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ABSTRACT

Interlaboratory Proficiency Test 07/2020

Proftest SYKE arranged the proficiency test (PT) for the measurements of the gross and 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 2020. In total, there were 31 participants in the PT. The participants could also estimate the emission factor for the peat and coal samples.

The robust mean or the median of the results reported by the participants was used as the assigned value for measurements. The performance evaluation was based on the z scores. In total, 89 % of the reported results were satisfactory, when the deviation of 1–30 % from the assigned value was accepted. For the gross calorific value measurements 79 % of the peat sample results, 80 % of the wood pellet sample results, and 90 % of the coal sample results were satisfactory. For the net calorific value measurements 83 % of the peat sample results, 76 % of the wood pellet results, and 82 % of the coal sample results were satisfactory. The performance evaluation was not done for the measurements of M_{ad} in all samples, N_d in the wood pellet sample, and emission factor in peat sample.
Warm thanks to all the participants in 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 07/2020

Proftest SYKE järjesti syyskuussa 2020 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 ja/tai laskea turve- ja kivihiilinäytteiden päästökerroin. Pätevyyskokeessa oli yhteensä 31 osallistujaa.

Testisuureiden vertailuarvoina käytettiin osallistujatulosten robustia keskiarvoa tai mediaania. Pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa hyväksyttäviä tuloksia oli 89 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 79 % (turve), 80 % (puupelletti) ja 90 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 83 % (turve), 76 % (puupelletti) ja 82 % (kivihiili). Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, puupelletin typen määrityksille ja päästökertoimelle turvenäytteessä.
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 07/2020

Proftest SYKE genomförde i september 2020 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 31 deltagarna deltog i jämförelsen.

Som referensvärde för analyternas koncentration användes det robusta medelvärdet eller den medianen av deltagarnas resultat. Resultaten värderades med hjälp av z värden. I jämförelsen var 89 % av alla resultaten acceptabel värderades, när en total deviation på 1–30 % från referensvärdet tilläts. Av det kalorimetriska värmevärdet var 79 % acceptabla (torv), 80 % (trädpellet) och 90 % (stenkol). För resultaten av det effektiva värmevärdet var 83 % (torv), 76 % (trädpellet) och 82 % (stenkol) acceptabla. Det var inte gjorts värdering till fuktighalt i alla prover, beräkning av väte i torv provet, nitrogen i trädpellet och emissionfaktor i torv provet.
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 2020 (CAL 07/2020). In the PT, gross and net calorific value, C_d, S_d, H_d, N_d, moisture content of the analysis sample (M_{ad}), ash content (Ash_d) as well as volatile matter (V_d) were tested in peat, wood pellet (not S) and coal samples. Additionally, the participants were asked to estimate the emission factors (EF) for the peat 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 standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
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Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Analytical expert

Eliisa Hatanpää	FTF Fuel Testing Finland Oy, *firstname.lastname@fueltest.fi*

Subcontracting	Sample homogenisation and dividing into subsamples, KVVY Tutkimus Oy, Tampere (T064, www.finas.fi/sites/en) Homogeneity testing: FTF Fuel Testing Finland Oy (T329, www.finas.fi/sites/en)

2.2 Participants

In total 31 laboratories participated in this proficiency test, of which 12 were from Finland and 19 from abroad (Appendix 1).

Altogether 71 % of the participants used accredited analytical methods at least for a part of the measurements. The samples were tested at the laboratory of FTF Fuel Testing Finland Oy and their participant code is 22 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}), ash content as well as volatile matter (V_d) were tested in peat, wood pellet (not S) and coal samples.

The material for the peat sample (B1) was collected from Finnish marshland. The material was air dried, ground with grinding mill and sieved with 500 µm sieve by Eurofins Labtium Ltd in Jyväskylä, Finland (T025, www.finas.fi/sites/en).

The wood pellet sample (B2) was provided by Vapo Oy and it was pre-treated by Eurofins Labtium Ltd, Jyväskylä. The raw material for wood pellets was spruce sawdust. The material was crushed with a cutting mill, ground with grinding mill and sieved with 1000 µm sieve.

The coal sample (K1) was pre-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 laboratory of FTF Fuel Testing Finland Oy tested all samples. 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 the measurements and to be stored in a dry place at room temperature. Further, the sample moisture content was instructed to be analyzed on every measurement day. 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 45.9 %,
- coal K1 9.8 %

The samples were dispatched to the participants on 1 September 2020. The samples arrived to fourteen participants latest on 4 September 2020. The used transportation service reported that there were difficulties especially in the international deliveries due to Covid-19 pandemic. Altogether 28 participants received the samples at the latest on 18 September 2020 and all samples were delivered at the latest on 28 September 2020. For some participants abroad new samples were dispatched using other transportation service. The delay in sample transportation was taken into account in the result evaluation.

Due to the sample transportation difficulties the reporting time of the participant results was extended. The original deadline of 22 September 2020 was prolonged until 30 September 2020. All the results were reported within the prolonged timetable. The preliminary results report was delivered to the participants via ProftestWEB and email on 6 October 2020.

2.4 Homogeneity and stability studies

Homogeneity of the samples 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. Based on the knowledge of the provider the samples have been considered stable during the PT. Further, based on the reported results the unforeseen delay in the sample delivery did not influence to the performance of the participants.

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 convergence to the given information with the results. Many participants reported their measurement uncertainties as absolute values not as relative values, as requested. The participants are advised to follow more carefully the instructions from the organizer. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. The replicate results were tested using the Cochran test. If the result was below limit of determination (LOD), it was not included to the data handling.

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 was used as the assigned value for measurands of the test samples, when there were at least 12 results ($n_{stat} \geq 12$). In cases, where the number of results was lower than 12 ($n_{stat} < 12$), the median (B1: EF, H_d, $q_{p,net,d}$, V_d; B2: N_d, V_d; K1: EF) or the mean (B1: C_d, N_d, S_d; B2: H_d) of participants' results was used as the assigned value. The expanded uncertainty of the assigned value was calculated using the robust standard deviation or the standard deviation of the reported results [1, 4].

When the robust mean, the mean, or the median was used as the assigned value, the uncertainty was calculated using the robust standard deviation or 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 0.4 %. For the other evaluated measurands the expanded uncertainty varied from 0.4 % to 7.6 % (Appendix 5).

After reporting the preliminary results report the assigned value of net calorific value in the coal sample (K1) is changed:

$q_{p,net,d}$ in K1: was 27 537 J/g → changed to 27 520 J/g.

This change caused no changes in the participants' performance evaluation, but changes in the numerical values of z scores occur.

2.6.3 Proficiency assessment procedure

The requirements for the reproducibility of the used standard methods were reported 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 results of this proficiency test were evaluated with the z scores. 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 given for analysis moisture content M_{ad} (all samples), and thus the results have not evaluated. Due to the high deviation of the results for nitrogen (N_d) in peat sample no performance evaluation is given for the results. Further, the number of results for emission factor (EF) in the peat sample was too low for results evaluation.

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

When using the robust mean, the median or the mean as the assigned value, the reliability 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 the reliability of the assigned value the criterion was fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standard deviation (s, $n_{stat}<12$) of the reported results (the criteria) [3]. The criterion s_{rob} (s) / $s_{pt} < 1.2$ was fulfilled.

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 scores are shown in Appendix 9 and the z scores in the ascending order in Appendix 10.

The robust standard deviations of the evaluated results varied from 0.4 to 12.9 % (Table 1). The robust standard deviation or the standard deviation was lower than 2 % for 52 % of the reported results and lower than 6 % for 85 % of the results (Table 1). For S_d in the sample B1, Ash_d and N_d in the sample B2 and M_{ad} in the sample K1 the robust standard deviation of the results was higher than 6 % (Table 1). The robust standard deviations and the standard deviations were approximately within the same range as in the previous similar proficiency test Proftest SYKE CAL 07/2019, where the standards deviations varied from 0.2 % to 12.7 % [5].

Table 1. The summary of the results in the proficiency test CAL 07/2020.

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%	4.58	4.59	4.58	4.60	0.15	3.4	7	13	92
	B2	w%	0.28	0.27	0.28	0.27	0.04	12.9	30	18	94
	K1	w%	14.7	14.7	14.7	14.7	0.1	0.7	2.5	20	95
C_d	B1	w%	54.6	54.6	54.6	54.6	0.6	1.1	2.5	10	100
	B2	w%	50.7	50.9	50.7	50.8	0.4	0.8	2.5	15	80
	K1	w%	69.0	69.0	69.0	69.0	0.5	0.7	2.5	20	100
EF	B1	t CO2/TJ	107	107	-	107	-	-	-	4	-
	K1	t CO2/TJ	92.9	92.9	92.9	92.9	0.8	0.9	4	9	89
H_d	B1	w%	5.79	5.79	5.90	5.79	0.31	5.2	7	10	80
	B2	w%	6.06	6.06	6.04	6.06	0.20	3.3	6	13	85
	K1	w%	4.65	4.64	4.65	4.62	0.15	3.1	6	18	83
M_{ad}	B1	w%	6.90	6.90	6.90	6.92	0.35	5.0	-	15	-
	B2	w%	8.15	8.16	8.15	8.19	0.14	1.7	-	21	-
	K1	w%	3.36	3.45	3.36	3.42	0.28	8.3	-	23	-
N_d	B1	w%	1.63	1.63	1.63	1.63	0.08	4.8	10	10	100
	B2	w%	0.073	0.076	0.082	0.073	0.036	44.2	-	12	-
	K1	w%	2.22	2.22	2.22	2.25	0.08	3.5	10	16	100
$q_{p,net,d}$	B1	J/g	20867	20891	20891	20867	122	0.6	1.5	12	83
	B2	J/g	18875	18858	18875	18873	86	0.5	1.6	17	76
	K1	J/g	27520	27510	27520	27465	141	0.5	1.2	17	82
$q_{V,gr,d}$	B1	J/g	22114	22104	22114	22105	81	0.4	1.4	14	79
	B2	J/g	20158	20134	20158	20153	137	0.7	1.4	20	80
	K1	J/g	28520	28527	28520	28518	119	0.4	1.0	21	90
S_d	B1	w%	0.15	0.15	0.15	0.16	0.01	9.3	15	10	90
	K1	w%	0.44	0.44	0.44	0.44	0.02	5.4	15	22	91
V_d	B1	w%	69.6	69.6	69.8	69.6	1.1	1.6	3	7	86
	B2	w%	85.1	85.1	85.1	85.1	1.2	1.4	3	11	91
	K1	w%	34.8	34.8	34.8	34.9	0.9	2.5	5	17	100

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, n_{all}: the number of the participants, Acc z %: the results (%), where $|z| \leq 2$.

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. Particularly, 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 0.54 % for the sample B1, 0.60 % for the sample B2 and 0.42 % for the sample K1 and in measurement of the net calorific value 0.48 %, 0.64 % and 0.44 %, 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 %).

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%	4.58	4.59	0.02	0.16	0.16	0.46	3.5	3.5	7.6
	B2	w%	0.28	0.27	0.02	0.04	0.04	5.7	14	15	2.4
	K1	w%	14.7	14.7	0.04	0.19	0.15	0.26	1.0	1.0	3.9
C_d	B1	w%	54.6	54.6	0.17	0.53	0.56	0.32	0.98	1.0	3.1
	B2	w%	50.7	50.9	0.13	0.66	0.68	0.26	1.3	1.3	5.0
	K1	w%	69.0	69.0	0.10	0.54	0.55	0.15	0.79	0.80	5.3
EF	B1	t CO2/TJ	107	107	0.21	1.02	1.04	0.20	0.96	0.98	4.9
	K1	t CO2/TJ	92.9	92.9	0.12	0.71	0.72	0.13	0.76	0.77	5.7
H_d	B1	w%	5.79	5.79	0.03	0.38	0.38	0.57	6.3	6.4	11
	B2	w%	6.06	6.06	0.06	0.30	0.31	0.95	5.0	5.1	5.3
	K1	w%	4.65	4.64	0.12	0.28	0.31	2.6	6.0	6.6	2.3
M_{ad}	B1	w%	6.90	6.90	0.06	0.40	0.40	0.90	5.8	5.8	6.4
	B2	w%	8.15	8.16	0.03	0.21	0.21	0.42	2.5	2.6	6.0
	K1	w%	3.36	3.45	0.06	0.53	0.53	1.7	16	16	9.3
N_d	B1	w%	1.63	1.63	0.01	0.08	0.076	0.71	4.6	4.7	6.5
	B2	w%	0.073	0.076	0.01	0.05	0.046	11	51	52	4.7
	K1	w%	2.22	2.22	0.01	0.08	0.08	0.54	3.5	3.5	6.5
$q_{p,net,d}$	B1	J/g	20867	20891	35.4	168	171	0.17	0.80	0.82	4.7
	B2	J/g	18875	18858	28.8	154	157	0.15	0.82	0.83	5.4
	K1	J/g	27520	27510	40.8	154	160	0.15	0.56	0.58	3.8
$q_{V,gr,d}$	B1	J/g	22114	22104	36.4	135	140	0.16	0.61	0.63	3.7
	B2	J/g	20158	20134	80.4	181	198	0.40	0.90	0.98	2.3
	K1	J/g	28520	28527	39.5	127	133	0.14	0.45	0.47	3.2
S_d	B1	w%	0.15	0.15	0.01	0.02	0.02	6.1	12	13	1.9
	K1	w%	0.44	0.44	0.01	0.03	0.03	1.7	7.5	7.7	4.3
V_d	B1	w%	69.6	69.6	0.32	2.32	2.34	0.45	3.3	3.3	7.3
	B2	w%	85.1	85.1	0.22	1.07	1.09	0.26	1.3	1.3	4.8
	K1	w%	34.8	34.8	0.09	0.78	0.78	0.25	2.2	2.3	8.9

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

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 3.7 (the sample B1), 2.3 (the sample B2) and 3.2 (the sample K1), for the net calorific values 4.7, 5.4 and 5.2, respectively. For the calorific values the ratio s_b/s_w was mainly higher than in the previous similar proficiency test CAL 07/2019 [5].

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. A survey of the used analytical methods was carried out along the proficiency test. The summary of the survey 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 ≥ 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 and 12.

Mostly standard methods were used for measurement of calorific values ($q_{V,gr,d}$ and $q_{p,net,d}$) (EN 14918 [6], EN ISO 18125 [7], ISO 1928 [8], Appendix 12). One participant used standard ASTM D 5865 [9] or DIN 51900 [10]. At maximum seven participants used standard method EN 15400 (solid recovered fuels) for the sample B1 and/or B2 (reported as *Other method*).

For 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). Also for the calculations of net calorific value ($q_{p,net,d}$), different combinations of correction factors were used depending of the test material (Appendix 11). Mainly nitrogen plus oxygen (N+O) and hydrogen (H) content was used for corrections. Based on the graphical evaluation no clear 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 [11], ISO 1171 [12], EN ISO 18122 [13], ASTM D 7582 [14]
C_d, H_d and N_d	ISO 29541 [15], ASTM D 5373 [16], EN ISO 16948 [17]
M_{ad} (analytical moisture content)	EN 14774-3 [18], ISO 589 [19], DIN 51718 [20], ASTM D 7582 [14], EN ISO 18134-3 [21], ISO 11722 [22]
S_d	EN ISO 16994 [23], ASTM D 4239 [24], ISO 334 [25], ISO 19579 [26]
V_{db}, (volatile matter)	EN 15148 [27], ISO 562 [28], EN ISO 18123 [29]

However, in some cases also other international and national standards or technical specifications (e.g. DIN 51719, EN 15403, ASTM D 4422, EN 15407, EN 15936, ASTM D 5291, EN 15400, EN 15414, EN 15934, EN 15408, ASTM D 7582, EN 15402, ASTM D 3175, ISO 19579) or internal methods (e.g. participant 31) were used. It was noticed, that in some cases the participants used withdrawn international standards e.g. EN 14775 [11] instead of EN ISO 18122 [13].

The ash content was determined mainly gravimetrically by heating at the temperature 550 °C or 815 °C (Samples B1 and B2), and at the temperature 750 °C or 815 °C (Sample K1). Ash content was measured also using TGA for the samples at the temperatures 550 °C, 750 °C and 815 °C (Appendix 11). In the international standard EN ISO 18122 the ashing temperature is mentioned to be 550 °C for solid biofuels [11, 13]. While in ISO 1711 for solid mineral fuels it is mentioned

to be 815 °C [12]. 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 105-108 °C. Moisture content was measured also using TGA at the temperatures of 105-107 °C (Appendix 11).

Most of the participants conducted CHN analyses from air dried samples, four to six participants used dried samples for all test samples and one participant used samples as received with correction for moisture (Appendix 11). For C_d results a statistically significant difference was observed between the international standard methods ASTM D 5373 (mean ± standard deviation, 69.4 ± 0.5, n = 6) and ISO 29541 (68.8 ± 0.5, n = 12) in the coal sample K1 (Appendices 12, 13). Based on the graphical result evaluation for others, 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 the detection limits for nitrogen and sulphur was collected (Appendix 11). The detection limits varied for N: 0.002-0.1 w% and for S: 0.001-0.1 w%.

3.3 Uncertainties of the results

At maximum 76 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 14). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for estimating of measurement uncertainty (Appendix 14). 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 uncertainty estimation for some measurands [30, 31]. 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 measurement uncertainties varied highly for all the tested measurands (Table 3). Especially, very low or high uncertainties can be considered very questionable. **It was evident, that some uncertainties had been reported erroneously for the measurands** (including calorific values, bolded italic numbers in Table 3, Appendix 13), **not as relative values as the provider of this proficiency test had requested**. The participants are advised to follow more carefully the instructions from the organizer. When reporting measurement uncertainties, the accuracy of the numeric values should correlate with the accuracy of the result. 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	4.4-18	0.11-50	1.5-5.9
C_d	0.6-3	0.34-40	0.42-10
EF	8-10	-	1-8
H_d	5-9	0.86-11	0.51-20
M_{ad}	1.28-12	0.08-27.9	0.02-17
N_d	8-17	0.24-57	0.24-20
$q_{p,net,d}$	0.6-4.3	0.36-5.4	0.13-5
$q_{V,gr,d}$	0.8-***4032***	0.36-***674***	0.11-***5503***
S_d	11-20	-	0.11-30
V_{db}	2.8-5	0.48-10	0.2-5

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 (4-9). Due to the low number of the reported results, the performance evaluation was not given for the peat sample (B1).

4 Evaluation of the results

The performance evaluation was based on the z 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

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). About 71 % of the participants used the accredited methods and 80 % of their results were satisfactory. In the previous similar proficiency test CAL 07/2019 the performance was satisfactory for 90 % 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 CAL 07/2020.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
Peat, B1	89	1.4-15	• Good performance. • Difficulties in measurements for $q_{p,gr,d}$ < 80% satisfactory results. • In the CAL 07/2019 the performance was satisfactory for 93 % of the results [5].
Wood pellet, B2	84	1.4-30	• Good performance. • Difficulties in measurements for $q_{p,net,d}$ < 80% satisfactory results. • In the CAL 07/2019 the performance was satisfactory for 89 % of the results [5].
Coal, K1	92	1-15	• Very good performance. • In the CAL 07/2019 the performance was satisfactory for 92 % of the results [5].

The summary of the performance evaluation is shown in Table 4. The percentage of the satisfactory results varied between 84 % and 92 % for the tested sample types. The criteria for performance evaluation was 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 07/2019) 93 % of the results were satisfactory for the peat sample (B1) when accepting 1.4–15 % deviation from the assigned value [5], and thus the performance was somewhat lower in this PT (89 %, Table 4). In the previous similar PT, the gross and the net calorific values 93 % and 82 % of the results, respectively, were satisfactory [5]. In this PT the satisfactory number of the results for the gross and net calorific values were 79 % and 83, respectively. Thus, there was lower number of satisfactory results for the gross calorific value and for the net calorific value at the same level in this PT. The results of analysis moisture (M_{ad}) and emission factor (EF) have not been evaluated, but the assigned values are presented (Table 1).

Wood pellet

In the previous similar PT (CAL 07/2019) the satisfactory results of the wood pellet sample (B2) were in total 89 %, when accepting deviation 1.4–30 % from the assigned value, thus the performance in this PT was slightly lower (84 %, Table 4) [5]. The satisfactory results varied between 76 % ($q_{p,net,d}$) and 94 % (Ash_d) for the wood pellet sample (Table 1). In the measurement of gross and net calorific values 80 % and 76 % of the results, respectively, were satisfactory when accepting deviations of 1.4 % and 1.6 % from the assigned values (Table 1). The number of satisfactory results was somewhat higher for the gross calorific values and lower for the net calorific value for wood pellet than in the previous similar PT (76 % and 88 %, respectively) [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 07/2019) the satisfactory results of the coal sample (K1) were in total 92 %, thus the performance was at the same level in this PT (92 %, Table 4) [5]. In the measurement of gross and net calorific values, 90 % and 82 % of results, respectively, were satisfactory, when accepting the deviations of 1 and 1.2 % from the assigned values (Table 1). The number of the satisfactory results was somewhat higher for the gross calorific value and lower for the net calorific value than in the previous similar PT (86 % and 93 %, respectively) [5]. The results of analysis moisture (M_{ad}) has 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 2020. Three types of samples were delivered to the participants: peat, wood pellet (not sulphur) and coal. Additionally, the participants also had the possibility to estimate or calculate the emission factor for peat and coal samples. In total 31 participants took part in the PT.

The robust mean, the mean or the median 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 or equal to 0.4 % for calorific values and at maximum 7.6 % 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. The evaluation of performance was not done for the measurement of M_{ad} in all samples, N_d in the wood pellet sample, and EF for peat 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 71 % of the participants used the accredited methods and 80 % of their results were satisfactory. In measurements of the gross calorific value from the peat, the wood pellet and the coal samples, 79 %, 80 % and 90 % of the results were satisfactory, respectively. In measurements of the net calorific value from the peat, the wood pellet and the coal samples, 83 %, 76 % and 82 % of the results were satisfactory, respectively. In the present PT the number of the satisfactory results for the gross caloric value was lower in the peat (B1) sample and slightly higher for the wood pellet (B2) and the coal (K1) samples than in the previous similar PT CAL 07/2019 [5]. For the net calorific value the number of the satisfactory results was at the same level in the peat (B1) sample, and somewhat lower in the wood pellet (B2) and coal samples in the present PT than in the previous PT [5].

6 Summary in Finnish

Proftest SYKE järjesti syyskuussa 2020 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. Pätevyyskokeessa oli 31osallistujaa.

Testisuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai niiden keskiarvoa tai mediaania. Vertailuarvon epävarmuus oli lämpöarvomäärityksissä pienempi tai yhtä suuri kuin 0,4 % ja muiden määritysten osalta korkeintaan 7,6 %.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, typen määritykselle puupelletistä eikä turpeen päästökertoimelle. Koko tulosaineistossa hyväksyttäviä tuloksia oli 89 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Noin 71 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 80 %. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 79 % (turve), 80 % (puupelletti) ja 90 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 83 % (turve), 76 % (puupelletti) ja 82 % (kivihiili). Kalorimetrisen lämpöarvon määritysten osalta menestyminen oli turvenäytteessä alhaisempi sekä puupelletin ja kivihiilen osalta jonkin verran parempi kuin edellisessä vastaavassa pätevyyskokeessa CAL 07/2019 [5]. Tehollisen lämpöarvon määrityksissä menestyminen oli turvenäytteen osalta samalla tasolla, mutta alhaisempi puupelletti- ja kivihiilinäytteen osalta kuin edellisessä vastaavassa pätevyyskokeessa [5].

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Bulgary	AES-3C Maritza East 1 EOOD; Testing Laboratory "Energy Materials"
	Brikel EAD, Solid Fuels Test Laboratory
Estonia	Enefit Energiatootmine AS Chemical Laboratory
	Estonian Environmental Research Center
Finland	Eurofins Labtium Oy, Jyväskylä
	Finnsementti Oy
	Fortum Waste Solutions Oy, Riihimäki
	FTF Fuel Testing Finland Oy
	Helen Ltd
	Kaakkois-Suomen ammattikorkeakoulu Oy / KymiLabs
	Kuopion Energia Oy / Tuotanto-osasto
	Kymen Ympäristölaboratorio Oy
	Neste Corporation, Technology Center, Kilpilahti
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	SeiLab Oy Haapaveden toimipiste
	SYNLAB Analytics & Services Finland Oy
France	ArcelorMittal Fos sur Mer
	Eurofins Analyses des Materiaux et Combustibles France
	SOCOR Dechy France
Lithuania	Cement testing laboratory Co Akmenes cementas Lithuania
Republic of Ireland	Edenderry Power Ltd
Romania	HeidelbergCement Romania S.A
	Holcim (Romania) SA Cement Plant Campulung
	INCDE ICEMENERG Bucharest, National Research and Development Institute for Energy
	Romcontrol
	SC EUROTOTAL COMP SRL
	Waste Analysis Laboratory INCD ECOIND Bucuresti-Romania
Slovenia	Salonit Anhovo
Spain	Centro de Investigacion Elias Masaveu S.A.
	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 collected from Finnish marshland.
The peat was air-dried (35 ºC), ground with grinding mill and sieved with 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, then ground with grinding mill and sieved 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

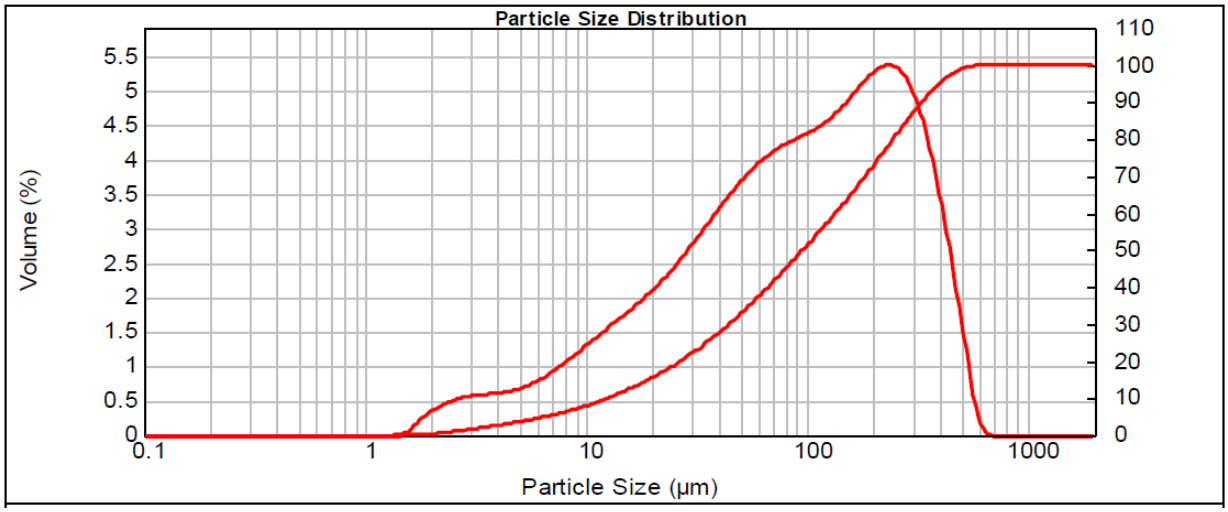
Sample K1 was Russian steam coal. The coal was dried at room temperature and ground to particle size < 212 µm at Helen Ltd (Finland). The dried and sieved sample was mixed by a mechanized sample mixer and distributed into subsamples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory the laboratory of KVVY Tutkimus Oy (Tampere). The particle size distribution of coal was measured by 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 95.5 µm and ca. 98 % of the particles were smaller than 550 µm. For coal sample K1 the mean size of particles was 54.8 µm and 100 % 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)



b)

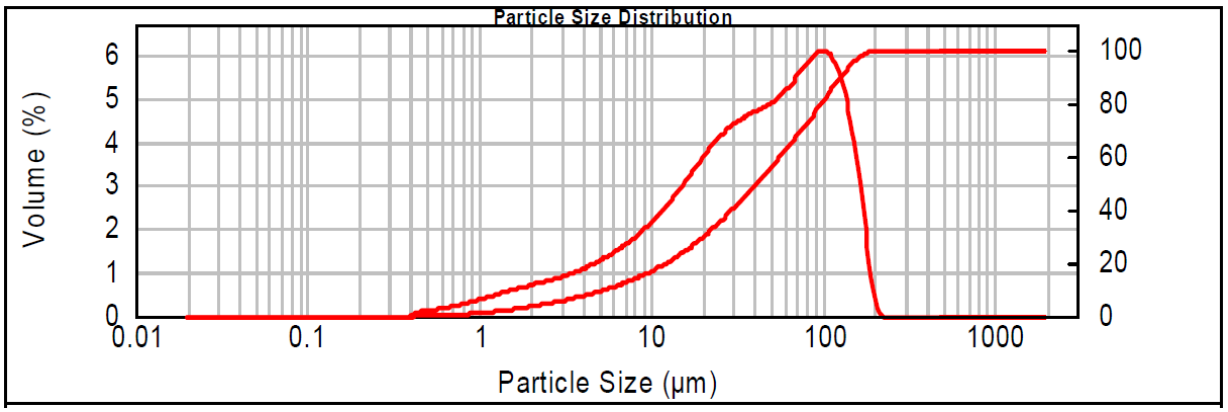


Figure 1. The particle size distribution of the fuel samples a) the peat (B1) and b) the coal (K1) sample.

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	n	Mean	s_h%	s_{pt}%	s_h	s_{an}	s_{an}/s_h	Is $s_{an}/s_h<0.5$?	s_{sam}	s_{sam}^2	c	Is $s_{sam}^2<c$?
Peat (B1)												
Gross calorific value, J/g	5	22146	0.7	0.7	155	35.3	0.23	yes	83.6	6990	7750	yes
Net calorific value, J/g	5	20877	0.7	0.8	146	35.6	0.24	yes	83.6	6990	7220	yes
Pellet (B2)												
Gross calorific value, J/g	5	20230	0.5	0.7	101	49.2	0.49	yes	25.4	647	6950	yes
Net calorific value, J/g	5	18911	0.3	0.8	56.7	24.8	0.44	yes	22.1	490	1910	yes
Coal (K1)												
Gross calorific value, J/g	5	28799	0.3	0.5	86.4	32.2	0.37	yes	0	0	3770	yes
Net calorific value, J/g	5	27793	0.3	0.6	83.4	31.6	0.38	yes	0	0	3580	yes

n= number of tested samples

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
8, 21	The participants received the sample package as scheduled, at the latest on 4 September 2020.	The used distributor (Posti) reported they had difficulties in the international deliveries due to the Covid-19 pandemic. The provider extended the reporting time of the participant results from 22 September until 30 September 2020.
1, 3, 13, 15, 17, 26, 31	The participants received the sample package on 5 - 11 September 2020.	
5, 6, 12, 14, 20, 30, 32	The participants received the sample package on 12 - 18 September 2020.	
10	The participant received the sample package on 21 September 2020.	
7, 16, 29	The participants did not receive the sample package. The provider dispatched new sample packages with different distributor on 18 September 2020. These packages arrived to the participant on 21 and on 28 September 2020.	

Participant	Comments to the results	Action / Proftest SYKE
9	The participant reported erroneously their results of net calorific value. Their corrected values were: B1: 20867 J/g B2: 18875 J/g K1: 27537 J/g	The provider does not correct the results after delivering the preliminary result report. The erroneous results for samples B1 and B2 were handled as manual outliers in the statistical treatment and they did not affect to performace of the other participants. In the final data handling the result of sample K1 was set as an outlier for the statistical calculations. See more information in Chapter 2.6.2. If the results 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 reported their results in wrong unit. Their corrected gross calorific values were: B2: 19871 J/g K1: 28340 J/g Their corrected net calorific values were: B2: 18811 J/g K1: 27361 J/g	The provider does not correct the results after delivering the preliminary results. The erroneous results were handled as manual outliers in the statistical treatment. They did not affect to the assigned value evaluation. If the gross and net calorific values value had been reported correctly, they would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
1, 3, 10, 12, 14, 16, 21, 31	The participants did not report the expanded measurement uncertainties for some measurands. The measurement uncertainty should be reported with the results obtained with accredited method.
8, 10, 14, 30, 32	The participant did not inform the accreditation status of their method for some measurands. The participants should follow the instructions of the provider.
3, 10, 12, 14, 21, 24, 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 for replicate measurements.
12, 14, 15, 18, 19, 32	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%	4.58	0.11	2.3	Robust mean	0.33
	B2	w%	0.28	0.02	7.6	Robust mean	0.25
	K1	w%	14.7	0.1	0.4	Robust mean	0.16
C_d	B1	w%	54.6	0.3	0.6	Mean	0.24
	B2	w%	50.7	0.3	0.6	Robust mean	0.24
	K1	w%	69.0	0.3	0.4	Robust mean	0.16
EF	B1	t CO2/TJ	107	1	1.1	Median	
	K1	t CO2/TJ	92.9	0.5	0.5	Median	0.13
H_d	B1	w%	5.79	0.10	1.7	Median	0.24
	B2	w%	6.06	0.09	1.5	Mean	0.25
	K1	w%	4.65	0.08	1.8	Robust mean	0.30
M_{ad}	B1	w%	6.90	0.23	3.4	Robust mean	
	B2	w%	8.15	0.08	1.0	Robust mean	
	K1	w%	3.36	0.14	4.3	Robust mean	
N_d	B1	w%	1.63	0.05	2.9	Mean	0.29
	B2	w%	0.073	0.018	24.0	Median	
	K1	w%	2.22	0.05	2.2	Robust mean	0.22
$q_{p,net,d}$	B1	J/g	20867	42	0.2	Median	0.13
	B2	J/g	18875	57	0.3	Robust mean	0.19
	K1	J/g	27520	83	0.3	Robust mean	0.25
$q_{V,gr,d}$	B1	J/g	22114	66	0.3	Robust mean	0.21
	B2	J/g	20158	81	0.4	Robust mean	0.29
	K1	J/g	28520	57	0.2	Robust mean	0.20
S_d	B1	w%	0.15	0.01	4.6	Mean	0.31
	K1	w%	0.44	0.01	2.9	Robust mean	0.19
V_d	B1	w%	69.6	0.6	0.8	Median	0.27
	B2	w%	85.1	0.7	0.8	Median	0.27
	K1	w%	34.8	0.5	1.5	Robust mean	0.30

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
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n_{stat}	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i ($i = 1, 2, \ldots, p$)
s^* = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

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%	K1		0.05	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
M_{ad}	w%	K1			3.36		3.26	3.42	3.45	0.33	9.5	23
$q_{v,gr,d}$	J/g	K1		-0.31	28520	1	28476	28518	28527	130	0.5	19
S_d	w%	K1		0.14	0.44	15	0.44	0.44	0.44	0.03	6.1	22
V_d	w%	K1		0.12	34.8	5	34.9	34.9	34.8	0.8	2.2	17

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%	B2		0.95	0.28	30	0.32	0.27	0.27	0.04	14.4	18
	w%	K1		0.38	14.7	2,5	14.8	14.7	14.7	0.1	0.6	20
C_d	w%	B2		-0.09	50.7	2,5	50.6	50.8	50.9	0.3	0.6	14
	w%	K1		0.28	69.0	2,5	69.2	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	K1		0.02	92.9	4	92.9	92.9	92.9	0.7	0.8	8
H_d	w%	B2		0.69	6.06	6	6.19	6.06	6.06	0.15	2.6	11
	w%	K1		-0.30	4.65	6	4.61	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B2			8.15		3.28	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.45	3.42	3.45	0.33	9.5	23
N_d	w%	B2			0.073		*<0,1*	0.073	0.076	0.027	35.8	9
	w%	K1		-0.64	2.22	10	2.15	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B2		0.15	18875	1,6	18897	18873	18858	86	0.5	14
	J/g	K1		0.26	27520	1,2	27563	27465	27510	157	0.6	15
$q_{v,gr,d}$	J/g	B2		0.47	20158	1,4	20225	20153	20134	139	0.7	18
	J/g	K1		0.19	28520	1	28548	28518	28527	130	0.5	19
S_d	w%	K1		0.76	0.44	15	0.47	0.44	0.44	0.03	6.1	22
V_d	w%	B2		-0.60	85.1	3	84.3	85.1	85.1	1.1	1.3	10
	w%	K1		0.72	34.8	5	35.4	34.9	34.8	0.8	2.2	17

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		2.15	4.58	7	4.93	4.60	4.59	0.16	3.5	13
	w%	K1		-0.16	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	B1		-0.40	54.6	2,5	54.3	54.6	54.6	0.5	1.0	10
	w%	K1		-0.39	69.0	2,5	68.7	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	B1			107		12	107	107	1	1.0	3
	t CO2/TJ	K1		-39.24	92.9	4	20.0	92.9	92.9	0.7	0.8	8
H_d	w%	B1		0.36	5.79	7	5.86	5.79	5.79	0.14	2.4	8
	w%	K1		5.65	4.65	6	5.44	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		7.68	6.92	6.90	0.26	3.8	14
	w%	K1			3.36		4.38	3.42	3.45	0.33	9.5	23
N_d	w%	B1		0.66	1.63	10	1.68	1.63	1.63	0.08	4.6	10
	w%	K1		0.05	2.22	10	2.23	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		-0.20	20867	1,5	20835	20867	20891	78	0.4	9
	J/g	K1		-2.40	27520	1,2	27124	27465	27510	157	0.6	15

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$q_{V,gr,d}$	J/g	B1		-0.06	22114	1,4	22105	22105	22104	79	0.4	12
	J/g	K1		-1.66	28520	1	28283	28518	28527	130	0.5	19
S_d	w%	B1		1.47	0.15	15	0.17	0.16	0.15	0.01	6.9	9
	w%	K1		-0.55	0.44	15	0.42	0.44	0.44	0.03	6.1	22
V_d	w%	B1		0.87	69.6	3	70.5	69.6	69.6	0.7	1.0	6
	w%	K1		0.10	34.8	5	34.9	34.9	34.8	0.8	2.2	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}
C_d	w%	B1		-0.89	54.6	2,5	54.0	54.6	54.6	0.5	1.0	10
	w%	K1		-1.72	69.0	2,5	67.5	69.0	69.0	0.5	0.8	20
H_d	w%	B1		3.08	5.79	7	6.42	5.79	5.79	0.14	2.4	8
	w%	K1		-0.57	4.65	6	4.57	4.62	4.64	0.10	2.1	18
N_d	w%	B1		0.31	1.63	10	1.66	1.63	1.63	0.08	4.6	10
	w%	K1		0.45	2.22	10	2.27	2.25	2.22	0.08	3.5	16

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		-1.09	4.58	7	4.41	4.60	4.59	0.16	3.5	13
	w%	B2		-0.60	0.28	30	0.26	0.27	0.27	0.04	14.4	18
	w%	K1		-0.08	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
M_{ad}	w%	B1			6.90		6.90	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.13	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.38	3.42	3.45	0.33	9.5	23
$q_{V,gr,d}$	J/g	B1		-1.01	22114	1,4	21957	22105	22104	79	0.4	12
	J/g	B2		-0.91	20158	1,4	20029	20153	20134	139	0.7	18
	J/g	K1		0.03	28520	1	28524	28518	28527	130	0.5	19
S_d	w%	K1		-1.67	0.44	15	0.39	0.44	0.44	0.03	6.1	22
V_d	w%	B1		-1.01	69.6	3	68.6	69.6	69.6	0.7	1.0	6
	w%	B2		-1.36	85.1	3	83.4	85.1	85.1	1.1	1.3	10
	w%	K1		-1.34	34.8	5	33.6	34.9	34.8	0.8	2.2	17

Participant 6												
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		0.16	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	B2		-2.54	50.7	2,5	49.1	50.8	50.9	0.3	0.6	14
	w%	K1		-0.44	69.0	2,5	68.6	69.0	69.0	0.5	0.8	20
M_{ad}	w%	B2			8.15		8.33	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		4.17	3.42	3.45	0.33	9.5	23
$q_{V,gr,d}$	J/g	B2		-2.62	20158	1,4	19789	20153	20134	139	0.7	18
	J/g	K1		2.00	28520	1	28805	28518	28527	130	0.5	19
S_d	w%	K1		-0.45	0.44	15	0.43	0.44	0.44	0.03	6.1	22
V_d	w%	K1		-1.53	34.8	5	33.5	34.9	34.8	0.8	2.2	17

Participant 7												
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		-0.87	14.7	2,5	14.5	14.7	14.7	0.1	0.6	20
C_d	w%	K1		-0.23	69.0	2,5	68.8	69.0	69.0	0.5	0.8	20
H_d	w%	K1		0.72	4.65	6	4.75	4.62	4.64	0.10	2.1	18
M_{ad}	w%	K1			3.36		2.95	3.42	3.45	0.33	9.5	23
N_d	w%	K1		0.59	2.22	10	2.29	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	K1		-0.76	27520	1,2	27395	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	K1		-1.03	28520	1	28373	28518	28527	130	0.5	19
S_d	w%	K1		1.36	0.44	15	0.49	0.44	0.44	0.03	6.1	22
V_d	w%	K1		1.37	34.8	5	36.0	34.9	34.8	0.8	2.2	17

Participant 8												
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		0.66	4.58	7	4.69	4.60	4.59	0.16	3.5	13
	w%	B2		-0.36	0.28	30	0.27	0.27	0.27	0.04	14.4	18
	w%	K1		0.08	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	B1		1.00	54.6	2,5	55.3	54.6	54.6	0.5	1.0	10
	w%	B2		0.63	50.7	2,5	51.1	50.8	50.9	0.3	0.6	14
	w%	K1		0.09	69.0	2,5	69.1	69.0	69.0	0.5	0.8	20
H_d	w%	B1		-1.12	5.79	7	5.56	5.79	5.79	0.14	2.4	8
	w%	B2		-0.42	6.06	6	5.98	6.06	6.06	0.15	2.6	11
	w%	K1		-0.59	4.65	6	4.57	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		7.03	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.20	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.23	3.42	3.45	0.33	9.5	23
N_d	w%	B1		0.74	1.63	10	1.69	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		0.060	0.073	0.076	0.027	35.8	9
$q_{p,net,d}$	J/g	B1		0.31	20867	1,5	20915	20867	20891	78	0.4	9
	J/g	B2		-0.17	18875	1,6	18849	18873	18858	86	0.5	14
	J/g	K1		0.00	27520	1,2	27520	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		0.06	22114	1,4	22123	22105	22104	79	0.4	12
	J/g	B2		-0.04	20158	1,4	20153	20153	20134	139	0.7	18
	J/g	K1		-0.02	28520	1	28518	28518	28527	130	0.5	19
S_d	w%	B1		-0.71	0.15	15	0.14	0.16	0.15	0.01	6.9	9
	w%	K1		-0.06	0.44	15	0.44	0.44	0.44	0.03	6.1	22
V_d	w%	K1		-0.56	34.8	5	34.3	34.9	34.8	0.8	2.2	17

Participant 9												
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		-0.16	4.58	7	4.56	4.60	4.59	0.16	3.5	13
	w%	B2		0.36	0.28	30	0.30	0.27	0.27	0.04	14.4	18
	w%	K1		-0.63	14.7	2,5	14.6	14.7	14.7	0.1	0.6	20
M_{ad}	w%	B1			6.90		6.67	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		7.75	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		1.49	3.42	3.45	0.33	9.5	23
$q_{p,net,d}$	J/g	B1		6.78	20867	1,5	21929	20867	20891	78	0.4	9
	J/g	B2		8.26	18875	1,6	20122	18873	18858	86	0.5	14
	J/g	K1		3.42	27520	1,2	28085	27465	27510	157	0.6	15

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
S_d	w%	B1		1.60	0.15	15	0.17	0.16	0.15	0.01	6.9	9
	w%	K1		-0.15	0.44	15	0.44	0.44	0.44	0.03	6.1	22
V_d	w%	B1		0.39	69.6	3	70.0	69.6	69.6	0.7	1.0	6
	w%	B2		0.89	85.1	3	86.2	85.1	85.1	1.1	1.3	10
	w%	K1		1.18	34.8	5	35.8	34.9	34.8	0.8	2.2	17

Participant 10												
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		0.87	4.58	7	4.72	4.60	4.59	0.16	3.5	13
	w%	B2		0.60	0.28	30	0.31	0.27	0.27	0.04	14.4	18
	w%	K1		0.60	14.7	2,5	14.8	14.7	14.7	0.1	0.6	20
C_d	w%	B1		-0.28	54.6	2,5	54.4	54.6	54.6	0.5	1.0	10
	w%	B2		-0.43	50.7	2,5	50.4	50.8	50.9	0.3	0.6	14
	w%	K1		0.01	69.0	2,5	69.0	69.0	69.0	0.5	0.8	20
H_d	w%	B1		0.13	5.79	7	5.82	5.79	5.79	0.14	2.4	8
	w%	B2		0.91	6.06	6	6.23	6.06	6.06	0.15	2.6	11
	w%	K1		0.97	4.65	6	4.79	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		7.00	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.26	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.42	3.42	3.45	0.33	9.5	23
N_d	w%	B1		-1.83	1.63	10	1.48	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		0.064	0.073	0.076	0.027	35.8	9
	w%	K1		-1.21	2.22	10	2.09	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		1.14	20867	1,5	21046	20867	20891	78	0.4	9
	J/g	B2		0.78	18875	1,6	18994	18873	18858	86	0.5	14
	J/g	K1		1.47	27520	1,2	27763	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		1.07	22114	1,4	22280	22105	22104	79	0.4	12
	J/g	B2		1.10	20158	1,4	20314	20153	20134	139	0.7	18
	J/g	K1		1.81	28520	1	28779	28518	28527	130	0.5	19
S_d	w%	B1		-1.11	0.15	15	0.14	0.16	0.15	0.01	6.9	9
	w%	K1		-0.35	0.44	15	0.43	0.44	0.44	0.03	6.1	22

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
M_{ad}	w%	B1			6.90		6.99	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		7.88	8.19	8.16	0.11	1.3	20
$q_{V,gr,d}$	J/g	B1		8.30	22114	1,4	23399	22105	22104	79	0.4	12
	J/g	B2		9.91	20158	1,4	21556	20153	20134	139	0.7	18

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		0.12	0.28	30	0.29	0.27	0.27	0.04	14.4	18
	w%	K1		-0.95	14.7	2,5	14.5	14.7	14.7	0.1	0.6	20
C_d	w%	B2		1.33	50.7	2,5	51.5	50.8	50.9	0.3	0.6	14
	w%	K1		0.06	69.0	2,5	69.1	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	K1		0.11	92.9	4	93.1	92.9	92.9	0.7	0.8	8
H_d	w%	B2		-0.45	6.06	6	5.98	6.06	6.06	0.15	2.6	11
	w%	K1		-0.22	4.65	6	4.62	4.62	4.64	0.10	2.1	18

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}	w%	B2			8.15		8.03	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.14	3.42	3.45	0.33	9.5	23
N_d	w%	B2			0.073		0.086	0.073	0.076	0.027	35.8	9
	w%	K1		0.71	2.22	10	2.30	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B2		-0.37	18875	1,6	18819	18873	18858	86	0.5	14
	J/g	K1		-0.37	27520	1,2	27459	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B2		-0.42	20158	1,4	20099	20153	20134	139	0.7	18
	J/g	K1		-0.48	28520	1	28452	28518	28527	130	0.5	19
S_d	w%	K1		0.27	0.44	15	0.45	0.44	0.44	0.03	6.1	22
V_d	w%	B2		0.33	85.1	3	85.5	85.1	85.1	1.1	1.3	10
	w%	K1		0.10	34.8	5	34.9	34.9	34.8	0.8	2.2	17

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%	B2		-1.67	0.28	30	0.21	0.27	0.27	0.04	14.4	18
C_d	w%	B2		0.10	50.7	2,5	50.8	50.8	50.9	0.3	0.6	14
H_d	w%	B2		-1.28	6.06	6	5.83	6.06	6.06	0.15	2.6	11
M_{ad}	w%	B2			8.15		8.25	8.19	8.16	0.11	1.3	20
$q_{p,net,d}$	J/g	B2		0.05	18875	1,6	18882	18873	18858	86	0.5	14
$q_{V,gr,d}$	J/g	B2		1.17	20158	1,4	20323	20153	20134	139	0.7	18
V_d	w%	B2		1.21	85.1	3	86.6	85.1	85.1	1.1	1.3	10

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		-0.71	0.28	30	0.25	0.27	0.27	0.04	14.4	18
	w%	K1		-2.99	14.7	2,5	14.2	14.7	14.7	0.1	0.6	20
C_d	w%	B2		-5.21	50.7	2,5	47.4	50.8	50.9	0.3	0.6	14
	w%	K1		1.23	69.0	2,5	70.1	69.0	69.0	0.5	0.8	20
H_d	w%	B2		-5.01	6.06	6	5.15	6.06	6.06	0.15	2.6	11
	w%	K1		0.72	4.65	6	4.75	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B2			8.15		8.28	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.72	3.42	3.45	0.33	9.5	23
N_d	w%	B2			0.073		0.110	0.073	0.076	0.027	35.8	9
	w%	K1		0.09	2.22	10	2.23	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B2		-95.25	18875	1,6	4493	18873	18858	86	0.5	14
	J/g	K1		-127.09	27520	1,2	6535	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B2		-109.22	20158	1,4	4746	20153	20134	139	0.7	18
	J/g	K1		-152.53	28520	1	6769	28518	28527	130	0.5	19
S_d	w%	K1		0.11	0.44	15	0.44	0.44	0.44	0.03	6.1	22
V_d	w%	B2		0.92	85.1	3	86.3	85.1	85.1	1.1	1.3	10
	w%	K1		1.10	34.8	5	35.8	34.9	34.8	0.8	2.2	17

Participant 15												
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		0.49	14.7	2,5	14.8	14.7	14.7	0.1	0.6	20
C_d	w%	K1		-0.22	69.0	2,5	68.8	69.0	69.0	0.5	0.8	20
M_{ad}	w%	K1			3.36		3.54	3.42	3.45	0.33	9.5	23
$q_{p,net,d}$	J/g	K1		-0.34	27520	1,2	27465	27465	27510	157	0.6	15

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$q_{V,gr,d}$	J/g	K1		-0.46	28520	1	28455	28518	28527	130	0.5	19
S_d	w%	K1		-0.17	0.44	15	0.43	0.44	0.44	0.03	6.1	22
V_d	w%	K1		-1.29	34.8	5	33.7	34.9	34.8	0.8	2.2	17

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
C_d	w%	K1		0.44	69.0	2,5	69.4	69.0	69.0	0.5	0.8	20
H_d	w%	K1		-0.50	4.65	6	4.58	4.62	4.64	0.10	2.1	18
M_{ad}	w%	K1			3.36		3.37	3.42	3.45	0.33	9.5	23
N_d	w%	K1		0.36	2.22	10	2.26	2.25	2.22	0.08	3.5	16
S_d	w%	K1		-0.76	0.44	15	0.42	0.44	0.44	0.03	6.1	22

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	K1		-0.11	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	K1		-0.24	69.0	2,5	68.8	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	K1		-0.32	92.9	4	92.3	92.9	92.9	0.7	0.8	8
H_d	w%	K1		-1.60	4.65	6	4.43	4.62	4.64	0.10	2.1	18
M_{ad}	w%	K1			3.36		3.30	3.42	3.45	0.33	9.5	23
$q_{p,net,d}$	J/g	K1		-0.58	27520	1,2	27425	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	K1		-0.61	28520	1	28434	28518	28527	130	0.5	19
S_d	w%	K1		-0.70	0.44	15	0.42	0.44	0.44	0.03	6.1	22
V_d	w%	K1		0.34	34.8	5	35.1	34.9	34.8	0.8	2.2	17

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
M_{ad}	w%	B1			6.90		7.05	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.28	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		2.74	3.42	3.45	0.33	9.5	23
$q_{p,net,d}$	J/g	B1		2.68	20867	1,5	21287	20867	20891	78	0.4	9
	J/g	B2		3.16	18875	1,6	19352	18873	18858	86	0.5	14
$q_{V,gr,d}$	J/g	B1		2.52	22114	1,4	22504	22105	22104	79	0.4	12
	J/g	B2		3.85	20158	1,4	20702	20153	20134	139	0.7	18
	J/g	K1		-0.32	28520	1	28474	28518	28527	130	0.5	19

Participant 19												
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		0.66	4.58	7	4.69	4.60	4.59	0.16	3.5	13
	w%	B2		-0.24	0.28	30	0.27	0.27	0.27	0.04	14.4	18
M_{ad}	w%	B1			6.90		7.48	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.60	8.19	8.16	0.11	1.3	20
$q_{p,net,d}$	J/g	B1		0.74	20867	1,5	20983	20867	20891	78	0.4	9
	J/g	B2		-0.32	18875	1,6	18826	18873	18858	86	0.5	14
$q_{V,gr,d}$	J/g	B1		0.18	22114	1,4	22142	22105	22104	79	0.4	12
	J/g	B2		0.09	20158	1,4	20170	20153	20134	139	0.7	18

Participant 20												
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		0.48	0.28	30	0.30	0.27	0.27	0.04	14.4	18
	w%	K1		-0.08	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	B2		0.19	50.7	2,5	50.8	50.8	50.9	0.3	0.6	14
	w%	K1		0.74	69.0	2,5	69.6	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	K1		0.57	92.9	4	94.0	92.9	92.9	0.7	0.8	8
H_d	w%	B2		0.00	6.06	6	6.06	6.06	6.06	0.15	2.6	11
	w%	K1		-0.39	4.65	6	4.60	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B2			8.15		8.09	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.22	3.42	3.45	0.33	9.5	23
N_d	w%	B2			0.073		0.073	0.073	0.076	0.027	35.8	9
	w%	K1		0.30	2.22	10	2.25	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B2		0.00	18875	1,6	18876	18873	18858	86	0.5	14
	J/g	K1		-0.58	27520	1,2	27424	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B2		0.27	20158	1,4	20197	20153	20134	139	0.7	18
	J/g	K1		-0.79	28520	1	28407	28518	28527	130	0.5	19
S_d	w%	K1		-0.09	0.44	15	0.44	0.44	0.44	0.03	6.1	22

Participant 21												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ash_d	w%	B1		-0.31	4.58	7	4.53	4.60	4.59	0.16	3.5	13
	w%	B2		0.60	0.28	30	0.31	0.27	0.27	0.04	14.4	18
	w%	K1		0.16	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	B1		0.78	54.6	2,5	55.1	54.6	54.6	0.5	1.0	10
	w%	B2		0.50	50.7	2,5	51.0	50.8	50.9	0.3	0.6	14
	w%	K1		0.72	69.0	2,5	69.6	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	B1			107		107	107	107	1	1.0	3
	t CO2/TJ	K1		-0.03	92.9	4	92.9	92.9	92.9	0.7	0.8	8
H_d	w%	B1		-0.15	5.79	7	5.76	5.79	5.79	0.14	2.4	8
	w%	B2		0.80	6.06	6	6.21	6.06	6.06	0.15	2.6	11
	w%	K1		-3.66	4.65	6	4.14	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		6.94	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.19	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.54	3.42	3.45	0.33	9.5	23
N_d	w%	B1		-0.45	1.63	10	1.59	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		0.060	0.073	0.076	0.027	35.8	9
	w%	K1		-1.51	2.22	10	2.05	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		0.00	20867	1,5	20867	20867	20891	78	0.4	9
	J/g	B2		0.36	18875	1,6	18930	18873	18858	86	0.5	14
	J/g	K1		1.32	27520	1,2	27739	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		0.01	22114	1,4	22115	22105	22104	79	0.4	12
	J/g	B2		0.87	20158	1,4	20281	20153	20134	139	0.7	18
	J/g	K1		0.74	28520	1	28626	28518	28527	130	0.5	19
S_d	w%	B1		0.76	0.15	15	0.16	0.16	0.15	0.01	6.9	9
	w%	K1		0.45	0.44	15	0.46	0.44	0.44	0.03	6.1	22

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		0.47	4.58	7	4.66	4.60	4.59	0.16	3.5	13
	w%	B2		0.83	0.28	30	0.32	0.27	0.27	0.04	14.4	18
	w%	K1		0.87	14.7	2,5	14.9	14.7	14.7	0.1	0.6	20
C_d	w%	B1		-0.96	54.6	2,5	53.9	54.6	54.6	0.5	1.0	10
	w%	B2		-0.50	50.7	2,5	50.4	50.8	50.9	0.3	0.6	14
	w%	K1		-0.51	69.0	2,5	68.6	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	B1			107		105	107	107	1	1.0	3
	t CO2/TJ	K1		-0.59	92.9	4	91.8	92.9	92.9	0.7	0.8	8
H_d	w%	B1		-0.77	5.79	7	5.63	5.79	5.79	0.14	2.4	8
	w%	B2		-1.33	6.06	6	5.82	6.06	6.06	0.15	2.6	11
	w%	K1		-0.45	4.65	6	4.59	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		6.78	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.11	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.53	3.42	3.45	0.33	9.5	23
N_d	w%	B1		-0.37	1.63	10	1.60	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		0.122	0.073	0.076	0.027	35.8	9
	w%	K1		0.85	2.22	10	2.31	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		-0.32	20867	1,5	20817	20867	20891	78	0.4	9
	J/g	B2		0.50	18875	1,6	18950	18873	18858	86	0.5	14
	J/g	K1		0.57	27520	1,2	27614	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		-0.47	22114	1,4	22041	22105	22104	79	0.4	12
	J/g	B2		0.61	20158	1,4	20244	20153	20134	139	0.7	18
	J/g	K1		0.54	28520	1	28597	28518	28527	130	0.5	19
S_d	w%	B1		0.62	0.15	15	0.16	0.16	0.15	0.01	6.9	9
	w%	K1		0.08	0.44	15	0.44	0.44	0.44	0.03	6.1	22
V_d	w%	B1		0.11	69.6	3	69.7	69.6	69.6	0.7	1.0	6
	w%	B2		-0.74	85.1	3	84.2	85.1	85.1	1.1	1.3	10
	w%	K1		-0.06	34.8	5	34.8	34.9	34.8	0.8	2.2	17

Participant 23												
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		-0.72	4.58	7	4.47	4.60	4.59	0.16	3.5	13
	w%	B2		-2.50	0.28	30	0.18	0.27	0.27	0.04	14.4	18
$q_{p,net,d}$	J/g	B1		-0.25	20867	1,5	20828	20867	20891	78	0.4	9
	J/g	B2		-1.49	18875	1,6	18651	18873	18858	86	0.5	14
$q_{V,gr,d}$	J/g	B1		-0.08	22114	1,4	22101	22105	22104	79	0.4	12
	J/g	B2		-0.63	20158	1,4	20070	20153	20134	139	0.7	18

Participant 24												
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		-1.68	4.58	7	4.31	4.60	4.59	0.16	3.5	13
	w%	B2		-0.83	0.28	30	0.25	0.27	0.27	0.04	14.4	18
	w%	K1		0.54	14.7	2,5	14.8	14.7	14.7	0.1	0.6	20
C_d	w%	B1		0.81	54.6	2,5	55.2	54.6	54.6	0.5	1.0	10
	w%	B2		0.58	50.7	2,5	51.1	50.8	50.9	0.3	0.6	14
	w%	K1		-0.23	69.0	2,5	68.8	69.0	69.0	0.5	0.8	20

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
H_d	w%	B1		4.98	5.79	7	6.80	5.79	5.79	0.14	2.4	8
	w%	B2		6.75	6.06	6	7.29	6.06	6.06	0.15	2.6	11
	w%	K1		5.09	4.65	6	5.36	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		6.85	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.10	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.45	3.42	3.45	0.33	9.5	23
N_d	w%	B1		-0.34	1.63	10	1.60	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		0.033	0.073	0.076	0.027	35.8	9
	w%	K1		-0.43	2.22	10	2.17	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		-1.68	20867	1,5	20604	20867	20891	78	0.4	9
	J/g	B2		-3.57	18875	1,6	18336	18873	18858	86	0.5	14
	J/g	K1		-0.41	27520	1,2	27452	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		-0.30	22114	1,4	22068	22105	22104	79	0.4	12
	J/g	B2		-1.75	20158	1,4	19912	20153	20134	139	0.7	18
	J/g	K1		0.57	28520	1	28602	28518	28527	130	0.5	19
S_d	w%	B1		0.76	0.15	15	0.16	0.16	0.15	0.01	6.9	9
	w%	K1		2.20	0.44	15	0.51	0.44	0.44	0.03	6.1	22
V_d	w%	B1		5.65	69.6	3	75.5	69.6	69.6	0.7	1.0	6
	w%	B2		3.30	85.1	3	89.3	85.1	85.1	1.1	1.3	10
	w%	K1		0.08	34.8	5	34.9	34.9	34.8	0.8	2.2	17

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
C_d	w%	B2		-2.21	50.7	2,5	49.3	50.8	50.9	0.3	0.6	14
M_{ad}	w%	B2			8.15		7.64	8.19	8.16	0.11	1.3	20
$q_{V,gr,d}$	J/g	B2		-0.68	20158	1,4	20062	20153	20134	139	0.7	18

Participant 26												
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	4.58	7	4.46	4.60	4.59	0.16	3.5	13
	w%	B2		-0.24	0.28	30	0.27	0.27	0.27	0.04	14.4	18
M_{ad}	w%	B1			6.90		6.04	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.14	8.19	8.16	0.11	1.3	20

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
C_d	w%	B1		-1.14	54.6	2,5	53.8	54.6	54.6	0.5	1.0	10
	w%	K1		-0.74	69.0	2,5	68.4	69.0	69.0	0.5	0.8	20
H_d	w%	B1		0.64	5.79	7	5.92	5.79	5.79	0.14	2.4	8
	w%	K1		1.08	4.65	6	4.80	4.62	4.64	0.10	2.1	18
N_d	w%	B1		0.55	1.63	10	1.68	1.63	1.63	0.08	4.6	10
	w%	K1		0.27	2.22	10	2.25	2.25	2.22	0.08	3.5	16
S_d	w%	B1		-3.91	0.15	15	0.11	0.16	0.15	0.01	6.9	9
	w%	K1		-2.89	0.44	15	0.34	0.44	0.44	0.03	6.1	22

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		0.50	4.58	7	4.66	4.60	4.59	0.16	3.5	13
	w%	B2		1.31	0.28	30	0.34	0.27	0.27	0.04	14.4	18
	w%	K1		-0.35	14.7	2,5	14.6	14.7	14.7	0.1	0.6	20
C_d	w%	B1		0.42	54.6	2,5	54.9	54.6	54.6	0.5	1.0	10
	w%	B2		0.10	50.7	2,5	50.8	50.8	50.9	0.3	0.6	14
	w%	K1		0.16	69.0	2,5	69.1	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	B1			107		107	107	107	1	1.0	3
	t CO2/TJ	K1		-0.22	92.9	4	92.5	92.9	92.9	0.7	0.8	8
H_d	w%	B1		-0.10	5.79	7	5.77	5.79	5.79	0.14	2.4	8
	w%	B2		0.26	6.06	6	6.11	6.06	6.06	0.15	2.6	11
	w%	K1		0.11	4.65	6	4.67	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		6.79	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.20	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.50	3.42	3.45	0.33	9.5	23
N_d	w%	B1		1.26	1.63	10	1.73	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		0.194	0.073	0.076	0.027	35.8	9
	w%	K1		0.52	2.22	10	2.28	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		0.13	20867	1,5	20888	20867	20891	78	0.4	9
	J/g	B2		-0.69	18875	1,6	18772	18873	18858	86	0.5	14
	J/g	K1		0.70	27520	1,2	27635	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		0.21	22114	1,4	22147	22105	22104	79	0.4	12
	J/g	B2		-0.41	20158	1,4	20101	20153	20134	139	0.7	18
	J/g	K1		0.85	28520	1	28642	28518	28527	130	0.5	19
S_d	w%	B1		0.84	0.15	15	0.16	0.16	0.15	0.01	6.9	9
	w%	K1		-0.50	0.44	15	0.42	0.44	0.44	0.03	6.1	22
V_d	w%	B1		-0.03	69.6	3	69.6	69.6	69.6	0.7	1.0	6
	w%	B2		0.15	85.1	3	85.3	85.1	85.1	1.1	1.3	10
	w%	K1		0.51	34.8	5	35.2	34.9	34.8	0.8	2.2	17

Participant 30												
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		-0.36	0.28	30	0.27	0.27	0.27	0.04	14.4	18
	w%	K1		-0.22	14.7	2,5	14.7	14.7	14.7	0.1	0.6	20
C_d	w%	B2		0.31	50.7	2,5	50.9	50.8	50.9	0.3	0.6	14
	w%	K1		0.64	69.0	2,5	69.6	69.0	69.0	0.5	0.8	20
EF	t CO2/TJ	K1		0.44	92.9	4	93.7	92.9	92.9	0.7	0.8	8
H_d	w%	B2		-0.12	6.06	6	6.04	6.06	6.06	0.15	2.6	11
	w%	K1		-0.16	4.65	6	4.63	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B2			8.15		8.10	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.19	3.42	3.45	0.33	9.5	23
N_d	w%	B2			0.073		0.077	0.073	0.076	0.027	35.8	9
	w%	K1		0.28	2.22	10	2.25	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B2		-0.01	18875	1,6	18873	18873	18858	86	0.5	14
	J/g	K1		-0.38	27520	1,2	27457	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B2		0.22	20158	1,4	20189	20153	20134	139	0.7	18
	J/g	K1		-0.51	28520	1	28447	28518	28527	130	0.5	19
S_d	w%	K1		0.18	0.44	15	0.45	0.44	0.44	0.03	6.1	22

Participant 30												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
V_d	w%	B2		-0.18	85.1	3	84.9	85.1	85.1	1.1	1.3	10
	w%	K1		0.08	34.8	5	34.9	34.9	34.8	0.8	2.2	17

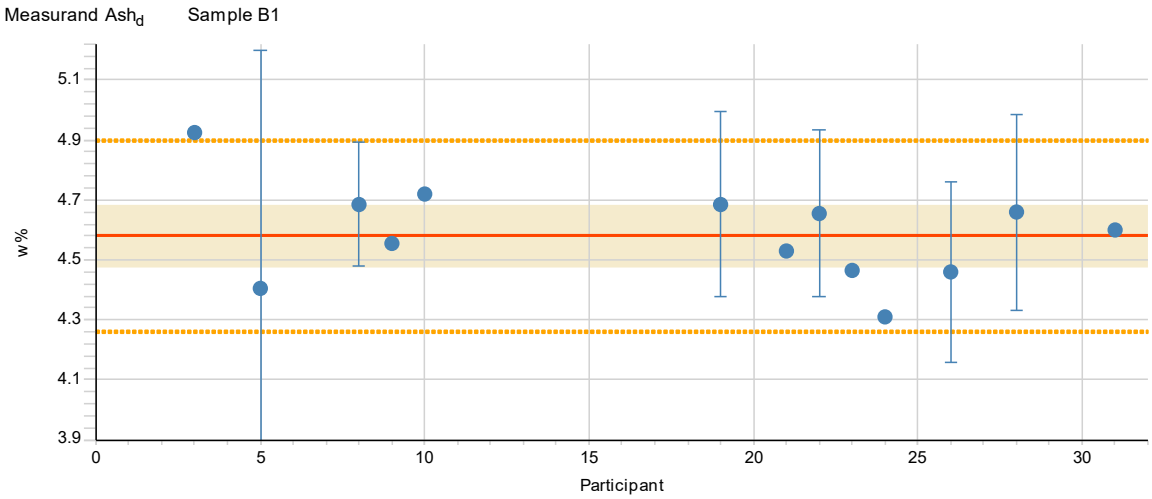
Participant 31												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		0.12	4.58	7	4.60	4.60	4.59	0.16	3.5	13
	w%	B2		-0.12	0.28	30	0.28	0.27	0.27	0.04	14.4	18
	w%	K1		-0.54	14.7	2,5	14.6	14.7	14.7	0.1	0.6	20
C_d	w%	B1		0.29	54.6	2,5	54.8	54.6	54.6	0.5	1.0	10
	w%	B2		0.24	50.7	2,5	50.9	50.8	50.9	0.3	0.6	14
	w%	K1		0.29	69.0	2,5	69.3	69.0	69.0	0.5	0.8	20
H_d	w%	B1		0.86	5.79	7	5.97	5.79	5.79	0.14	2.4	8
	w%	B2		1.21	6.06	6	6.28	6.06	6.06	0.15	2.6	11
	w%	K1		-0.07	4.65	6	4.64	4.62	4.64	0.10	2.1	18
M_{ad}	w%	B1			6.90		45.90	6.92	6.90	0.26	3.8	14
	w%	B2			8.15		8.19	8.19	8.16	0.11	1.3	20
	w%	K1			3.36		3.59	3.42	3.45	0.33	9.5	23
N_d	w%	B1		-0.98	1.63	10	1.55	1.63	1.63	0.08	4.6	10
	w%	B2			0.073		*<0.1*	0.073	0.076	0.027	35.8	9
	w%	K1		-0.81	2.22	10	2.13	2.25	2.22	0.08	3.5	16
$q_{p,net,d}$	J/g	B1		-0.19	20867	1,5	20838	20867	20891	78	0.4	9
	J/g	B2		-0.25	18875	1,6	18837	18873	18858	86	0.5	14
	J/g	K1		0.58	27520	1,2	27617	27465	27510	157	0.6	15
$q_{V,gr,d}$	J/g	B1		-0.31	22114	1,4	22067	22105	22104	79	0.4	12
	J/g	B2		-0.21	20158	1,4	20128	20153	20134	139	0.7	18
	J/g	K1		0.37	28520	1	28573	28518	28527	130	0.5	19
S_d	w%	B1		-0.36	0.15	15	0.15	0.16	0.15	0.01	6.9	9
	w%	K1		0.91	0.44	15	0.47	0.44	0.44	0.03	6.1	22
V_d	w%	B1		-0.57	69.6	3	69.0	69.6	69.6	0.7	1.0	6
	w%	B2		-0.63	85.1	3	84.3	85.1	85.1	1.1	1.3	10
	w%	K1		-1.15	34.8	5	33.8	34.9	34.8	0.8	2.2	17

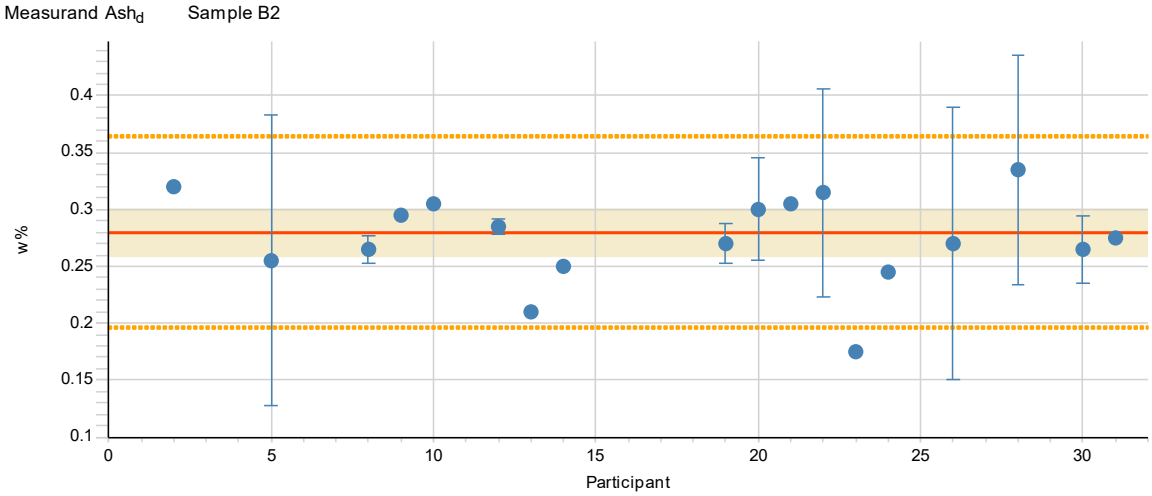
Participant 32												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
M_{ad}	w%	B1			6.90		6.39	6.92	6.90	0.26	3.8	14
	w%	K1			3.36		3.20	3.42	3.45	0.33	9.5	23
$q_{V,gr,d}$	J/g	B1		-12.67	22114	1,4	20153	22105	22104	79	0.4	12
	J/g	K1		-6.74	28520	1	27560	28518	28527	130	0.5	19

APPENDIX 8: Results of participants and their uncertainties

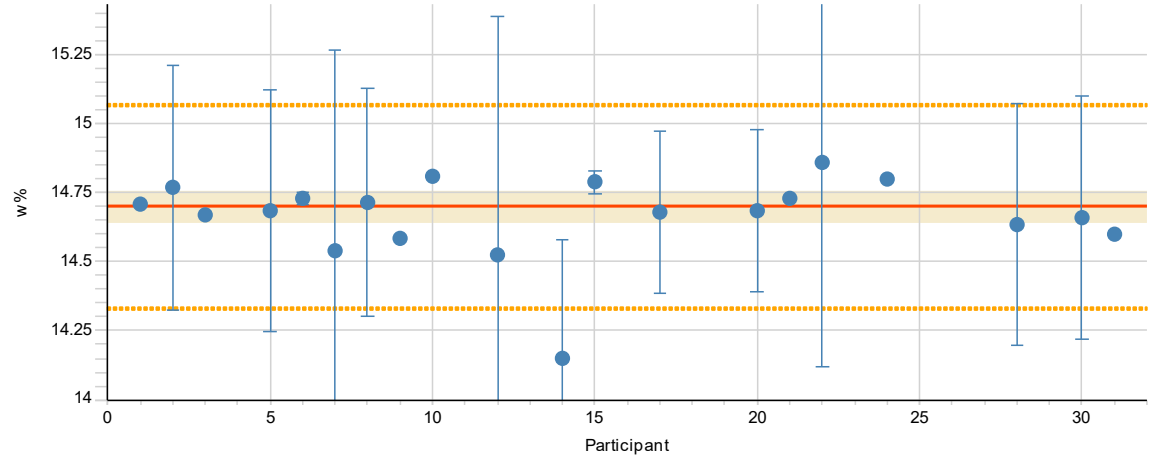
In figures:

- 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.

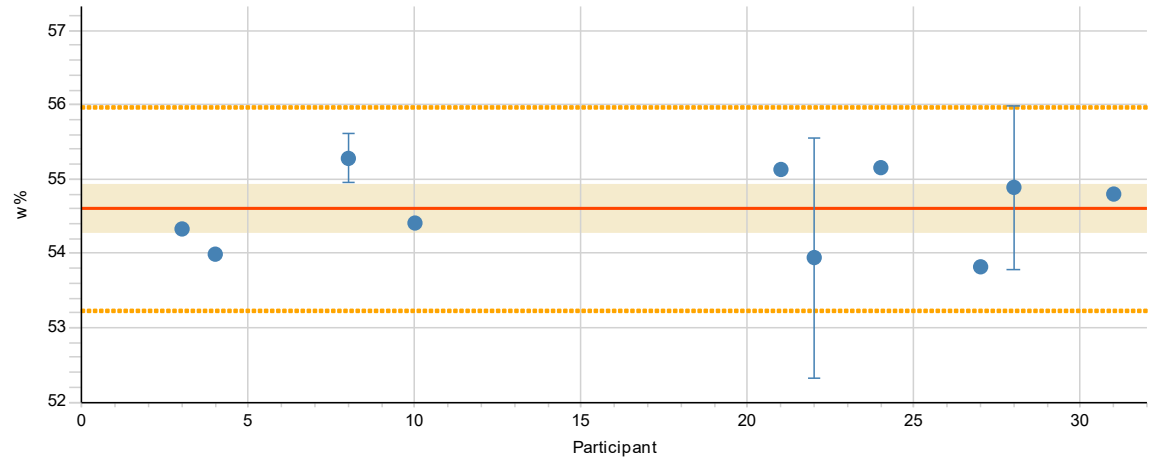




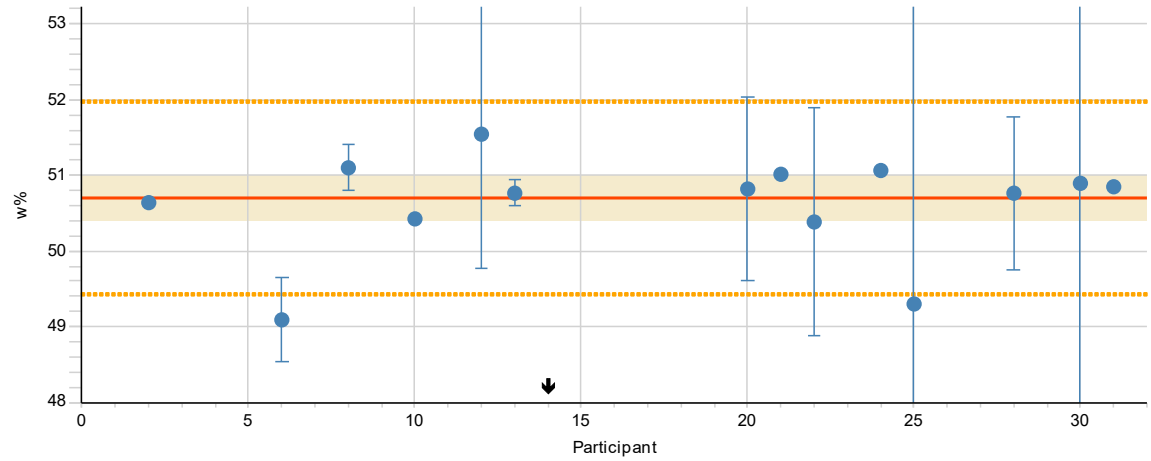
Measurand Ash_d Sample K1



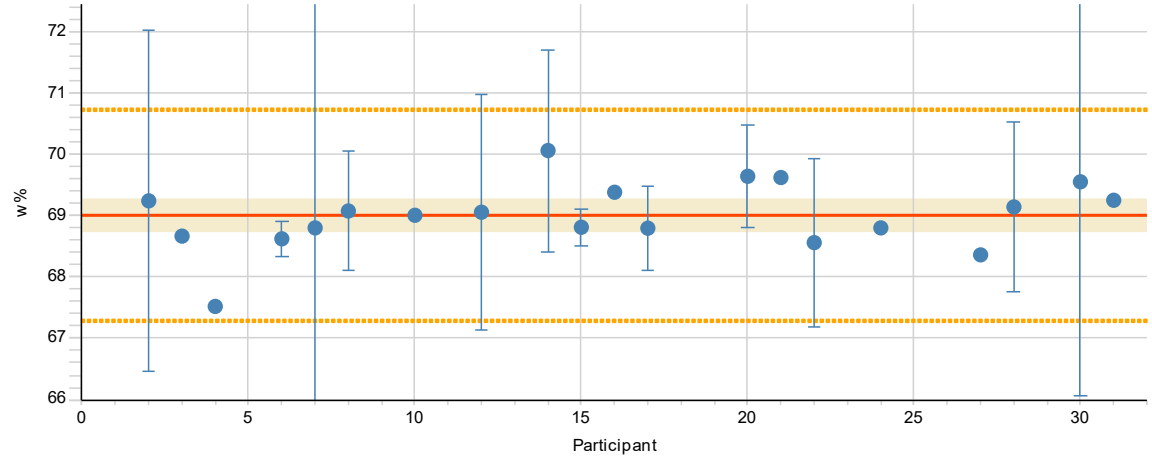
Measurand C_d Sample B1



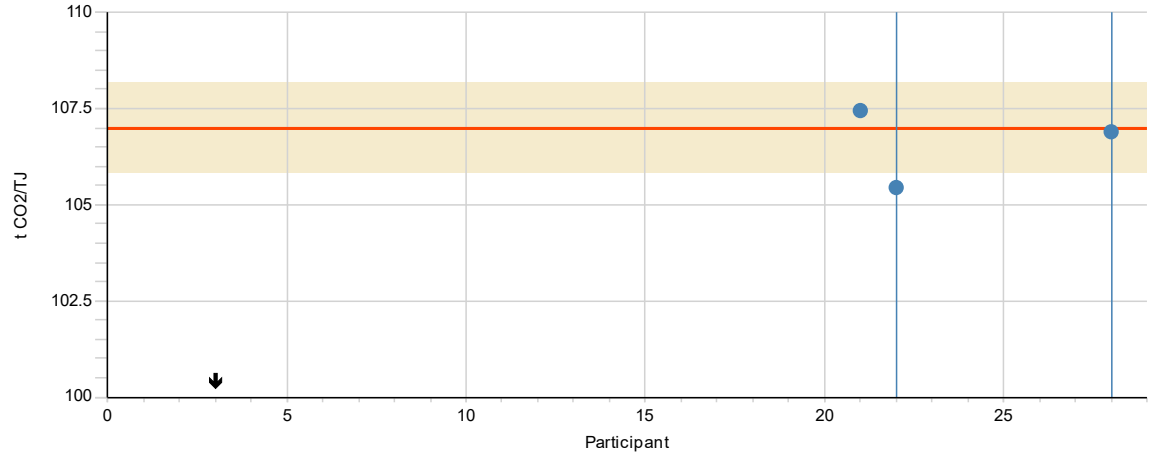
Measurand C_d Sample B2



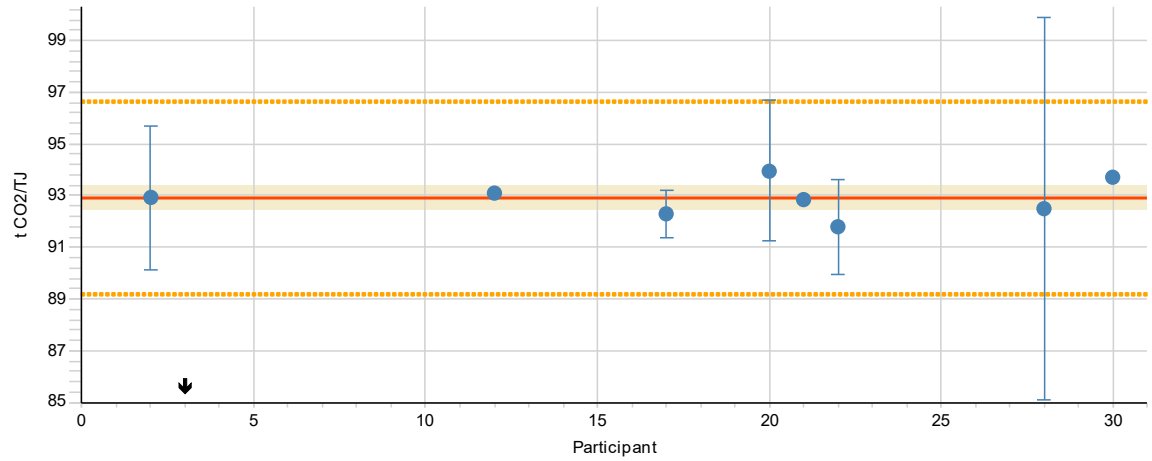
Measurand C_d Sample K1

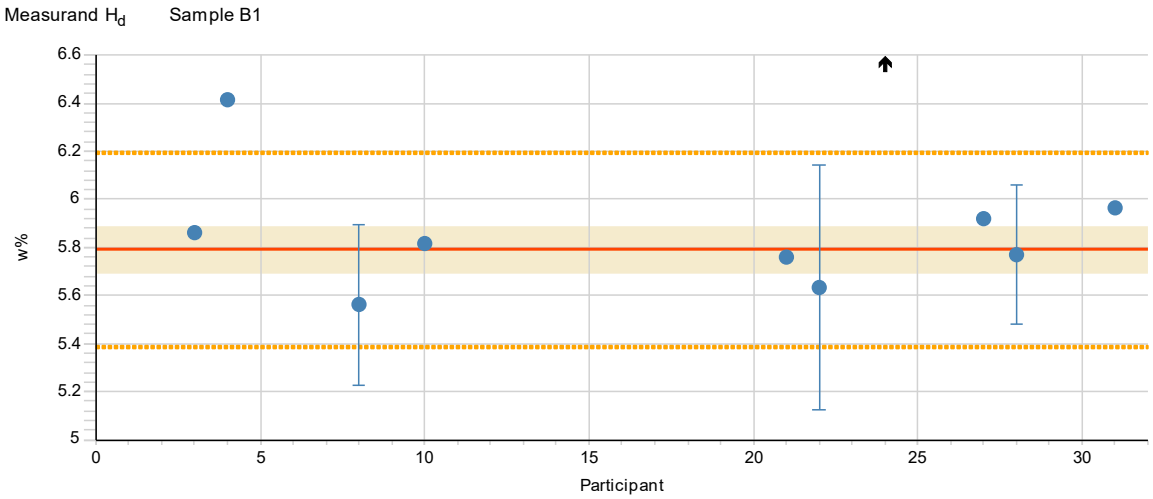


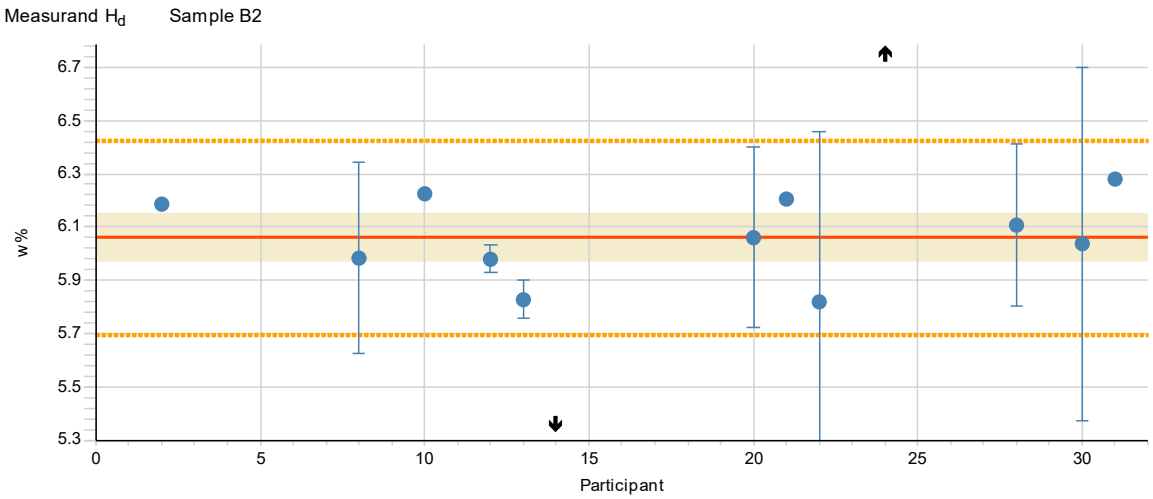
Measurand EF Sample B1

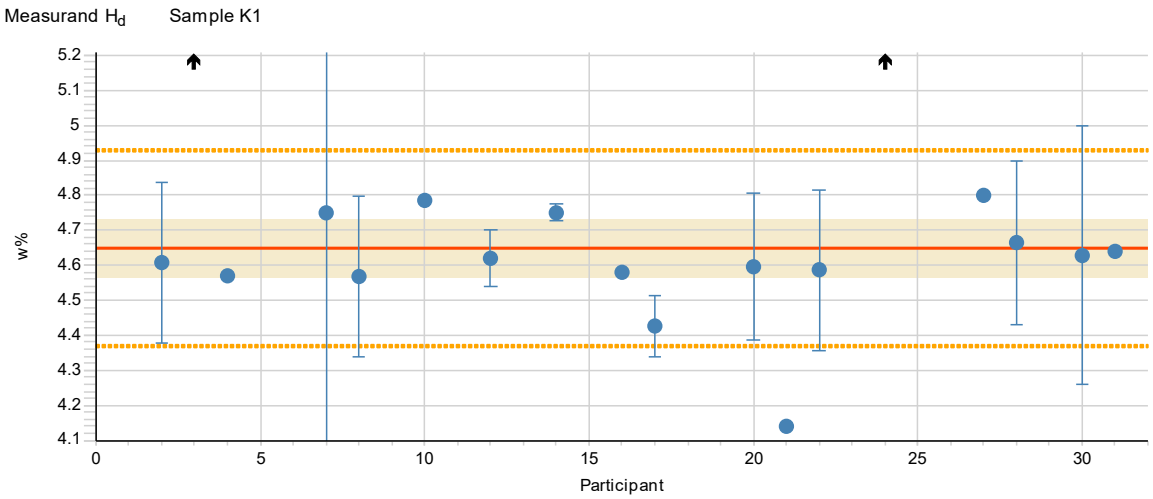


Measurand EF Sample K1

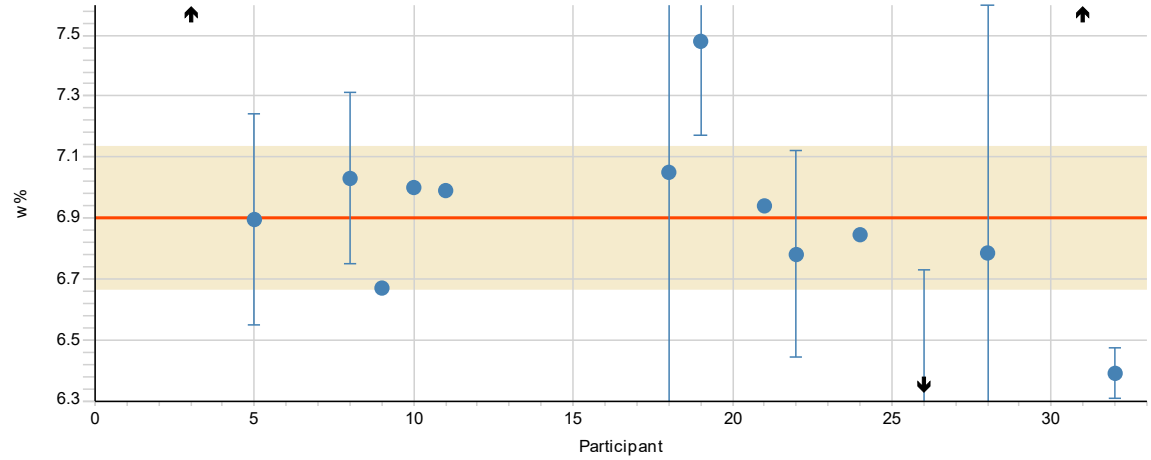



Measurand H_d Sample B1
w%
6.6
6.4
6.2
6
5.8
5.6
5.4
5.2
5
0
5
10
15
20
25
30
Participant

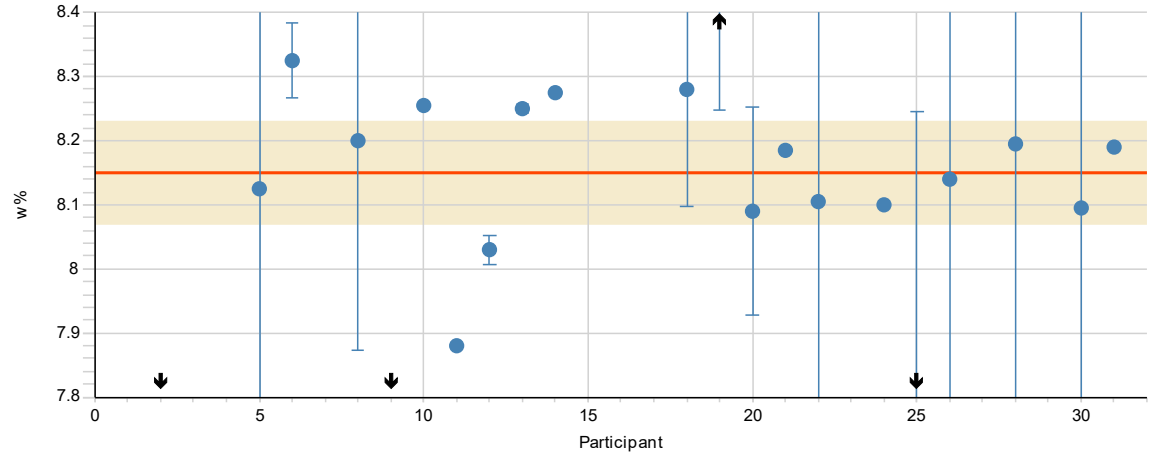

Measurand H_d Sample B2
w%
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
0
5
10
15
20
25
30
Participant


Measurand H_d Sample K1
w%
5.2
5.1
5
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
0
5
10
15
20
25
30
Participant

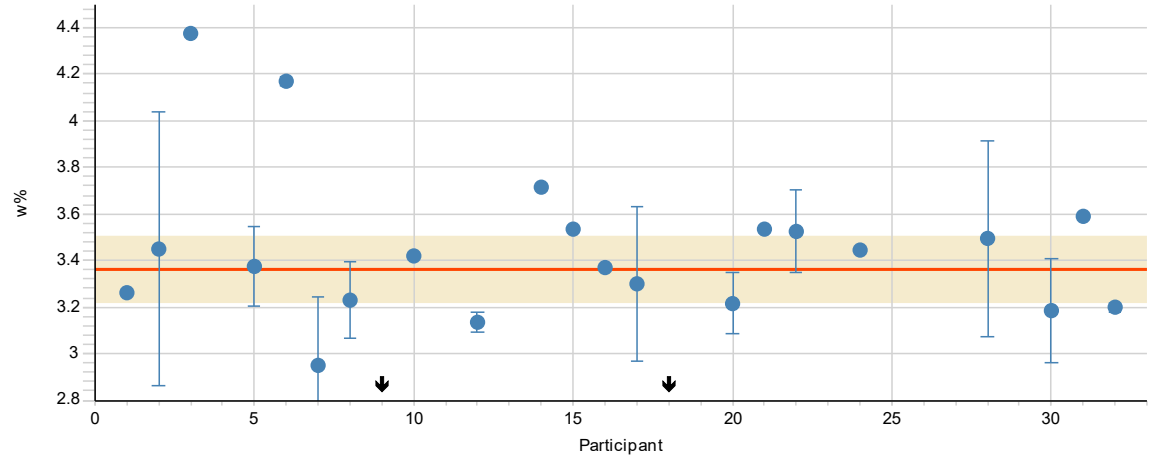
Measurand M_{ad} Sample B1



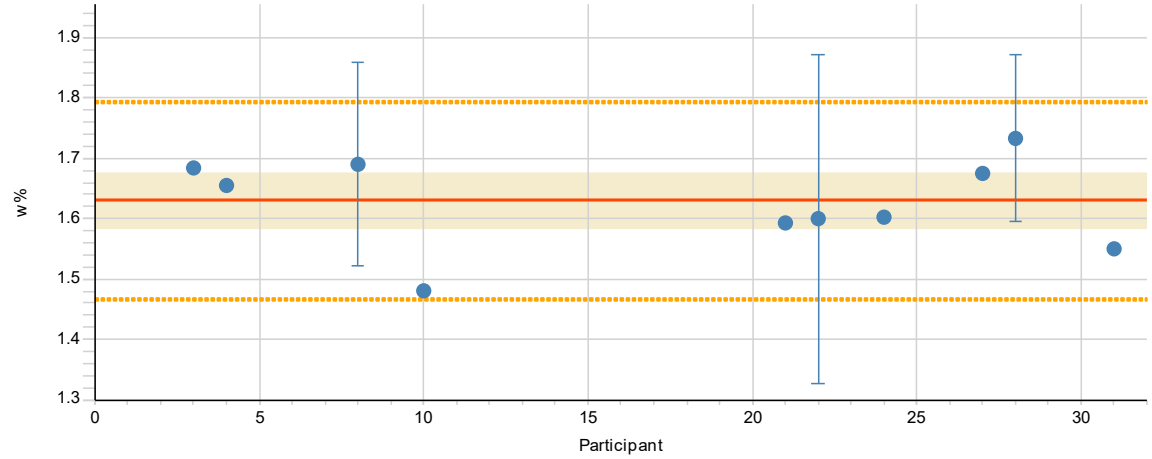
Measurand M_{ad} Sample B2



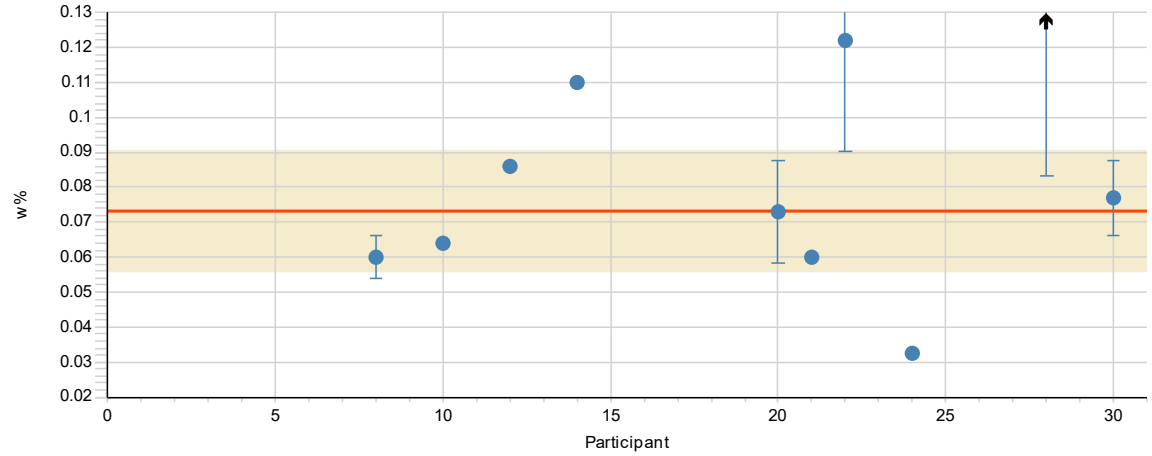
Measurand M_{ad} Sample K1



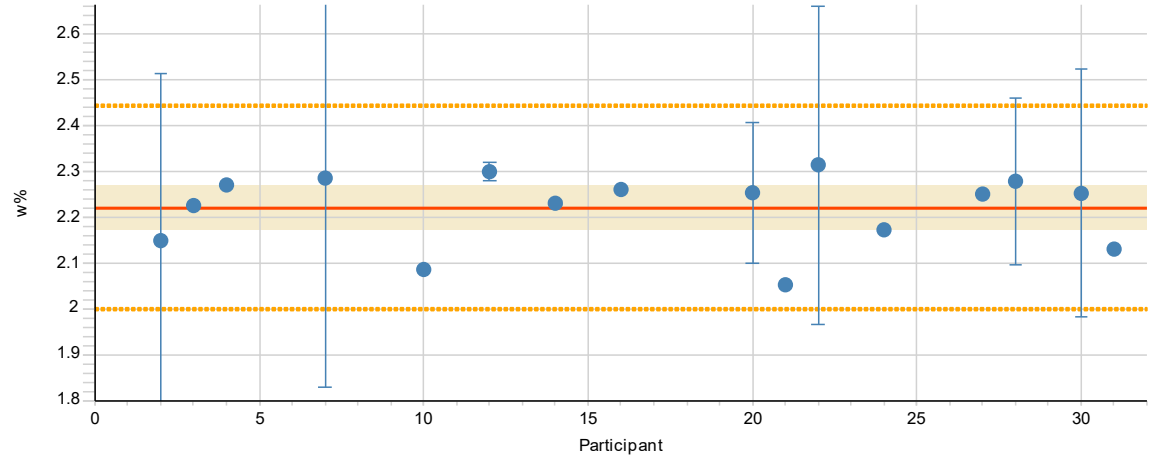
Measurand N_d Sample B1

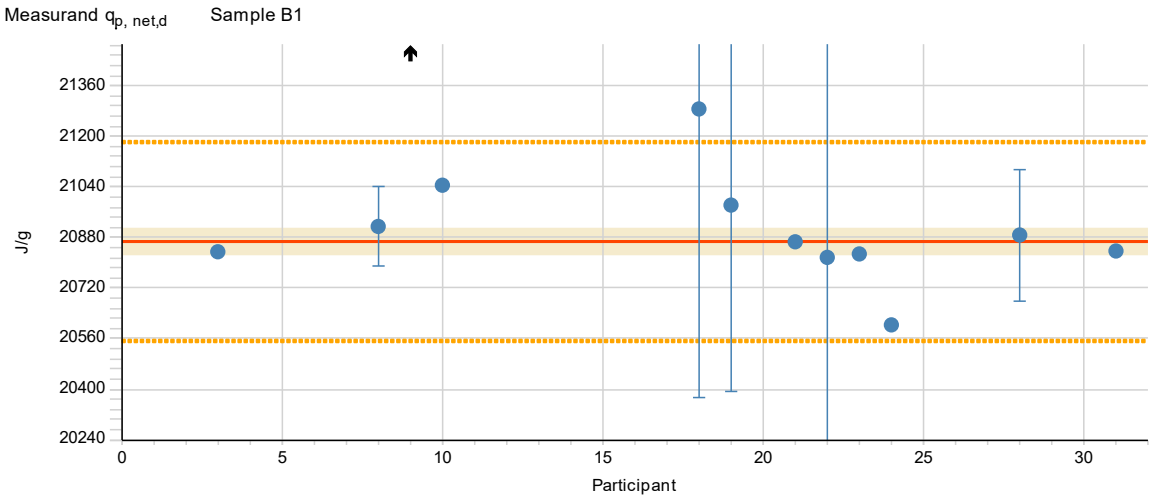


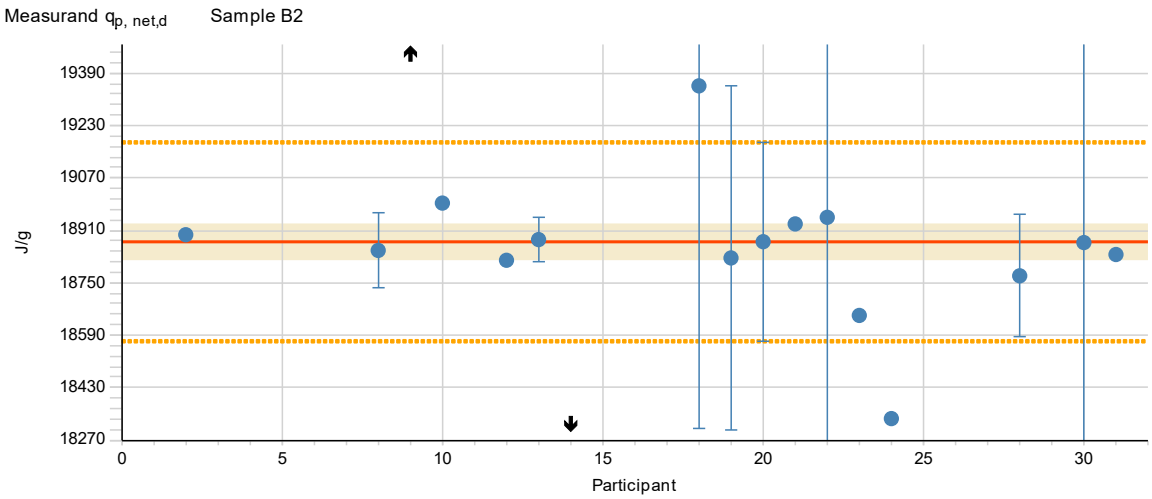
Measurand N_d Sample B2

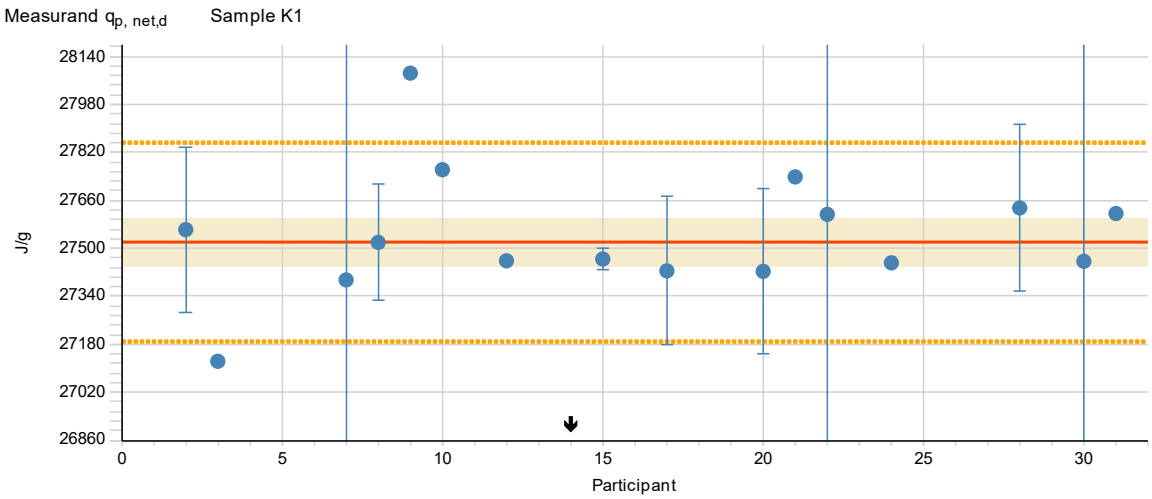


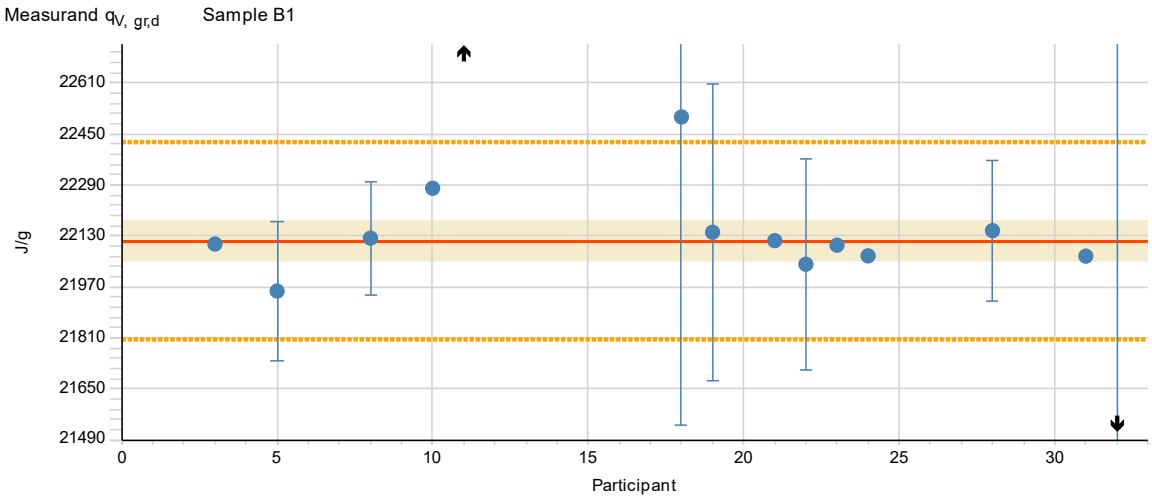
Measurand N_d Sample K1

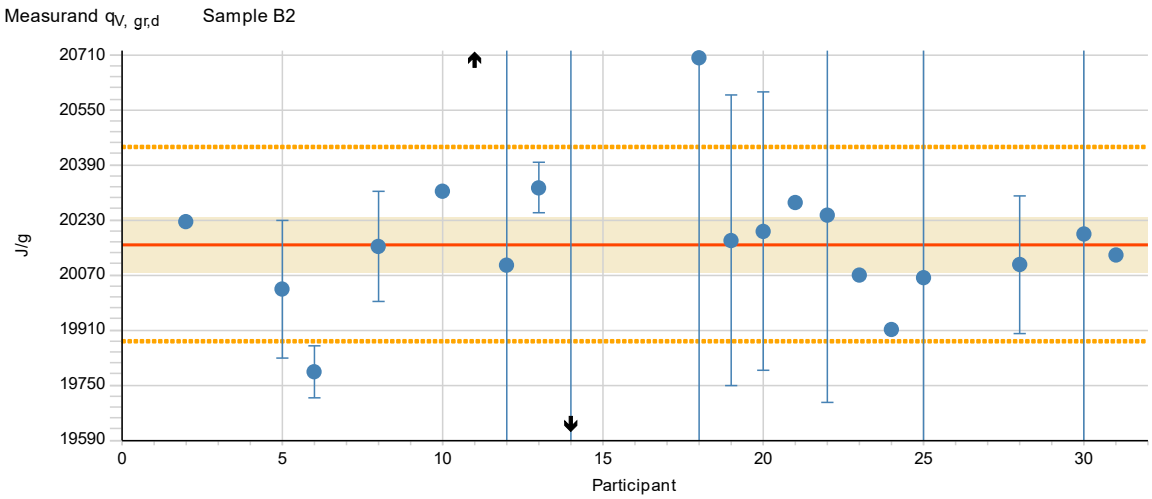


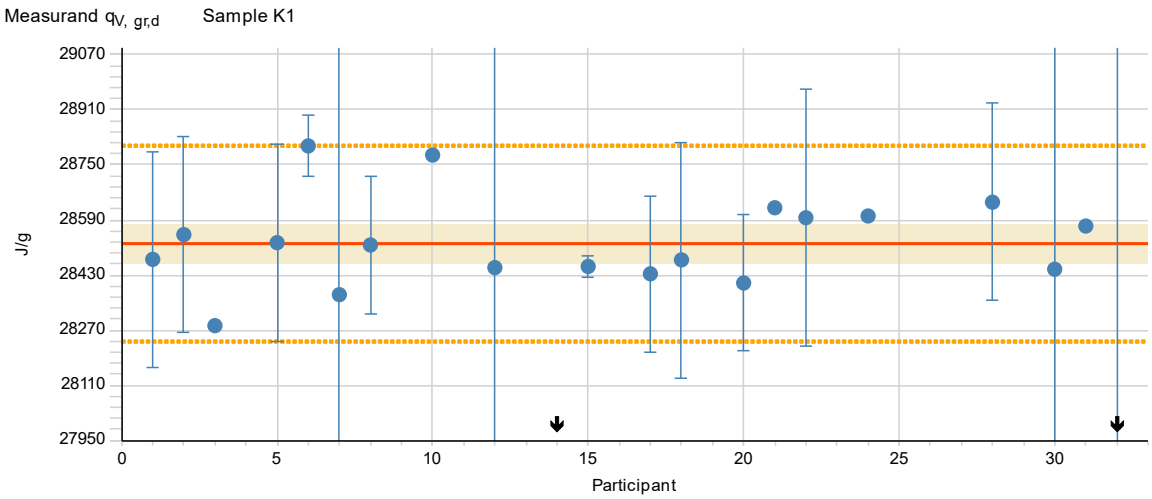

Measurand $q_{p, net,d}$
Sample B1
J/g
21360
21200
21040
20880
20720
20560
20400
20240
0
5
10
15
20
25
30
Participant


Measurand $q_{p, net,d}$
Sample B2
J/g
19390
19230
19070
18910
18750
18590
18430
18270
0
5
10
15
20
25
30
Participant

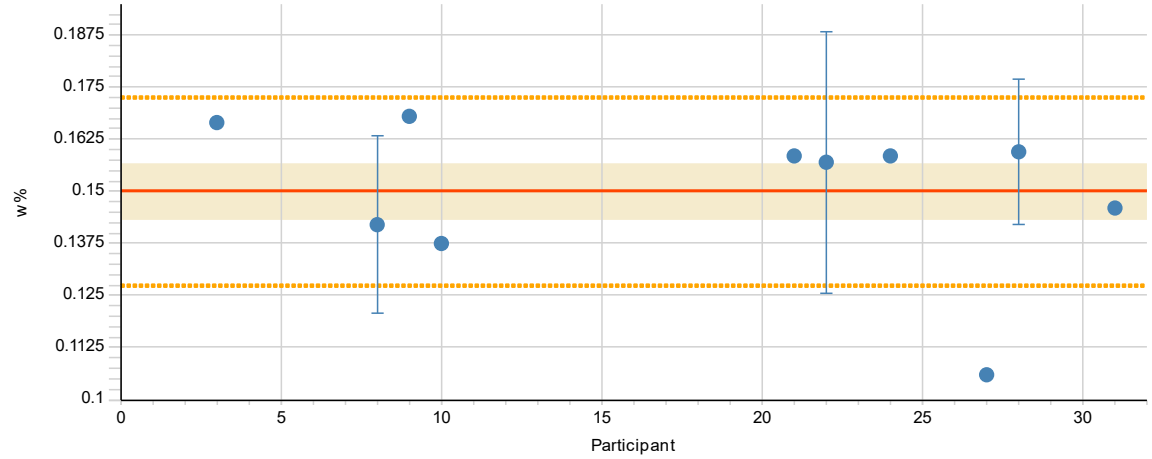

Measurand $q_{p, net,d}$
Sample K1
J/g
28140
27980
27820
27660
27500
27340
27180
27020
26860
0
5
10
15
20
25
30
Participant


Measurand $q_{V,\ gr,d}$
Sample B1
22610
22450
22290
22130
21970
21810
21650
21490
J/g
0
5
10
15
20
25
30
Participant

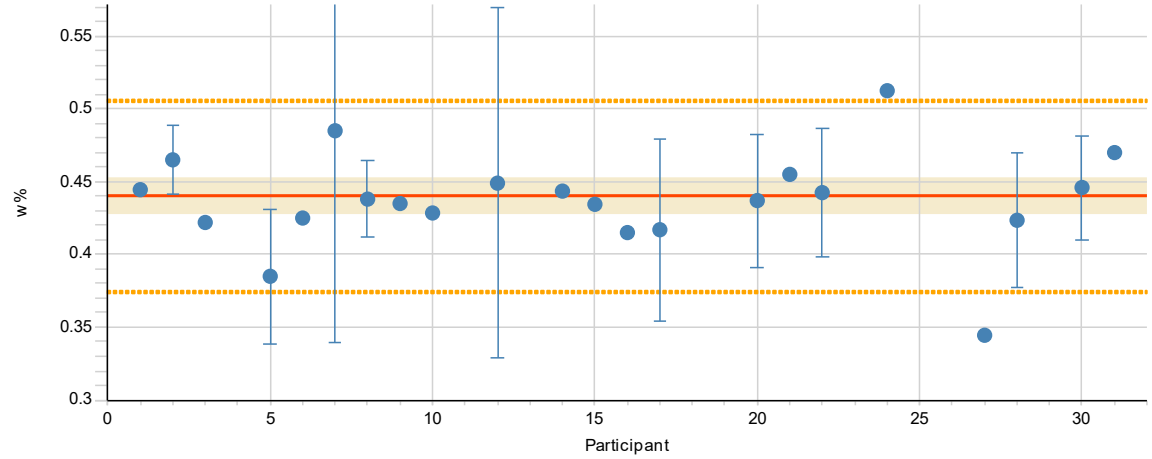

Measurand $q_{V,\ gr,d}$
Sample B2
20710
20550
20390
20230
20070
19910
19750
19590
J/g
0
5
10
15
20
25
30
Participant


Measurand $q_{V,\ gr,d}$
Sample K1
29070
28910
28750
28590
28430
28270
28110
27950
J/g
0
5
10
15
20
25
30
Participant

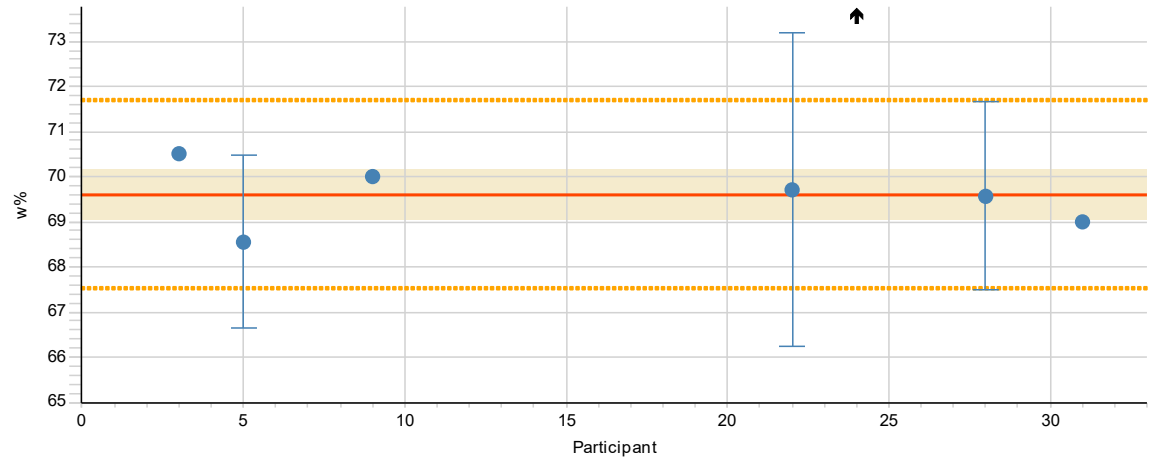
Measurand S_d Sample B1



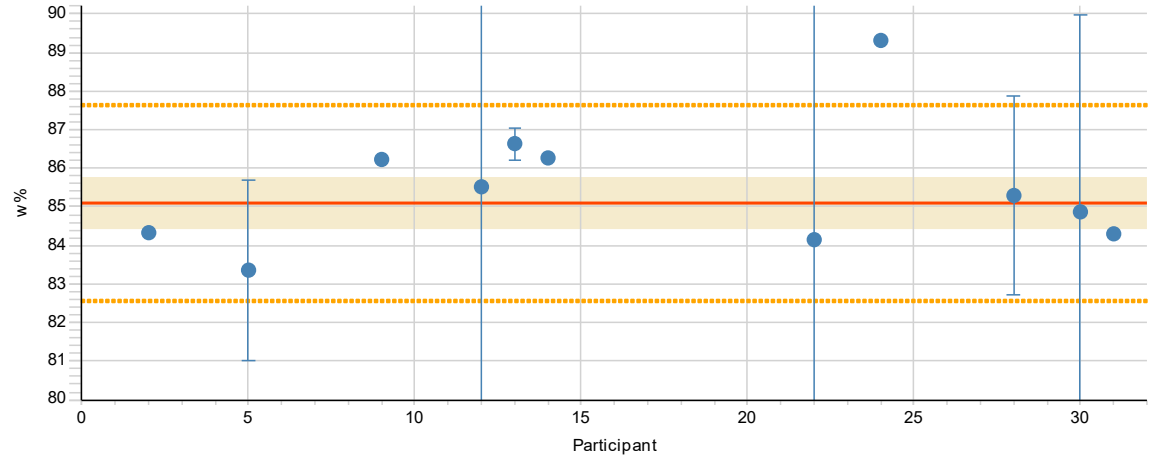
Measurand S_d Sample K1



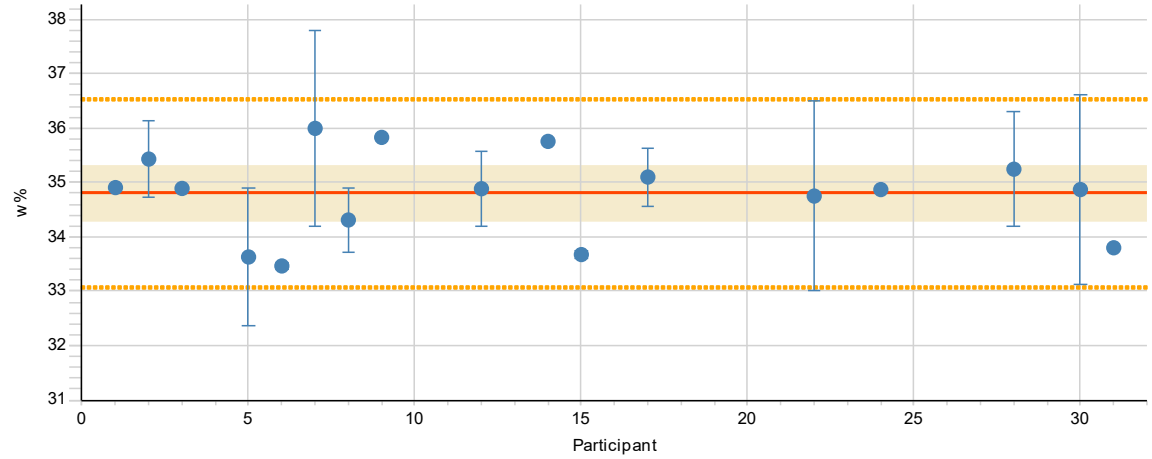
Measurand V_d Sample B1



Measurand V_d Sample B2



Measurand V_d Sample K1



APPENDIX 9: Summary of the z scores

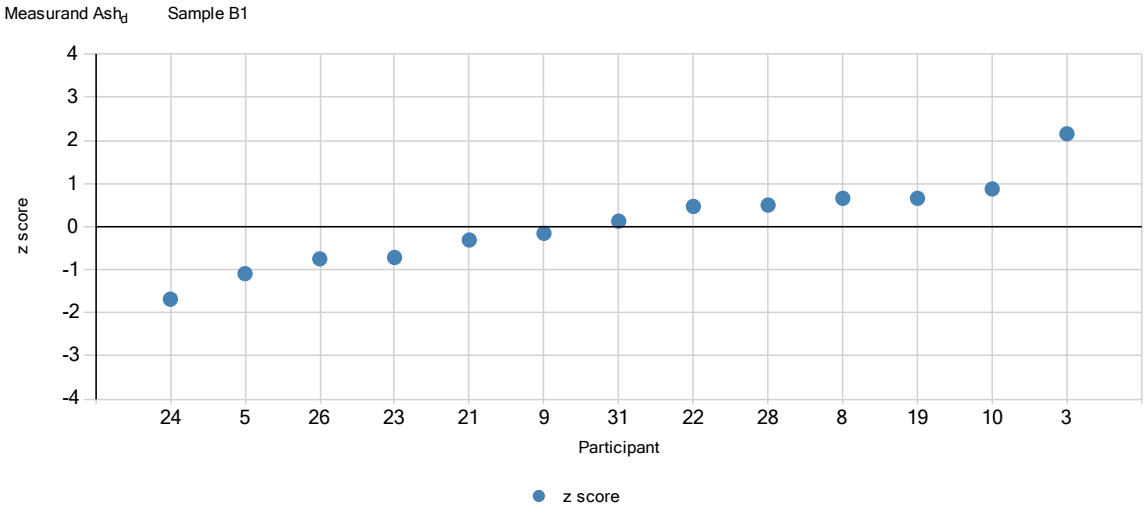
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Ash_d	B1	.	.	Q	.	**S**	.	.	**S**	*S*	**S**	.	.	.	.	.	.	.	.	**S**	.	**S**	**S**	*S*	92.3
	B2	.	*S*	.	.	**S**	.	.	**S**	*S*	**S**	.	**S**	**S**	*S*	.	.	.	.	**S**	**S**	**S**	**S**	*q*	94.4
	K1	*S*	**S**	**S**	.	**S**	**S**	**S**	*S*	*S*	**S**	.	**S**	.	**q**	*S*	.	**S**	.	.	**S**	**S**	**S**	.	95.0
C_d	B1	.	.	*S*	*S*	.	.	.	**S**	.	**S**	.	.	.	.	.	.	.	.	.	.	**S**	**S**	.	100
	B2	.	*S*	.	.	.	**q**	.	**S**	.	**S**	.	**S**	**S**	*u*	.	.	.	.	.	**S**	**S**	**S**	.	80.0
	K1	.	**S**	**S**	*S*	.	**S**	**S**	S	.	**S**	.	**S**	.	**S**	*S*	**S**	**S**	.	.	**S**	**S**	**S**	.	100
EF	K1	.	**S**	**u**	.	.	.	.	.	.	.	.	*S*	.	.	.	.	*S*	.	.	*S*	*S*	**S**	.	88.9
H_d	B1	.	.	*S*	*U*	.	.	.	**S**	.	**S**	.	.	.	.	.	.	.	.	.	.	**S**	**S**	.	80.0
	B2	.	*S*	.	.	.	.	.	**S**	.	**S**	.	**S**	*S*	*u*	.	.	.	.	.	**S**	**S**	**S**	.	84.6
	K1	.	**S**	**U**	*S*	.	.	**S**	S	.	**S**	.	**S**	.	S	.	*S*	*S*	.	.	**S**	**u**	**S**	.	83.3
N_d	B1	.	.	*S*	*S*	.	.	.	**S**	.	**S**	.	.	.	.	.	.	.	.	.	.	**S**	**S**	.	100
	K1	.	**S**	**S**	*S*	.	.	**S**	.	.	**S**	.	**S**	.	**S**	.	*S*	.	.	.	**S**	**S**	**S**	.	100
$q_{p,net,d}$	B1	.	.	*S*	.	.	.	.	**S**	*U*	**S**	.	.	.	.	.	.	.	**Q**	**S**	.	**S**	**S**	*S*	83.3
	B2	.	*S*	.	.	.	.	.	S	*U*	**S**	.	**S**	**S**	**u**	.	.	.	**U**	**S**	**S**	**S**	**S**	*S*	76.5
	K1	.	**S**	**q**	.	.	.	**S**	S	*U*	**S**	.	**S**	.	**u**	*S*	.	**S**	.	.	**S**	**S**	**S**	.	82.4
$q_{V,gr,d}$	B1	.	.	*S*	.	**S**	.	.	**S**	.	**S**	*U*	.	.	.	.	.	.	**Q**	**S**	.	**S**	**S**	*S*	78.6
	B2	.	*S*	.	.	**S**	**q**	.	**S**	.	**S**	*U*	**S**	**S**	u	.	.	.	**U**	**S**	**S**	**S**	**S**	*S*	80.0
	K1	**S**	**S**	**S**	.	**S**	**S**	**S**	**S**	.	**S**	.	**S**	.	**u**	*S*	.	**S**	*S*	.	**S**	**S**	**S**	.	90.5
S_d	B1	.	.	*S*	.	.	.	.	**S**	*S*	*S*	.	.	.	.	.	.	.	.	.	.	**S**	**S**	.	90.0
	K1	*S*	**S**	**S**	.	**S**	**S**	**S**	**S**	*S*	*S*	.	**S**	.	**S**	*S*	*S*	**S**	.	.	**S**	**S**	**S**	.	90.9
V_d	B1	.	.	*S*	.	**S**	.	.	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	**S**	.	85.7
	B2	.	*S*	.	.	**S**	.	.	.	*S*	.	.	**S**	**S**	*S*	.	.	.	.	.	.	.	**S**	.	90.9
	K1	*S*	**S**	**S**	.	**S**	**S**	*S*	*S*	*S*	.	.	**S**	.	*S*	*S*	.	**S**	.	.	.	.	**S**	.	100
%		100	100	76	83	100	71	100	100	73	100	0	100	100	50	100	100	100	20	100	100	95	100	83	
accredited		1	9	9		10	7	7	13		17		14	5	7		1	6	4	6	12	19	23		

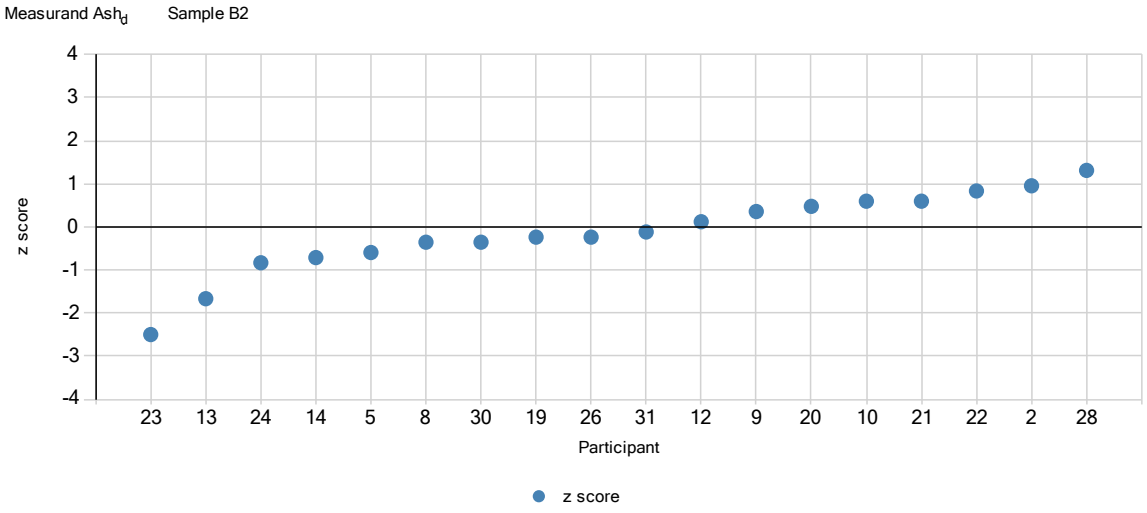
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
Ash_d	B1	*S*	.	**S**	.	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	92.3
	B2	*S*	.	**S**	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	94.4
	K1	*S*	.	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	95.0
C_d	B1	*S*	.	.	*S*	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	*S*	*q*	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	80.0
	K1	*S*	.	.	*S*	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	**S**	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	88.9
H_d	B1	*U*	.	.	*S*	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	80.0
	B2	*U*	.	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	84.6
	K1	*U*	.	.	*S*	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	83.3
M_{ad}	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
N_d	B1	*S*	.	.	*S*	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	*S*	.	.	*S*	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
$q_{p,net,d}$	B1	*S*	.	.	.	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	83.3
	B2	*u*	.	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	76.5
	K1	*S*	.	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	82.4
$q_{V,gr,d}$	B1	*S*	.	.	.	**S**	.	.	**S**	u	.	.	.	.	.	.	.	.	.	.	.	.	.	.	78.6
	B2	*S*	*S*	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	80.0
	K1	*S*	.	.	.	**S**	.	**S**	**S**	u	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.5
S_d	B1	*S*	.	.	*u*	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.0
	K1	*Q*	.	.	*q*	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.9
V_d	B1	*U*	.	.	.	**S**	.	.	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	85.7
	B2	*U*	.	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.9
	K1	*S*	.	.	.	**S**	.	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
%		68	50	100	75	100		100	100	0															
accredited				2		23		14	22																

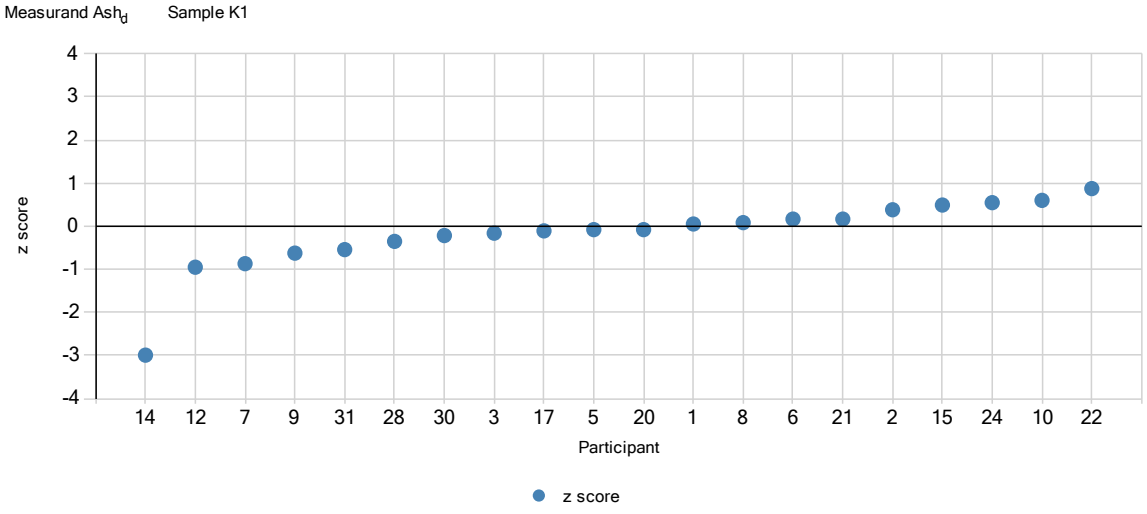
S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 89 % in accredited: 94 % in non-accredited: 80

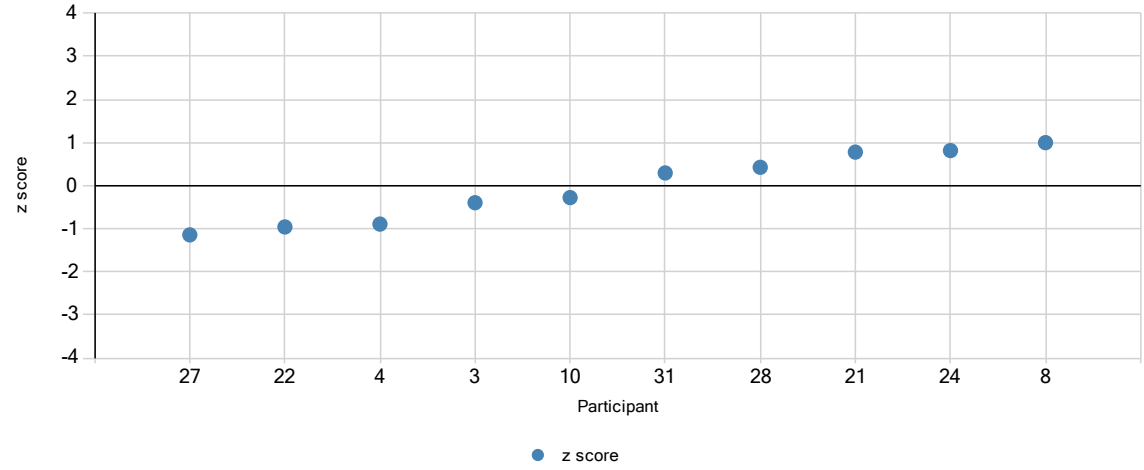
APPENDIX 10: z scores in ascending order



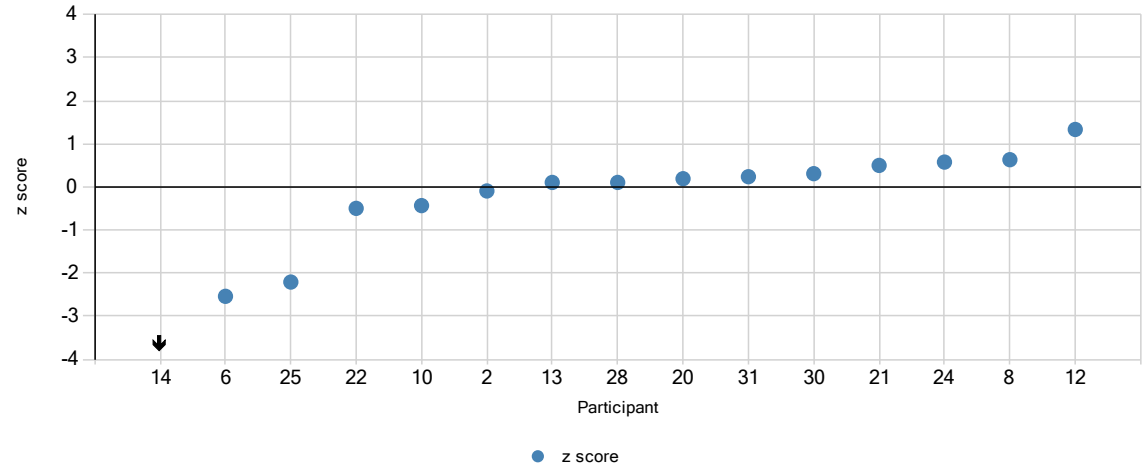




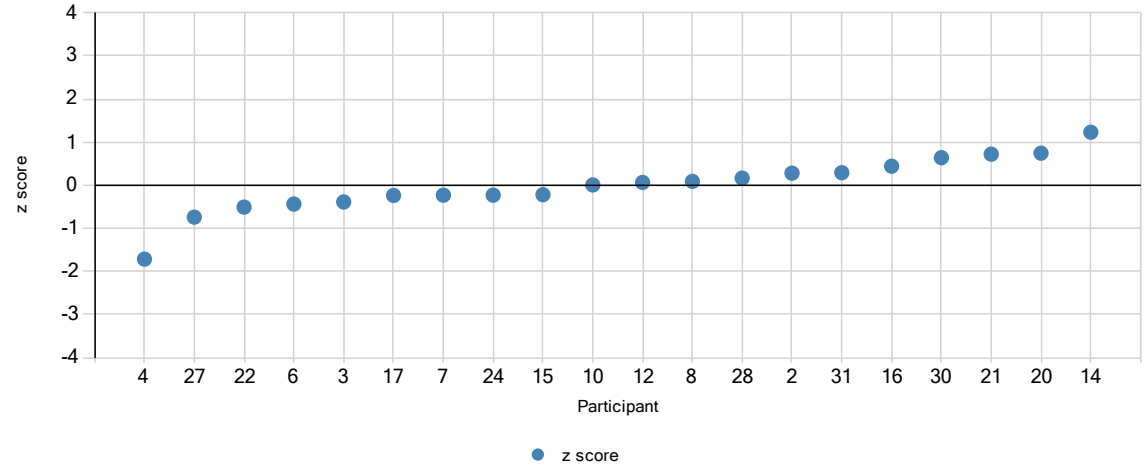
Measurand C_d Sample B1



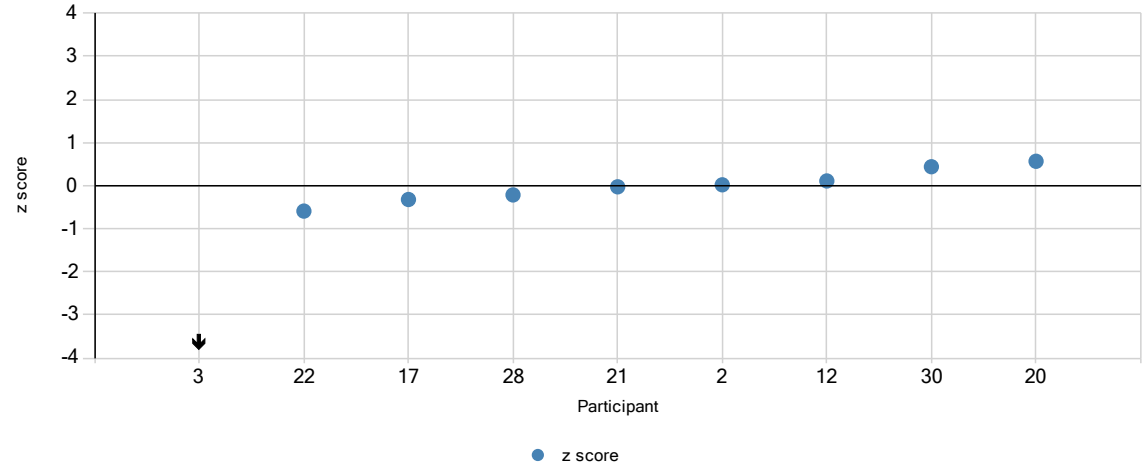
Measurand C_d Sample B2



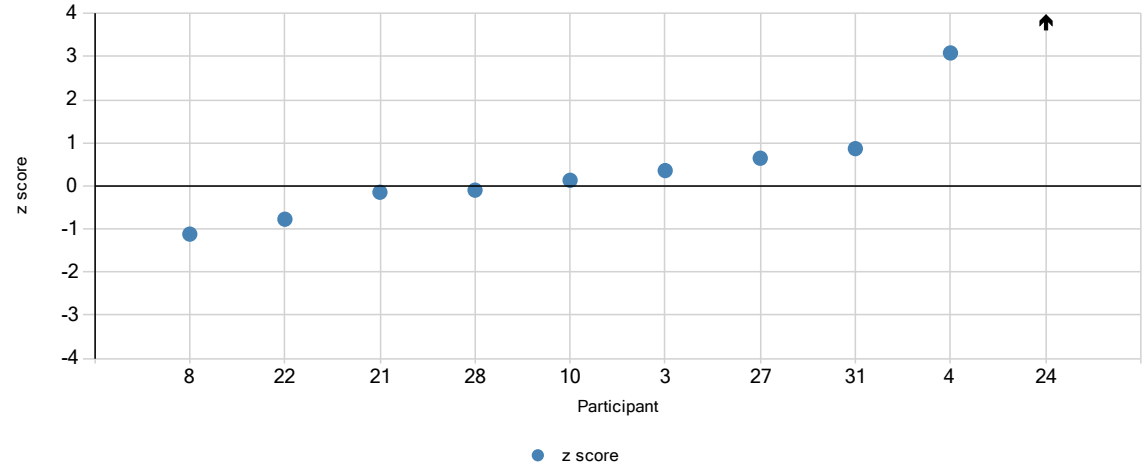
Measurand C_d Sample K1



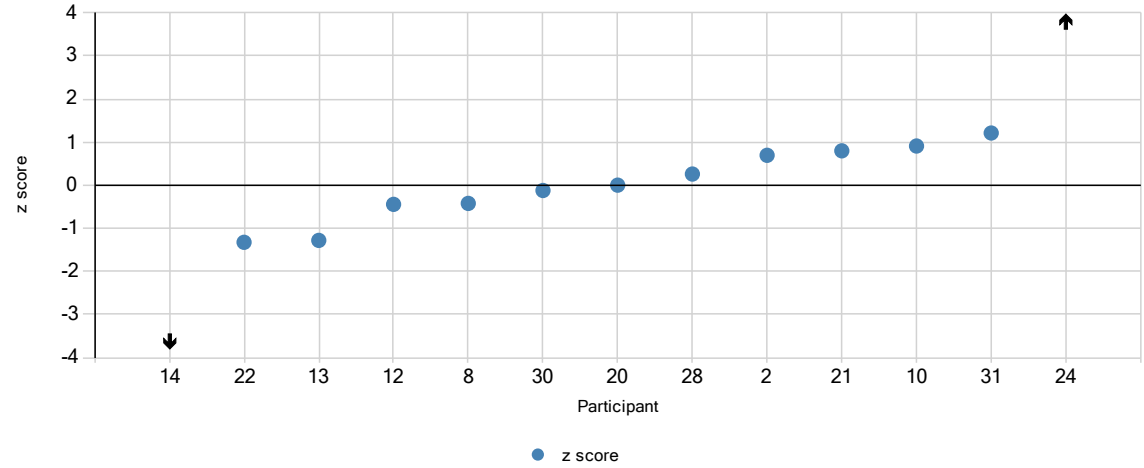
Measurand EF Sample K1



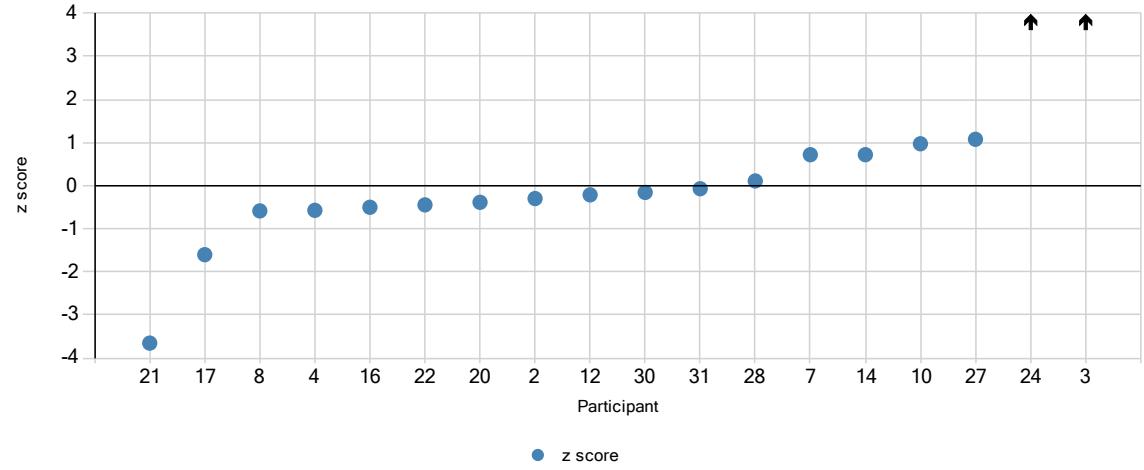
Measurand H_d Sample B1



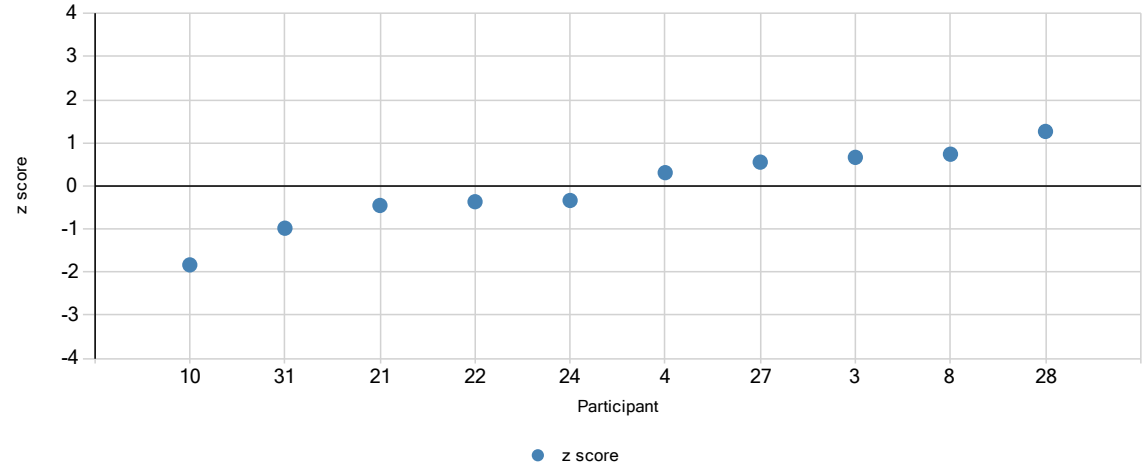
Measurand H_d Sample B2



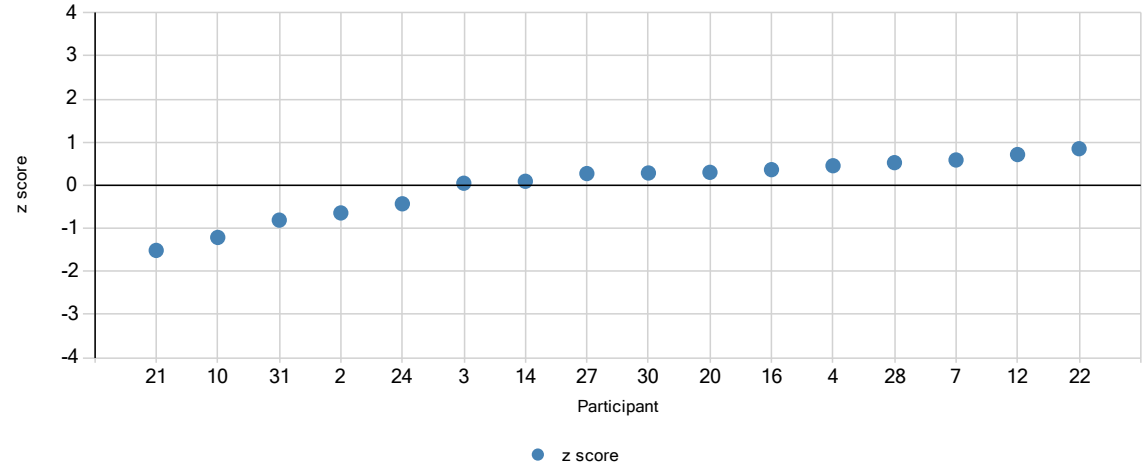
Measurand H_d Sample K1



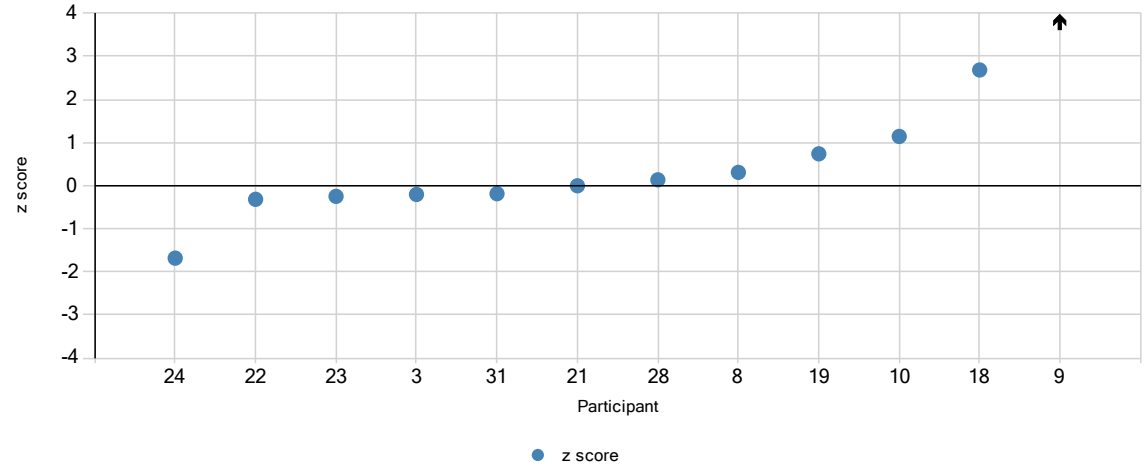
Measurand N_d Sample B1



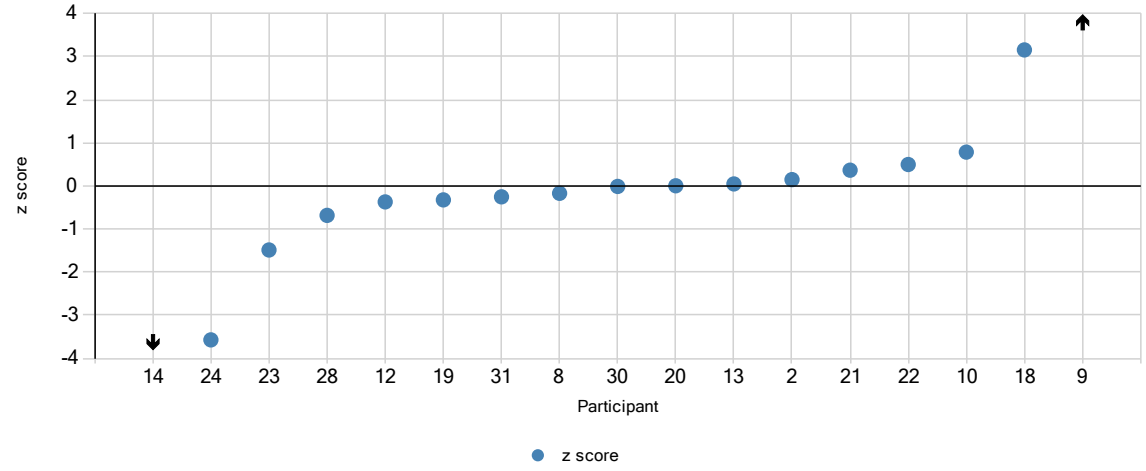
Measurand N_d Sample K1



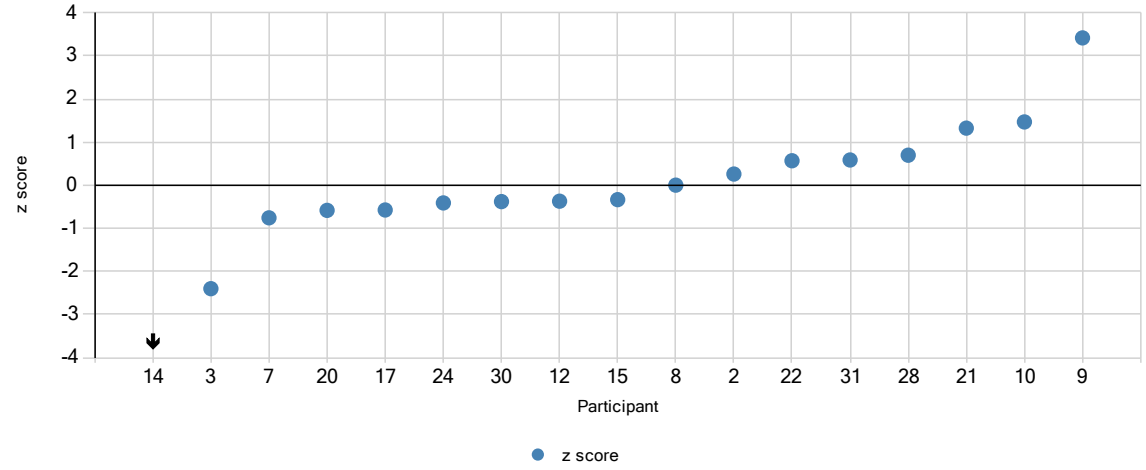
Measurand $q_{p,\ net,d}$ Sample B1

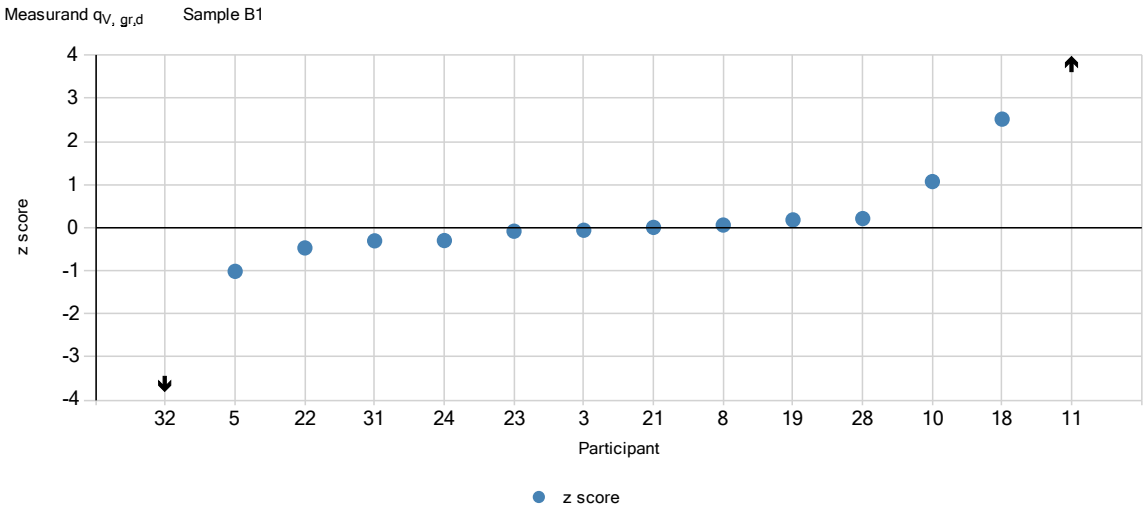


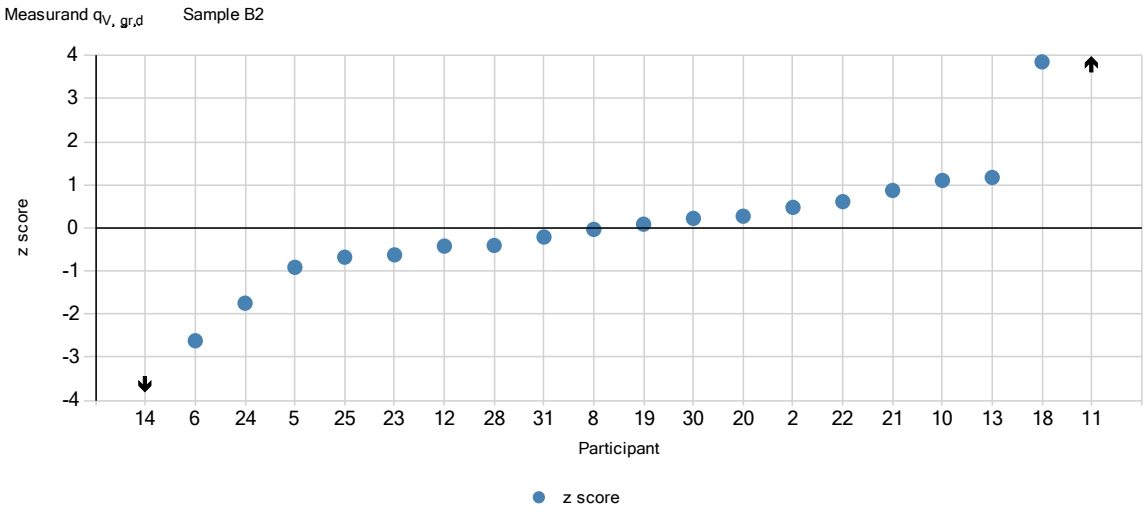
Measurand $q_{p,\ net,d}$ Sample B2

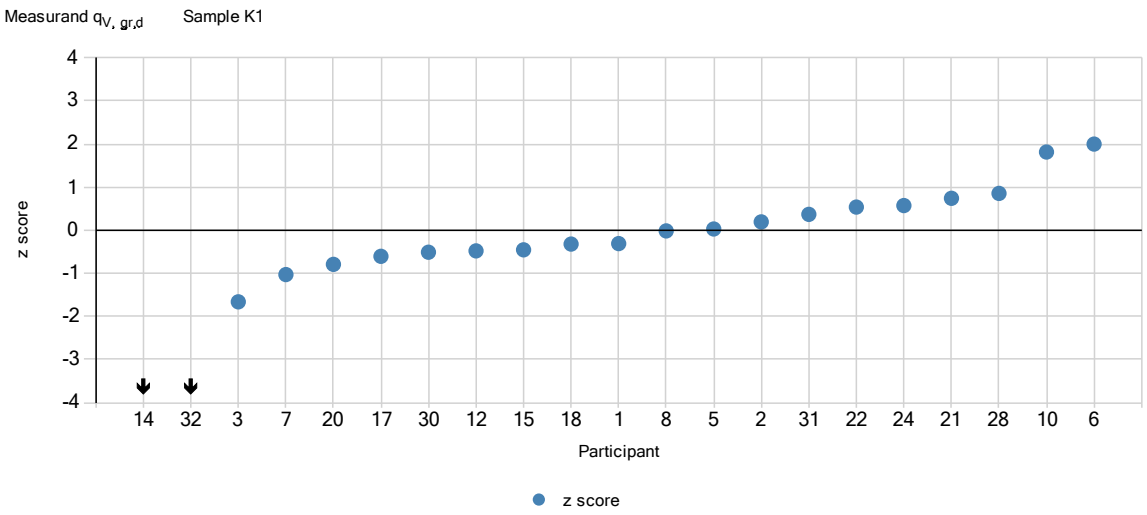


Measurand $q_{p,\ net,d}$ Sample K1

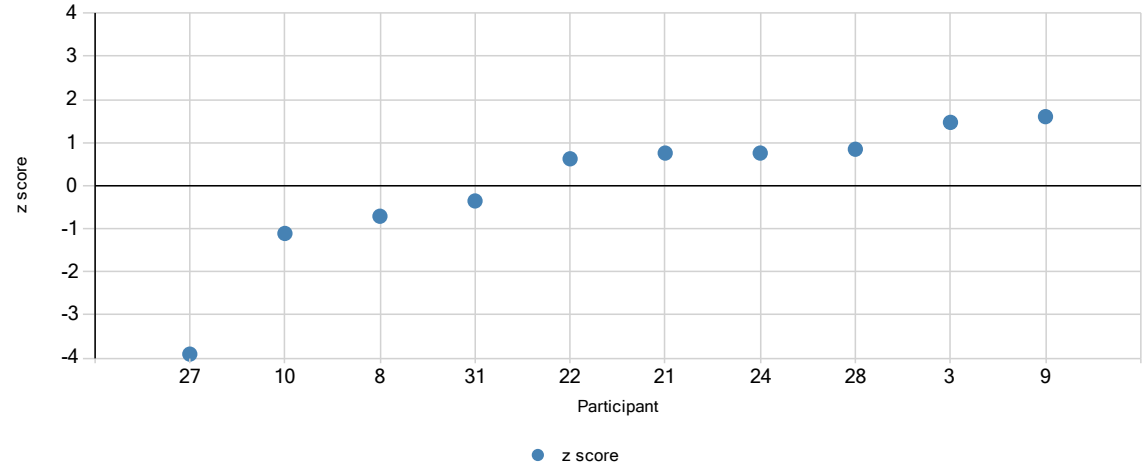



Measurand $q_{V,\ gr,d}$
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
32 5 22 31 24 23 3 21 8 19 28 10 18 11
Participant
z score

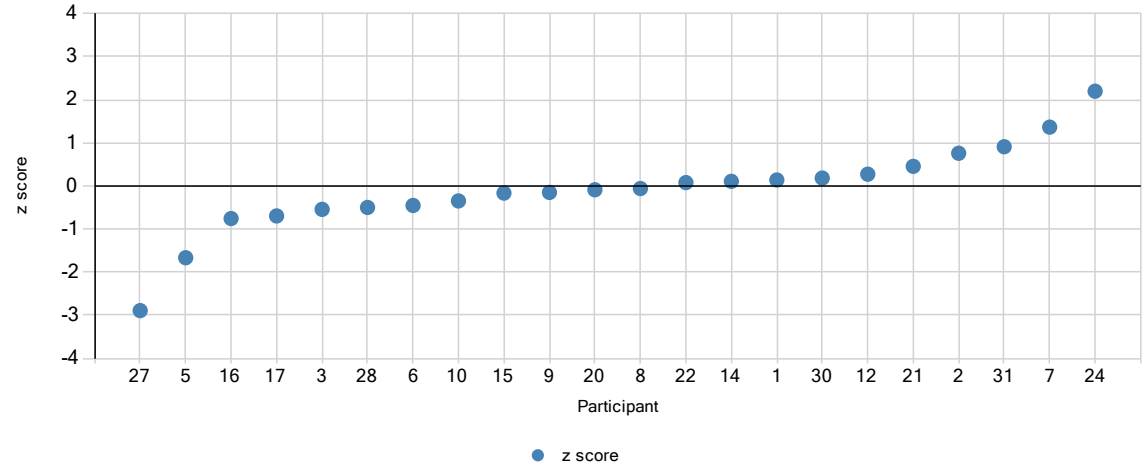

Measurand $q_{V,\ gr,d}$
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
14 6 24 5 25 23 12 28 31 8 19 30 20 2 22 21 10 13 18 11
Participant
z score


Measurand $q_{V,\ gr,d}$
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
14 32 3 7 20 17 30 12 15 18 1 8 5 2 31 22 24 21 28 10 6
Participant
z score

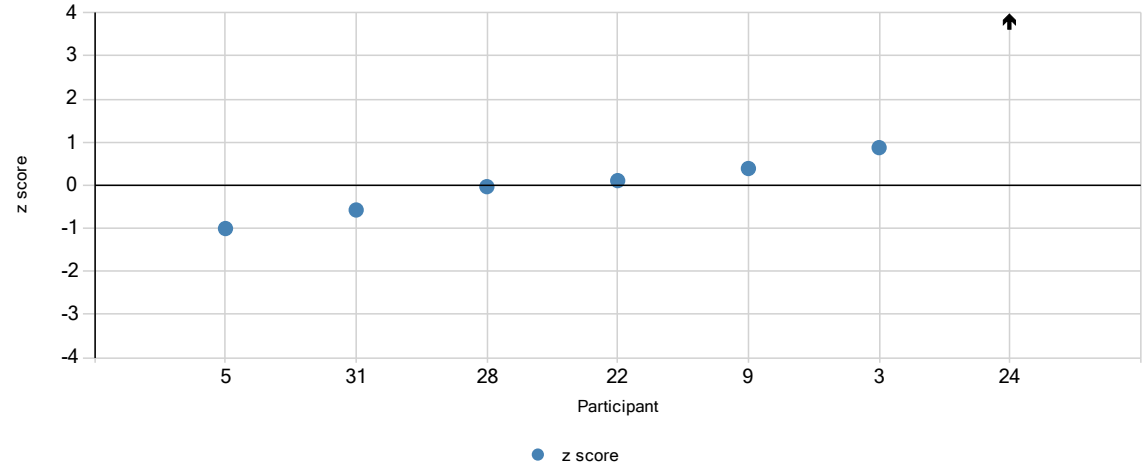
Measurand S_d Sample B1

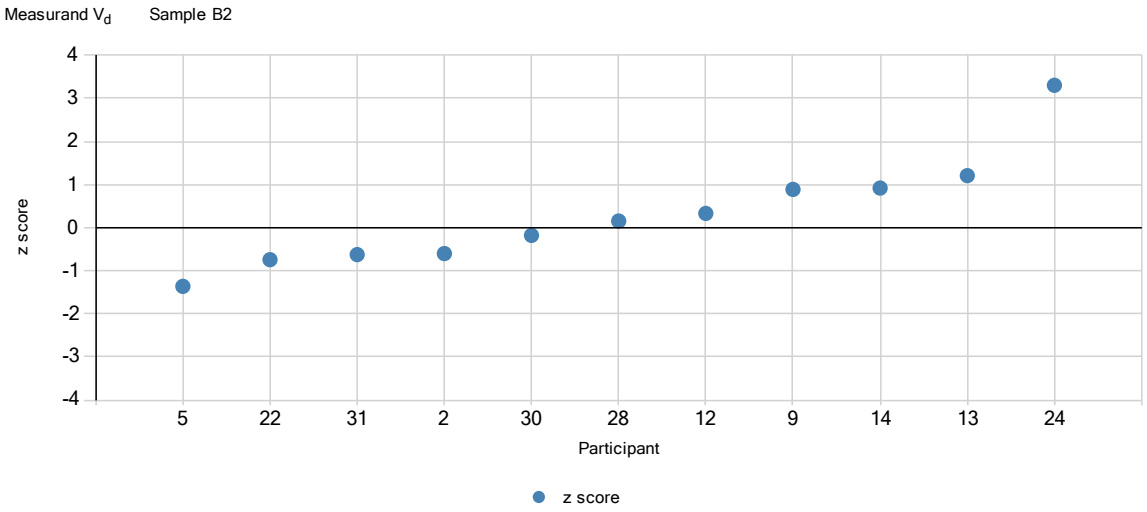


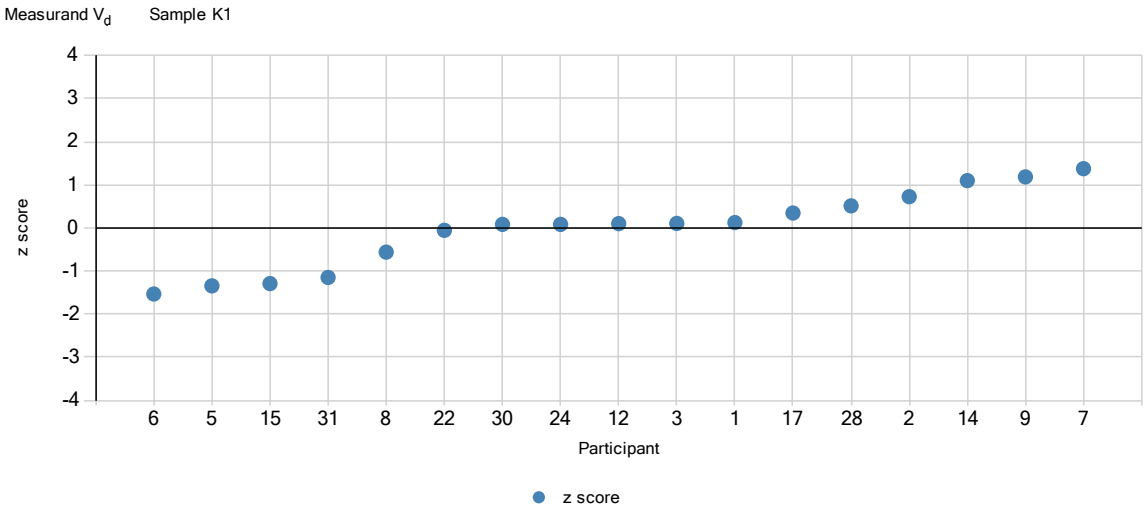
Measurand S_d Sample K1



Measurand V_d Sample B1




Measurand V_d Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
5
22
31
2
30
28
12
9
14
13
24
Participant
z score


Measurand V_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
6
5
15
31
8
22
30
24
12
3
1
17
28
2
14
9
7
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 8, 22, 24	participants 8, 12, 13, 20, 22, 24, 25, 30	participants 1, 8, 12, 16, 17, 20, 22, 24, 28, 30
Drying in 105 °C:	participants 3, 5, 11, 23, 27, 28,	participants 5, 6, 11, 14, 23, 26, 28,	participants 3, 5, 6, 14, 15, 27
Other:	participants 9: not dried sample 21: as received 26: 108 °C	participants 9: not dried sample 21: as received	participants 9: not dried sample 21: as received

Correction taken into account in calculations:

Gross calorific value			
Participants and correction factors used	**Sample**		
	B1 (peat)	**B2 (wood pellet)**	**K1 (coal)**
1: wire, ignition, S, N, analysis moisture			x
3: ignition, S, N, acid correction, analysis moisture	x		x
5: wire, ignition, S, N	x	x	x
6: wire		x	x
8: wire, ignition, acid correction, analysis moisture	x	x	
8: wire, ignition, S, acid correction, analysis moisture			x
9: wire, S, N, analysis moisture	x	x	x
11: ignition, analysis moisture	x	x	
12: wire, ignition, S, acid correction, analysis moisture		x	x
13: wire, ignition, acid correction, analysis moisture		x	
14: wire, S, acid correction, analysis moisture		x	x
15: ignition, acid correction, analysis moisture			x
17: wire, ignition, S, analysis moisture			x
20: wire, ignition, N, analysis moisture		x	
20: wire, ignition, S, N, analysis moisture			x
21: wire, ignition, S, analysis moisture	x	x	x
22: wire, ignition, S, acid correction, analysis moisture	x		x
22: wire, ignition, acid correction, analysis moisture		x	
23: wire, ignition	x	x	
24: wire, S, analysis moisture	x		
24: wire, analysis moisture		x	
24: wire, S, N, analysis moisture			x
25: wire, ignition, acid correction, analysis moisture		x	
28: wire, S, acid correction	x	x	
28: wire, S, acid correction, analysis moisture			x
30: ignition, S, N, analysis moisture		x	x

Correction taken into account in calculations:

Net calorific value (literature value in brackets)			
Participant	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
3	H		H
8	N+O, H	N+O, H	H
12		N+O, H	N+O, H
13		N+O, H	
14		H	H
15			H calculated, N+O literature (ISO 17247)
17			H calculated
20		N+O, H	N+O, H
21	N+O, H	N+O, H	N+O, H
22	N+O, H	N+O, H	N+O, H
23	H literature[1] Other[2]	H literature[1] Other[2]	
24	N+O, H	N+O, H	N+O, H
28	N+O, H	N+O, H	N+O, H
30		N+O, H	N+O, H

[1] 5.58 %:1.217 MJ/Kg for B1 and 6.4 %: 1.396 MJ/kg for B2

[2] Acid correction with sodium carbonate and literature value sulfur correction for B1 0.2%: 0.019 MJ/kg

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 3: 0.99 5: 1 8: 1 9: 1.1 21: 1.5 22: 1.5 23: 1 24: 0.8 26: 1 28: 1	participants 5: 1 6: 1 8: 1 9: 2 12: 1 13: 1 14: 1 20: 2 21: 1.5 22:1.5 23: 1 24: 0.8 26: 1 28: 1 30: 2	participants 1: 1 3: 0.95 5: 1 6: 1 8: 1 9: 1.1 12: 1 14: 5 15: 1 17: 1 20: 1 21: 1.5 22: 1 24: 1 28: 1 30: 1
Measurement	Method	°C	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Ash content (ashing temperature ℃)	Gravimetric:	550	parts 3, 5, 8, 9, 22	parts 5, 8, 9, 12, 13, 14, 20, 22, 26, 30	
		750			part 14
		815	part 23, 26	part 6, 23	parts 1, 3, 5, 6, 9, 12, 17, 20, 22, 30
	TGA:	550	parts 21, 24, 28	parts 21, 24, 28	
		750			part 8
		815			parts 15, 21, 24, 28
Moisture content of analysis sample, M_{ad}	Air:		parts 3, 5, 8, 9, 11, 24, 22, 26, 28	parts 5, 8, 9, 11, 12, 13, 14, 20, 22, 24, 25, 26, 28, 30	parts 1, 3, 5, 8, 9, 12, 14, 15, 20, 24, 30
	N_2 atmosphere:		part 21	part 21	parts 8, 16, 17, 21, 22, 28
	Gravimetric:	21	part 11	part 11	
		105	parts 3, 5, 8, 9, 22	parts 5, 6, 8, 9, 12, 13, 14, 20, 22, 25, 26, 30	parts 1, 3, 5, 6, 8, 9, 12, 14, 20, 22, 30
		107			part 17
		108	part 26		
	TGA:	105	parts 21, 24, 28	parts 21, 24, 28	parts 8, 15, 21, 24
		107			part 28
	Other				part 16: Oven

CHN-measurements carried out by:

	Sample		
	B1	**B2**	**K1**
Air dried samples:	parts 22, 24, 28	parts 12, 20, 22, 24, 25, 28, 30	parts 8, 12, 16, 17, 20, 22, 24, 28, 30
Drying in 105 °C:	part 3, 4, 8, 27	parts 6, 8, 13, 14	parts 3, 4, 6, 14, 15, 27
Other	part 21: As received and correction for moisture	part 21: As received and correction for moisture	part 21: As received and correction for moisture

Detection limits in nitrogen and sulphur measurements:

Participant	Detection limit for N (w%)	Participant	Detection limit for S (w%)
3	0.002	1	0.01
12	0.01	3	0.02
20	0.015	8	0.06
21	0.02	12	0.001
22	0.1	15	7.0
24	0.02	17	0.05
27	0.015	20	0.1
28	0.1	21	0.02
		22	0.03
		24	0.1
		27	0.001
		28	0.01

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 3, 28,	parts 3, 12, 17, 20, 28, 30,
No:	parts 8 Indicator is not used in practice 21 (national guide) 22[1]	parts 8 Indicator is not used in practice 15 21 (national guide) 22[1]

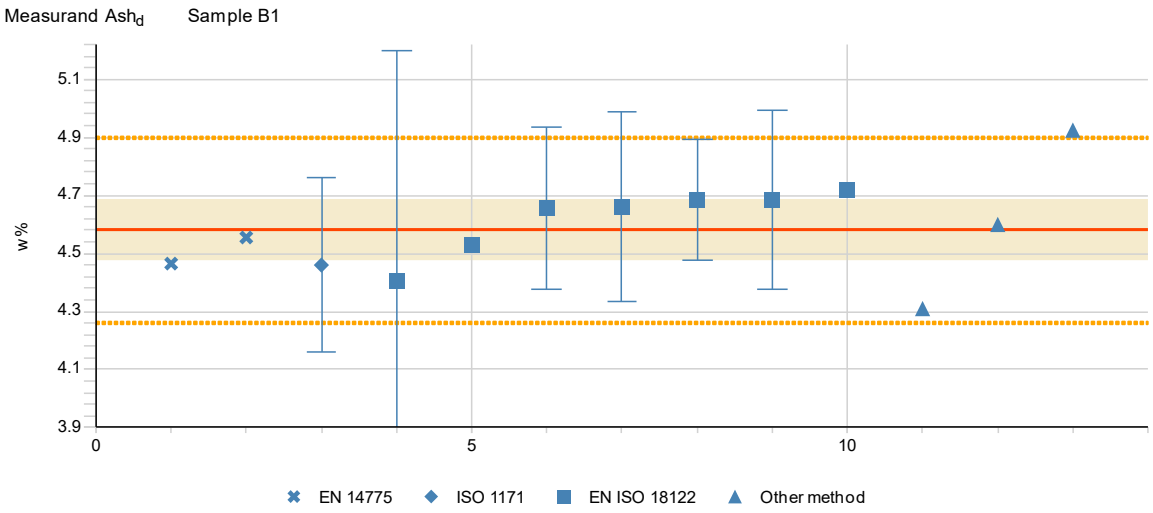
[1] In the cover letter the provider gave the participants the possibility to calculate the EF-value using the procedure presented in the EC directive and using the total moisture content as presented in the letter. The EC directive is not giving the detailed equation for calculation of EF-values. Therefore,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

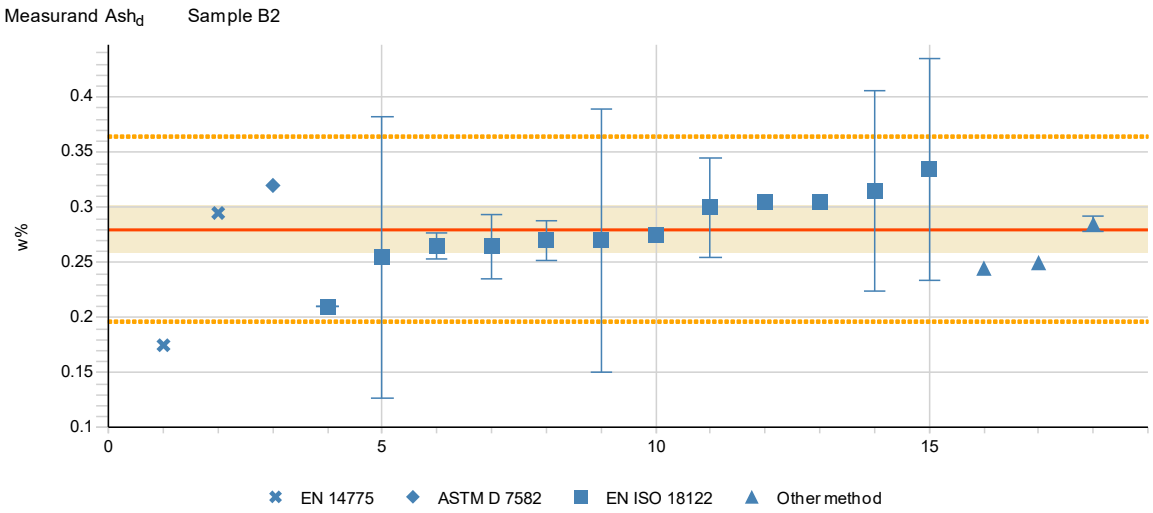
$EF = 1000 \times 3.664 \times (C/100) \times (1 - M_{ar}/100)/Q_{net.ar}$, where

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
(https://energiavirasto.fi/documents/11120570/12803724/Ohje-p%C3%A4%C3%A4st%C3%B6kertoimen-laskenta.pdf/5b0d50c9-c60d-e8b6-6820-92f0024d351e)

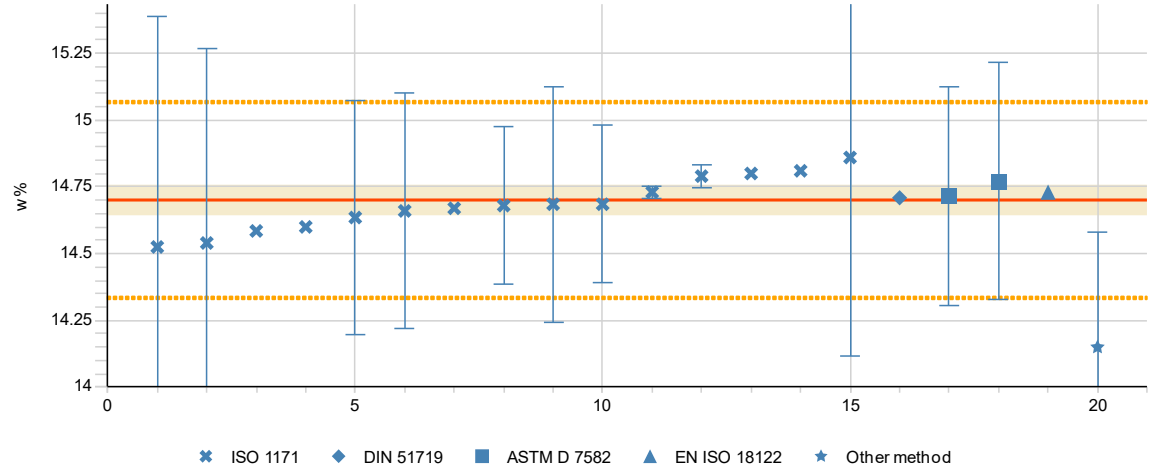
APPENDIX 12: Results grouped according to the methods

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

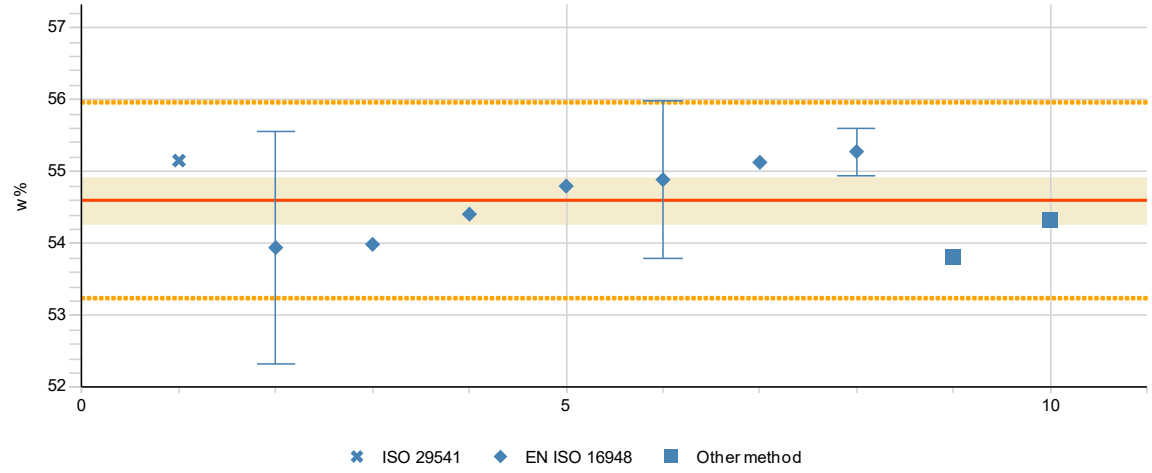




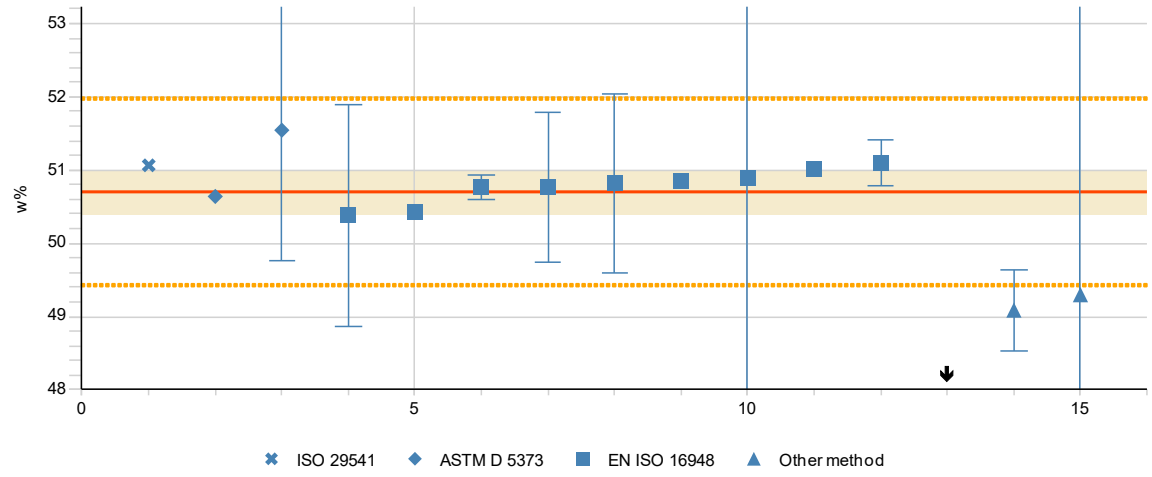
Measurand Ash_d Sample K1



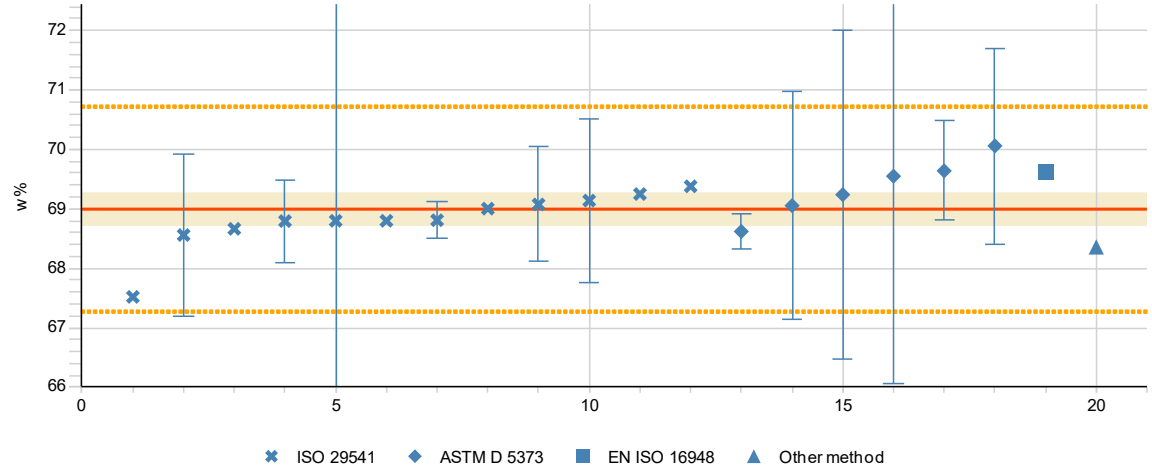
Measurand C_d Sample B1



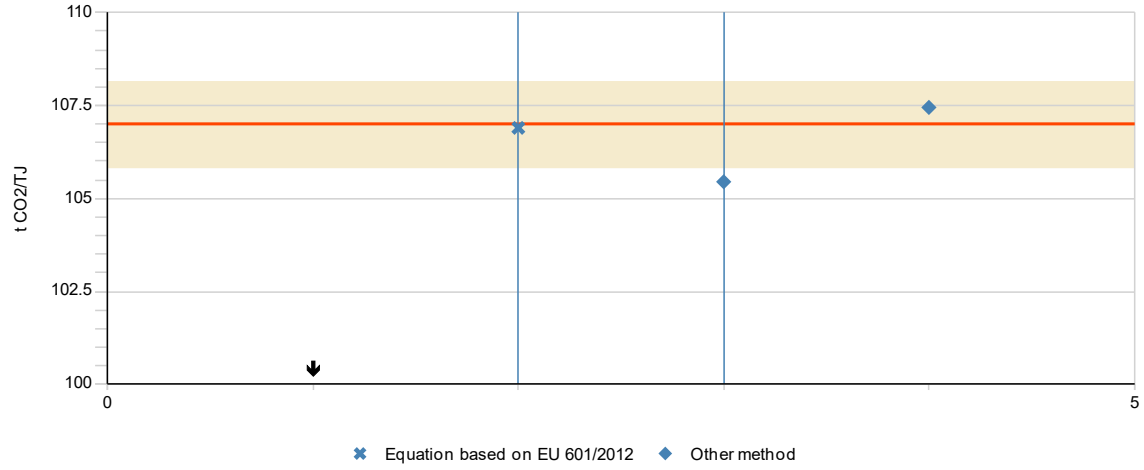
Measurand C_d Sample B2



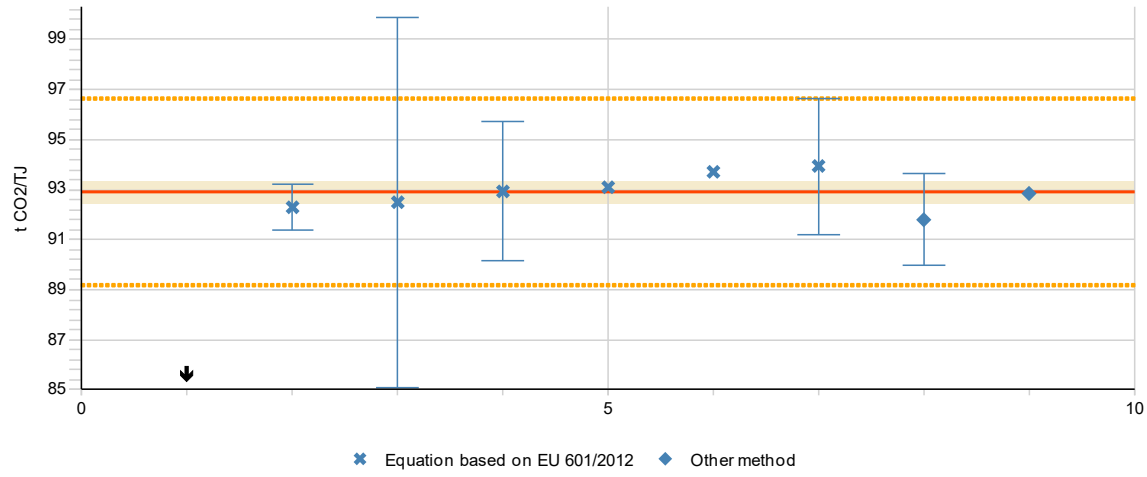
Measurand C_d Sample K1



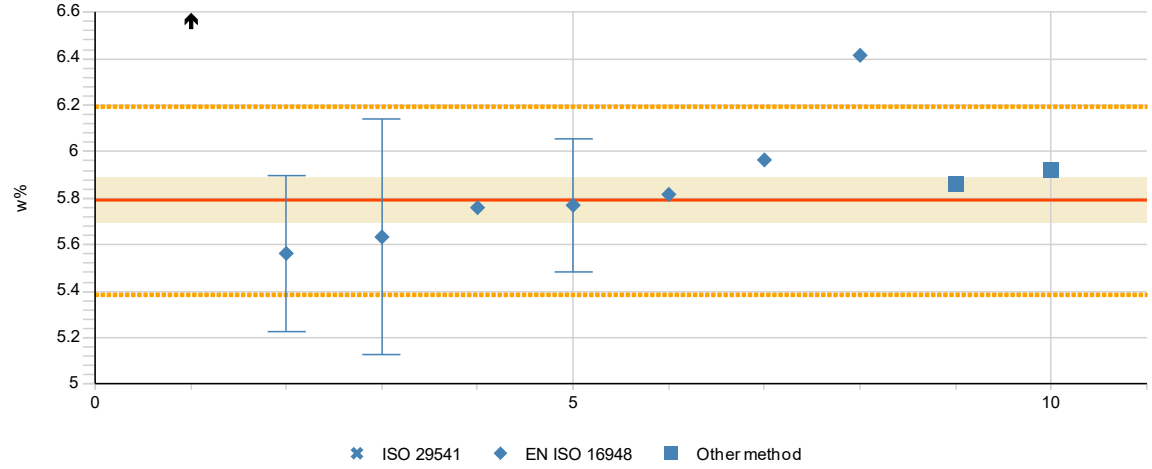
Measurand EF Sample B1



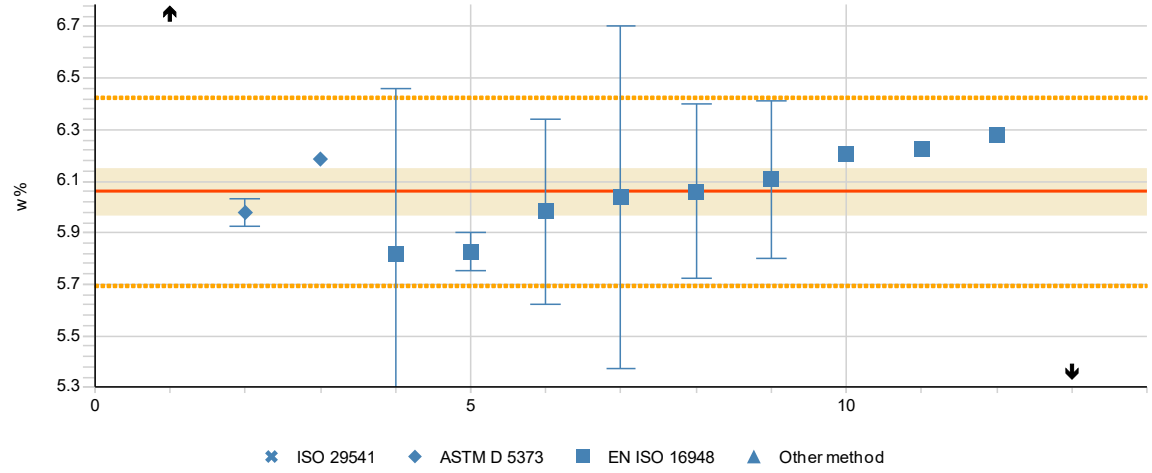
Measurand EF Sample K1



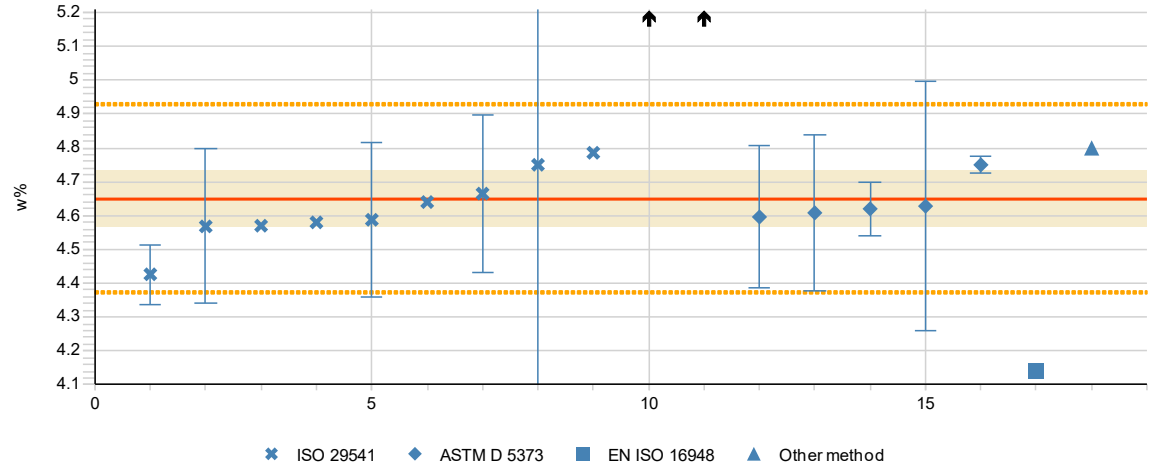
Measurand H_d Sample B1



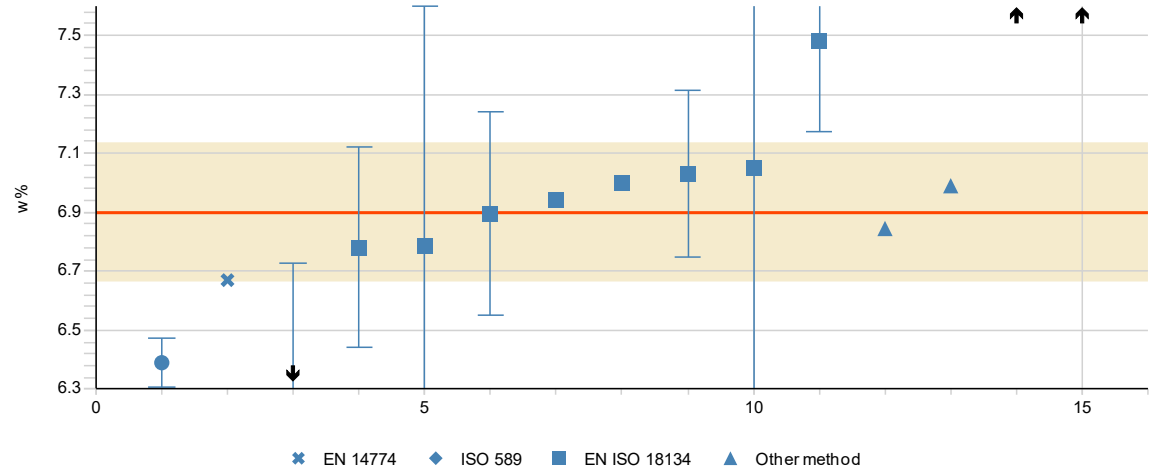
Measurand H_d Sample B2



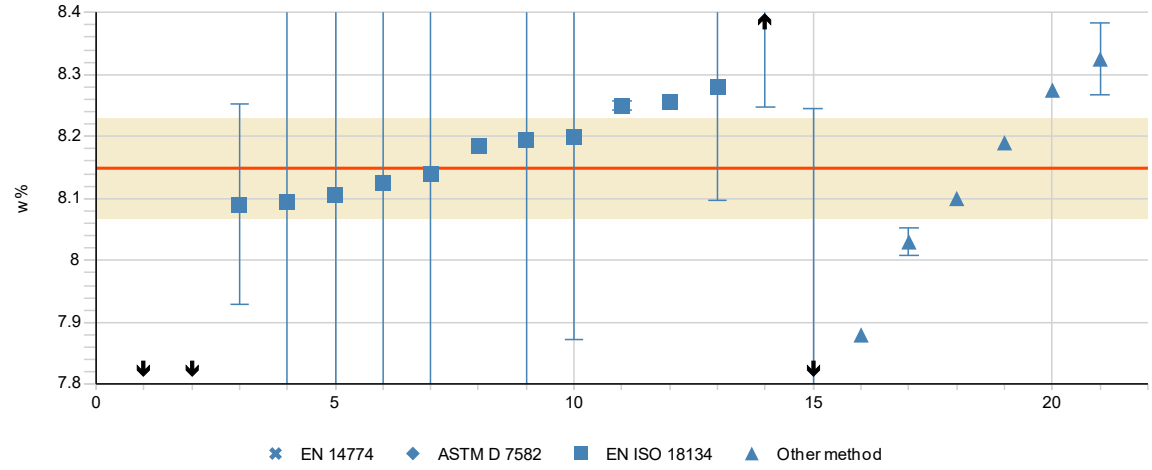
Measurand H_d Sample K1



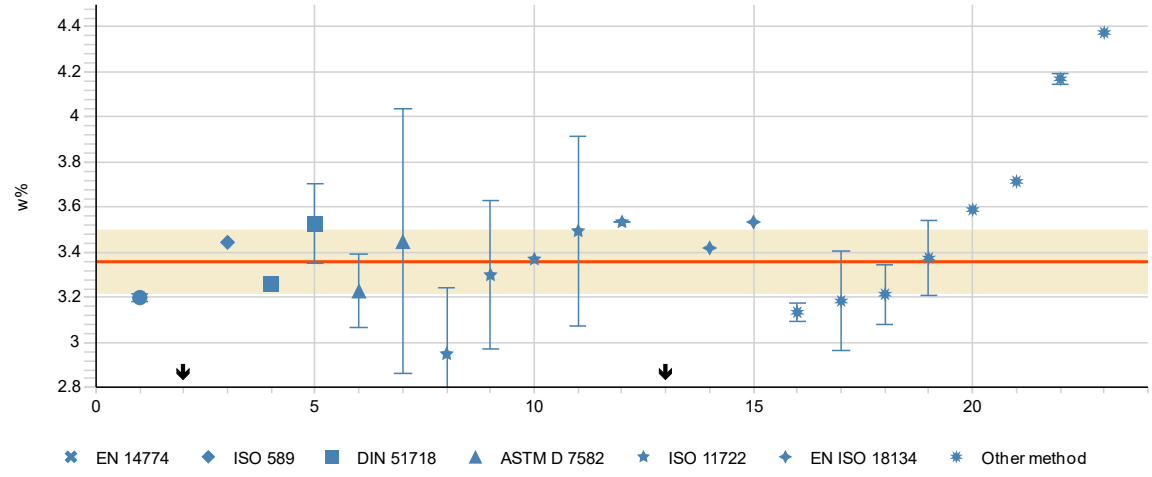
Measurand M_{ad} Sample B1



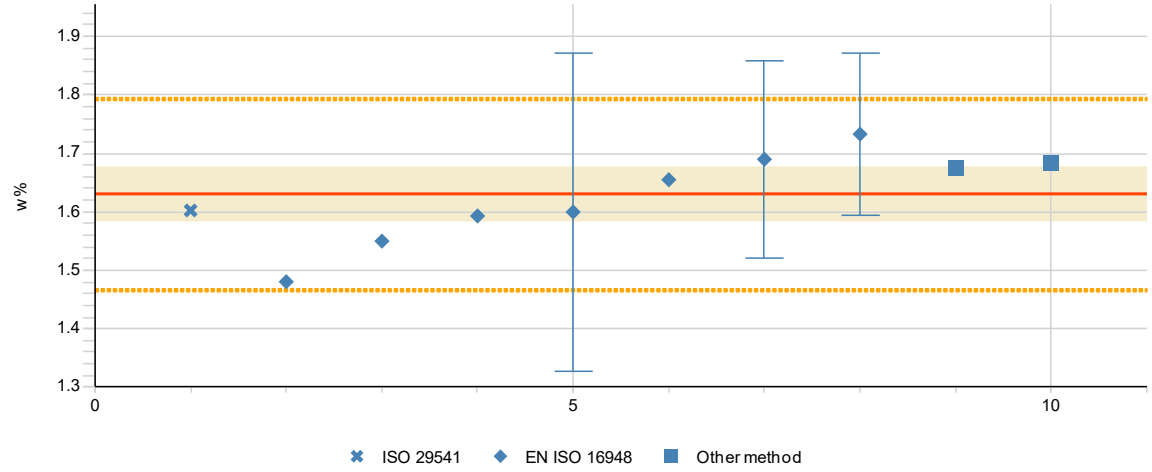
Measurand M_{ad} Sample B2



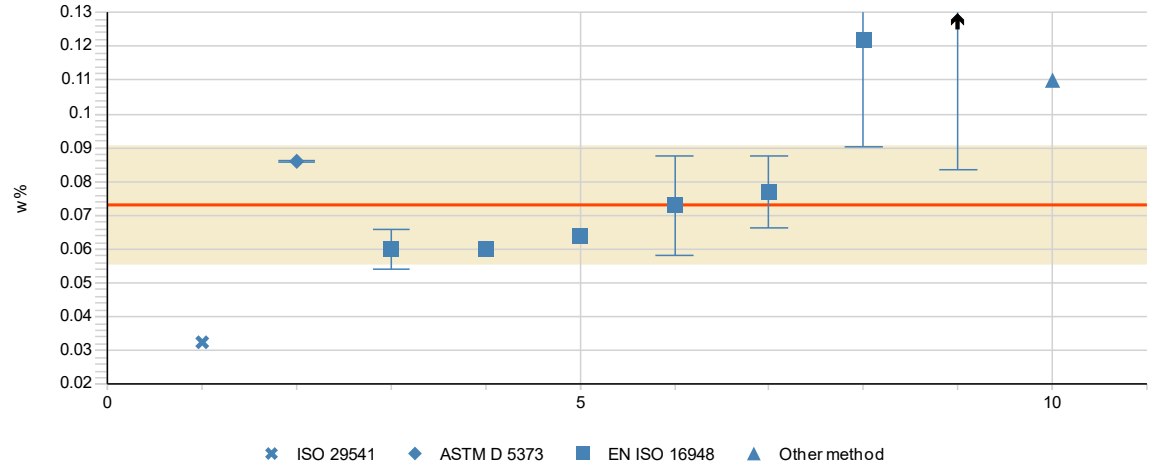
Measurand M_{ad} Sample K1



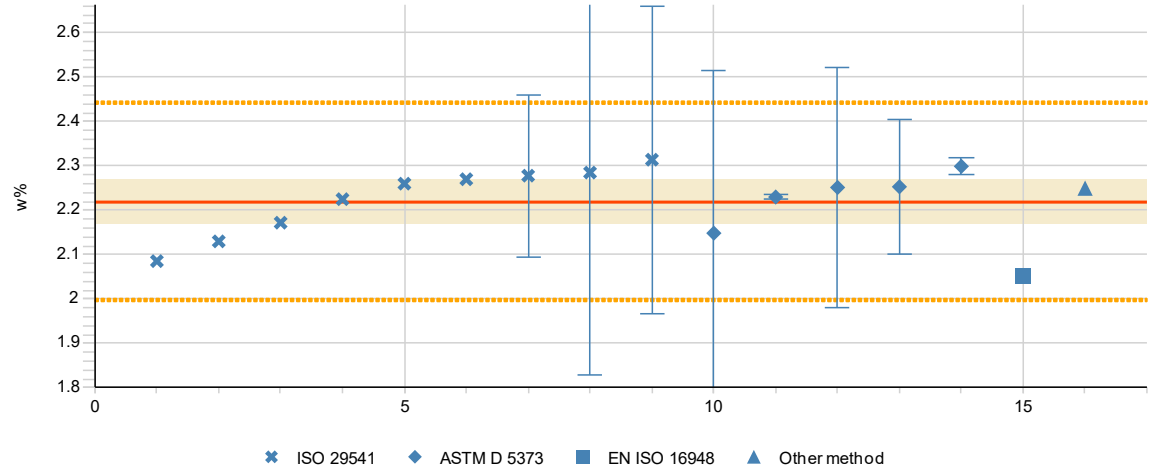
Measurand N_d Sample B1

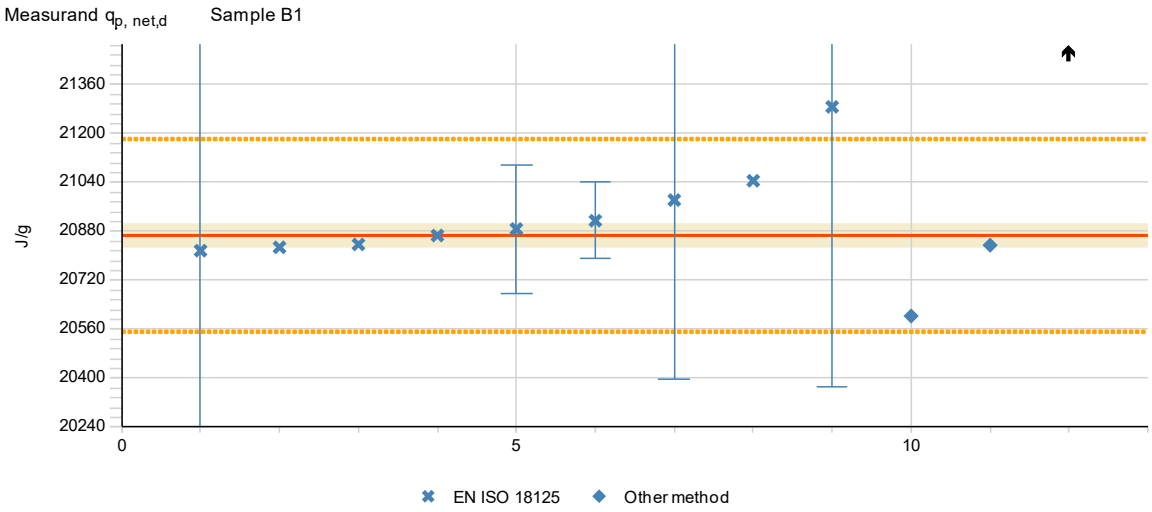


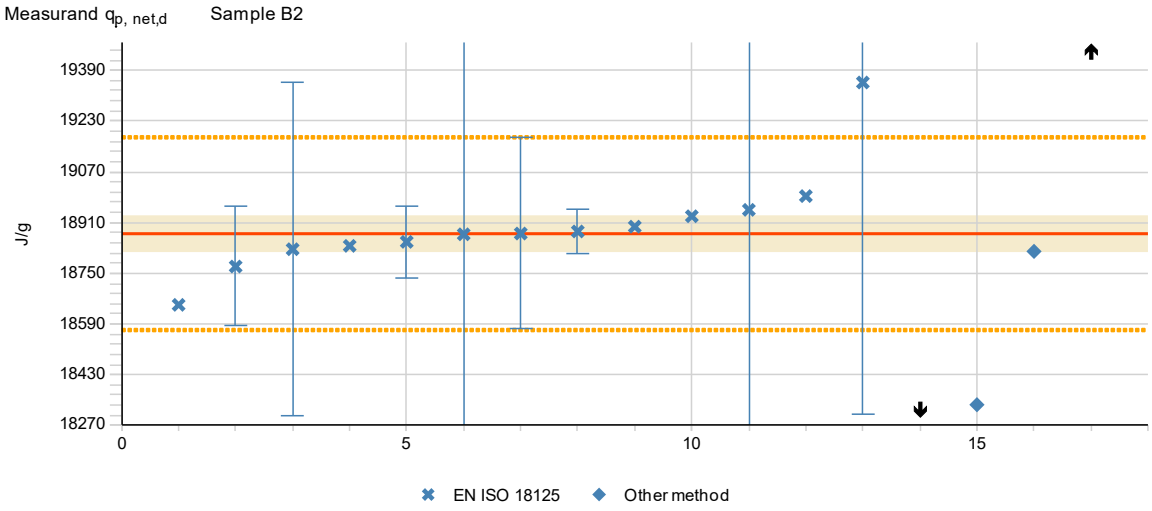
Measurand N_d Sample B2

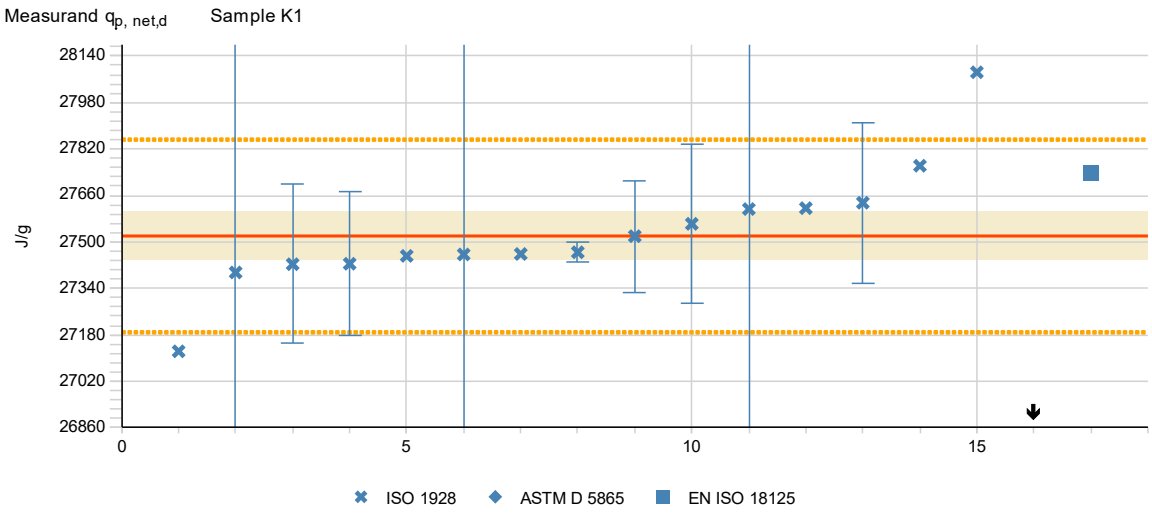


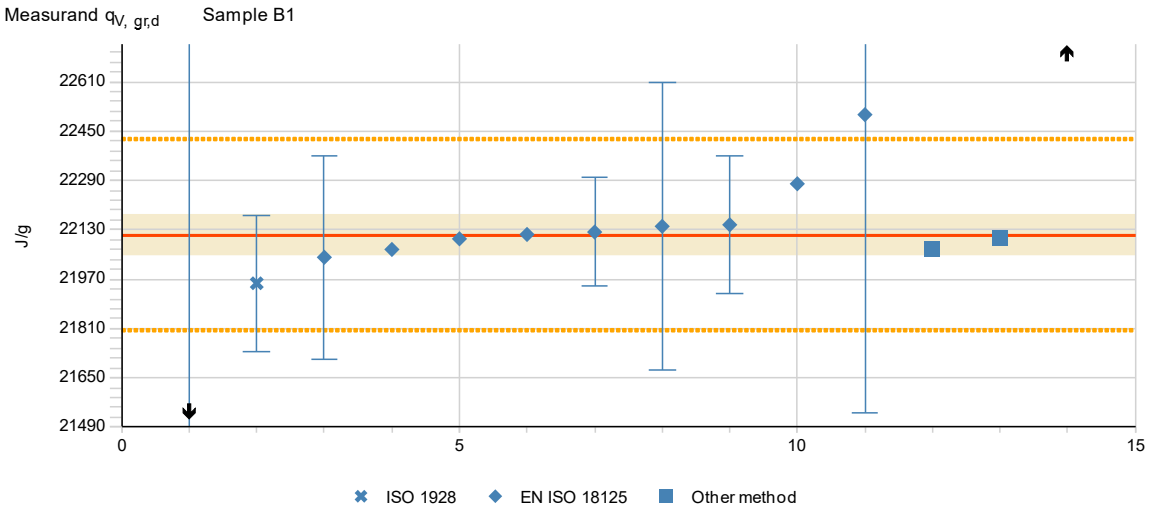
Measurand N_d Sample K1

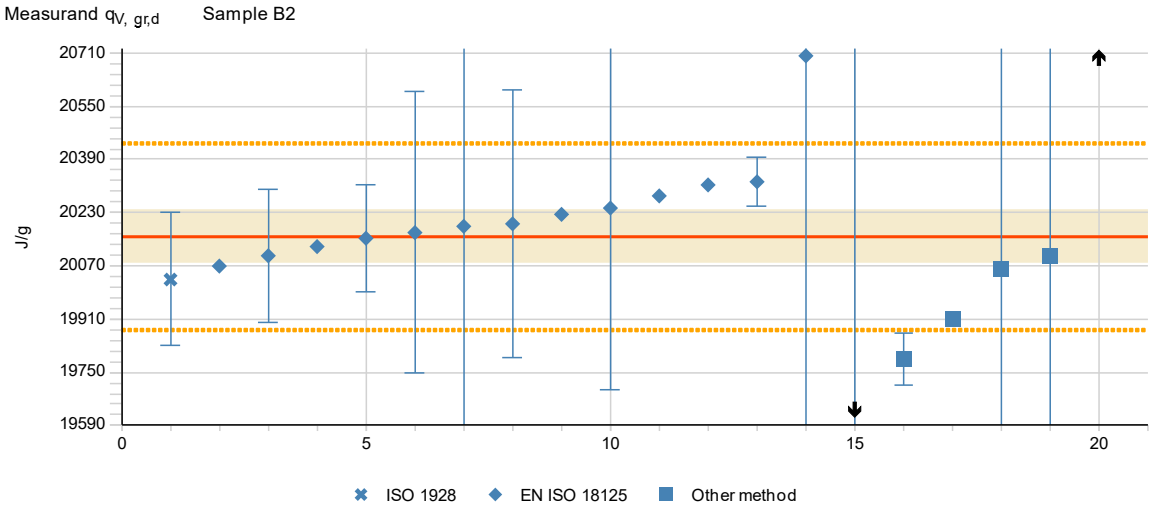


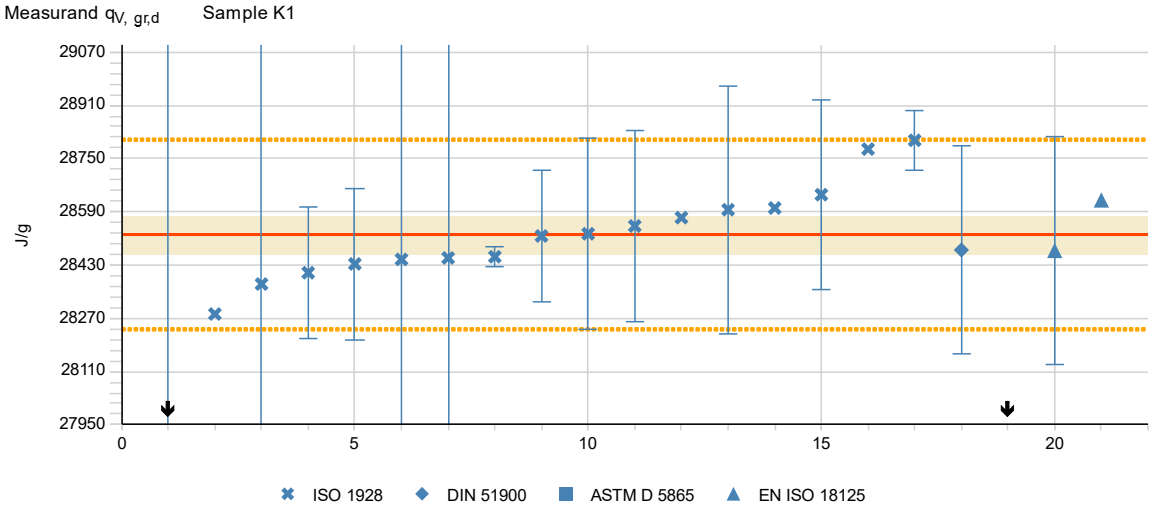

Measurand $q_{p, net,d}$
Sample B1
J/g
21360
21200
21040
20880
20720
20560
20400
20240
0
5
10
EN ISO 18125
Other method

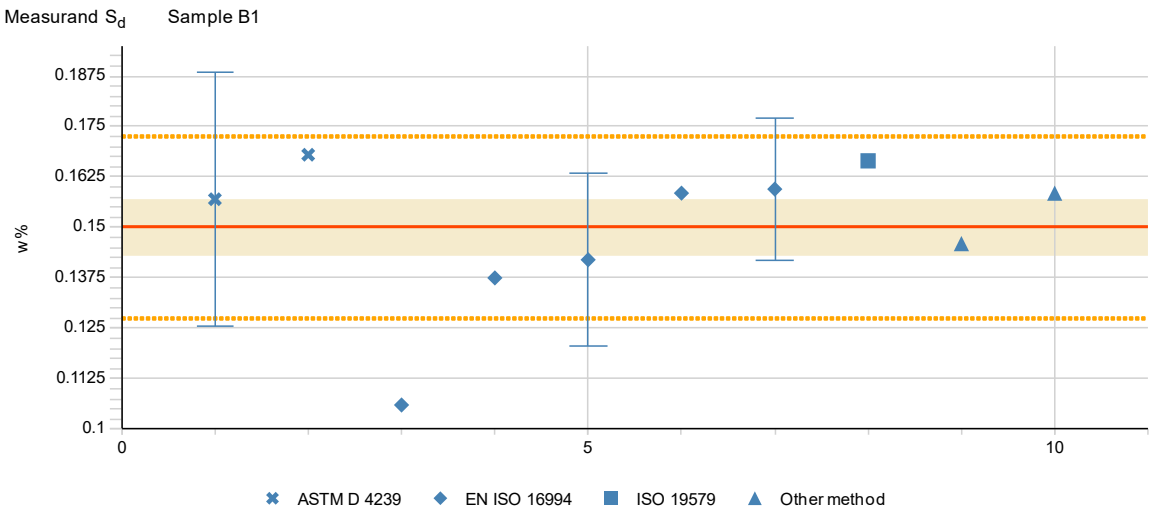

Measurand $q_{p, net,d}$
Sample B2
J/g
19390
19230
19070
18910
18750
18590
18430
18270
0
5
10
15
EN ISO 18125
Other method

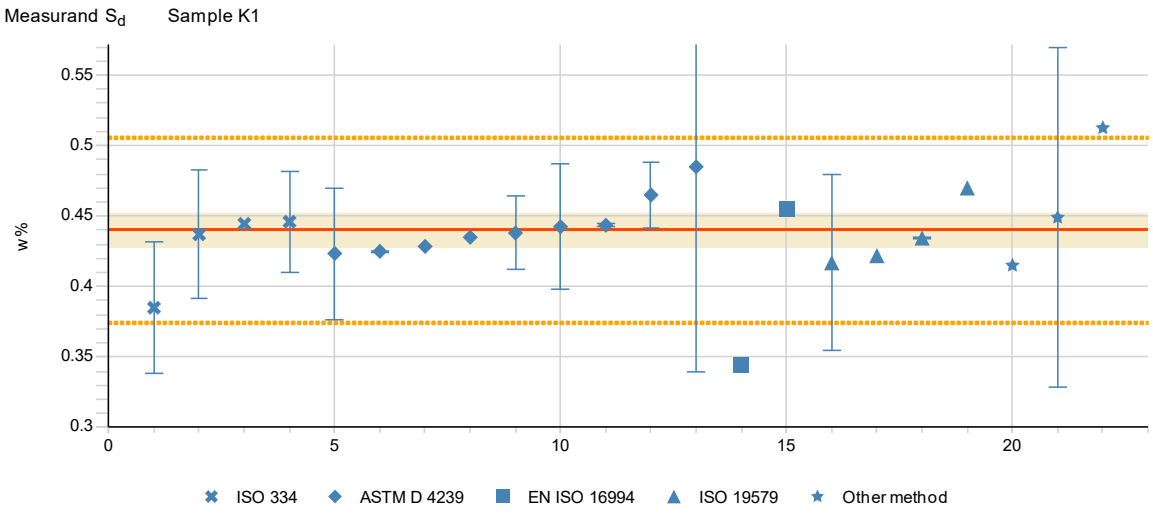

Measurand $q_{p, net,d}$
Sample K1
J/g
28140
27980
27820
27660
27500
27340
27180
27020
26860
0
5
10
15
ISO 1928
ASTM D 5865
EN ISO 18125

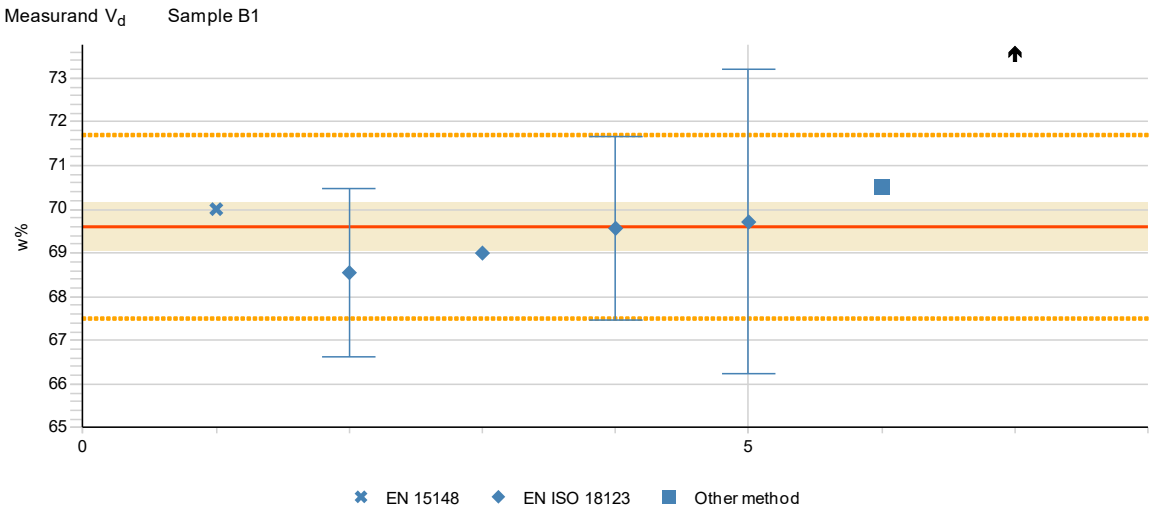

Measurand $q_{V,\ gr,d}$
Sample B1
J/g
22610
22450
22290
22130
21970
21810
21650
21490
0
5
10
15
ISO 1928
EN ISO 18125
Other method


Measurand $q_{V,\ gr,d}$
Sample B2
J/g
20710
20550
20390
20230
20070
19910
19750
19590
0
5
10
15
20
ISO 1928
EN ISO 18125
Other method

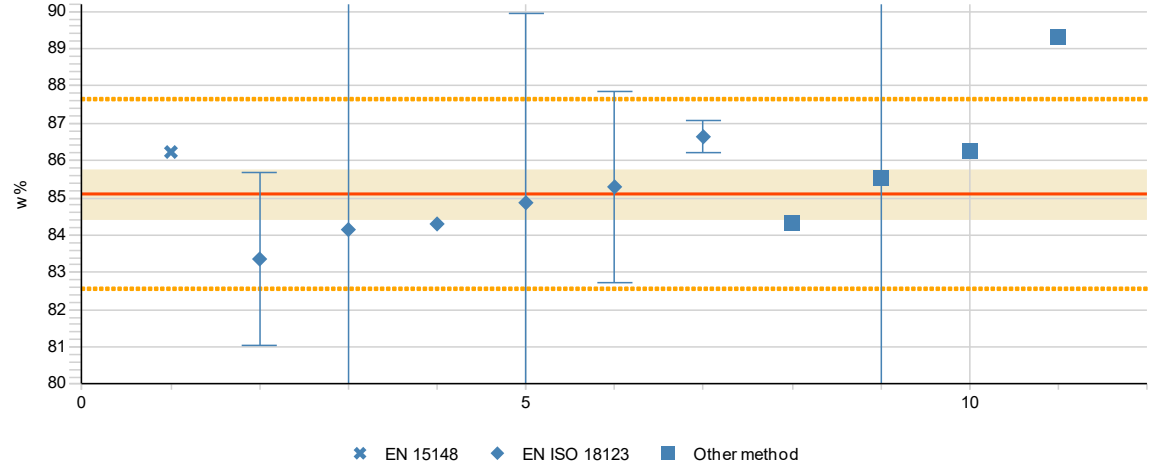

Measurand $q_{V,\ gr,d}$
Sample K1
J/g
29070
28910
28750
28590
28430
28270
28110
27950
0
5
10
15
20
ISO 1928
DIN 51900
ASTM D 5865
EN ISO 18125


Measurand S_d Sample B1
0.1875
0.175
0.1625
0.15
0.1375
0.125
0.1125
0.1
w%
0
5
10
ASTM D 4239
EN ISO 16994
ISO 19579
Other method

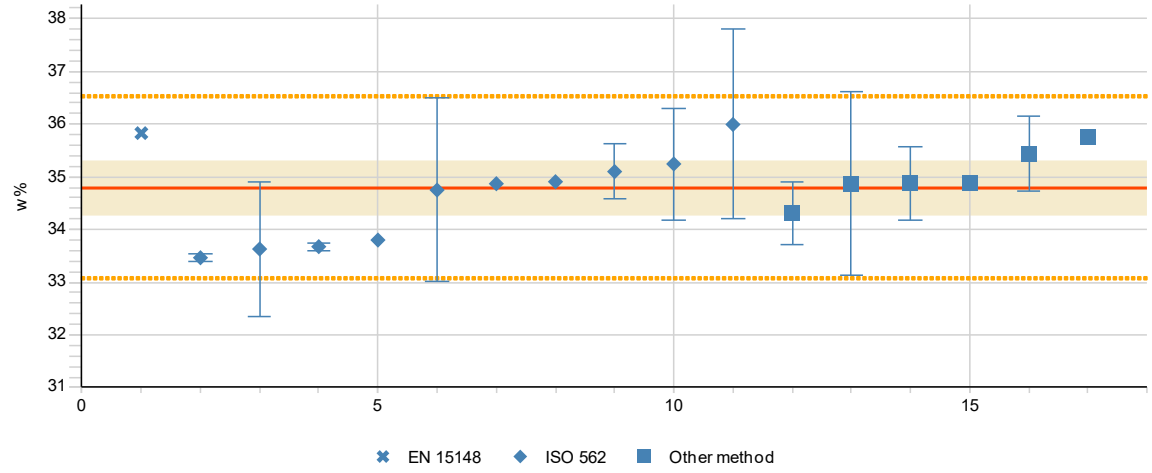

Measurand S_d Sample K1
0.55
0.5
0.45
0.4
0.35
0.3
w%
0
5
10
15
20
ISO 334
ASTM D 4239
EN ISO 16994
ISO 19579
Other method


Measurand V_d Sample B1
73
72
71
70
69
68
67
66
65
w%
0
5
EN 15148
EN ISO 18123
Other method

Measurand V_d Sample B2

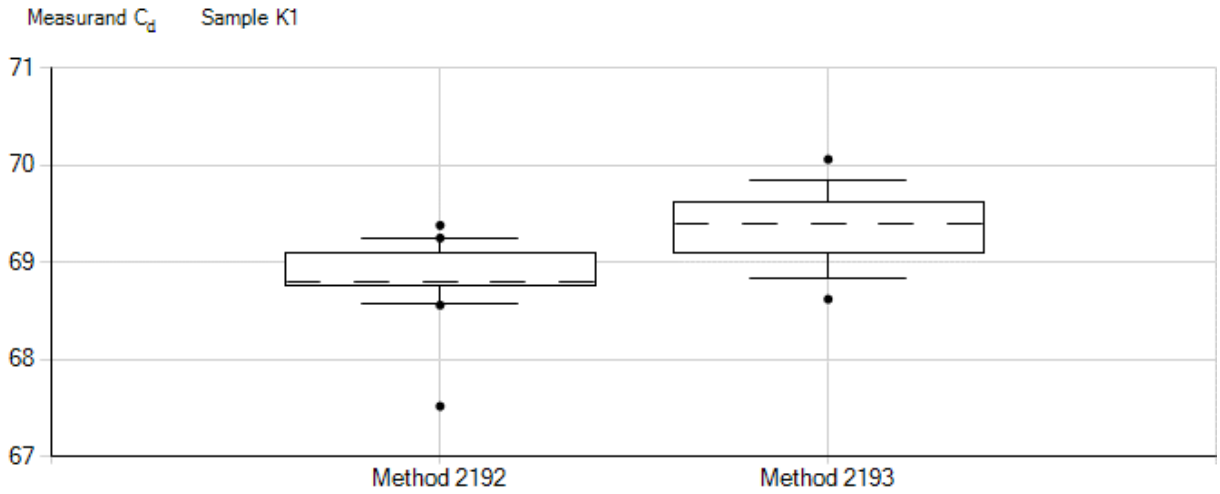


Measurand V_d Sample K1



APPENDIX 13: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.

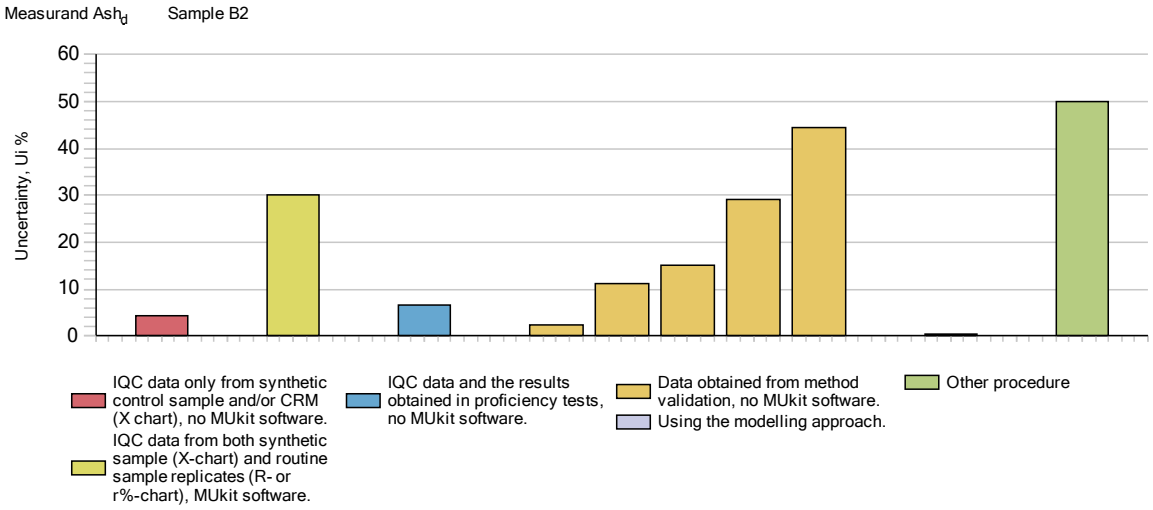


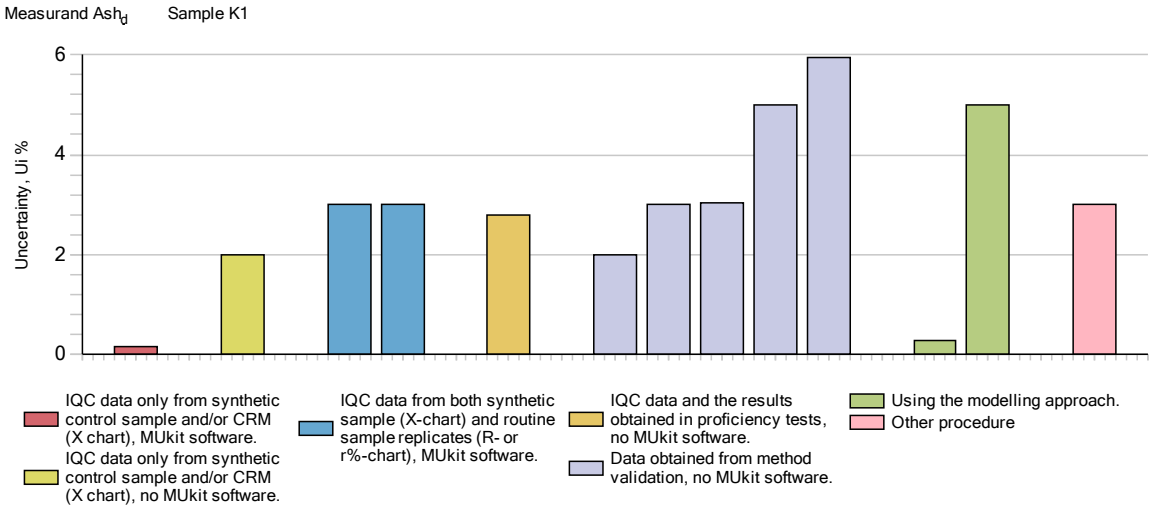
C_d: K1 Method	n	Mean	Median	s
Method 2192: ISO 29541	12	68.8	68.8	0.5
Method 2193: ASTM D 5373	6	69.4	69.4	0.5

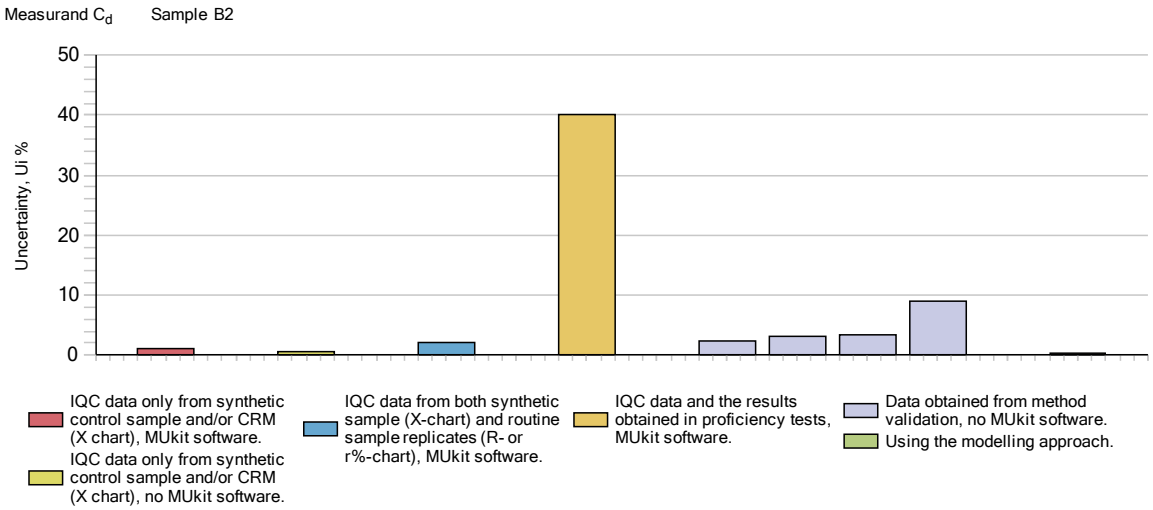
n:number of results. s: standard deviation

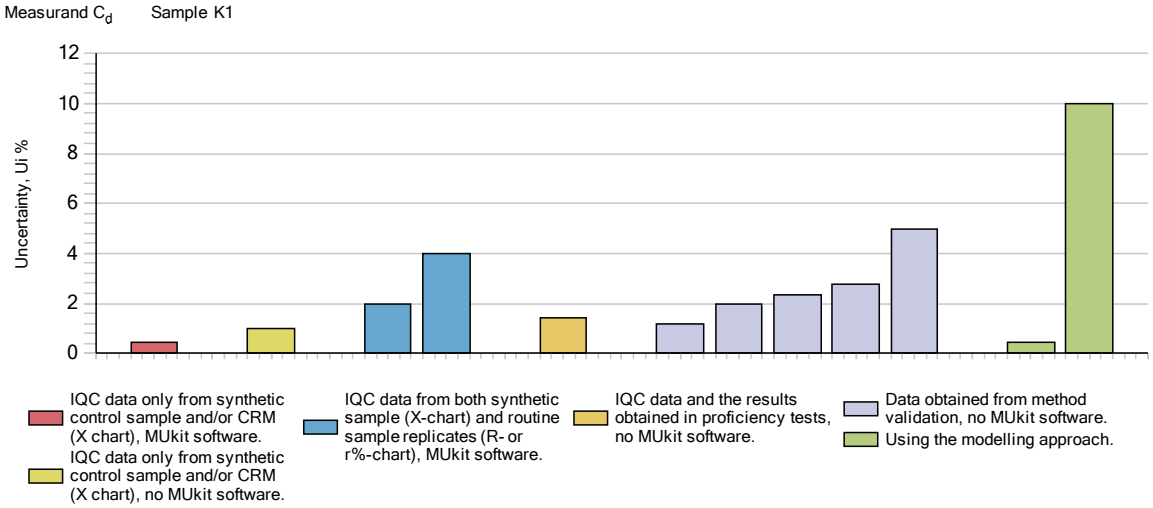
APPENDIX 14: Examples of measurement uncertainties reported by the participants

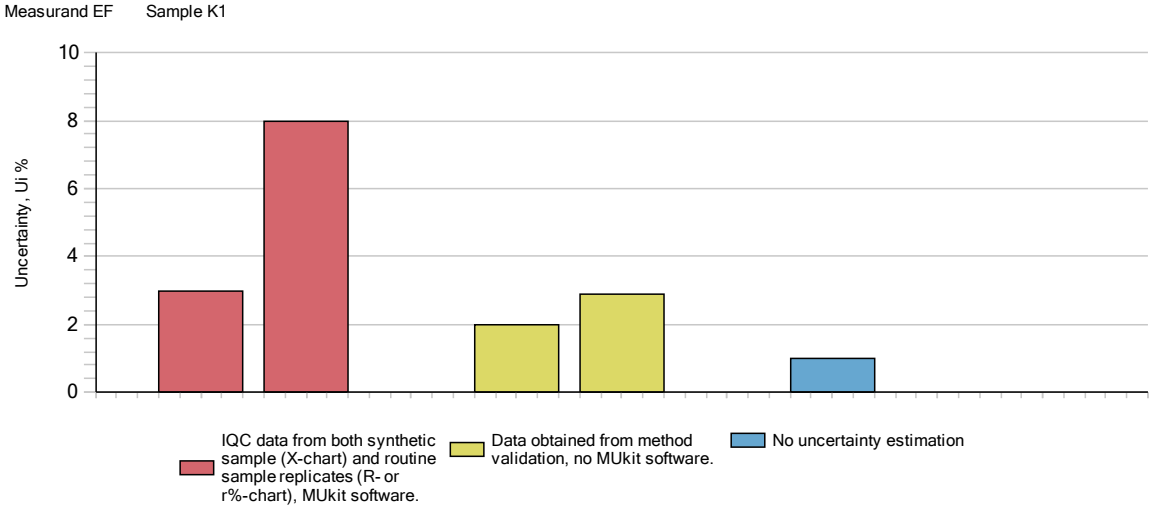
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [30, 31] or using a modelling approach based [32, 33].

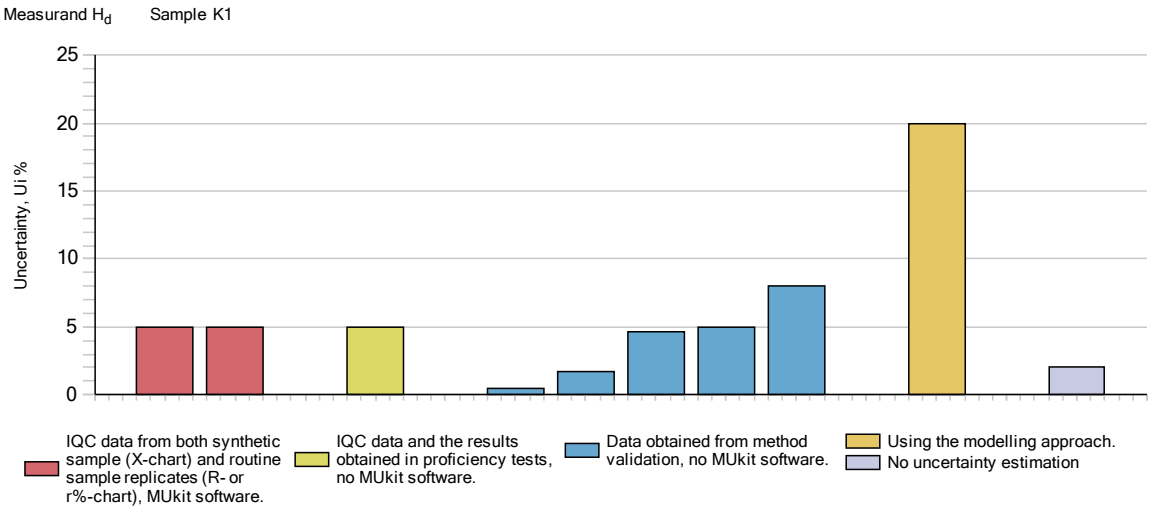


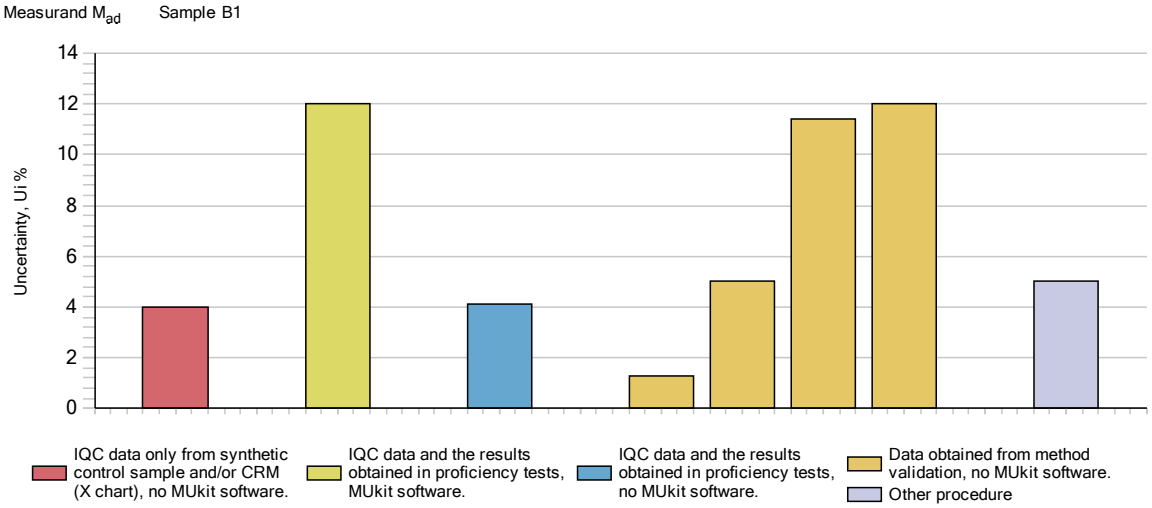


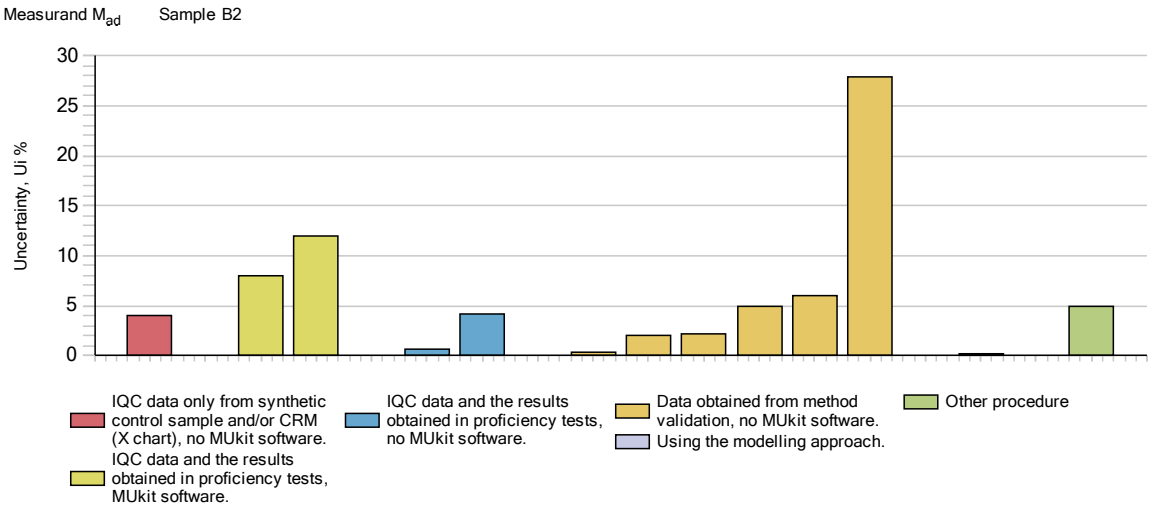

Measurand C_d Sample B2
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.

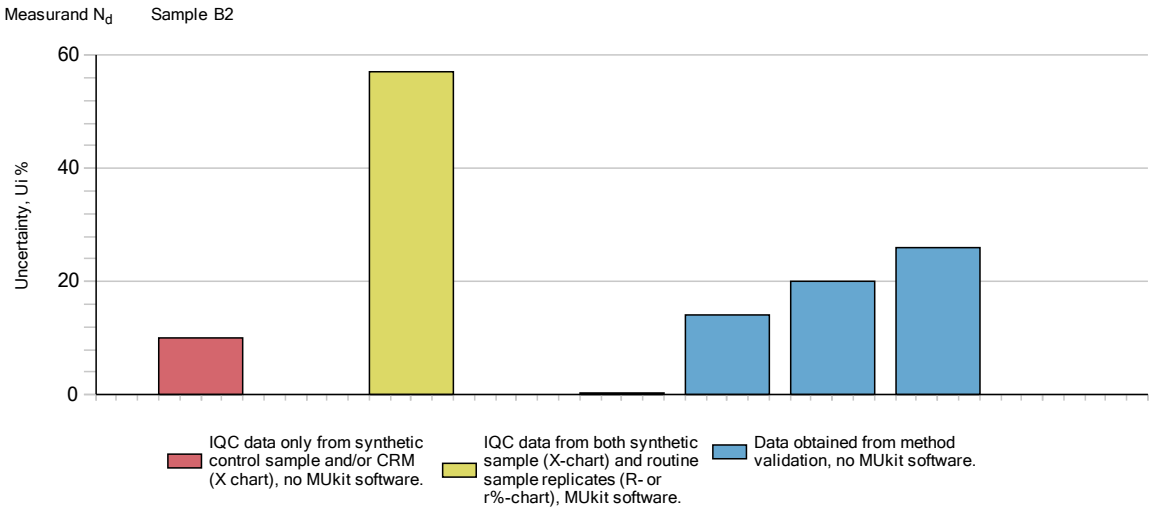

Measurand C_d Sample K1
Uncertainty, Ui %
12
10
8
6
4
2
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests,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

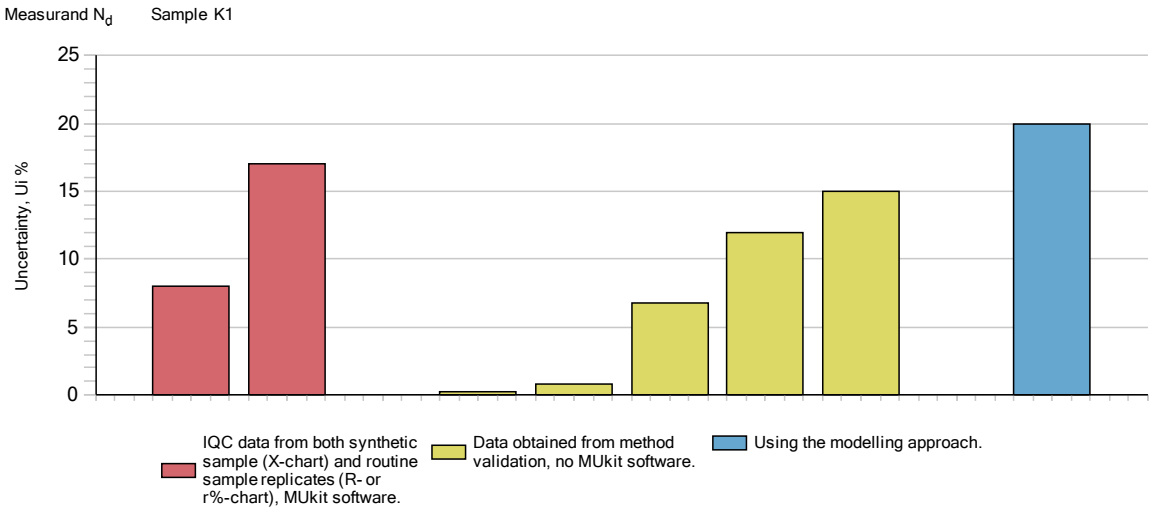

Measurand EF Sample K1
Uncertainty, Ui %
10
8
6
4
2
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.
No uncertainty estimation

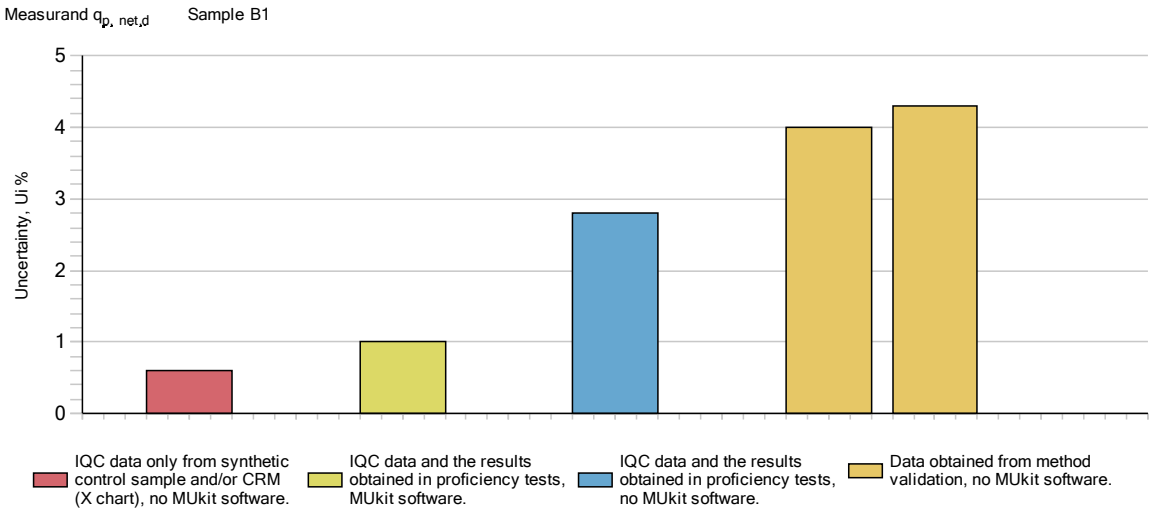

Measurand H_d Sample K1
Uncertainty, Ui %
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
No uncertainty estimation

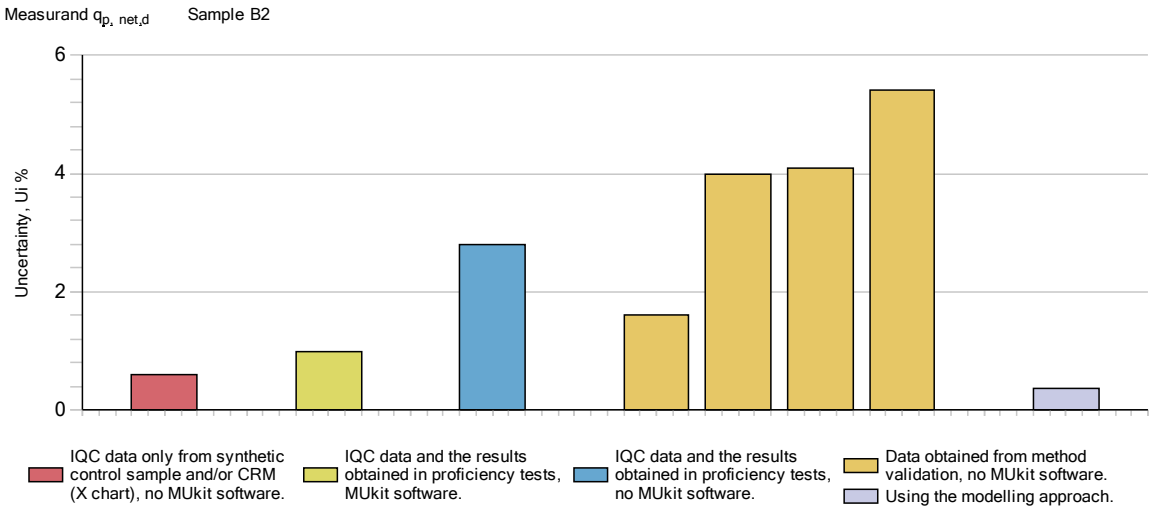

Measurand M_{ad} Sample B1
Uncertainty, Ui %
14
12
10
8
6
4
2
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure

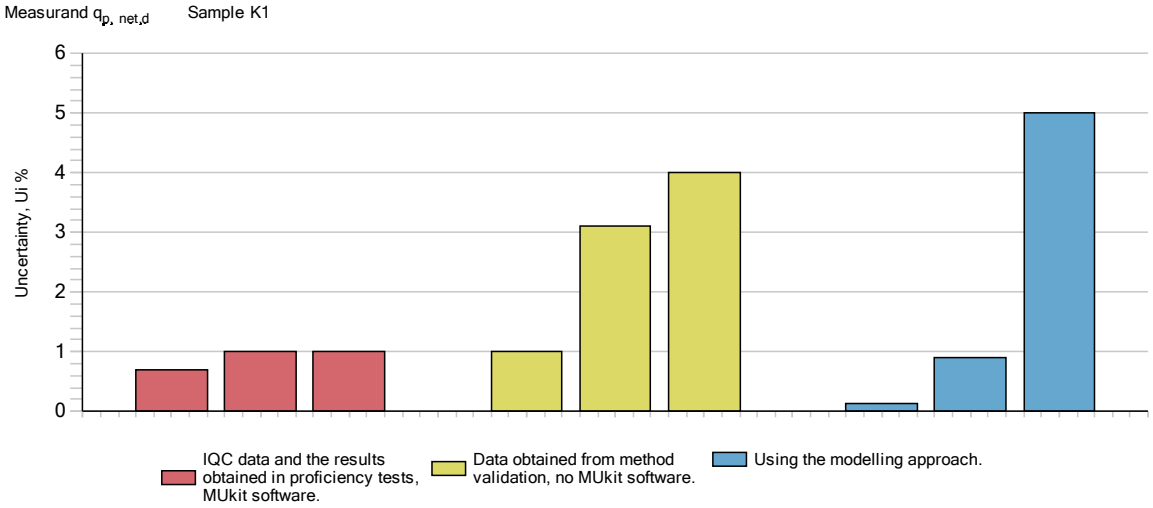

Measurand M_{ad} Sample B2
Uncertainty, Ui %
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure
Using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

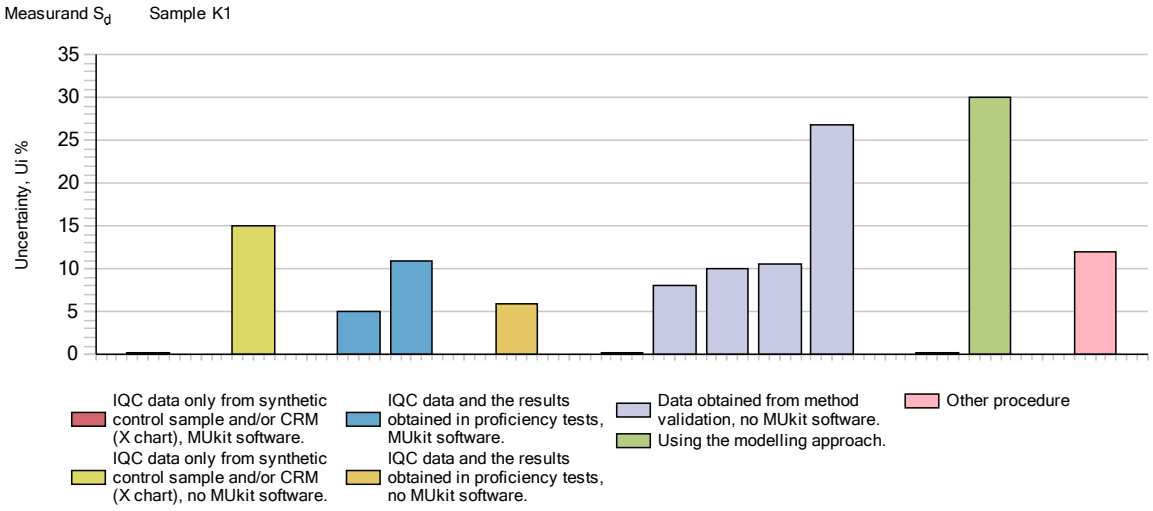

Measurand N_d Sample B2
Uncertainty, Ui %
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.

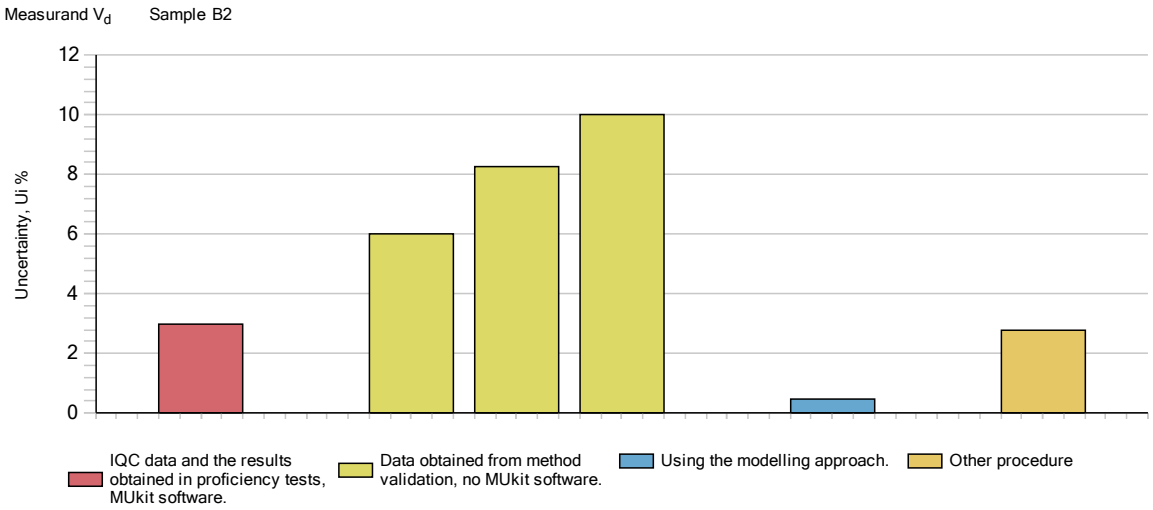

Measurand N_d Sample K1
Uncertainty, Ui %
25
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

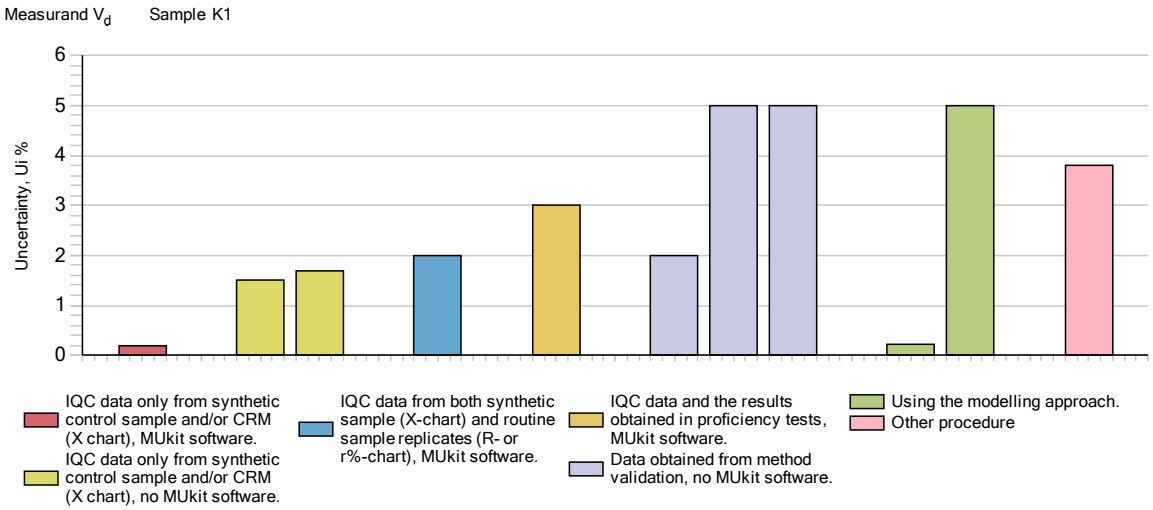

Measurand $q_{p,\ net,d}$ Sample B1
Uncertainty, Ui %
5
4
3
2
1
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand $q_{p,\ net,d}$ Sample B2
Uncertainty, Ui %
0
2
4
6
IQC data only from synthetic control sample and/or CRM (X 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.
Using the modelling approach.


Measurand $q_{p,\ net,d}$ Sample K1
Uncertainty, Ui %
0
1
2
3
4
5
6
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand S_d Sample K1
Uncertainty, Ui %
0
5
10
15
20
25
30
35
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Using the modelling approach.


Measurand V_d Sample B2
Uncertainty, Ui %
12
10
8
6
4
2
0
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
Other procedure


Measurand V_d Sample K1
Uncertainty, Ui %
6
5
4
3
2
1
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no 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, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
Other procedure

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