) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus arvioida/laskea turve- ja kivihiilinäytteiden päästökerroin. Pätevyyskokeessa oli yhteensä 26 osallistujaa.

Vertailuarvona käytettiin osallistujatulosten robustia keskiarvoa, keskiarvoa tai mediaania. Pätevyyden arviointi tehtiin z- ja E_n -arvojen avulla. Koko tulosaineistossa hyväksyttäviä tuloksia oli 89 % z-arvolla arvioituna, kun vertailuarvosta sallittiin 1–30 % poikkeama. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 92 % (turve), 83 % (puupelletti) ja 88 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 82 % (turve), 73 % (puupelletti) ja 79 % (kivihiili). E_n-arvolla arvioidut tulokset olivat kaikki hyväksyttäviä. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle ja puupelletin typen määrityksille.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: pätevyyskoe, vertailumittaus, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, päästökerroin, tuhka, kosteus, hiili, rikki, typpi, haihtuvat yhdisteet ja vety, turve, puupelletti, hiili, ympäristölaboratoriot

SAMMANDRAG

Provningsjämförelse 07/2018

Proftest SYKE genomförde i september 2018 en provningsjämförelse som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, svavel, väte, kol, kväve, askhalt, flykthalt och fukthalt i torv, träd pellet (inte svavel) och stenkol. Det var en möjlighet att beräkna emissionfaktor i torv och stenkol prover. Totalt 26 deltagarna deltog i jämförelsen.

Som referensvärde för analyternas koncentration användes det robusta medelvärdet, medelvärdet eller median av deltagarnas resultat. Resultaten värderades med hjälp av z och E_n värden. I jämförelsen var 89 % av alla resultaten acceptabel värderades med z värden, när en total deviation på 1–30 % från referensvärdet tilläts. Av det kalorimetriska värmevärdet var 92 % acceptabla (torv), 83 % (träd pellet) och 88 % (stenkol). För resultaten av det effektiva värmevärdet var 82 % (torv), 73 % (träd pellet) och 79 % (stenkol) acceptabla. Alla resultaten var acceptabel värderades med E_n värden. Det var inte gjorts värdering till fuktighalt i alla prover, beräkning av väte i torv provet och nitrogen i träd pellet.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: provningsjämförelse, kalorimetriskt och effektivt värmevärde, emissionfaktor, svavel, väte, kol, nitrogen, askhalt, flykthalt fukthalt stenkol, torv, träd pellet, miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of gross and net calorific value in fuels in September 2018 (CAL 07/2018). In the PT, gross and net calorific value, C_d, S_d, H_d, N_d, moisture content of the analysis sample ($M_{ad,d}$), ash content as well as volatile matter (V_{db}) were tested in peat, wood pellet (not S) and coal samples.

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/IEC17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE is accredited by the Finnish Accreditation Service (FINAS) 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 (formerly Hakuninmaantie 6), FI-00430 Helsinki, Finland
Phone: +358 295 251 000, e-mail: proftest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

Mirja Leivuori	coordinator
Riitta Koivikko	substitute of coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Co-operation partner and analytical expert:

Eliisa Hatanpää, Eurofins Environment Testing Finland Ltd, Vantaa (formerly Ramboll Finland Ltd, Ramboll Analytics), eliisahatanpää@eurofins.fi.
Also Minna Rantanen was the analytical expert in this PT.

Subcontracting:
The peat, wood pellet and coal samples were homogenated and divided into sub-samples at the laboratory of KVVY Tutkimus Oy (Tampere, Finland, T064 accredited by FINAS, www.finas.fi/sites/en). Samples were tested by Eurofins Environment Testing Finland Ltd, Vantaa (T039 accredited by FINAS, www.finas.fi/sites/en).

2.2 Participants

In total 26 participants took part in this proficiency test, of which 12 were from Finland and 14 from abroad (Appendix 1).

Altogether 69 % of the participants used accredited analytical methods at least for a part of the measurements. The samples were tested at the laboratory of Eurofins Environment Testing Finland Oy, Vantaa and their participant code is 6 in the result tables.

2.3 Samples and delivery

Three different fuel samples were delivered to the participants: peat (B1), wood pellet (B2) and coal (K1) samples. Gross ($q_{V,gr,d}$) and net ($q_{p,net,d}$) calorific value, C_d, S_d, H_d, N_d, moisture content of the analysis sample ($M_{ad,d}$), ash content as well as volatile matter (V_{db}) were tested in peat, wood pellet (not S) and coal samples.

The material for the peat sample (B1) was collected from the Finnish marshland. The material was air dried and ground by the mill with 500 µm sieve before homogenization and sample dividing. The peat sample was prepared by Eurofins Labtium Ltd in Jyväskylä (Finland).

The wood pellet sample (B2) was provided by Vapo and it was pre-treated (grinding) by Eurofins Labtium Ltd. The raw material for wood pellets was spruce sawdust. The material was first crushed with a cutting mill and then grounded by the mill with 1000 µm sieve before homogenization and sample dividing. The wood pellet sample was prepared by Eurofins Labtium Ltd in Jyväskylä (Finland).

The coal sample (K1) was prepared from Russian steam coal by the Helen Ltd (Finland).

All samples were homogenized and divided into sub-samples at the laboratory of KVVY Tutkimus Oy. The sample preparation is described in details in the Appendix 2.

In the cover letter delivered with the samples, the participants were instructed first to store the samples closed for one day after their arrival and then to measure the moisture content of the analysis sample (M_{ad}) as the first measurement. The samples were instructed to be homogenized before measurements and to be stored in a dry place at room temperature. Further, the moisture content of the analysis sample was instructed to be measured on every day of measurements. This was important as it eliminates the influence of humidity on the measurements.

Participants could also estimate/calculate the emission factor (as received), EF, for peat and coal samples. For this estimation/calculation the total moisture contents of the samples as received (M_{ar}) were given:

- peat B1 46.9 %,
- coal K1 10.9 %

The samples were delivered to the participants on 3 September 2018. The samples arrived to the participants mainly latest on 6 September 2018. One participant informed the arrival of the samples on 12 September 2018, but the tracking system of the delivery showed the sample arrival at the service point on 7 September 2018.

The samples were requested to be measured and the results to be reported latest on 25 September 2018. All the results were reported accordingly. The preliminary results were delivered to the participants via ProftestWEB and email on 1 October 2018.

2.4 Homogeneity

Homogeneity of the samples B1, B2 and K1 was tested by measuring the gross and net calorific value and ash content as duplicate determinations from five subsamples (Appendix 3). Moreover, the other measurands were tested from two subsamples as duplicate measurements. According to the homogeneity test results, all samples were considered homogenous.

Particle size distribution was also tested from one sub sample of peat (B1) and coal (K1). The requirement of particle sizes given in the international standards was fulfilled (Appendix 2).

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with sample delivery and participants' reporting errors. The comments from the provider are mainly focused to the lacking conversancy to the given information with the samples. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. Also before the statistical results handling some outliers were rejected in cases, where the result differed from the data more than $s_{rob} \times 5$ or 50 % from the robust mean. The rejection of results was partly based on the rather strict requirements for the reproducibility given in the standards for analysis described in the cover letter of the samples. The duplicate results were tested using the Cochran test. If the result was reported lower than the limit of determination, it has not been included in calculations.

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

2.6.2 Assigned values

Mainly the robust mean value of the participant results was used as the assigned value for measurands of the test samples, when there were at least 12 results (n(stat)≥12). In calculation of the robust mean the outliers are normally not rejected, but they are iterated before the final calculation of the robust mean. Also the mean and the median values of the data were calculated and they mainly differed only slightly from the robust means used as the assigned values (Table 1). In cases, where the number of results was lower than 12, the median of participants' results was used as the assigned value: the peat sample B1 all measurands with the exception of Ash_d (robust mean) and H_d (mean value). The median was used as the assigned value for the wood pellet sample B2 measurands: C_d, H_d, N_d, $q_{p,net,d}$, V_{dp} and for the coal sample K1 measurands: N_d, $q_{p,net,d}$. The assigned value of emission factor EF in the peat sample B1 was based on the median value of the results. For nitrogen (N_d) in the pellet sample (B2) the informative assigned value is given, but due to the high deviation of results the performance evaluation was not done. In cases, where the number of results was less than 6 (n(stat)<6), the performance evaluation was done using E_n score, if the assigned value and its uncertainty was set i.e. for emission factor (EF) for the peat sample (B1).

When the robust mean was used as the assigned value, the uncertainty was calculated using the robust standard deviation. When the median or the mean value was used as the assigned value, the expanded uncertainty was estimated based on the standard deviation [2, 4].

When using the robust mean, the mean or the median of the participant results as the assigned value, the expanded uncertainties of the assigned values for calorific values were between 0.2 % and 0.3 %. For the other evaluated measurands the uncertainty varied from 0.4 % to 7.8 % (Appendix 5).

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

2.6.3 Standard deviation for proficiency assessment and result evaluation

The requirements for the reproducibility of the used standard methods were informed in the cover letter of the samples and they were used for estimation of standard deviation for proficiency assessment in this PT. The reproducibility required for the standard methods was mainly fulfilled for gross calorific values. The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 1–30 % depending on the measurements. Standard deviation for proficiency assessment was not set for analysis moisture content $M_{ad,d}$ (all samples), for N_d in the wood pellet sample (B2) and for EF in the peat sample (B1), and thus the results have not evaluated.

After reporting the preliminary **results the standard deviation of the proficiency assessment (s_{pt}) has been cross-checked for S_d in the coal (K1) sample and changed from 17 to 15 %**.

This caused **minor numerical changes for z score values, but no changes to the participants' performance evaluation**. For other measurands and samples **no changes** have been done for the standard deviations of the proficiency assessment**.**

Additionally, when the number of reported results was low and the uncertainty was set for the assigned value, and the participant reported measurement uncertainty, the performance was estimated by means of E_n scores ('*Error, normalized*', Appendix 9). These are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

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

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

E_n scores of $-1.0 < E_n < 1.0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1.0$ or $E_n \leq -1.0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

The reliability of the 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 and s_{pt} is the standard deviation for proficiency assessment [3]. When testing these reliabilities the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation for proficiency assessment and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standard deviation (s) of the reported results [3]. The criterion s_{rob} (or s)/ $s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned was not met and, therefore, the evaluation of the performance is reduced in this proficiency test:

Sample	Measurand
B1	N_d
K1	V_{dp}

3 Results and conclusions

3.1 Results

The summary of the results of this proficiency test is presented in Table 1. Explanations to terms used in the result tables are presented in Appendix 6.The results and the performance of each participant are presented in Appendix 7. The reported results with their expanded uncertainties (*k*=2) are presented in Appendix 8. The summaries of the z and E_n scores are shown in Appendix 9 and the z scores in the ascending order in Appendix 10. If the participant did not report the requested parallel results for measurands, the evaluation scores are not available. When needed the participant can calculate their own z scores [4].

The robust standard deviations and standard deviations of the results varied from 0.3 to 13.3 % (Table 1). The robust standard deviation or standard deviation was lower than 2 % for 42 % of the results and lower than 6 % for 92 % of the results (Table 1). For Ash_d and S_d the robust standard deviation of the results was higher than 6 % (B2 and B1, respectively, Table 1). The robust standard deviations and standard deviations were approximately within the same range as in the previous similar proficiency test Proftest SYKE CAL 7/2017, where the deviations varied from 0.3 % to 30.7 % [5].

Table 1. The summary of the results in the proficiency test CAL 07/2018.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n (all)	Acc z %
Ash_d	B1	w%	6.65	6.65	6.65	6.69	0.17	2.6	8	14	100
	B2	w%	0.30	0.30	0.30	0.30	0.04	13.3	30	20	95
	K1	w%	11.1	11.1	11.1	11.1	0.1	1.1	2.5	19	89
C_d	B1	w%	54.4	54.4	54.4	54.4	0.3	0.5	3	7	100
	B2	w%	50.5	50.5	50.4	50.5	0.5	1.1	2.5	11	73
	K1	w%	70.7	70.7	70.7	70.6	0.7	1.0	2.5	16	94
EF	B1	t CO2/TJ	108	107		108			-	5	-
	K1	t CO2/TJ	94.7	94.7	94.7	94.3	0.8	0.8	4	8	88
H_d	B1	w%	5.63	5.63	5.62	5.62	0.11	2.0	7	7	100
	B2	w%	6.01	6.04	6.04	6.01	0.18	3.0	6	10	90
	K1	w%	4.60	4.58	4.60	4.58	0.09	1.9	6	13	85
$M_{ad,d}$	B1	w%	10.7	10.7	10.7	10.7	0.3	3.3	-	13	-
	B2	w%	8.10	8.11	8.10	8.10	0.20	2.4	-	20	-
	K1	w%	5.54	5.56	5.54	5.58	0.30	5.5	-	20	-
N_d	B1	w%	1.93	1.89	1.89	1.93	0.11	5.7	10	7	86
	B2	w%	0.11	0.10		0.11			-	10	-
	K1	w%	2.13	2.11	2.11	2.13	0.06	2.8	10	11	100
$q_{p,net,d}$	B1	J/g	20720	20718	20718	20720	122	0.6	1.5	11	82
	B2	J/g	18869	18864	18872	18869	85	0.4	1.7	15	73
	K1	J/g	27725	27707	27704	27725	140	0.5	1.2	14	79
$q_{V,gr,d}$	B1	J/g	21945	21933	21933	21945	98	0.4	1.3	12	92
	B2	J/g	20207	20203	20207	20222	62	0.3	1.4	18	83
	K1	J/g	28743	28745	28743	28748	135	0.5	1.0	17	88
S_d	B1	w%	0.21	0.21	0.21	0.21	0.02	10.8	20	9	100
	K1	w%	0.45	0.45	0.45	0.45	0.03	5.8	15	18	94
V_{db}	B1	w%	66.1	66.2	66.2	66.1	0.4	0.6	3	7	100
	B2	w%	85.0	85.1	84.7	85.0	1.2	1.4	3	12	83
	K1	w%	36.1	36.1	36.1	36.0	0.8	2.2	4	16	81

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 $|z| \le 2$, n(all): the total number of the participants.

In this proficiency test the participants were requested to report replicate results for all measurements. The results of the replicate determinations based on the ANOVA statistics are presented in Table 2. The targets for the repeatability are the ones recommended in the international standards or technical specifications related to the measurements of fuels.In particular, in measurements of the calorific values, the requirement for the repeatability is ± 120 J/g. In this proficiency test the requirements for the repeatability of the measurements of the gross calorific value were 0.55 % for the sample B1, 0.59 % for the sample B2 and 0.42 % for the sample K1 and in measurement of the net calorific value 0.58 %, 0.64 % and 0.43 %, respectively. In each case, the obtained repeatability of the measurement of the gross calorific value and the net calorific value was lower than the repeatability requirement (Table 2, the column s_w %).

The estimation of the robustness of the methods could be done by the ratio s_b/s_w. The ratio s_b/s_w should not exceed the value 3 for robust methods. Here, however, the robustness exceeded the value 3 in many cases (Table 2). For the gross calorific value, the ratio s_b/s_w, was 1.9 (the sample B1), 1.8 (the sample B2) and 5.5 (the sample K1), for the net calorific values 3.4, 3.8 and 5.5, respectively. For the calorific values the ratio s_b/s_w was mainly within the same range than in the previous similar proficiency test CAL 07/2017, with the exception of somewhat lower values for the peat (B1) and wood pellet (B2) and higher ratio in the coal sample (K1) [5].

Table 2. The summary of repeatability on the basis of replicate determinations (ANOVA statistics).

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
Ash_d	B1	w%	6.65	6.65	0.055	0.150	0.159	0.83	2.3	2.4	2.7
	B2	w%	0.30	0.30	0.016	0.041	0.044	5.3	14	15	2.6
	K1	w%	11.1	11.1	0.059	0.233	0.240	0.53	2.1	2.2	4.0
C_d	B1	w%	54.4	54.4	0.330	0.114	0.349	0.61	0.21	0.64	0.34
	B2	w%	50.5	50.5	0.121	0.685	0.696	0.24	1.4	1.4	5.7
	K1	w%	70.7	70.7	0.185	0.649	0.674	0.26	0.92	0.95	3.5
EF	B1	t CO2/TJ	108	107	0.285	0.504	0.579	0.26	0.47	0.54	1.8
	K1	t CO2/TJ	94.7	94.7	0.378	0.642	0.745	0.40	0.68	0.79	1.7
H_d	B1	w%	5.63	5.63	0.066	0.108	0.127	1.2	1.9	2.3	1.6
	B2	w%	6.01	6.04	0.041	0.162	0.167	0.68	2.7	2.8	3.9
	K1	w%	4.60	4.58	0.035	0.246	0.249	0.75	5.3	5.3	7.0
$M_{ad,d}$	B1	w%	10.7	10.7	0.055	0.304	0.309	0.51	2.8	2.9	5.6
	B2	w%	8.10	8.11	0.066	0.187	0.199	0.82	2.3	2.5	2.8
	K1	w%	5.54	5.56	0.046	0.393	0.396	0.84	7.2	7.2	8.5
N_d	B1	w%	1.93	1.89	0.017	0.103	0.104	0.92	5.4	5.5	5.9
	B2	w%	0.11	0.10	0.007	0.122	0.123	5.1	86	86	17
	K1	w%	2.13	2.11	0.022	0.066	0.069	1.0	3.1	3.3	3.1
$q_{p,net,d}$	B1	J/g	20720	20718	31.0	105	110	0.15	0.51	0.53	3.4
	B2	J/g	18869	18864	23.9	91.1	94.2	0.13	0.48	0.50	3.8
	K1	J/g	27725	27707	28.2	156	159	0.10	0.56	0.57	5.5
$q_{V,gr,d}$	B1	J/g	21945	21933	41.9	80.7	91.0	0.19	0.37	0.41	1.9
	B2	J/g	20207	20203	32.2	57.8	66.2	0.16	0.29	0.33	1.8
	K1	J/g	28743	28745	24.7	135	137	0.086	0.47	0.48	5.5
S_d	B1	w%	0.21	0.21	0.004	0.020	0.020	2.0	9.4	9.6	4.7
	K1	w%	0.45	0.45	0.011	0.033	0.034	2.4	7.1	7.5	2.9
V_{db}	B1	w%	66.1	66.2	0.117	0.357	0.375	0.18	0.54	0.57	3.0
	B2	w%	85.0	85.1	0.352	1.98	2.01	0.42	2.3	2.4	5.6
	K1	w%	36.1	36.1	0.205	0.767	0.794	0.57	2.1	2.2	3.7

Ass.val.: assigned value; s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t**:** reproducibility standard error.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. A questionnaire related to the used analytical methods was carried out along the proficiency test. The summary of the answers is shown in Appendix 11. The used analytical methods and the results of the participants grouped by methods are shown in more detail in Appendix 12. The statistical comparison of the analytical methods was possible for the data where the number of the results was $\geq$ 5 (several cases in this PT). In those cases the comparison is based on the graphical result evaluation.

3.2.1 Gross and net calorific value

The analytical methods based on different standard methods were used for the measurements in this PT. The used analytical methods of the participants are shown in more detail in Appendices 11-12.

Mostly, standard methods were used for measurement of calorific values ($q_{V,gr,d}$, $q_{p,net,d}$) (EN 14918 [6], EN ISO 18125 [7], ISO 1928 [8], Appendix 12). One participant used standard ASTM D 5865 [9]. One participant (13) used other standard method (EN 15400) and one reported to used isoperibolic calorimeter (participant 22).

In the calculations of gross calorific value ($q_{V,gr,d}$), various correction factors were used. Fuse wire, ignition, acid, moisture, nitrogen and sulphur corrections were most commonly used in several different combinations depending of the test material (Appendix 11). For the calculation of net calorific value ($q_{p,net,d}$), different combinations of correction factors were used as well depending of the test material (Appendix 11). Mainly nitrogen plus oxygen (N+O) and hydrogen (H) content was used for corrections. Based on the statistical comparison and the graphical evaluation no differences between the used methods in gross and net calorific value measurements could be concluded (Appendix 12).

3.2.2 Measurement of ash, carbon, hydrogen, moisture, nitrogen, sulphur, and volatile matter

In the PT mainly the following standard methods or technical specifications were used for measurements of different parameters:

Measurand	Method
Ash_d	EN 14775 [10], ISO 1171 [11], EN ISO 18122 [12], ASTM D 7582 [13]
C_d, H_d and N_d	ISO 29541 [14], ASTM D 5373 [15], EN ISO 16948 [16]
M_{ad} (analytical moisture content)	EN 14774-3 [17], ISO 589 [18], DIN 51718 [19], ASTM D 7582 [13], EN ISO 18134-3 [20], ISO 11722 [21]
S_d	EN ISO 16994 [22], ASTM D 4239 [23]
V_{db}, (volatile matter)	EN 15148 [24], ISO 562 [25], EN ISO 18123 [26]

However, in some cases also other international and national standards or technical specifications (e.g. EN 15403, ASTM D 7582, EN 15414, EN 15402, ISO 19579) or internal methods (e.g. participants 1, 22, 15) were used.

The ash content was determined mainly gravimetrically by heating at the temperature 550 °C (Samples B1 and B2), at the temperature 750 °C or 815 °C (Sample K1) or at the temperature 950 °C (Samples B2 and K1). Ash content was measured also using TGA for samples at the temperatures between 550 °C and 815 °C (Appendix 11). In the international standards EN 14775 and EN ISO 18122 the ashing temperature is mentioned to be 550 °C for solid biofuels [10, 12]. While in ISO 1711 for solid mineral fuels it is mentioned to be 815 °C [11]. Based on the graphical result evaluation, clear differences between the used methods in measurements could not be concluded (Appendix 12).

Moisture content was determined gravimetrically by heating in air or N_2 atmosphere at the temperatures of 105-107.5 °C. Moisture content was measured also using TGA at the temperatures of 105-108 °C (Appendix 11).

Most of the participants conducted CHN analyses from air dried samples, one participant used dried B1 sample, and two participants used dried B2 and K1 samples (Appendix 11). Based on the graphical result evaluation, clear differences between the used methods in CHN measurements could not be concluded (Appendix 12). Also for S_d and V_{db} no clear differences between the used methods were noticed (Appendix 12).

In the PT also information of detection limits for nitrogen and sulphur was collected (Appendix 11). The detection limits varied for N: 0.0074-0.3 w% and for S: 0.0004-0.1 w%.

3.3 Uncertainties of the results

At maximum 88 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for estimating of measurement uncertainty (Appendix 13). The most used approaches were based on IQC data and method validation data. Three participants reported the usage of the MUkit measurement uncertainty software for the estimation of their uncertainties [27]. The free software is available on the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The estimated uncertainties varied highly for all the tested measurands (Table 3). Especially, very low or high uncertainties can be considered questionable. It was evident, that some uncertainties had been reported erroneously for the measurands (including calorific values, Appendix 13), **not as relative values as the provider of this proficiency test had requested**. It is evident that harmonization is still needed for the estimation of the expanded measurement uncertainties.

Table 3. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurement	Uncertainty B1,%	Uncertainty B2, %	Uncertainty K1, %
Ash_d	4.59-11.9	0.02-40	0.07-6
C_d	0.6-10	0.2-10	0.12-10
EF	3-10	-	1-10
H_d	5-10	0.18-11	0.17-10
N_d	6-14	2.46-30	0.14-17
$q_{p,net,d}$	0.9-10	0.44-182	0.12-465
$q_{V,gr,d}$	0.9-10	0.36-182	0.12-465
S_d	8-30	-	0.001-14
V_{db}	2-10	0.33-10	0.01-5

3.4 Estimation of emission factor

Additionally, the participants were asked to estimate the emission factors for the peat and coal samples distributed in the PT by taking into account their own net calorific values and the total moisture values as received, which was informed in the cover letter of the samples. The calculation of the emission factor of the wood pellet sample (B2) was not done as it is a CO_2 neutral fuel. In this PT, very few participants reported their results for the emission factor (5-8). Due to the low number of the reported results, the peat sample (B1) was evaluated based on E_n score (Appendix 9).

4 Evaluation of the results

The evaluation of participants was based on the z scores and E_n scores, which were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

In total, 89 % of the results evaluated based on z scores were satisfactory when accepting the deviation of 1–30 % from the assigned value (Appendix 9). All results evaluated based on E_n scores were satisfactory (Appendix 9). About 69 % of the participants used the accredited methods and 92 % of their results were satisfactory. In the previous similar proficiency test CAL 07/2017 the performance was satisfactory for 89 % of the results when deviation 1–30 % from the assigned value was accepted [5].

Table 4. Summary of the performance evaluation in the proficiency test 07/2018.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
Peat, B1	95	1.3-20	• Very good performance. • Only approximate assessment for N_d. • In the CAL 07/17 the performance was satisfactory for 100 % of the results, when accepting 1.3-15 % deviation from the assigned value [5].
Wood pellet, B2	83	1.4-30	• Difficulties in measurements for C_d and $q_{p,net,d}$ < 80% satisfactory results. • In the CAL 07/17 the performance was satisfactory for 85 % of the results, when accepting 1.3-30 % deviation from the assigned value [5].
Coal, K1	89	1-15	• Difficulties in measurements for $q_{p,net,d}$ < 80 % satisfactory results. • Only approximate assessment for V_{db}. • In the CAL 07/17 the performance was satisfactory for 88 % of the results [5].

The summary of the performance evaluation is shown in Table 4. The percentage of the satisfactory results varied between 83 % and 95 % for the tested sample types. The criteria for performance evaluation is mainly set according to the target value for reproducibility recommended in international standards or technical specifications for measurement of the calorific values and other determinants. The reproducibility required in the standards was fulfilled for the gross calorific values. For the net calorific value increased reproducibility from the value for the gross caloric value was used. There was no criterion for reproducibility for the net calorific value in standards methods.

Peat

In the previous similar PT (CAL 07/2017) 100 % of the results were satisfactory for the peat sample (B1) when accepting 1.3–30 % deviation from the assigned value [5]. In this PT the number of satisfactory results is slightly lower (95 %, Table 4). The number of satisfactory results of the gross and net calorific values for peat sample was lower for the gross calorific value and the net calorific value when compared to the previous similar PT (100 % for both) [5]. The results of analysis moisture (M_{ad}) have not been evaluated, but the assigned values are presented (Table 1). The results of EF were evaluated based on the E_n scores, which were all satisfactory (Appendix 9).

Wood pellet

In the previous similar PT CAL 07/2017 the satisfactory results of the wood pellet sample (B2) were in total 85 %, when accepting deviation 1.3–30 % from the assigned value [5], thus the performance in this PT was slightly lower (83 %, Table 4). The satisfactory results varied between 73 % (C_d, $q_{p,net,d}$) and 95 % (Ash_d) for the wood pellet sample (Table 1). In the measurement of gross and net calorific values 83 % and 73 % of the results, respectively, were satisfactory when accepting deviations of 1.4 % and 1.7 % from the assigned values (Table 1). The number of satisfactory results of the gross and net calorific values for wood pellet was at the same level for the gross calorific value and lower for the net calorific value than in the previous similar PT CAL 07/2017 (83 % for the both) [5]. The estimation of EF was not done as it is a CO_2 neutral fuel. Also the results of analysis moisture (M_{ad}) and nitrogen (N_d) have not been evaluated, but the assigned value is given (Table 1).

Coal

In the previous similar PT CAL 07/2017 the satisfactory results of the coal sample (K1) were in total 88 % [5], thus the performance was at the same level in this PT (89 %, Table 4). In the measurement of gross and net calorific values, 88 % and 79 % of results, respectively, were satisfactory, when accepting the deviations of 1 and 1.2 % from the assigned values (Table 1). These were lower than in the previous similar PT CAL 07/2017 (94 % and 92 %, respectively) [5]. From the calculated emission factor results 88 % were satisfactory and it was lower than in the previous similar PT CAL 07/2017 (100 %) [5]. The results of analysis moisture (M_{ad}) have not been evaluated, but the assigned value is given (Table 1).

5 Summary

Proftest SYKE carried out the proficiency test (PT) for the analysis of the gross and the net calorific value as well as for content of ash, carbon, hydrogen, nitrogen, sulphur, analytical moisture content and volatile matter in fuels in September 2018. Three types of samples were delivered to the participants: peat, wood pellet (not sulphur) and coal. In total 26 participants took part in the PT. The participants also had the possibility to estimate or calculate the emission factor for peat and coal samples.

The robust means, medians or means of the results reported by the participants were used as the assigned values for measurands. The uncertainty for the assigned value was estimated at the 95 % confidence level and it was less than 0.4 % for calorific values and at maximum 8 % for the other measurands.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. In some cases the number of the reported results was low and the performance was evaluated by using E_n scores (EF in the peat sample). The evaluation of performance was not done for the measurement of M_{ad} in all samples and N_d in the wood pellet sample. In this proficiency test 89 % of the data was regarded to be satisfactory when, depending on the measurand and sample, the result was accepted to deviate from the assigned value from 1 to 30 %. About 69 % of the participants used the accredited methods and 92 % of their results were satisfactory. In measurements of the gross calorific value from the peat, wood pellet and coal samples, 92 %, 83 % and 88 % of the results were satisfactory, respectively. In measurements of the net calorific value from the peat, wood pellet and coal samples, 82 %, 73 % and 79 % of the results were satisfactory, respectively. In general, the results were in the same range as in the previous similar Proftest SYKE proficiency test, CAL 07/2017 [5], but the performance in the gross and net calorific value was somewhat lower for peat and coal samples and also for the net calorific value for wood pellet sample in the present PT. The evaluation of data based on E_n scores for the peat sample show satisfactory performance for all results.

6 Summary in Finnish

Proftest SYKE järjesti syyskuussa 2018 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, hiilen, vedyn, typen, rikin, kosteuden ja haihtuvien yhdisteiden määrittämiseksi turpeesta, puupelletistä (ei rikkiä) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus laskea päästökerroin turve- ja kivihiilinäytteistä.

Pätevyyskokeeseen osallistui yhteensä 26 laboratoriota. Osallistujien pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat määrityksestä ja näytteestä riippuen välillä 1–30 %. Turvenäytteen päästökerrointulokset arvioitiin käyttäen E_n-arvoa tulosten vähyyden vuoksi. Testisuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai niiden mediaania ja keskiarvoa, jos tuloksia oli vähän (n<12). Vertailuarvon epävarmuus oli lämpöarvomäärityksissä alhaisempi kuin 0,4 % ja muiden määritysten osalta korkeintaan 8 %. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle eikä typen määritykselle puupelletistä.

Koko tulosaineistossa hyväksyttäviä tuloksia oli 89 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Noin 69 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 92 %. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 92 % (turve), 73 % (puupelletti) ja 79 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 92 % (turve), 83 % (puupelletti) ja 88 % (kivihiili). Hyväksyttäviä tuloksia oli lähes saman verran kuin edellisessä vastaavassa pätevyyskokeessa CAL 07/2017 [5]. Turve- ja hiilinäytteen osalta kalorimetrisen ja tehollisen lämpöarvon menestyminen sekä puupellettinäytteen tehollisen lämpöarvon menestyminen olivat jonkin verran alhaisempia kuin edellisellä kierroksella. E_n-arvolla arvioidut turvenäytteen päästökertoimen tulokset olivat kaikki hyväksyttäviä.

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).

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

5. Leivuori, M., Rantanen, M., Koivikko, R., Tervonen, K., Lanteri, S., Ilmakunnas, M., Proficiency test 07/2017. Gross and net calorific value in fuels. Reports of Finnish Environment Institute 35/2017. 75 pp. (http://hdl.handle.net/10138/228806)

6. EN 14918, 2010. Solid Biofuels. Method for the determination of calorific value.

7. EN ISO 18125. 2017. Solid biofuels- Determination of calorific value.

8. ISO 1928, 2009. Solid mineral fuels - Determination of gross calorific value by a bomb calorimetric method, and calculation of net calorific value.

9. ASTM D 5865. 2013. Test method for gross calorific value of coal and coke.

10. EN 14775, 2010. Solid biofuels. Determination of ash content (withdrawn).

11. ISO 1171, 2010 Solid mineral fuels - Determination of ash.

12. EN ISO 18122, 2015. Solid biofuels - Determination of ash content.

13. ASTM D 7582, 2015. Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis.

14. ISO 29541, 2010. Solid mineral fuels - Determination of total carbon, hydrogen and nitrogen content - Instrumental methods.

15. ASTM D 5373, 2013. Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke.

16. EN ISO 16948, 2015. Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen.

17. EN 14774-3, 2010. Solid biofuels. Methods for the determination of moisture content. Oven dry method. Part 3: Moisture in general analysis sample (withdrawn).

18. ISO 589, 2008. Hard coal - Determination of total moisture.

19. DIN 51718, 2002. Determining the moisture content of solid fuels.

20. EN ISO 18134-3, 2015. Solid biofuels - Determination of moisture content - Oven dry method - Part 3: Moisture in general analysis sample.

21. ISO 11722, 2013. Solid mineral fuels - Hard coal - Determination of moisture in the general analysis test sample by drying in nitrogen.

22. EN ISO 16994, 2015. Solid biofuels - Determination of total content of sulfur and chlorine.

23. ASTM D 4239, 2013. Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High - Temperature Combustion and Infrared Absorption.

24. EN 15148, 2010. Biofuels, Solid fuels, Biomass, Fuels, Chemical analysis and testing, Volatile matter determination, Gravimetric analysis (withdrawn).

25. ISO 562, 2010. Hard coal and coke - Determination of volatile matter.

26. EN ISO 18123, 2015. Solid biofuels - Determination of the content of volatile matter.

27. 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.*

28. Magnusson, B. Näykki. T., Hovind, H. and Krysell, M., 2012. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. NT Technical Report 537. Nordtest.

29. 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.

30. 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
Bulgary	AES-3C Maritza East 1 EOOD; Testing Laboratory "Energy Materials"
Czech Republic	ALS Czech Republic s.r.o.
Estonia	Enefit Energiatootmine AS Chemical Laboratory
Finland	Eurofins Ahma Oy, Oulu
	Eurofins Environment Testing Finland Oy, Vantaa, Industry and Power Plant Chemistry
	Eurofins Labtium Oy, Jyväskylä
	Finnsementti Oy
	Fortum Waste Solutions Oy, Riihimäki
	Helen Ltd
	Kuopion Energia Oy / Tuotanto-osasto
	KVVY-Botnialab, Vaasa
	Kymen Ympäristölaboratorio Oy
	Kymenlaakson ammattikorkeakoulu
	Luonnonvarakeskus Kokkolan laboratorio
	SSAB Europe Raahe, Raahe
France	ArcelorMittal Fos sur Mer
	SOCOR Dechy France
Lithuania	Axioma servisas, Biofuel researh laboratory
	Cement testing laboratory Co Akmenes cementas Lithuania
Republic of Ireland	Edenderry Power Ltd
Republic of Korea	Intertek KIMSCO Ulsan Testing Center, South Korea
Romania	Holcim(Romania) SA Ciment Campulung
	ICSI Ramnicu Valcea
	Romcontrol
Spain	Laboratorio Central de Calidad - LCC
Sweden	RISE Research Institutes of Sweden AB

APPENDIX 2: Preparation of the samples

Sample B1, peat

Sample B1 was prepared from peat taken from Finnish marshland.

The peat was air-dried (35 ºC) and ground in a mill with a 500 µm sieve at the laboratory of Eurofins Labtium Ltd (Jyväskylä, Finland). The dried and sieved sample was mixed by a mechanized sample mixer and distributed to sub-samples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of KVVY Tutkimus Oy (Tampere). The particle size distribution of peat was measured by the laboratory of Eurofins Labtium Ltd using laser diffraction (Malvern).

Sample B2, wood pellet

Sample B2 was prepared from spruce sawdust. The wood pellets were first crushed with a cutting mill and then ground by the mill with 1000 µm sieve at the laboratory of Eurofins Labtium Ltd. The sieved sample was mixed by a mechanized sample mixer and distributed to subsamples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of KVVY Tutkimus Oy (Tampere).

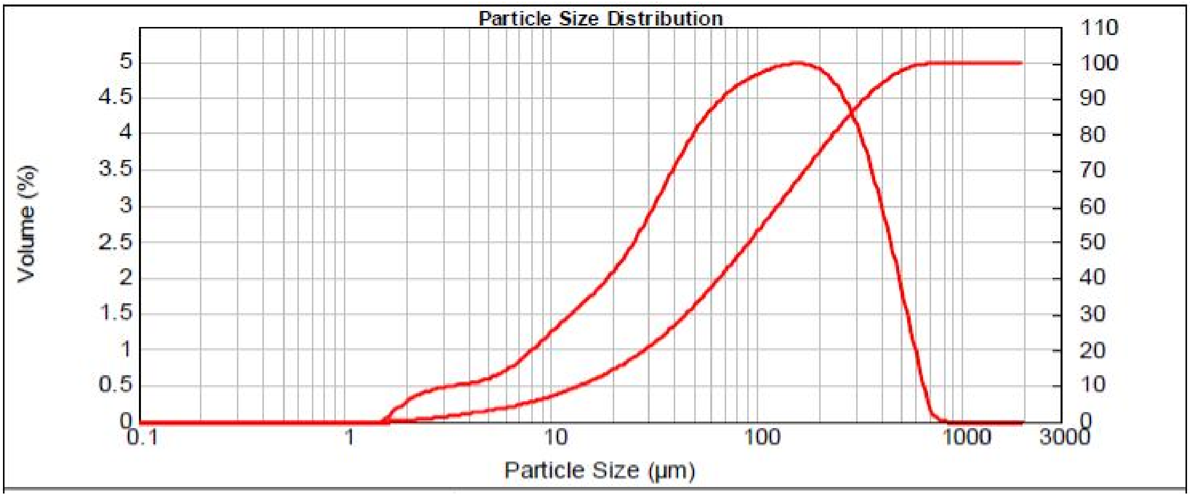
Sample K1, steam coal fuel

Sample K1 was a Russian steam coal. The coal was dried at room temperature and ground to particle size < 212 µm at the the Helen Ltd (Finland). The dried and sieved sample was mixed by a mechanized sample mixer and distributed into subsamples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory the laboratory of KVVY Tutkimus Oy (Tampere). The particle size distribution of coal was measured by the Helen Ltd, Power Plant Chemistry using laser diffraction (Malvern).

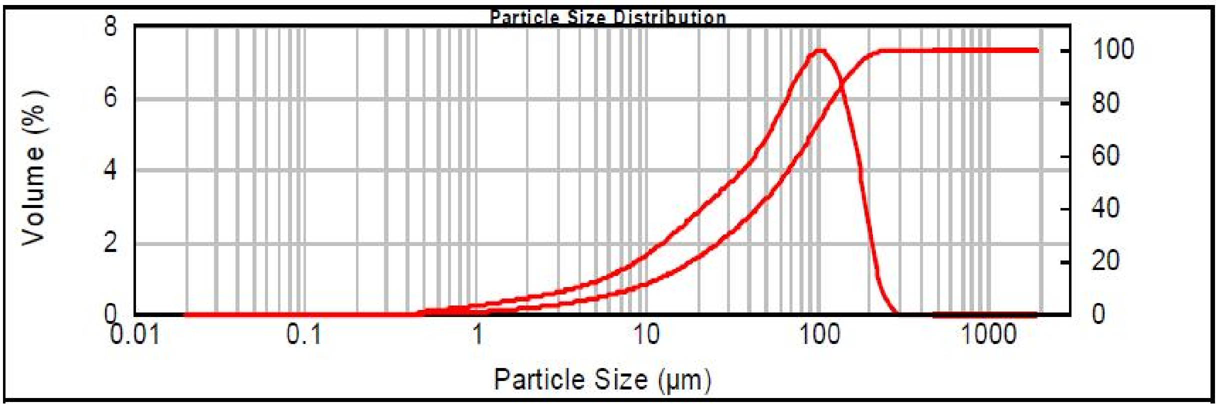
Particle size

To test the particle size of peat (B1) and coal (K1) samples, they were tested using laser diffraction (Malvern).

Figure 1 is showing the distribution of particle size for the samples B1 and K1. For peat sample B1 the mean size of particles was 92 µm and ca. 98.5 % of the particles were smaller than 550 µm. For coal sample K1 the mean size of particles was 60.9 µm and 99 % of the particles were smaller than 212 µm. The requirements of particle sizes given in the international standards were mainly fulfilled for the tested material [6, 8].



a) The particle size distribution of peat B1.



b) The particle size distribution of coal K1.

Figure 1. The particle size distribution of the fuel samples a) the peat (B1) and b) the coal (K1) sample.

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements of calorific value (Table 1) and ash content in five samples, which were homogenised before sampling. Additionally, the other measurands from two samples was tested.

Criteria for homogeneity:

$s_{anal}/s_h<0.5$ and $s_{sam}^2<c$, where

s_h % = standard deviation for testing of homogeneity
s_{anal} = analytical deviation, standard deviation of the results within sub samples
s_{pt}% = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$,
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Table 1. Results from the homogeneity testing of the peat (B1), pellet (B2) and coal (K1) samples.

Measurements	Mean	s_h%	s_{pt}%	s_h	s_{anal}	s_{anal}/s_h	Is s_{anal}/s_h<0.5?	s_{sam}	s_{sam}^2	c	Is s_{sam}^2<c?
Peat (B1)											
Gross calorific value, J/g	21744	0.3	0.65	65.2	24.7	0.37	yes	26.3	690	2190	yes
Net calorific value, J/g	20529	0.3	0.75	61.6	24.7	0.40	yes	26.3	700	2090	yes
Pellet (B2)											
Gross calorific value, J/g	20046	0.5	0.7	100	42.5	0.42	yes	63.8	4070	5760	yes
Net calorific value, J/g	18717	0.5	0.85	93.6	42.6	0.45	yes	63.6	4000	5460	yes
Coal (K1)											
Gross calorific value, J/g	28908	0.2	0.5	57.8	22.2	0.38	yes	18.4	340	1750	yes
Net calorific value, J/g	27899	0.2	0.6	55.8	22.2	0.40	yes	18.4	300	1700	yes

Conclusion: In each case, the criteria were fulfilled. **Thus, all the samples could be regarded as homogenous.** Also the results of the other tested measurands confirm the homogeneity of the samples.

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest SYKE
1	The participant informed receiving the samples on 10th September.	The used distributor (Posti) did not deliver the samples according to the agreed schedule.
22	The participant informed receiving the samples on 12th September.	According to the distributor's (Posti) tracking system the samples arrived to the participant on 7th September. The provider recommends to check the internal package delivery procedures.

Participant	Comments to the results	Action / Proftest SYKE
5	The participant reported only one result (Ash_d, Mad_d), though replicate results were requested.	The provider recommends the participant to follow the given guidelines.
14, 24	The participant did not deliver the results to Proftest SYKE by selecting ”Send results” on ProftestWEB.	The provider accepted the results.
23	The participant reported erroneously their results of gross calorific value for net calorific value. Their correct values were: B1: 21849 J/g, 21858 J/g B2: 20185 J/g, 20152 J/g K1: 28204 J/g, 28275 J/g.	The provider does not correct the results after delivering the preliminary results. The erroneous results were handled as outliers in the statistical treatment. They did not affect to the assigned value evaluation. If the gross calorific values value had been reported correctly they would have been satisfactory, with exception of coal sample. The participant can re-calculate the z scores according to the Guide for participants [4].
14	The participant contacted the provider due to their performance in the PT. The participant requested further information for the carbon and calorific value results.	The provider discussed with the participants about their performance, but clear explanation for the reason was not concluded.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
5	The participant reported only one result instead of replicate results for some measurands. The results have been excluded from the calculation of the assigned values, and results are not evaluated. The participants should follow more carefully the instructions given by the provider.
1, 6, 13, 14, 17, 22, 25	For these participants the deviation of replicate measurements for some measurands and samples was high and their results were Cochran outliers. The provider recommends the participants to validate their accepted deviation of replicate measurements.
4, 12, 14, 22	It was evident, that some uncertainties had been reported erroneously for the measurands (including calorific values), not as relative values as the provider of this proficiency test had requested. The provider recommends the participants to validate the calculation of measurement uncertainties and follow more carefully the instructions given by the provider.

APPENDIX 5: 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}
Ash_d	B1	w%	6.65	0.12	1.8	Robust mean	0.23
	B2	w%	0.30	0.02	7.8	Robust mean	0.26
	K1	w%	11.1	0.1	0.6	Robust mean	0.24
C_d	B1	w%	54.4	0.2	0.4	Median	0.13
	B2	w%	50.5	0.3	0.5	Median	0.20
	K1	w%	70.7	0.4	0.6	Robust mean	0.24
EF	B1	t CO2/TJ	108	1	0.5	Median	
	K1	t CO2/TJ	94.7	0.6	0.6	Mean	0.15
H_d	B1	w%	5.63	0.09	1.6	Mean	0.23
	B2	w%	6.01	0.11	1.8	Median	0.30
	K1	w%	4.60	0.06	1.3	Robust mean	0.22
$M_{ad,d}$	B1	w%	10.7			Median	
	B2	w%	8.10			Robust mean	
	K1	w%	5.54			Robust mean	
N_d	B1	w%	1.93	0.08	4.1	Median	0.41
	B2	w%	0.11			Median	
	K1	w%	2.13	0.04	1.9	Median	0.19
$q_{p,net,d}$	B1	J/g	20720	70	0.3	Median	0.23
	B2	J/g	18869	57	0.3	Median	0.18
	K1	J/g	27725	83	0.3	Median	0.25
$q_{V,gr,d}$	B1	J/g	21945	53	0.2	Median	0.18
	B2	J/g	20207	40	0.2	Robust mean	0.14
	K1	J/g	28743	86	0.3	Robust mean	0.30
S_d	B1	w%	0.21	0.01	6.3	Median	0.32
	K1	w%	0.45	0.02	3.4	Robust mean	0.23
V_{db}	B1	w%	66.1	0.3	0.4	Median	0.13
	B2	w%	85.0	0.5	0.6	Median	0.20
	K1	w%	36.1	0.54	1.5	Robust mean	0.38

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 and the z scores are qualified.

APPENDIX 6: 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
Participants'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 ($-2 \leq z \leq 2$)
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 ($z \geq 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \leq -3$), 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 $(i = 1, 2 \ldots p)$:

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

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

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

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

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

APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B1		-0.75	6.65	8	6.45	6.69	6.65	0.15	2.3	13
	w%	B2		0.33	0.30	30	0.32	0.30	0.30	0.04	14.3	18
	w%	K1		0.00	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	B1		-0.12	54.4	3	54.3	54.4	54.4	0.3	0.5	7
	w%	B2		0.40	50.5	2,5	50.8	50.5	50.5	0.4	0.8	8
	w%	K1		-0.11	70.7	2,5	70.6	70.6	70.7	0.7	0.9	15
H_d	w%	B1		-0.05	5.63	7	5.62	5.62	5.63	0.12	2.1	7
	w%	B2		-0.03	6.01	6	6.01	6.01	6.04	0.16	2.7	9
	w%	K1		-0.29	4.60	6	4.56	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B1			10.7		10.6	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.25	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.75	5.58	5.56	0.25	4.6	19
N_d	w%	B1		-1.35	1.93	10	1.80	1.93	1.89	0.10	5.5	7
	w%	B2			0.11		*<0.1*	0.11	0.10	0.04	46.1	5
	w%	K1		-1.55	2.13	10	1.97	2.13	2.11	0.07	3.2	11
$q_{V,gr,d}$	J/g	B1		0.54	21945	1,3	22023	21945	21933	86	0.4	11
	J/g	B2		0.49	20207	1,4	20277	20222	20203	62	0.3	15
	J/g	K1		0.59	28743	1	28828	28748	28745	136	0.5	15
S_d	w%	B1		-0.74	0.21	20	0.19	0.21	0.21	0.02	9.5	9
	w%	K1		1.04	0.45	15	0.49	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		0.00	66.1	3	66.1	66.1	66.2	0.4	0.6	7
	w%	B2		-0.16	85.0	3	84.8	85.0	85.1	0.8	0.9	10
	w%	K1		-0.28	36.1	4	35.90	36.0	36.1	0.8	2.2	14

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B1		0.34	6.65	8	6.74	6.69	6.65	0.15	2.3	13
	w%	B2		0.44	0.30	30	0.32	0.30	0.30	0.04	14.3	18
	w%	K1		1.19	11.1	2,5	11.3	11.1	11.1	0.1	0.9	18
C_d	w%	B1		0.40	54.4	3	54.7	54.4	54.4	0.3	0.5	7
	w%	B2		0.74	50.5	2,5	51.0	50.5	50.5	0.4	0.8	8
	w%	K1		-0.10	70.7	2,5	70.6	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	B1			108		108	108	107	1	0.5	5
	t CO2/TJ	K1		-0.24	94.7	4	94.3	94.3	94.7	0.7	0.7	7
H_d	w%	B1		-0.05	5.63	7	5.62	5.62	5.63	0.12	2.1	7
	w%	B2		0.26	6.01	6	6.06	6.01	6.04	0.16	2.7	9
	w%	K1		0.51	4.60	6	4.67	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B1			10.7		11.2	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.55	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.86	5.58	5.56	0.25	4.6	19
N_d	w%	B1		0.35	1.93	10	1.96	1.93	1.89	0.10	5.5	7
	w%	B2			0.11		0.11	0.11	0.10	0.04	46.1	5
	w%	K1		-0.01	2.13	10	2.13	2.13	2.11	0.07	3.2	11

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$q_{p,net,d}$	J/g	B1		0.55	20720	1,5	20806	20720	20718	107	0.5	9
	J/g	B2		0.56	18869	1,7	18959	18869	18864	93	0.5	11
	J/g	K1		0.15	27725	1,2	27750	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		0.56	21945	1,3	22025	21945	21933	86	0.4	11
	J/g	B2		0.50	20207	1,4	20278	20222	20203	62	0.3	15
	J/g	K1		0.05	28743	1	28751	28748	28745	136	0.5	15
S_d	w%	B1		-0.21	0.21	20	0.21	0.21	0.21	0.02	9.5	9
	w%	K1		-0.70	0.45	15	0.43	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		-0.19	66.1	3	65.9	66.1	66.2	0.4	0.6	7
	w%	B2		0.02	85.0	3	85.0	85.0	85.1	0.8	0.9	10
	w%	K1		-0.91	36.1	4	35.44	36.0	36.1	0.8	2.2	14

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B1		-0.41	6.65	8	6.54	6.69	6.65	0.15	2.3	13
	w%	B2		-0.11	0.30	30	0.30	0.30	0.30	0.04	14.3	18
$M_{ad,d}$	w%	B1			10.7		11.1	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.20	8.10	8.11	0.19	2.4	17

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	K1		-0.36	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	K1		-0.63	70.7	2,5	70.1	70.6	70.7	0.7	0.9	15
$M_{ad,d}$	w%	K1			5.54		5.62	5.58	5.56	0.25	4.6	19
$q_{p,net,d}$	J/g	K1		-0.48	27725	1,2	27645	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	K1		-0.70	28743	1	28642	28748	28745	136	0.5	15
S_d	w%	K1		-0.59	0.45	15	0.43	0.45	0.45	0.03	5.7	18
V_{db}	w%	K1		-1.41	36.1	4	35.08	36.0	36.1	0.8	2.2	14

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B1			6.65	8	*6,3*	6.69	6.65	0.15	2.3	13
	w%	B2			0.30	30	*0*	0.30	0.30	0.04	14.3	18
	w%	K1			11.1	2,5	*8,9*	11.1	11.1	0.1	0.9	18
$M_{ad,d}$	w%	B1			10.7		*10,3*	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		*8,3*	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		*5,0*	5.58	5.56	0.25	4.6	19
$q_{p,net,d}$	J/g	B1		-0.55	20720	1,5	20635	20720	20718	107	0.5	9
	J/g	B2		-2.85	18869	1,7	18413	18869	18864	93	0.5	11
	J/g	K1		-3.65	27725	1,2	27118	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		-0.64	21945	1,3	21853	21945	21933	86	0.4	11
	J/g	B2		-3.04	20207	1,4	19777	20222	20203	62	0.3	15
	J/g	K1		-4.85	28743	1	28046	28748	28745	136	0.5	15

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)
Ash_d	w%	B1		0.28	6.65	8	6.73	6.69	6.65	0.15	2.3	13
	w%	B2		0.67	0.30	30	0.33	0.30	0.30	0.04	14.3	18
	w%	K1		0.97	11.1	2,5	11.2	11.1	11.1	0.1	0.9	18
C_d	w%	B1		-0.15	54.4	3	54.3	54.4	54.4	0.3	0.5	7
	w%	B2		-0.64	50.5	2,5	50.1	50.5	50.5	0.4	0.8	8
	w%	K1		1.46	70.7	2,5	72.0	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	B1			108		107	108	107	1	0.5	5
	t CO2/TJ	K1		0.34	94.7	4	95.4	94.3	94.7	0.7	0.7	7
H_d	w%	B1		0.08	5.63	7	5.65	5.62	5.63	0.12	2.1	7
	w%	B2		-0.59	6.01	6	5.90	6.01	6.04	0.16	2.7	9
	w%	K1		-0.42	4.60	6	4.54	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B1			10.7		10.7	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.11	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.67	5.58	5.56	0.25	4.6	19
N_d	w%	B1		-2.38	1.93	10	1.70	1.93	1.89	0.10	5.5	7
	w%	B2			0.11		*<0,1*	0.11	0.10	0.04	46.1	5
	w%	K1		0.15	2.13	10	2.15	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B1		0.00	20720	1,5	20720	20720	20718	107	0.5	9
	J/g	B2		0.66	18869	1,7	18976	18869	18864	93	0.5	11
	J/g	K1		0.28	27725	1,2	27772	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		0.00	21945	1,3	21945	21945	21933	86	0.4	11
	J/g	B2		0.40	20207	1,4	20264	20222	20203	62	0.3	15
	J/g	K1		0.15	28743	1	28764	28748	28745	136	0.5	15
S_d	w%	B1		1.52	0.21	20	0.24	0.21	0.21	0.02	9.5	9
	w%	K1		1.29	0.45	15	0.49	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		0.45	66.1	3	66.5	66.1	66.2	0.4	0.6	7
	w%	B2		-0.08	85.0	3	84.9	85.0	85.1	0.8	0.9	10
	w%	K1		0.13	36.1	4	36.20	36.0	36.1	0.8	2.2	14

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)
Ash_d	w%	B1		0.13	6.65	8	6.69	6.69	6.65	0.15	2.3	13
	w%	B2		-0.22	0.30	30	0.29	0.30	0.30	0.04	14.3	18
$M_{ad,d}$	w%	B1			10.7		10.4	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		7.81	8.10	8.11	0.19	2.4	17
$q_{p,net,d}$	J/g	B1		-0.68	20720	1,5	20614	20720	20718	107	0.5	9
	J/g	B2		-0.68	18869	1,7	18760	18869	18864	93	0.5	11
$q_{V,gr,d}$	J/g	B1		-0.31	21945	1,3	21901	21945	21933	86	0.4	11
	J/g	B2		-0.36	20207	1,4	20156	20222	20203	62	0.3	15

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)
Ash_d	w%	B2		-0.89	0.30	30	0.26	0.30	0.30	0.04	14.3	18
	w%	K1		0.65	11.1	2,5	11.2	11.1	11.1	0.1	0.9	18
$M_{ad,d}$	w%	B2			8.10		8.05	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.66	5.58	5.56	0.25	4.6	19
$q_{V,gr,d}$	J/g	B2		0.13	20207	1,4	20225	20222	20203	62	0.3	15
	J/g	K1		1.16	28743	1	28910	28748	28745	136	0.5	15

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)
V_{db}	w%	B2		-0.89	85.0	3	83.9	85.0	85.1	0.8	0.9	10
	w%	K1		-0.93	36.1	4	35.43	36.0	36.1	0.8	2.2	14

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)
Ash_d	w%	B1		-0.34	6.65	8	6.56	6.69	6.65	0.15	2.3	13
	w%	B2		0.67	0.30	30	0.33	0.30	0.30	0.04	14.3	18
	w%	K1		0.68	11.1	2,5	11.2	11.1	11.1	0.1	0.9	18
C_d	w%	B1		-0.01	54.4	3	54.4	54.4	54.4	0.3	0.5	7
	w%	B2		0.14	50.5	2,5	50.6	50.5	50.5	0.4	0.8	8
	w%	K1		0.48	70.7	2,5	71.1	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	B1			108		108	108	107	1	0.5	5
	t CO2/TJ	K1		0.26	94.7	4	95.2	94.3	94.7	0.7	0.7	7
H_d	w%	B1		-0.24	5.63	7	5.58	5.62	5.63	0.12	2.1	7
	w%	B2		0.07	6.01	6	6.02	6.01	6.04	0.16	2.7	9
	w%	K1		-0.54	4.60	6	4.53	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B1			10.7		10.7	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.10	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.53	5.58	5.56	0.25	4.6	19
N_d	w%	B1		0.00	1.93	10	1.93	1.93	1.89	0.10	5.5	7
	w%	B2			0.11		0.11	0.11	0.10	0.04	46.1	5
	w%	K1		-0.52	2.13	10	2.08	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B1		-0.91	20720	1,5	20579	20720	20718	107	0.5	9
	J/g	B2		0.32	18869	1,7	18921	18869	18864	93	0.5	11
	J/g	K1		-0.40	27725	1,2	27659	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		-1.06	21945	1,3	21794	21945	21933	86	0.4	11
	J/g	B2		0.16	20207	1,4	20229	20222	20203	62	0.3	15
	J/g	K1		-0.83	28743	1	28624	28748	28745	136	0.5	15
S_d	w%	B1		-0.05	0.21	20	0.21	0.21	0.21	0.02	9.5	9
	w%	K1		-0.57	0.45	15	0.43	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		-0.41	66.1	3	65.7	66.1	66.2	0.4	0.6	7
	w%	B2		-0.07	85.0	3	84.9	85.0	85.1	0.8	0.9	10
	w%	K1		-0.47	36.1	4	35.76	36.0	36.1	0.8	2.2	14

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)
Ash_d	w%	B1		0.45	6.65	8	6.77	6.69	6.65	0.15	2.3	13
	w%	B2		0.78	0.30	30	0.34	0.30	0.30	0.04	14.3	18
	w%	K1		-0.40	11.1	2,5	11.0	11.1	11.1	0.1	0.9	18
C_d	w%	B1		-0.59	54.4	3	53.9	54.4	54.4	0.3	0.5	7
	w%	B2		-0.48	50.5	2,5	50.2	50.5	50.5	0.4	0.8	8
	w%	K1		-1.01	70.7	2,5	69.8	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	B1			108		107	108	107	1	0.5	5
	t CO2/TJ	K1		-0.21	94.7	4	94.3	94.3	94.7	0.7	0.7	7
H_d	w%	B1		1.11	5.63	7	5.85	5.62	5.63	0.12	2.1	7
	w%	B2		1.76	6.01	6	6.33	6.01	6.04	0.16	2.7	9
	w%	K1		2.62	4.60	6	4.96	4.58	4.58	0.06	1.3	13

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$M_{ad,d}$	w%	B1			10.7		10.5	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.00	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.06	5.58	5.56	0.25	4.6	19
N_d	w%	B1		0.64	1.93	10	1.99	1.93	1.89	0.10	5.5	7
	w%	B2			0.11		0.16	0.11	0.10	0.04	46.1	5
	w%	K1		0.03	2.13	10	2.13	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B1		-0.42	20720	1,5	20655	20720	20718	107	0.5	9
	J/g	B2		-0.15	18869	1,7	18845	18869	18864	93	0.5	11
	J/g	K1		-1.84	27725	1,2	27420	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		-0.13	21945	1,3	21927	21945	21933	86	0.4	11
	J/g	B2		0.11	20207	1,4	20222	20222	20203	62	0.3	15
	J/g	K1		-1.75	28743	1	28492	28748	28745	136	0.5	15
S_d	w%	B1		1.52	0.21	20	0.24	0.21	0.21	0.02	9.5	9
	w%	K1		0.25	0.45	15	0.46	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		0.15	66.1	3	66.2	66.1	66.2	0.4	0.6	7
	w%	B2		0.31	85.0	3	85.4	85.0	85.1	0.8	0.9	10
	w%	K1		-0.01	36.1	4	36.10	36.0	36.1	0.8	2.2	14

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B2		0.11	0.30	30	0.31	0.30	0.30	0.04	14.3	18
	w%	K1		0.22	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	B2		-0.17	50.5	2,5	50.4	50.5	50.5	0.4	0.8	8
	w%	K1		-0.17	70.7	2,5	70.6	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	K1		-0.36	94.7	4	94.0	94.3	94.7	0.7	0.7	7
H_d	w%	B2		-0.63	6.01	6	5.90	6.01	6.04	0.16	2.7	9
	w%	K1		-1.12	4.60	6	4.45	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B2			8.10		3.67	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.59	5.58	5.56	0.25	4.6	19
N_d	w%	B2			0.11		*<0.300*	0.11	0.10	0.04	46.1	5
	w%	K1		-0.41	2.13	10	2.09	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B2		0.00	18869	1,7	18869	18869	18864	93	0.5	11
	J/g	K1		0.41	27725	1,2	27794	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B2		-0.07	20207	1,4	20198	20222	20203	62	0.3	15
	J/g	K1		0.03	28743	1	28748	28748	28745	136	0.5	15
S_d	w%	K1		0.56	0.45	15	0.47	0.45	0.45	0.03	5.7	18
V_{db}	w%	B2		-0.59	85.0	3	84.2	85.0	85.1	0.8	0.9	10
	w%	K1		0.51	36.1	4	36.47	36.0	36.1	0.8	2.2	14

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B2		0.44	0.30	30	0.32	0.30	0.30	0.04	14.3	18
	w%	K1		-0.22	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	B2		-0.79	50.5	2,5	50.0	50.5	50.5	0.4	0.8	8
	w%	K1		-1.36	70.7	2,5	69.5	70.6	70.7	0.7	0.9	15
H_d	w%	B2		1.55	6.01	6	6.29	6.01	6.04	0.16	2.7	9
	w%	K1		5.72	4.60	6	5.39	4.58	4.58	0.06	1.3	13

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$M_{ad,d}$	w%	B2			8.10		7.97	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.47	5.58	5.56	0.25	4.6	19
N_d	w%	B2			0.11		0.05	0.11	0.10	0.04	46.1	5
	w%	K1		-0.38	2.13	10	2.09	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B2		0.19	18869	1,7	18899	18869	18864	93	0.5	11
	J/g	K1		-0.16	27725	1,2	27699	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B2		0.43	20207	1,4	20268	20222	20203	62	0.3	15
	J/g	K1		-0.11	28743	1	28727	28748	28745	136	0.5	15
S_d	w%	K1		0.89	0.45	15	0.48	0.45	0.45	0.03	5.7	18
V_{db}	w%	B2		0.39	85.0	3	85.5	85.0	85.1	0.8	0.9	10
	w%	K1		2.35	36.1	4	37.80	36.0	36.1	0.8	2.2	14

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B1		-1.03	6.65	8	6.38	6.69	6.65	0.15	2.3	13
	w%	B2		-1.78	0.30	30	0.22	0.30	0.30	0.04	14.3	18
	w%	K1		0.83	11.1	2,5	11.2	11.1	11.1	0.1	0.9	18
$M_{ad,d}$	w%	B1			10.7		10.2	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		7.87	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.27	5.58	5.56	0.25	4.6	19
$q_{V,gr,d}$	J/g	B1		-0.95	21945	1,3	21810	21945	21933	86	0.4	11
	J/g	B2		-0.72	20207	1,4	20105	20222	20203	62	0.3	15
	J/g	K1		-0.41	28743	1	28684	28748	28745	136	0.5	15
S_d	w%	B1		0.21	0.21	20	0.21	0.21	0.21	0.02	9.5	9
	w%	K1		0.27	0.45	15	0.46	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		-0.21	66.1	3	65.9	66.1	66.2	0.4	0.6	7
	w%	B2		-2.96	85.0	3	81.2	85.0	85.1	0.8	0.9	10
	w%	K1		-5.00	36.1	4	32.49	36.0	36.1	0.8	2.2	14

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B2		-0.67	0.30	30	0.27	0.30	0.30	0.04	14.3	18
	w%	K1		-4.29	11.1	2,5	10.5	11.1	11.1	0.1	0.9	18
C_d	w%	B2		-5.83	50.5	2,5	46.8	50.5	50.5	0.4	0.8	8
	w%	K1		-4.71	70.7	2,5	66.5	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	K1		-49.95	94.7	4	0.1	94.3	94.7	0.7	0.7	7
H_d	w%	B2		-0.67	6.01	6	5.89	6.01	6.04	0.16	2.7	9
	w%	K1		-0.29	4.60	6	4.56	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B2			8.10		8.12	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.48	5.58	5.56	0.25	4.6	19
N_d	w%	B2			0.11		0.38	0.11	0.10	0.04	46.1	5
	w%	K1		0.89	2.13	10	2.23	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B2		-11.17	18869	1,7	17078	18869	18864	93	0.5	11
	J/g	K1		-9.24	27725	1,2	26188	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B2		-13.03	20207	1,4	18364	20222	20203	62	0.3	15
	J/g	K1		-11.04	28743	1	27156	28748	28745	136	0.5	15
S_d	w%	K1		2.81	0.45	15	0.55	0.45	0.45	0.03	5.7	18

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)
V_{db}	w%	B2		-4.33	85.0	3	79.5	85.0	85.1	0.8	0.9	10
	w%	K1		-4.40	36.1	4	32.93	36.0	36.1	0.8	2.2	14

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)
Ash_d	w%	K1		-0.07	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	K1		-0.18	70.7	2,5	70.5	70.6	70.7	0.7	0.9	15
$M_{ad,d}$	w%	K1			5.54		5.36	5.58	5.56	0.25	4.6	19
S_d	w%	K1		-0.16	0.45	15	0.44	0.45	0.45	0.03	5.7	18

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)
Ash_d	w%	B1		-0.51	6.65	8	6.52	6.69	6.65	0.15	2.3	13
	w%	B2		-0.44	0.30	30	0.28	0.30	0.30	0.04	14.3	18
	w%	K1		0.22	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	B1		0.25	54.4	3	54.6	54.4	54.4	0.3	0.5	7
	w%	B2		0.80	50.5	2,5	51.0	50.5	50.5	0.4	0.8	8
	w%	K1		-0.09	70.7	2,5	70.6	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	B1			108		108	108	107	1	0.5	5
	t CO2/TJ	K1		-0.28	94.7	4	94.2	94.3	94.7	0.7	0.7	7
H_d	w%	B1		0.00	5.63	7	5.63	5.62	5.63	0.12	2.1	7
	w%	B2		-0.33	6.01	6	5.95	6.01	6.04	0.16	2.7	9
	w%	K1		0.07	4.60	6	4.61	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B1			10.7		10.6	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.05	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.55	5.58	5.56	0.25	4.6	19
N_d	w%	B1		-0.50	1.93	10	1.88	1.93	1.89	0.10	5.5	7
	w%	B2			0.11		0.06	0.11	0.10	0.04	46.1	5
	w%	K1		-0.85	2.13	10	2.04	2.13	2.11	0.07	3.2	11
$q_{p,net,d}$	J/g	B1		0.07	20720	1,5	20732	20720	20718	107	0.5	9
	J/g	B2		0.39	18869	1,7	18931	18869	18864	93	0.5	11
	J/g	K1		0.33	27725	1,2	27781	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		0.05	21945	1,3	21952	21945	21933	86	0.4	11
	J/g	B2		0.14	20207	1,4	20227	20222	20203	62	0.3	15
	J/g	K1		0.17	28743	1	28768	28748	28745	136	0.5	15
S_d	w%	B1		-0.05	0.21	20	0.21	0.21	0.21	0.02	9.5	9
	w%	K1		0.04	0.45	15	0.45	0.45	0.45	0.03	5.7	18

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)
Ash_d	w%	B1		-0.24	6.65	8	6.59	6.69	6.65	0.15	2.3	13
	w%	B2		-1.89	0.30	30	0.22	0.30	0.30	0.04	14.3	18
$q_{p,net,d}$	J/g	B1		-3.18	20720	1,5	20226	20720	20718	107	0.5	9
	J/g	B2		-1.33	18869	1,7	18656	18869	18864	93	0.5	11
$q_{V,gr,d}$	J/g	B1		-3.20	21945	1,3	21489	21945	21933	86	0.4	11
	J/g	B2		-0.98	20207	1,4	20068	20222	20203	62	0.3	15

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)
Ash_d	w%	B1		0.52	6.65	8	6.79	6.69	6.65	0.15	2.3	13
	w%	B2		-0.26	0.30	30	0.29	0.30	0.30	0.04	14.3	18
$M_{ad,d}$	w%	B1			10.7		11.1	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		8.38	8.10	8.11	0.19	2.4	17
$q_{p,net,d}$	J/g	B1		1.16	20720	1,5	20900	20720	20718	107	0.5	9
	J/g	B2		-0.09	18869	1,7	18855	18869	18864	93	0.5	11
$q_{V,gr,d}$	J/g	B1		0.62	21945	1,3	22034	21945	21933	86	0.4	11
	J/g	B2		-0.06	20207	1,4	20199	20222	20203	62	0.3	15

Participant 20													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B1		0.64	6.65	8	6.82	6.69	6.65	0.15	2.3	13
	w%	K1		-0.18	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	B1		0.02	54.4	3	54.4	54.4	54.4	0.3	0.5	7
	w%	K1		1.01	70.7	2,5	71.6	70.6	70.7	0.7	0.9	15
H_d	w%	B1		-0.92	5.63	7	5.45	5.62	5.63	0.12	2.1	7
	w%	K1		-0.12	4.60	6	4.58	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B1			10.7		10.7	10.7	10.7	0.3	2.9	12
	w%	K1			5.54		5.99	5.58	5.56	0.25	4.6	19
N_d	w%	B1		0.10	1.93	10	1.94	1.93	1.89	0.10	5.5	7
$q_{p,net,d}$	J/g	B1		0.65	20720	1,5	20821	20720	20718	107	0.5	9
	J/g	K1		1.80	27725	1,2	28025	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B1		0.41	21945	1,3	22004	21945	21933	86	0.4	11
	J/g	K1		1.97	28743	1	29026	28748	28745	136	0.5	15
S_d	w%	B1		-1.48	0.21	20	0.18	0.21	0.21	0.02	9.5	9
	w%	K1		0.36	0.45	15	0.46	0.45	0.45	0.03	5.7	18
V_{db}	w%	K1		-0.44	36.1	4	35.79	36.0	36.1	0.8	2.2	14

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)
C_d	w%	K1		-0.23	70.7	2,5	70.5	70.6	70.7	0.7	0.9	15
H_d	w%	K1		0.14	4.60	6	4.62	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	K1			5.54		5.57	5.58	5.56	0.25	4.6	19
N_d	w%	K1		0.09	2.13	10	2.14	2.13	2.11	0.07	3.2	11
S_d	w%	K1		-0.30	0.45	15	0.44	0.45	0.45	0.03	5.7	18

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)
Ash_d	w%	B2		-3.89	0.30	30	0.13	0.30	0.30	0.04	14.3	18
	w%	K1		-0.90	11.1	2,5	11.0	11.1	11.1	0.1	0.9	18
C_d	w%	B2		-4.12	50.5	2,5	47.9	50.5	50.5	0.4	0.8	8
	w%	K1		0.65	70.7	2,5	71.3	70.6	70.7	0.7	0.9	15
H_d	w%	B2		2.61	6.01	6	6.48	6.01	6.04	0.16	2.7	9
	w%	K1		0.25	4.60	6	4.64	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	B2			8.10		4.10	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.97	5.58	5.56	0.25	4.6	19
N_d	w%	B2			0.11		0.00	0.11	0.10	0.04	46.1	5
	w%	K1		0.14	2.13	10	2.15	2.13	2.11	0.07	3.2	11

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)
$q_{p,net,d}$	J/g	B2		-10.00	18869	1,7	17266	18869	18864	93	0.5	11
	J/g	K1		0.00	27725	1,2	27725	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	B2		-10.91	20207	1,4	18664	20222	20203	62	0.3	15
	J/g	K1		-0.46	28743	1	28678	28748	28745	136	0.5	15
S_d	w%	K1		-1.93	0.45	15	0.39	0.45	0.45	0.03	5.7	18
V_{db}	w%	B2		1.38	85.0	3	86.8	85.0	85.1	0.8	0.9	10
	w%	K1		0.08	36.1	4	36.16	36.0	36.1	0.8	2.2	14

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)
Ash_d	w%	B1		0.85	6.65	8	6.88	6.69	6.65	0.15	2.3	13
	w%	B2		1.92	0.30	30	0.39	0.30	0.30	0.04	14.3	18
	w%	K1		4.91	11.1	2,5	11.8	11.1	11.1	0.1	0.9	18
$M_{ad,d}$	w%	B1			10.7		10.3	10.7	10.7	0.3	2.9	12
	w%	B2			8.10		7.93	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		4.22	5.58	5.56	0.25	4.6	19
$q_{p,net,d}$	J/g	B1		7.29	20720	1,5	21854	20720	20718	107	0.5	9
	J/g	B2		8.10	18869	1,7	20169	18869	18864	93	0.5	11
	J/g	K1		3.09	27725	1,2	28240	27725	27707	158	0.6	11
S_d	w%	B1		0.17	0.21	20	0.21	0.21	0.21	0.02	9.5	9
	w%	K1		-0.06	0.45	15	0.45	0.45	0.45	0.03	5.7	18
V_{db}	w%	B1		0.61	66.1	3	66.7	66.1	66.2	0.4	0.6	7
	w%	B2		0.13	85.0	3	85.2	85.0	85.1	0.8	0.9	10
	w%	K1		1.51	36.1	4	37.19	36.0	36.1	0.8	2.2	14

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)
Ash_d	w%	B2		0.11	0.30	30	0.31	0.30	0.30	0.04	14.3	18
$M_{ad,d}$	w%	B2			8.10		8.31	8.10	8.11	0.19	2.4	17
$q_{p,net,d}$	J/g	B2		-0.21	18869	1,7	18835	18869	18864	93	0.5	11
$q_{V,gr,d}$	J/g	B2		-0.16	20207	1,4	20185	20222	20203	62	0.3	15

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)
Ash_d	w%	K1		-0.22	11.1	2,5	11.1	11.1	11.1	0.1	0.9	18
C_d	w%	K1		0.73	70.7	2,5	71.3	70.6	70.7	0.7	0.9	15
EF	t CO2/TJ	K1		0.56	94.7	4	95.8	94.3	94.7	0.7	0.7	7
H_d	w%	K1		-0.07	4.60	6	4.59	4.58	4.58	0.06	1.3	13
$M_{ad,d}$	w%	K1			5.54		5.11	5.58	5.56	0.25	4.6	19
$q_{p,net,d}$	J/g	K1		-1.29	27725	1,2	27510	27725	27707	158	0.6	11
$q_{V,gr,d}$	J/g	K1		-0.89	28743	1	28615	28748	28745	136	0.5	15
S_d	w%	K1		-0.36	0.45	15	0.44	0.45	0.45	0.03	5.7	18
V_{db}	w%	K1		1.10	36.1	4	36.90	36.0	36.1	0.8	2.2	14

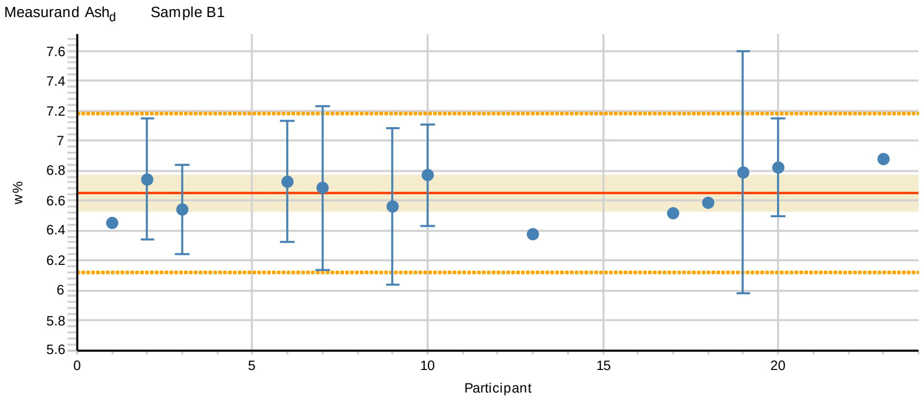
Participant 26													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2 \times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n (stat)
$M_{ad,d}$	w%	B2			8.10		8.23	8.10	8.11	0.19	2.4	17

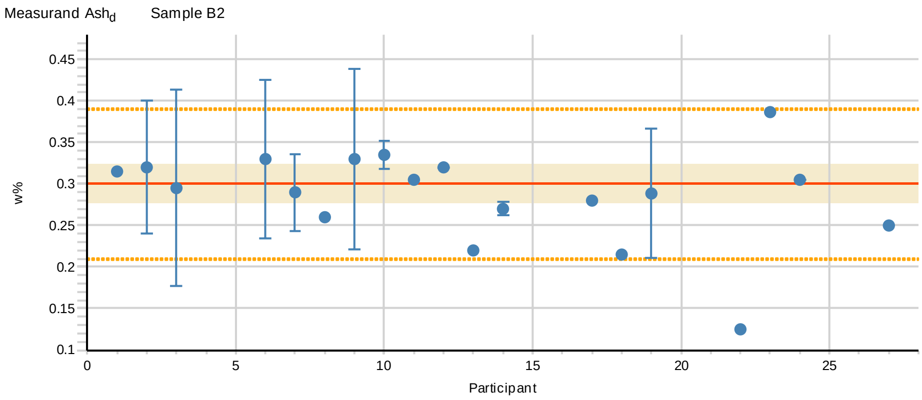
Participant 27													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Ash_d	w%	B2		-1.11	0.30	30	0.25	0.30	0.30	0.04	14.3	18
	w%	K1		1.69	11.1	2,5	11.3	11.1	11.1	0.1	0.9	18
C_d	w%	B2		-2.79	50.5	2,5	48.7	50.5	50.5	0.4	0.8	8
	w%	K1		-0.35	70.7	2,5	70.4	70.6	70.7	0.7	0.9	15
$M_{ad,d}$	w%	B2			8.10		7.94	8.10	8.11	0.19	2.4	17
	w%	K1			5.54		5.66	5.58	5.56	0.25	4.6	19
$q_{V,gr,d}$	J/g	B2		-0.38	20207	1,4	20153	20222	20203	62	0.3	15
	J/g	K1		1.24	28743	1	28922	28748	28745	136	0.5	15
S_d	w%	K1		0.30	0.45	15	0.46	0.45	0.45	0.03	5.7	18
V_{db}	w%	K1		-1.30	36.1	4	35.16	36.0	36.1	0.8	2.2	14

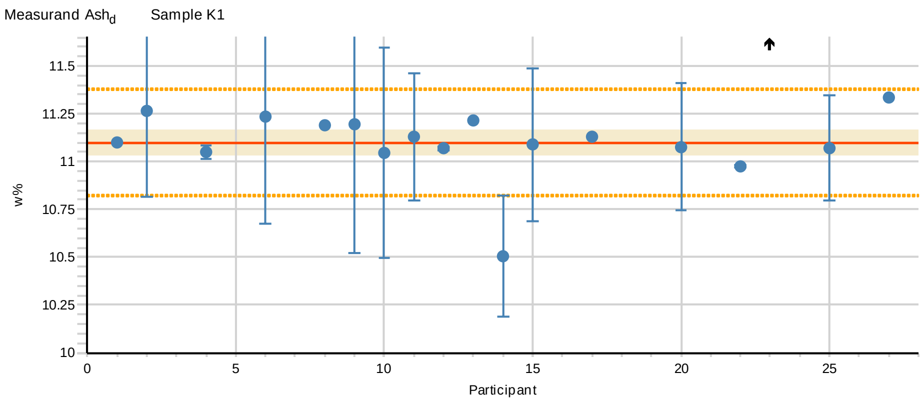
APPENDIX 8: Results of participants and their uncertainties

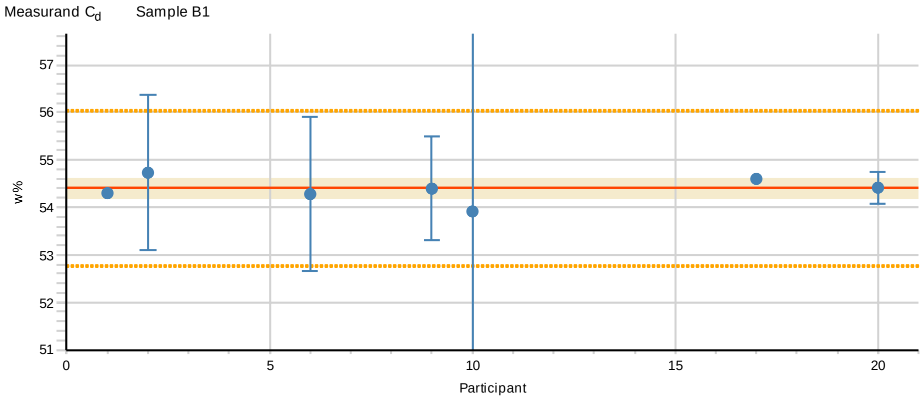
In figures:

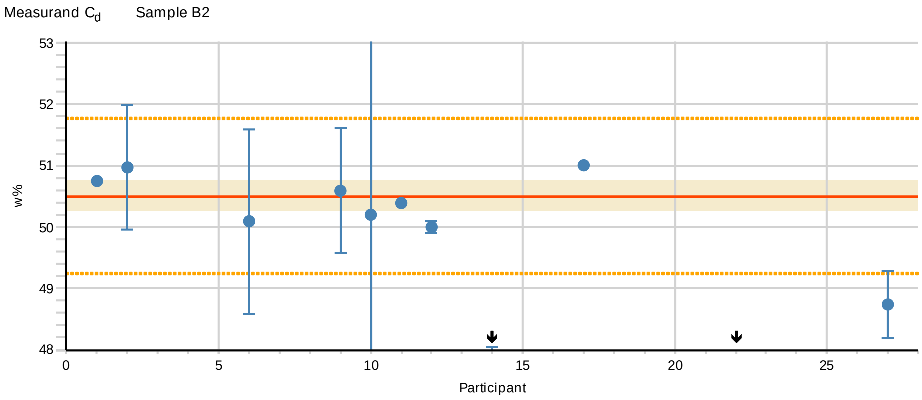
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

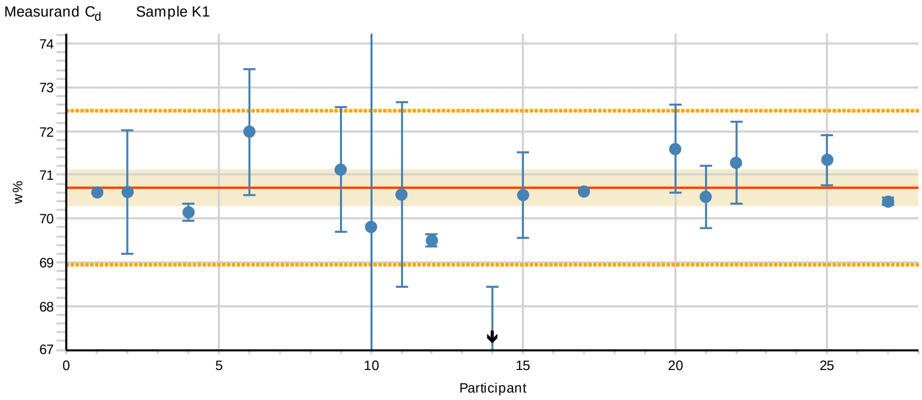


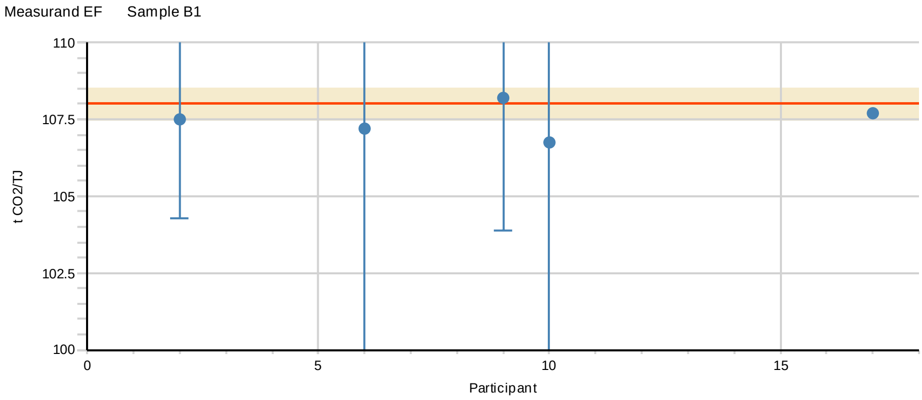


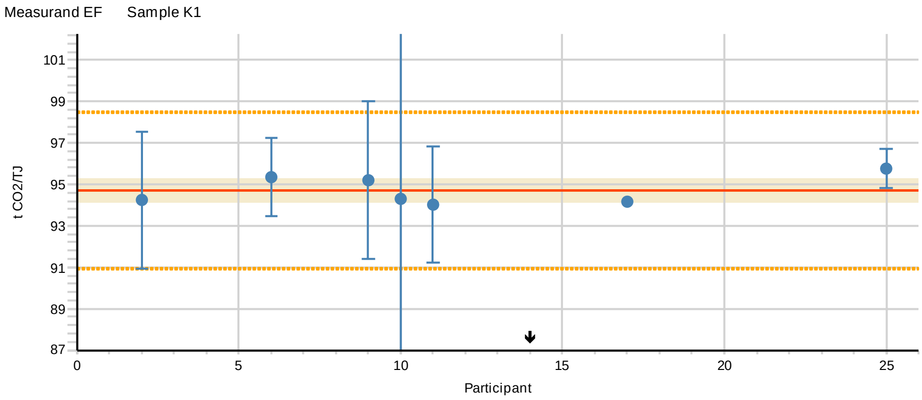


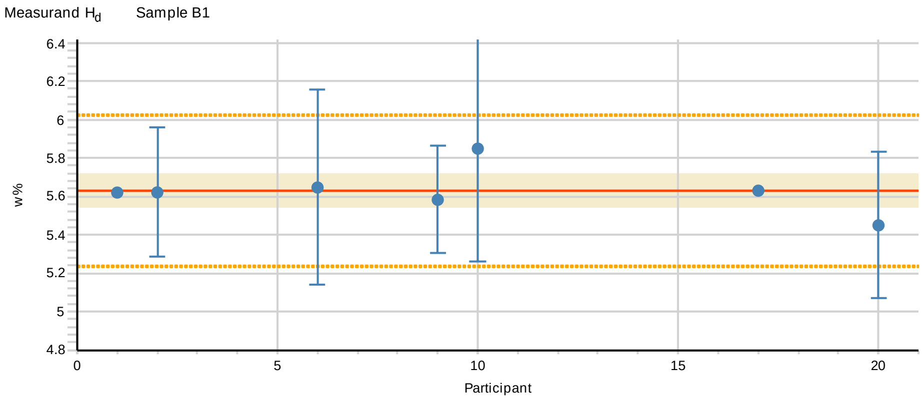

Measurand C_d Sample B1
w%
57
56
55
54
53
52
51
0
5
10
15
20
Participant

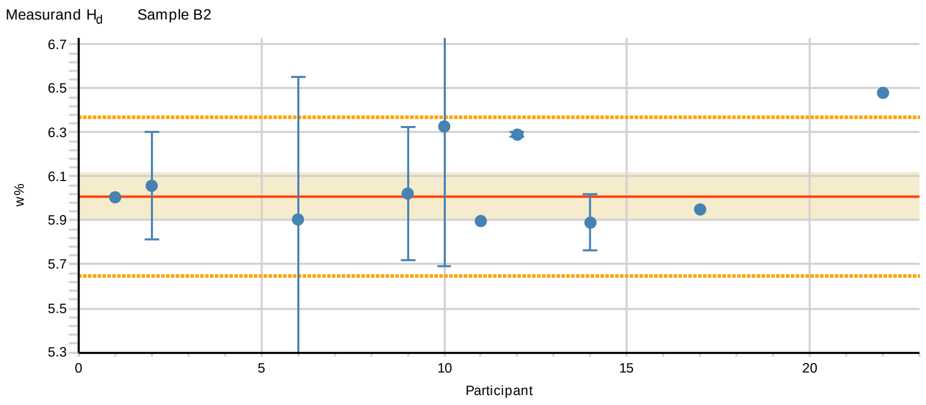

Measurand C_d Sample B2
w%
53
52
51
50
49
48
0
5
10
15
20
25
Participant

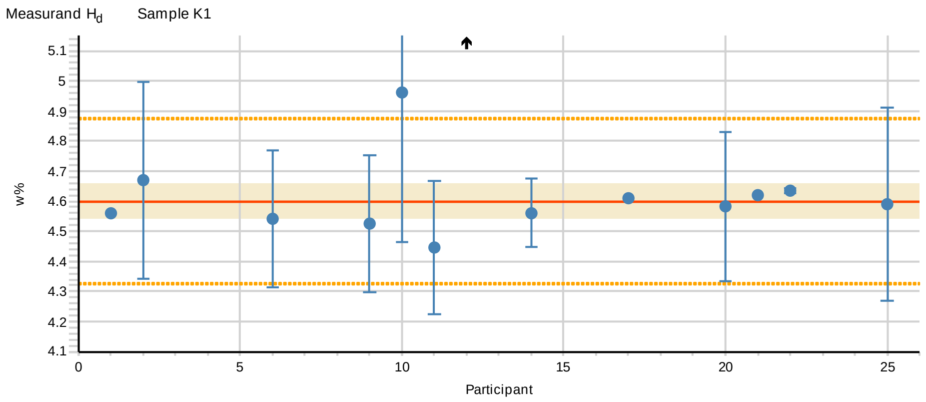

Measurand C_d Sample K1
w%
74
73
72
71
70
69
68
67
0
5
10
15
20
25
Participant

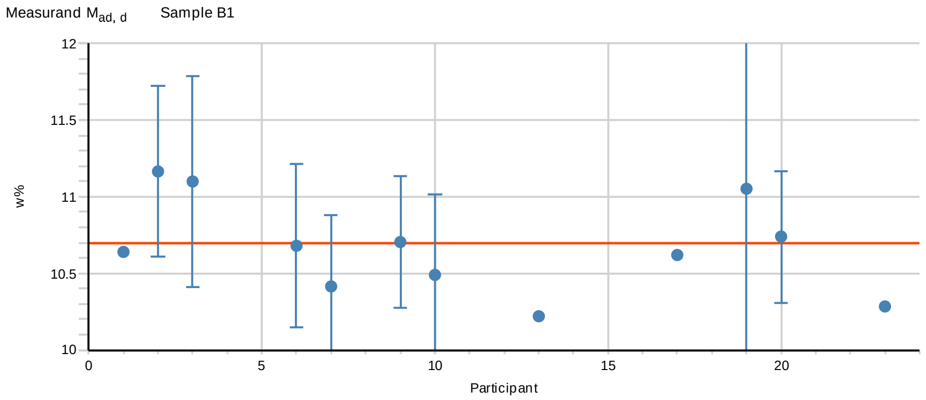

Measurand EF Sample B1
110
107.5
105
102.5
100
t CO2/TJ
0
5
10
15
Participant


Measurand EF Sample K1
101
99
97
95
93
91
89
87
t CO2/TJ
0
5
10
15
20
25
Participant

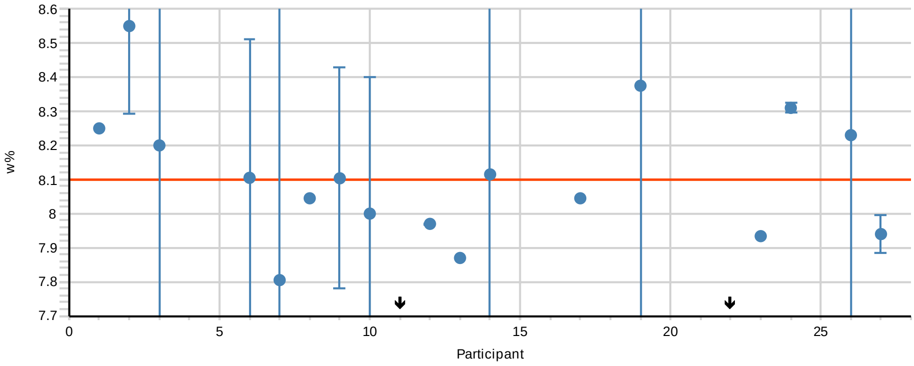

Measurand H_d Sample B1
6.4
6.2
6
5.8
5.6
5.4
5.2
5
4.8
w%
0
5
10
15
20
Participant


Measurand H_d Sample B2
w%
Participant

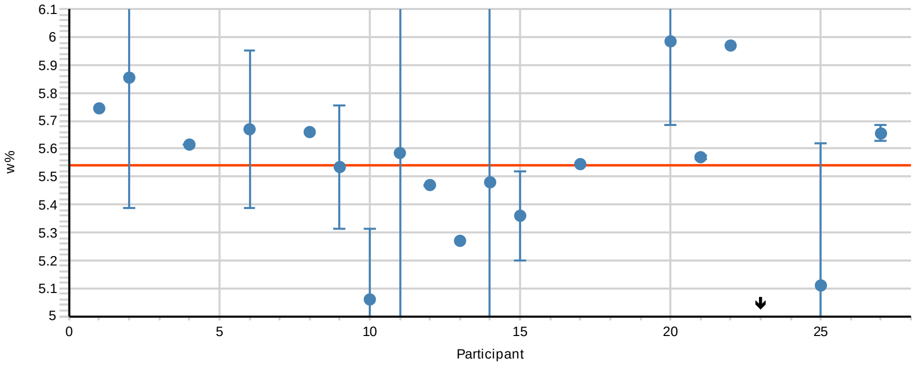

Measurand H_d Sample K1
w%
Participant


Measurand $M_{ad, d}$ Sample B1
w%
Participant

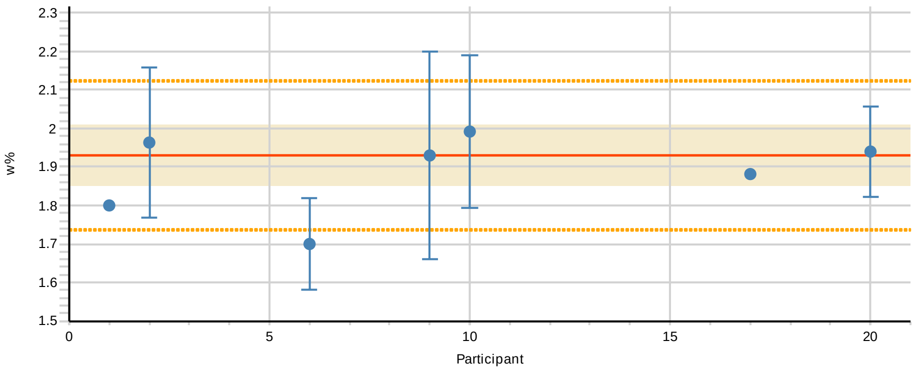
Measurand $M_{ad,\,d}$ Sample B2

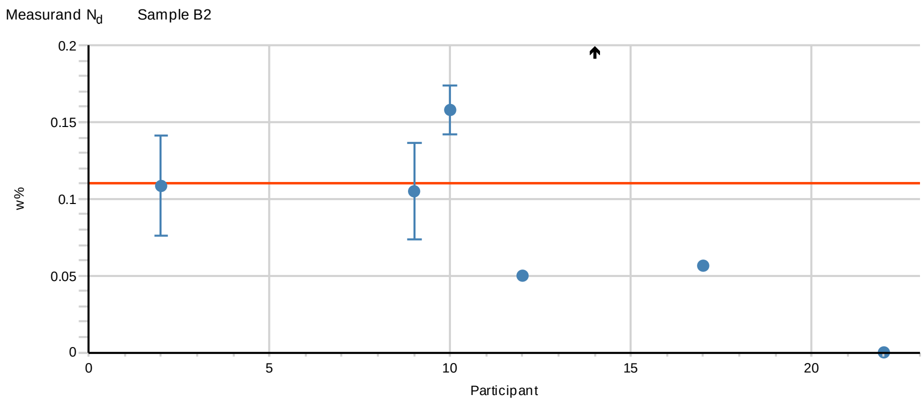


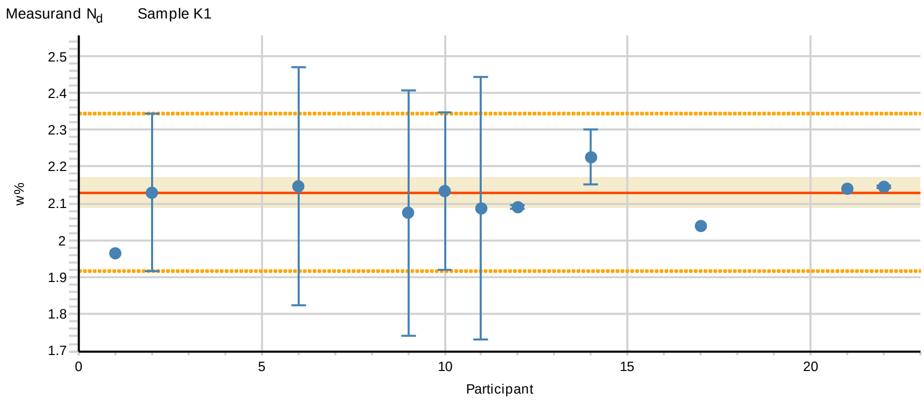
Measurand $M_{ad,\,d}$ Sample K1

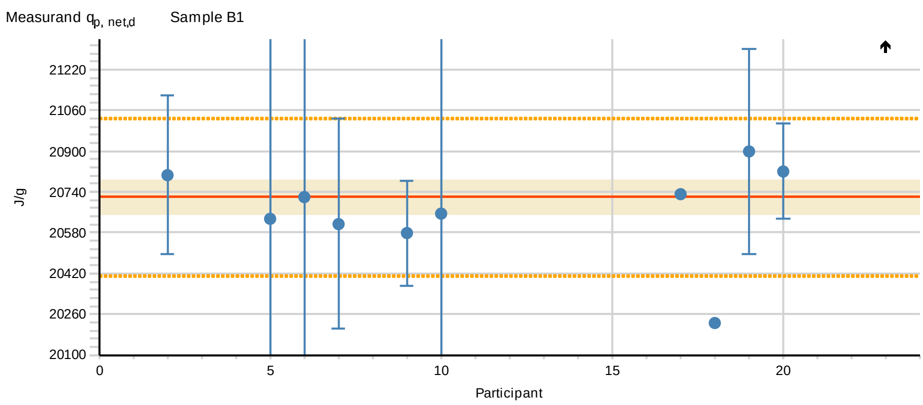


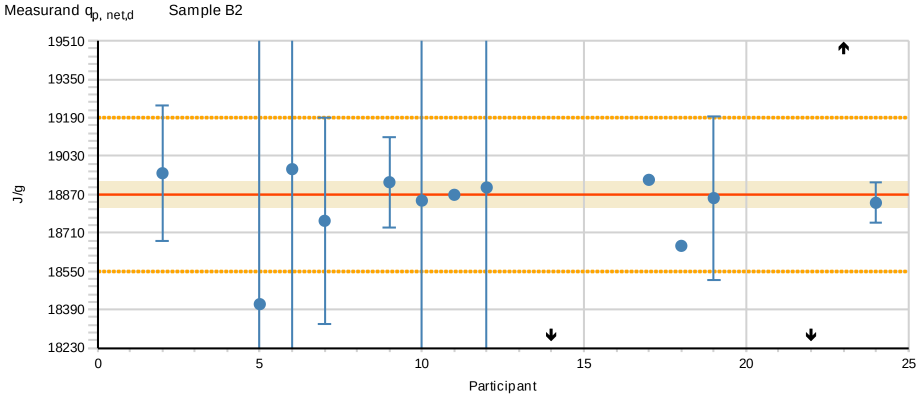
Measurand N_d Sample B1

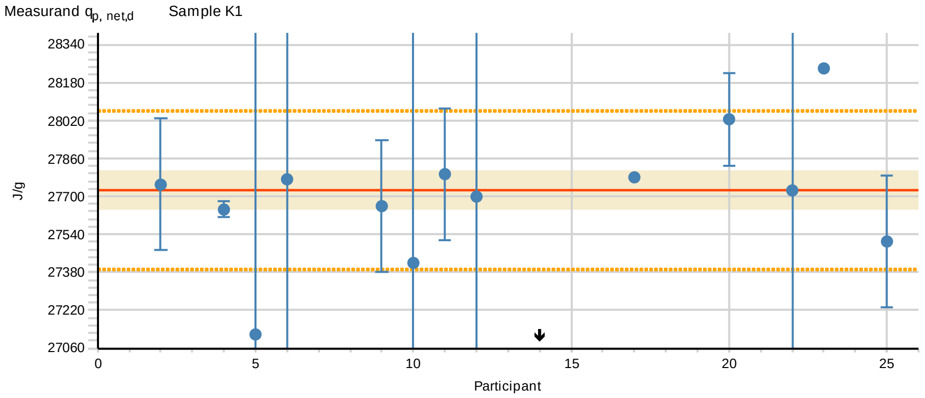


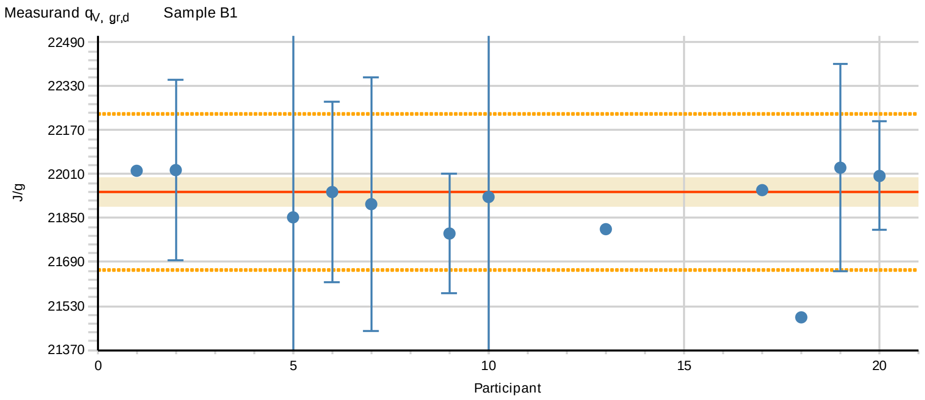

Measurand N_d
Sample B2
0.2
0.15
0.1
0.05
0
w%
0
5
10
15
20
Participant

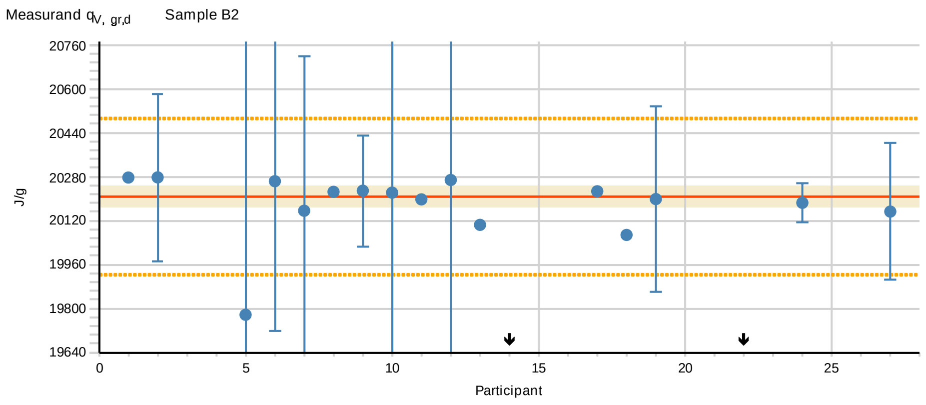

Measurand N_d
Sample K1
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
w%
0
5
10
15
20
Participant

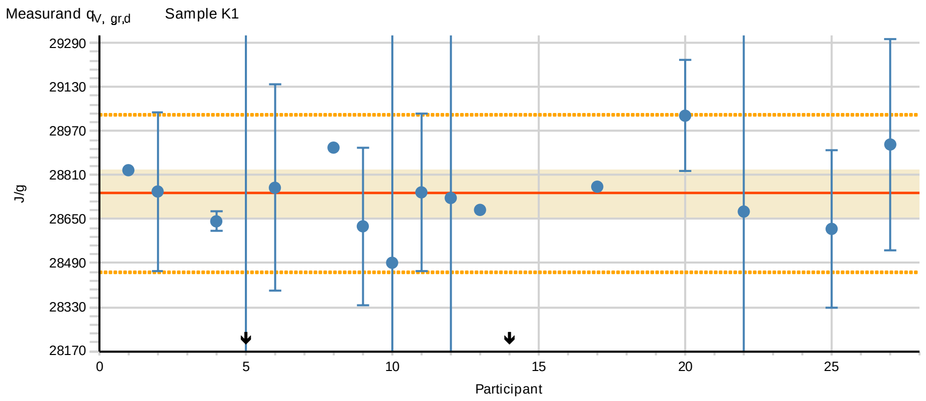

Measurand $q_{p, net,d}$
Sample B1
21220
21060
20900
20740
20580
20420
20260
20100
J/g
0
5
10
15
20
Participant

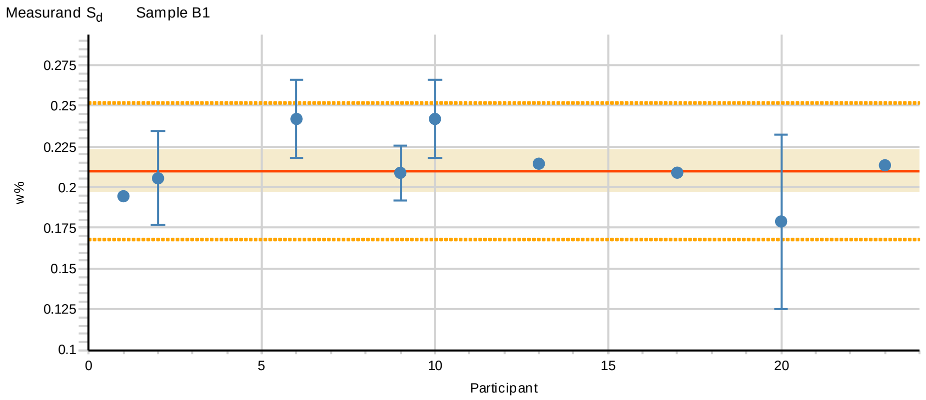

Measurand qp, net,d
Sample B2
19510
19350
19190
19030
18870
18710
18550
18390
18230
J/g
0
5
10
15
20
25
Participant


Measurand qp, net,d
Sample K1
28340
28180
28020
27860
27700
27540
27380
27220
27060
J/g
0
5
10
15
20
25
Participant

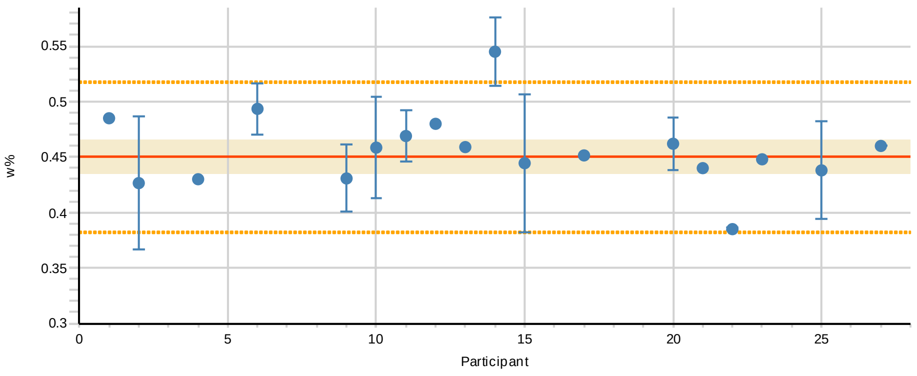

Measurand qV, gr,d
Sample B1
22490
22330
22170
22010
21850
21690
21530
21370
J/g
0
5
10
15
20
Participant


Measurand qV, gr,d
Sample B2
J/g
20760
20600
20440
20280
20120
19960
19800
19640
0
5
10
15
20
25
Participant

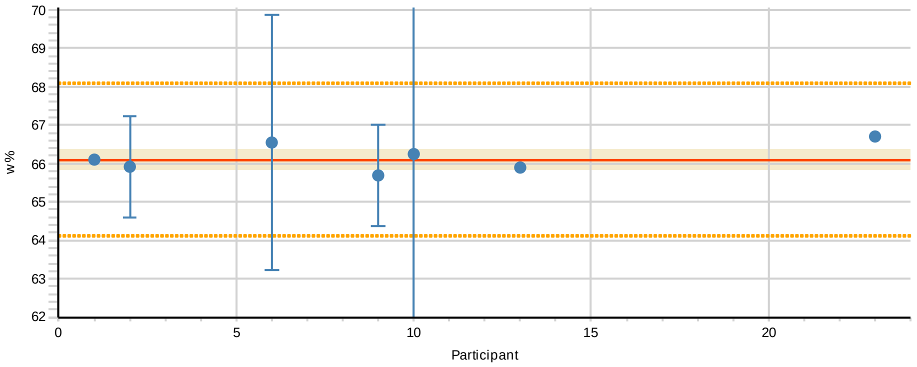

Measurand qV, gr,d
Sample K1
J/g
29290
29130
28970
28810
28650
28490
28330
28170
0
5
10
15
20
25
Participant


Measurand Sd
Sample B1
w%
0.275
0.25
0.225
0.2
0.175
0.15
0.125
0.1
0
5
10
15
20
Participant

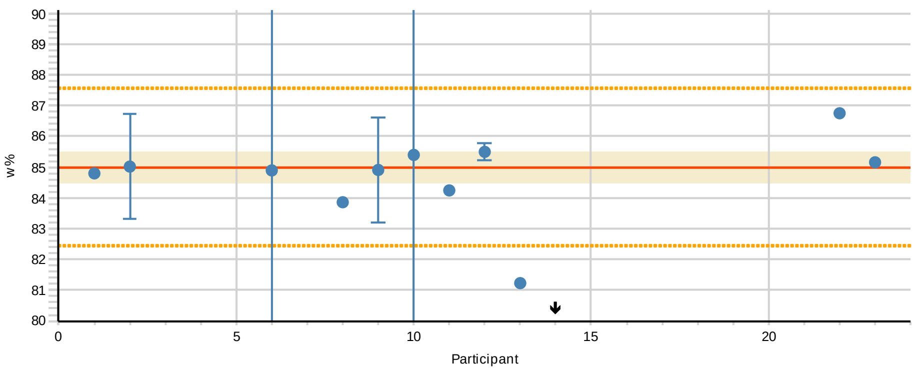
Measurand S_d Sample K1

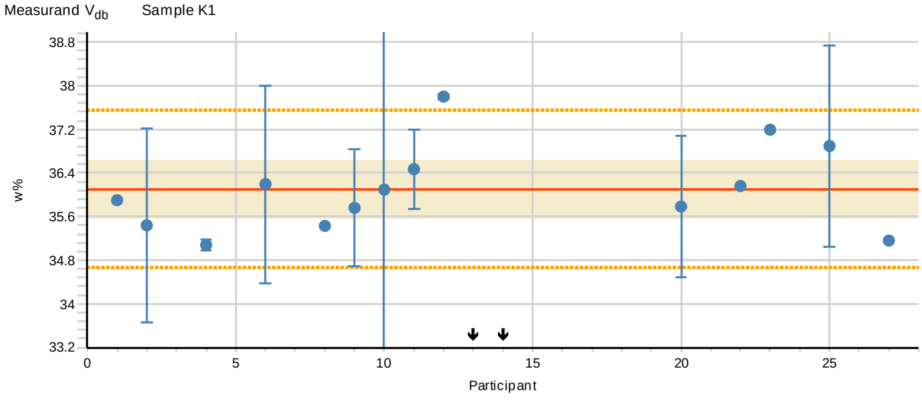


Measurand V_{db} Sample B1



Measurand V_{db} Sample B2




Measurand V_{db}
Sample K1
w%
38.8
38
37.2
36.4
35.6
34.8
34
33.2
0
5
10
15
20
25
Participant

APPENDIX 9: Summary of the z and E_n scores

z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	17	18	19	20	21	22	23	24	25	26	27	%
Ash_d	B1	S	S	S	.	.	S	*S*	.	S	S	.	.	*S*	.	.	S	*S*	S	S	.	.	*S*	.	.	.	.	100
	B2	S	S	S	.	.	S	*S*	*S*	S	S	*S*	S	*S*	S	.	S	*S*	S	.	.	*u*	*S*	*S*	.	.	*S*	94.7
	K1	S	S	.	*S*	.	S	.	*S*	S	S	S	S	*S*	u	*S*	S	.	.	*S*	.	*S*	*U*	.	*S*	.	*S*	88.9
C_d	B1	S	S	.	.	.	S	.	.	S	S	.	.	.	.	.	S	.	.	S	.	.	.	.	.	.	.	100
	B2	S	S	.	.	.	S	.	.	S	S	*S*	S	.	u	.	S	.	.	.	.	*u*	.	.	.	.	*q*	72.7
	K1	S	S	.	*S*	.	S	.	.	S	S	S	S	.	u	S	S	.	.	S	*S*	S	.	.	S	.	*S*	93.8
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	S	.	.	.	S	.	.	S	S	S	.	.	*u*	.	*S*	.	.	.	.	.	.	.	*S*	.	.	87.5
H_d	B1	S	S	.	.	.	S	.	.	S	S	.	.	.	.	.	S	.	.	S	.	.	.	.	.	.	.	100
	B2	S	S	.	.	.	S	.	.	S	S	*S*	S	.	S	.	S	.	.	.	.	*Q*	.	.	.	.	.	90.0
	K1	S	S	.	.	.	S	.	.	S	Q	S	U	.	S	.	S	.	.	*S*	*S*	S	.	.	*S*	.	.	84.6
$M_{ad,d}$	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
N_d	B1	S	S	.	.	.	q	.	.	S	S	.	.	.	.	.	S	.	.	S	.	.	.	.	.	.	.	85.7
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	S	S	.	.	.	S	.	.	S	S	S	S	.	S	.	S	.	.	.	*S*	S	.	.	.	.	.	100
$q_{p,net,d}$	B1	.	S	.	.	S	S	*S*	.	S	S	.	.	.	.	.	S	*u*	S	S	.	.	*U*	.	.	.	.	81.8
	B2	.	S	.	.	q	S	*S*	.	S	S	*S*	*S*	.	u	.	S	*S*	S	.	.	*u*	*U*	S	.	.	.	73.3
	K1	.	S	.	*S*	u	S	.	.	S	S	S	S	.	u	.	S	.	.	S	.	S	*U*	.	S	.	.	78.6
$q_{V,gr,d}$	B1	S	S	.	.	S	S	*S*	.	S	S	.	.	*S*	.	.	S	*u*	S	S	.	.	.	.	.	.	.	91.7
	B2	S	S	.	.	u	S	*S*	*S*	S	S	*S*	*S*	*S*	u	.	S	*S*	S	.	.	*u*	.	S	.	.	*S*	83.3
	K1	S	S	.	*S*	u	S	.	*S*	S	S	S	S	*S*	u	.	S	.	.	*S*	.	S	.	.	S	.	S	88.2
S_d	B1	S	S	.	.	.	S	.	.	S	S	.	.	*S*	.	.	S	.	.	S	.	.	*S*	.	.	.	.	100
	K1	S	S	.	*S*	.	S	.	.	S	S	S	*S*	*S*	Q	*S*	S	.	.	S	*S*	S	*S*	.	S	.	*S*	94.4
V_{db}	B1	S	*S*	.	.	.	S	.	.	S	S	.	.	*S*	.	.	.	.	.	.	.	.	*S*	.	.	.	.	100
	B2	S	*S*	.	.	.	S	.	*S*	S	S	*S*	*S*	*q*	*u*	.	.	.	.	.	.	*S*	*S*	.	.	.	.	83.3
	K1	S	*S*	.	*S*	.	S	.	*S*	S	S	S	Q	*u*	*u*	.	.	.	.	*S*	.	*S*	*S*	.	S	.	*S*	81.3
%		100	100	100	100	33	96	100	100	100	96	100	86	82	27	100	100	67	100	100	100	64	64	100	100		88	
accredited		19	20	2		6	23			23	23	9	10		12	1	19		6	10		6		3	6		1	

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

Totally satisfactory, % in all: 89 % in accredited: 92 % in non-accredited: 81

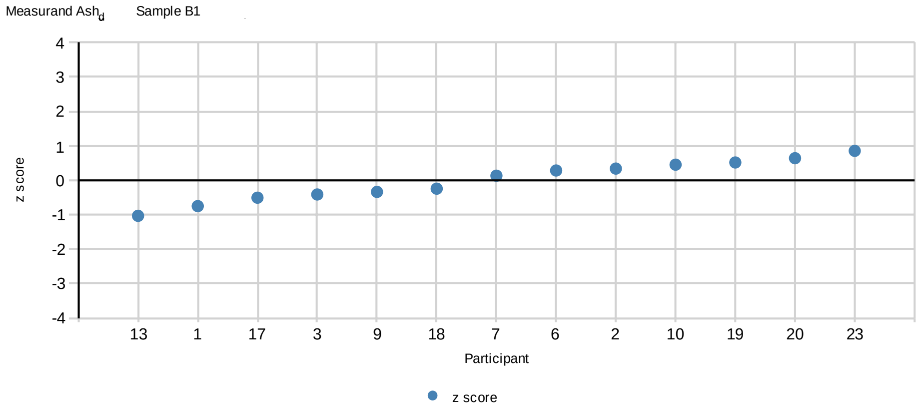
E_n scores

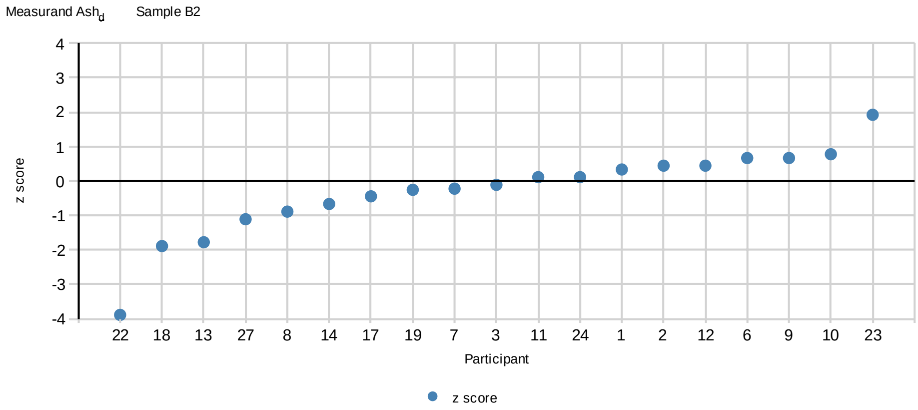
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
EF	B1	-0.2	.	.	.	.	.	.	-0.1	.	.	0.0	-0.1	.	.	.	.	.	.	.	.	.	.	.	100

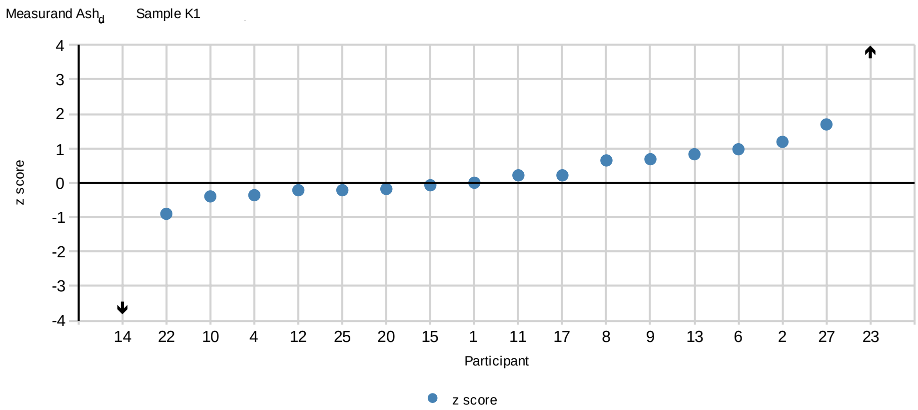
E_n scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty
Scores of $-1.0 < E_n < 1.0$ indicate successful performance
Scores of $E_n \ge 1.0$ or $E_n \le -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

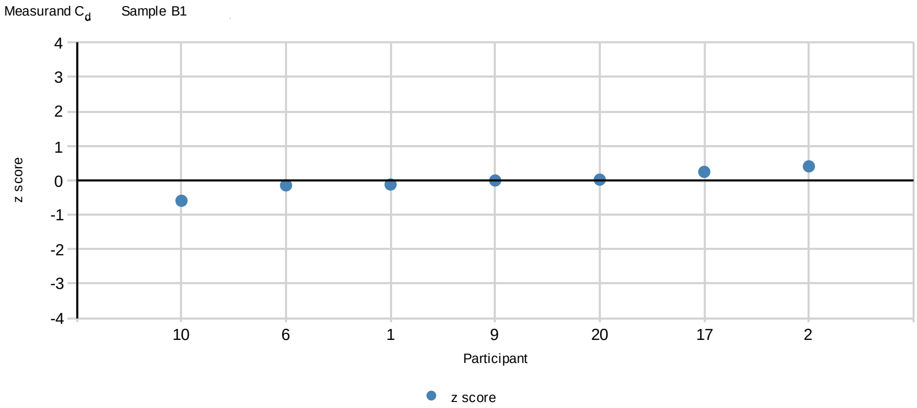
Totally satisfactory, % in all: 100

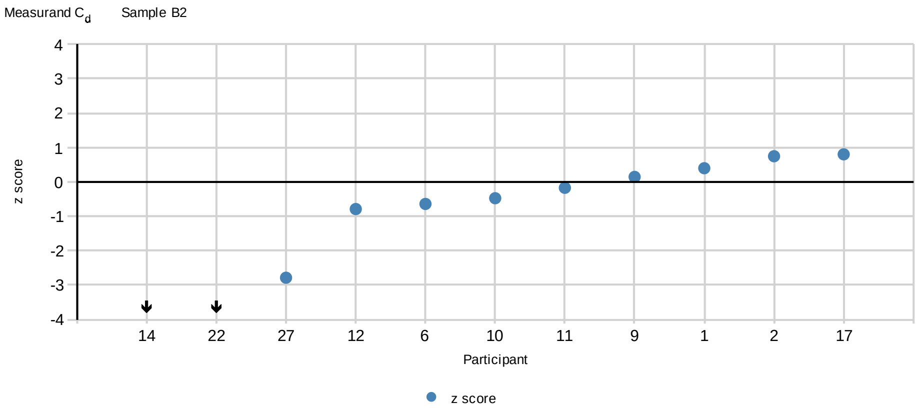
APPENDIX 10: z scores in ascending order

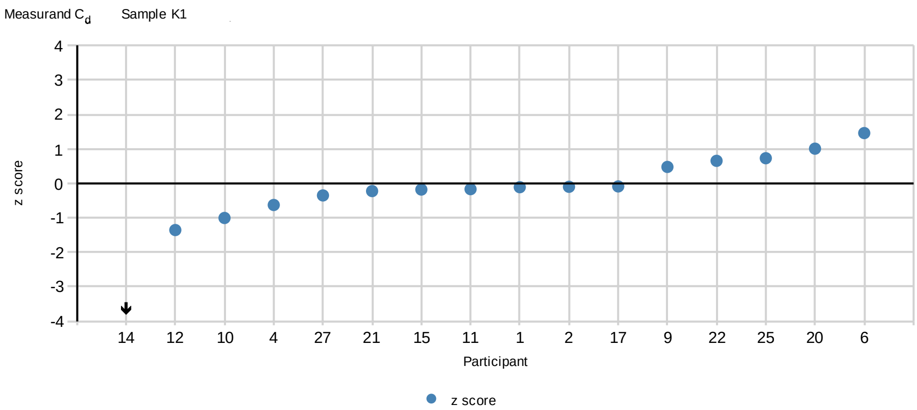


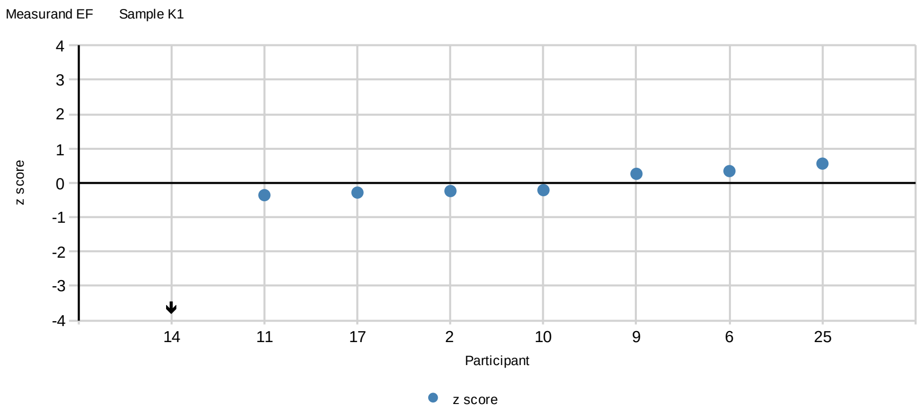


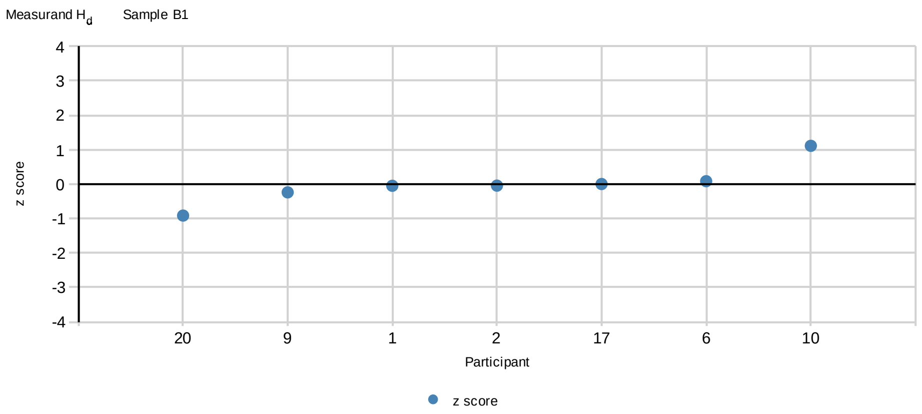


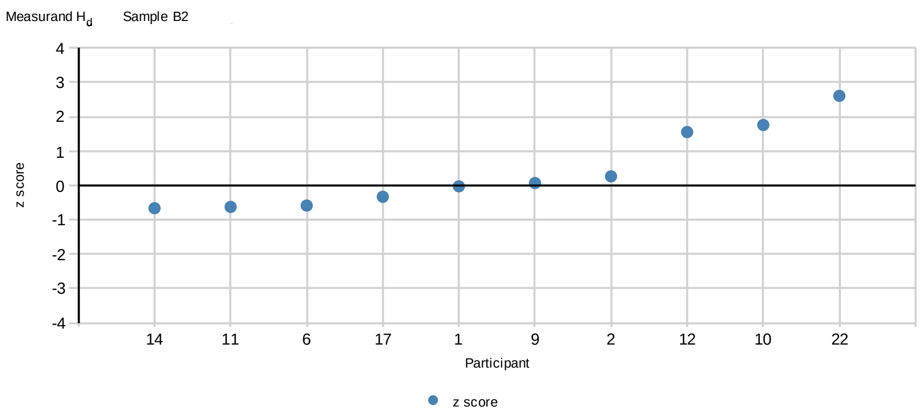

Measurand C_d
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
10
6
1
9
20
17
2
Participant
z score


Measurand C_d
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
14
22
27
12
6
10
11
9
1
2
17
Participant
z score

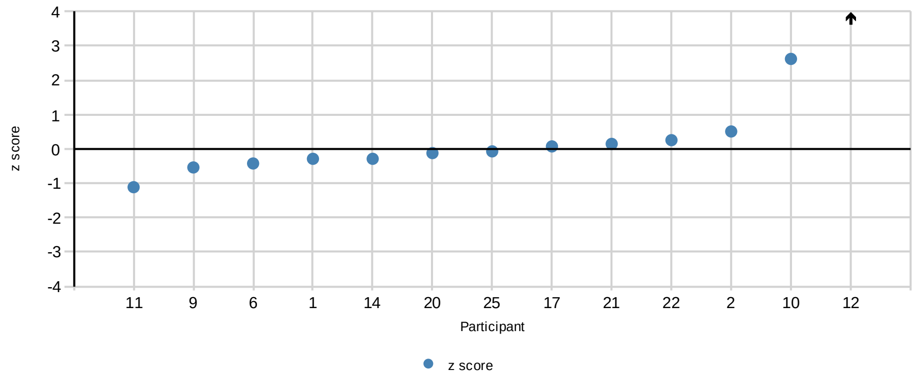

Measurand C_d
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
14
12
10
4
27
21
15
11
1
2
17
9
22
25
20
6
Participant
z score


Measurand EF
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
14
11
17
2
10
9
6
25
Participant
z score

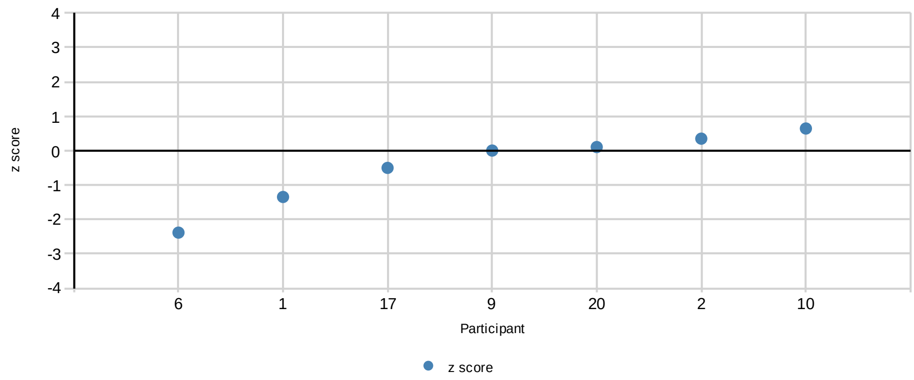

Measurand H_d
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
20
9
1
2
17
6
10
Participant
z score


Measurand H_d
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
14
11
6
17
1
9
2
12
10
22
Participant
z score

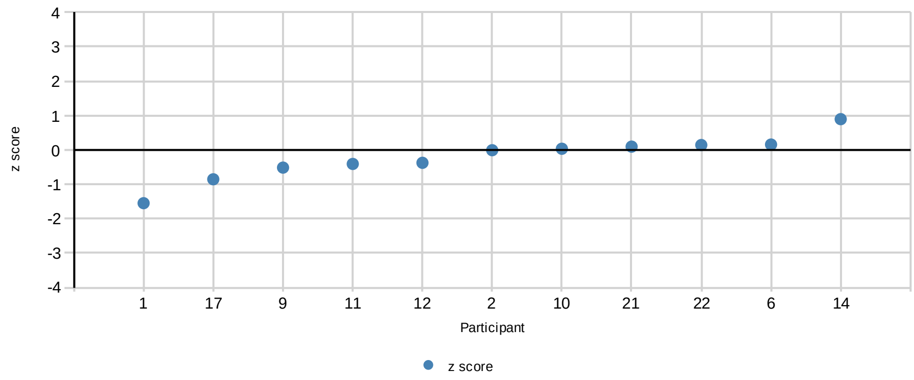
Measurand H_d Sample K1

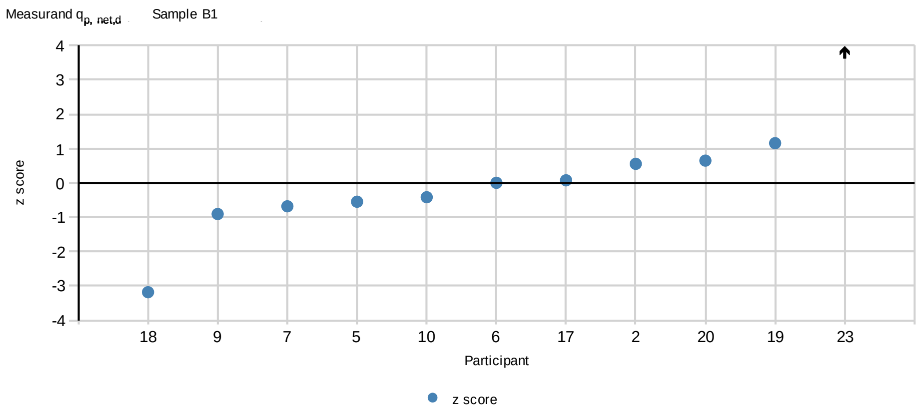


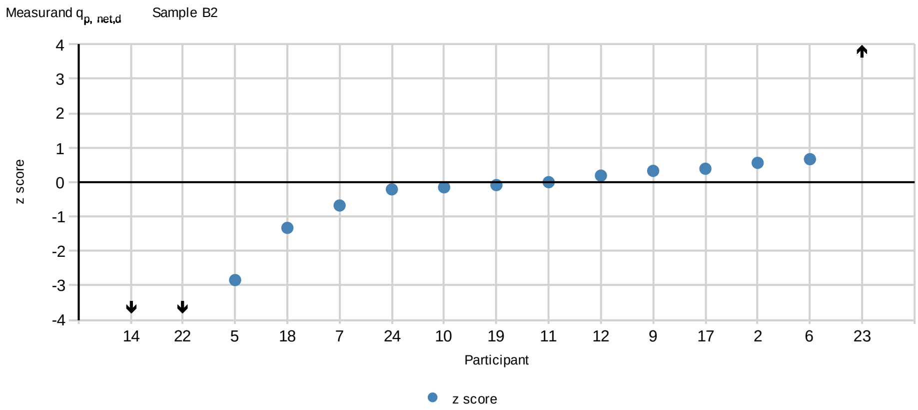
Measurand N_d Sample B1

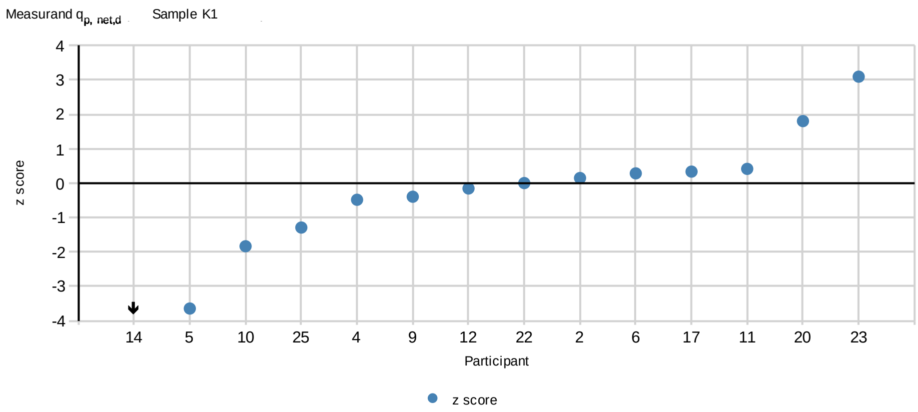


Measurand N_d Sample K1

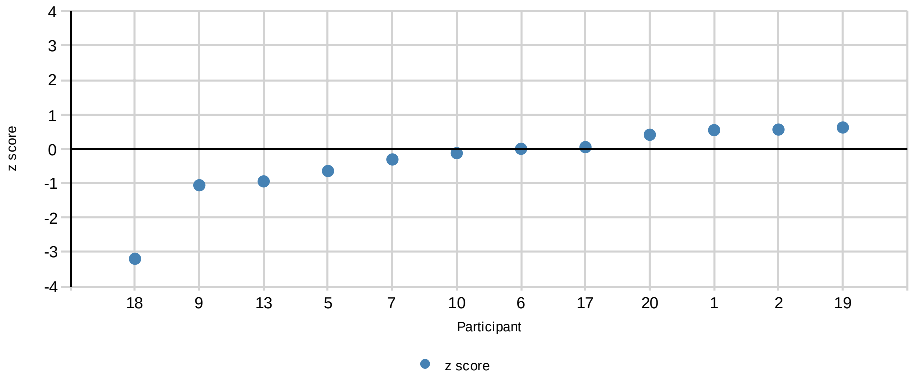



Measurand $q_{p,\ net,d}$
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
18
9
7
5
10
6
17
2
20
19
23
Participant
z score

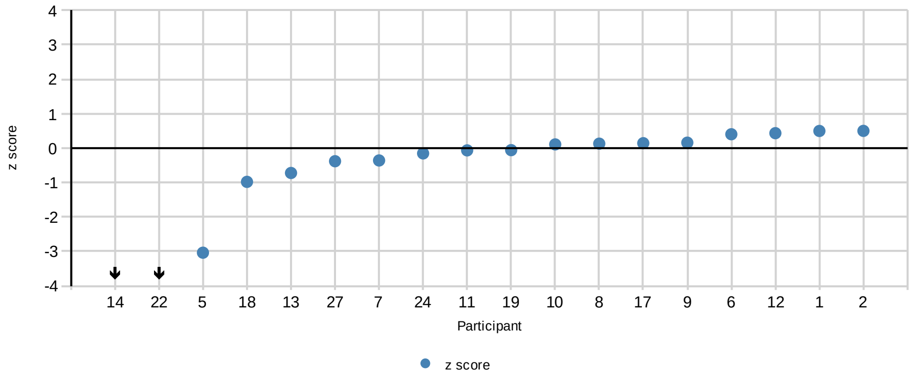

Measurand $q_{p,\ net,d}$
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
14
22
5
18
7
24
10
19
11
12
9
17
2
6
23
Participant
z score


Measurand $q_{p,\ net,d}$
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
14
5
10
25
4
9
12
22
2
6
17
11
20
23
Participant
z score

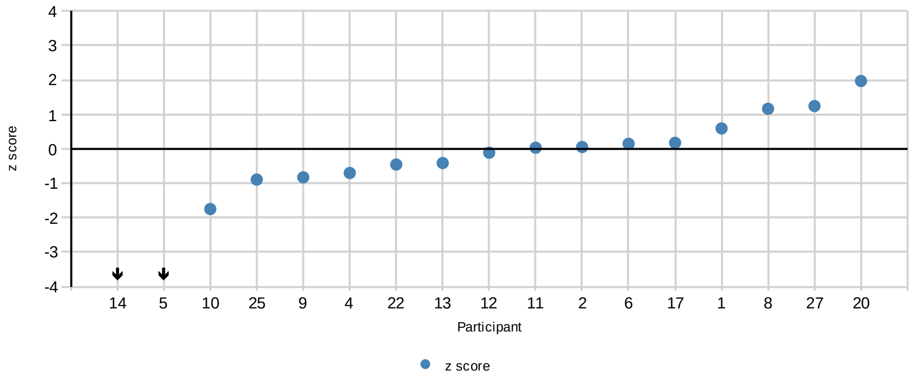
Measurand $q_{V, gr,d}$ Sample B1



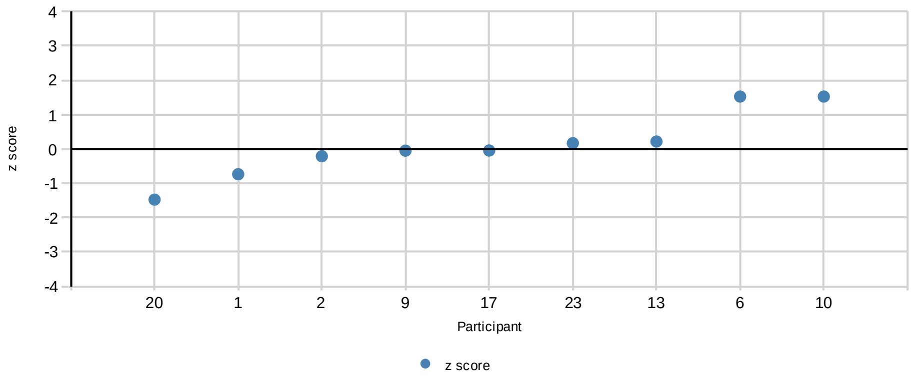
Measurand $q_{V, gr,d}$ Sample B2



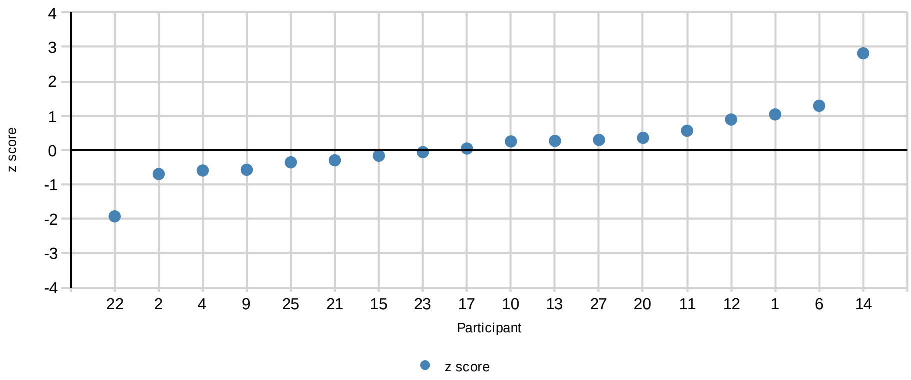
Measurand $q_{V, gr,d}$ Sample K1



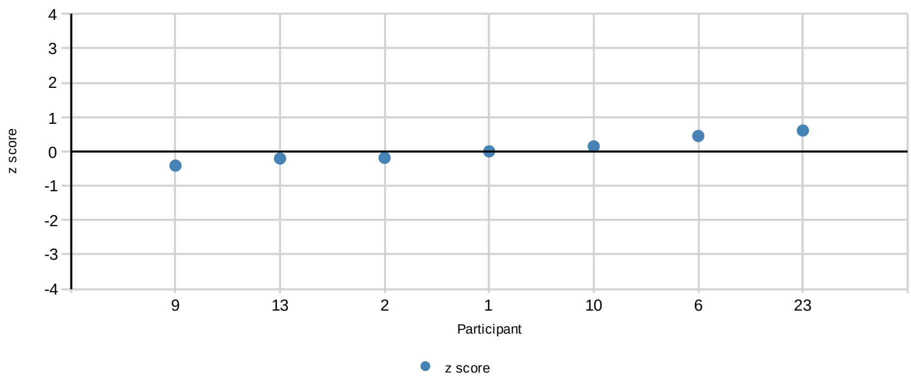
Measurand S_d Sample B1

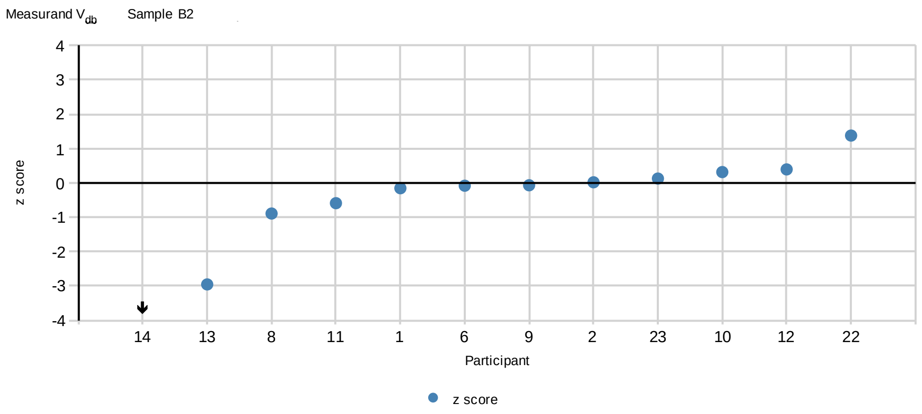


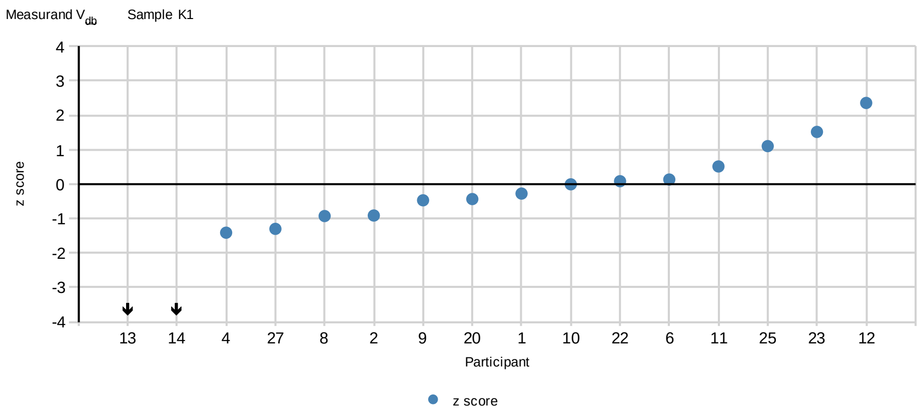
Measurand S_d Sample K1



Measurand V_{db} Sample B1




Measurand V db
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
14
13
8
11
1
6
9
2
23
10
12
22
Participant
z score


Measurand V db
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
13
14
4
27
8
2
9
20
1
10
22
6
11
25
23
12
Participant
z score

APPENDIX 11: Analytical measurements and background information for calculations

Reported details of the measurements:

Analysis carried out from	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Air dried samples:	participants 1, 2, 6, 7, 13, 20	participants 1, 2, 6, 7, 12, 13, 24	participants 1, 2, 6, 9, 11, 12, 13, 20, 25
Drying in 105 °C:	participant 9	participants 3, 9, 11, 22,	participants 4, 22
Other:	participants 3: 108 °C dried samples 17: as received 23: not dried sample	participants 17: as received 23: not dried sample	participants 15: as received 17: as received 21: ISO 11722 23: not dried sample

Correction taken into account in calculations:

Gross calorific value $q_{V,gr,d}$			
Participants and correction factors used	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
1: wire, ignition, S, acid correction, analysis moisture	x	x	x
2: wire, ignition, acid correction, analysis moisture	x	x	x
4: wire, acid correction, analysis moisture			x
6: wire, ignition, acid correction, analysis moisture	x	x	x
6: S	x		x
7: wire, analysis moisture	x		
9: wire, S, acid correction	x	x	x
9: analysis moisture			x
11: wire, ignition, analysis moisture		x	x
11: S			x
12: wire, S, acid correction, analysis moisture		x	x
13: wire, analysis moisture	x	x	x
13: S	x		x
13: N			x
17: wire, ignition, S, analysis moisture	x	x	x
20: wire, ignition, S, analysis moisture	x		x
20: N	x		
20: acid correction			x
22: wire, S		x	x
22: N, acid correction			x
23: wire, S, N, analysis moisture	x	x	x
24: wire, ignition, S, analysis moisture		x	
25: wire, acid correction, analysis moisture			x

Correction taken into account in calculations:

Net calorific value $q_{p,net,d}$ (literature value in brackets)			
Participant	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
2	N+O, H	N+O, H	N+O, H
4			H, values of N + O if literature values are used
6	N+O, H	N+O, H	N+O, H
7	H	H	
9	N+O, H	N+O, H	N+O, H
11		values of H if literature values are used	N+O, H
12		N+O, H	N+O, H
17	N+O, H	N+O, H	N+O, H
20	N+O, H		H
22			H
24		values of N +O and H if literature values are used	
25			O, H

Methods used in ash_d and moisture (M_{ad}) measurements:

Ash_d	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Sample amount (g)	participants 1: 1 g 2: 2,5 g 3: 1 g 6: 1,6 g 7:1 g 9: 1 g 13: 0,8 g 17:1,5 g 20: 1 g 23: 1,1 g	participants 1: 2 g 2: 2,5 g 3: 1 g 6: 1,6 g 7: 1 g 9: 1 g 11:1 g 12: 1 g 13: 0,8 g 15:1,6 g 17: 1,5 g 22: 1 g 24: 1 g	participants 1: 1 g 2: 2,5 g 4: 1 g 6: 1 g 7: 1 g 9: 1 g 11: 1 g 12: 1 g 13: 1 g 15: 1,1 g 17: 1,5 g 20: 1 g 23: 1,5 g

Measurement	Method	°C	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Ash content (ashing temperature ℃)	Gravimetric:	550	parts 2, 6, 7, 20, 23	parts 1, 2, 6, 7, 11, 12, 23	
		750			parts 11, 12
		815			parts 1, 2, 6, 23, 25
		950		part 22	part 22
	TGA:	550	parts 9, 13, 17	parts 3, 9, 13, 17, 24	part 17
		750			parts 12, 15
		815	parts 1, 3		parts 4, 9, 13
Moisture content of analysis sample, M_{ad} (temperature °C)	Air:		parts 2, 3, 6, 7, 9, 13, 15, 20, 23	parts 2, 6, 3, 7, 9, 13, 22, 23, 26	parts 12, 13, 23, 25
	N_2 atmosphere:		parts 1,17	parts 1, 11, 12, 17	parts 1, 2, 4, 6, 9, 11, 17, 20, 21, 22
	Gravimetric:	105	parts 2,6, 7, 9, 20, 23	parts 2, 6, 7, 9, 12, 22, 23, 26	parts 6, 12, 15, 22, 23, 25
		107			parts 9, 20
		107.5			part 2
	TGA:	105	parts 13,17	parts 3, 13, 17, 24	parts 4, 13, 17
		107	part 1	parts 1, 11	parts 1, 11
		108	part 3		

CHN-measurements carried out by:

	Sample		
	B1	B2	K1
Air dried samples:	parts 1, 2, 6,9	parts 1, 2, 6, 9, 12	parts 1, 2, 6,9, 11, 12, 20, 25
Drying in 105 °C:	part 20	parts 11, 22	parts 4, 22
Other	part: 17: as received	part: 17: as received	parts: 15: as received 17: as received 21: ISO 11722

Detection limits in nitrogen and sulphur measurements:

Participant	Detection limit for N_d (w%)	Participant	Detection limit for S_d (w%)
1	0.1	1	0.1
2	0.03	2	0.002
6	0.1	6	0.03
9	0.1	9	0.01
11	0.3	11	0.1
12	0.01	12	0.01
17	0.02	13	0.1
22	0.0074	17	0.02
		20	0.06
		22	0.0004
		25	0.001

Calculations of Emission factor (EF)[1]:

We have used the equation based on the decision EU601/2012(21.6.2012).

If no, describe how?

	Sample B1 (peat)	Sample K1 (coal)
Yes:	parts 2, 6, 9	parts 2, 6, 9, 11, 25
No:	20, 26	parts 17, 20

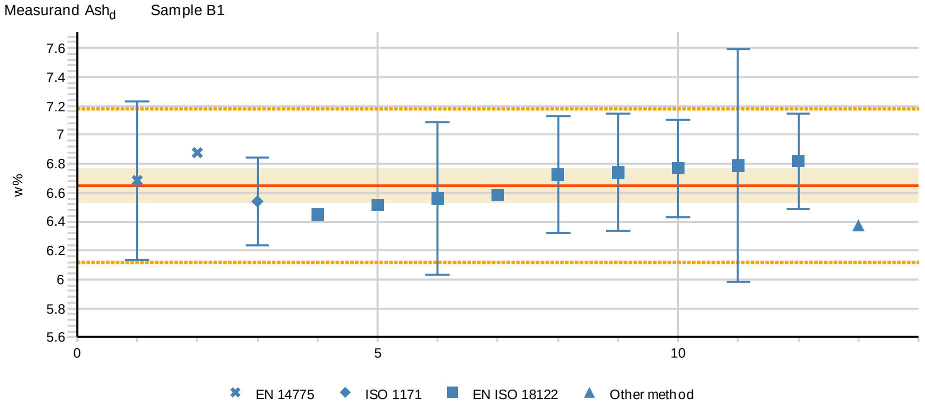
[1]In the cover letter the provider gave the participants the possibility to calculate the EF-value using the procedure presented in the EC directive and using the total moisture content as presented in the letter. Later it was obtained, that the EC directive is not giving the detailed equation for calculation of EF-values. Therefore, some national guides for the equation of EF value calculation have been produced.
As a result from this, the Energy Market Authority in Finland has made the guideline for the calculation of emission factor for fossile fuels as follows:

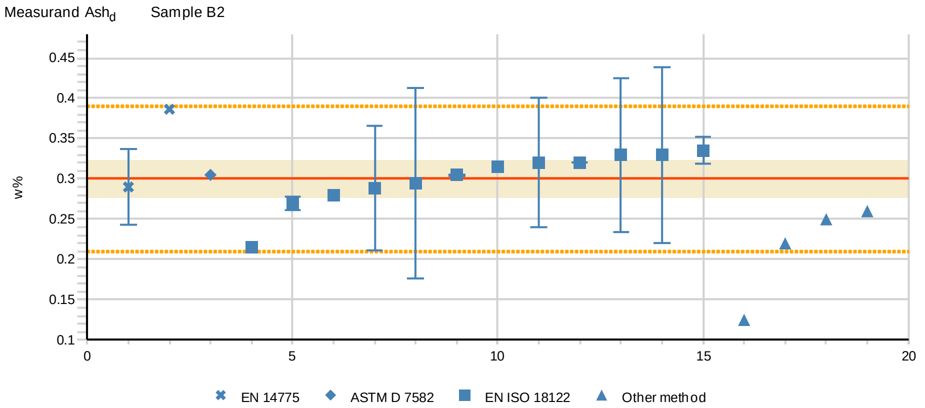
$EF = 1000 \times 3.664 \times (C/100) \times (1 - M_{ar}/100)/Q_{net.ar}$, where

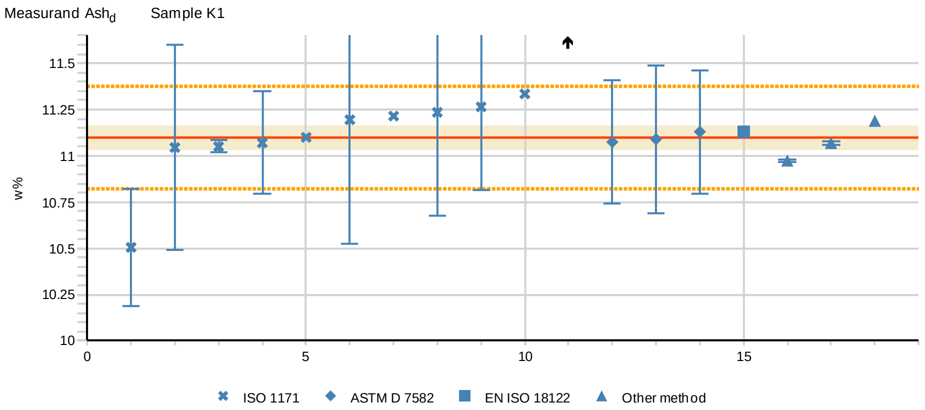
EF emission factor, g CO_2/MJ
C carbon content as dry, %
M_{ar} total moisture as received, %
$Q_{net.ar}$ net calorific value as received, MJ/kg
(http://www.energiavirasto.fi/documents/10179/132665/Paastokertoimen+laskentaohje.pdf)

APPENDIX 12: Results grouped according to the methods

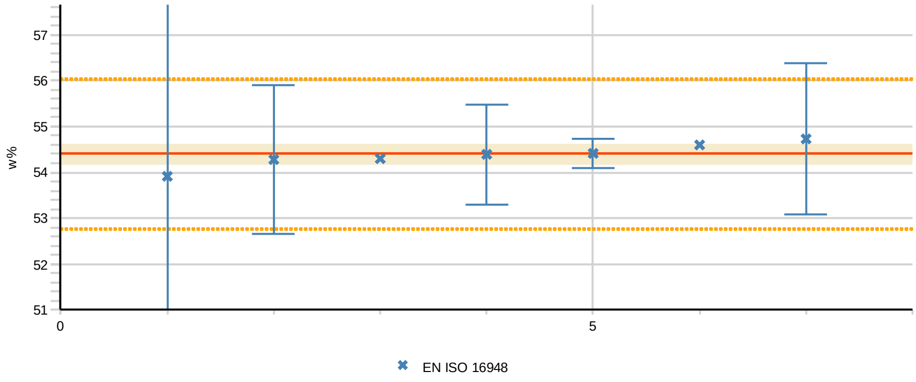
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



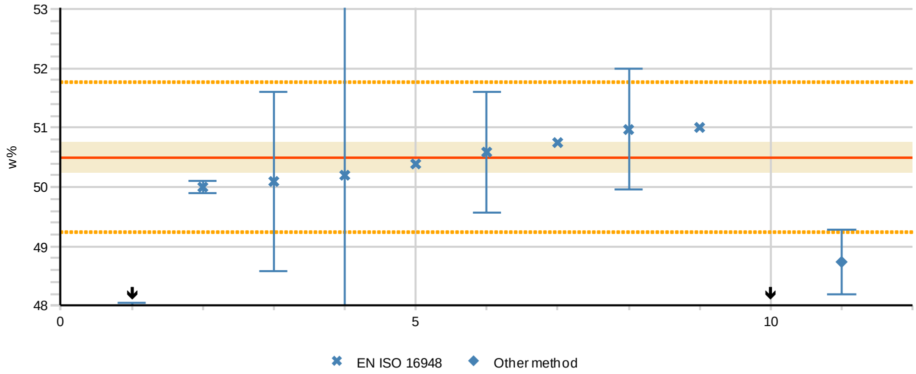




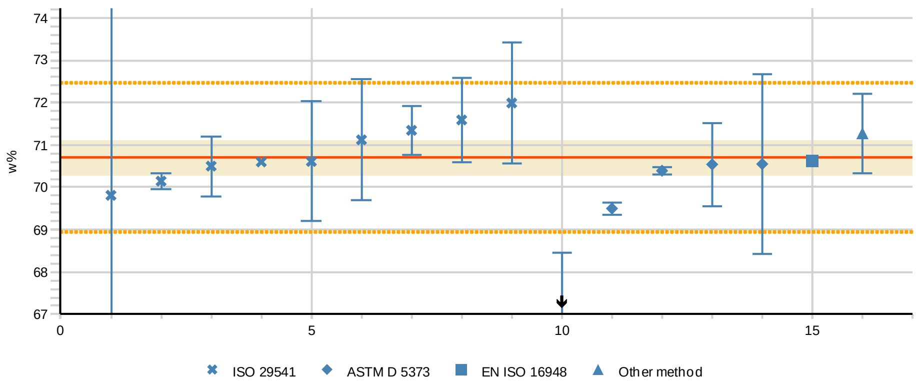
Measurand C_d Sample B1

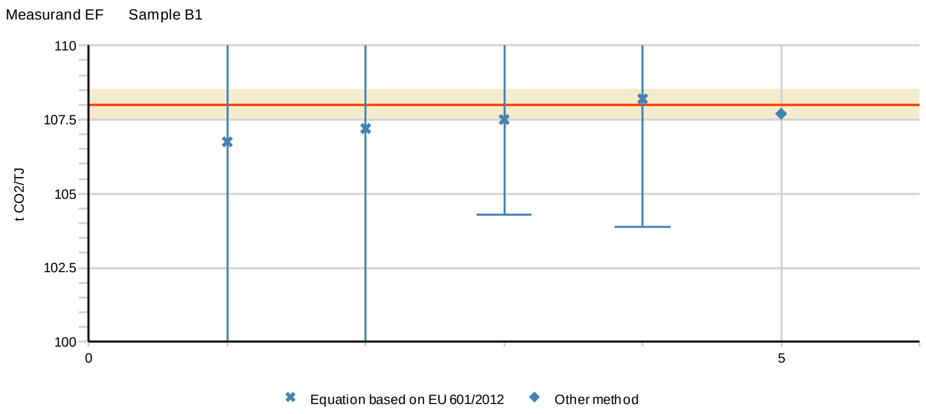


Measurand C_d Sample B2

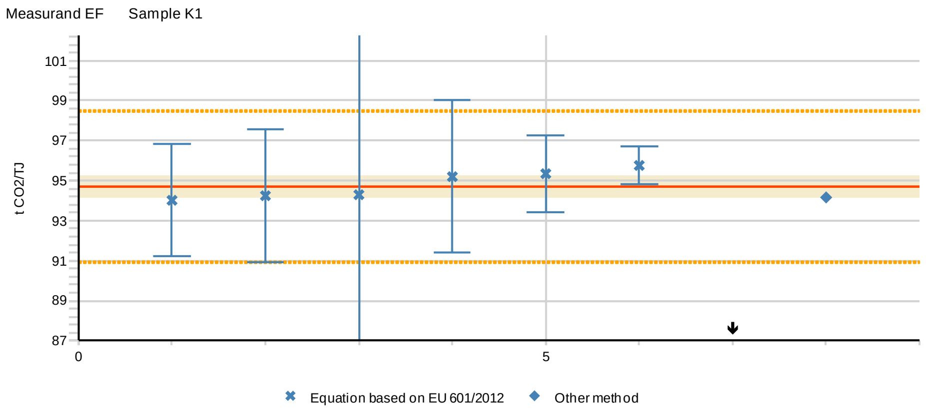


Measurand C_d Sample K1

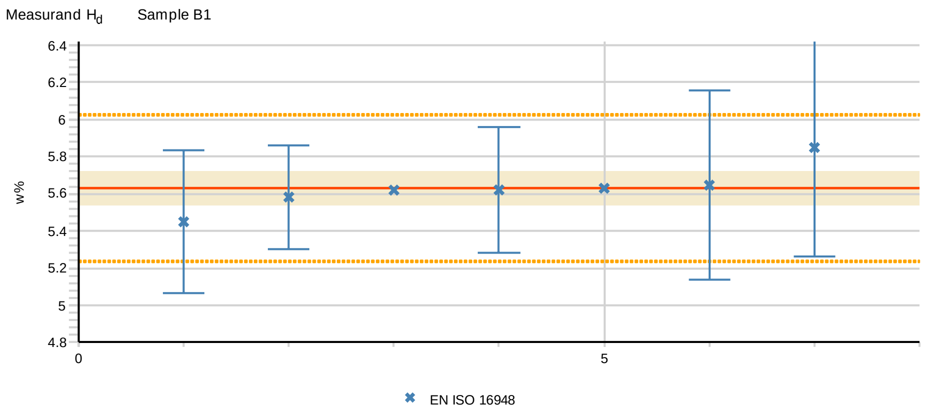




Measurand EF
Sample B1
110
107.5
105
102.5
100
t CO2/TJ
0
5
Equation based on EU 601/2012
Other method

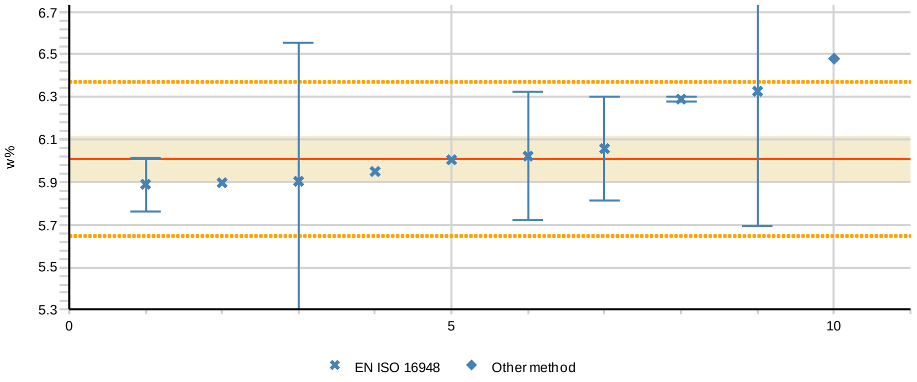


Measurand EF
Sample K1
101
99
97
95
93
91
89
87
t CO2/TJ
0
5
Equation based on EU 601/2012
Other method

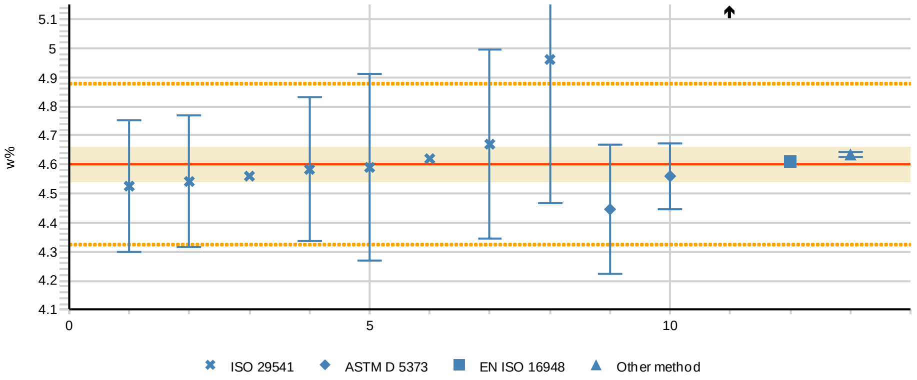


Measurand H_d
Sample B1
6.4
6.2
6
5.8
5.6
5.4
5.2
5
4.8
w%
0
5
EN ISO 16948

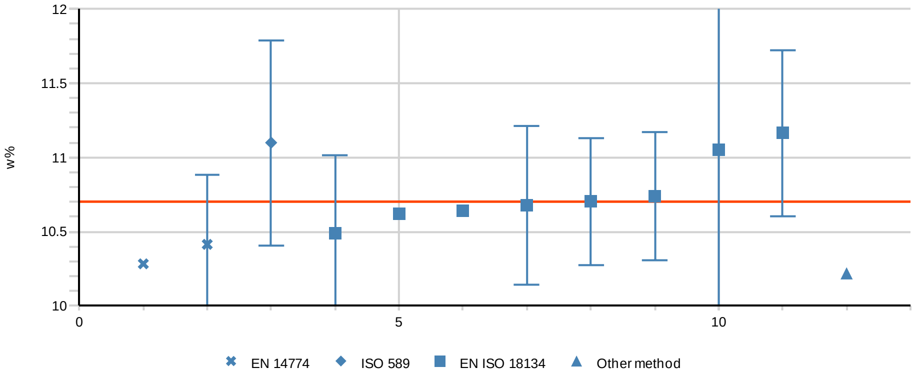
Measurand H_d Sample B2

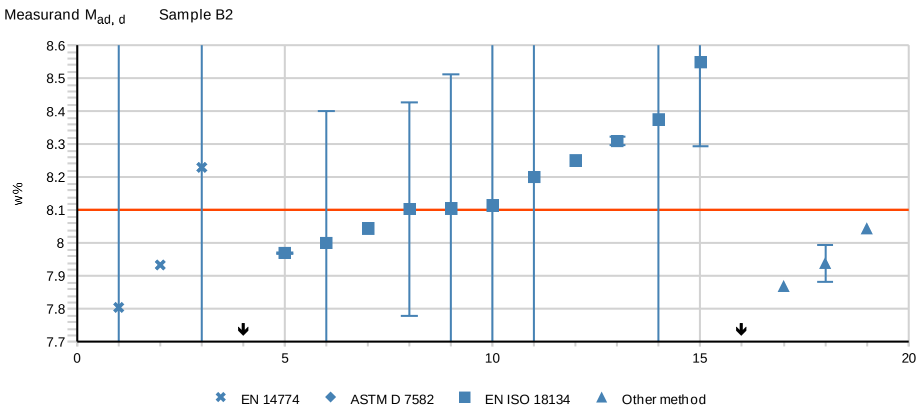


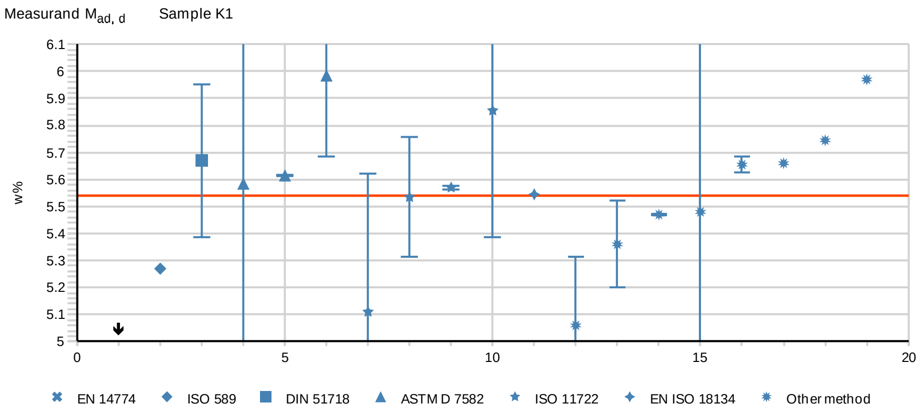
Measurand H_d Sample K1

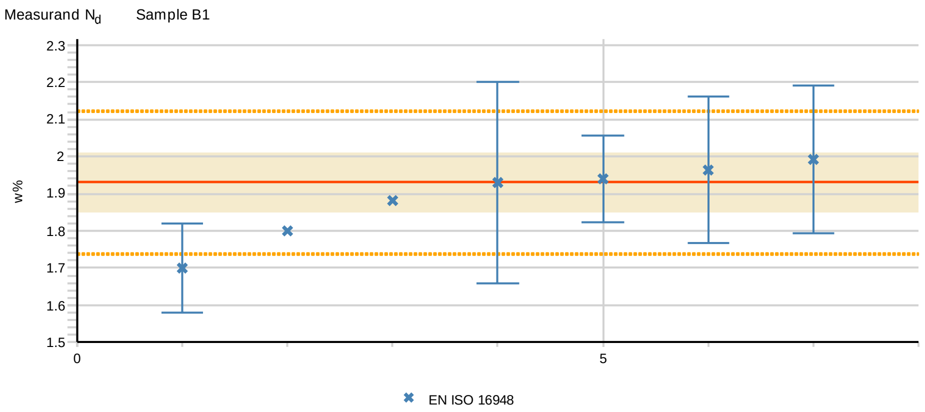


Measurand $M_{ad, d}$ Sample B1

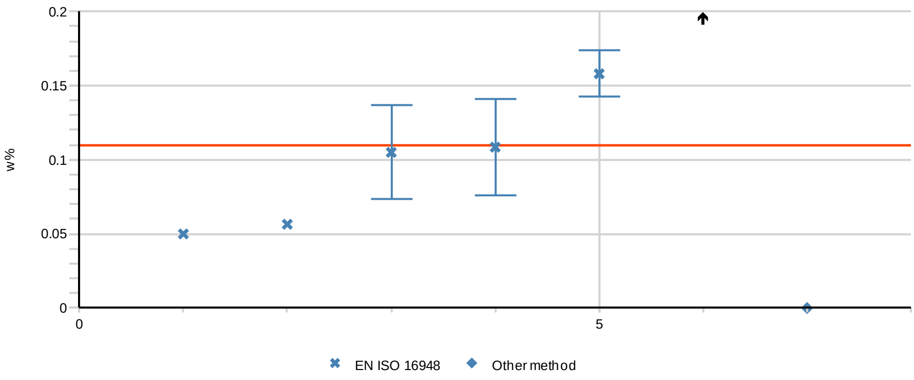



Measurand M ad, d
Sample B2
w%
EN 14774
ASTM D 7582
EN ISO 18134
Other method

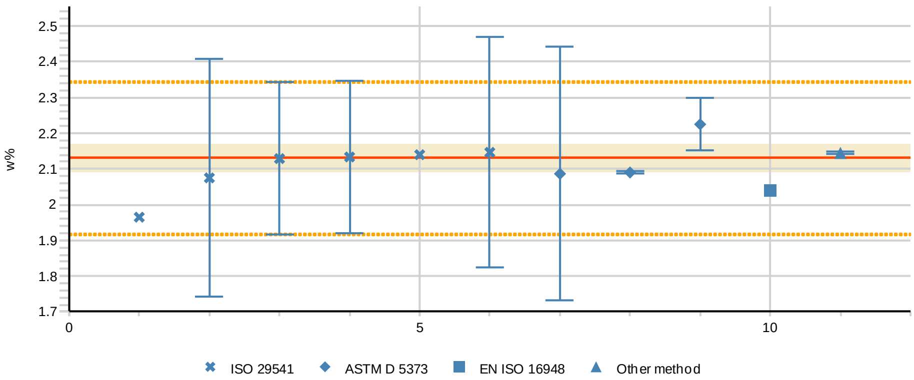

Measurand M ad, d
Sample K1
w%
EN 14774
ISO 589
DIN 51718
ASTM D 7582
ISO 11722
EN ISO 18134
Other method


Measurand N d
Sample B1
w%
EN ISO 16948

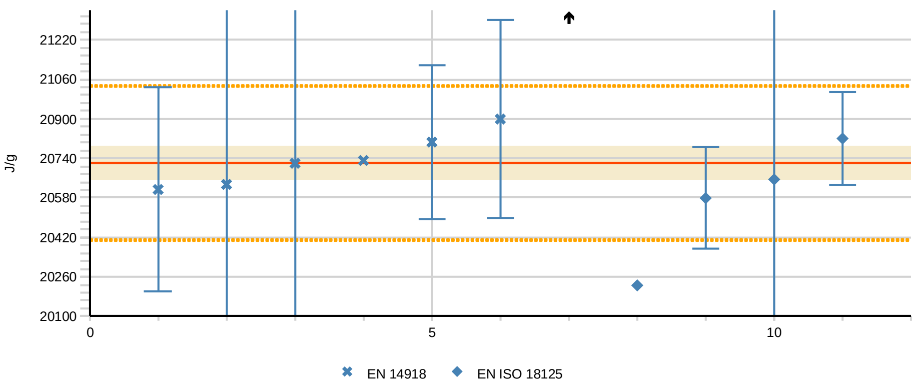
Measurand N_d Sample B2

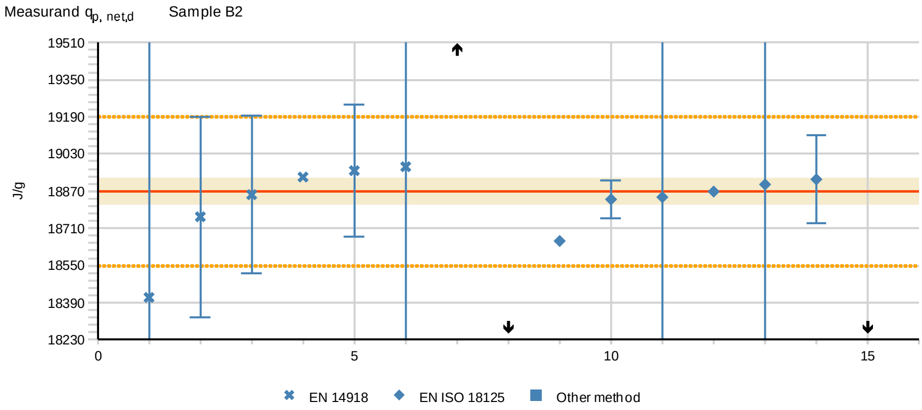


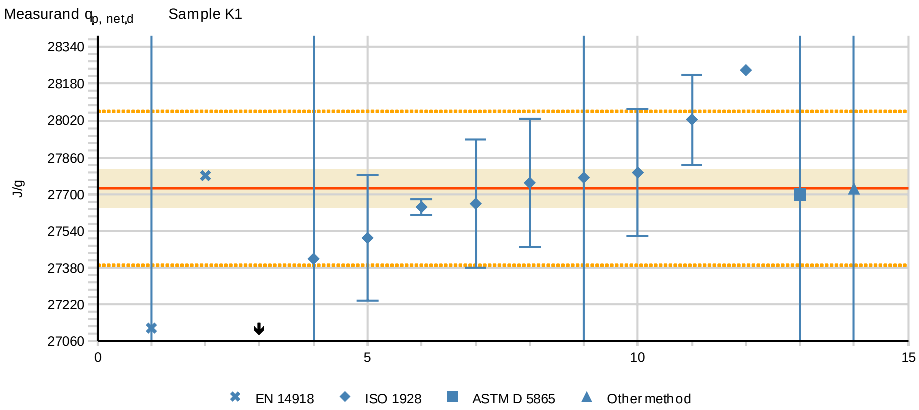
Measurand N_d Sample K1

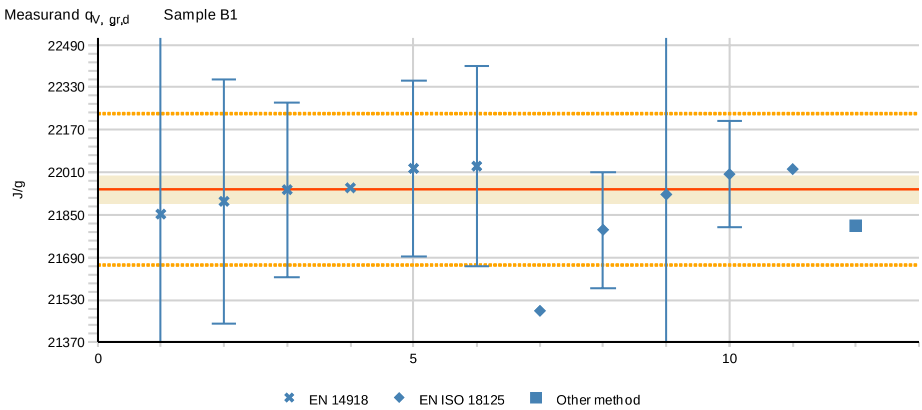


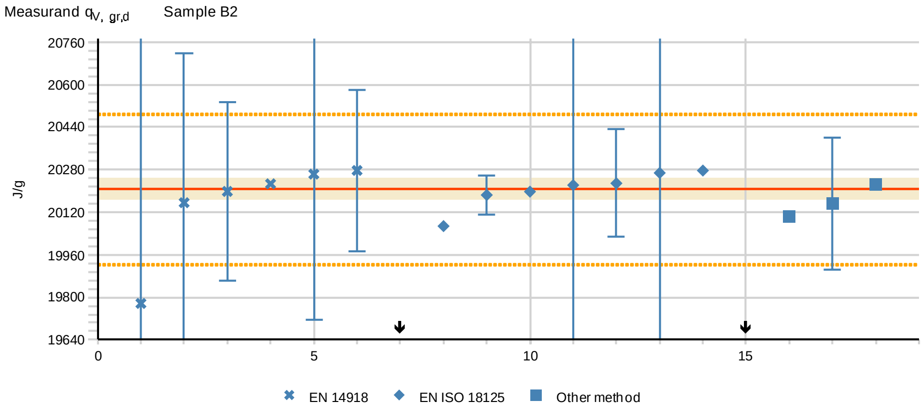
Measurand $q_{p, net,d}$ Sample B1

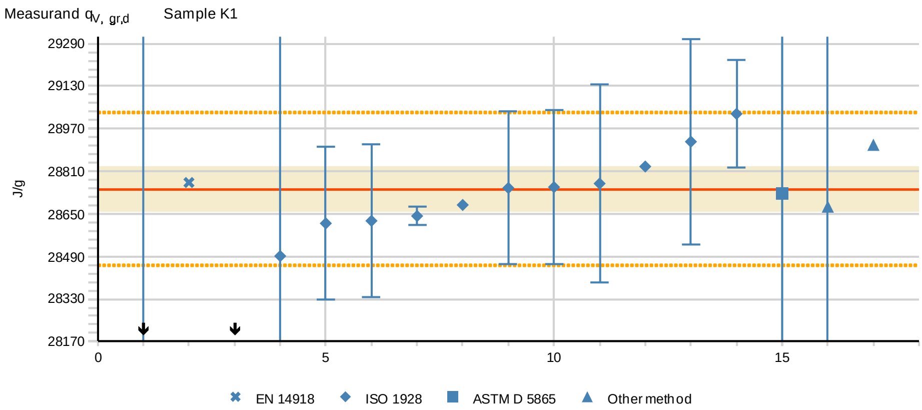


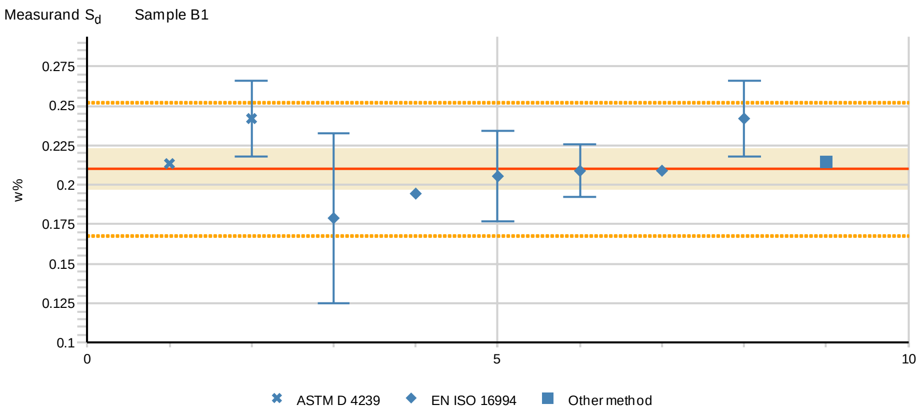

Measurand $q_{p, net,d}$ Sample B2
J/g
19510
19350
19190
19030
18870
18710
18550
18390
18230
0
5
10
15
EN 14918
EN ISO 18125
Other method


Measurand $q_{p, net,d}$ Sample K1
J/g
28340
28180
28020
27860
27700
27540
27380
27220
27060
0
5
10
15
EN 14918
ISO 1928
ASTM D 5865
Other method

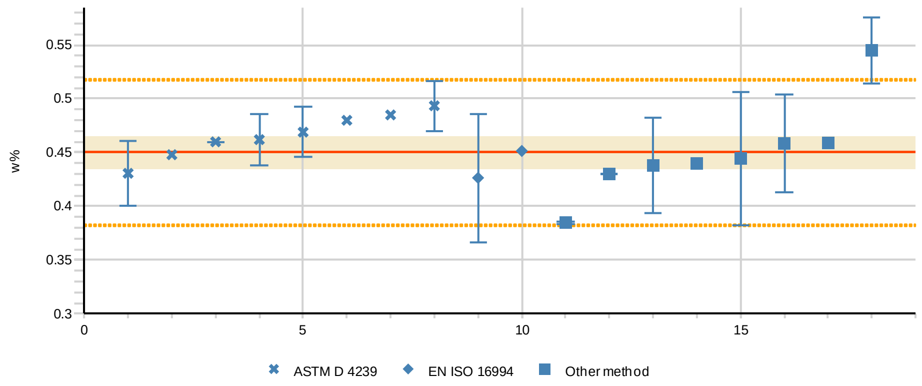

Measurand $q_{V, gr,d}$ Sample B1
J/g
22490
22330
22170
22010
21850
21690
21530
21370
0
5
10
EN 14918
EN ISO 18125
Other method


Measurand $q_{V, gr,d}$ Sample B2
J/g
20760
20600
20440
20280
20120
19960
19800
19640
0
5
10
15
EN 14918
EN ISO 18125
Other method

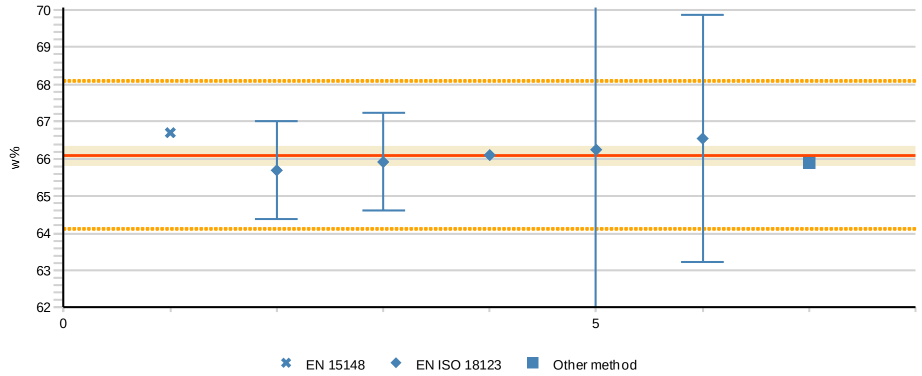

Measurand $q_{V, gr,d}$ Sample K1
J/g
29290
29130
28970
28810
28650
28490
28330
28170
0
5
10
15
EN 14918
ISO 1928
ASTM D 5865
Other method


Measurand S_d Sample B1
w%
0.275
0.25
0.225
0.2
0.175
0.15
0.125
0.1
0
5
10
ASTM D 4239
EN ISO 16994
Other method

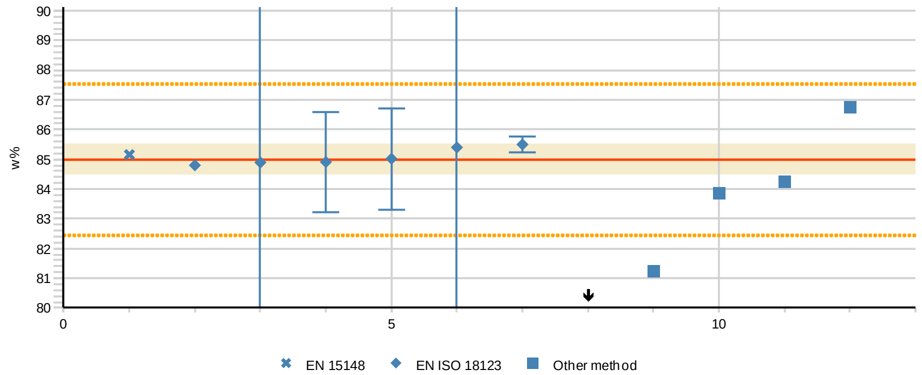
Measurand S_d Sample K1

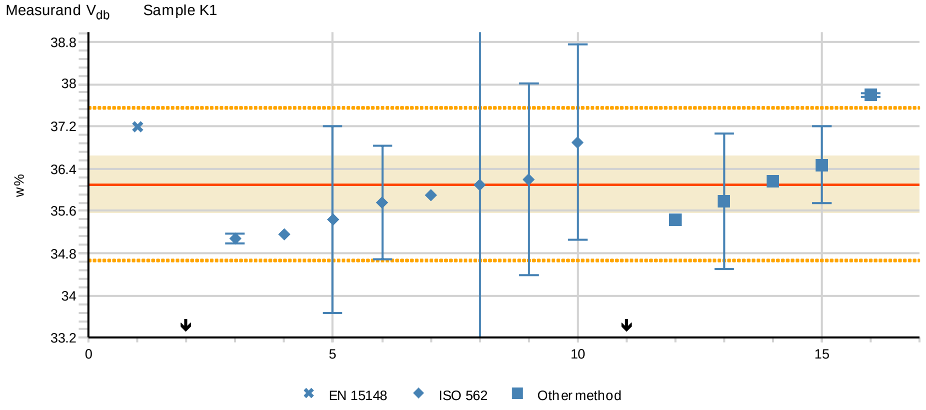


Measurand V_{db} Sample B1



Measurand V_{db} Sample B2

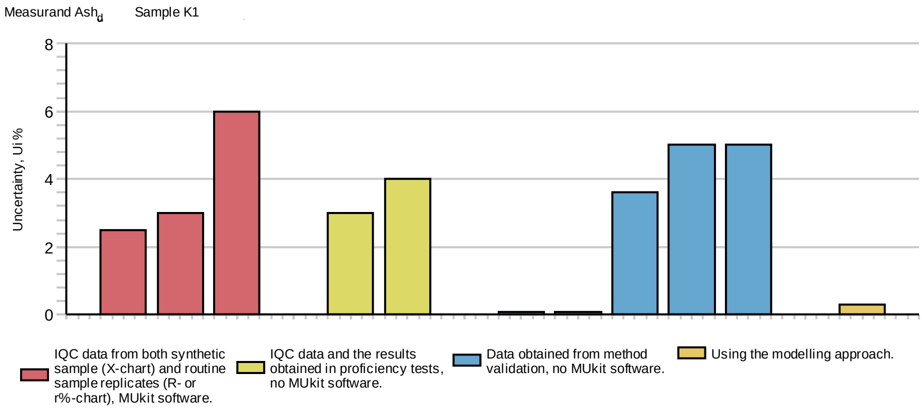


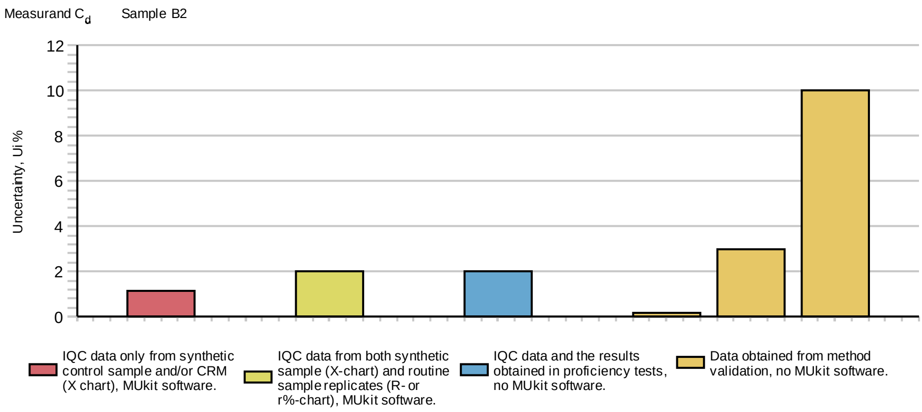


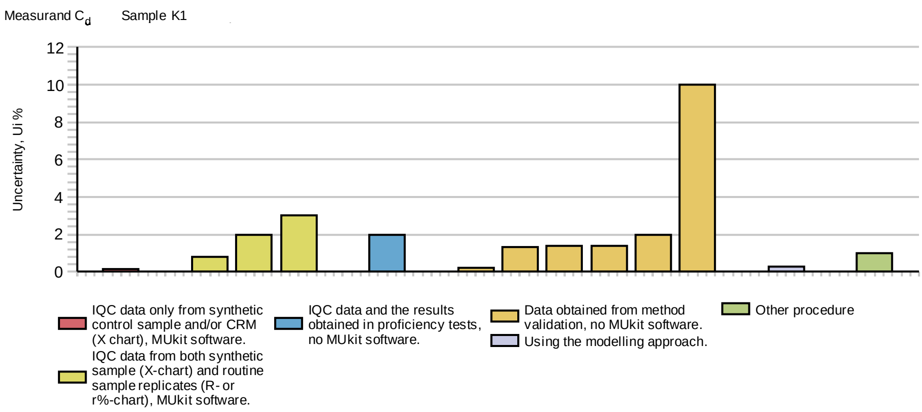
Measurand V db
Sample K1
w%
38.8
38
37.2
36.4
35.6
34.8
34
33.2
0
5
10
15
EN 15148
ISO 562
Other method

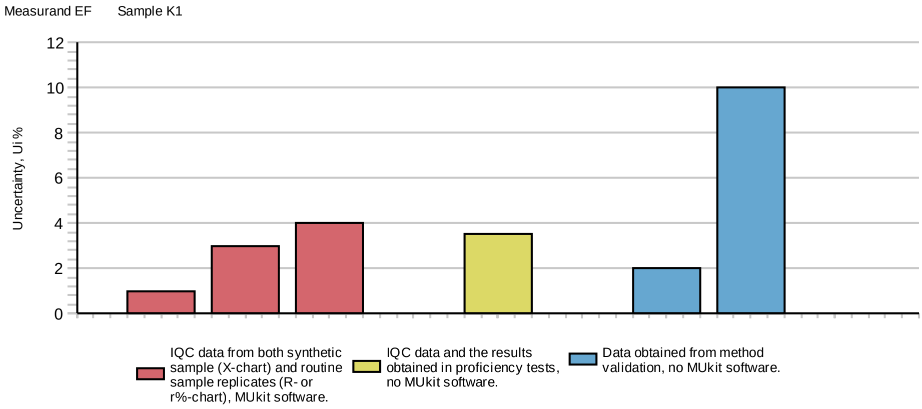
APPENDIX 13: Examples of measurement uncertainties reported by the participants

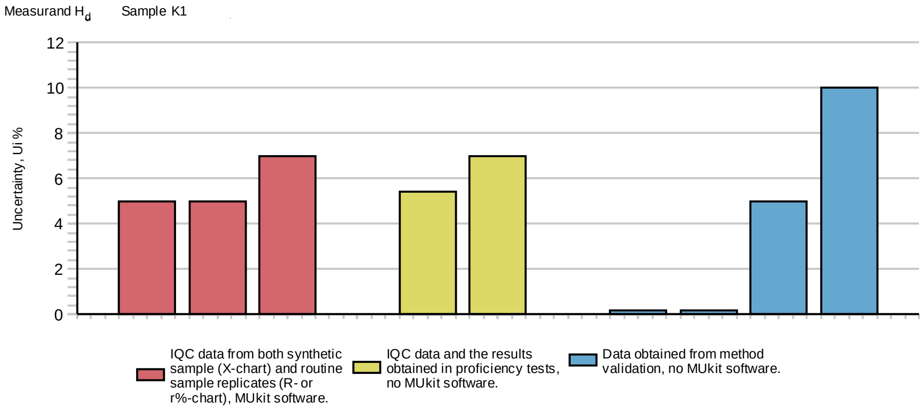
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (*k*=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [27, 28] or using a modelling approach based [29, 30].

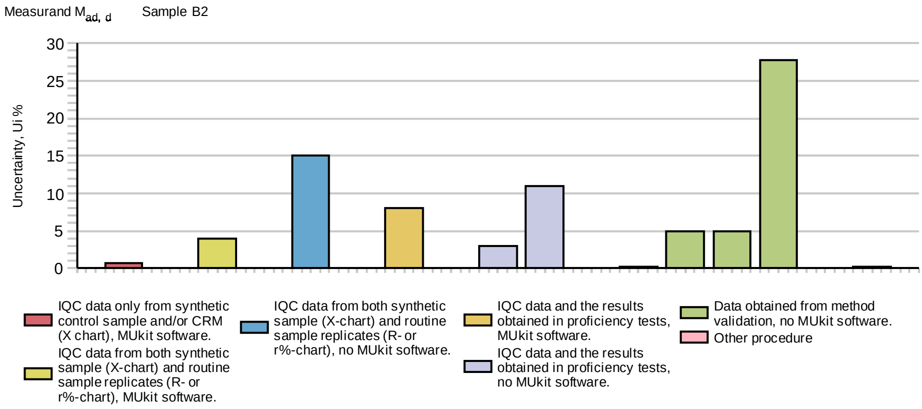


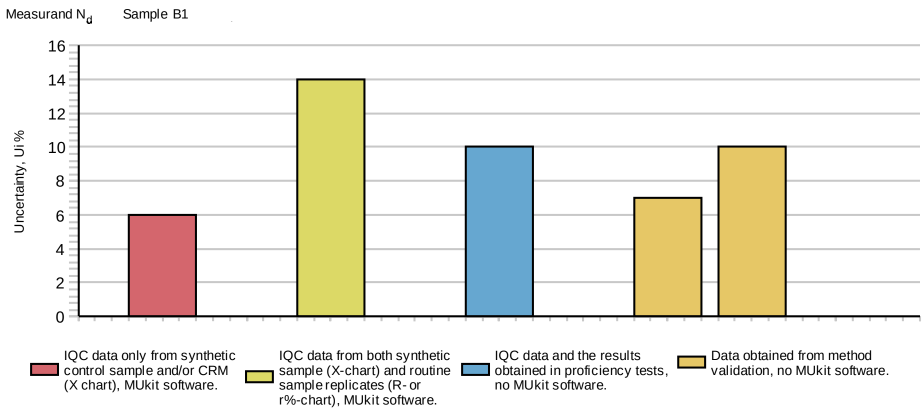


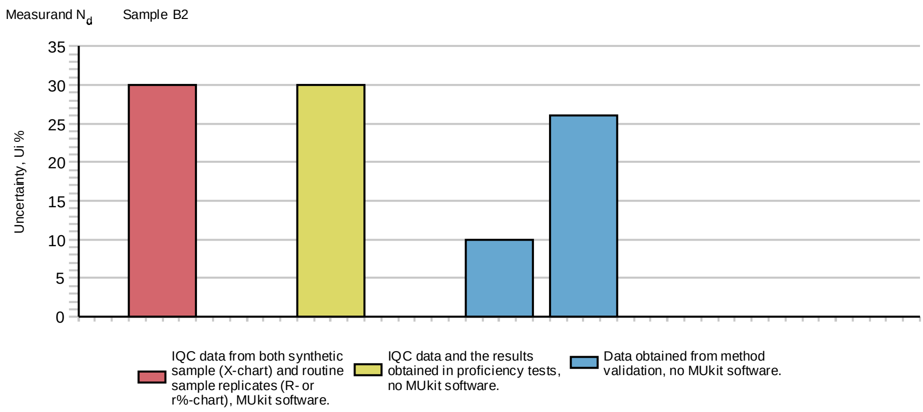


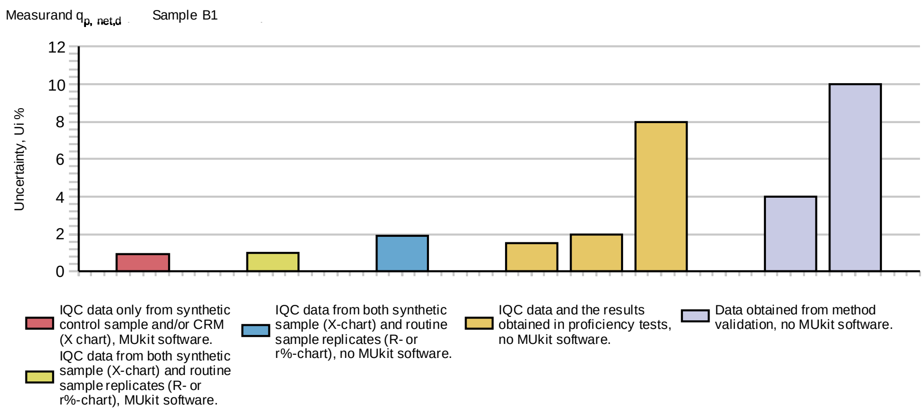

Measurand EF
Sample K1
Uncertainty, Ui %
0
2
4
6
8
10
12
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand H_d
Sample K1
Uncertainty, Ui %
0
2
4
6
8
10
12
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

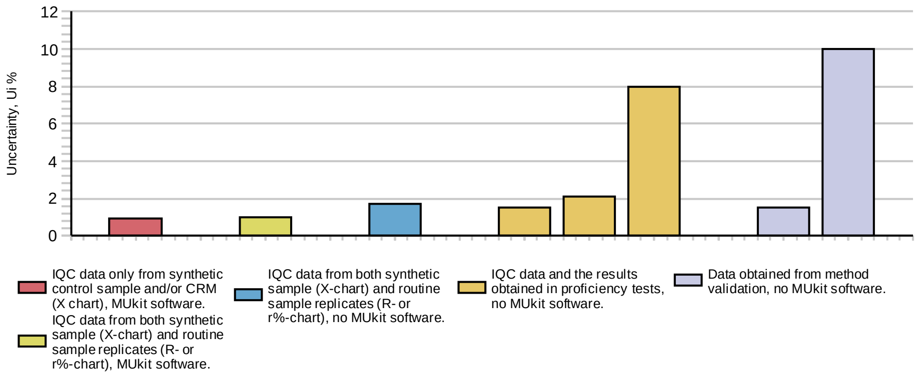

Measurand $M_{ad, d}$
Sample B2
Uncertainty, Ui %
0
5
10
15
20
25
30
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure


Measurand N_d Sample B1
Uncertainty, Ui %
0
2
4
6
8
10
12
14
16
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

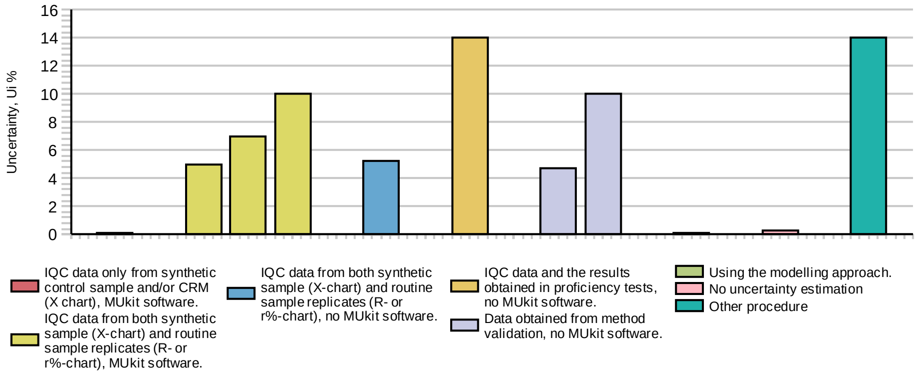

Measurand N_d Sample B2
Uncertainty, Ui %
0
5
10
15
20
25
30
35
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand $q_{p, net,d}$ Sample B1
Uncertainty, Ui %
0
2
4
6
8
10
12
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

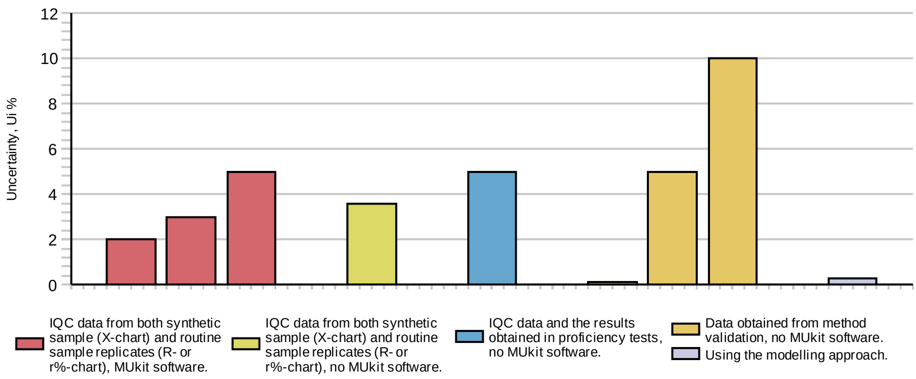
Measurand $q_{V, gr,d}$ Sample B1



Measurand S_d Sample K1



Measurand V_{db} Sample K1



INTERLABORATORY PROFICIENCY TEST SYKE 07/2018

FINNISH ENVIRONMENT INSTITUTE

SYKE

Proftest SYKE

ISBN 978-952-11-4975-7 (pbk.)
ISBN 978-952-11-4976-4 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)