Reports of the Finnish Environment Institute 7 | 2022

Interlaboratory Proficiency Test 07/2021

Gross and net calorific values in fuels

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

PROF TEST SYKE

Finnish Environment Institute

Reports of the Finnish Environment Institute 7 | 2022

Interlaboratory Proficiency Test 07/2021

Gross and net calorific values in fuels

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

PROF TEST SYKE

ilac-MRA

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

Reports of the Finnish Environment Institute 7 | 2022
Finnish Environment Institute
Laboratory Centre

Author(s): Mirja Leivuori[1], Eliisa Hatanpää[2], Riitta Koivikko[1], Keijo Tervonen[1], Sari Lanteri[1] and Markku Ilmakunnas[1]
[1)] Finnish Environment Institute, Laboratory Centre
[2)] FTF Fuel Testing Finland Oy

Publisher and financier of publication: Finnish Environment Institute SYKE
Latokartanonkaari 11, 00790 Helsinki, Finland, Phone +358 295 251 000, syke.fi

Layout: Markku Ilmakunnas
Cover photo: Adobe Stock

The publication is available in the internet (pdf): syke.fi/publications | helda.helsinki.fi/syke

ISBN 978-952-11-5463-8 (PDF)
ISSN 1796-1726 (online)

Year of issue: 2022

Abstract

Interlaboratory Proficiency Test 07/2021

Proftest SYKE carried out the proficiency test (PT) for the measurements of gross and net calorific value, moisture, the content of ash, bromide, chloride, fluoride, sulphur, carbon, hydrogen, nitrogen, and volatile matter in peat (not Br, F), wood pellet (not Br, Cl, F, S), recycled wood (not Br, F) and coal samples in September–October 2021. In total, there were 35 participants in the PT. The participants could also estimate the emission factor for the peat and coal samples.

The robust mean, the mean, or the median of the results reported by the participants was used as the assigned value for the measurements. The performance evaluation was based on the z scores. In total, 87 % of the reported results were satisfactory, when the deviation of 1–35 % from the assigned value was accepted. For the gross calorific value measurements 75 % of the peat sample, 75 % of the wood pellet sample, 71 % of the recycled wood, and 95 % of the coal sample results were satisfactory. For the net calorific value measurements 73 % of the peat sample, 73 % of the wood pellet, 71 % of the recycled wood, and 94 % of the coal sample results were satisfactory. The performance evaluation was not done for the measurement of moisture content in all samples, chlorine in peat, nitrogen in wood pellet sample, bromide and fluoride in the coal, and emission factor for peat sample. Warm thanks to all the participants in this proficiency test!

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

Tiivistelmä

Laboratorioiden välinen pätevyyskoe 07/2021

Proftest SYKE järjesti syys–lokakuussa 2021 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä analyysikosteuden, tuhkan, bromin, fluorin, kloorin, rikin, hiilen, typen, vedyn ja haihtuvien aineiden määrittämiseksi turpeesta (ei Br, F), puupelletistä (ei Br, Cl, F, S), kierrätyspuusta (ei Br, F) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus arvioida ja/tai laskea turve- ja kivihiilinäytteiden päästökerroin. Pätevyyskokeessa oli yhteensä 35 osallistujaa.

Testisuureiden vertailuarvoina käytettiin osallistujatulosten robustia keskiarvoa, keskiarvoa tai mediaania. Pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa hyväksyttäviä tuloksia oli 87 %, kun vertailuarvosta sallittiin 1–35 % poikkeama. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 77 % (turvenäyte), 75 % (puupelletti), 71 % (kierrätyspuu) ja 95 % (kivihiili). Tehollisen lämpöarvon tuloksista hyväksyttäviä oli 73 % (turvenäyte), 73 % (puupelletti), 71 % (kierrätyspuu) ja 94 % (kivihiili). Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, turpeen kloorin, puupelletin typen sekä kivihiilen bromin ja fluorin määrityksille, eikä päästökertoimelle turvenäytteessä. Kiitos pätevyyskokeen osallistujille!

Avainsanat: pätevyyskoe, vertailumittaus, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, päästökerroin, bromi, fluori, hiili, haihtuvat aineet, kloori, kosteus, tuhka, rikki, typpi, vety, kierrätyspuu, turve, puupelletti, ympäristölaboratoriot

Sammandrag

Provningsjämförelse 07/2021

Proftest SYKE genomförde i september–oktober 2021 en provningsjämförelse som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, askhalt, fukthalt, brom, fluor, klor, svavel, kol, kväve, väte och flyktiga föreningar i torv (inte Br, F), träd pellet (inte Br, Cl. F, S), stenkol och återvunnet trä (inte Br, F). Det var en möjlighet att beräkna emissionfaktor i torv och stenkol prover. Totalt 35 deltagarna deltog i jämförelsen.

Som referensvärde för analyternas koncentration användes det robusta medelvärdet, det medelvärdet eller den medianen av deltagarnas resultat. Resultaten värderades med hjälp av z värden. I jämförelsen var 87 % av alla resultaten acceptabla värderades, när en total deviation på 1–35 % från referensvärdet tilläts. Av de kalorimetriska värmevärdesresultaten var 75 % (torvprov), 75 % (trädpellet), 95 % (stenkol) och 71 % (återvunnet trä) acceptabla. Av de effektiva värmevärdesresultaten var 73 % (torvprov), 73 % (trädpellet), 84 % (stenkol) och 71 % (återvunnet trä) acceptabla. Utvärdering var inte gjort till resultaten av fukthalt i alla prover, beräkning av klor i torv, nitrogen i trädpellet, brom och fluor i stenkol och emissionfaktor i torv provet. Ett varmt tack till alla deltagarna i testet!

Nyckelord: provningsjämförelse, kalorimetriskt och effektivt värmevärde, emissionfaktor, askhalt, brom, fluor, flyktiga föreningar, fukthalt, klor, kol, nitrogen, svavel, väte, stenkol, torv, träd pellet, återvunnet träd, miljölaboratorier

Contents

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of gross and net calorific value in fuels in September–October 2021 (CAL 07/2021). In the PT, gross and net calorific value ($q_{p,net,d}$, $q_{V,gr,d}$), Br_d, C_d, Cl_d, F_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 (not Br, F), wood pellet (not Br, Cl, F, S), recycled wood (not Br, F), 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 with the exception of Br, Cl, and F measurements.

2 Organizing the proficiency test

2.1 Responsibilities

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

The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
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 (no wood pellet): 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 35 laboratories participated in this PT (Appendix 1), 13 from Finland and 22 from abroad. One participant reported two result sets. 66 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025, while one participant did not report their accreditation status. Altogether 80 % 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 20 in result tables.

2.3 Samples and delivery

Four different fuel samples were delivered to the participants: peat (B1), wood pellet (B2), recycled wood (B3), and coal (K1) samples. Gross and net calorific value ($q_{p,net,d}$, $q_{V,gr,d}$), Br_d, C_d, Cl_d, F_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 (not Br, F), recycled wood (not Br, F) wood pellet (not Br, Cl, F, 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 Environment Testing Finland Ltd, Jyväskylä (T025, www.finas.fi/sites/en). The dry recycled wood (B3) was first crushed and then grounded with a cutting mill through the 500 µm sieve at the laboratory of Eurofins Ltd.

The wood pellet sample (B2) was the sample from the previous PT CAL 06/2012 [4]. The sample was rehomogenated and divided again in the laboratory of Proftest SYKE.

The coal sample (K1) was pre-prepared from Polish duff coal by the Helen Ltd (Finland).

The samples were homogenized and divided into sub-samples at the laboratory of KVVY Tutkimus Oy with the exception of wood pellet. 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 46.2 %,
- coal K1 10.8 %

The samples were dispatched to the participants abroad mainly on 6 September 2021 and to the national participants on 7 September 2021. The samples arrived to the participants mainly by 10 September 2021, and some participants received the samples at the latest on 14 September 2021. The samples of one participant abroad were returned to the provider. The samples were re-delivered, and they arrived to the participant on 23 September 2021.

The results were reported at the latest on 6 October 2021, as requested. The preliminary results report was delivered to the participants via ProftestWEB and email on 13 October 2021.

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 three to six 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 experience of the provider the samples are known to be stable over the given time period of the test.

Particle size distribution was also tested from one sub sample of both 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 dealt with the sample delivery problems or the results reporting. The comments from the provider focused mainly on the missing background information or reporting the data contrary to the instructions of the organizer. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Hampel or the Grubbs test before calculating the mean. The results which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

The participants were to report replicate results for all the measurements. The replicate results were tested using the Cochran's test, which compares the within-laboratory deviation of each participant to the standard deviation of the replicate results of all the participants. The replicate results which differ significantly from others are outliers. The Cochran's test rejects the results having significantly higher within-laboratory deviation than the results the average, regardless their z score evaluation. When two results were to be reported for the analysis and the participant reported only one, the result was not included in the statistical calculations and it was not evaluated.

More information about the statistical handling of the data is available from the Guide for participant [5].

2.6.2 Assigned values

Mainly the robust mean of the results reported by the participants 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: Cl_d, Ma_d, S_d, V_d; B2: N_d, K1: F_d) or the mean (B1: C_d, EF, H_d, N_d, $q_{p,net,d}$, $q_{V,gr,d}$; B2: $q_{p,net,d}$, V_d; B3: C_d, Cl_d, H_d, $q_{p,net,d}$, V_d; K1: Cl_d, EF, $q_{p,gr,d}$) of

participants' results was used as the assigned value. Assigned value was not set for Br_d in the coal sample due to high variation of the results. Detailed information of the assigned values, their uncertainties, and reliabilities is shown in Appendix 5.

The assigned values based on the robust mean, the mean, or the median are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned values was statistically tested [2, 3].

When the robust mean, the mean, or the median of the results reported by the participants was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation [2, 5].

When using the robust mean, the mean or the median of the participant results as the assigned value, the uncertainties of the assigned values varied between 0.2 % and 0.5 % for calorific values. For the other evaluated measurands the expanded uncertainty varied from 0.4 % to 14 % (Appendix 5). **After reporting the preliminary results report no changes have been done for the assigned values.**

2.6.3 Proficiency assessment procedure

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

The requirements for the reproducibility given in the used standard methods, and also listed in the cover letter of the samples, were used for estimation of standard deviation for proficiency assessment in this PT. The reproducibility required by the standard methods was mainly fulfilled for gross calorific values. The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 1–35 % depending on the measurements. Standard deviation for proficiency assessment was not given for analysis moisture content M_{ad} (all samples), and thus the results were not evaluated. Due to the high deviation of the results for nitrogen (N_d) in wood pellet sample and bromide (Br_d) and fluoride (F_d) in the coal sample no evaluation is given. The number of results for chlorine and emission factor (EF) in the peat sample was too low for result evaluation.

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

When using the robust mean, the mean or the median 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 [2, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

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

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

Sample	Measurand
B3	S_d

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 22 % for the evaluated results (Table 1). The robust standard deviation or the standard deviation was lower than 2 % for 43 % of the reported results and lower than 6 % for 71 % of the results (Table 1). For Cl_d, S_d in the sample B1, Ash_d and N_d in the sample B2, Cl_d, M_{ad}, N_d and S_d in the sample B3, and Br_d, Cl_d, F_d, N_d in the sample K1 the robust standard or the 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 for the same measurands tested as in the previous similar PT Proftest SYKE CAL 07/2020, where the standards deviations varied from 0.2 % to 12.9 % [6].

In this PT 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 the technical specifications related to the measurements of fuels. Particularly, for measurements of the calorific values, the requirement for the repeatability is ± 120 J/g. In this PT the requirements for the repeatability of the measurements for the gross calorific value were 0.53 % for the sample B1, 0.59 % for the sample B2, 0.61 % for the sample B3, and 0.45 % for the sample K1 and for the net calorific value 0.56 %, 0.59 %, 0.65 %, and 0.46 %, respectively. 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 %) with exception of the gross calorific value in the recycled wood (B3).

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 3.2 in the sample B1, 2.7 in the sample B2, 0.45 in the sample B3 and 4.2 in the sample K1, for the net calorific values 2.7, 3.0, 3.4 and 4.4, respectively. For the calorific values the ratio s_b/s_w was almost in the same range than in the previous similar PT CAL 07/2020 [6].

Table 1. The summary of the results in the proficiency test CAL 07/2021.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} % / s%	2 x s_{pt} %	n_{all}	Acc z %
Ash_d	B1	w%	4.32	4.29	4.32	4.34	0.14	3.3	7	13	85
	B2	w%	0.30	0.30	0.30	0.30	0.04	15.2	30	17	94
	B3	w%	3.17	3.18	3.17	3.16	0.18	5.8	15	16	88
	K1	w%	17.8	17.8	17.8	17.8	0.1	0.7	2.5	25	96
Br_d	K1	mg/kg		16.1	-	11.8	*9.0*	*55.9*	-	8	-
C_d	B1	w%	55.3	55.3	55.3	55.2	0.5	0.9	2.5	8	100
	B2	w%	50.4	50.5	50.4	50.5	0.6	1.1	2.5	12	92
	B3	w%	49.0	49.0	49.0	49.0	0.5	1.0	2.5	12	92
	K1	w%	66.2	66.2	66.2	66.1	0.8	1.2	2.5	22	95
Cl_d	B1	mg/kg	255	251	-	255	*35*	*14.1*	-	6	-
	B3	mg/kg	572	572	570	577	124	21.8	35	11	82
	K1	mg/kg	569	569	569	571	38	6.7	20	13	54
EF	B1	t CO2/TJ	106	106	-	107	*1.0*	*1.3*	-	6	-
	K1	t CO2/TJ	94.3	94.3	94.3	94.3	1.5	1.6	4	10	80
F_d	K1	mg/kg	114	121	-	114	*13.0*	*11.0*	-	8	-
H_d	B1	w%	5.99	5.99	5.97	5.97	0.15	2.5	7	9	100
	B2	w%	6.18	6.18	6.18	6.18	0.13	2.0	6	13	100
	B3	w%	6.07	6.08	6.07	6.02	0.14	2.3	6	13	100
	K1	w%	4.28	4.27	4.28	4.30	0.15	3.5	7	19	89
M_{ad}	B1	w%	4.57	4.51	4.44	4.57	0.26	5.8	-	12	-
	B2	w%	6.20	6.20	6.20	6.26	0.23	3.7	-	16	-
	B3	w%	4.54	4.56	4.54	4.69	0.55	12.1	-	16	-
	K1	w%	3.46	3.47	3.46	3.43	0.14	4.2	-	26	-
N_d	B1	w%	1.76	1.76	1.75	1.74	0.05	3.0	10	9	100
	B2	w%	0.07	0.11	0.10	0.07	0.07	75.4	-	11	-
	B3	w%	1.05	1.04	1.04	1.05	0.10	9.8	20	12	91
	K1	w%	1.18	1.18	1.18	1.20	0.07	6.2	15	16	93
$q_{p,net,d}$	B1	J/g	21348	21348	21348	21369	111	0.5	1.5	11	73
	B2	J/g	18847	18847	18849	18864	86	0.5	1.6	15	73
	B3	J/g	18434	18434	18434	18420	136	0.7	1.7	14	71
	K1	J/g	25978	25975	25978	25998	99	0.4	1.2	18	94
$q_{V,gr,d}$	B1	J/g	22598	22598	22583	22593	95	0.4	1.3	12	75
	B2	J/g	20176	20170	20176	20189	98	0.5	1.4	16	75
	B3	J/g	19737	19727	19737	19748	155	0.8	1.5	17	71
	K1	J/g	26881	26881	26887	26895	117	0.4	1.1	23	95
S_d	B1	w%	0.17	0.17	0.17	0.17	0.02	10.1	20	10	80
	B3	w%	0.06	0.06	0.06	0.06	0.01	19.9	35	16	75
	K1	w%	0.90	0.92	0.90	0.91	0.05	5.5	10	25	83
V_d	B1	w%	70.5	71.0	-	70.5	*0.8*	*1.2*	3	7	100
	B2	w%	84.7	84.7	84.7	84.7	0.7	0.8	3	10	90
	B3	w%	79.7	79.7	79.7	79.8	0.8	1.0	3	11	100
	K1	w%	31.4	31.4	31.4	31.3	0.8	2.6	5	21	85

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, *s: the standard deviation, s %: the standard deviation as percent*, 2×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 $|z| \leq 2$.

Table 2. The summary of repeatability based on 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%	4.32	4.29	0.05	0.25	0.26	1.2	5.8	5.9	4.7
	B2	w%	0.30	0.30	0.02	0.05	0.05	5.8	15	16	2.6
	B3	w%	3.17	3.18	0.08	0.21	0.23	2.4	6.7	7.1	2.8
	K1	w%	17.8	17.8	0.07	0.16	0.17	0.37	0.89	0.96	2.4
Br_d	K1	mg/kg	-	16.1	0.52	8.98	9.00	3.3	56	56	17
C_d	B1	w%	55.3	55.3	0.11	0.42	0.43	0.20	0.75	0.78	3.8
	B2	w%	50.4	50.5	0.12	0.61	0.63	0.24	1.2	1.2	5.1
	B3	w%	49.0	49.0	0.21	0.41	0.46	0.42	0.83	0.93	2.0
	K1	w%	66.2	66.2	0.14	0.73	0.74	0.21	1.1	1.1	5.3
Cl_d	B1	mg/kg	255	251	7.19	35.1	35.8	2.9	14	14	4.9
	B3	mg/kg	572	572	28.5	111	114	5.0	19	20	3.9
	K1	mg/kg	569	569	15.7	31.9	35.5	2.8	5.6	6.2	2.0
EF	B1	t CO2/TJ	106	106	0.35	1.31	1.36	0.33	1.2	1.3	3.7
	K1	t CO2/TJ	94.3	94.3	0.20	1.30	1.31	0.21	1.4	1.4	6.5
F_d	K1	mg/kg	114	121	7.36	12.2	14.3	6.1	10	12	1.7
H_d	B1	w%	5.99	5.99	0.09	0.22	0.23	1.4	3.6	3.9	2.6
	B2	w%	6.18	6.18	0.04	0.14	0.14	0.68	2.2	2.3	3.2
	B3	w%	6.07	6.08	0.04	0.18	0.18	0.63	2.9	3.0	4.6
	K1	w%	4.28	4.27	0.06	0.14	0.15	1.3	3.4	3.6	2.6
M_{ad}	B1	w%	4.57	4.51	0.03	0.37	0.37	0.61	8.4	8.5	14
	B2	w%	6.20	6.20	0.04	0.26	0.26	0.64	4.2	4.2	6.5
	B3	w%	4.54	4.56	0.07	0.54	0.54	1.6	12	12	7.5
	K1	w%	3.46	3.47	0.02	0.21	0.21	0.67	6.0	6.0	9.0
N_d	B1	w%	1.76	1.76	0.01	0.07	0.07	0.79	3.7	3.8	4.7
	B2	w%	0.07	0.11	0.01	0.08	0.08	10	78	78	7.5
	B3	w%	1.05	1.04	0.04	0.11	0.12	3.5	10	11	2.9
	K1	w%	1.18	1.18	0.0206	0.06	0.06	1.7	5.2	5.5	3.0
$q_{p,net,d}$	B1	J/g	21348	21348	34.4	94.7	101	0.16	0.44	0.47	2.7
	B2	J/g	18847	18847	25.5	77.0	81.1	0.14	0.41	0.43	3.0
	B3	J/g	18434	18434	35.1	118	123	0.19	0.64	0.67	3.4
	K1	J/g	25978	25975	24.4	106	109	0.09	0.41	0.42	4.4
$q_{V,gr,d}$	B1	J/g	22598	22598	38.0	123	129	0.17	0.55	0.57	3.2
	B2	J/g	20176	20170	35.7	95.6	102	0.18	0.47	0.51	2.7
	B3	J/g	19737	19727	188	84.9	207	0.95	0.43	1.0	0.45
	K1	J/g	26881	26881	27.7	116	119	0.10	0.43	0.44	4.2
S_d	B1	w%	0.17	0.17	0.005	0.01	0.02	3.0	8.6	9.1	2.9
	B3	w%	0.06	0.06	0.006	0.01	0.01	9.7	18	20	1.8
	K1	w%	0.90	0.92	0.011	0.14	0.14	1.3	17	17	13
V_d	B1	w%	70.5	71.0	0.32	0.81	0.87	0.45	1.1	1.2	2.5
	B2	w%	84.7	84.7	0.22	0.60	0.64	0.26	0.71	0.76	2.8
	B3	w%	79.7	79.7	0.15	0.77	0.79	0.19	0.97	0.99	5.2
	K1	w%	31.4	31.4	0.18	0.80	0.82	0.58	2.5	2.6	4.3

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

3.2 Analytical methods

The participants could use different analytical methods for the measurements in the PT. A survey of the used analytical methods was carried out along the PT. 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 was possible for the methods where the number of the results was ≥ 5 (only C_d, S_d, V_d in the sample K1). In the other 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 ISO 18125 [7], ISO 1928 [8], EN 15400 [9] Appendix 12). One participant used standard ASTM D 5865 [10] or DIN 51900 [11]. Reported other used methods were mainly internal methods.

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 on 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 on 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 the additional measurands

In the PT mainly the following standard methods or technical specifications were used for measurements of different parameters (Table 3).

Table 3. Used international standard in the measurements of the additional measurands.

Measurand	Method
Ash_d	EN 14775 [12], ISO 1171 [13], EN ISO 18122 [14], ASTM D 7582 [15], EN 15403 [16]
C_d, H_d and N_d	ISO 29541 [17], ASTM D 5373 [18], EN ISO 16948 [19], EN 15407 [20],
M_{ad} (analytical moisture content)	ISO 589 [21], DIN 51718 [22], ASTM D 7582 [15], EN ISO 18134-3 [23], ISO 11722 [24]
S_d	EN ISO 16994 [25], ASTM D 4239 [26], ISO 334 [27], ISO 19579 [28], EN 15408 [29], EN 15289 [30]
V_d, (volatile matter)	ISO 562 [31], EN ISO 18123 [32], EN 15402 [33]
Br_d	EN ISO 16994 [25], ASTM D 8247 [34]
Cl_d	EN ISO 16994 [25}, EN 15408 [29], ASTM D 8247 [34], ASTM D 4208 [35]
F_d	EN ISO 16994 [25], EN 15408 [29], ASTM D 8247 [34]

However, in some cases also other international and national standards or technical specifications (e.g. DIN 51719, ASTM D 3174, ASTM D 4422, ASTM D 5291, EN ISO 21663 (see [20]), EN 15414, ASTM D 3173, ASTM D 4239, ASTM D 6376, ASTM D 7359, EN ISO 16173, EN 14582, ISO 5071-1, ASTM D 7582, ASTM D 3175, ASTM D 5291, ISO 10304-1, ISO 11724) or internal methods were used.

Moisture content was determined gravimetrically or by using TGA in air or N_2 atmosphere (Appendix 11). The ash content was determined mainly gravimetrically by heating at the temperature 550 °C or 815 °C (Samples B1, B2 and B3), and at the temperature 750 °C, 750 °C or 815 °C (Sample K1, Appendix 11). 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, while in ISO 1171 for solid mineral fuels it is mentioned to be 815 °C [13, 14]. Based on the graphical result evaluation, clear differences between the used methods in measurements could not be concluded (Appendix 12).

Most of the participants conducted CHN analyses as received and correction for moisture, while from one to four participants used dried samples at the temperature 105 °C depending the sample type (Appendix 11). No statistical difference between the used methods was noticed for C, S, and V in the sample K1. Based on the graphical result evaluation clear differences between the used methods for CHN, S or V measurands could not be concluded (Appendix 12).

Also Br, Cl, and F from suitable samples were to be measured in the PT (Tables 1 and 3, Appendices 11 and 12). Mostly, those were measured using the international standards EN ISO 16994 [25], EN 15408 [29] or ASTM D 8247 [34], but also some others methods were used (Table 3, Appendices 11 and 12). Mainly the samples were digested in oxygen bomb using water, KOH, $NaOH+H_2O_2$ or Na_2CO_3. Mostly the measurands were measured by ion chromatography, but also titration and potentiometric measurements were used (Appendix 11). There were only few results for bromine and fluorine and the variation of those was high.

Further, information of the detection limits was collected for some measurands (Appendix 11). The ranges of the reported detection limits were for Br:10-50 mg/kg, for Cl: 0.04-500 mg/kg, for F: 10-50 mg/kg, N: 0.0001-1.87 w%, and for S: 0.0001-0.995 w%. The wide ranges suggest that the detection limits are probably reported in several different units.

3.3 Uncertainties of the results

At maximum 59 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 4, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for evaluating the measurement uncertainty (Appendix 13). The most used approaches were based on method validation data and IQC data. Three participants reported the usage of the MUkit measurement uncertainty software for the uncertainty estimation for some measurands [36, 37]. The free software is available on the webpage: www.syke.fi/envical/en. Generally, the used approach for evaluating the measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 4. The ranges of the reported expanded uncertainties by participants as percent (k=2, U_i%).

Measurement	Uncertainty % B1	Uncertainty % B2	Uncertainty % B3	Uncertainty % K1
Ash_d	4-18	0.09-41.4	0.66-37	0.18-10
Br_d	-	-	-	1.0-45
C_d	0.6-5	0.6-5	0.6-12	0.39-5.6
Cl_d	25-35	-	20-49	25-48
EF	8-10	-	-	2-8
F_d	-	-	-	10-45
H_d	5-10	0.37-10	0.41-20	0.14-10
M_{ad}	4-13.5	0.1-33.9	0.2-13	0.02-36
N_d	8-17	0.01-**100**	0.06-50	0.06-17
$q_{p,net,d}$	0.6-5	0.6-***277***	0.6-***292***	0.08-***371***
$q_{v,gr,d}$	0.8-***150***	0.8-***150***	0.8-***150***	0.08-***165***
S_d	10-30	-	0.0058-37	0.05-30
V_d	3-5	0.2-6	0.6-6	0.24-5.5

[1)] In table with bold the values of expanded measurement uncertainty over 50 % and with italic the values over 100 %.

The evaluated measurement uncertainties varied highly for all the tested measurands (Table 4). Especially, very low or high uncertainties can be considered very questionable. **It was evident, that some uncertainties had been reported erroneously** (including calorific values, bolded italic numbers in Table 4, 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. Harmonization of the uncertainties' estimation should be continued.

3.4 Estimation of emission factor

The participants were to estimate also the emission factors [38, 39] 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 were 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, some participants (6-10 participants, depending on the sample) reported their results for the emission factor (Table 1, Appendices 8, 11 and 12). Due to the low number of the reported results and the high variation between the results, the performance evaluation was not given for the peat sample (B1).

4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for proficiency assessment (Appendix 7). The z scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 87 % of the results evaluated based on z scores were satisfactory when accepting the deviation of 1–35 % from the assigned value (Appendix 9). About 80 % of the participants used the accredited methods and 71 % of their results were satisfactory. In the previous proficiency test CAL 07/2020 the performance was satisfactory for 89 % of the results when deviation 1–30 % from the assigned value

was accepted [6]. The summary of the performance evaluation is shown in Table 5. The percentage of the satisfactory results varied between 84 % and 89 % for the tested sample types.

The criteria for performance evaluation were mainly set according to the target value for reproducibility recommended in international standards for measurement of the calorific values and other determinations. 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 PT (CAL 07/2020) 89 % of the results were satisfactory for the peat sample (B1) when accepting 1.4–15 % deviation from the assigned value [6], and the performance was at the same level in this PT (Table 5). In the previous PT, the gross and the net calorific values 79 % and 83 % of the results, respectively, were satisfactory [6]. In this PT the satisfactory number of the results for the gross and net calorific values were 75 % and 73 %, respectively. Thus, there was lower number of satisfactory results for the calorific values in this PT. The results of analysis moisture (M_{ad}), chlorine and emission factor (EF) have not been evaluated, but the assigned values are presented (Table 1).

Wood pellet

In the previous PT (CAL 07/2020) the satisfactory results of the wood pellet sample (B2) were in total 84 %, when accepting deviation 1.4–30 % from the assigned value [6], thus the performance in this PT was slightly higher (87 %, Table 5). The satisfactory results varied between 73 % ($q_{p,net,d}$) and 100 % (H_d) for the wood pellet sample (Table 1). In the measurement of gross and net calorific values 75 % and 73 % 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 lower for the calorific values for wood pellet than in the previous PT (80 % and 76 %, respectively) [6]. 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).

Table 5. Summary of the performance evaluation in the proficiency test CAL 07/2021.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
Peat, B1	89	1.3 – 20	• Good performance. • Difficulties in measurements for $q_{p,net,d}$ and $q_{p,gr,d}$, < 80% satisfactory results. • In the CAL 07/2020 the performance was satisfactory for 89 % of the results, when accepting deviation of 1.4-15 % from the assigned value [6].
Wood pellet, B2	87	1.4 – 30	• Good performance. • Difficulties in measurements for $q_{p,net,d}$ and $q_{Vgr,d}$ < 80% satisfactory results. • In the CAL 07/2020 the performance was satisfactory for 84 % of the results [6].
Recycled wood, B3	85	1.5 – 35	• Good performance. • Difficulties in measurements for $q_{p,net,d}$, $q_{V,gr,d}$, and S_d, < 80% satisfactory results. • Informative evaluation for S_d.
Coal, K1	87	1.1 – 20	• Good performance. • Difficulties in measurements for Cl_d, < 80% satisfactory results. • In the CAL 07/2020 the performance was satisfactory for 92 % of the results when accepting deviation of 1-15 % from the assigned value [6].

Recycled wood
In the PT the satisfactory results of the recycled wood sample (B3) were in total 85 %, when accepting deviation 1.5–50 % from the assigned value The satisfactory results varied between 71 % ($q_{p,net,d}$, $q_{p,gr,d}$) and 100 % (H_d, V_d) for the recycled wood sample (Table 1). The estimation of EF was not done as it is a CO_2 neutral fuel. Also, the results of analysis moisture (M_{ad}) have not been evaluated, but the assigned value is given (Table 1).

Coal
In the previous PT (CAL 07/2020) the satisfactory results of the coal sample (K1) were in total 92 %, thus the performance was somewhat lower in this PT (87 %, Table 5) [6]. The satisfactory results varied between 54 % (Cl_d) and 96 % (Ash_d) (Table 1). In the measurement of gross and net calorific values, 95 % and 94 % of results, respectively, were satisfactory, when accepting the deviations of 1.1 and 1.2 % from the assigned values (Table 1). The number of the satisfactory results was higher for the gross and net calorific values for the coal samples than in the previous PT (90 % and 82 %, respectively) [6]. The results of analysis moisture (M_{ad}), bromide (Br_d) and fluoride (F_d) have not been evaluated, but the assigned value is given (Table 1).

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of gross and net calorific value in fuels in September 2021 (CAL 07/2021). In the PT, gross and net calorific value ($q_{p,net,d}$, $q_{v,gr,d}$), Br_d, C_d, Cl_d, F_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 (not Br, F), wood pellet (not Br, Cl, F, S), recycled wood (not Br, F), and coal samples. Additionally, the participants were asked to estimate the emission factors (EF) for the peat and coal samples. In total 35 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 0.5 % for calorific values and at maximum 14 % 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 moisture content (M_{ad}) in all samples, nitrogen (N_d) in wood pellet sample, bromide (Br_d) and fluoride (F_d) in the coal, and chlorine and emission factor for peat sample. In the PT 87 % 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 35 %. About 80 % of the participants used the accredited methods and 71 % of their results were satisfactory. In measurements of the gross calorific value from the peat, the wood pellet, the recycled wood, and the coal samples, 75 %, 75 %, 71 % and 95 % of the results were satisfactory, respectively. In measurements of the net calorific value from the peat, the wood pellet, the recycled wood, and the coal samples, 73 %, 73 %, 71 % and 94 % of the results were satisfactory, respectively. In the PT the number of the satisfactory results for the gross and net caloric values was lower in the peat (B1) and wood pellet (B2) samples, while they were higher for the coal (K1) sample than in the previous PT CAL 07/2020 [6].

6 Summary in Finnish

Proftest SYKE järjesti pätevyyskokeen kalorimetrista ja tehollista lämpöarvoa polttoaineista analysoiville laboratorioille syys-lokakuussa 2021 (CAL 07/2021). Pätevyyskokeessa testattiin kalorimetrinen ja tehollinen lämpöarvo ($q_{p,net,d}$, $q_{v,gr,d}$), Br_d-, C_d-, Cl_d-, F_d-, S_d-, H_d-, N_d-, analyysikosteus (M_{ad})- ja tuhkapitoisuus (Ash_d) sekä haihtuvat aineet(V_d) turpeesta (ei Br, F), puupelletistä (ei Br, Cl, F, S), kierrätyspuusta (ei Br, F) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus laskea päästökerroin turve- ja kivihiilinäytteistä. Pätevyyskokeessa oli 35osallistujaa.

Testisuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai niiden keskiarvoa tai mediaania. Vertailuarvon epävarmuus oli lämpöarvomäärityksissä pienempi tai yhtä suuri kuin 0,5 % ja muiden määritysten osalta korkeintaan 14 %.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, typen määritykselle puupelletistä, bromin ja fluorin määritykselle kivihiilestä eikä turpeen kloorimääritykselle ja päästökertoimelle. Koko tulosaineistossa hyväksyttäviä tuloksia oli 87 %, kun vertailuarvosta sallittiin 1–35 % poikkeama. Noin 80 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 71 %. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 75 % turve, 75 % puupelletti, 71 % kierrätyspuu ja 95 % kivihiili. Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 73 % turve, 73 % puupelletti, 71 % kierrätyspuu ja 94 % kivihiili. Kalorimetrisen ja tehollisen lämpöarvon määritysten osalta menestyminen oli turve- ja puupelletti näytteissä alhaisempi ja kivihiilessä parempi kuin edellisessä pätevyyskokeessa CAL 07/2020 [6].

References

1. SFS-EN ISO 17043, 2010. Conformity assessment – General requirements for Proficiency Testing.
2. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.
3. Thompson, M., Ellison, S. L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report).
4. Leivuori, M., Rantanen, M., Björklöf, K., Tervonen, K., Lanteri, S. and Ilmakunnas, M. 2012. SYKE Proficiency Test 6/2012. Gross and net calorific value in fuels. Reports of Finnish Environment Institute 4/2013. (https://helda.helsinki.fi/handle/10138/40180*)*.
5. Proftest SYKE Guide for laboratories: www.syke.fi/proftest/en → Running proficiency test (www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886).
6. Leivuori, M., Hatanpää, E., Koivikko, R., Tervonen, K., Lanteri, S., and Ilmakunnas, M. 2020. Proficiency test 07/2020. Gross and net calorific value in fuels. Reports of Finnish Environment Institute 46/2020. 82 pp. (http://hdl.handle.net/10138/322340).
7. EN ISO 18125, 2017. Solid biofuels- Determination of calorific value.
8. ISO 1928, 2009. Solid mineral fuels - Determination of gross calorific value by a bomb calorimetric method, and calculation of net calorific value.
9. EN 15400, 2011. Solid recovered fuels – Determination of calorific value (withdrawn – replaced with EN ISO 21654:2021).
10. ASTM D 5865, 2013. Test method for gross calorific value of coal and coke.
11. DIN 51900, 2000. Determining the gross calorific value of solid and liquid fuels using the bomb calorimeter, and calculation of net calorific value.
12. EN 14775, withdrawn on 31.10.2017. Solid biofuels. Determination of ash content.
13. ISO 1171, 2010 Solid mineral fuels - Determination of ash.
14. EN ISO 18122, 2015. Solid biofuels - Determination of ash content.
15. ASTM D 7582, 2015. Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis.
16. EN 15403, 2011. Solid recovered fuels - Determination of ash content (withdrawn- replaced with EN ISO 21656: 2021).
17. ISO 29541, 2010. Solid mineral fuels - Determination of total carbon, hydrogen and nitrogen content - Instrumental methods.
18. ASTM D 5373, 2013. Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke.

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

20. EN 15407, 2011. Solid recovered fuels - Methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content (withdrawn – replaced with EN ISO 21663:2020).

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

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

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

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

25. EN ISO 16994, 2016. Solid biofuels - Determination of total content of sulfur and chlorine.

26. ASTM D 4239, 2018. Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High - Temperature Combustion and Infrared Absorption.

27. ISO 334, 2013. Solid mineral fuels — Determination of total sulfur — Eschka method.

28. ISO 19579, 2006. Solid mineral fuels – Determination of total sulfur by IR spectrometry.

29. EN 15408, 2011. Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content.

30. EN 15289, 2011. Solid biofuels - Determination of total content of sulfur and chlorine (withdrawn-replaced with EN ISO 16994:2016).

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

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

33. EN 15402, 2011. Solid recovered fuels - Determination of the content of volatile matter (withdrawn- replaced with EN ISO 22167:2021)..

34. ASTM D 8247, 2019. Standard Test Method for Determination of Total Fluorine and Total Chlorine in Coal by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection.

35. ASTM D 4208, 2019. Standard Test Method for Total Chlorine in Coal by the Oxygen Vessel Combustion/Ion Selective Electrode Method.

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

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

38. EU 2018/2066, 2018. Commission Implementing Regulation (EU) 2018/2066 of 19 December 2018 on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of

the European Parliament and of the Council and amending Commission Regulation (EU) No 601/2012 (19.10.2018). (http://data.europa.eu/eli/reg_impl/2018/2066/oj)

39. Guidance Document No. 1, 2017. The Monitoring and Reporting Regulation- General guidance for installations. European Commission. (https://ec.europa.eu/clima/system/files/2018-07/gd1_guidance_installations_en.pdf)

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

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

42. JCGM GUM-6, 2020. Guide to Expression of Uncertainty in Measurements – Part 6: Developing and Using Measurement Models. (https://www.bipm.org/documents/20126/50065290/JCGM_GUM_6_2020.pdf/d4e77d99-3870-0908-ff37-c1b6a230a337)

Appendix 1. Participants in the proficiency test

Country	Participant
Bosnia-Hertsegovina	Rudnik uglja "Kreka" d.o.o.-Tuzla
Bulgary	AES-3C Maritza East 1 EOOD; Testing Laboratory "Energy Materials"
Estonia	Enefit Energiatootmine AS Chemical Laboratory
Finland	Eurofins Environment Testing Finland Oy, Energy & Water 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 Kuusakoski Recycling Neste Corporation, Technology Center, Kilpilahti Savo-Karjalan Ympäristötutkimus Oy, Joensuu Savo-Karjalan Ympäristötutkimus Oy, Kuopio SeiLab Oy Haapaveden toimipiste SSAB Europe Raahe, Raahe
France	ArcelorMittal Fos sur Mer Eurofins Analyses des Materiaux et Combustibles France SOCOR Dechy France
Italy	Nuova Tecnogest SRL
Republic of Ireland	Edenderry Power Ltd
Republic of Korea	Intertek KIMSCO Ulsan Testing Center, South Korea
Romania	Ceprocim S.A. Romania CRH Ciment (Romania)-Punct de lucru Hoghiz Holcim Romania -Ciment Alesd Laborator analize fizico-chimice apa si carbune, Romania Romcontrol Constanta Laboratory Rompetrol Quality Control SRL-Laborator Produse Petroliere
Slovakia	Ekolab s.r.o.
Slovenia	Salonit Anhovo
Spain	Centro de Investigacion Elias Masaveu S.A. Laboratorio Central de Calidad - LCC
Sweden	Cementa AB Eurofins Water Testing Sweden AB RISE Research Institutes of Sweden AB

Appendix 2. Sample preparation

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 Environment Testing Finland Ltd, (Jyväskylä, Finland). The dried and sieved sample was mixed by a mechanized sample mixer and distributed to sub-samples of ca. 25g 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 Environment Testing Finland Ltd (Jyväskylä) using laser diffraction (Malvern).

Sample B3, recycled wood
For the sample B3 the dry crushed recycled wood was grounded with grinding mill and sieved with 500 µm sieve at the laboratory of Eurofins Environment Testing Finland Ltd. The sieved sample was mixed by a mechanized sample mixer and distributed to subsamples of ca. 25 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of KVVY Tutkimus Oy (Tampere).

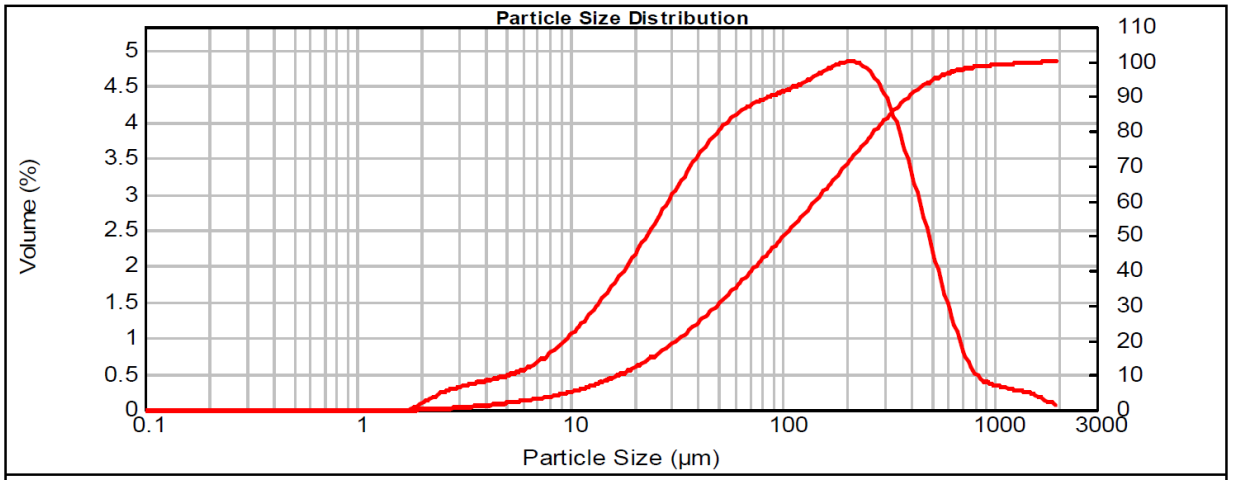
Sample K1, steam coal fuel
Sample K1 was Polish duff coal. The coal was dried at room temperature and ground to particle size < 212 µm at Helen Ltd (Finland). The dried and sieved sample was mixed by a mechanized sample mixer and distributed into subsamples of ca. 25 g using a rotary sample divider equipped 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 102 µm and ca. 98 % of the particles were smaller than 550 µm. For coal sample K1 the mean size of particles was 32.6 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 [7, 8].

a)



b)

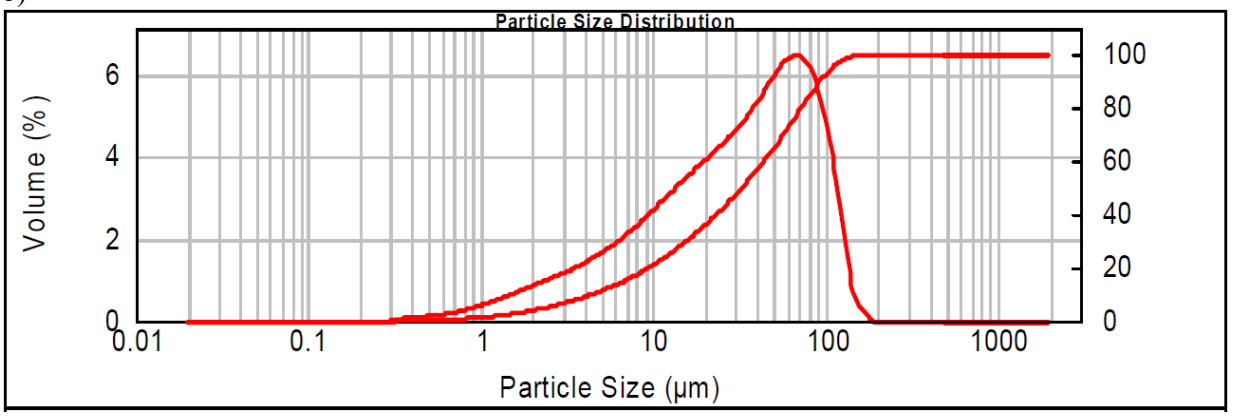


Figure 1. The particle size distribution of the fuel samples a) the peat (B1) and b) the coal (K1) sample

Appendix 3. Homogeneity of the samples

Homogeneity was tested from duplicate measurements of calorific value (Table 1) and ash content from the samples. Additionally, the other measurands from two samples was tested.

Criteria for homogeneity:

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

s_{pt} = standard deviation for proficiency assessment
s_{anal} = analytical deviation, standard deviation of the results in a sub samples
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
$s_{all}^2 = (0.3 \times s_{pt})^2$

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), wood pellet (B2), recycled wood (B3) and coal (K1) samples.

Measurements	n	Mean	s_{pt}%	s_{pt}	s_{anal}	s_{anal}/s_{pt}	Is $s_{anal}/s_{pt}<0.5$?	s_{sam}	s_{sam}^2	c	Is $s_{sam}^2<c$?
Peat (B1)											
Gross calorific value, J/g	5	22551	0.65	147	37.7	0.26	yes	47.5	2250	7560	yes
Net calorific value, J/g	5	21162	0.75	159	37.7	0.24	yes	47.5	2250	8350	yes
Wood pellet (B2)											
Gross calorific value, J/g	3	20073	0.7	141	35.5	0.25	yes	85.1	7230	10710	yes
Net calorific value, J/g	3	18756	0.8	150	35.5	0.24	yes	85.1	7240	11460	yes
Recycled wood (B3)											
Gross calorific value, J/g	6	19502	0.75	146	77.0	0.53	no[1]	80.1	6410	13820	yes
Net calorific value J/g	6	18187	0.85	155	64.1	0.41	yes	92.9	8630	11720	yes
Coal (K1)											
Gross calorific value, J/g	5	27049	0.55	149	22.6	0.15	yes	1.69	2.85	5790	yes
Net calorific value J/g	4	26167	0.6	157	22.2	0.14	yes	6.20	38	7830	yes

[1]Included within the analytical error. n= number of tested sample

Conclusion: All criteria for homogeneity were fulfilled and the samples could be considered 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 excecution	Action / Proftest SYKE
35	The samples of the participant were returned to the organizer.	The used distributor did not reach the participant. The provider delivered new samples to the participant.

Participant	Comments to the results	Action / Proftest SYKE
11	The results for chloride were reported in wrong unit. The corrected result for K1 were: 1) 708 mg/kg 2) 668 mg/kg	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the result had been reported correctly, the result would have been questionable. The participant can re-calculate the z scores according to the Guide for participants [5].

Feedback to the participants

Participant	Comments
18	The participant did not report the replicate result for their results, thus these results were not included in the statistical calculations and no performance evaluation was given. The participant should follow the instructions of the organizer.
2, 4, 6, 10, 15, 20, 21, 28, 31, 32, 35, 37	Some of the participants' results were Cochran outliers. The participants are recommended to check the allowed difference for the parallel results.
4	The participant informed they used an external accredited laboratory for some of their measurements (H, N). Those results were eliminated from the database. The proficiency test is to test the performance of the registered participant in the round and results from the subcontracted laboratory are not allowed.
4, 8, 9, 10, 11, 16, 21, 24, 25, 29, 36	The measurement uncertainty should be reported with the results obtained by accredited methods.
4, 6, 11, 14, 36	The participant did not inform the accreditation status of their method for some measurands. The participants should follow the instructions of the organizer.
14	The participant did not inform the requested background information with their results. The participants should follow the instructions of the organizer.
13, 34	The participants are recommended to check their limit of detection for Br in the coal sample K1.
7, 9, 12, 16, 25, 26, 35	The participant reported absolute measurement uncertainty for their calorific values and/or H, N, S, V results, but the request from the organizer was to report the relative measurement uncertainty. The participant should follow the instructions of the organizer.

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%	4.32	0.10	2.3	Robust mean	0.33
	B2	w%	0.30	0.03	9.2	Robust mean	0.31
	B3	w%	3.17	0.12	3.8	Robust mean	0.25
	K1	w%	17.8	0.1	0.4	Robust mean	0.16
C_d	B1	w%	55.3	0.3	0.5	Mean	0.20
	B2	w%	50.4	0.4	0.8	Robust mean	0.32
	B3	w%	49.0	0.2	0.5	Mean	0.20
	K1	w%	66.2	0.5	0.7	Robust mean	0.28
Cl_d	B1	mg/kg	255	-	-	Median	
	B3	mg/kg	572	74	13.0	Mean	0.37
	K1	mg/kg	569	26	4.5	Mean	0.23
EF	B1	t CO2/TJ	106	-	-	Mean	-
	K1	t CO2/TJ	94.3	0.9	1.0	Mean	0.25
F_d	K1	mg/kg	114	11	9.8	Median	-
H_d	B1	w%	5.99	0.13	2.1	Mean	0.30
	B2	w%	6.18	0.09	1.5	Robust mean	0.25
	B3	w%	6.07	0.10	1.7	Robust mean	0.28
	K1	w%	4.28	0.09	2.2	Robust mean	0.31
M_{ad}	B1	w%	4.57	0.12	2.6	Median	-
	B2	w%	6.20	0.15	2.4	Robust mean	-
	B3	w%	4.54	0.37	8.1	Robust mean	-
	K1	w%	3.46	0.08	2.2	Robust mean	-
N_d	B1	w%	1.76	0.04	2.4	Mean	0.24
	B2	w%	0.07	-	-	Median	-
	B3	w%	1.05	0.06	6.0	Mean	0.30
	K1	w%	1.18	0.05	4.1	Robust mean	0.27
$q_{p,net,d}$	B1	J/g	21348	64	0.3	Mean	0.20
	B2	J/g	18847	57	0.3	Mean	0.19
	B3	J/g	18434	74	0.4	Mean	0.24
	K1	J/g	25978	52	0.2	Robust mean	0.17
$q_{V,gr,d}$	B1	J/g	22598	47	0.2	Mean	0.16
	B2	J/g	20176	81	0.4	Robust mean	0.29
	B3	J/g	19737	99	0.5	Robust mean	0.33
	K1	J/g	26881	54	0.2	Mean	0.18
S_d	B1	w%	0.17	0.01	6.2	Median	0.31
	B3	w%	0.06	0.01	14	Robust mean	0.40
	K1	w%	0.90	0.03	2.8	Robust mean	0.28
V_d	B1	w%	70.5	0.7	1.0	Median	0.33
	B2	w%	84.7	0.4	0.5	Mean	0.17
	B3	w%	79.7	0.5	0.6	Mean	0.20
	K1	w%	31.4	0.5	1.6	Robust mean	0.32

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

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

Appendix 6. Terms in the results tables

The information could be applied according to the PT.

Measurand The tested parameter

Sample The code of the sample

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

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

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

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

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

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

Interpretation of the z scores

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

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

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

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

Interpretation of the E_n scores

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

Md Median

s Standard deviation

s % Standard deviation, %

n_{stat} Number of results in statistical processing

More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Proftest SYKE Guide for participants [1, 2, 5].

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		-0.11	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
C_d	w%	K1		1.11	66.2	2,5	67.1	66.1	66.2	0.7	1.1	20
M_{ad}	w%	K1			3.46		3.16	3.43	3.47	0.13	3.8	23
$q_{p,net,d}$	J/g	K1		-0.22	25978	1,2	25944	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	K1		-0.38	26881	1,1	26825	26895	26881	118	0.4	21

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		0.26	4.32	7	4.36	4.34	4.29	0.14	3.3	13
	w%	B2		0.33	0.30	30	0.32	0.30	0.30	0.05	15.5	17
	w%	B3		-0.06	3.17	15	3.16	3.16	3.18	0.22	6.9	15
	w%	K1		1.80	17.8	2,5	18.2	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					*<50*	11.8	16.1	9.0	55.9	3
C_d	w%	B1		0.87	55.3	2,5	55.9	55.2	55.3	0.4	0.8	8
	w%	B2		2.38	50.4	2,5	51.9	50.5	50.5	0.6	1.2	12
	w%	B3		-0.08	49.0	2,5	49.0	49.0	49.0	0.4	0.9	11
	w%	K1		-5.68	66.2	2,5	61.5	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B1			255		0	255	251	35	14.1	4
	mg/kg	B3		-5.71	572	35	0	577	572	113	19.7	9
	mg/kg	K1		-10.00	569	20	0	571	569	34	5.9	7
EF	t CO2/TJ	B1			106		97	107	106	1	1.3	4
	t CO2/TJ	K1		-3.74	94.3	4	87.3	94.3	94.3	1.3	1.4	8
F_d	mg/kg	K1			114		455	114	121	13	11.0	5
H_d	w%	B1		0.52	5.99	7	6.10	5.97	5.99	0.18	3.0	8
	w%	B2		0.92	6.18	6	6.35	6.18	6.18	0.11	1.8	12
	w%	B3		-0.38	6.07	6	6.00	6.02	6.08	0.14	2.2	12
	w%	K1		0.80	4.28	7	4.40	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.35	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.20	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.70	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.30	3.43	3.47	0.13	3.8	23
N_d	w%	B1		-0.06	1.76	10	1.76	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		0.12	0.07	0.11	0.09	79.5	9
	w%	B3		-0.10	1.05	20	1.04	1.05	1.04	0.10	9.5	10
	w%	K1		-5.42	1.18	15	0.70	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		-0.88	21348	1,5	21207	21369	21348	98	0.5	8
	J/g	B2		-0.96	18847	1,6	18702	18864	18847	79	0.4	11
	J/g	B3		-0.62	18434	1,7	18338	18420	18434	120	0.7	10
	J/g	K1		-0.93	25978	1,2	25834	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		-0.48	22598	1,3	22527	22593	22598	71	0.3	9
	J/g	B2		-0.70	20176	1,4	20078	20189	20170	99	0.5	12
	J/g	B3		-0.66	19737	1,5	19640	19748	19727	158	0.8	13
	J/g	K1		-0.71	26881	1,1	26776	26895	26881	118	0.4	21
S_d	w%	B1		-1.26	0.17	20	0.15	0.17	0.17	0.01	8.9	8
	w%	B3		-0.19	0.06	35	0.06	0.06	0.06	0.01	19.0	13
	w%	K1		0.16	0.90	10	0.91	0.91	0.92	0.04	4.1	24

Participant 2												
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%	B1		1.18	70.5	3	71.8	70.5	71.0	0.8	1.2	6
	w%	B2		-0.31	84.7	3	84.3	84.7	84.7	0.6	0.7	9
	w%	B3		0.54	79.7	3	80.4	79.8	79.7	0.8	1.0	11
	w%	K1		0.51	31.4	5	31.8	31.3	31.4	0.8	2.6	18

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		0.40	4.32	7	4.38	4.34	4.29	0.14	3.3	13
	w%	B2		-0.67	0.30	30	0.27	0.30	0.30	0.05	15.5	17
	w%	B3		-0.06	3.17	15	3.16	3.16	3.18	0.22	6.9	15
M_{ad}	w%	B1			4.57		4.18	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		5.91	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.22	4.69	4.56	0.54	11.8	14
$q_{p,net,d}$	J/g	B1		-0.06	21348	1,5	21339	21369	21348	98	0.5	8
	J/g	B2		-0.03	18847	1,6	18843	18864	18847	79	0.4	11
	J/g	B3		-0.30	18434	1,7	18387	18420	18434	120	0.7	10
$q_{V,gr,d}$	J/g	B1		-0.03	22598	1,3	22593	22593	22598	71	0.3	9
	J/g	B2		-0.08	20176	1,4	20165	20189	20170	99	0.5	12
	J/g	B3		-0.28	19737	1,5	19696	19748	19727	158	0.8	13

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		-2.15	4.32	7	4.00	4.34	4.29	0.14	3.3	13
	w%	B2		2.00	0.30	30	0.39	0.30	0.30	0.05	15.5	17
	w%	B3		-0.61	3.17	15	3.03	3.16	3.18	0.22	6.9	15
	w%	K1		-1.93	17.8	2,5	17.4	17.8	17.8	0.1	0.5	23
H_d	w%	B1			5.99	7	*5.55*	5.97	5.99	0.18	3.0	8
	w%	B2			6.18	6	*5.87*	6.18	6.18	0.11	1.8	12
	w%	B3			6.07	6	*5.64*	6.02	6.08	0.14	2.2	12
	w%	K1			4.28	7	*4.02*	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.32	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		5.94	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.60	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.36	3.43	3.47	0.13	3.8	23
N_d	w%	B1			1.76	10	*1.87*	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		*0.073*	0.07	0.11	0.09	79.5	9
	w%	B3			1.05	20	*1.25*	1.05	1.04	0.10	9.5	10
	w%	K1			1.18	15	*1.16*	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		-4.92	21348	1,5	20561	21369	21348	98	0.5	8
	J/g	B2		-4.01	18847	1,6	18243	18864	18847	79	0.4	11
	J/g	B3		-3.15	18434	1,7	17941	18420	18434	120	0.7	10
	J/g	K1		0.30	25978	1,2	26025	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		-5.85	22598	1,3	21739	22593	22598	71	0.3	9
	J/g	B2		-4.87	20176	1,4	19488	20189	20170	99	0.5	12
	J/g	B3		-4.05	19737	1,5	19138	19748	19727	158	0.8	13
	J/g	K1		-0.02	26881	1,1	26878	26895	26881	118	0.4	21

Participant 4												
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		3.24	0.17	20	0.23	0.17	0.17	0.01	8.9	8
	w%	B3		3.81	0.06	35	0.10	0.06	0.06	0.01	19.0	13
	w%	K1		2.11	0.90	10	1.00	0.91	0.92	0.04	4.1	24
V_d	w%	B1		-1.95	70.5	3	68.4	70.5	71.0	0.8	1.2	6
	w%	B2		-3.01	84.7	3	80.9	84.7	84.7	0.6	0.7	9
	w%	B3		-1.32	79.7	3	78.1	79.8	79.7	0.8	1.0	11
	w%	K1		-3.14	31.4	5	28.9	31.3	31.4	0.8	2.6	18

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		0.40	4.32	7	4.38	4.34	4.29	0.14	3.3	13
	w%	B2		-0.33	0.30	30	0.29	0.30	0.30	0.05	15.5	17
	w%	B3		-0.19	3.17	15	3.13	3.16	3.18	0.22	6.9	15
$q_{p,net,d}$	J/g	B1		0.81	21348	1,5	21477	21369	21348	98	0.5	8
	J/g	B2		0.16	18847	1,6	18871	18864	18847	79	0.4	11
	J/g	B3		0.64	18434	1,7	18534	18420	18434	120	0.7	10
$q_{V,gr,d}$	J/g	B1		0.33	22598	1,3	22647	22593	22598	71	0.3	9
	J/g	B2		0.28	20176	1,4	20216	20189	20170	99	0.5	12
	J/g	B3		0.29	19737	1,5	19781	19748	19727	158	0.8	13

Participant 6												
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	B3		-7.61	19737	1,5	18610	19748	19727	158	0.8	13

Participant 7												
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		-0.11	66.2	2,5	66.1	66.1	66.2	0.7	1.1	20
H_d	w%	K1		-1.60	4.28	7	4.04	4.30	4.27	0.14	3.3	16
M_{ad}	w%	K1			3.46		3.64	3.43	3.47	0.13	3.8	23
N_d	w%	K1		0.65	1.18	15	1.24	1.20	1.18	0.07	5.5	14
S_d	w%	K1		-0.39	0.90	10	0.88	0.91	0.92	0.04	4.1	24

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%	K1		-0.13	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
C_d	w%	K1		-0.24	66.2	2,5	66.0	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	K1		-0.95	569	20	515	571	569	34	5.9	7
H_d	w%	K1		-0.13	4.28	7	4.26	4.30	4.27	0.14	3.3	16
M_{ad}	w%	K1			3.46		3.42	3.43	3.47	0.13	3.8	23
N_d	w%	K1		-0.68	1.18	15	1.12	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	K1		0.26	25978	1,2	26019	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	K1		0.09	26881	1,1	26895	26895	26881	118	0.4	21
S_d	w%	K1		0.00	0.90	10	0.90	0.91	0.92	0.04	4.1	24
V_d	w%	K1		2.14	31.4	5	33.1	31.3	31.4	0.8	2.6	18

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%	B2		0.33	0.30	30	0.32	0.30	0.30	0.05	15.5	17
	w%	K1		-1.39	17.8	2,5	17.5	17.8	17.8	0.1	0.5	23
C_d	w%	B2		-0.12	50.4	2,5	50.3	50.5	50.5	0.6	1.2	12
	w%	K1		1.29	66.2	2,5	67.3	66.1	66.2	0.7	1.1	20
EF	t CO2/TJ	K1		1.09	94.3	4	96.4	94.3	94.3	1.3	1.4	8
H_d	w%	B2		-1.11	6.18	6	5.98	6.18	6.18	0.11	1.8	12
	w%	K1		0.40	4.28	7	4.34	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B2			6.20		6.27	6.26	6.20	0.26	4.2	15
	w%	K1			3.46		3.42	3.43	3.47	0.13	3.8	23
$q_{p,net,d}$	J/g	B2		-0.16	18847	1,6	18824	18864	18847	79	0.4	11
	J/g	K1		0.13	25978	1,2	25998	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B2		-0.40	20176	1,4	20120	20189	20170	99	0.5	12
	J/g	K1		0.26	26881	1,1	26920	26895	26881	118	0.4	21
S_d	w%	K1		-0.67	0.90	10	0.87	0.91	0.92	0.04	4.1	24

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%	K1		0.82	17.8	2,5	18.0	17.8	17.8	0.1	0.5	23
M_{ad}	w%	K1			3.46		3.42	3.43	3.47	0.13	3.8	23
$q_{V,gr,d}$	J/g	K1		-0.99	26881	1,1	26734	26895	26881	118	0.4	21
S_d	w%	K1		-0.17	0.90	10	0.89	0.91	0.92	0.04	4.1	24
V_d	w%	K1		0.40	31.4	5	31.7	31.3	31.4	0.8	2.6	18

Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ash_d	w%	K1		0.83	17.8	2,5	18.0	17.8	17.8	0.1	0.5	23
C_d	w%	K1		1.38	66.2	2,5	67.3	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	K1		-10.00	569	20	0	571	569	34	5.9	7
EF	t CO2/TJ	K1		0.76	94.3	4	95.7	94.3	94.3	1.3	1.4	8
M_{ad}	w%	K1			3.46		3.36	3.43	3.47	0.13	3.8	23
$q_{p,net,d}$	J/g	K1		-0.75	25978	1,2	25861	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	K1		-0.80	26881	1,1	26762	26895	26881	118	0.4	21
S_d	w%	K1		0.47	0.90	10	0.92	0.91	0.92	0.04	4.1	24
V_d	w%	K1		-0.92	31.4	5	30.7	31.3	31.4	0.8	2.6	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%	K1		-0.52	17.8	2,5	17.7	17.8	17.8	0.1	0.5	23
M_{ad}	w%	K1			3.46		3.45	3.43	3.47	0.13	3.8	23
$q_{V,gr,d}$	J/g	K1		-1.55	26881	1,1	26652	26895	26881	118	0.4	21
V_d	w%	K1		-0.80	31.4	5	30.8	31.3	31.4	0.8	2.6	18

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		-0.67	0.30	30	0.27	0.30	0.30	0.05	15.5	17
	w%	B3		0.25	3.17	15	3.23	3.16	3.18	0.22	6.9	15
	w%	K1		0.70	17.8	2,5	18.0	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					*< 10,00*	11.8	16.1	9.0	55.9	3
C_d	w%	B2		-0.09	50.4	2,5	50.3	50.5	50.5	0.6	1.2	12
	w%	B3		-0.28	49.0	2,5	48.8	49.0	49.0	0.4	0.9	11
	w%	K1		-0.30	66.2	2,5	66.0	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B3		-0.12	572	35	560	577	572	113	19.7	9
	mg/kg	K1		-0.50	569	20	541	571	569	34	5.9	7
EF	t CO2/TJ	K1		-0.87	94.3	4	92.7	94.3	94.3	1.3	1.4	8
F_d	mg/kg	K1			114		61	114	121	13	11.0	5
H_d	w%	B2		-0.17	6.18	6	6.15	6.18	6.18	0.11	1.8	12
	w%	B3		-0.62	6.07	6	5.96	6.02	6.08	0.14	2.2	12
	w%	K1		-0.25	4.28	7	4.24	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B2			6.20		6.28	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.69	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.55	3.43	3.47	0.13	3.8	23
N_d	w%	B2			0.07		0.03	0.07	0.11	0.09	79.5	9
	w%	B3		-1.29	1.05	20	0.92	1.05	1.04	0.10	9.5	10
	w%	K1		0.11	1.18	15	1.19	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B2		0.58	18847	1,6	18935	18864	18847	79	0.4	11
	J/g	B3		0.87	18434	1,7	18571	18420	18434	120	0.7	10
	J/g	K1		0.62	25978	1,2	26075	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B2		0.61	20176	1,4	20262	20189	20170	99	0.5	12
	J/g	B3		1.10	19737	1,5	19900	19748	19727	158	0.8	13
	J/g	K1		0.70	26881	1,1	26985	26895	26881	118	0.4	21
S_d	w%	B3		-0.90	0.06	35	0.05	0.06	0.06	0.01	19.0	13
	w%	K1		1.54	0.90	10	0.97	0.91	0.92	0.04	4.1	24
V_d	w%	B2		-0.15	84.7	3	84.5	84.7	84.7	0.6	0.7	9
	w%	B3		0.64	79.7	3	80.5	79.8	79.7	0.8	1.0	11
	w%	K1		0.55	31.4	5	31.8	31.3	31.4	0.8	2.6	18

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%	B1		0.53	4.32	7	4.40	4.34	4.29	0.14	3.3	13
	w%	B2		0.00	0.30	30	0.30	0.30	0.30	0.05	15.5	17
	w%	B3		-1.56	3.17	15	2.80	3.16	3.18	0.22	6.9	15
	w%	K1		0.00	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					373.0	11.8	16.1	9.0	55.9	3
C_d	w%	B1		-0.14	55.3	2,5	55.2	55.2	55.3	0.4	0.8	8
	w%	B2		0.16	50.4	2,5	50.5	50.5	50.5	0.6	1.2	12
	w%	B3		0.98	49.0	2,5	49.6	49.0	49.0	0.4	0.9	11
	w%	K1		-0.24	66.2	2,5	66.0	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B1			255		204	255	251	35	14.1	4
	mg/kg	B3		0.94	572	35	666	577	572	113	19.7	9
	mg/kg	K1		-3.44	569	20	373	571	569	34	5.9	7
EF	t CO2/TJ	B1			106		95	107	106	1	1.3	4
	t CO2/TJ	K1		24.23	94.3	4	140.0	94.3	94.3	1.3	1.4	8

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
F_d	mg/kg	K1			114		373	114	121	13	11.0	5
H_d	w%	B1		0.14	5.99	7	6.02	5.97	5.99	0.18	3.0	8
	w%	B2		0.65	6.18	6	6.30	6.18	6.18	0.11	1.8	12
	w%	B3		0.82	6.07	6	6.22	6.02	6.08	0.14	2.2	12
	w%	K1		1.34	4.28	7	4.48	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.20	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.10	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.10	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		4.70	3.43	3.47	0.13	3.8	23
N_d	w%	B1		1.36	1.76	10	1.88	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		0.19	0.07	0.11	0.09	79.5	9
	w%	B3		1.81	1.05	20	1.24	1.05	1.04	0.10	9.5	10
	w%	K1		0.79	1.18	15	1.25	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		0.32	21348	1,5	21400	21369	21348	98	0.5	8
	J/g	B2		-2.96	18847	1,6	18400	18864	18847	79	0.4	11
	J/g	B3		-9.15	18434	1,7	17000	18420	18434	120	0.7	10
	J/g	K1		-56.00	25978	1,2	17250	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		0.01	22598	1,3	22600	22593	22598	71	0.3	9
	J/g	B2		-3.37	20176	1,4	19700	20189	20170	99	0.5	12
	J/g	B3		-9.71	19737	1,5	18300	19748	19727	158	0.8	13
	J/g	K1		-58.72	26881	1,1	18200	26895	26881	118	0.4	21
S_d	w%	B1		0.59	0.17	20	0.18	0.17	0.17	0.01	8.9	8
	w%	B3		0.00	0.06	35	0.06	0.06	0.06	0.01	19.0	13
	w%	K1		1.11	0.90	10	0.95	0.91	0.92	0.04	4.1	24
V_d	w%	B1		-0.09	70.5	3	70.4	70.5	71.0	0.8	1.2	6
	w%	B2		0.47	84.7	3	85.3	84.7	84.7	0.6	0.7	9
	w%	B3		0.08	79.7	3	79.8	79.8	79.7	0.8	1.0	11
	w%	K1		-0.38	31.4	5	31.1	31.3	31.4	0.8	2.6	18

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%	B2		1.89	0.30	30	0.39	0.30	0.30	0.05	15.5	17
	w%	B3		2.38	3.17	15	3.74	3.16	3.18	0.22	6.9	15
C_d	w%	B2		-1.27	50.4	2,5	49.6	50.5	50.5	0.6	1.2	12
	w%	B3		-0.11	49.0	2,5	48.9	49.0	49.0	0.4	0.9	11
Cl_d	mg/kg	B3		3.81	572	35	954	577	572	113	19.7	9
H_d	w%	B2		0.19	6.18	6	6.22	6.18	6.18	0.11	1.8	12
	w%	B3		-0.38	6.07	6	6.00	6.02	6.08	0.14	2.2	12
M_{ad}	w%	B2			6.20		6.79	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		6.64	4.69	4.56	0.54	11.8	14
$q_{p,net,d}$	J/g	B2		20.48	18847	1,6	21935	18864	18847	79	0.4	11
	J/g	B3		27.32	18434	1,7	22715	18420	18434	120	0.7	10
$q_{V,gr,d}$	J/g	B2		21.45	20176	1,4	23205	20189	20170	99	0.5	12
	J/g	B3		28.56	19737	1,5	23965	19748	19727	158	0.8	13
S_d	w%	B3		7.05	0.06	35	0.13	0.06	0.06	0.01	19.0	13
V_d	w%	B2		-0.75	84.7	3	83.8	84.7	84.7	0.6	0.7	9
	w%	B3		-0.79	79.7	3	78.8	79.8	79.7	0.8	1.0	11

Participant 16												
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		0.89	0.30	30	0.34	0.30	0.30	0.05	15.5	17
	w%	B3		1.09	3.17	15	3.43	3.16	3.18	0.22	6.9	15
	w%	K1		0.00	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					10.0	11.8	16.1	9.0	55.9	3
C_d	w%	B2		-1.03	50.4	2,5	49.8	50.5	50.5	0.6	1.2	12
	w%	B3		-0.85	49.0	2,5	48.5	49.0	49.0	0.4	0.9	11
	w%	K1		-0.83	66.2	2,5	65.5	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B3		0.09	572	35	581	577	572	113	19.7	9
	mg/kg	K1		2.43	569	20	707	571	569	34	5.9	7
F_d	mg/kg	K1			114		124	114	121	13	11.0	5
H_d	w%	B2		0.32	6.18	6	6.24	6.18	6.18	0.11	1.8	12
	w%	B3		0.60	6.07	6	6.18	6.02	6.08	0.14	2.2	12
	w%	K1		-0.33	4.28	7	4.23	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B2			6.20		6.20	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		3.80	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.38	3.43	3.47	0.13	3.8	23
N_d	w%	B2			0.07		0.07	0.07	0.11	0.09	79.5	9
	w%	B3		-1.14	1.05	20	0.93	1.05	1.04	0.10	9.5	10
	w%	K1		-0.68	1.18	15	1.12	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B2		0.11	18847	1,6	18864	18864	18847	79	0.4	11
	J/g	B3		-0.21	18434	1,7	18401	18420	18434	120	0.7	10
	J/g	K1		-1.65	25978	1,2	25721	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B2		0.34	20176	1,4	20224	20189	20170	99	0.5	12
	J/g	B3		0.05	19737	1,5	19745	19748	19727	158	0.8	13
	J/g	K1		-1.70	26881	1,1	26629	26895	26881	118	0.4	21
S_d	w%	B3		0.70	0.06	35	0.07	0.06	0.06	0.01	19.0	13
	w%	K1		0.44	0.90	10	0.92	0.91	0.92	0.04	4.1	24
V_d	w%	B2		0.39	84.7	3	85.2	84.7	84.7	0.6	0.7	9
	w%	B3		0.25	79.7	3	80.0	79.8	79.7	0.8	1.0	11
	w%	K1		0.31	31.4	5	31.6	31.3	31.4	0.8	2.6	18

Participant 18												
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			17.8	2,5	*17.67*	17.8	17.8	0.1	0.5	23
C_d	w%	K1			66.2	2,5	*72.03*	66.1	66.2	0.7	1.1	20
M_{ad}	w%	K1			3.46		*3.48*	3.43	3.47	0.13	3.8	23
$q_{V,gr,d}$	J/g	K1			26881	1,1	*26050*	26895	26881	118	0.4	21
S_d	w%	K1			0.90	10	*0.84*	0.91	0.92	0.04	4.1	24
V_d	w%	K1			31.4	5	*30.54*	31.3	31.4	0.8	2.6	18

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		-1.75	4.32	7	4.06	4.34	4.29	0.14	3.3	13
	w%	B2		-0.22	0.30	30	0.29	0.30	0.30	0.05	15.5	17
M_{ad}	w%	B1			4.57		4.73	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		5.99	6.26	6.20	0.26	4.2	15

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	B1		0.66	4.32	7	4.42	4.34	4.29	0.14	3.3	13
	w%	B2		-0.78	0.30	30	0.27	0.30	0.30	0.05	15.5	17
	w%	B3		0.65	3.17	15	3.33	3.16	3.18	0.22	6.9	15
	w%	K1		-0.25	17.8	2,5	17.7	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					26.4	11.8	16.1	9.0	55.9	3
C_d	w%	B1		-0.56	55.3	2,5	54.9	55.2	55.3	0.4	0.8	8
	w%	B2		0.20	50.4	2,5	50.5	50.5	50.5	0.6	1.2	12
	w%	B3		0.37	49.0	2,5	49.2	49.0	49.0	0.4	0.9	11
	w%	K1		-0.16	66.2	2,5	66.1	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B1			255		258	255	251	35	14.1	4
	mg/kg	B3		-0.15	572	35	557	577	572	113	19.7	9
	mg/kg	K1		0.09	569	20	574	571	569	34	5.9	7
EF	t CO2/TJ	B1			106		104	107	106	1	1.3	4
	t CO2/TJ	K1		-0.42	94.3	4	93.5	94.3	94.3	1.3	1.4	8
F_d	mg/kg	K1			114		112	114	121	13	11.0	5
H_d	w%	B1		-0.64	5.99	7	5.86	5.97	5.99	0.18	3.0	8
	w%	B2		-0.21	6.18	6	6.14	6.18	6.18	0.11	1.8	12
	w%	B3		-0.69	6.07	6	5.94	6.02	6.08	0.14	2.2	12
	w%	K1		-1.39	4.28	7	4.07	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.59	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.32	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.78	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.73	3.43	3.47	0.13	3.8	23
N_d	w%	B1		-0.75	1.76	10	1.69	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		0.29	0.07	0.11	0.09	79.5	9
	w%	B3		-0.09	1.05	20	1.04	1.05	1.04	0.10	9.5	10
	w%	K1		1.31	1.18	15	1.30	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		0.38	21348	1,5	21409	21369	21348	98	0.5	8
	J/g	B2		0.82	18847	1,6	18971	18864	18847	79	0.4	11
	J/g	B3		0.72	18434	1,7	18547	18420	18434	120	0.7	10
	J/g	K1		1.33	25978	1,2	26185	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		0.61	22598	1,3	22687	22593	22598	71	0.3	9
	J/g	B2		0.96	20176	1,4	20312	20189	20170	99	0.5	12
	J/g	B3		0.73	19737	1,5	19845	19748	19727	158	0.8	13
	J/g	K1		1.31	26881	1,1	27074	26895	26881	118	0.4	21
S_d	w%	B1		0.12	0.17	20	0.17	0.17	0.17	0.01	8.9	8
	w%	B3		-0.38	0.06	35	0.06	0.06	0.06	0.01	19.0	13
	w%	K1		0.14	0.90	10	0.91	0.91	0.92	0.04	4.1	24
V_d	w%	B1		-0.07	70.5	3	70.4	70.5	71.0	0.8	1.2	6
	w%	B2		0.01	84.7	3	84.7	84.7	84.7	0.6	0.7	9
	w%	B3		0.06	79.7	3	79.8	79.8	79.7	0.8	1.0	11
	w%	K1		-0.10	31.4	5	31.3	31.3	31.4	0.8	2.6	18

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		-0.69	4.32	7	4.22	4.34	4.29	0.14	3.3	13
	w%	B2		0.33	0.30	30	0.32	0.30	0.30	0.05	15.5	17
	w%	K1		0.56	17.8	2,5	17.9	17.8	17.8	0.1	0.5	23
C_d	w%	B1		0.72	55.3	2,5	55.8	55.2	55.3	0.4	0.8	8
	w%	B2		1.01	50.4	2,5	51.0	50.5	50.5	0.6	1.2	12
	w%	K1		0.45	66.2	2,5	66.6	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B1			255		290	255	251	35	14.1	4
	mg/kg	K1		0.72	569	20	610	571	569	34	5.9	7
EF	t CO2/TJ	B1			106		107	107	106	1	1.3	4
	t CO2/TJ	K1		0.27	94.3	4	94.8	94.3	94.3	1.3	1.4	8
H_d	w%	B1		-0.07	5.99	7	5.98	5.97	5.99	0.18	3.0	8
	w%	B2		-0.30	6.18	6	6.13	6.18	6.18	0.11	1.8	12
	w%	K1		-1.90	4.28	7	4.00	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.54	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.31	6.26	6.20	0.26	4.2	15
	w%	K1			3.46		3.54	3.43	3.47	0.13	3.8	23
N_d	w%	B1		-0.20	1.76	10	1.74	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		0.05	0.07	0.11	0.09	79.5	9
	w%	K1		-1.15	1.18	15	1.08	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		-0.85	21348	1,5	21213	21369	21348	98	0.5	8
	J/g	B2		0.21	18847	1,6	18879	18864	18847	79	0.4	11
	J/g	K1		0.34	25978	1,2	26031	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		-0.62	22598	1,3	22507	22593	22598	71	0.3	9
	J/g	B2		0.26	20176	1,4	20213	20189	20170	99	0.5	12
	J/g	K1		0.04	26881	1,1	26887	26895	26881	118	0.4	21
S_d	w%	B1		0.91	0.17	20	0.19	0.17	0.17	0.01	8.9	8
	w%	K1		1.01	0.90	10	0.95	0.91	0.92	0.04	4.1	24

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		0.00	4.32	7	4.32	4.34	4.29	0.14	3.3	13
	w%	B2		0.22	0.30	30	0.31	0.30	0.30	0.05	15.5	17
	w%	B3		0.59	3.17	15	3.31	3.16	3.18	0.22	6.9	15
	w%	K1		0.11	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
C_d	w%	B1		-0.09	55.3	2,5	55.2	55.2	55.3	0.4	0.8	8
	w%	B2		0.26	50.4	2,5	50.6	50.5	50.5	0.6	1.2	12
	w%	B3		0.77	49.0	2,5	49.5	49.0	49.0	0.4	0.9	11
	w%	K1		-1.66	66.2	2,5	64.8	66.1	66.2	0.7	1.1	20
H_d	w%	B1		-0.12	5.99	7	5.96	5.97	5.99	0.18	3.0	8
	w%	B2		0.74	6.18	6	6.32	6.18	6.18	0.11	1.8	12
	w%	B3		-0.16	6.07	6	6.04	6.02	6.08	0.14	2.2	12
	w%	K1		1.41	4.28	7	4.49	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.57	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.26	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.70	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.56	3.43	3.47	0.13	3.8	23

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_d	w%	B1		-0.16	1.76	10	1.75	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		0.05	0.07	0.11	0.09	79.5	9
	w%	B3		0.15	1.05	20	1.07	1.05	1.04	0.10	9.5	10
$q_{p,net,d}$	J/g	B1		0.43	21348	1,5	21417	21369	21348	98	0.5	8
	J/g	B2		0.28	18847	1,6	18889	18864	18847	79	0.4	11
	J/g	B3		0.03	18434	1,7	18439	18420	18434	120	0.7	10
	J/g	K1		-0.27	25978	1,2	25936	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		0.76	22598	1,3	22710	22593	22598	71	0.3	9
	J/g	B2		0.62	20176	1,4	20264	20189	20170	99	0.5	12
	J/g	B3		0.11	19737	1,5	19754	19748	19727	158	0.8	13
	J/g	K1		0.24	26881	1,1	26917	26895	26881	118	0.4	21
S_d	w%	B1		-1.32	0.17	20	0.15	0.17	0.17	0.01	8.9	8
	w%	B3		0.86	0.06	35	0.07	0.06	0.06	0.01	19.0	13
	w%	K1		-0.02	0.90	10	0.90	0.91	0.92	0.04	4.1	24
V_d	w%	K1		-0.34	31.4	5	31.1	31.3	31.4	0.8	2.6	18

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		-0.25	4.32	7	4.28	4.34	4.29	0.14	3.3	13
	w%	B2		-1.33	0.30	30	0.24	0.30	0.30	0.05	15.5	17
M_{ad}	w%	B1			4.57		0.00	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		0.00	6.26	6.20	0.26	4.2	15
$q_{p,net,d}$	J/g	B1		-133.20	21348	1,5	21	21369	21348	98	0.5	8
	J/g	B2		-124.88	18847	1,6	19	18864	18847	79	0.4	11
$q_{V,gr,d}$	J/g	B1		-153.69	22598	1,3	23	22593	22598	71	0.3	9
	J/g	B2		-142.71	20176	1,4	20	20189	20170	99	0.5	12

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%	K1		0.04	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
C_d	w%	K1		-0.48	66.2	2,5	65.8	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	K1		-0.07	569	20	565	571	569	34	5.9	7
H_d	w%	K1		0.13	4.28	7	4.30	4.30	4.27	0.14	3.3	16
M_{ad}	w%	K1			3.46		3.41	3.43	3.47	0.13	3.8	23
N_d	w%	K1		-0.56	1.18	15	1.13	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	K1		0.50	25978	1,2	26056	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	K1		0.41	26881	1,1	26942	26895	26881	118	0.4	21
S_d	w%	K1		0.44	0.90	10	0.92	0.91	0.92	0.04	4.1	24
V_d	w%	K1		1.15	31.4	5	32.3	31.3	31.4	0.8	2.6	18

Participant 25												
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%	B3		-0.55	3.17	15	3.04	3.16	3.18	0.22	6.9	15
	w%	K1		-0.29	17.8	2,5	17.7	17.8	17.8	0.1	0.5	23
C_d	w%	B3		-0.85	49.0	2,5	48.5	49.0	49.0	0.4	0.9	11
	w%	K1		-0.42	66.2	2,5	65.9	66.1	66.2	0.7	1.1	20
EF	t CO2/TJ	K1		-0.74	94.3	4	92.9	94.3	94.3	1.3	1.4	8

Participant 25												
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%	B3		0.95	6.07	6	6.24	6.02	6.08	0.14	2.2	12
	w%	K1		0.37	4.28	7	4.34	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B3			4.54		2.29	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.61	3.43	3.47	0.13	3.8	23
N_d	w%	B3		-2.39	1.05	20	0.80	1.05	1.04	0.10	9.5	10
	w%	K1		-0.90	1.18	15	1.10	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B3		-2.19	18434	1,7	18091	18420	18434	120	0.7	10
	J/g	K1		0.10	25978	1,2	25994	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B3		-2.44	19737	1,5	19377	19748	19727	158	0.8	13
	J/g	K1		0.04	26881	1,1	26888	26895	26881	118	0.4	21
S_d	w%	B3		2.25	0.06	35	0.08	0.06	0.06	0.01	19.0	13
	w%	K1		0.12	0.90	10	0.91	0.91	0.92	0.04	4.1	24
V_d	w%	B3		0.78	79.7	3	80.6	79.8	79.7	0.8	1.0	11
	w%	K1		2.44	31.4	5	33.3	31.3	31.4	0.8	2.6	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%	K1		0.09	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
C_d	w%	K1		0.86	66.2	2,5	66.9	66.1	66.2	0.7	1.1	20
M_{ad}	w%	K1			3.46		3.63	3.43	3.47	0.13	3.8	23
$q_{p,net,d}$	J/g	K1		-0.09	25978	1,2	25964	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	K1		-0.14	26881	1,1	26861	26895	26881	118	0.4	21
S_d	w%	K1		0.81	0.90	10	0.94	0.91	0.92	0.04	4.1	24
V_d	w%	K1		-1.75	31.4	5	30.0	31.3	31.4	0.8	2.6	18

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ash_d	w%	K1		0.27	17.8	2,5	17.9	17.8	17.8	0.1	0.5	23
C_d	w%	K1		0.86	66.2	2,5	66.9	66.1	66.2	0.7	1.1	20
M_{ad}	w%	K1			3.46		3.40	3.43	3.47	0.13	3.8	23
S_d	w%	K1		0.30	0.90	10	0.91	0.91	0.92	0.04	4.1	24
V_d	w%	K1		1.76	31.4	5	32.8	31.3	31.4	0.8	2.6	18

Participant 28												
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		-0.38	55.3	2,5	55.0	55.2	55.3	0.4	0.8	8
	w%	B2		-0.88	50.4	2,5	49.8	50.5	50.5	0.6	1.2	12
	w%	K1		-1.83	66.2	2,5	64.7	66.1	66.2	0.7	1.1	20
H_d	w%	B1		-0.83	5.99	7	5.82	5.97	5.99	0.18	3.0	8
	w%	B2		-0.59	6.18	6	6.07	6.18	6.18	0.11	1.8	12
	w%	K1		-3.44	4.28	7	3.77	4.30	4.27	0.14	3.3	16
N_d	w%	B1		-0.40	1.76	10	1.73	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		0.06	0.07	0.11	0.09	79.5	9
	w%	K1		0.23	1.18	15	1.20	1.20	1.18	0.07	5.5	14

Participant 29												
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		0.22	17.8	2,5	17.9	17.8	17.8	0.1	0.5	23
H_d	w%	K1		0.00	4.28	7	4.28	4.30	4.27	0.14	3.3	16
M_{ad}	w%	K1			3.46		3.61	3.43	3.47	0.13	3.8	23
$q_{V,gr,d}$	J/g	K1		1.21	26881	1,1	27060	26895	26881	118	0.4	21
S_d	w%	K1		-8.67	0.90	10	0.51	0.91	0.92	0.04	4.1	24
V_d	w%	K1		-0.83	31.4	5	30.8	31.3	31.4	0.8	2.6	18

Participant 30												
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		0.35	0.17	20	0.18	0.17	0.17	0.01	8.9	8
	w%	B3		1.33	0.06	35	0.07	0.06	0.06	0.01	19.0	13
	w%	K1		-0.20	0.90	10	0.89	0.91	0.92	0.04	4.1	24

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		4.93	4.32	7	5.07	4.34	4.29	0.14	3.3	13
	w%	K1		-0.34	17.8	2,5	17.7	17.8	17.8	0.1	0.5	23
C_d	w%	B1		-0.69	55.3	2,5	54.8	55.2	55.3	0.4	0.8	8
	w%	K1		-0.19	66.2	2,5	66.0	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B1			255		602	255	251	35	14.1	4
	mg/kg	K1		-5.00	569	20	285	571	569	34	5.9	7
EF	t CO2/TJ	B1			106		107	107	106	1	1.3	4
	t CO2/TJ	K1		0.11	94.3	4	94.5	94.3	94.3	1.3	1.4	8
H_d	w%	B1		1.83	5.99	7	6.37	5.97	5.99	0.18	3.0	8
	w%	K1		4.39	4.28	7	4.94	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		3.42	4.57	4.51	0.18	3.9	9
	w%	K1			3.46		3.38	3.43	3.47	0.13	3.8	23
N_d	w%	B1		-0.36	1.76	10	1.73	1.74	1.76	0.06	3.3	8
	w%	K1		0.25	1.18	15	1.20	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		-2.58	21348	1,5	20935	21369	21348	98	0.5	8
	J/g	K1		-0.66	25978	1,2	25875	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		-2.30	22598	1,3	22260	22593	22598	71	0.3	9
	J/g	K1		0.32	26881	1,1	26929	26895	26881	118	0.4	21
S_d	w%	B1		-3.59	0.17	20	0.11	0.17	0.17	0.01	8.9	8
	w%	K1		-0.22	0.90	10	0.89	0.91	0.92	0.04	4.1	24
V_d	w%	B1		1.74	70.5	3	72.3	70.5	71.0	0.8	1.2	6
	w%	K1		0.90	31.4	5	32.1	31.3	31.4	0.8	2.6	18

Participant 32												
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%	B3		0.13	3.17	15	3.20	3.16	3.18	0.22	6.9	15
	w%	K1		-5.08	17.8	2,5	16.7	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					11.8	11.8	16.1	9.0	55.9	3
C_d	w%	B3		-0.64	49.0	2,5	48.6	49.0	49.0	0.4	0.9	11
	w%	K1		-0.83	66.2	2,5	65.5	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B3		-1.63	572	35	409	577	572	113	19.7	9
	mg/kg	K1		-4.09	569	20	336	571	569	34	5.9	7
F_d	mg/kg	K1			114		143	114	121	13	11.0	5

Participant 32												
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%	B3		-0.09	6.07	6	6.05	6.02	6.08	0.14	2.2	12
	w%	K1		0.23	4.28	7	4.31	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B3			4.54		3.72	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		2.29	3.43	3.47	0.13	3.8	23
N_d	w%	B3		0.19	1.05	20	1.07	1.05	1.04	0.10	9.5	10
	w%	K1		0.68	1.18	15	1.24	1.20	1.18	0.07	5.5	14
S_d	w%	B3		-1.52	0.06	35	0.04	0.06	0.06	0.01	19.0	13
	w%	K1		-9.32	0.90	10	0.48	0.91	0.92	0.04	4.1	24

Participant 33												
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%	B3		-4.90	3.17	15	2.01	3.16	3.18	0.22	6.9	15
C_d	w%	B3		3.80	49.0	2,5	51.3	49.0	49.0	0.4	0.9	11
Cl_d	mg/kg	B3		0.37	572	35	609	577	572	113	19.7	9
H_d	w%	B3		1.53	6.07	6	6.35	6.02	6.08	0.14	2.2	12
M_{ad}	w%	B3			4.54		5.74	4.69	4.56	0.54	11.8	14
N_d	w%	B3		0.80	1.05	20	1.13	1.05	1.04	0.10	9.5	10
$q_{p,net,d}$	J/g	B3		0.94	18434	1,7	18582	18420	18434	120	0.7	10
$q_{V,gr,d}$	J/g	B3		1.52	19737	1,5	19962	19748	19727	158	0.8	13
S_d	w%	B3		0.29	0.06	35	0.06	0.06	0.06	0.01	19.0	13

Participant 34												
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		0.60	4.32	7	4.41	4.34	4.29	0.14	3.3	13
	w%	B2		0.11	0.30	30	0.31	0.30	0.30	0.05	15.5	17
	w%	B3		-0.13	3.17	15	3.14	3.16	3.18	0.22	6.9	15
	w%	K1		0.29	17.8	2,5	17.9	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					*<10*	11.8	16.1	9.0	55.9	3
C_d	w%	B1		0.64	55.3	2,5	55.7	55.2	55.3	0.4	0.8	8
	w%	B2		0.71	50.4	2,5	50.9	50.5	50.5	0.6	1.2	12
	w%	B3		1.10	49.0	2,5	49.7	49.0	49.0	0.4	0.9	11
	w%	K1		-0.11	66.2	2,5	66.1	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B1			255		253	255	251	35	14.1	4
	mg/kg	B3		0.05	572	35	577	577	572	113	19.7	9
	mg/kg	K1		0.03	569	20	571	571	569	34	5.9	7
EF	t CO2/TJ	B1			106		106	107	106	1	1.3	4
	t CO2/TJ	K1		-0.13	94.3	4	94.1	94.3	94.3	1.3	1.4	8
F_d	mg/kg	K1			114		114	114	121	13	11.0	5
H_d	w%	B1		-0.69	5.99	7	5.85	5.97	5.99	0.18	3.0	8
	w%	B2		-0.61	6.18	6	6.07	6.18	6.18	0.11	1.8	12
	w%	B3		-0.68	6.07	6	5.95	6.02	6.08	0.14	2.2	12
	w%	K1		0.08	4.28	7	4.29	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B1			4.57		4.66	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.49	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.87	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.60	3.43	3.47	0.13	3.8	23

Participant 34												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_d	w%	B1		0.58	1.76	10	1.81	1.74	1.76	0.06	3.3	8
	w%	B2			0.07		*<0,2*	0.07	0.11	0.09	79.5	9
	w%	B3		0.21	1.05	20	1.07	1.05	1.04	0.10	9.5	10
	w%	K1		0.56	1.18	15	1.23	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B1		-0.16	21348	1,5	21323	21369	21348	98	0.5	8
	J/g	B2		-0.26	18847	1,6	18808	18864	18847	79	0.4	11
	J/g	B3		-0.94	18434	1,7	18287	18420	18434	120	0.7	10
	J/g	K1		0.40	25978	1,2	26041	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B1		-0.12	22598	1,3	22581	22593	22598	71	0.3	9
	J/g	B2		-0.28	20176	1,4	20137	20189	20170	99	0.5	12
	J/g	B3		-0.98	19737	1,5	19593	19748	19727	158	0.8	13
	J/g	K1		0.40	26881	1,1	26941	26895	26881	118	0.4	21
S_d	w%	B1		0.29	0.17	20	0.18	0.17	0.17	0.01	8.9	8
	w%	B3		-0.05	0.06	35	0.06	0.06	0.06	0.01	19.0	13
	w%	K1		-1.54	0.90	10	0.83	0.91	0.92	0.04	4.1	24
V_d	w%	B1		0.00	70.5	3	70.5	70.5	71.0	0.8	1.2	6
	w%	B2		0.38	84.7	3	85.2	84.7	84.7	0.6	0.7	9
	w%	B3		0.49	79.7	3	80.3	79.8	79.7	0.8	1.0	11
	w%	K1		-0.09	31.4	5	31.3	31.3	31.4	0.8	2.6	18

Participant 35												
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		-0.53	4.32	7	4.24	4.34	4.29	0.14	3.3	13
	w%	B2		-1.22	0.30	30	0.25	0.30	0.30	0.05	15.5	17
	w%	B3		-0.44	3.17	15	3.07	3.16	3.18	0.22	6.9	15
	w%	K1		0.20	17.8	2,5	17.8	17.8	17.8	0.1	0.5	23
M_{ad}	w%	B1			4.57		4.64	4.57	4.51	0.18	3.9	9
	w%	B2			6.20		6.30	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.73	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		3.45	3.43	3.47	0.13	3.8	23
$q_{V,gr,d}$	J/g	B1		-0.43	22598	1,3	22535	22593	22598	71	0.3	9
	J/g	B2		-1.55	20176	1,4	19958	20189	20170	99	0.5	12
	J/g	B3		0.07	19737	1,5	19748	19748	19727	158	0.8	13
	J/g	K1		0.81	26881	1,1	27001	26895	26881	118	0.4	21
S_d	w%	B1		-0.88	0.17	20	0.16	0.17	0.17	0.01	8.9	8
	w%	B3		-1.43	0.06	35	0.05	0.06	0.06	0.01	19.0	13
	w%	K1		-8.33	0.90	10	0.53	0.91	0.92	0.04	4.1	24
V_d	w%	B1		0.00	70.5	3	70.5	70.5	71.0	0.8	1.2	6
	w%	B2		0.46	84.7	3	85.3	84.7	84.7	0.6	0.7	9
	w%	B3		-0.25	79.7	3	79.4	79.8	79.7	0.8	1.0	11
	w%	K1		-0.79	31.4	5	30.8	31.3	31.4	0.8	2.6	18

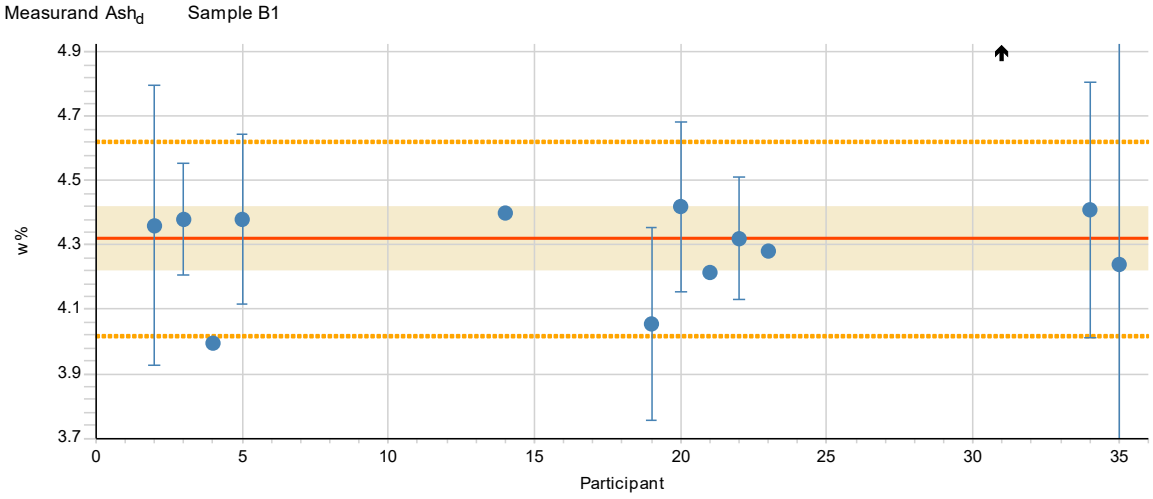
Participant 36												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Ash_d	w%	B2		-1.78	0.30	30	0.22	0.30	0.30	0.05	15.5	17
	w%	B3		-0.93	3.17	15	2.95	3.16	3.18	0.22	6.9	15
	w%	K1		-0.45	17.8	2,5	17.7	17.8	17.8	0.1	0.5	23
Br_d	mg/kg	K1					*<20*	11.8	16.1	9.0	55.9	3
C_d	w%	B2		0.24	50.4	2,5	50.6	50.5	50.5	0.6	1.2	12
	w%	B3		0.49	49.0	2,5	49.3	49.0	49.0	0.4	0.9	11
	w%	K1		0.54	66.2	2,5	66.7	66.1	66.2	0.7	1.1	20
Cl_d	mg/kg	B3		-1.57	572	35	415	577	572	113	19.7	9
	mg/kg	K1		0.65	569	20	606	571	569	34	5.9	7
F_d	mg/kg	K1			114		112	114	121	13	11.0	5
H_d	w%	B2		0.32	6.18	6	6.24	6.18	6.18	0.11	1.8	12
	w%	B3		-0.49	6.07	6	5.98	6.02	6.08	0.14	2.2	12
	w%	K1		0.13	4.28	7	4.30	4.30	4.27	0.14	3.3	16
M_{ad}	w%	B2			6.20		5.70	6.26	6.20	0.26	4.2	15
	w%	B3			4.54		4.10	4.69	4.56	0.54	11.8	14
	w%	K1			3.46		2.70	3.43	3.47	0.13	3.8	23
N_d	w%	B2			0.07		0.12	0.07	0.11	0.09	79.5	9
	w%	B3		-1.05	1.05	20	0.94	1.05	1.04	0.10	9.5	10
	w%	K1		-0.11	1.18	15	1.17	1.20	1.18	0.07	5.5	14
$q_{p,net,d}$	J/g	B2		-0.75	18847	1,6	18734	18864	18847	79	0.4	11
	J/g	B3		-1.15	18434	1,7	18254	18420	18434	120	0.7	10
	J/g	K1		0.30	25978	1,2	26025	25998	25975	108	0.4	17
$q_{V,gr,d}$	J/g	B2		-0.59	20176	1,4	20093	20189	20170	99	0.5	12
	J/g	B3		-1.22	19737	1,5	19557	19748	19727	158	0.8	13
	J/g	K1		0.44	26881	1,1	26946	26895	26881	118	0.4	21
S_d	w%	B3		-0.86	0.06	35	0.05	0.06	0.06	0.01	19.0	13
	w%	K1		1.56	0.90	10	0.97	0.91	0.92	0.04	4.1	24
V_d	w%	B2		-0.71	84.7	3	83.8	84.7	84.7	0.6	0.7	9
	w%	B3		-0.46	79.7	3	79.2	79.8	79.7	0.8	1.0	11
	w%	K1		-1.08	31.4	5	30.6	31.3	31.4	0.8	2.6	18

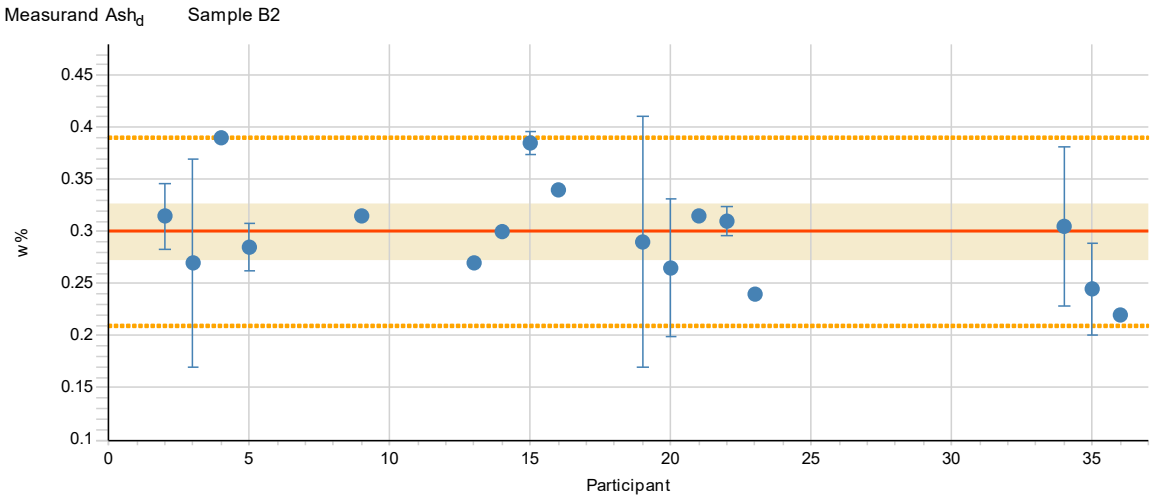
Participant 37												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cl_d	mg/kg	B3		1.99	572	35	771	577	572	113	19.7	9
M_{ad}	w%	B3			4.54		5.17	4.69	4.56	0.54	11.8	14
$q_{V,gr,d}$	J/g	B3		0.83	19737	1,5	19860	19748	19727	158	0.8	13
S_d	w%	B3		58470.48	0.06	35	614.00	0.06	0.06	0.01	19.0	13

Appendix 8. Results of participants and their uncertainties

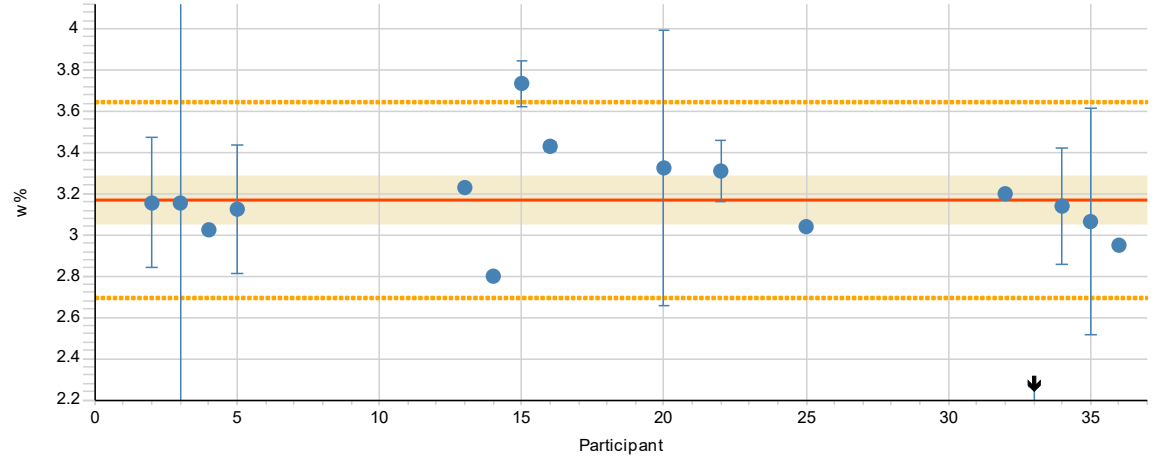
In figures:

- 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.

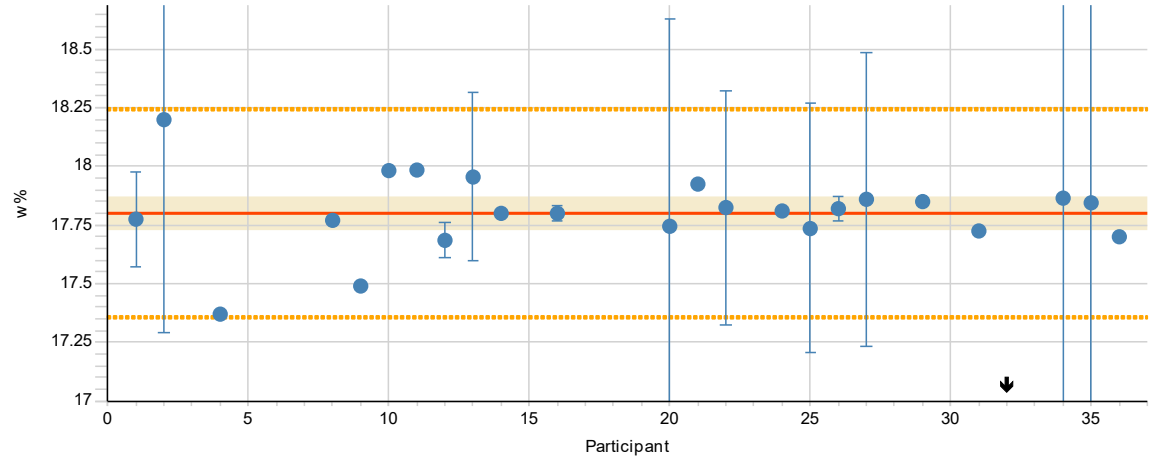




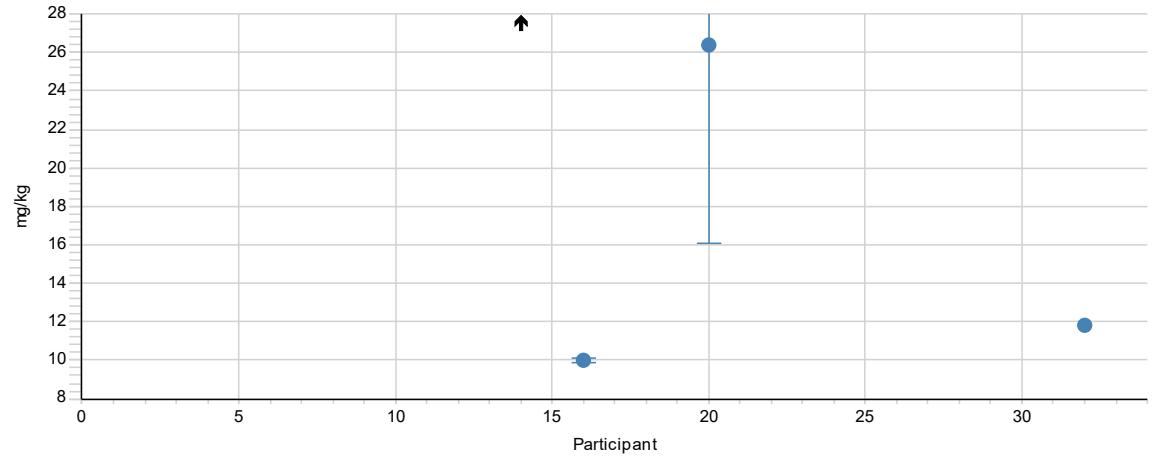
Measurand Ash_d Sample B3



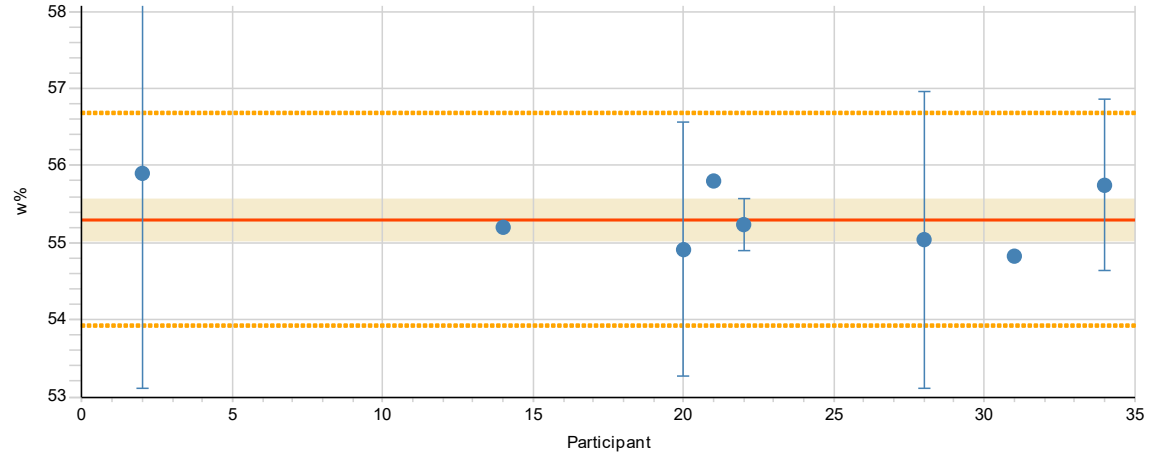
Measurand Ash_d Sample K1



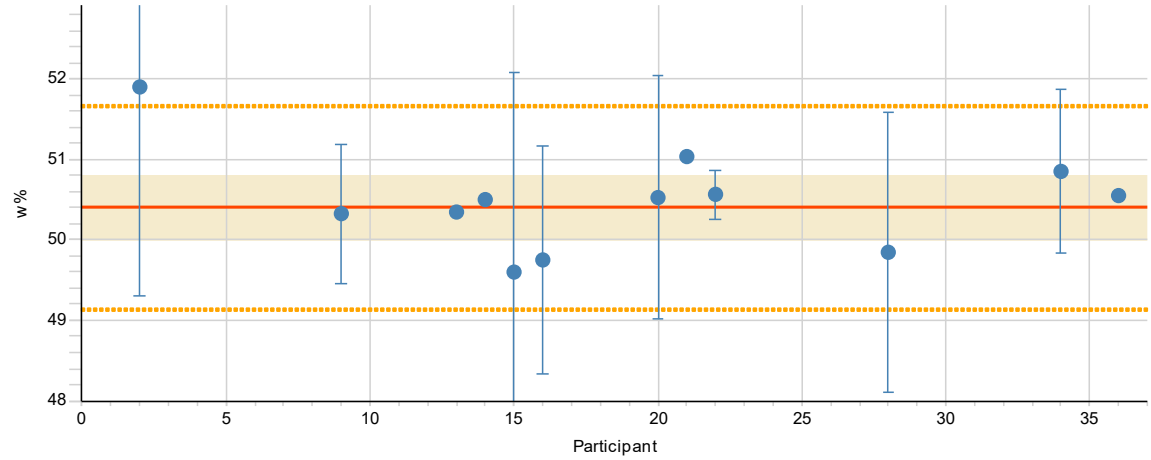
Measurand Br_d Sample K1



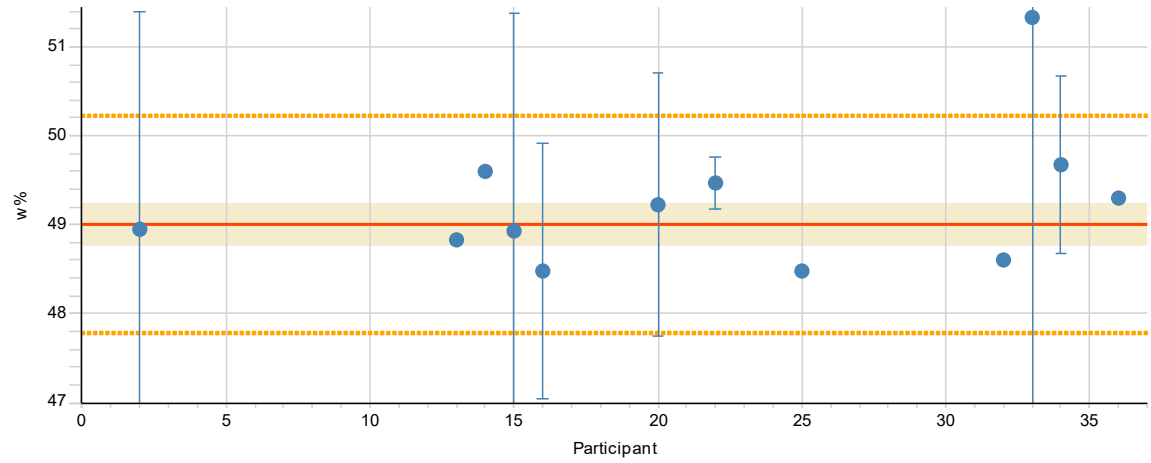
Measurand C_d Sample B1



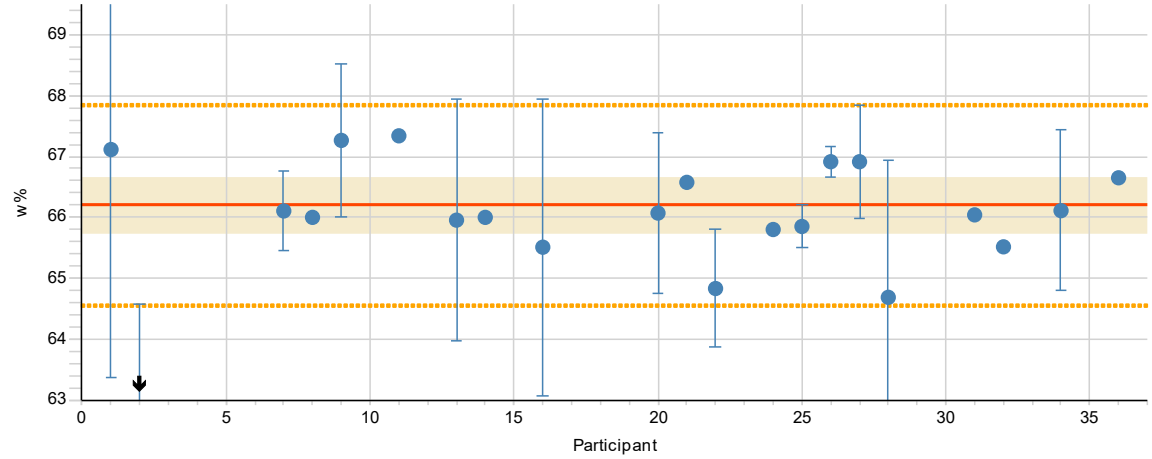
Measurand C_d Sample B2



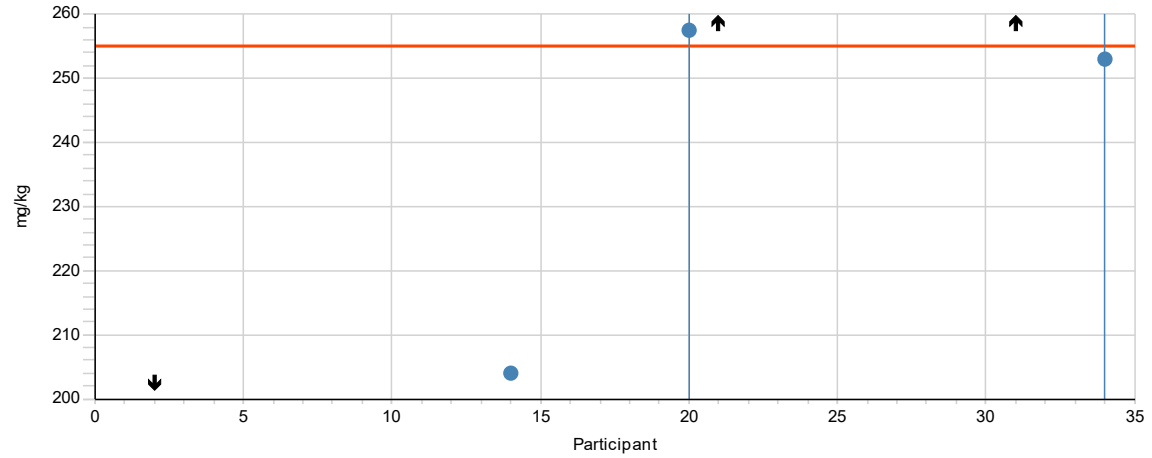
Measurand C_d Sample B3



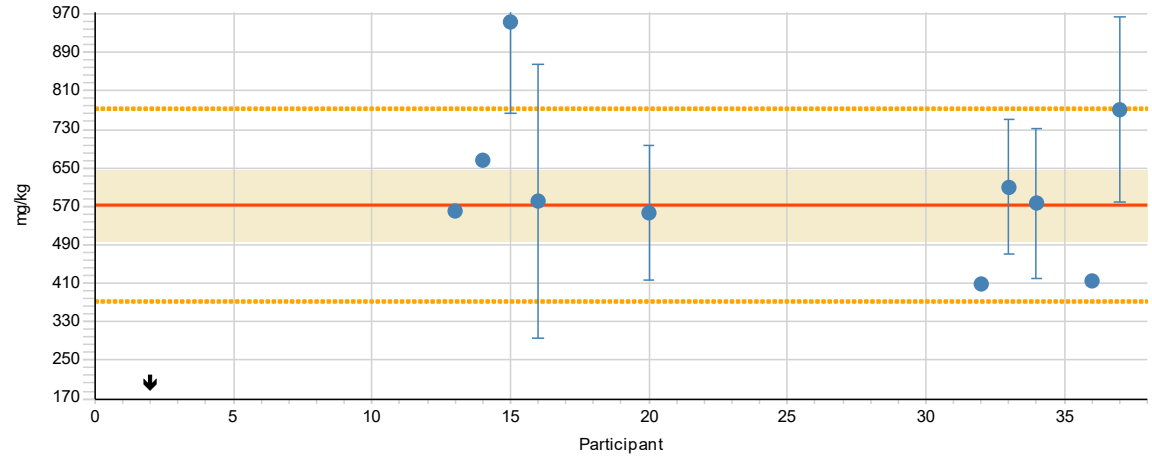
Measurand C_d Sample K1



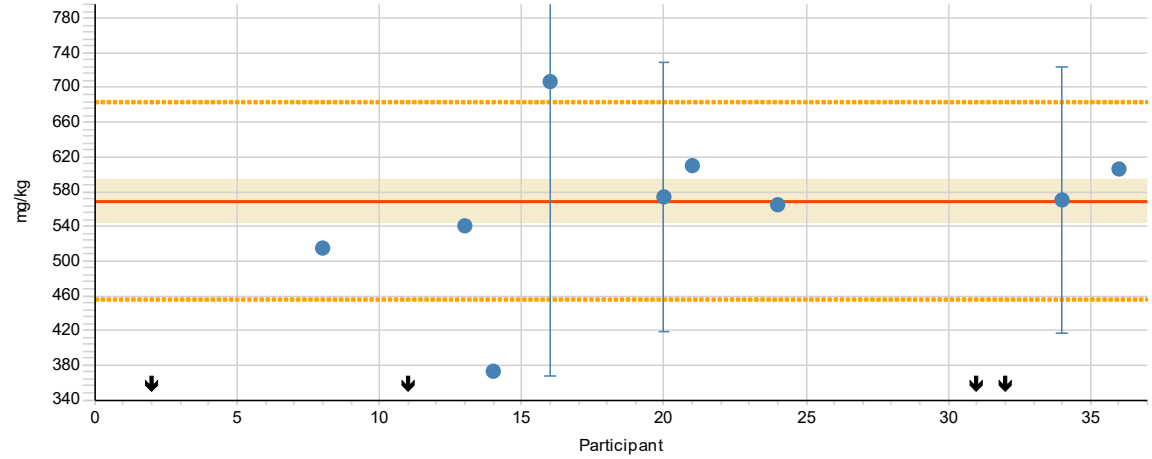
Measurand Cl_d Sample B1



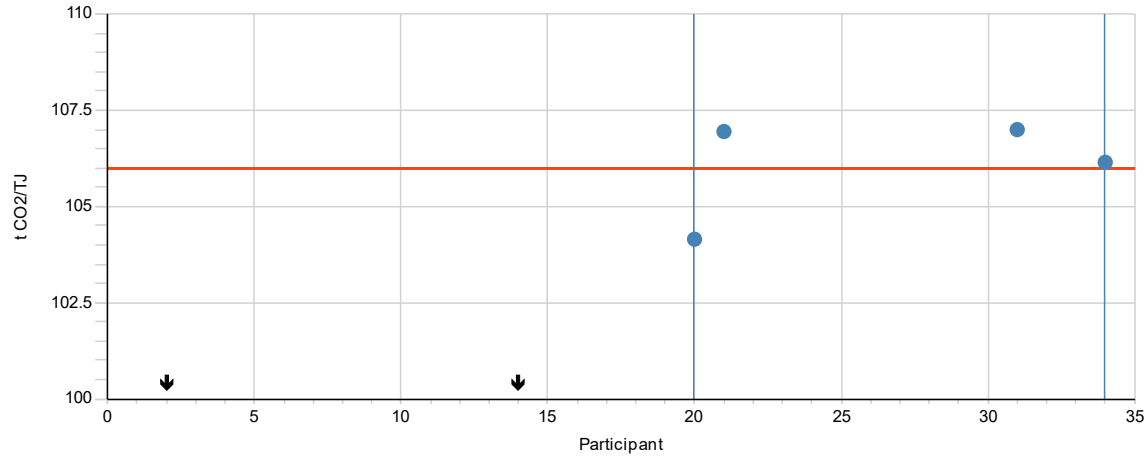
Measurand Cl_d Sample B3



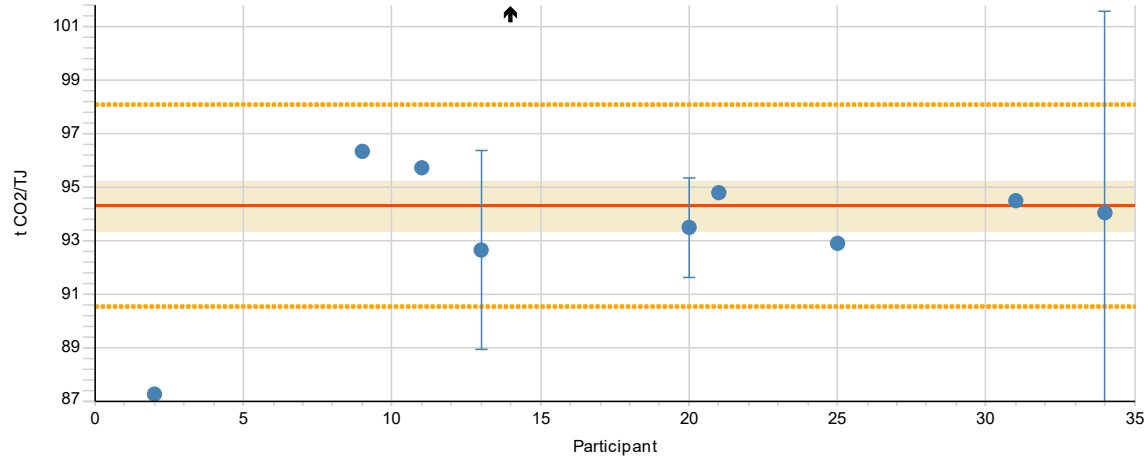
Measurand Cl_d Sample K1



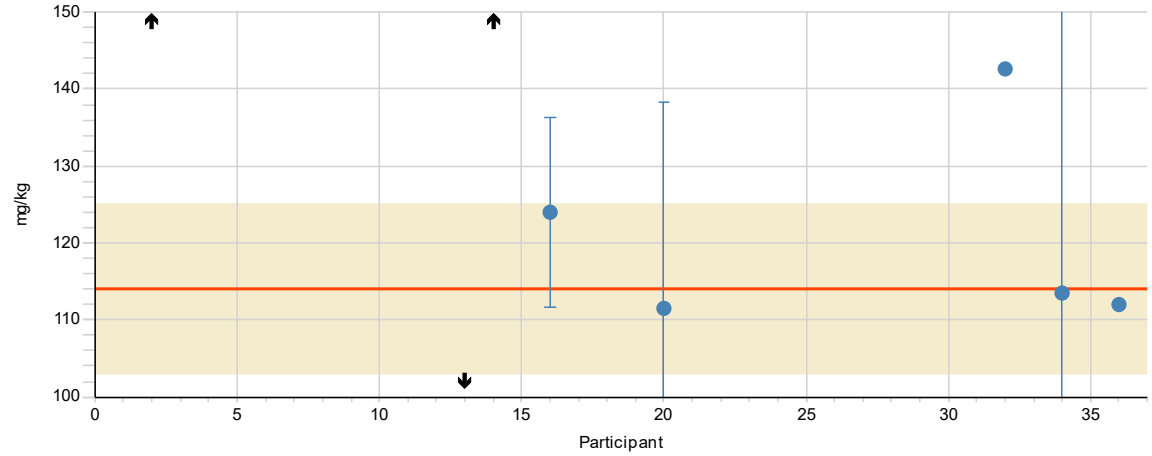
Measurand EF Sample B1



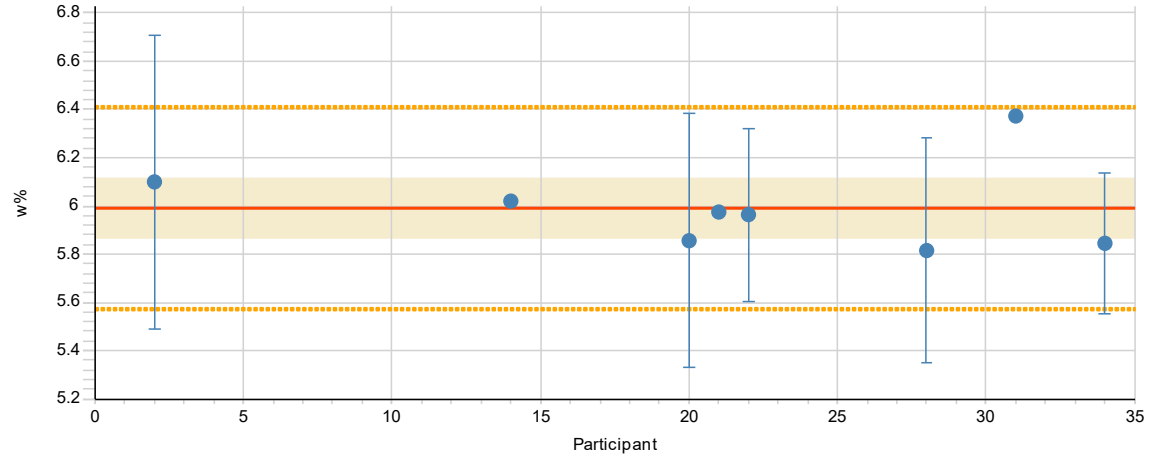
Measurand EF Sample K1



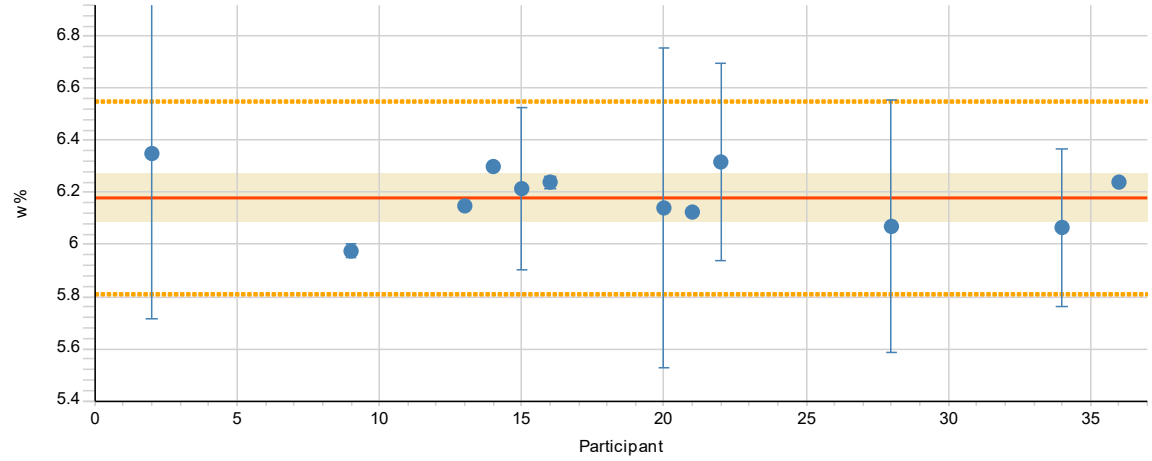
Measurand F_d Sample K1



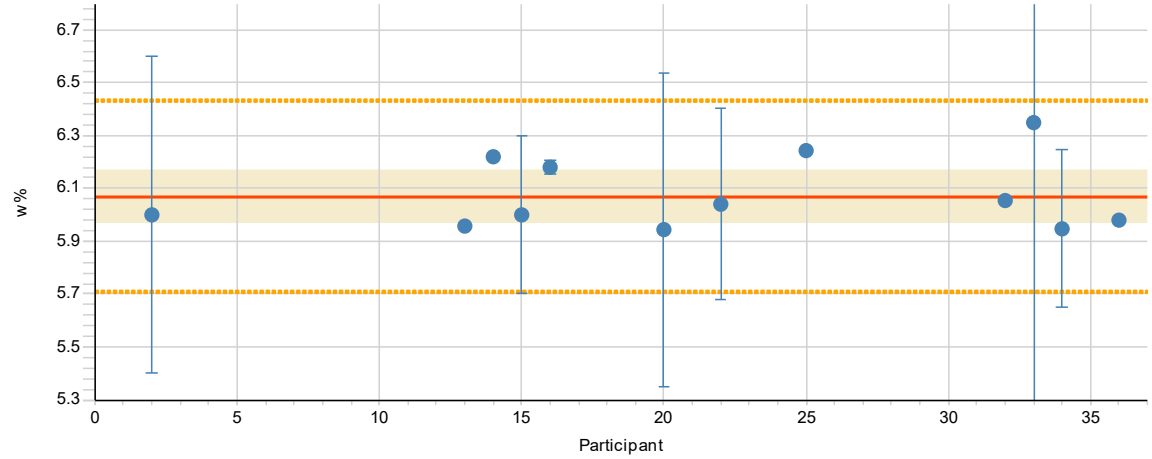
Measurand H_d Sample B1



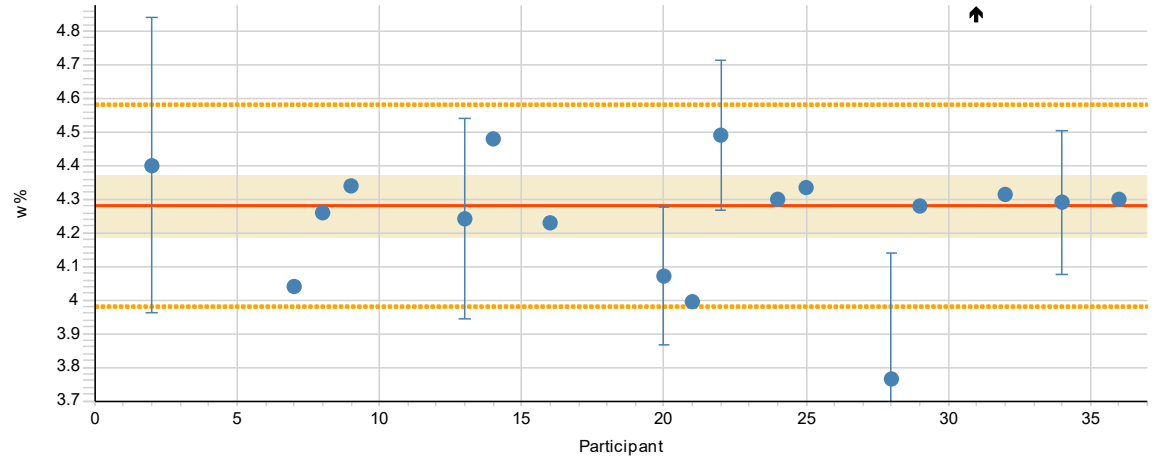
Measurand H_d Sample B2



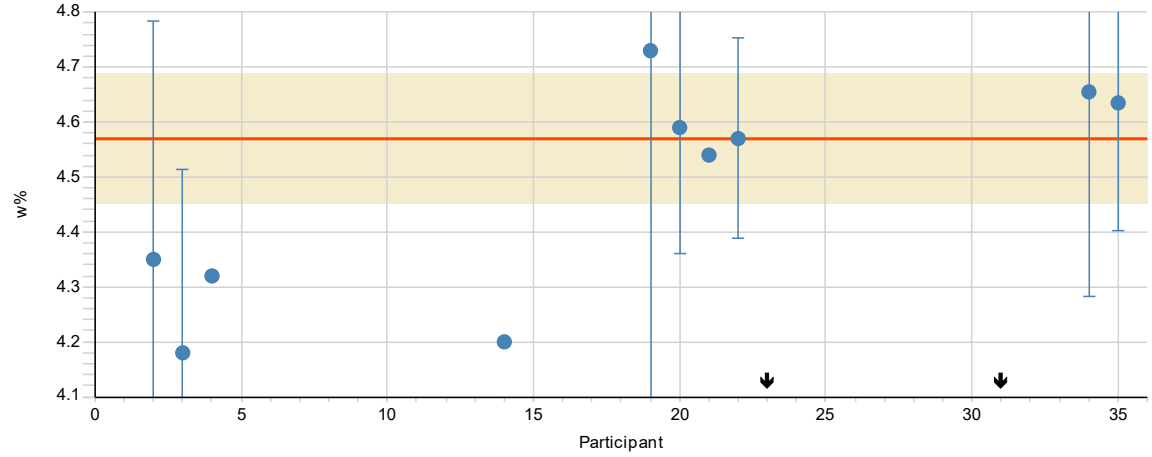
Measurand H_d Sample B3



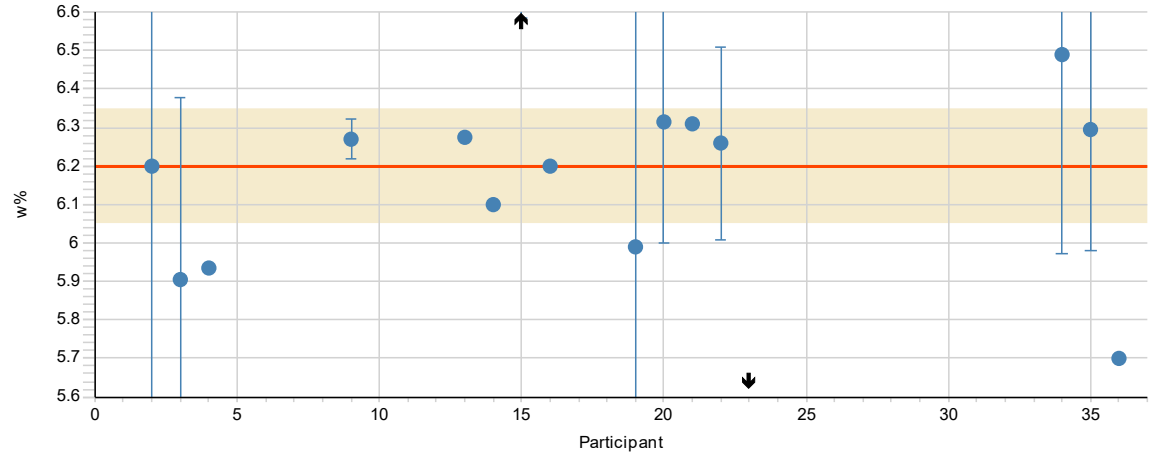
Measurand H_d Sample K1



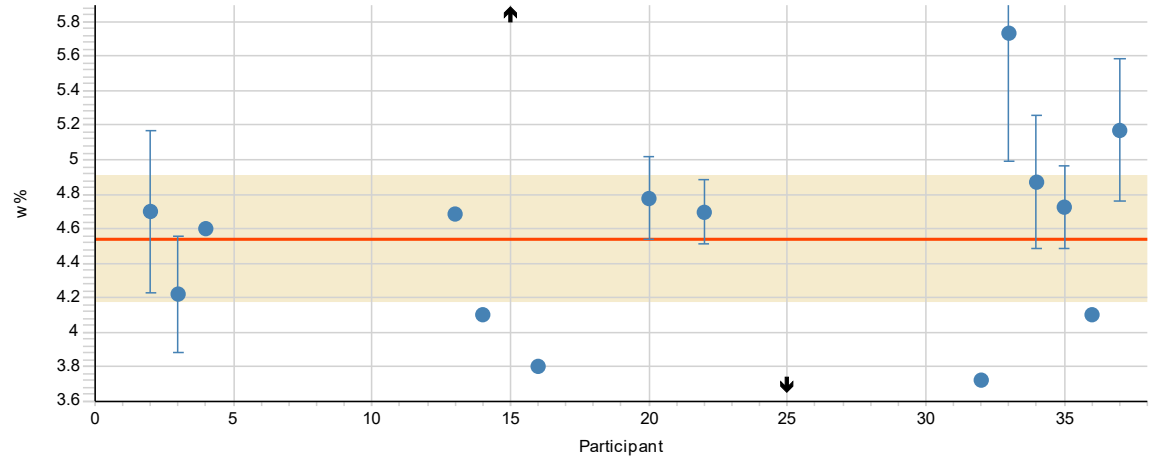
Measurand M_{ad} Sample B1



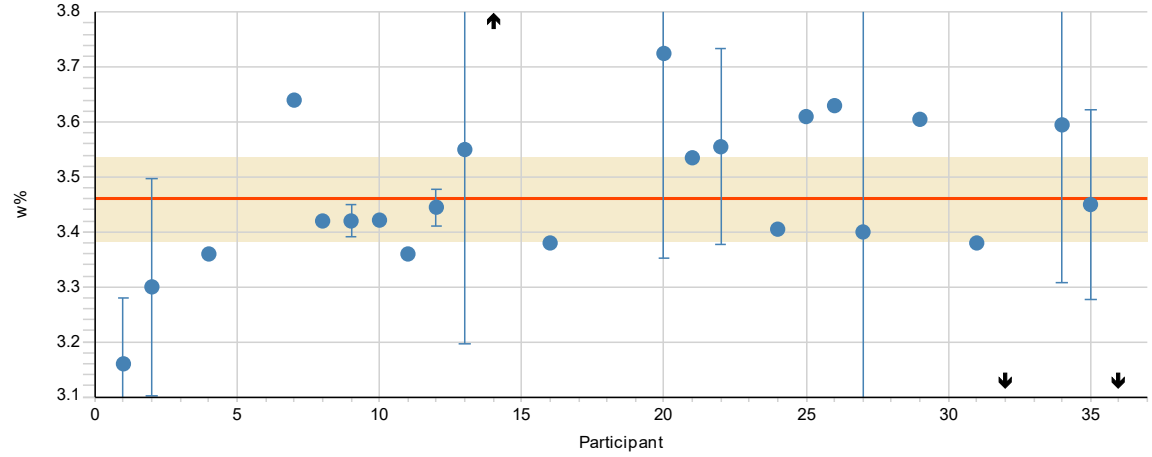
Measurand M_{ad} Sample B2



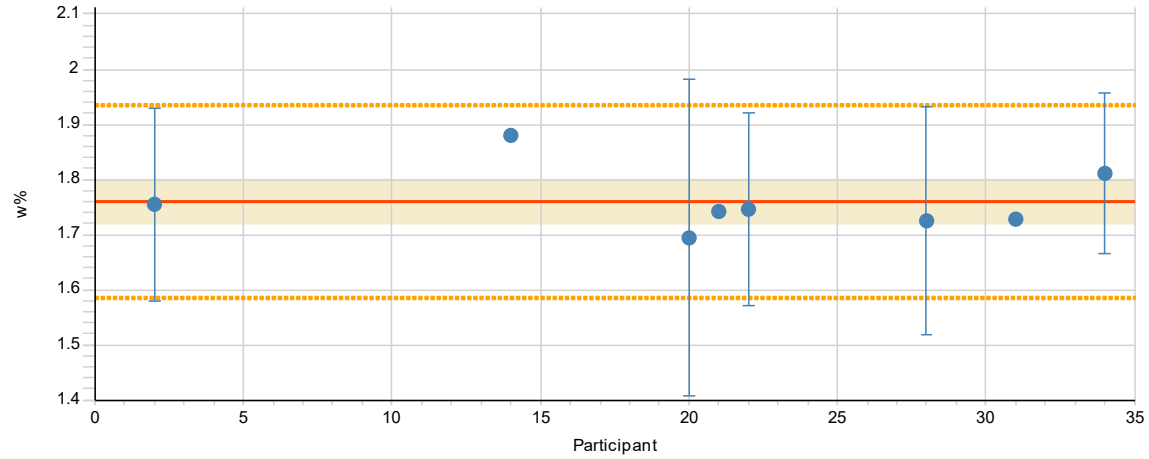
Measurand M_{ad} Sample B3



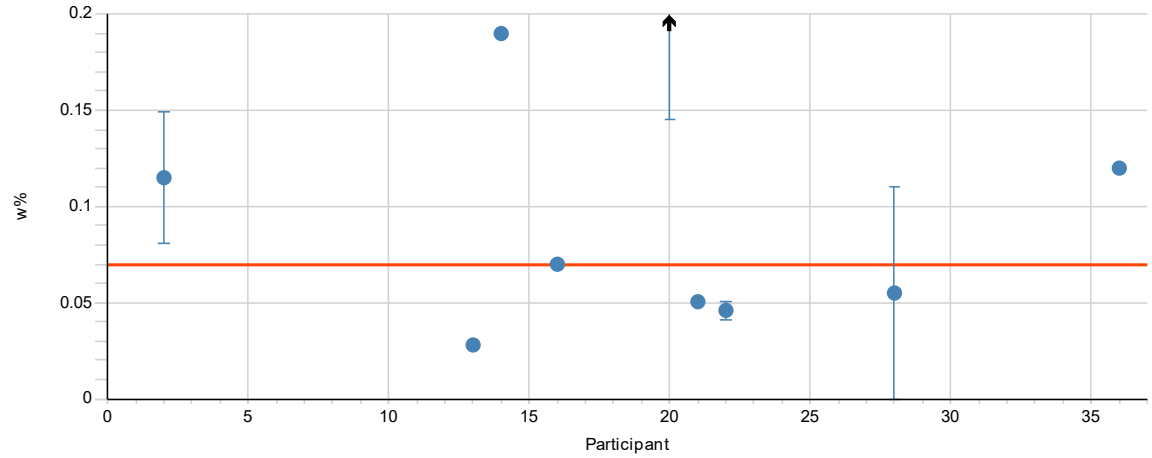
Measurand M_{ad} Sample K1



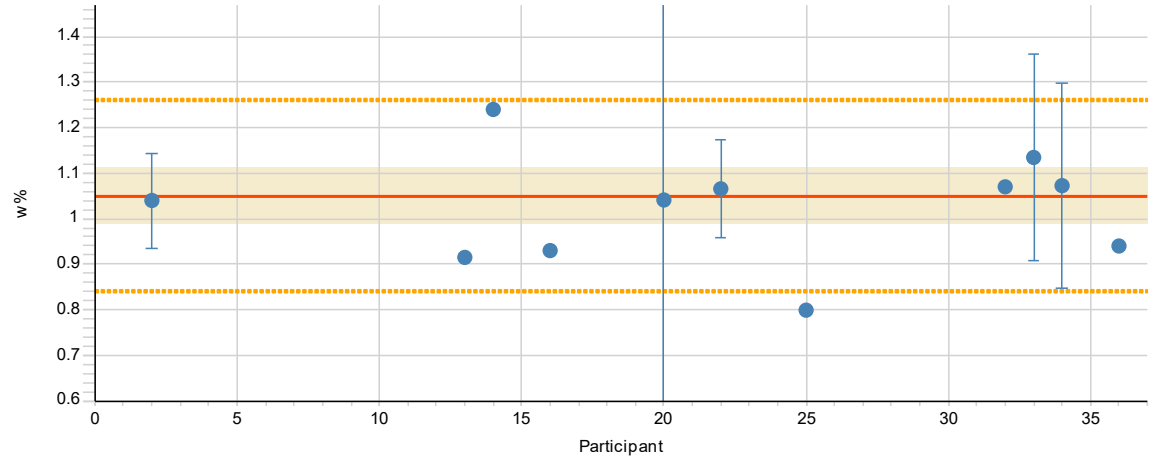
Measurand N_d Sample B1



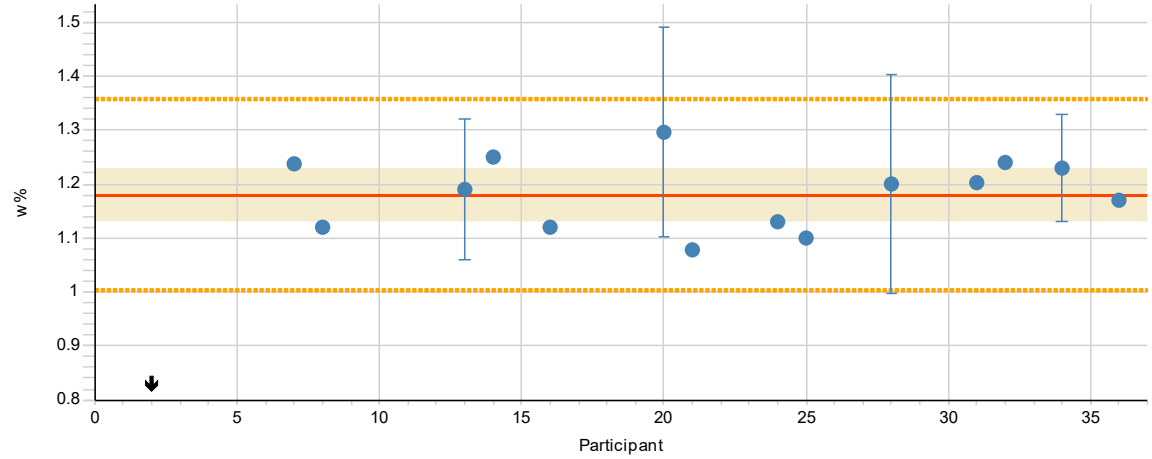
Measurand N_d Sample B2



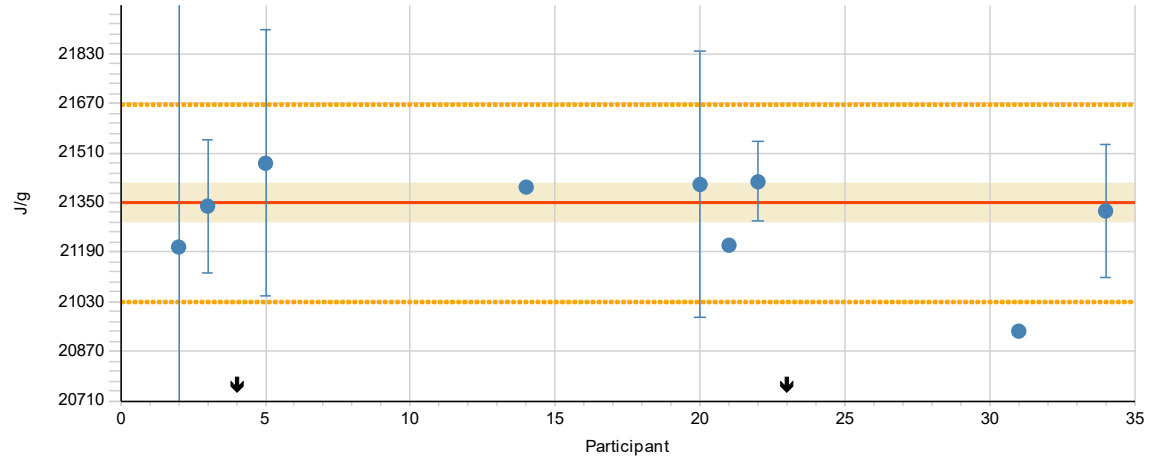
Measurand N_d Sample B3



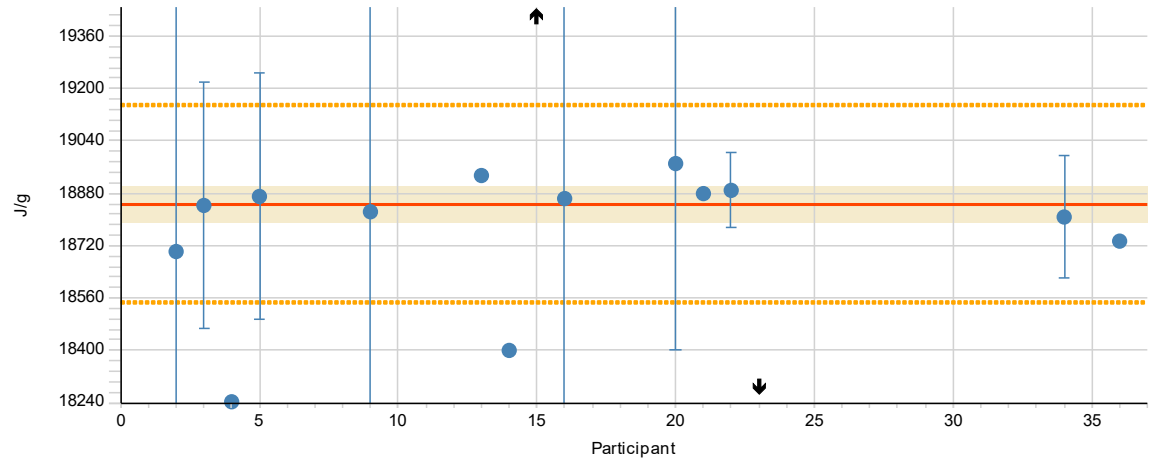
Measurand N_d Sample K1



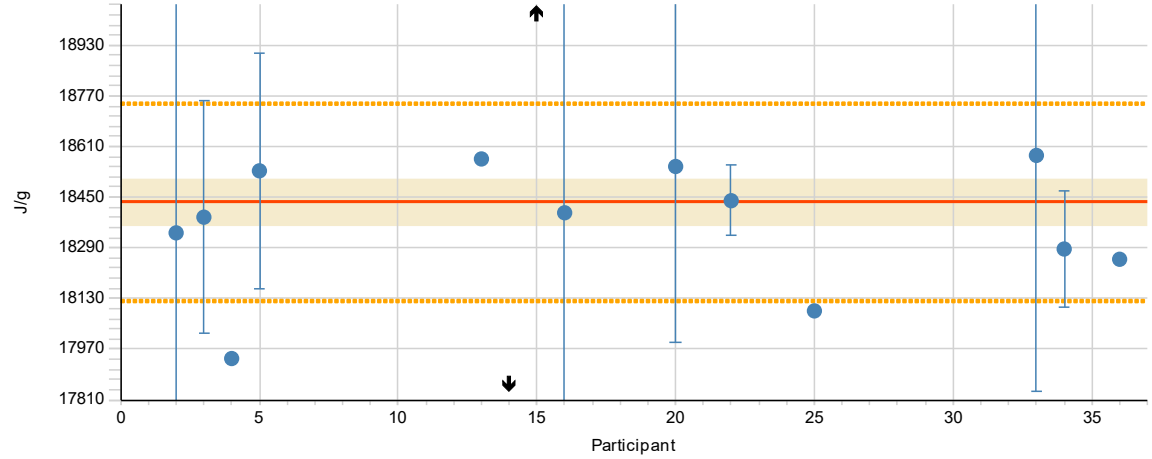
Measurand $q_{p,\,net,d}$ Sample B1



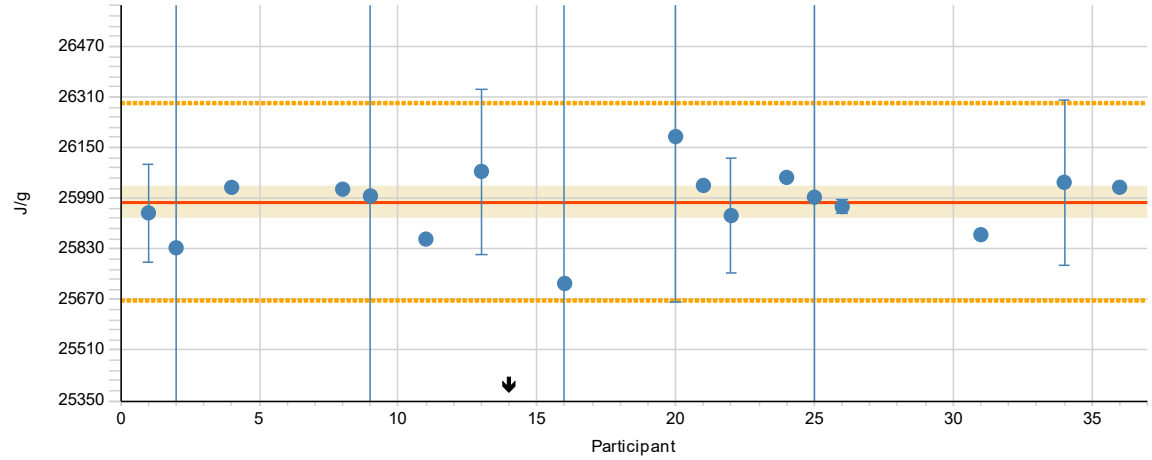
Measurand $q_{p,\,net,d}$ Sample B2



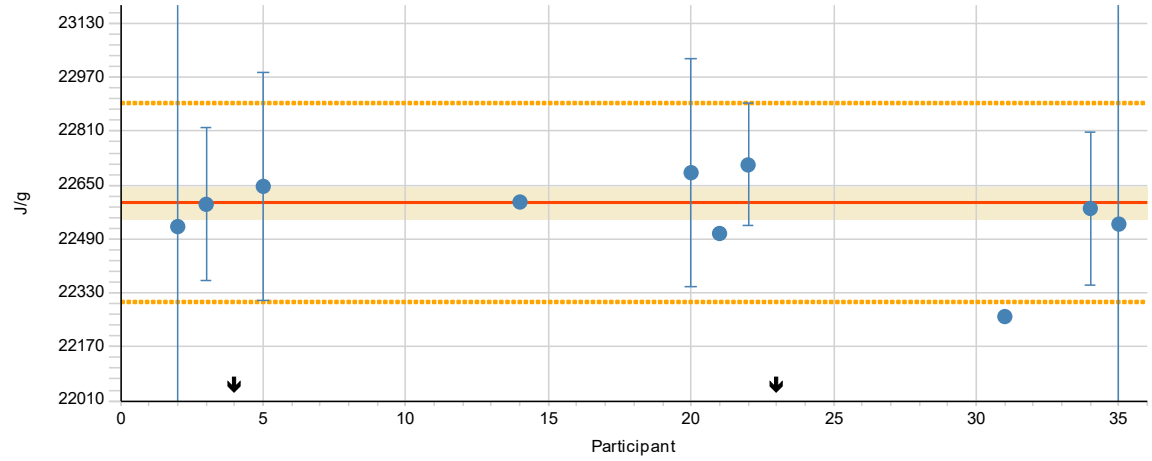
Measurand $q_{p,\,net,d}$ Sample B3

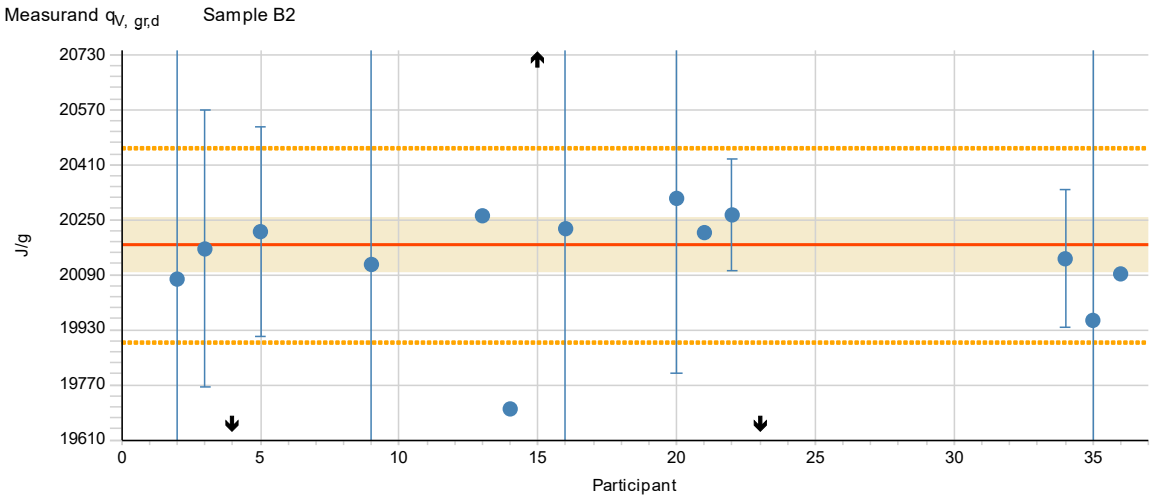


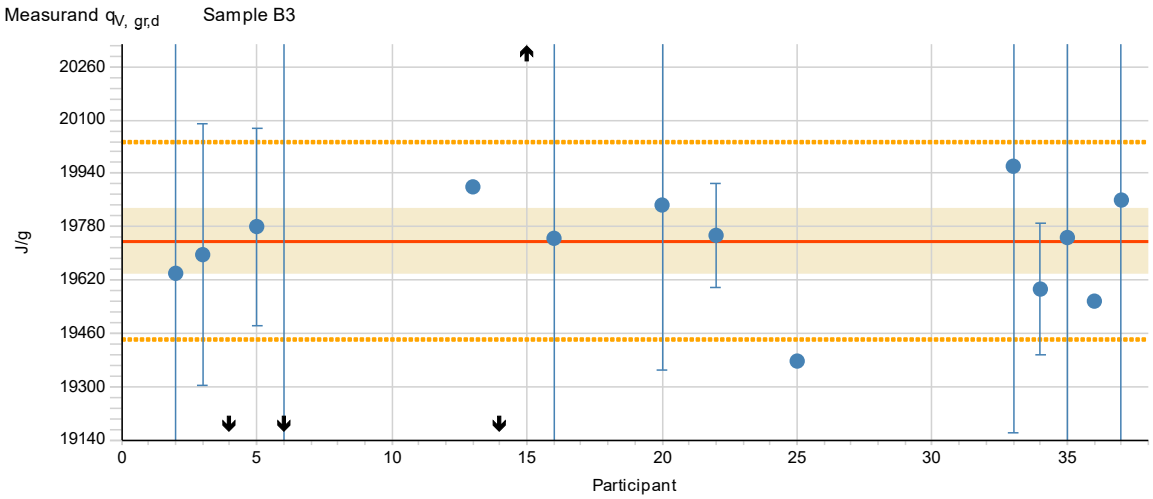
Measurand $q_{p,\,net,d}$ Sample K1

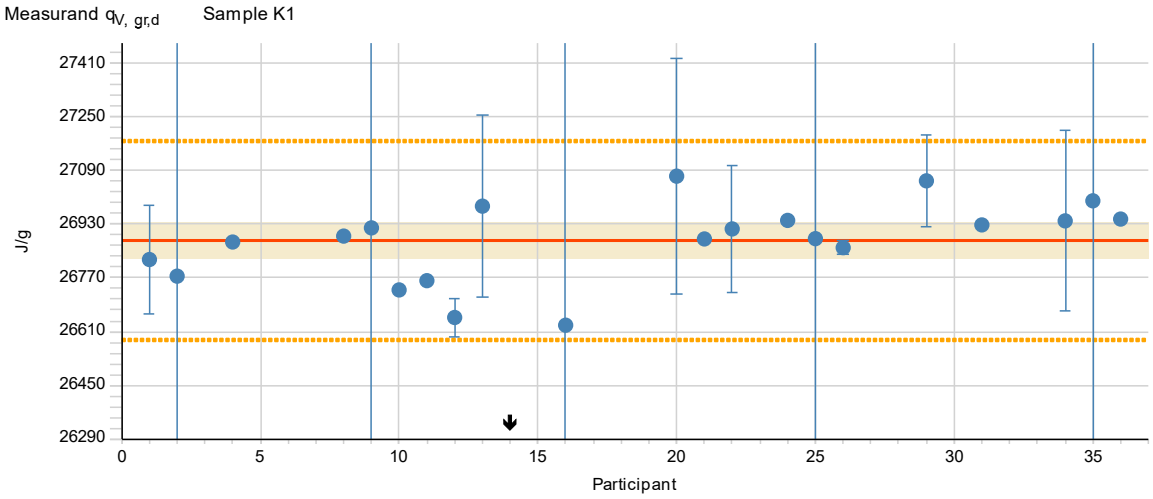


Measurand $q_{V,\,gr,d}$ Sample B1

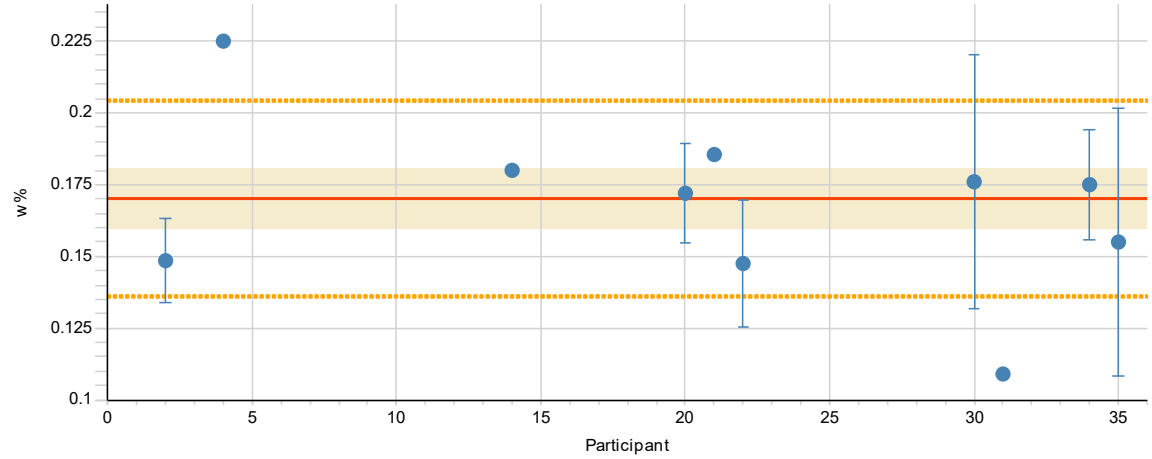



Measurand $q_{V,\ gr,d}$
Sample B2
20730
20570
20410
20250
20090
19930
19770
19610
J/g
0
5
10
15
20
25
30
35
Participant

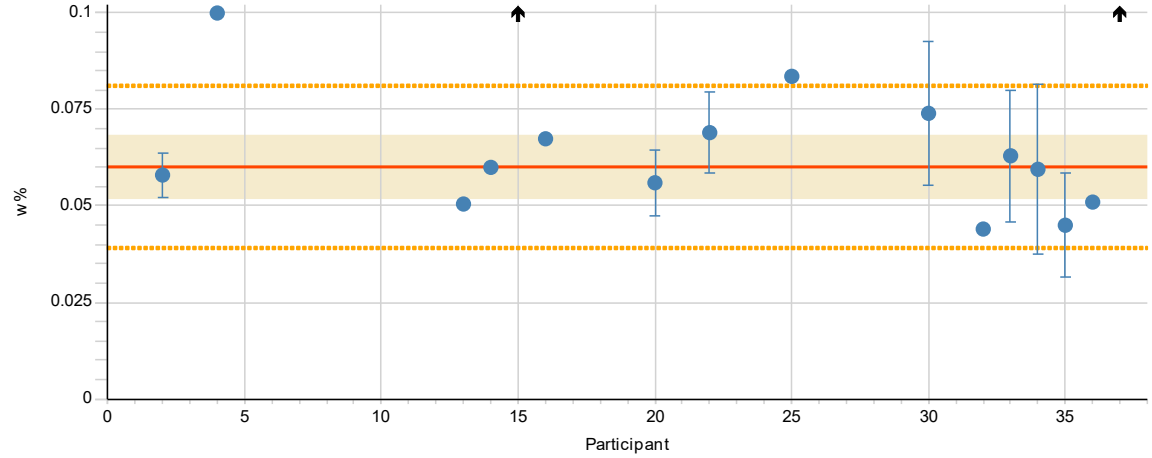

Measurand $q_{V,\ gr,d}$
Sample B3
20260
20100
19940
19780
19620
19460
19300
19140
J/g
0
5
10
15
20
25
30
35
Participant


Measurand $q_{V,\ gr,d}$
Sample K1
27410
27250
27090
26930
26770
26610
26450
26290
J/g
0
5
10
15
20
25
30
35
Participant

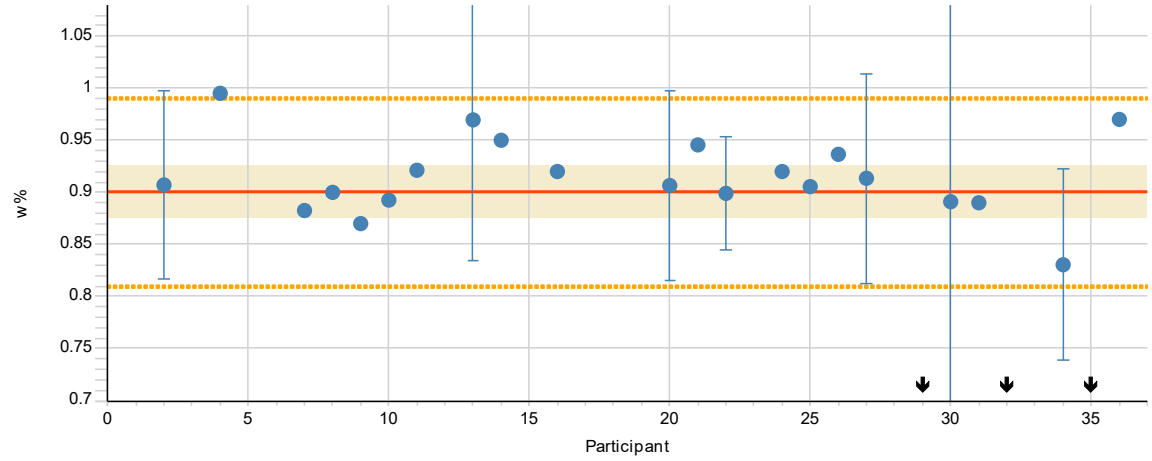
Measurand S_d Sample B1



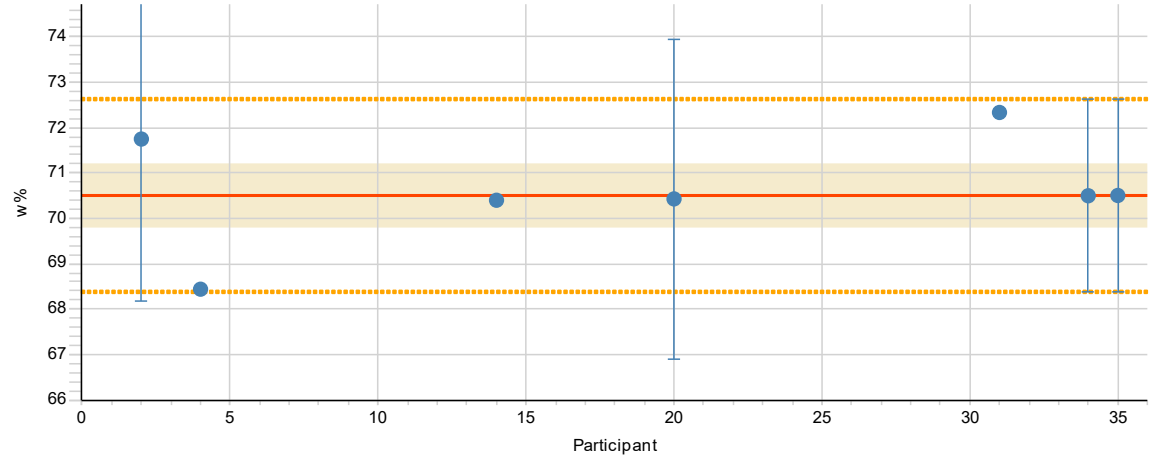
Measurand S_d Sample B3



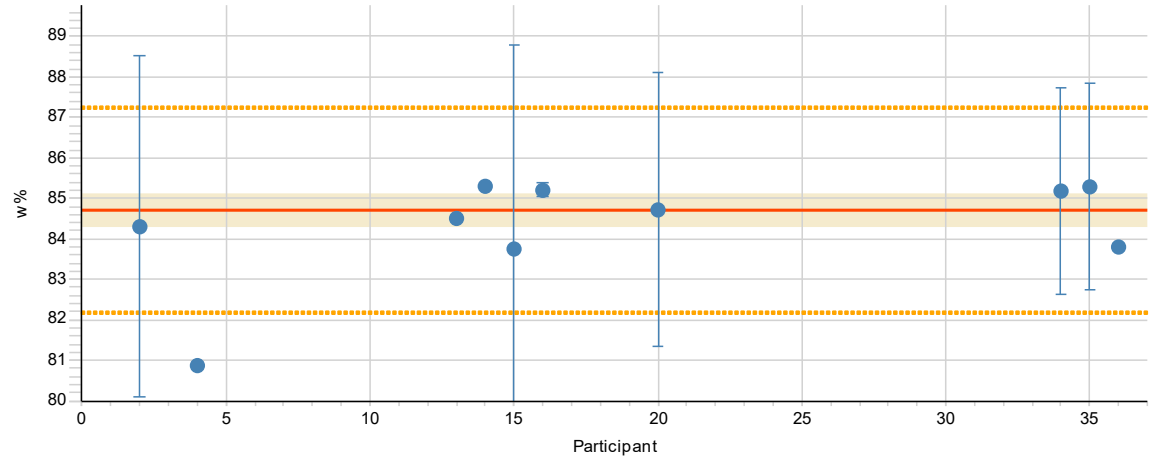
Measurand S_d Sample K1



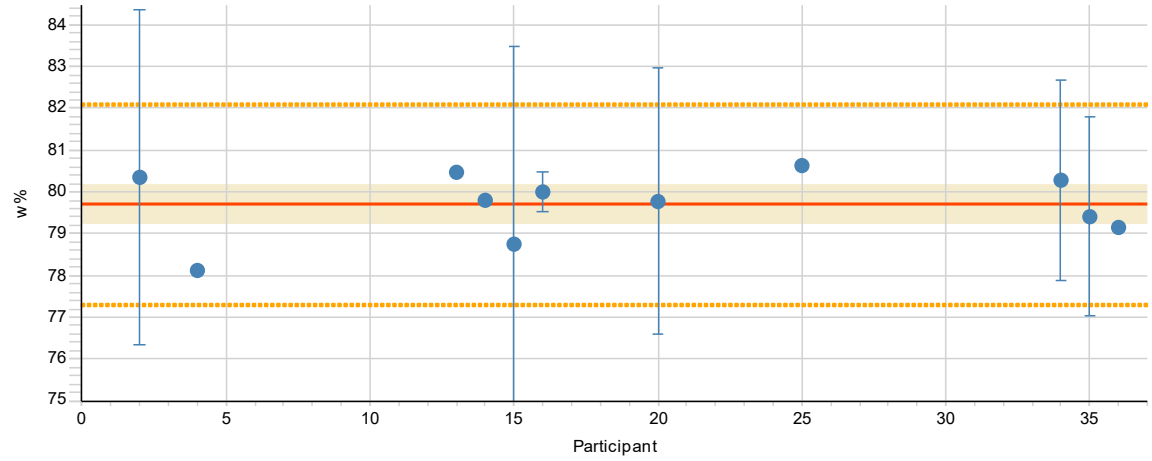
Measurand V_d Sample B1

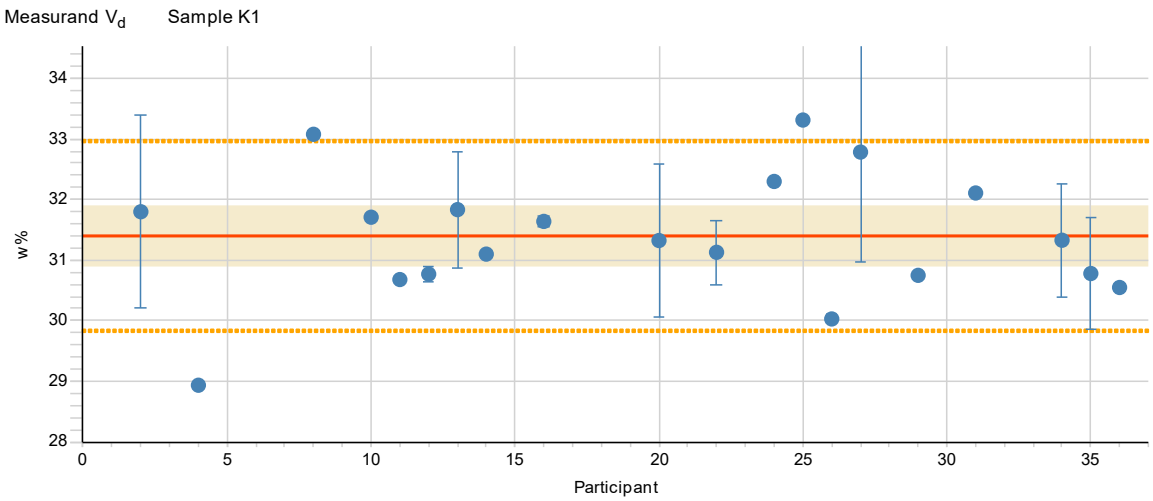


Measurand V_d Sample B2



Measurand V_d Sample B3




Measurand V_d
Sample K1
w%
34
33
32
31
30
29
28
0
5
10
15
20
25
30
35
Participant

Appendix 9. Summary of the z scores

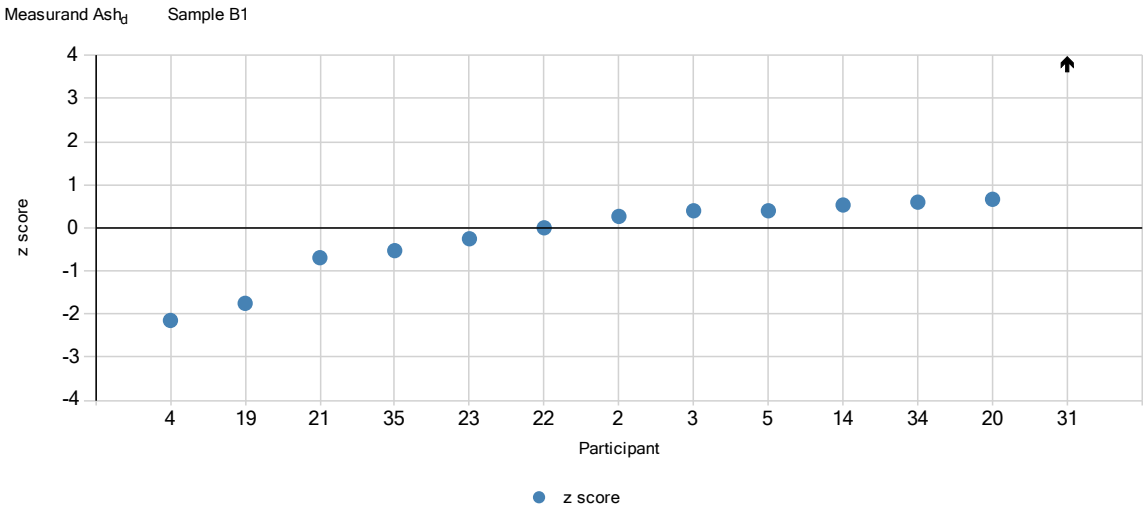
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	18	19	20	21	22	23	%
Ash_d	B1	.	**S**	**S**	*q*	**S**	.	.	.	.	.	.	.	.	S	.	.	.	**S**	**S**	**S**	**S**	*S*	84.6
	B2	.	**S**	**S**	*Q*	**S**	.	.	.	*S*	.	.	.	*S*	S	**S**	**S**	.	**S**	**S**	**S**	**S**	*S*	94.1
	B3	.	**S**	**S**	*S*	**S**	.	.	.	.	.	.	.	*S*	S	**Q**	**S**	.	.	**S**	.	**S**	.	87.5
	K1	**S**	**S**	.	*S*	.	.	.	**S**	*S*	*S*	**S**	**S**	**S**	S	.	**S**	.	.	**S**	**S**	*S*	.	95.8
C_d	B1	.	**S**	.	.	.	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	**S**	**S**	.	100
	B2	.	**Q**	.	.	.	.	.	.	**S**	.	.	.	*S*	S	**S**	**S**	.	.	**S**	**S**	**S**	.	91.7
	B3	.	**S**	.	.	.	.	.	.	.	.	.	.	*S*	S	**S**	**S**	.	.	**S**	.	**S**	.	91.7
	K1	**S**	**u**	.	.	.	.	**S**	**S**	**S**	.	**S**	.	**S**	S	.	**S**	.	.	**S**	**S**	**S**	.	95.2
Cl_d	B3	.	**u**	.	.	.	.	.	.	.	.	.	.	*S*	S	**U**	**S**	.	.	**S**	.	.	.	81.8
	K1	.	**u**	.	.	.	.	.	**S**	.	.	*u*	.	*S*	u	.	*Q*	.	.	**S**	**S**	.	.	53.8
EF	K1	.	*u*	.	.	.	.	.	.	*S*	.	S	.	**S**	U	.	.	.	.	**S**	*S*	.	.	80.0
H_d	B1	.	**S**	.	.	.	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	**S**	**S**	.	100
	B2	.	**S**	.	.	.	.	.	.	**S**	.	.	.	*S*	S	**S**	**S**	.	.	**S**	**S**	**S**	.	100
	B3	.	**S**	.	.	.	.	.	.	.	.	.	.	*S*	S	**S**	**S**	.	.	**S**	.	**S**	.	100
	K1	.	**S**	.	.	.	.	*S*	**S**	**S**	.	.	.	**S**	S	.	**S**	.	.	**S**	**S**	**S**	.	88.9
N_d	B1	.	**S**	.	.	.	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	**S**	**S**	.	100
	B3	.	**S**	.	.	.	.	.	.	.	.	.	.	*S*	S	.	S	.	.	**S**	.	**S**	.	90.9
	K1	.	**u**	.	.	.	.	*S*	**S**	.	.	.	.	**S**	S	.	**S**	.	.	**S**	**S**	.	.	93.3
$q_{p,net,d}$	B1	.	**S**	**S**	u	**S**	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	**S**	**S**	*u*	72.7
	B2	.	**S**	**S**	u	**S**	.	.	.	**S**	.	.	.	*S*	q	**U**	**S**	.	.	**S**	**S**	**S**	*u*	73.3
	B3	.	**S**	**S**	u	**S**	.	.	.	.	.	.	.	*S*	u	**U**	**S**	.	.	**S**	.	**S**	.	71.4
	K1	**S**	**S**	.	S	.	.	.	**S**	**S**	.	**S**	.	**S**	u	.	*S*	.	.	**S**	**S**	*S*	.	94.4
$q_{V,gr,d}$	B1	.	**S**	**S**	*u*	**S**	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	**S**	**S**	*u*	75.0
	B2	.	**S**	**S**	*u*	**S**	.	.	.	**S**	.	.	.	*S*	u	**U**	**S**	.	.	**S**	**S**	**S**	*u*	75.0
	B3	.	**S**	**S**	*u*	**S**	u	.	.	.	.	.	.	*S*	u	U	**S**	.	.	**S**	.	**S**	.	70.6
	K1	**S**	**S**	.	**S**	.	.	.	**S**	**S**	**S**	**S**	**S**	**S**	u	.	*S*	.	.	**S**	**S**	**S**	.	95.5
S_d	B1	.	**S**	.	*U*	.	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	**S**	**S**	.	80.0
	B3	.	**S**	.	*U*	.	.	.	.	.	.	.	.	*S*	S	**U**	**S**	.	.	**S**	.	**S**	.	75.0
	K1	.	**S**	.	*Q*	.	.	*S*	**S**	**S**	*S*	**S**	.	**S**	S	.	**S**	.	.	**S**	**S**	**S**	.	83.3
V_d	B1	.	**S**	.	*S*	.	.	.	.	.	.	.	.	.	S	.	.	.	.	**S**	.	.	.	100
	B2	.	**S**	.	*u*	.	.	.	.	.	.	.	.	*S*	S	**S**	*S*	.	.	**S**	.	.	.	90.0
	B3	.	**S**	.	*S*	.	.	.	.	.	.	.	.	*S*	S	S	*S*	.	.	**S**	.	.	.	100
	K1	.	**S**	.	*u*	.	.	.	*Q*	.	*S*	**S**	S	**S**	S	.	**S**	.	.	**S**	.	*S*	.	85.0
%		100	82	100	32	100	0	100	89	100	100	88	100	100	76	50	96		100	100	100	100	33	
accredited		4	32	9	1	9		1	8	9	1	6	2	9		12	18		2	33	20	23		

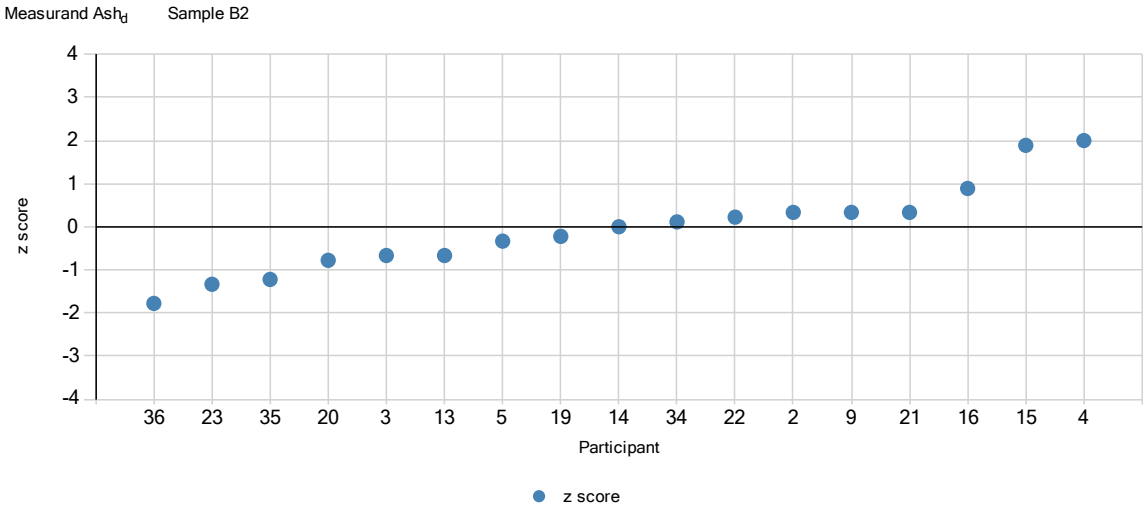
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	%
Ash_d	B1	.	.	.	.	.	.	.	*U*	.	.	**S**	**S**	.	.	84.6
	B2	.	.	.	.	.	.	.	.	.	.	**S**	**S**	**S**	.	94.1
	B3	.	*S*	.	.	.	.	.	.	*S*	**u**	**S**	**S**	**S**	.	87.5
	K1	**S**	**S**	*S*	*S*	.	**S**	.	*S*	*u*	.	**S**	**S**	**S**	.	95.8
C_d	B1	.	.	.	.	**S**	.	.	*S*	.	.	**S**	.	.	.	100
	B2	.	.	.	.	*S*	.	.	.	.	.	**S**	.	**S**	.	91.7
	B3	.	*S*	.	.	.	.	.	.	*S*	*U*	**S**	.	**S**	.	91.7
	K1	**S**	**S**	*S*	**S**	*S*	.	.	*S*	*S*	.	**S**	.	**S**	.	95.2
Cl_d	B3	.	.	.	.	.	.	.	.	*S*	**S**	**S**	.	**S**	**S**	81.8
	K1	**S**	.	.	.	.	.	.	*u*	*u*	.	*S*	.	*S*	.	53.8
EF	K1	.	*S*	.	.	.	.	.	*S*	.	.	**S**	.	.	.	80.0
H_d	B1	.	.	.	.	**S**	.	.	*S*	.	.	**S**	.	.	.	100
	B2	.	.	.	.	*S*	.	.	.	.	.	**S**	.	**S**	.	100
	B3	.	*S*	.	.	.	.	.	.	*S*	*S*	**S**	.	**S**	.	100
	K1	**S**	**S**	.	.	*u*	*S*	.	*U*	*S*	.	**S**	.	**S**	.	88.9
N_d	B1	.	.	.	.	**S**	.	.	*S*	.	.	**S**	.	.	.	100
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B3	.	*q*	.	.	.	.	.	.	*S*	*S*	**S**	.	S	.	90.9
	K1	**S**	**S**	.	.	*S*	.	.	S	*S*	.	**S**	.	**S**	.	93.3
$q_{p,net,d}$	B1	.	.	.	.	.	.	.	*q*	.	.	**S**	.	.	.	72.7
	B2	.	.	.	.	.	.	.	.	.	.	**S**	.	S	.	73.3
	B3	.	*q*	.	.	.	.	.	.	.	**S**	**S**	.	S	.	71.4
	K1	**S**	**S**	*S*	.	.	.	.	*S*	.	.	**S**	.	S	.	94.4
$q_{V,gr,d}$	B1	.	.	.	.	.	.	.	*q*	.	.	**S**	**S**	.	.	75.0
	B2	.	.	.	.	.	.	.	.	.	.	**S**	**S**	**S**	.	75.0
	B3	.	*q*	.	.	.	.	.	.	.	**S**	**S**	**S**	**S**	*S*	70.6
	K1	**S**	**S**	*S*	.	.	**S**	.	*S*	.	.	**S**	**S**	**S**	.	95.5
S_d	B1	.	.	.	.	.	.	**S**	*u*	.	.	**S**	**S**	.	.	80.0
	B3	.	Q	.	.	.	.	**S**	.	S	**S**	**S**	**S**	**S**	**U**	75.0
	K1	**S**	**S**	*S*	*S*	.	**u**	**S**	*S*	*u*	.	**S**	**u**	**S**	.	83.3
V_d	B1	.	.	.	.	.	.	.	*S*	.	.	**S**	**S**	.	.	100
	B2	.	.	.	.	.	.	.	.	.	.	**S**	**S**	**S**	.	90.0
	B3	.	*S*	.	.	.	.	.	.	.	.	**S**	**S**	S	.	100
	K1	*S*	*Q*	*S*	*S*	.	**S**	.	*S*	.	.	**S**	**S**	**S**	.	85.0
%		100	71	100	100	88	80	100	67	75	75	100	93	100	67	
accredited		8	7		1	3	4	3			5	32	15	18	2	

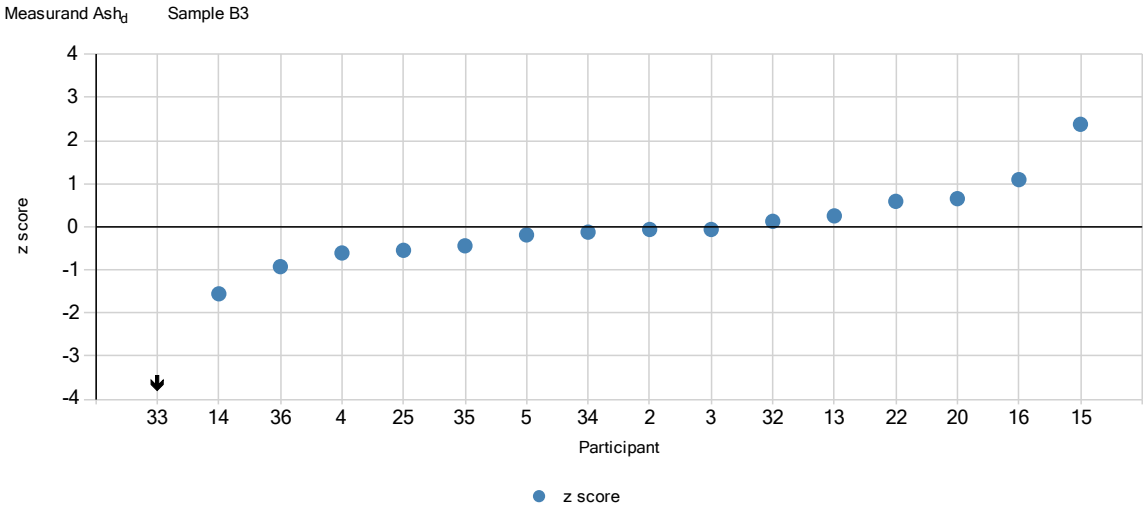
S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Satisfactory results, in total %: 87 in accredited %: 95 in non-accredited %: 71

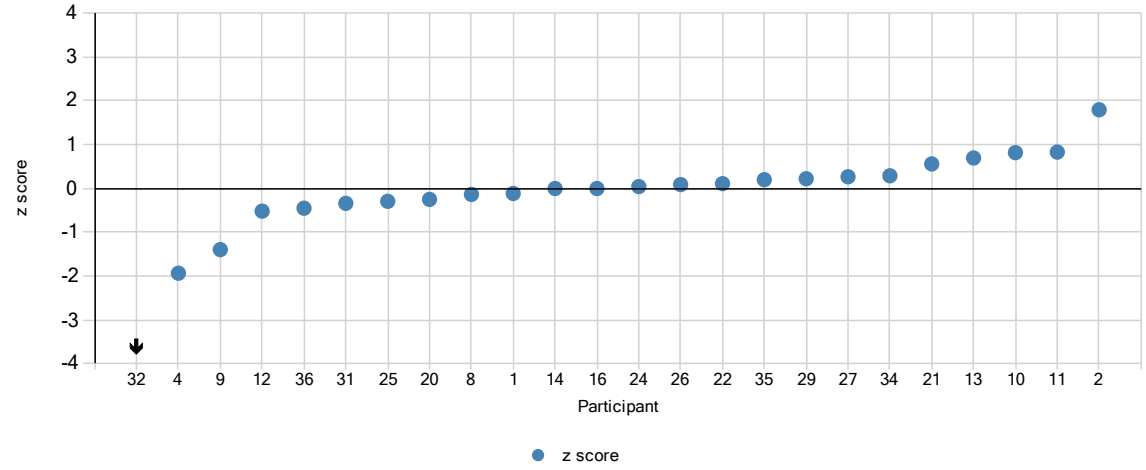
Appendix 10. z scores in ascending order



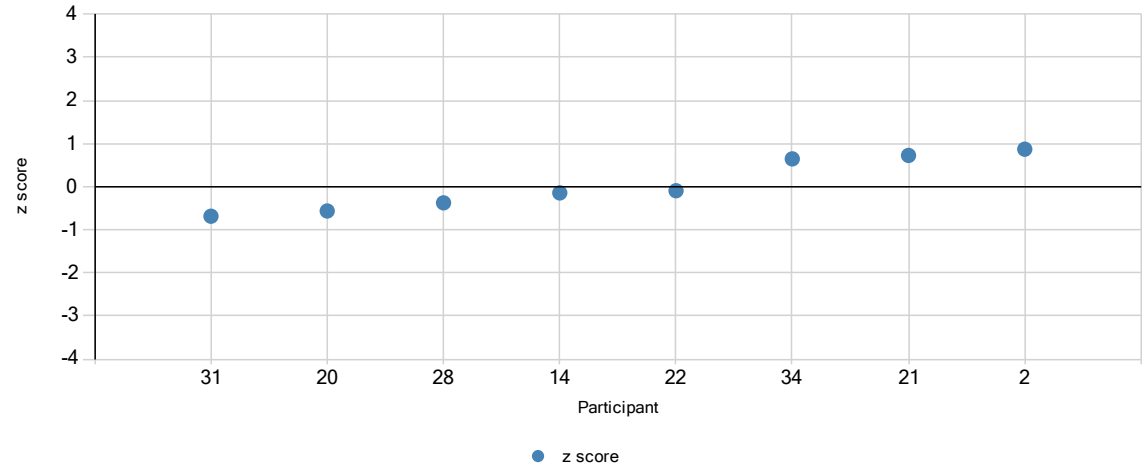




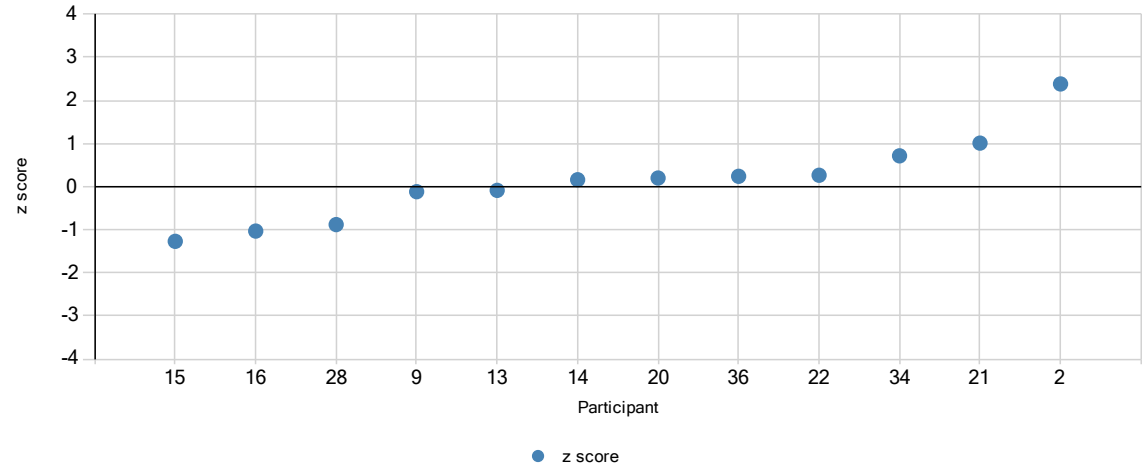
Measurand Ash_d Sample K1



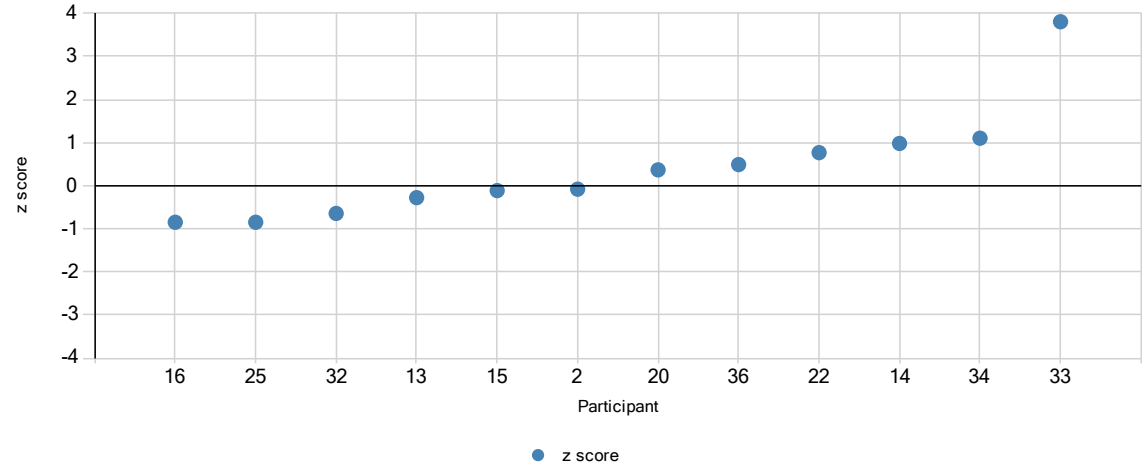
Measurand C_d Sample B1



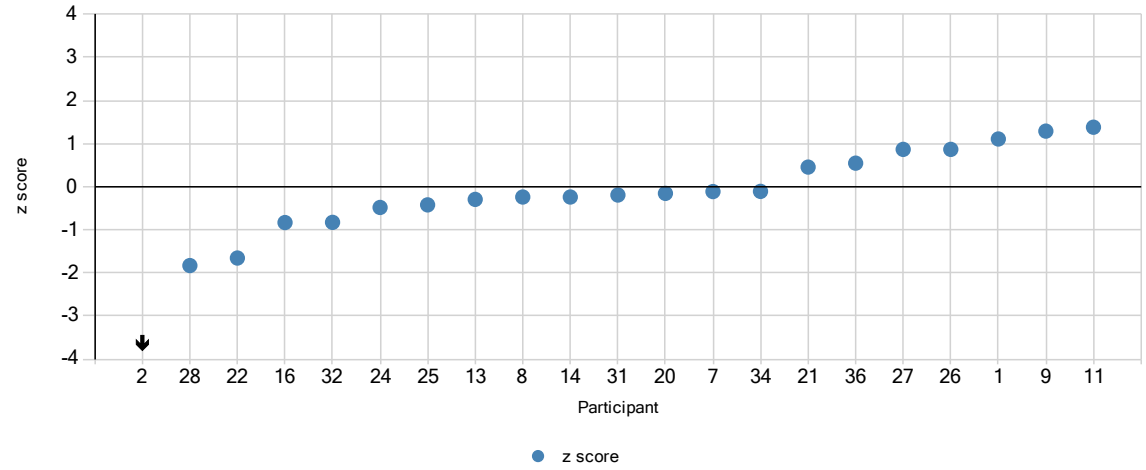
Measurand C_d Sample B2



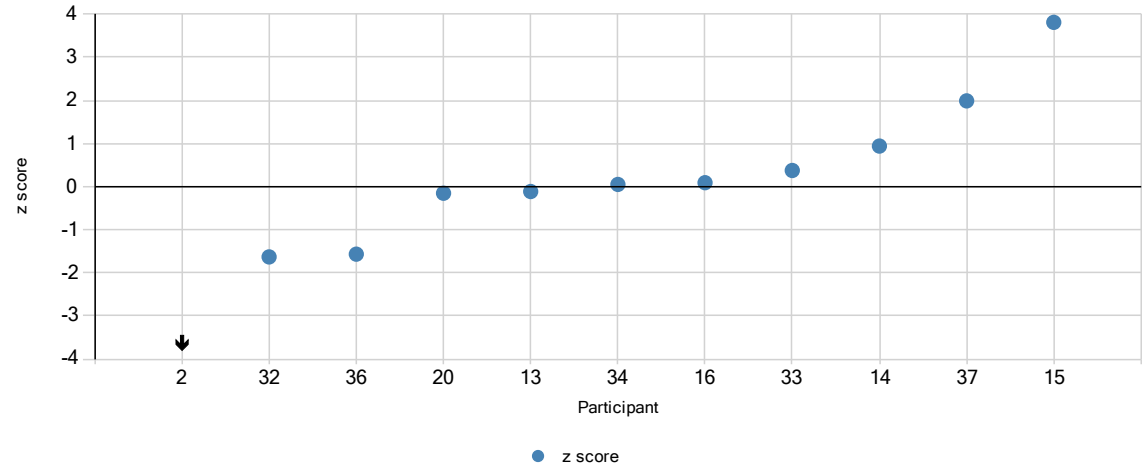
Measurand C_d Sample B3



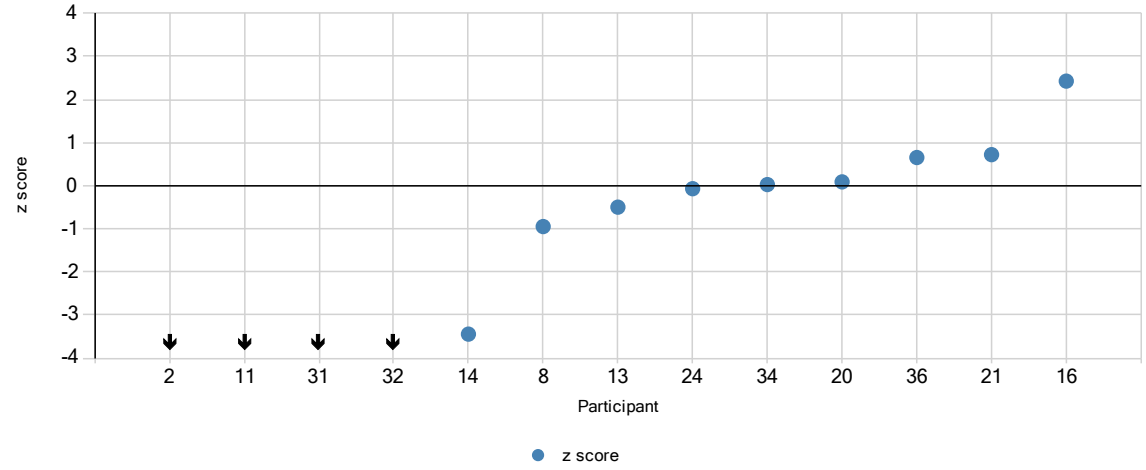
Measurand C_d Sample K1



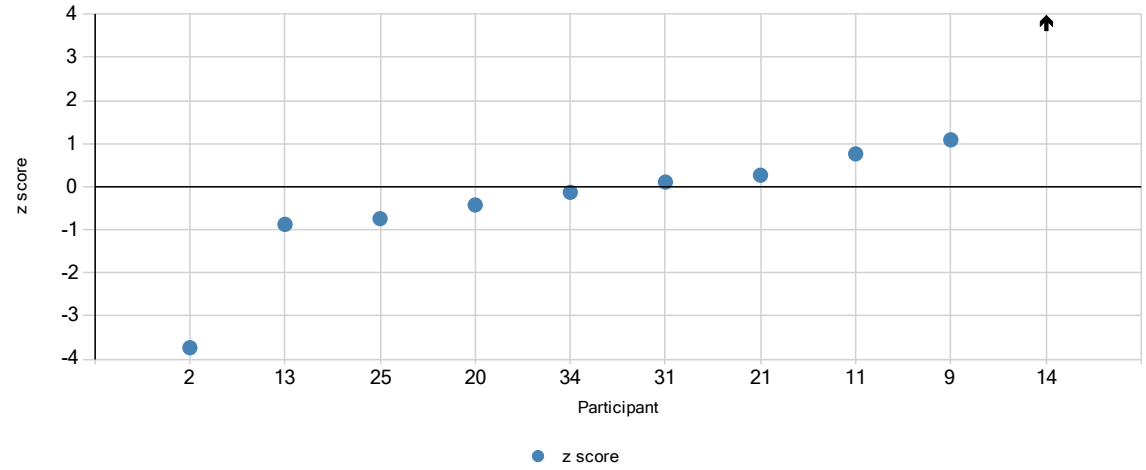
Measurand Cl_d Sample B3



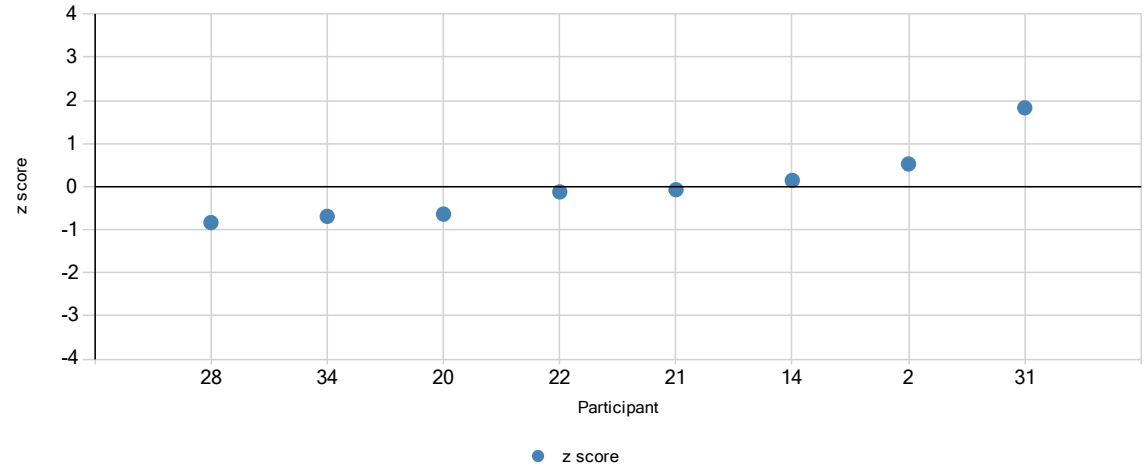
Measurand Cl_d Sample K1

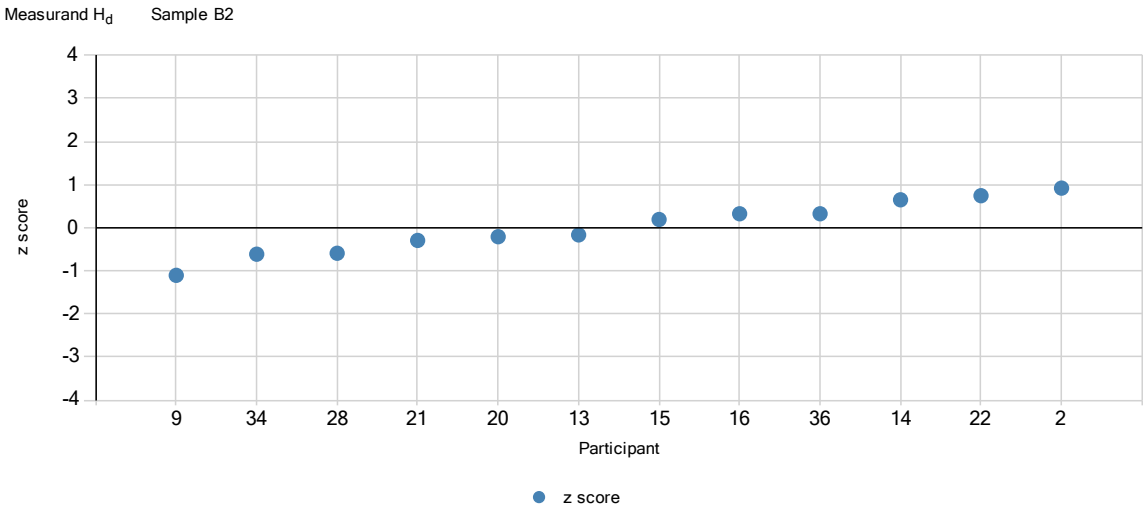


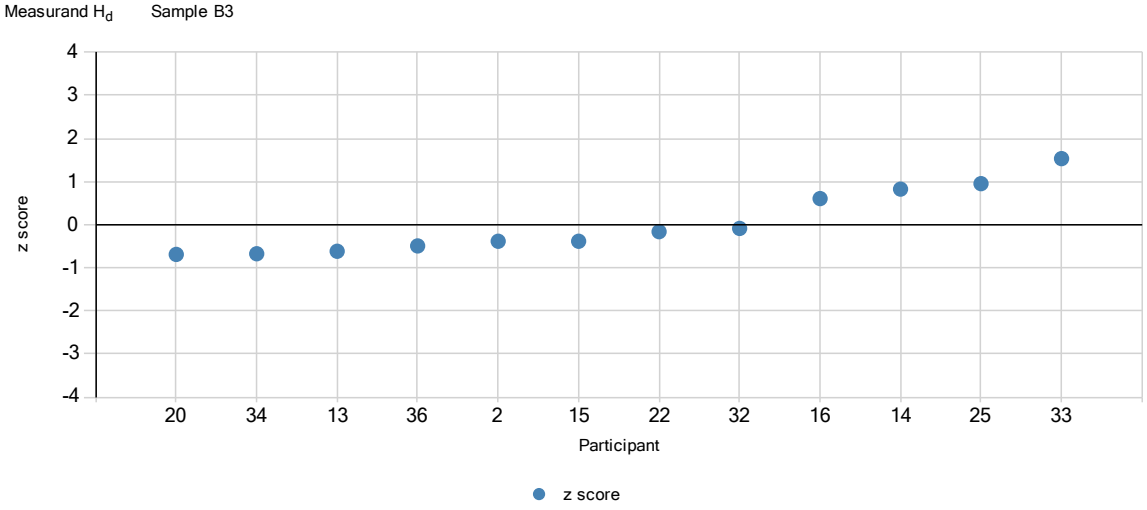
Measurand EF Sample K1

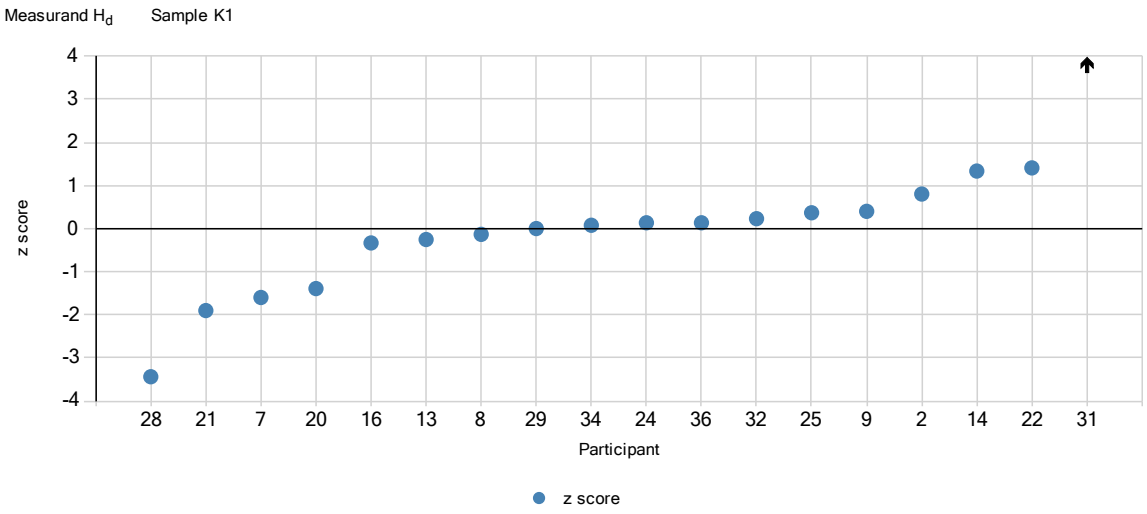


Measurand H_d Sample B1

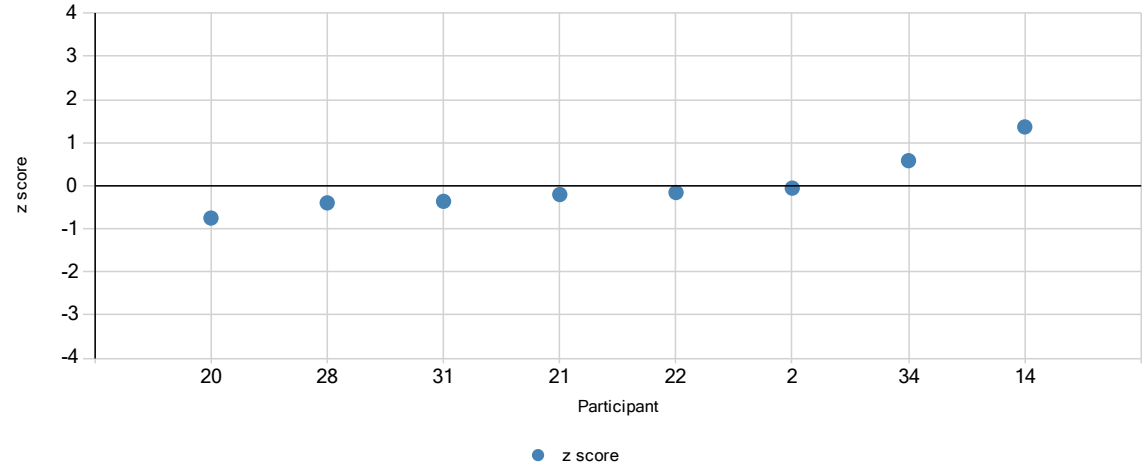



Measurand H_d Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
9 34 28 21 20 13 15 16 36 14 22 2
Participant
z score

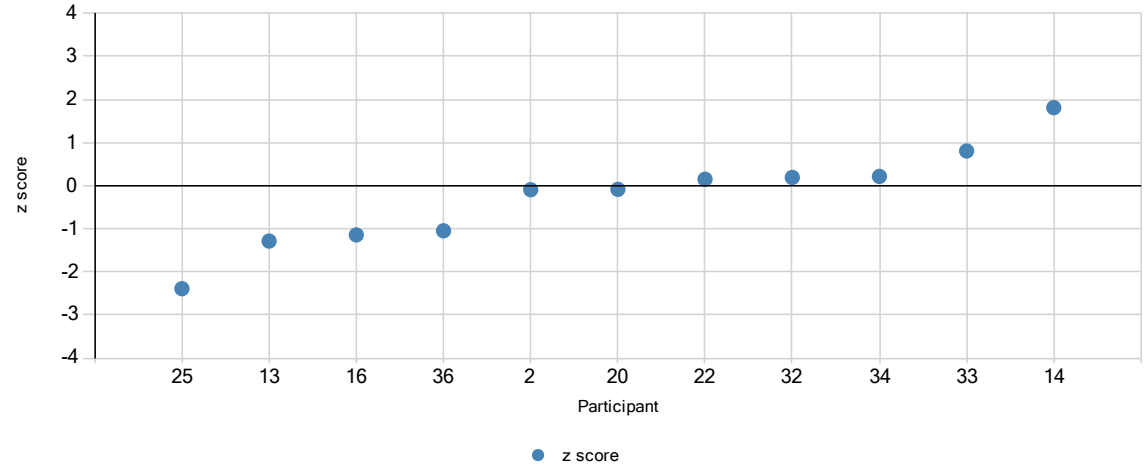

Measurand H_d Sample B3
z score
4
3
2
1
0
-1
-2
-3
-4
20 34 13 36 2 15 22 32 16 14 25 33
Participant
z score


Measurand H_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
28 21 7 20 16 13 8 29 34 24 36 32 25 9 2 14 22 31
Participant
z score

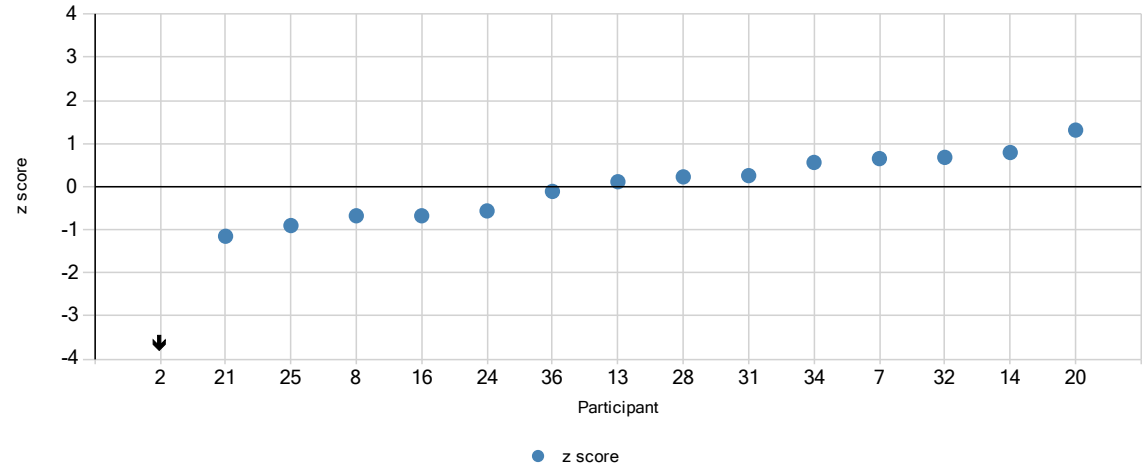
Measurand N_d Sample B1

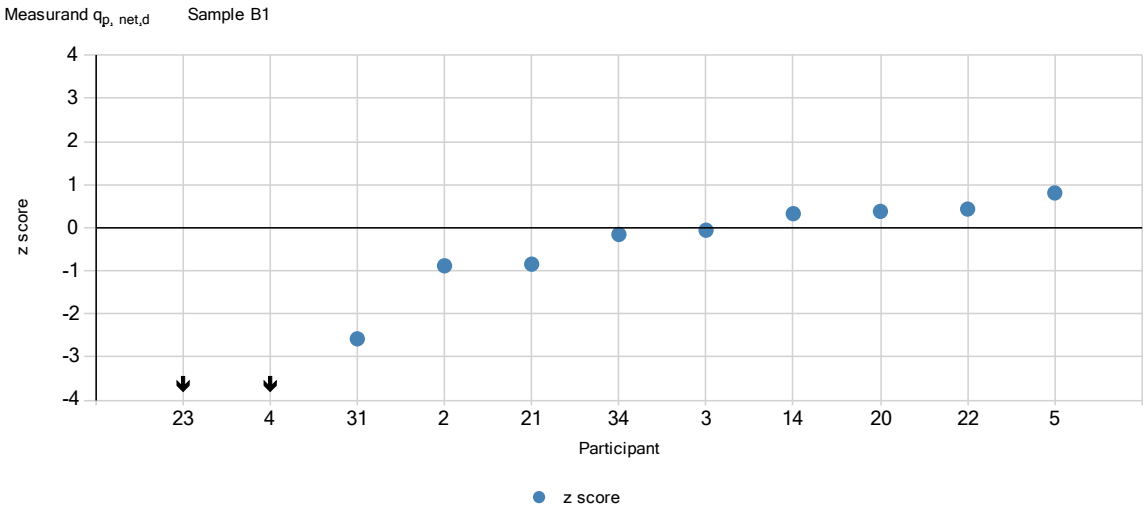


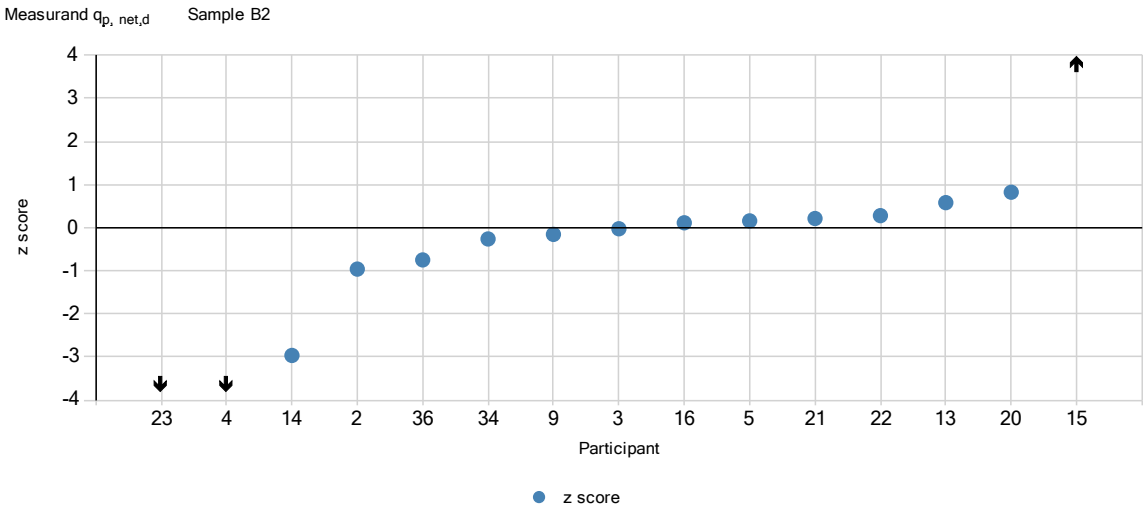
Measurand N_d Sample B3

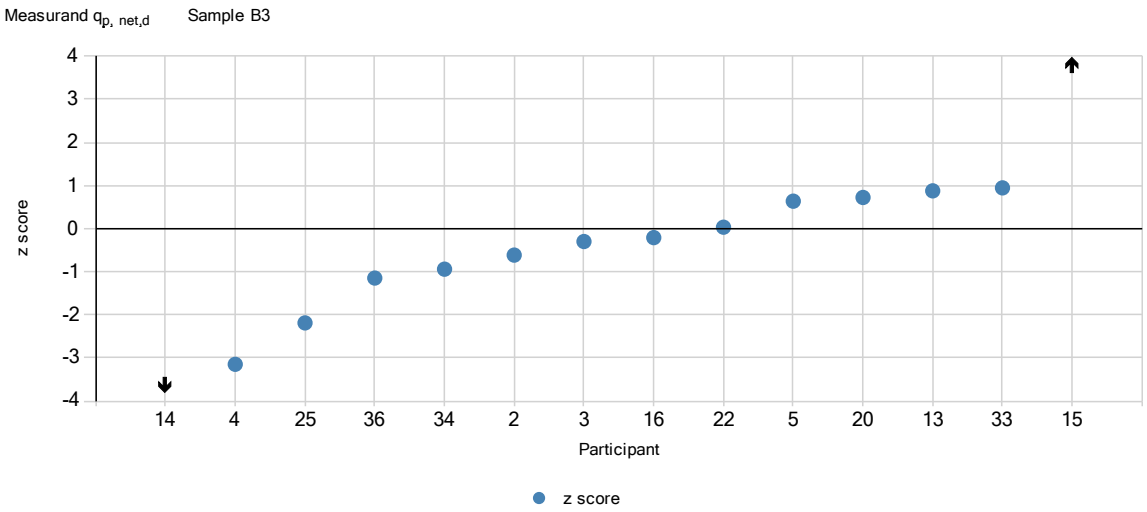


Measurand N_d Sample K1

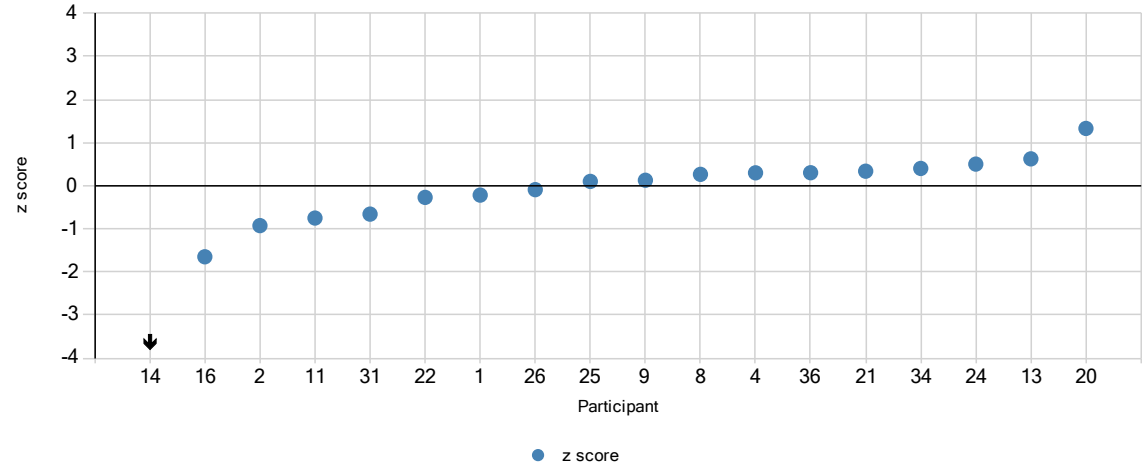



Measurand $q_{p,\ net,d}$
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
23
4
31
2
21
34
3
14
20
22
5
Participant
z score

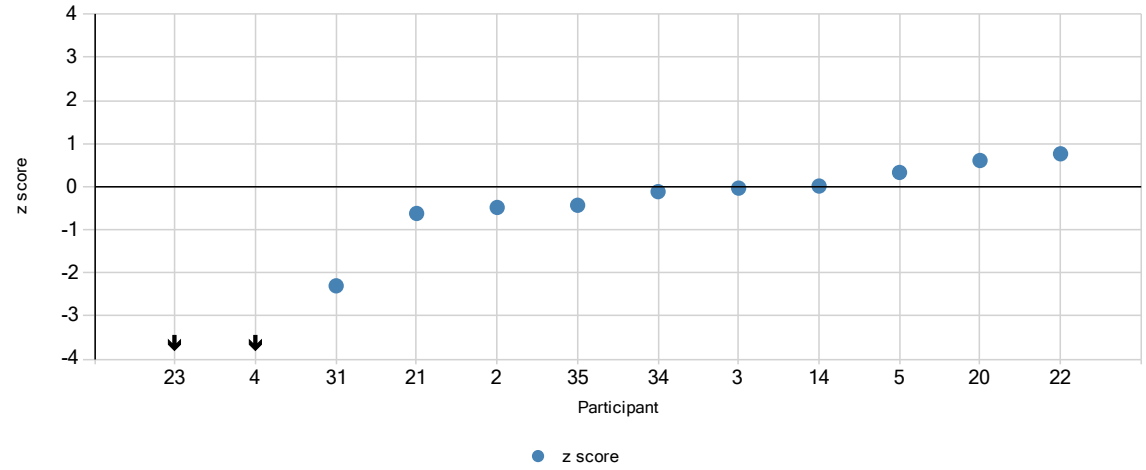

Measurand $q_{p,\ net,d}$
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
23
4
14
2
36
34
9
3
16
5
21
22
13
20
15
Participant
z score


Measurand $q_{p,\ net,d}$
Sample B3
z score
4
3
2
1
0
-1
-2
-3
-4
14
4
25
36
34
2
3
16
22
5
20
13
33
15
Participant
z score

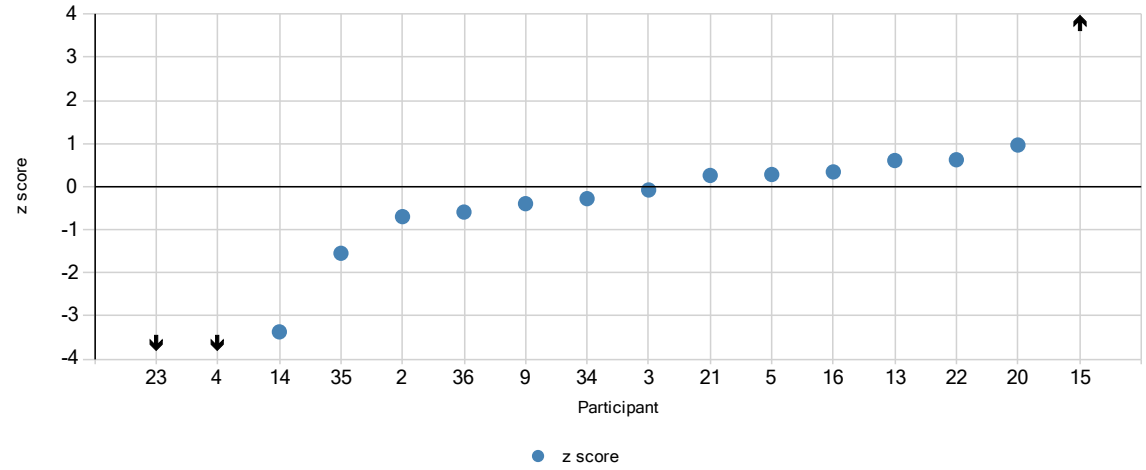
Measurand $q_{p,\ net,d}$ Sample K1



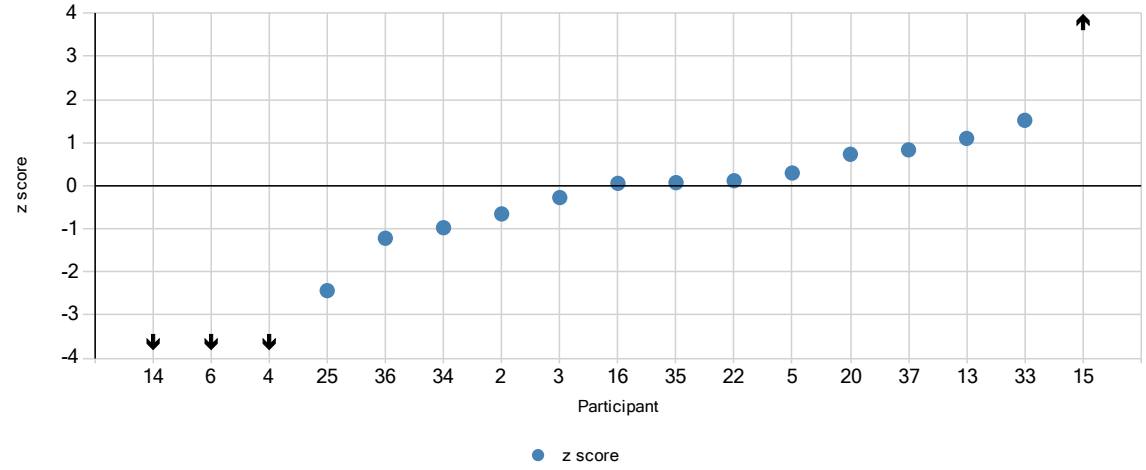
Measurand $q_{V,\ gr,d}$ Sample B1



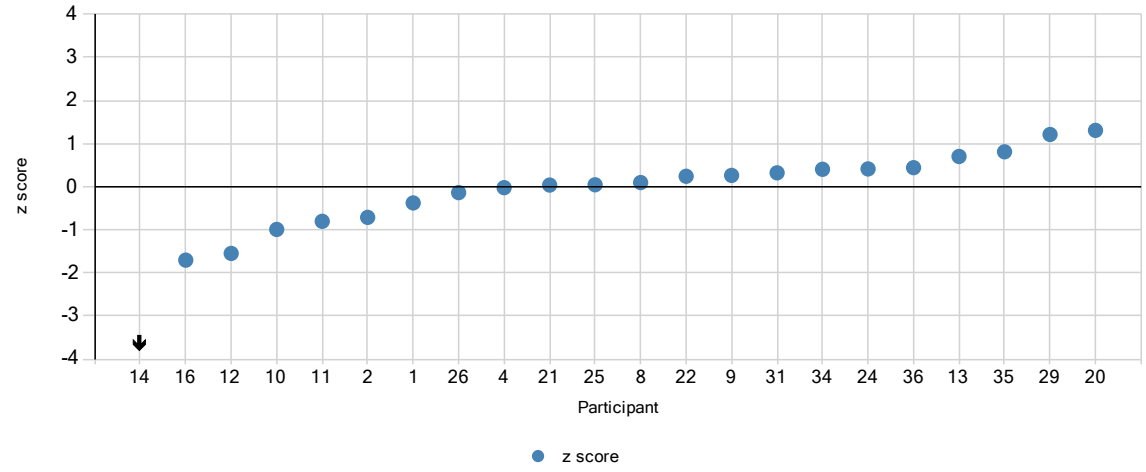
Measurand $q_{V,\ gr,d}$ Sample B2



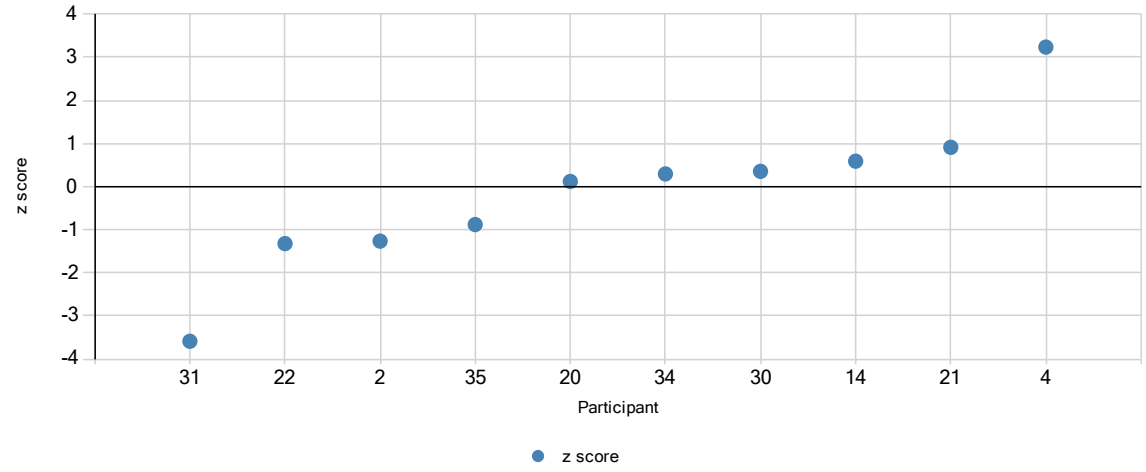
Measurand $q_{V,\,gr,d}$ Sample B3



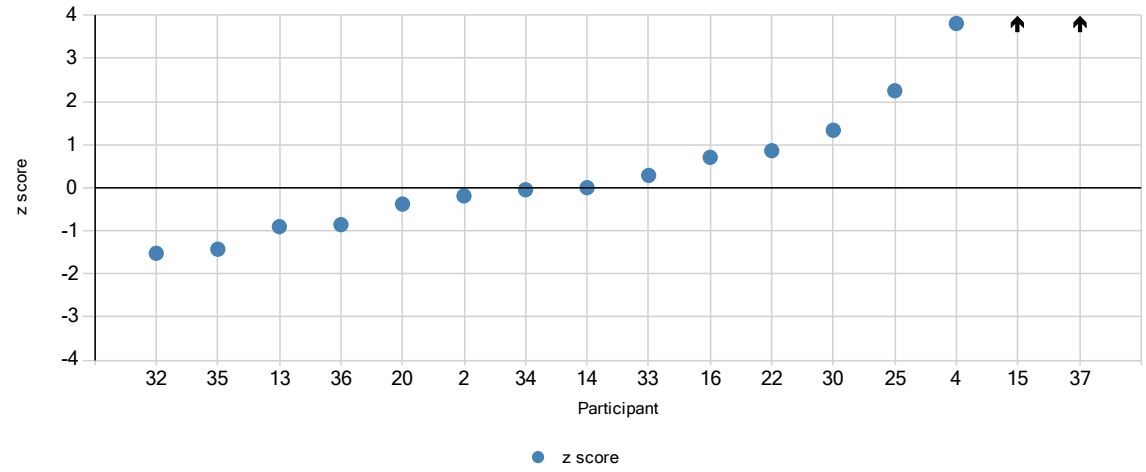
Measurand $q_{V,\,gr,d}$ Sample K1



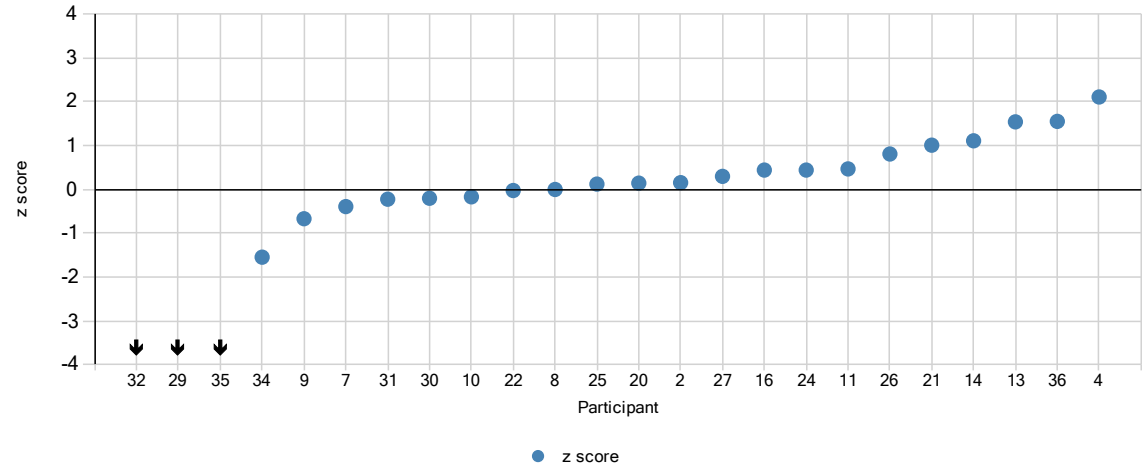
Measurand S_d Sample B1



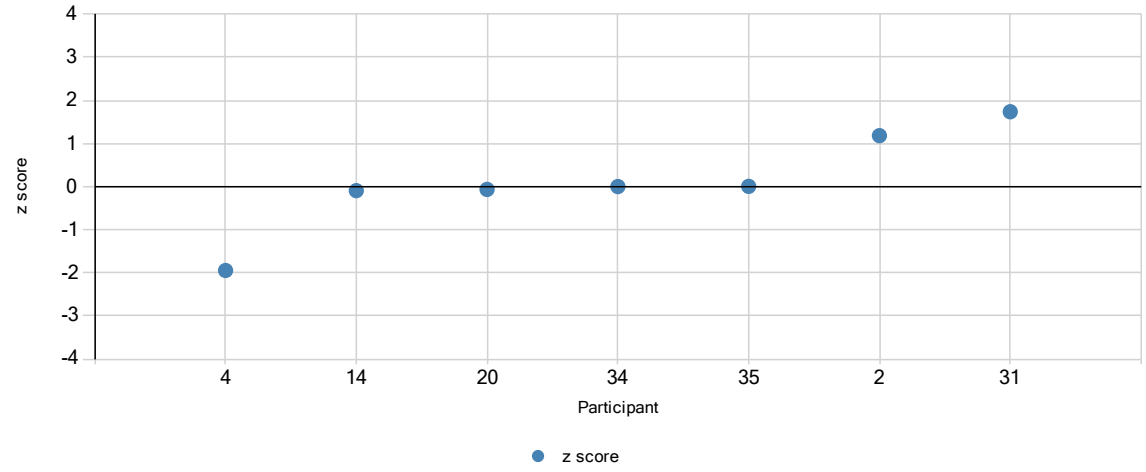
Measurand S_d Sample B3

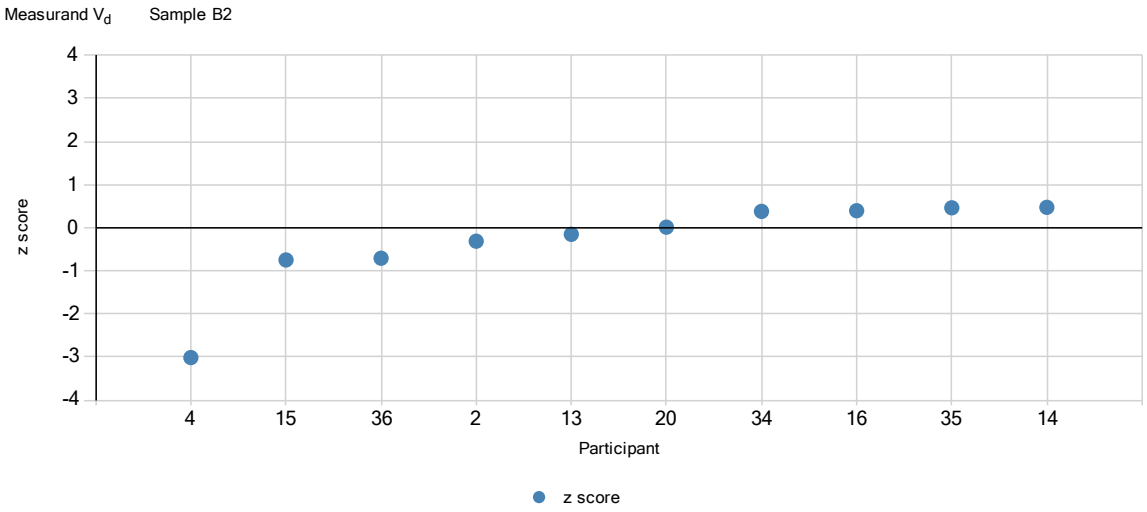


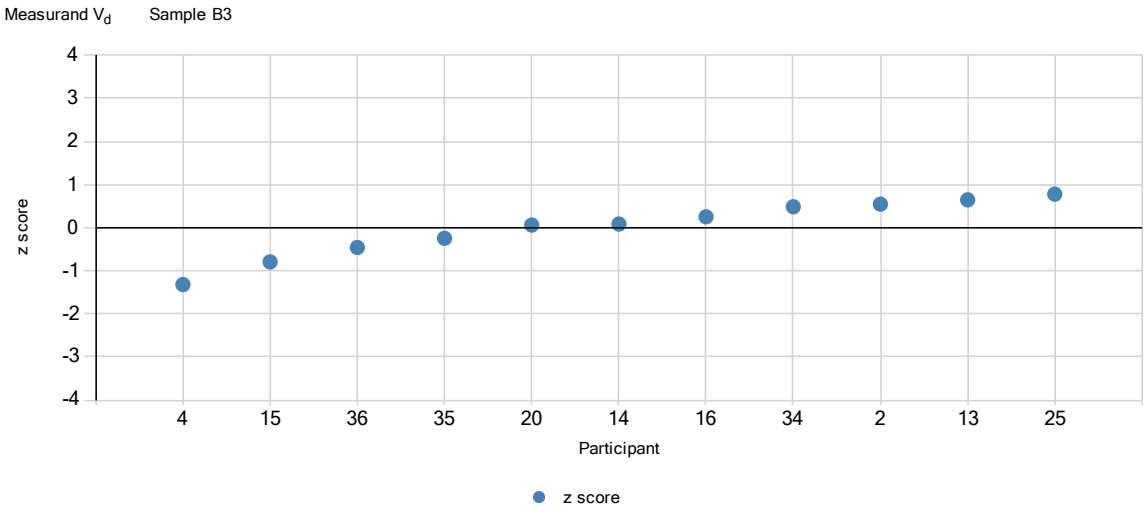
Measurand S_d Sample K1

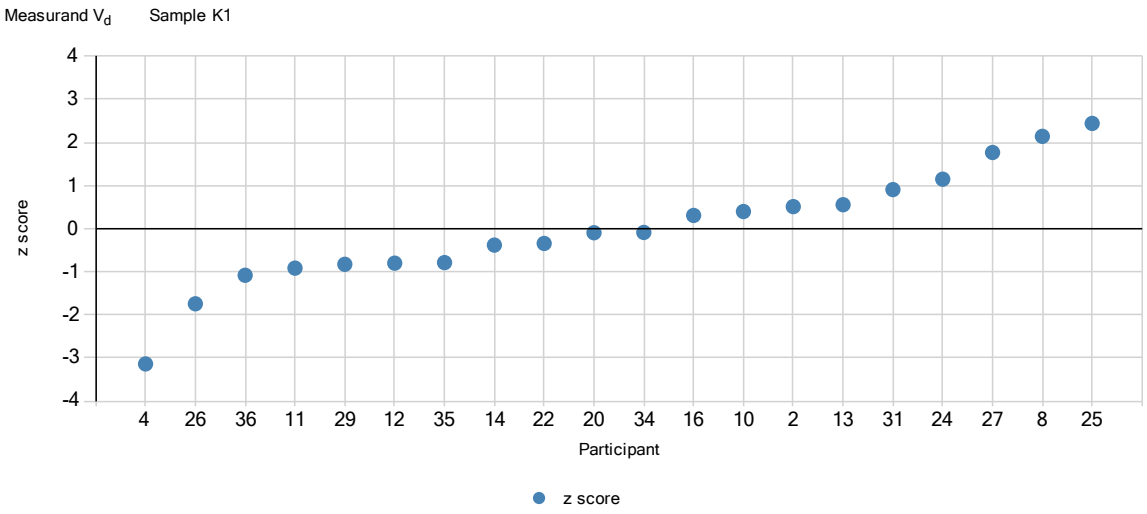


Measurand V_d Sample B1




Measurand V_d Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
4 15 36 2 13 20 34 16 35 14
Participant
z score


Measurand V_d Sample B3
z score
4
3
2
1
0
-1
-2
-3
-4
4 15 36 35 20 14 16 34 2 13 25
Participant
z score


Measurand V_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
4 26 36 11 29 12 35 14 22 20 34 16 10 2 13 31 24 27 8 25
Participant
z score

Appendix 11. Analytical measurements and background information for calculations

Reported details of the measurements:

Analyses carried out from:	Sample B1 (peat)	Sample B2 (wood pellet)	Sample B3 (recycled wood)	Sample K1 (coal)
As received and correction for moisture:	participants 20, 31, 35	participants 20, 35, 36	participants 6, 20, 33, 35, 36, 37	participants 1, 7, 10, 11, 16, 20, 29, 31, 34, 35, 36
105 °C dried samples:	participants 4, 5, 23, 34	participants 4, 5, 15, 16, 23, 34	participants 4, 5, 15, 16, 25, 32, 34	participants 4, 18, 25, 32
Other:	participants	participants	participants	participants

Correction taken into account in calculations:

Gross calorific value				
Participants and correction factors used	**Sample**			
	B1 (peat)	**B2 (wood pellet)**	**B3 (recycled wood)**	**K1 (coal)**
1: wire, ignition, analysis moisture				x
4: wire, ignition, S, acid correction	x	x	x	x
5: wire, ignition, S, acid correction	x	x	x	
6: wire, ignition, analysis moisture			x	
10: wire, ignition, S, N, analysis moisture				x
11: wire, ignition, S, N, analysis moisture				x
12: wire, ignition, S, N, analysis moisture				x
15: wire, S, acid correction, analysis moisture		x	x	
16: wire, S, acid correction, analysis moisture		x	x	x
16: analysis moisture				x
18: wire, ignition, S, acid correction, analysis moisture				x
20: wire, ignition, acid correction, analysis moisture	x	x	x	x
20: S	x			x
23: wire, ignition	x	x		
25: wire, ignition, S, N			x	x
29: wire, ignition, S, acid correction, analysis moisture				x
31: wire, S, analysis moisture	x			x
31: N				x
33: wire, ignition, S, N, analysis moisture			x	
34: wire, ignition, S, acid correction	x	x	x	x
34: analysis moisture				x
35: wire, ignition, S, N	x	x	x	x
36: wire, ignition, S, N, acid correction, analysis moisture		x	x	x
37: wire, ignition, analysis moisture			x	

Correction taken into account in calculations:

Net calorific value (literature value in brackets)				
Participant	Sample			
	B1 (peat)	B2 (wood pellet)	B3 (recycled wood)	K1 (coal)
1				H calculated, literature (4.035)
4	N+O, H	N+O, H	N+O, H	N+O, H
5	N+O literature (40/35/39) H literature (6.0/5.6/5.9)	N+O literature (40/35/39) H literature (6.0/5.6/5.9)	N+O literature (40/35/39) H literature (6.0/5.6/5.9)	
11				N+O literature (4.84), H calculated
15		H	H	
16		N+O, H calculated	N+O, H calculated	N+O, H calculated
20	H	H	H	H
23	N+O, H literature (1217 J/g for S)	N+O, H literature		
25			H	H
31	N+O, H			N+O, H
33			N+O, H	
34	N+O, H	N+O, H	N+O, H	N+O, H
36	N+O, H	N+O, H	N+O, H	N+O, H

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

Measurement	Method	°C	Sample B1 (peat)	Sample B2 (wood pellet)	Sample B3 (recycled wood)	Sample K1 (coal)
Ash content (ashing temperature ℃)	Gravimetric:	550	parts 5, 20, 35	parts 5, 15, 16, 19, 20, 35, 36	parts 5, 15, 16, 20, 25, 32, 33, 35	
		700				part 25
		750				part 16
		815	part 19			parts 1, 10, 12, 20, 29, 32, 35
	TGA:	550	parts 4, 31, 34	parts 4, 34	parts 4, 34	
		750				part 27
		815			part 36	parts 4, 11, 31, 34, 36
Moisture content of analysis sample, M_{ad} (temperature °C)	Air:		parts 4, 19, 20, 23, 31, 34, 35	parts 4, 15, 16, 19, 20, 23, 34, 35	parts 4, 15, 16, 20, 25, 32, 33, 34, 35, 37	parts 1, 4, 10, 16, 18, 29, 31, 32, 35
	N_2 atmosphere:			part 36	part 36	parts 7, 11, 12, 20, 25, 27, 34, 36
	Gravimetric:		parts 20, 35	parts 15, 16, 20, 35, 36	parts 15, 16, 20, 25, 32, 33, 35, 36, 37	parts 1, 10, 12, 16, 18, 20, 25, 29, 32, 35, 36
	TGA:		parts 4, 19, 31, 34	parts 4, 19, 34	parts 4, 34	parts 4, 11, 27, 31, 34

CHN-measurements carried out by:

	Sample			
	B1	**B2**	**B3**	**K1**
As received and correction for moisture:	parts 4, 20, 31, 34	parts 4, 16, 20, 34, 36	parts 4, 16, 20, 33, 34, 36	parts 1, 4, 7, 11, 16, 20, 27, 31, 34, 36
105 °C dried samples:	part 28	parts 15, 28	parts 15, 25, 32	parts 18, 25, 28, 32
Other	part 23	part 23		part 21

Detection limits:

Parts	**for B1**			**for B2**	**for B3**			**for K1**				
	Cl_d (mg/kg)	N_d (w%)	S_d (w%)	N_d (w%)	Cl_d (mg/kg)	N_d (w%)	S_d (w%)	Br_d (mg/kg)	Cl_d (mg/kg)	F_d (mg/kg)	N_d (w%)	S_d (w%)
4		1.87	0.225	0.073		1.25	0.105				1.16	0.995
7											0.0001	0.0001
15				0.1	1	0.1	0.01					
16				0.1	100	0.1	0.01	30	30	30	0.1	0.01
20	50	0.1	0.03	0.1	50	0.1	0.01	50	50	50	0.1	0.03
27												0.05
28		0.2		0.2							0.2	
30			0.1				0.1					0.1
31	0.2	0.02	0.1						0.04		0.02	0.1
32					20	0.2	0.002	20	20	20	0.2	0.002
33					500	0.01	0.02					
34	10	0.2	0.01	0.2	10	0.2	0.01	10	10	10	0.2	0.01

Calculations of Emission factor (EF)[1]:

We have used the equation based on the decision EU 2018/2066 [38].

	Sample B1 (peat)	**Sample K1 (coal)**
Yes:	parts 20, 25, 34	parts 20, 25, 34
No:	parts 10, 23, 27, 31	parts 10, 11, 12, 18, 23, 27, 31

[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 [38, 39] and using the total moisture content as presented in the letter. Additionally, 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)

Measurements of additional measurands

What standard(s) (international/national or other) you have used to measure Cl_d and Br_d:

Participant	for measure Cl_d in B1	for measure Cl_d in B3	for measure Br_d in K1	for measure Cl_d in K1
11	-	-	-	ASTM 4208-19
15	-	EN 15408	-	-
16	-	-	ERM-EC680m, ERM-EC681m	-
20	SFS-EN ISO16994 modified	-	SFS-EN ISO 16994 modified	-
31	-	-	-	ISO 9297
32	-	ASTM D7359	ASTM D7359 modified	-
33	-	SFS-EN ISO 10304-1	-	-
34	SFS-EN ISO 16994	-	SFS-EN 15408	-
36	-	inhouse method	NF EN 14582	-
37	-	SFS-EN 14582	-	-

Sample pretreatment method:

Pretreatment method	for measure Cl_d in B1	for measure Cl_d in B3	for measure Br_d in K1	for measure Cl_d in K1
Digestion in oxygen bomb	parts 20 (water) 31 (0.2 M KOH) 34	parts 15 33 (water) 36 (water) 37 (0.25 M $NaOH+H_2O_2$)	parts 20 (water) 34 36 (water)	parts 11 (2 % Na_2CO_3) 31 (water)
Other		part 32 (Combusted in pyrohydrolytic environment and trapped in an absorption solution)	part 32 (Combusted in pyrohydrolytic environment and trapped in an absorption solution)	

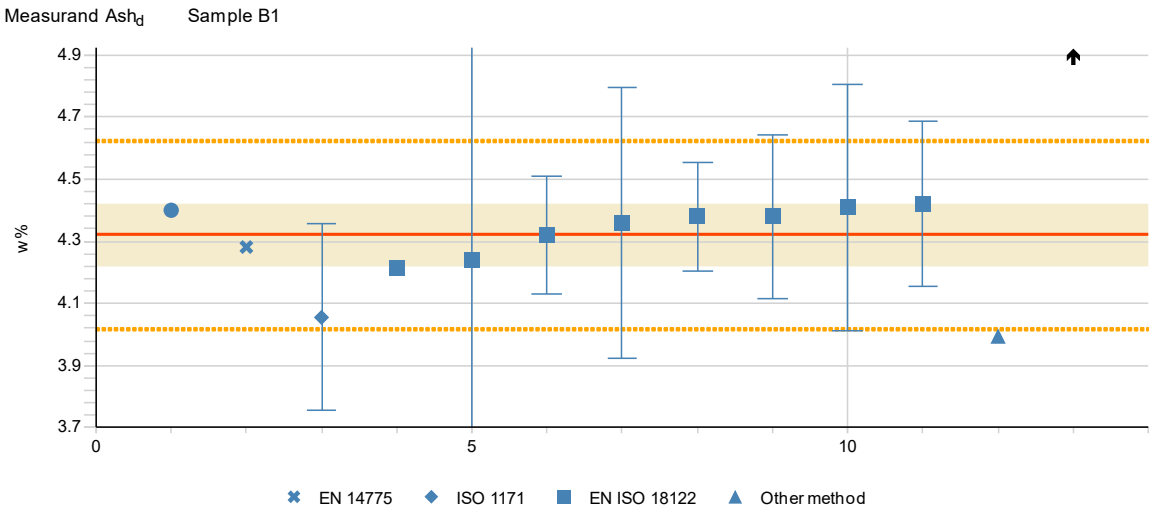
Measurement:

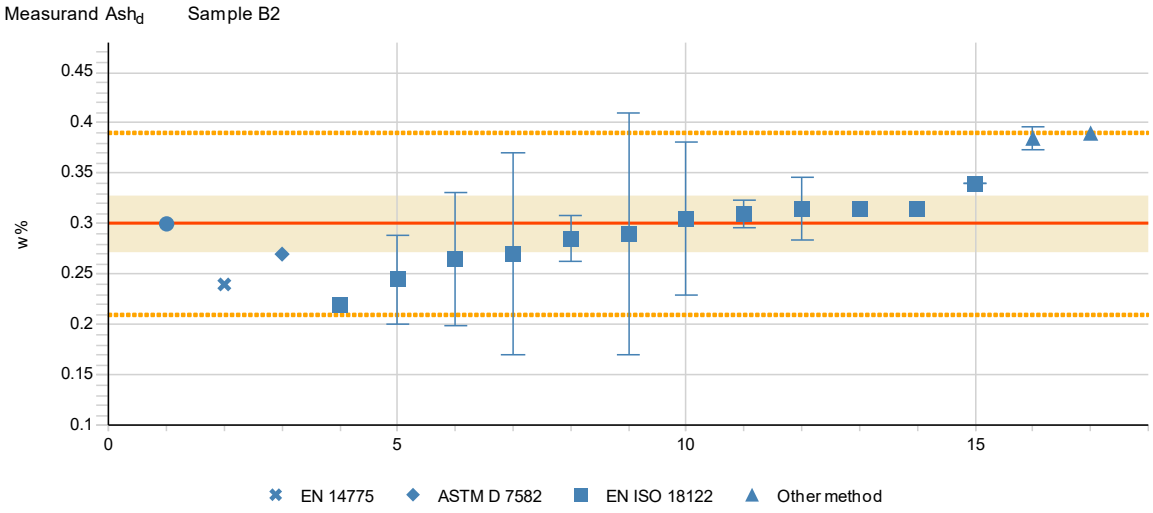
Measurement	for measure Cl_d in B1	for measure Cl_d in B3	for measure Br_d in K1	for measure Cl_d in K1
by ion chromatography/IC	parts 20, 34	parts 15, 32, 33, 36, 37	parts 20, 32, 34, 36	part 11
by titration	-	-	-	part 31
Other	part 31 (potentiometric)	-	part 16 (combustion-IC without pretreatment)	-

Question	Yes	No
Have you digested and measured Cl_d in recycled wood sample B3 using same methods than in peat sample B1?	parts 16, 20, 34	parts 32, 33, 35, 36, 37
Coal sample K1: Have you used for Cl_d the same digestion and measurements than for Br_d?	parts 16, 20, 32, 34, 36	part 31
Coal sample K1: Have you used for F_d the same digestion and measurements than for Br_d or Cl_d?	parts 16, 20, 32, 34 (same as for Cl_d) 36 (same as for Br_d)	

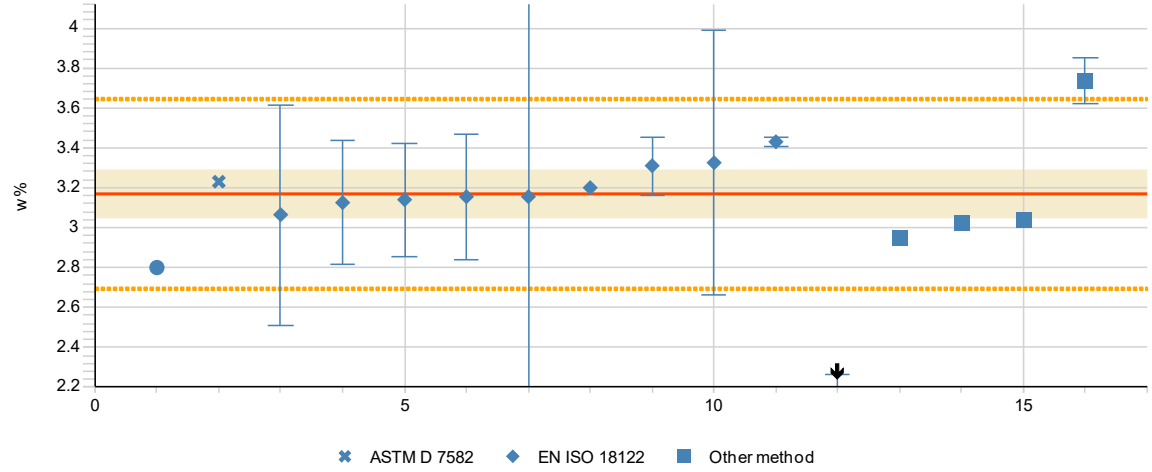
Appendix 12. Results grouped according to the methods

The explanations for the figures are described in the Appendix 8. The results are shown in ascending order.

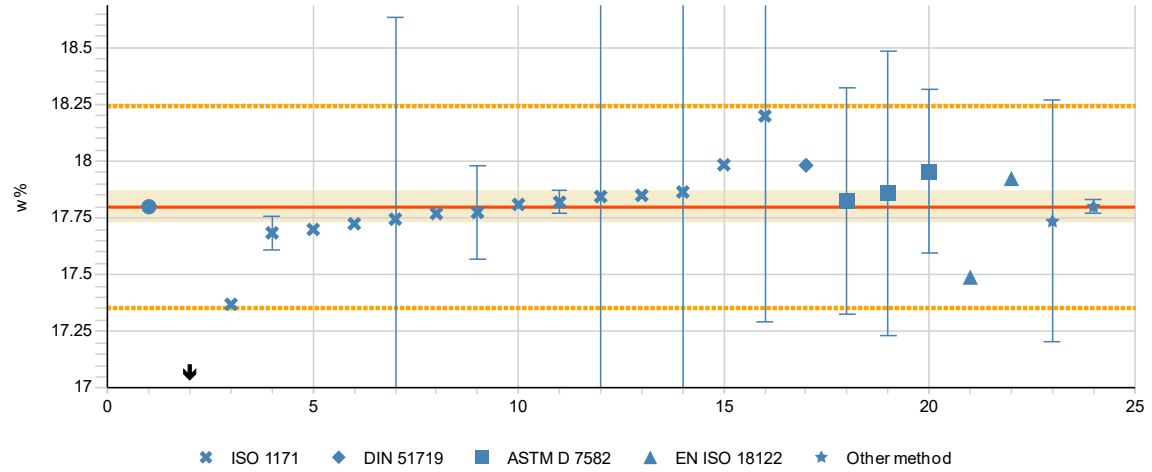




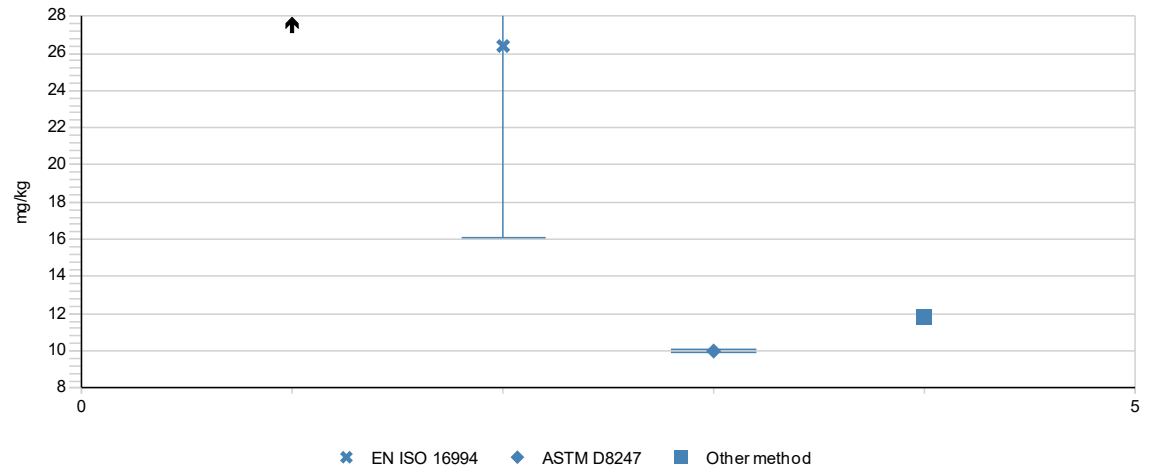
Measurand Ash_d Sample B3



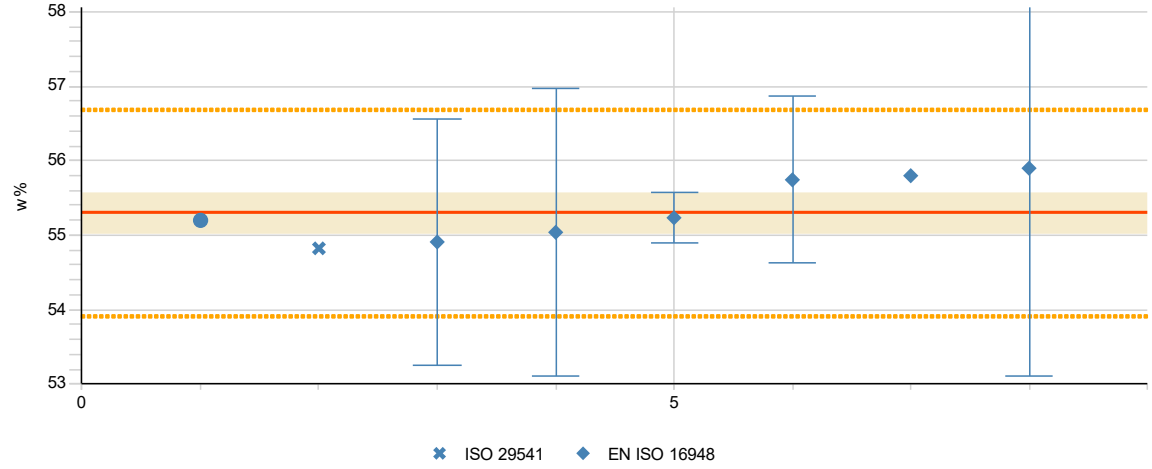
Measurand Ash_d Sample K1



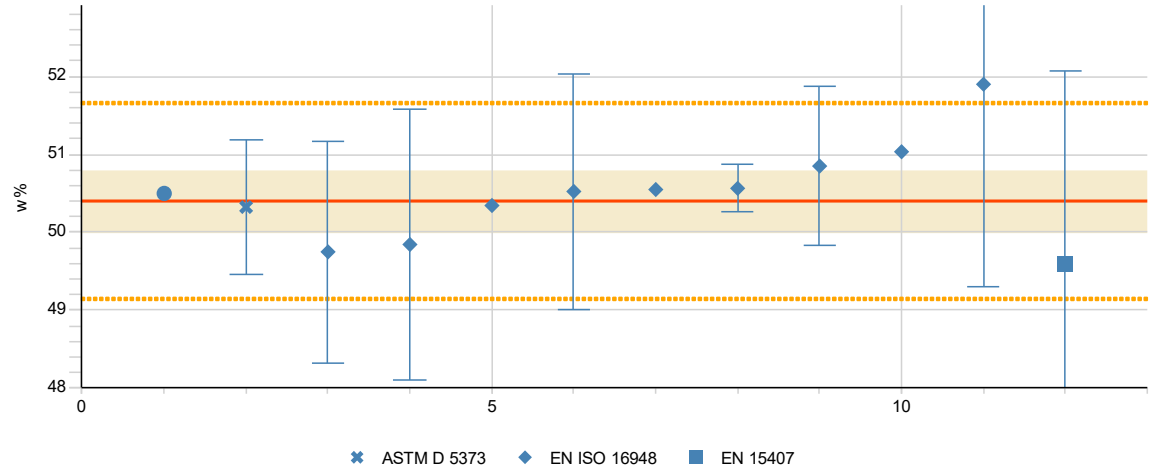
Measurand Br_d Sample K1



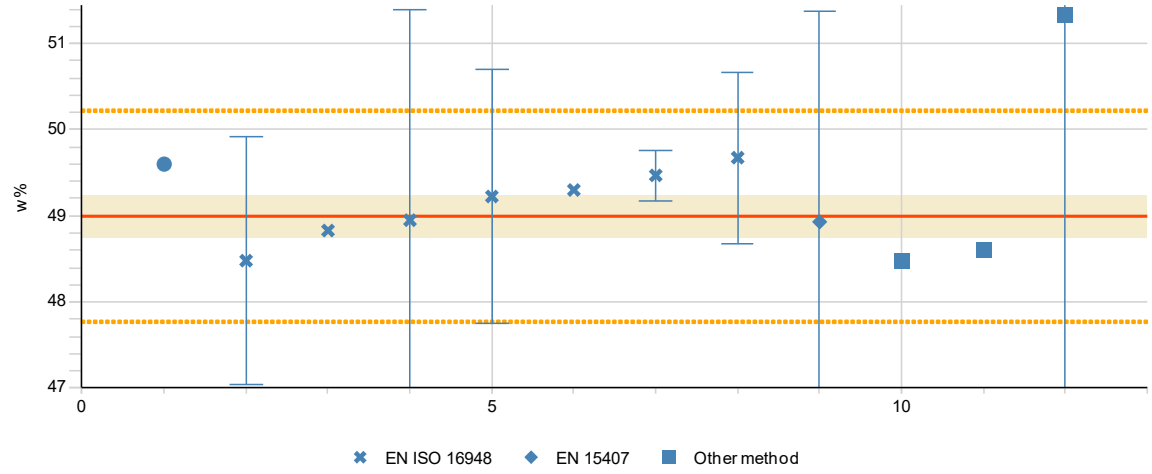
Measurand C_d Sample B1



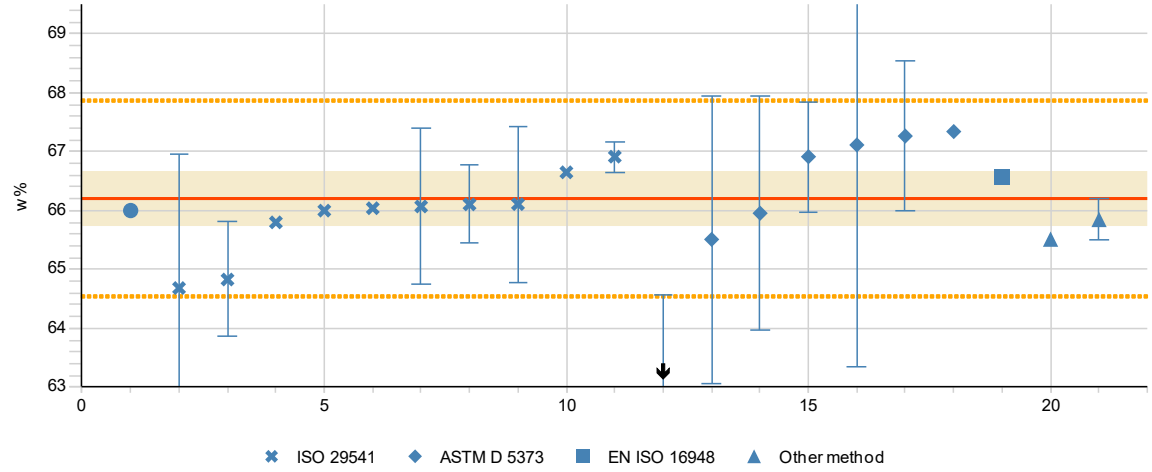
Measurand C_d Sample B2



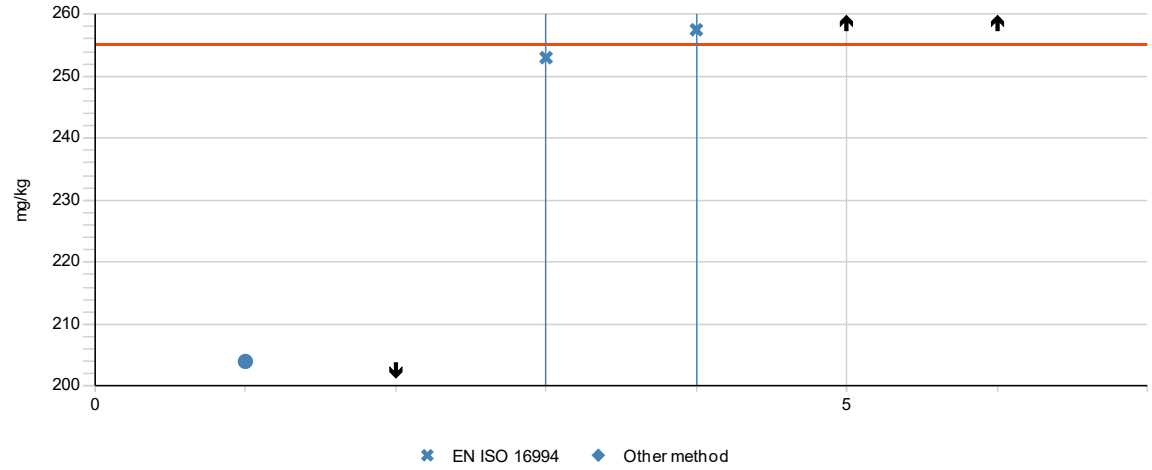
Measurand C_d Sample B3



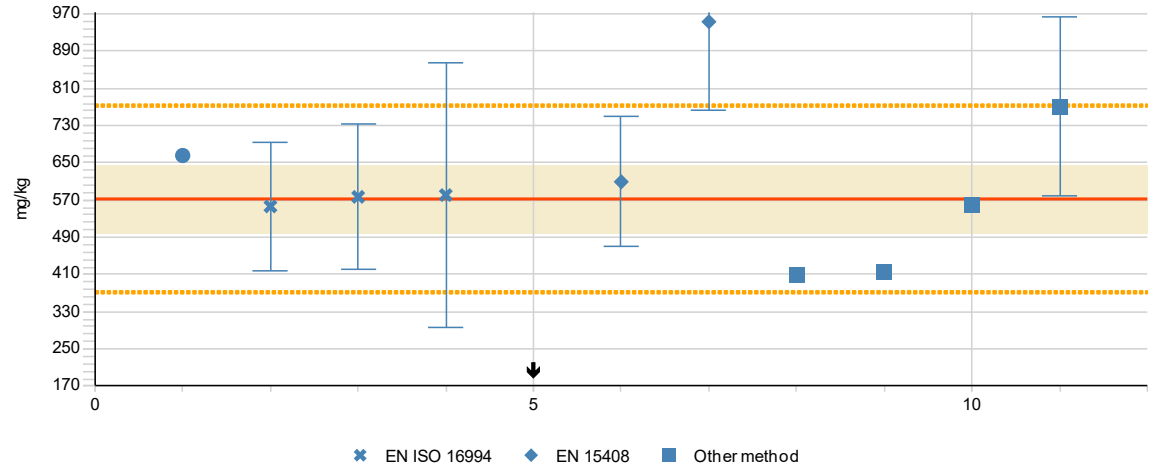
Measurand C_d Sample K1



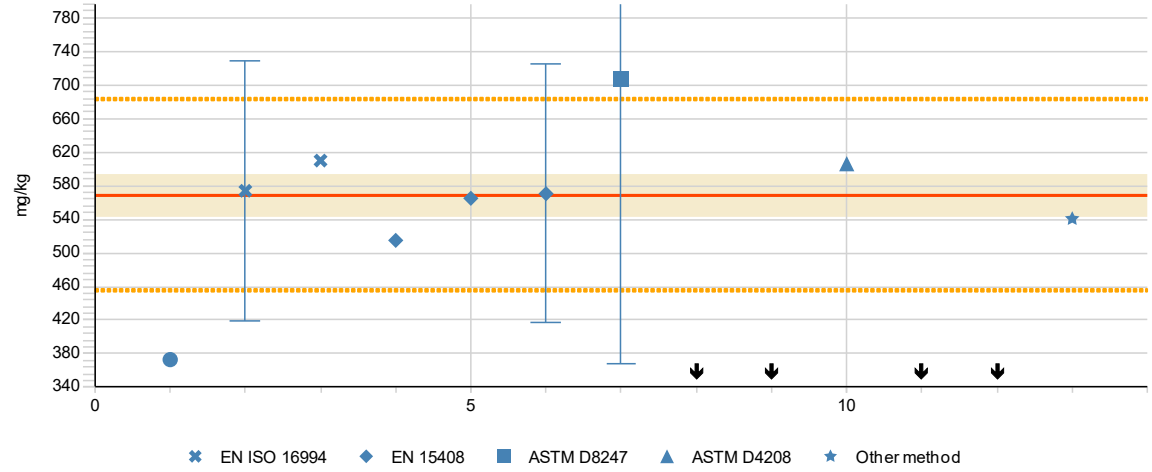
Measurand Cl_d Sample B1



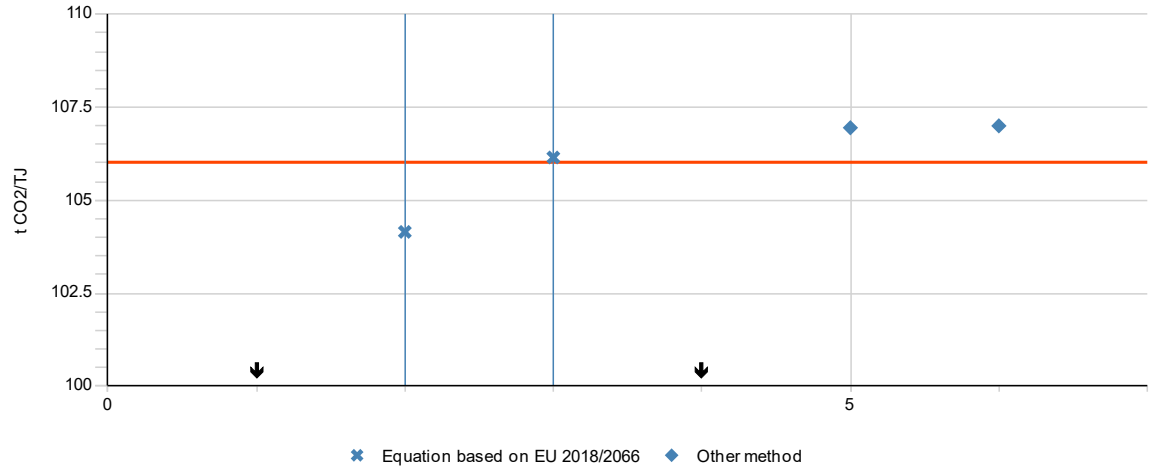
Measurand Cl_d Sample B3



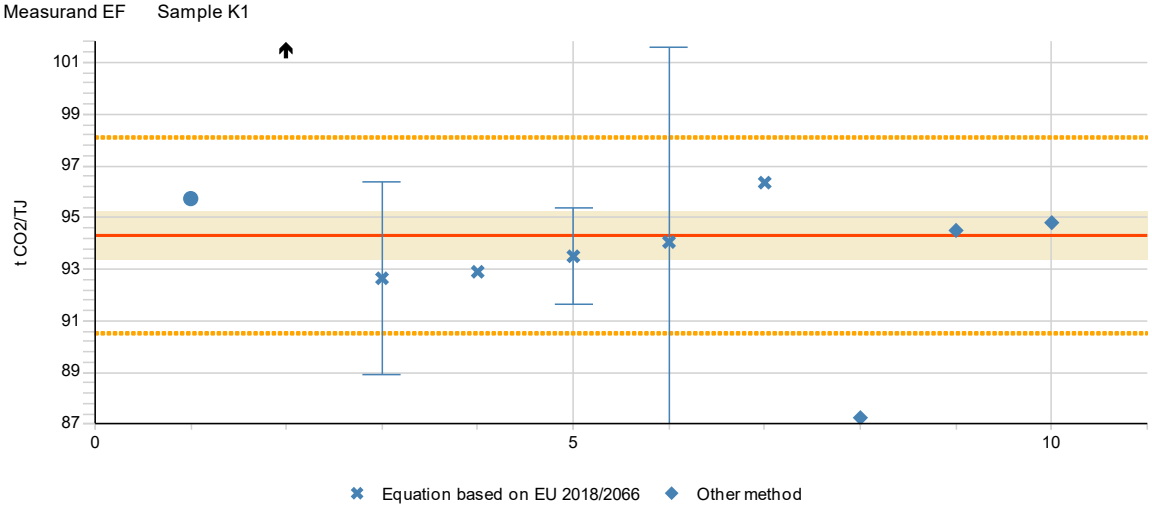
Measurand Cl_d Sample K1



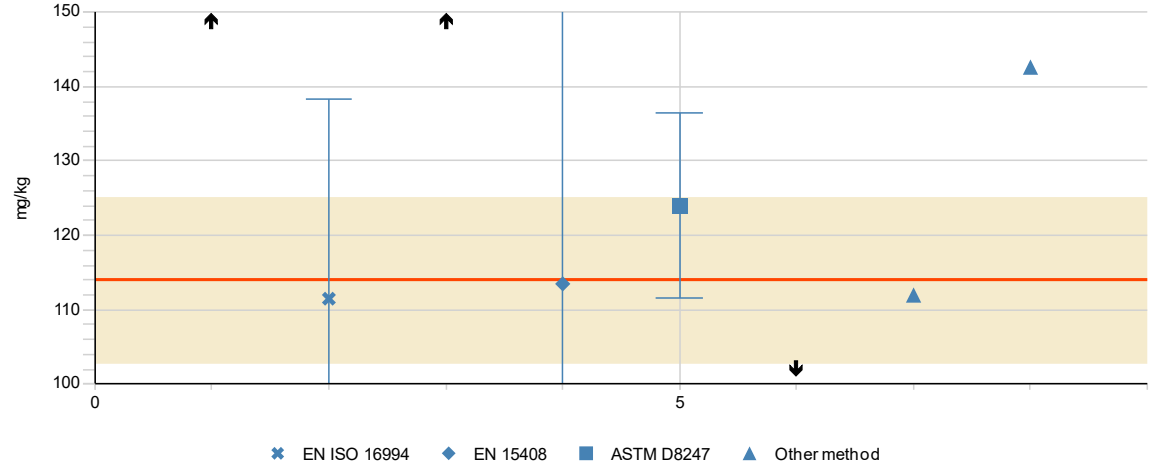
Measurand EF Sample B1



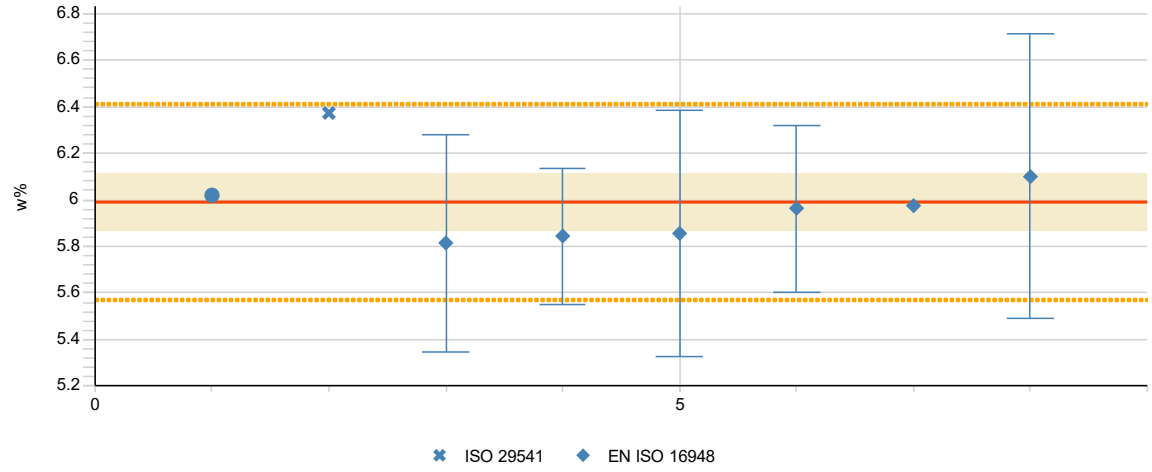
Measurand EF Sample K1



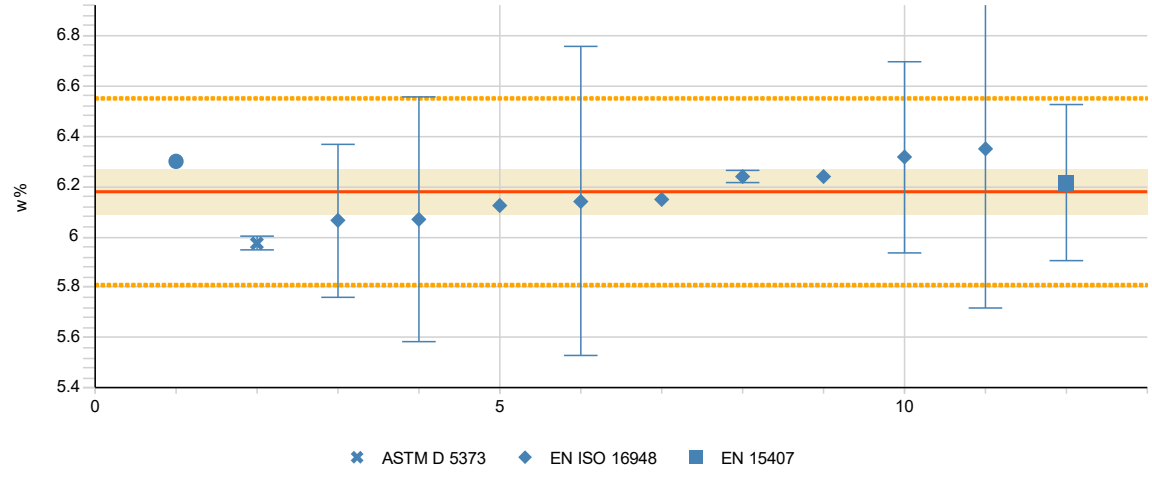
Measurand F_d Sample K1



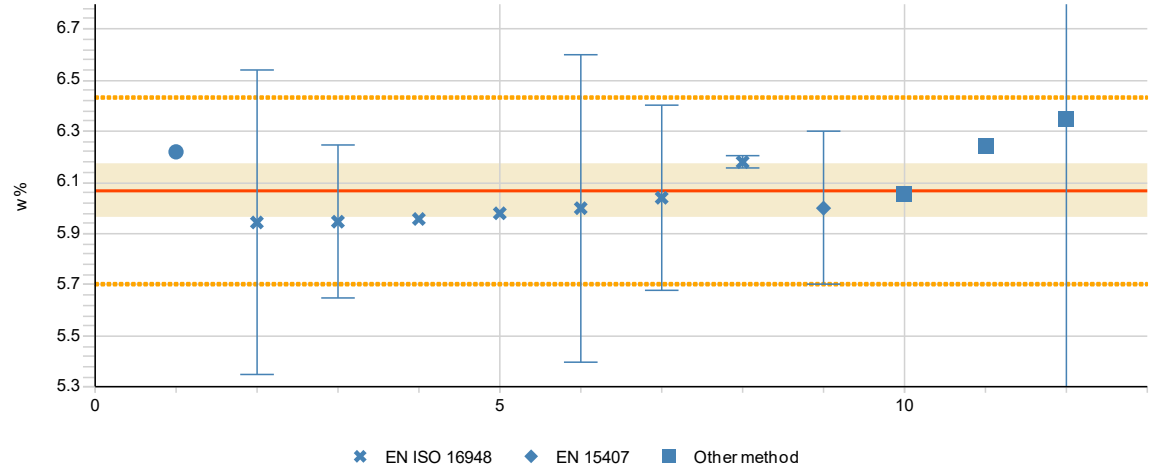
Measurand H_d Sample B1



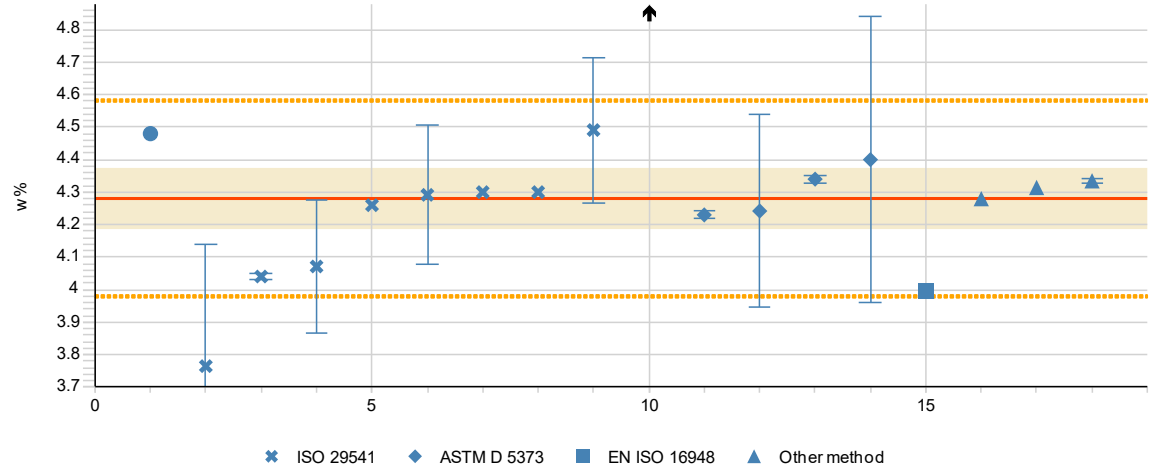
Measurand H_d Sample B2



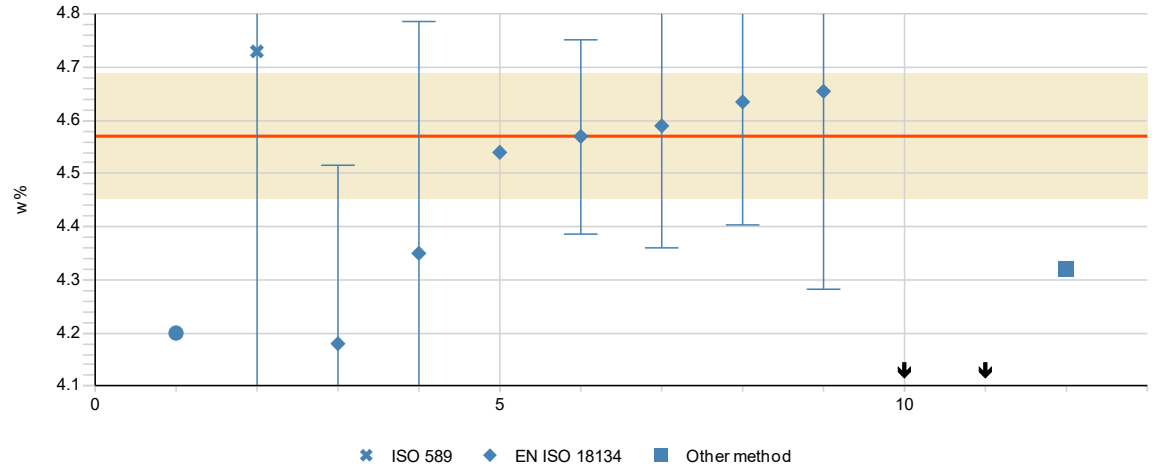
Measurand H_d Sample B3



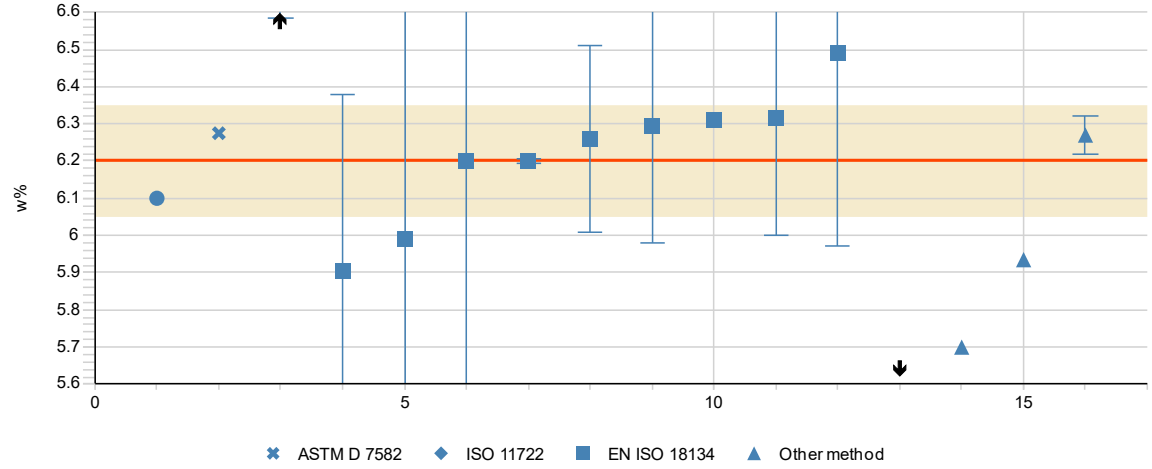
Measurand H_d Sample K1



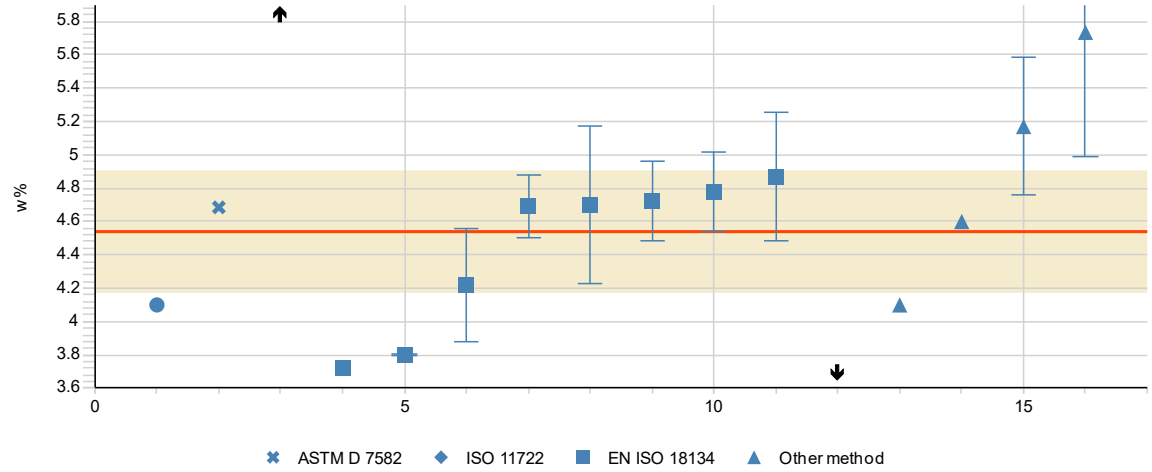
Measurand M_{ad} Sample B1



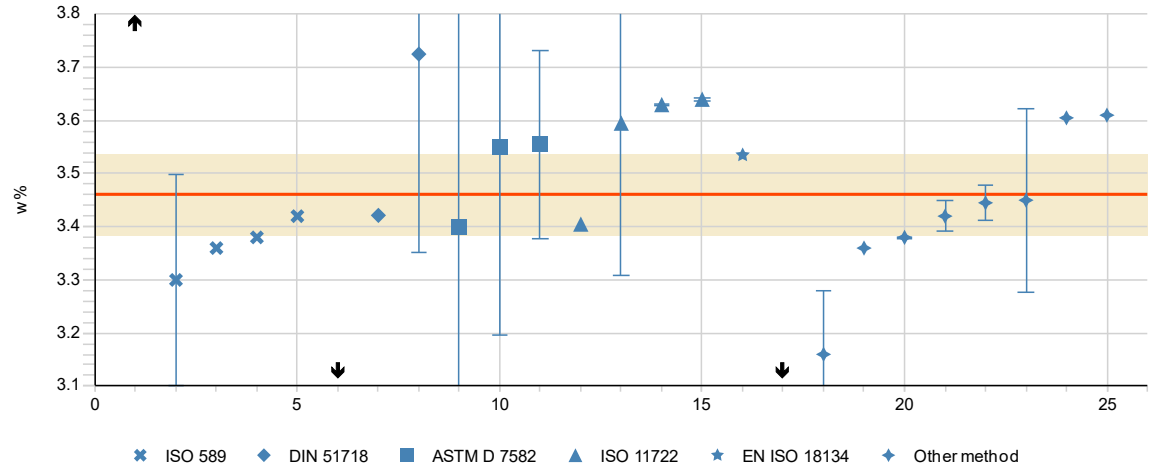
Measurand M_{ad} Sample B2



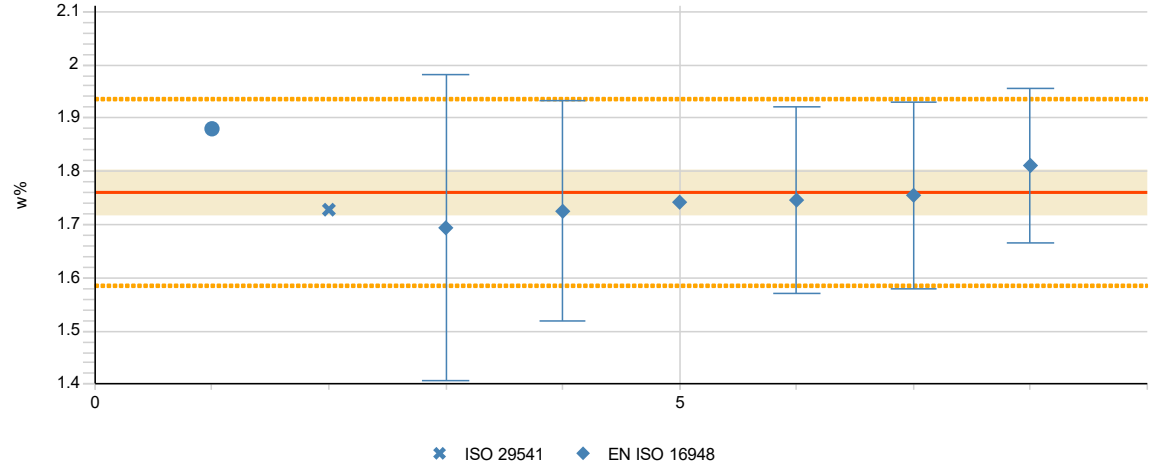
Measurand M_{ad} Sample B3



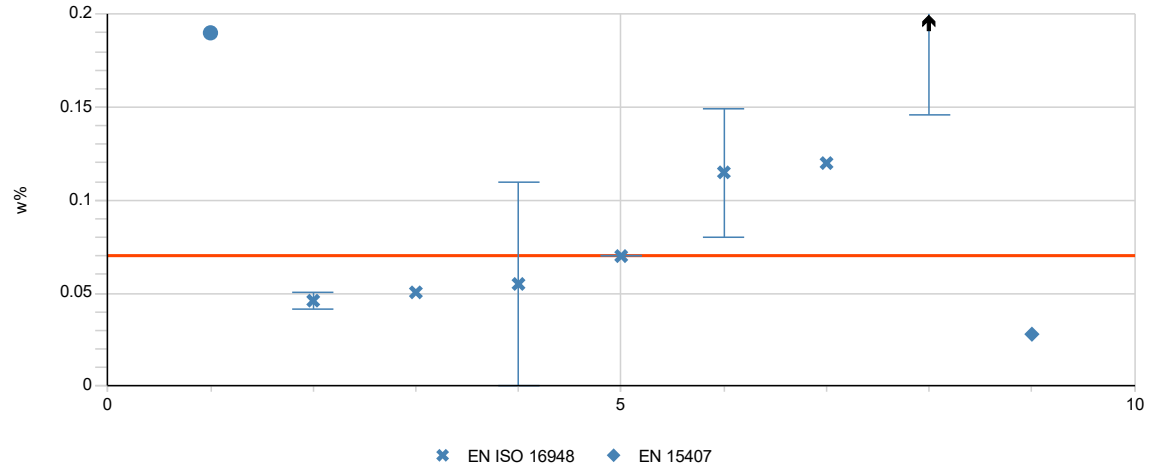
Measurand M_{ad} Sample K1



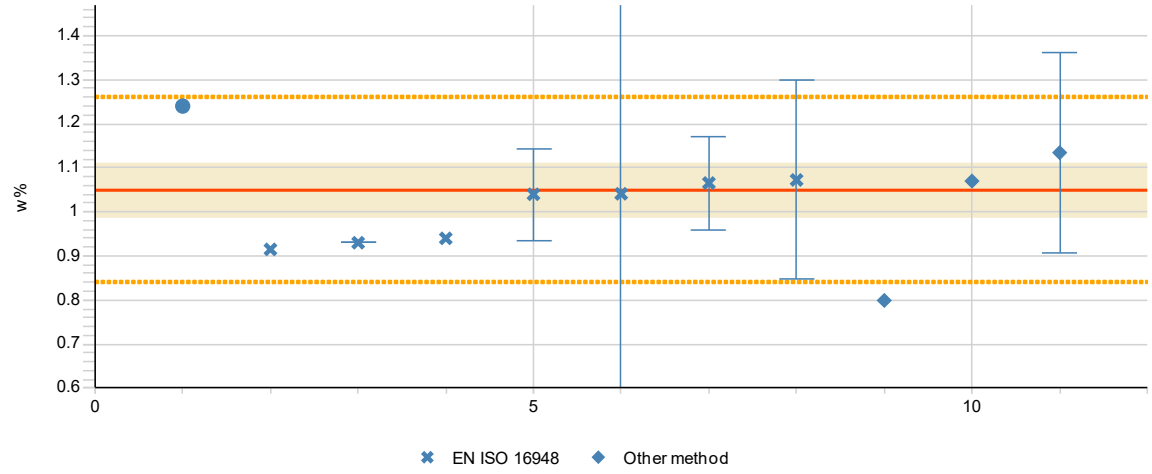
Measurand N_d Sample B1



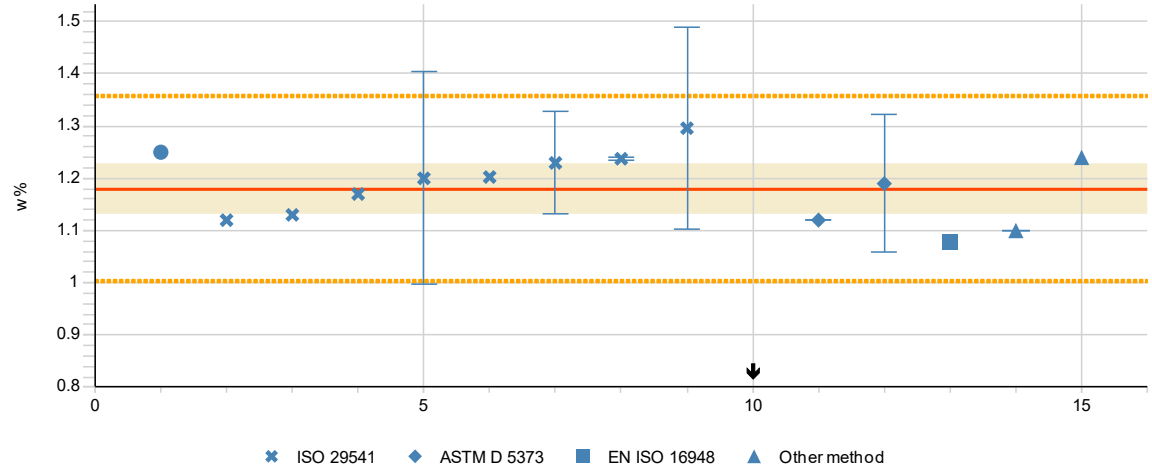
Measurand N_d Sample B2



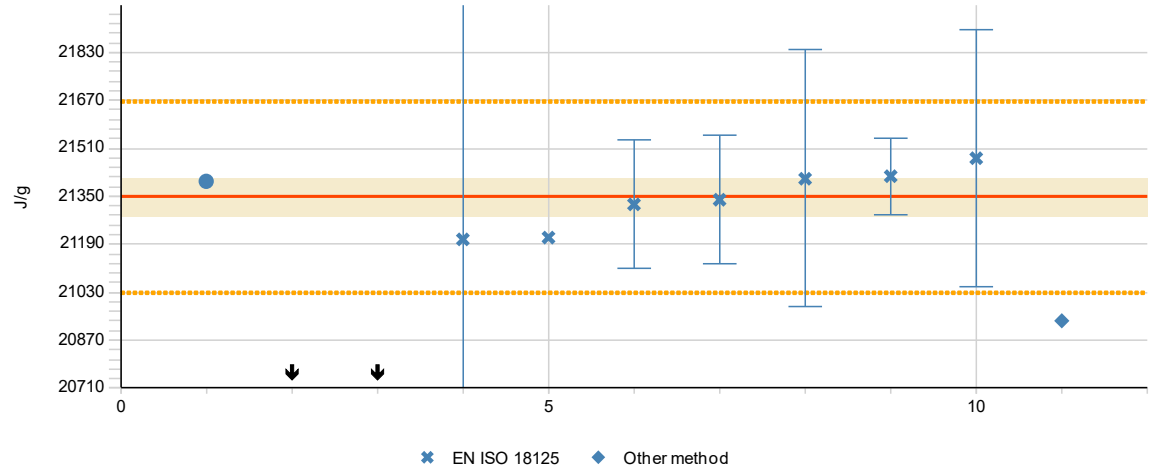
Measurand N_d Sample B3



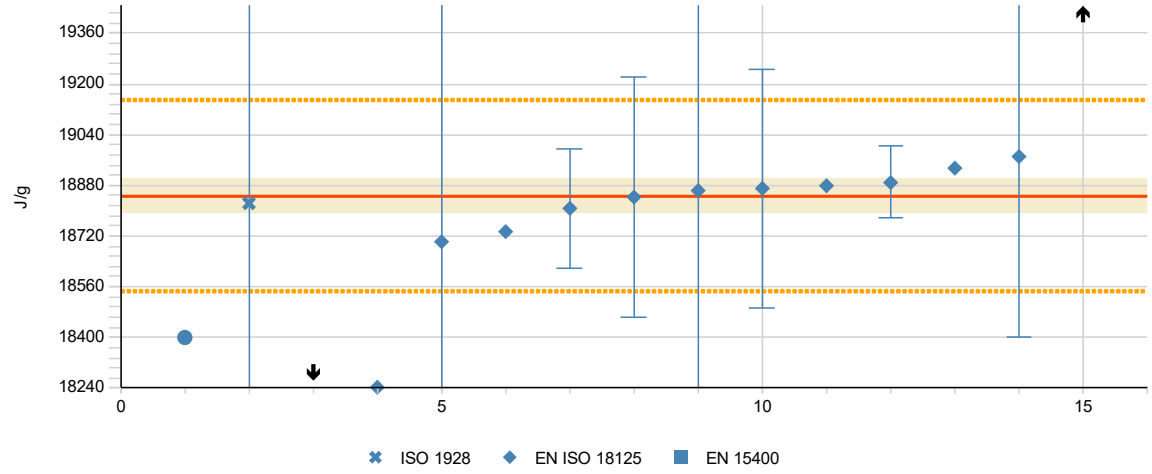
Measurand N_d Sample K1



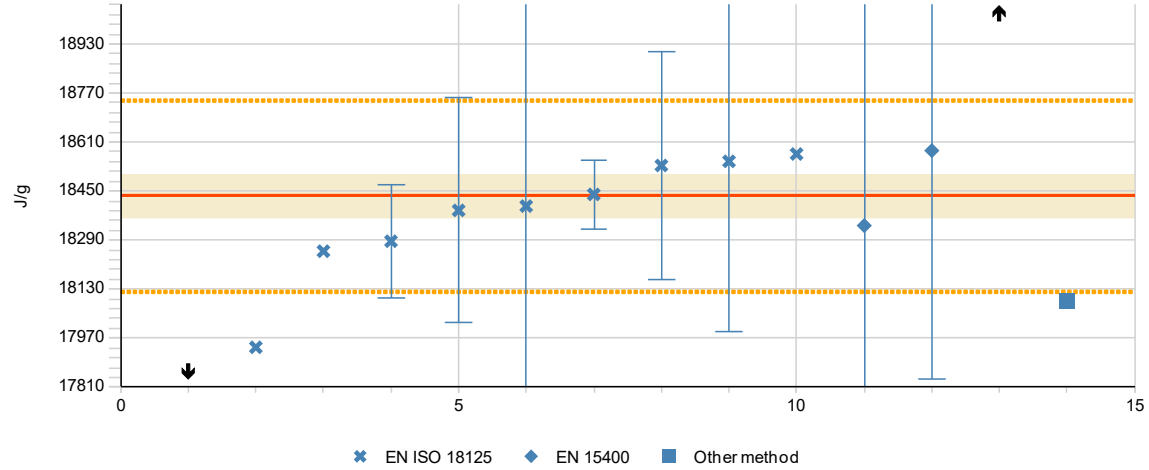
Measurand $q_{p,\,net,d}$ Sample B1



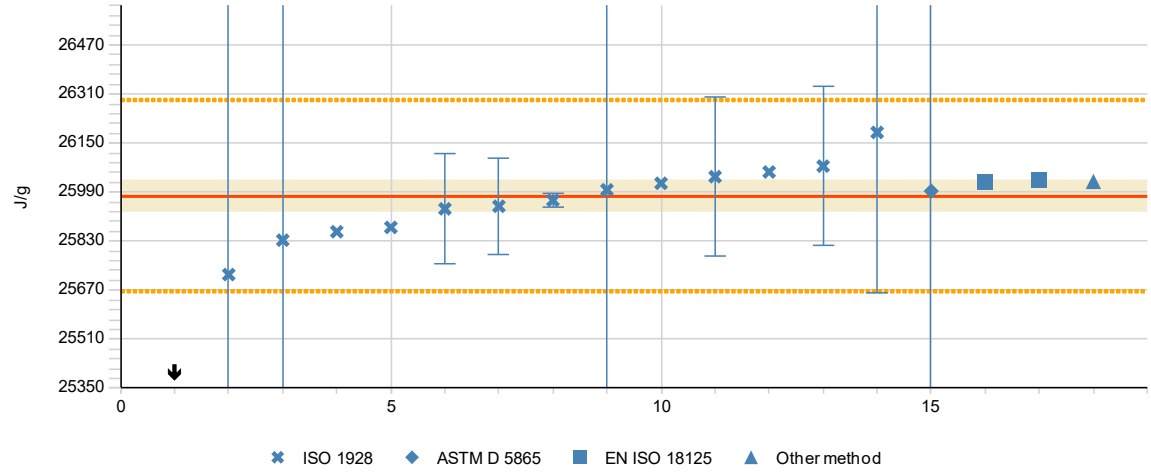
Measurand $q_{p,\,net,d}$ Sample B2



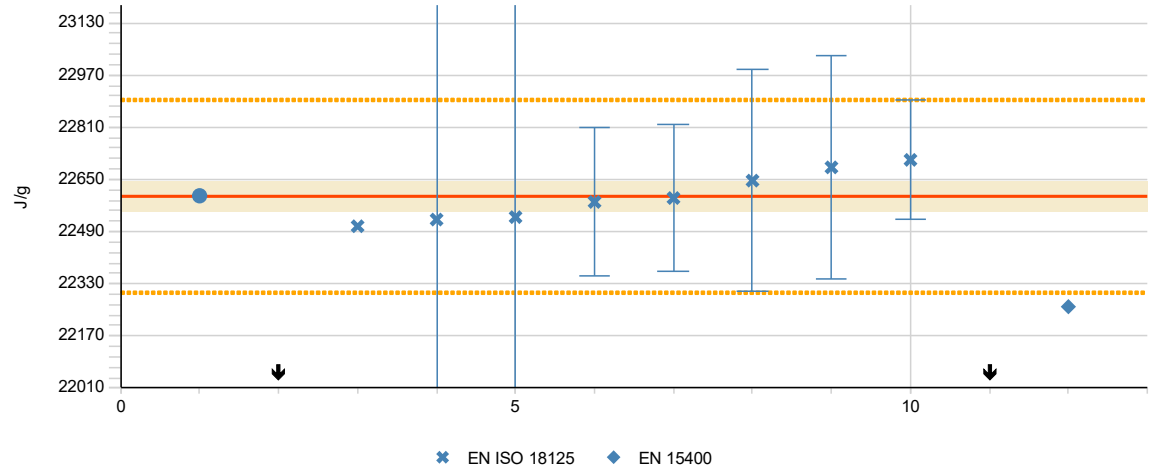
Measurand $q_{p,\,net,d}$ Sample B3

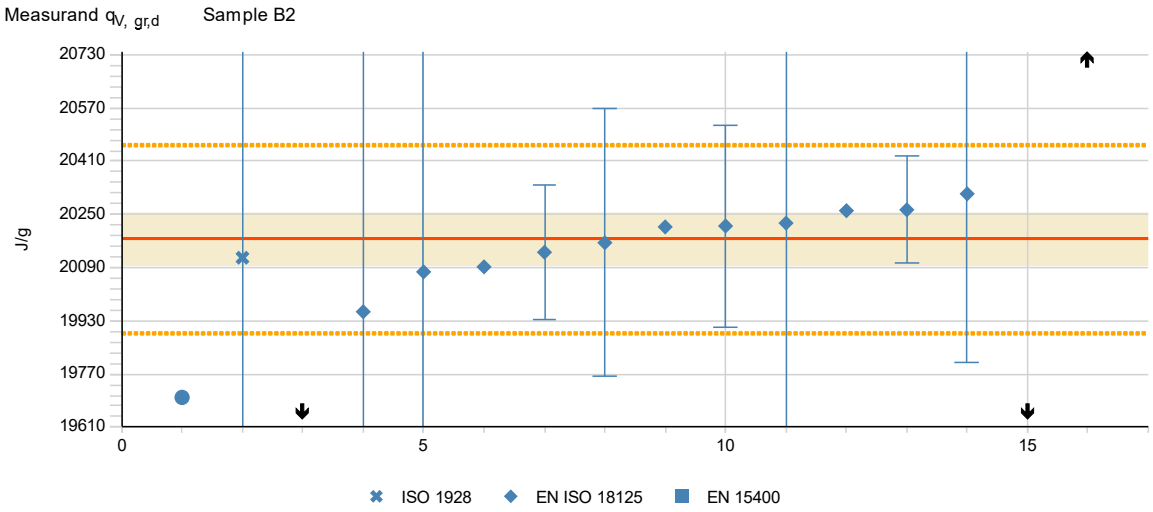


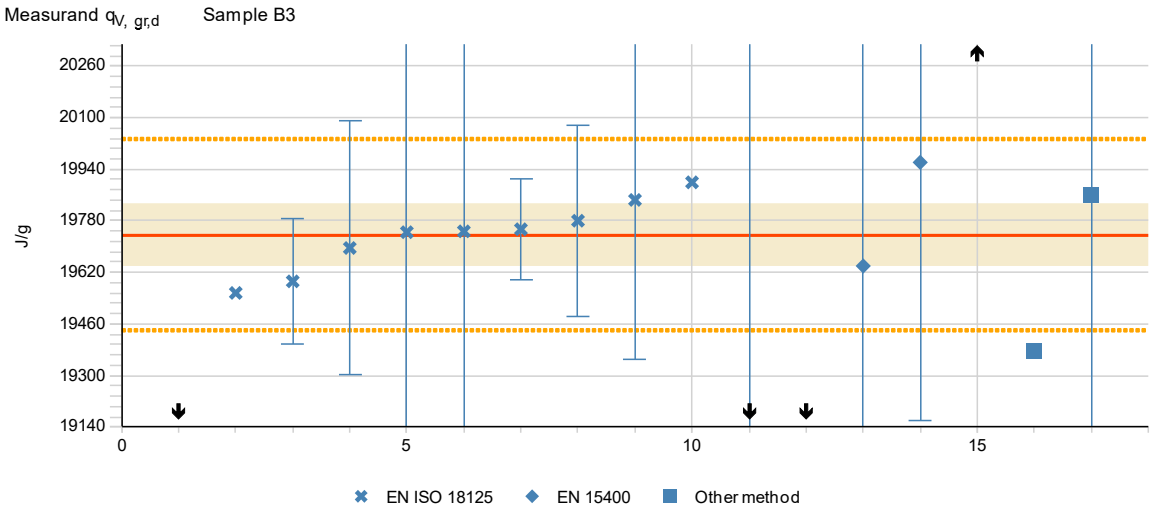
Measurand $q_{p,\,net,d}$ Sample K1

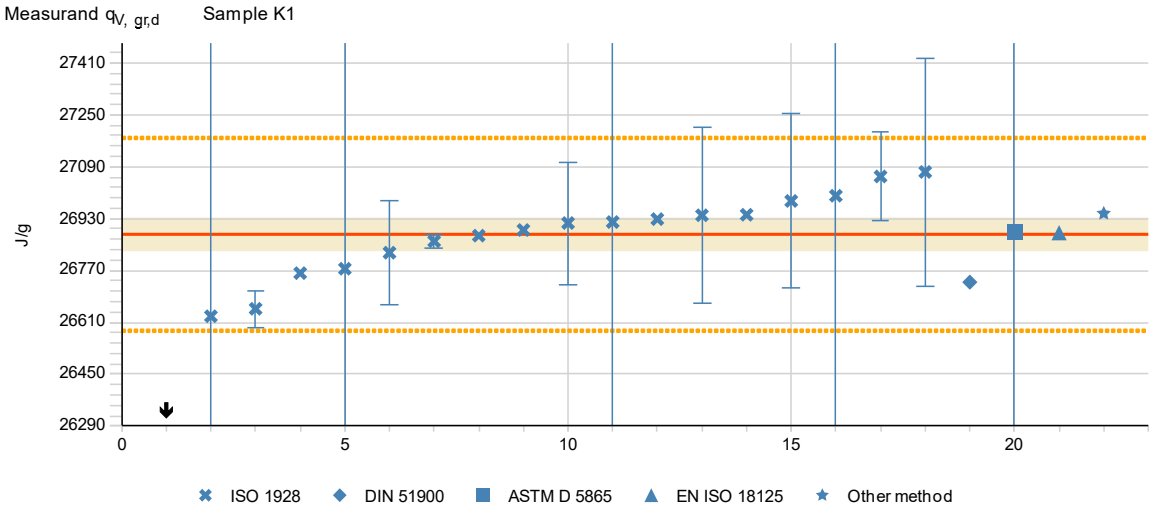


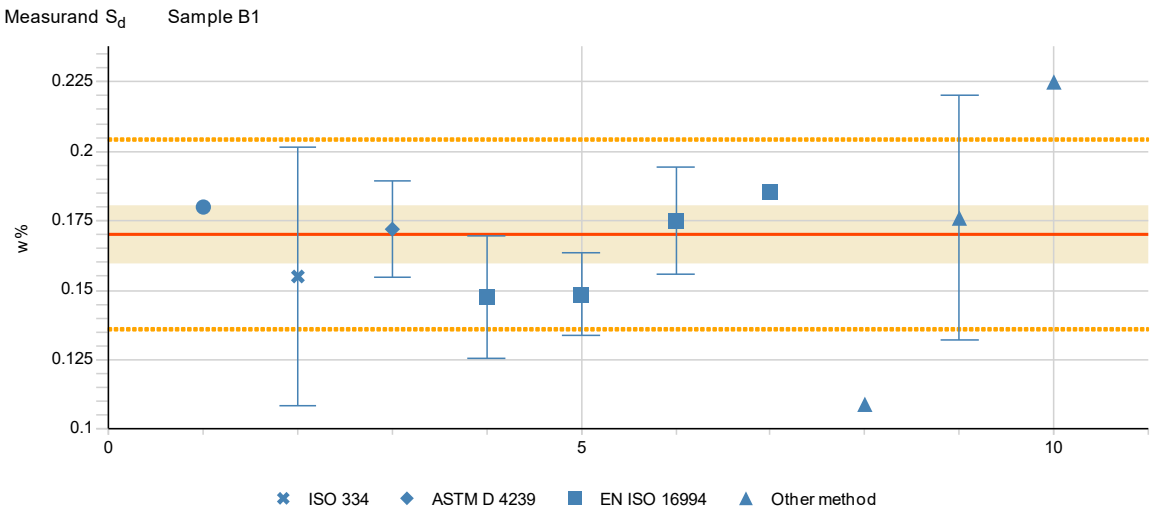
Measurand $q_{V,\,gr,d}$ Sample B1

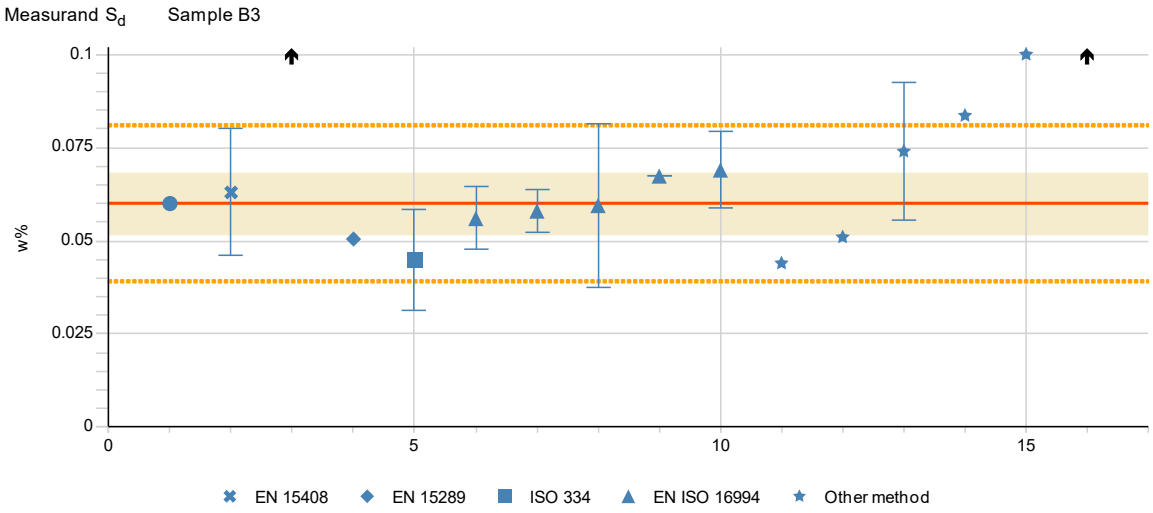


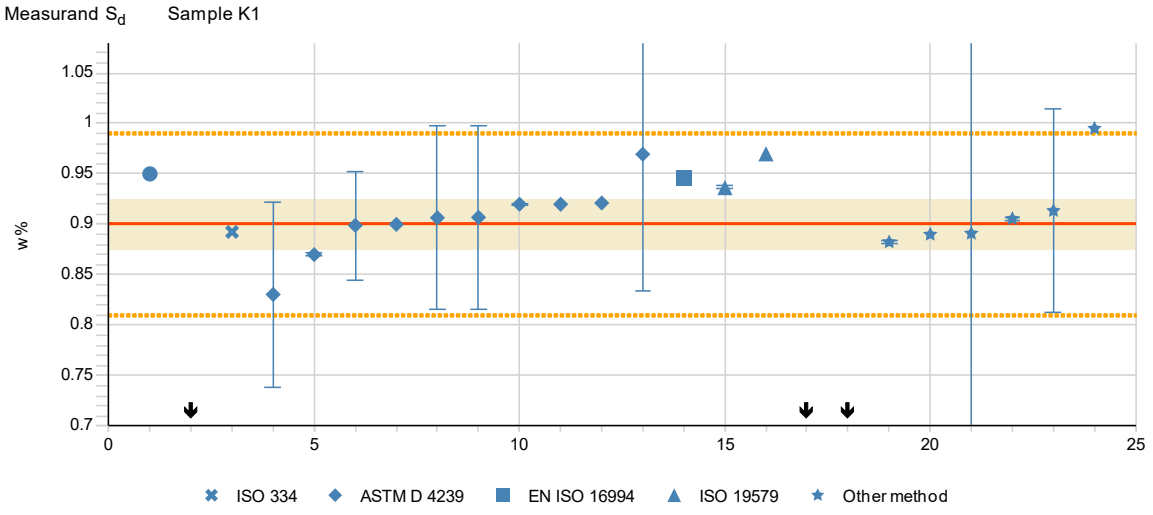

Measurand $q_{V,\ gr,d}$
Sample B2
J/g
20730
20570
20410
20250
20090
19930
19770
19610
0
5
10
15
ISO 1928
EN ISO 18125
EN 15400


Measurand $q_{V,\ gr,d}$
Sample B3
J/g
20260
20100
19940
19780
19620
19460
19300
19140
0
5
10
15
EN ISO 18125
EN 15400
Other method

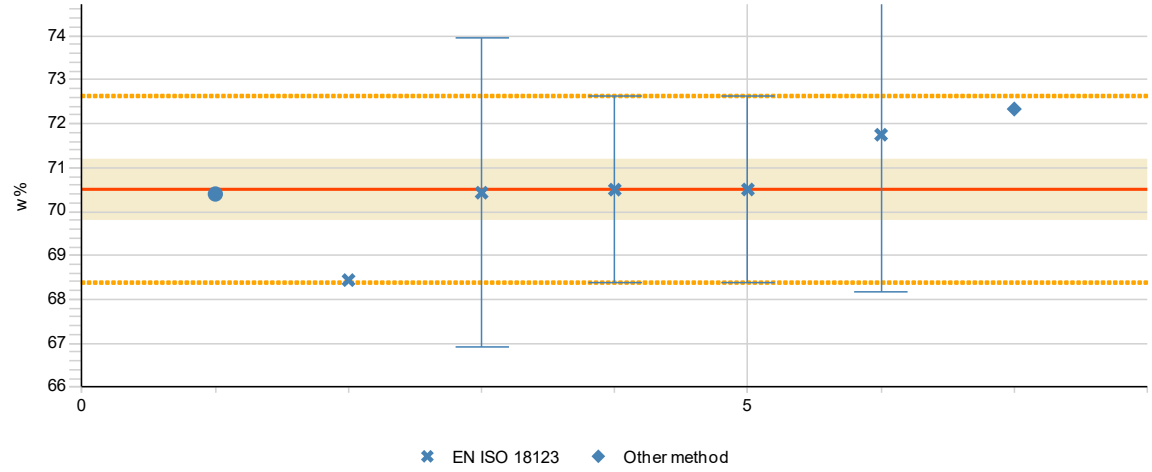

Measurand $q_{V,\ gr,d}$
Sample K1
J/g
27410
27250
27090
26930
26770
26610
26450
26290
0
5
10
15
20
ISO 1928
DIN 51900
ASTM D 5865
EN ISO 18125
Other method


Measurand S_d Sample B1
w %
0.225
0.2
0.175
0.15
0.125
0.1
0
5
10
ISO 334
ASTM D 4239
EN ISO 16994
Other method

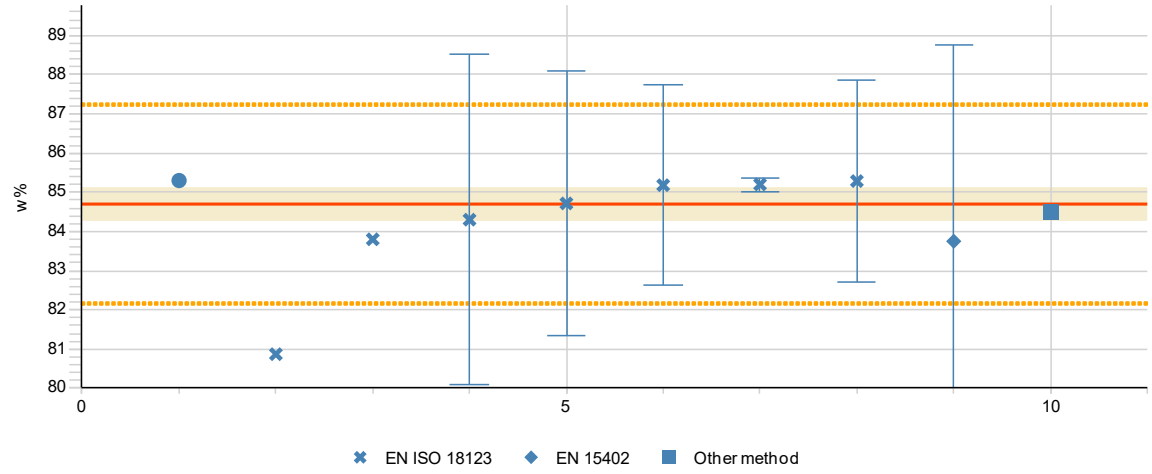

Measurand S_d Sample B3
w %
0.1
0.075
0.05
0.025
0
0
5
10
15
EN 15408
EN 15289
ISO 334
EN ISO 16994
Other method


Measurand S_d Sample K1
w %
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0
5
10
15
20
25
ISO 334
ASTM D 4239
EN ISO 16994
ISO 19579
Other method

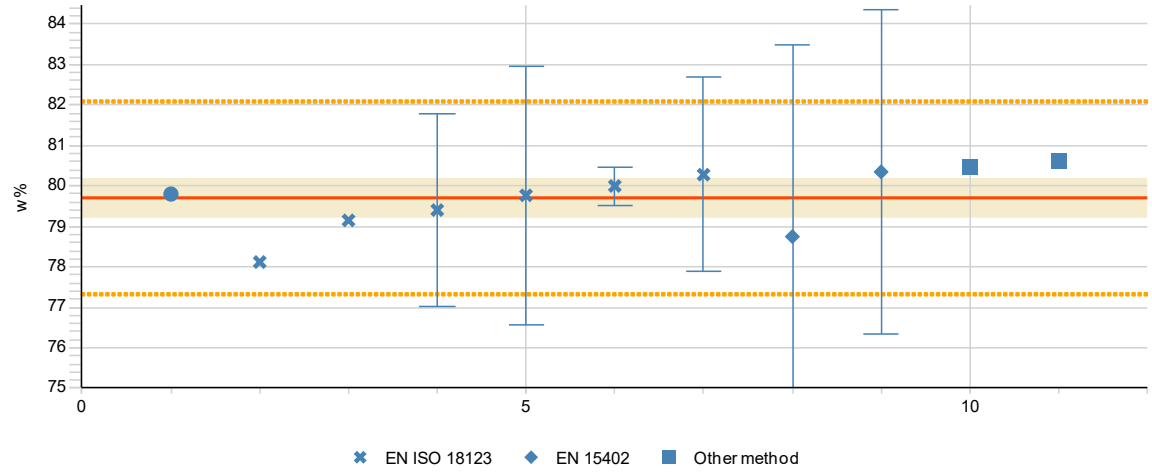
Measurand V_d Sample B1

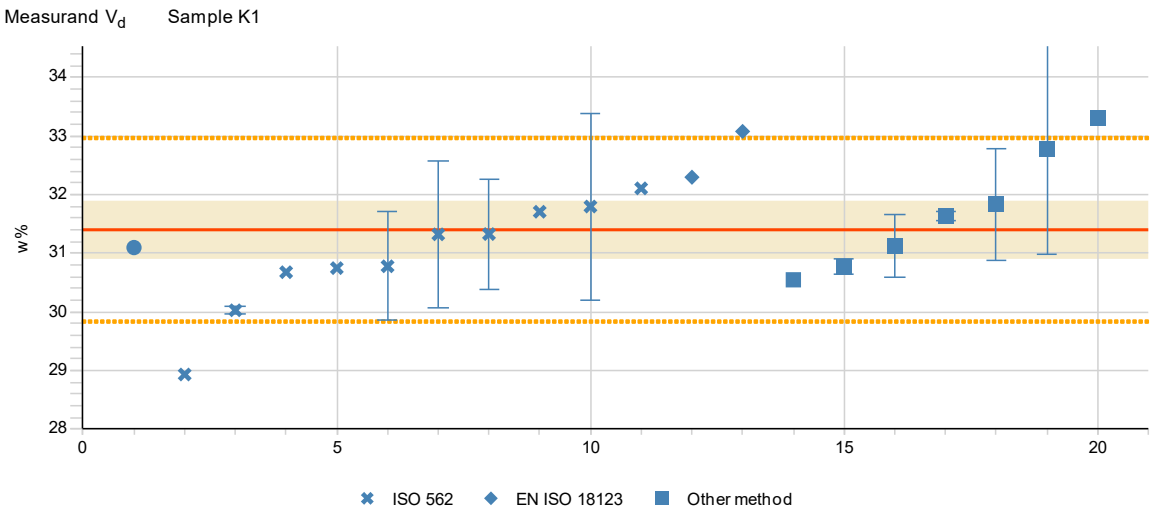


Measurand V_d Sample B2



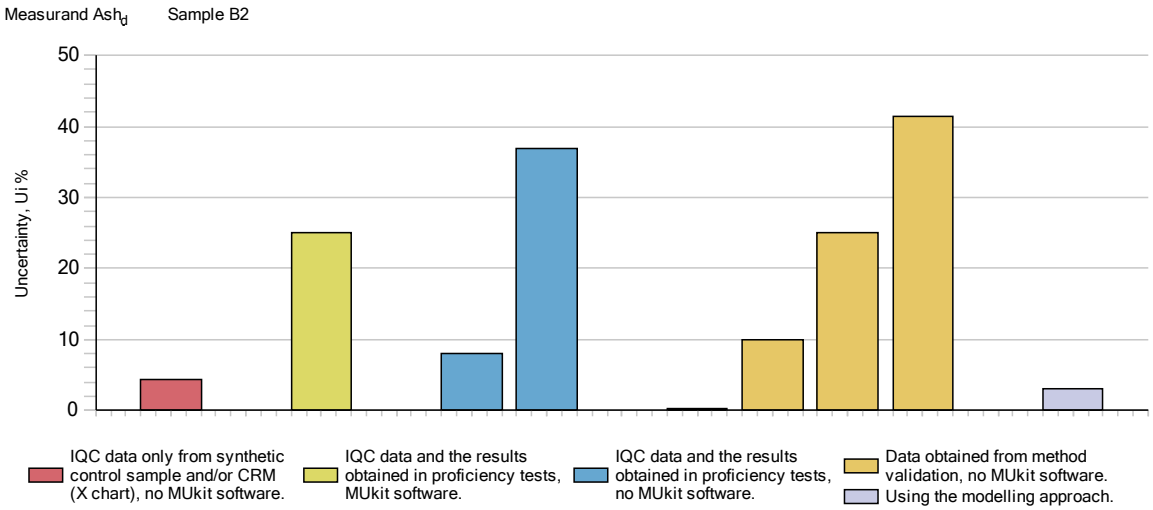
Measurand V_d Sample B3

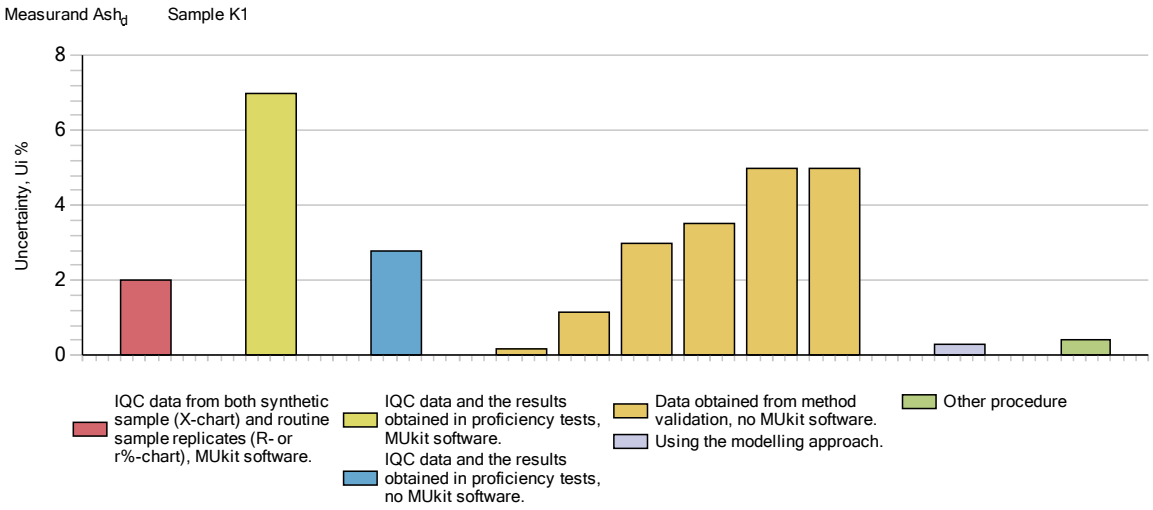


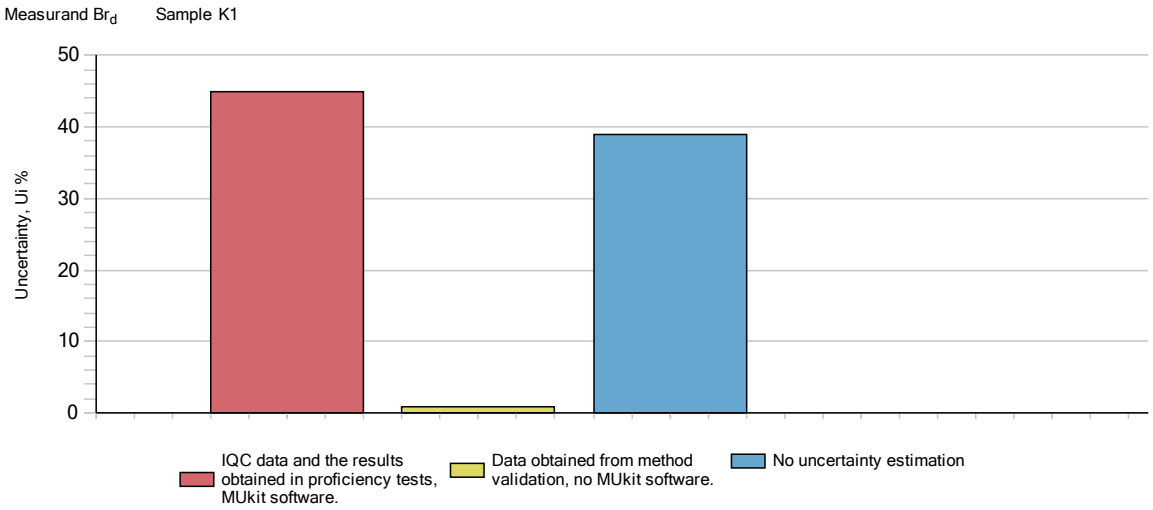

Measurand V_d
Sample K1
w %
34
33
32
31
30
29
28
0
5
10
15
20
ISO 562
EN ISO 18123
Other method

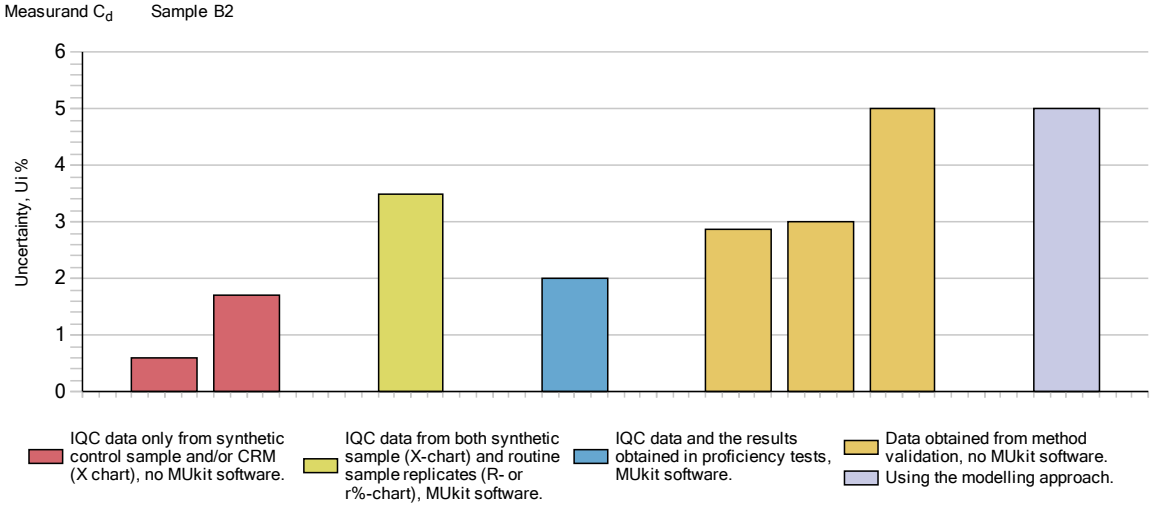
Appendix 13. Examples of measurement uncertainties reported by the participants

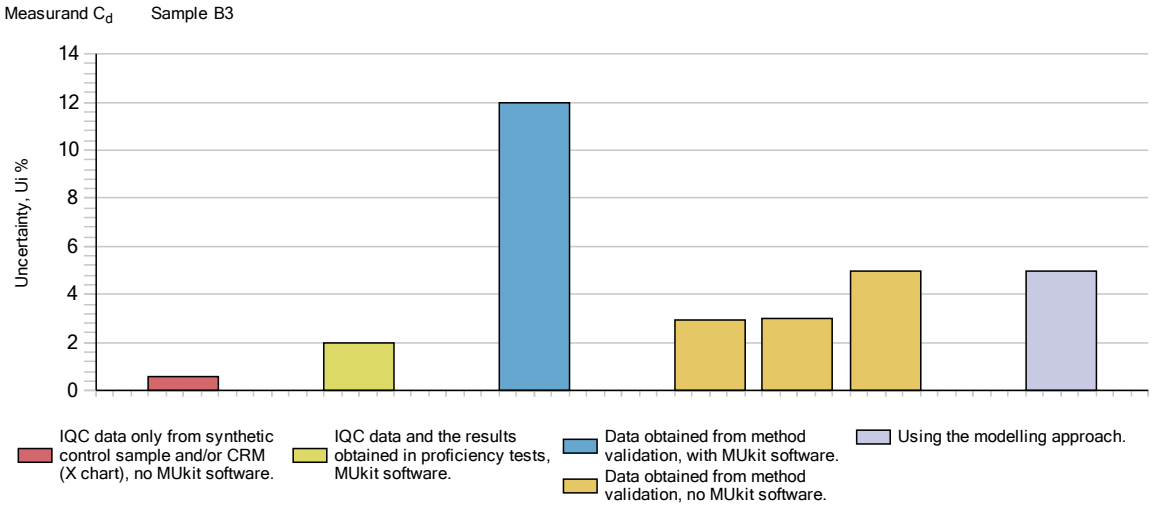
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [36, 37] or using a modelling approach based [40-42].



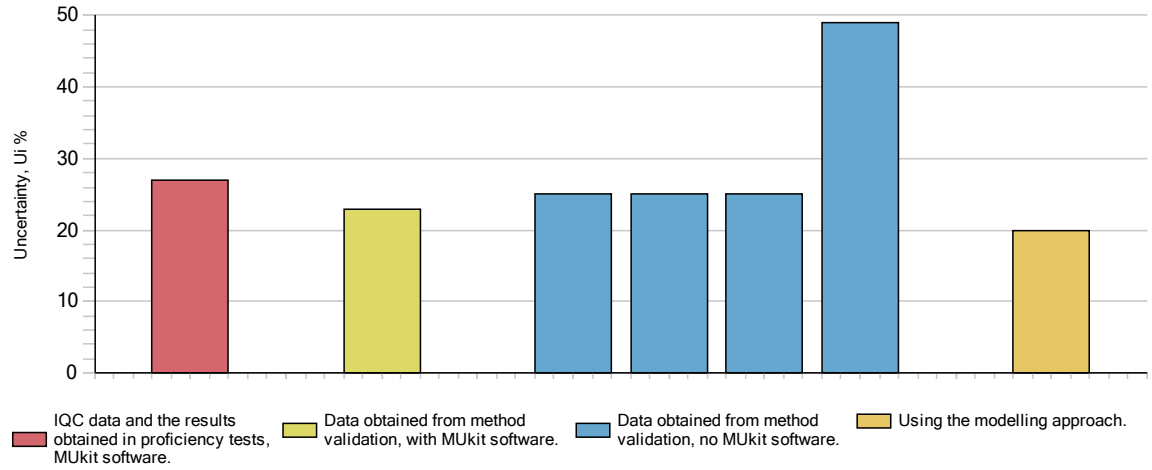



Measurand Br_d
Sample K1
Uncertainty, Ui %
50
40
30
20
10
0
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
No uncertainty estimation

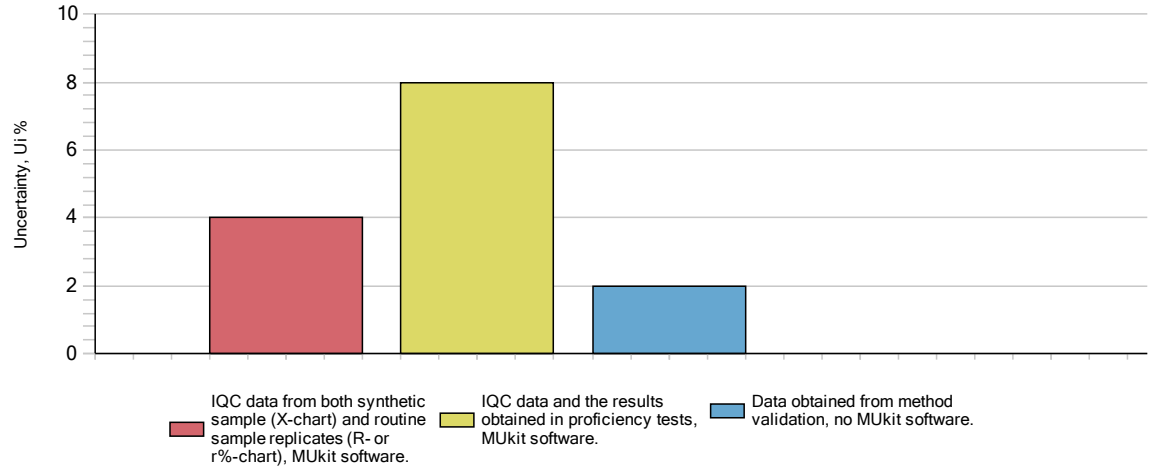

Measurand C_d
Sample B2
Uncertainty, Ui %
6
5
4
3
2
1
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand C_d
Sample B3
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.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

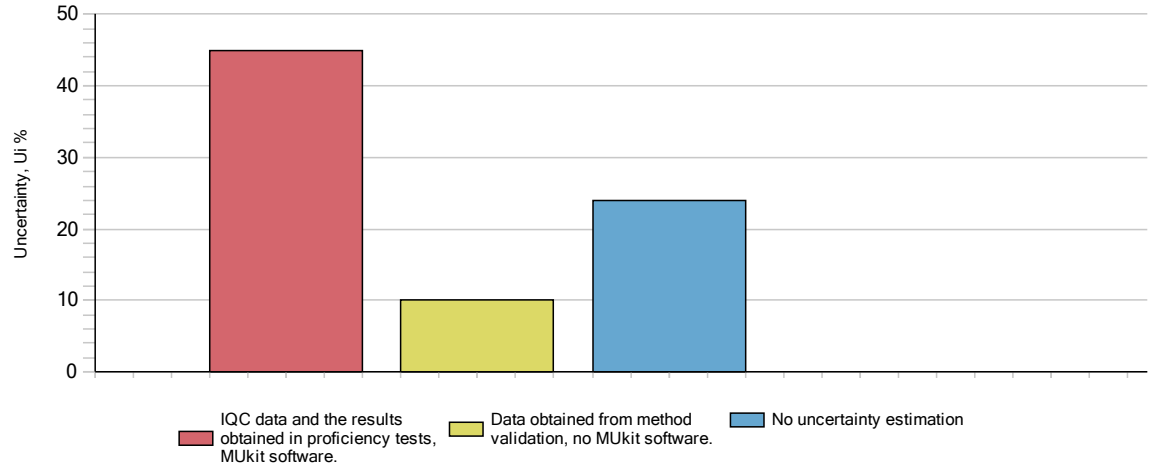
Measurand Cl_d Sample B3



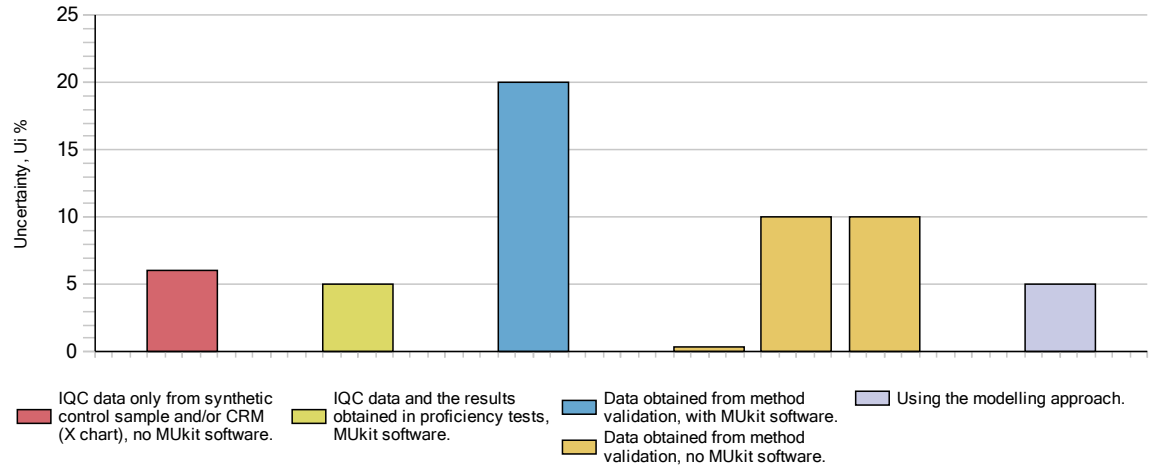
Measurand EF Sample K1



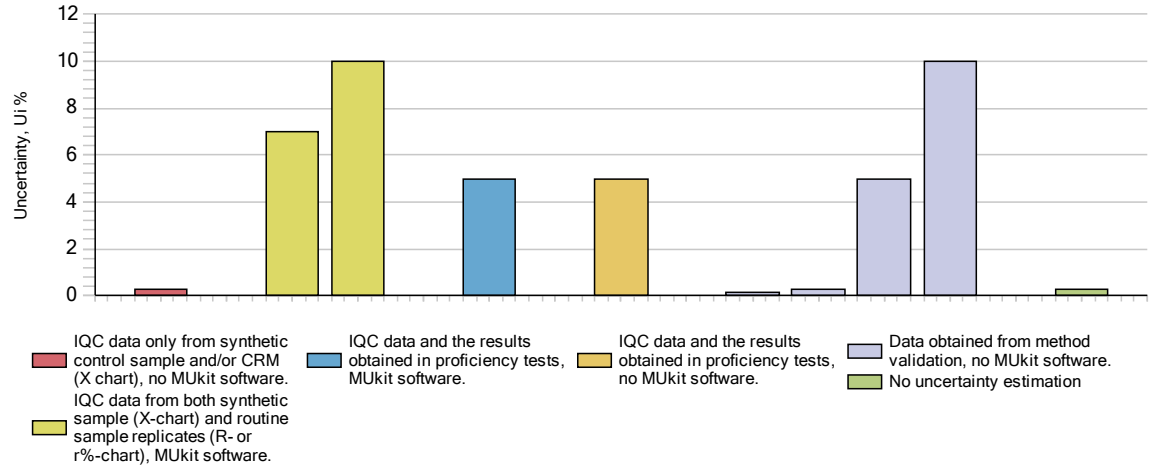
Measurand F_d Sample K1



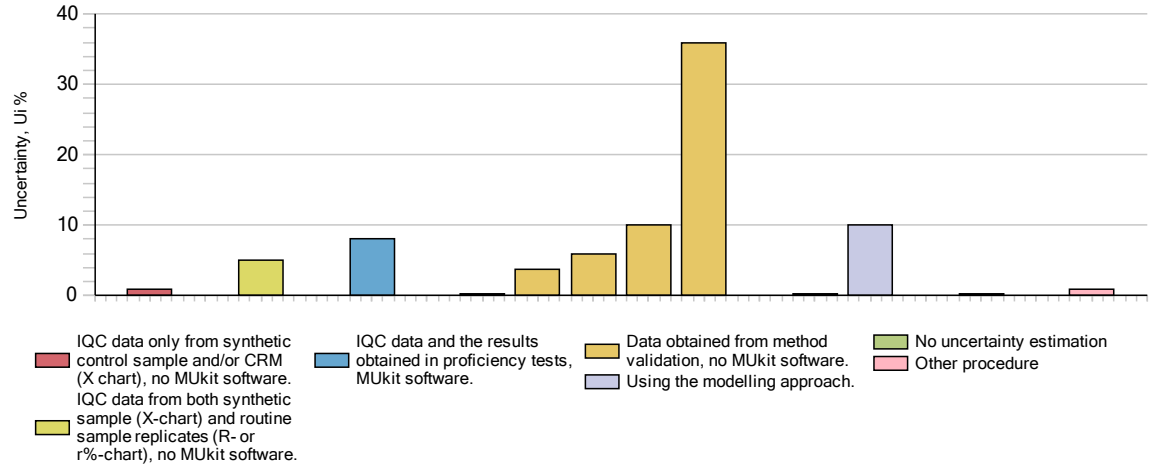
Measurand H_d Sample B3

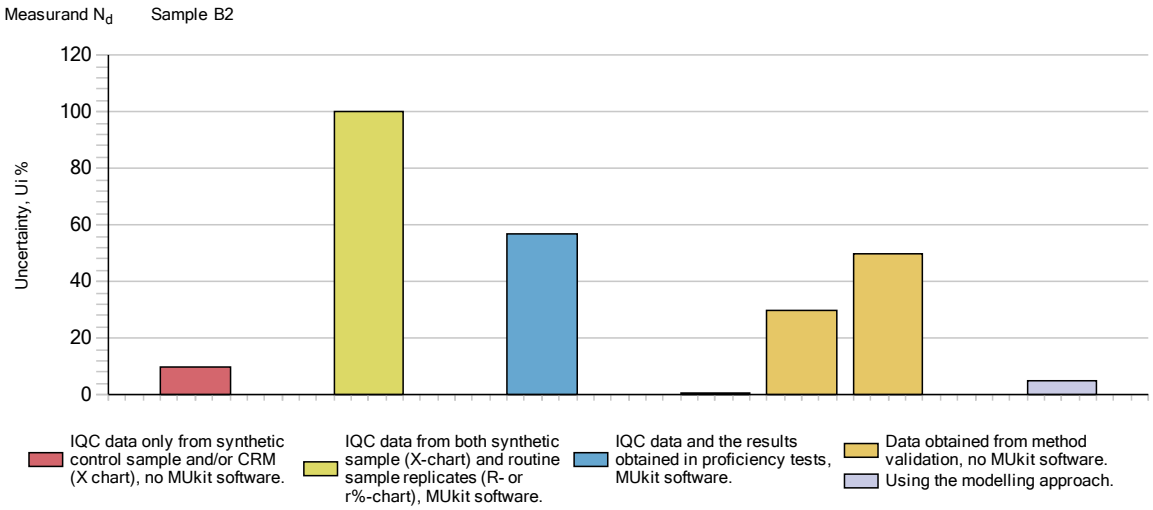


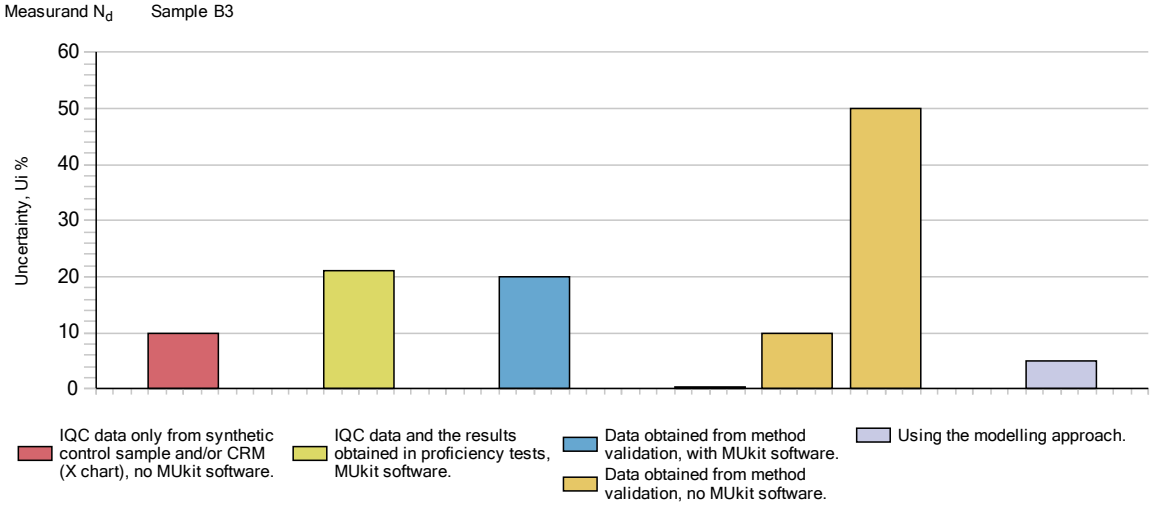
Measurand H_d Sample K1

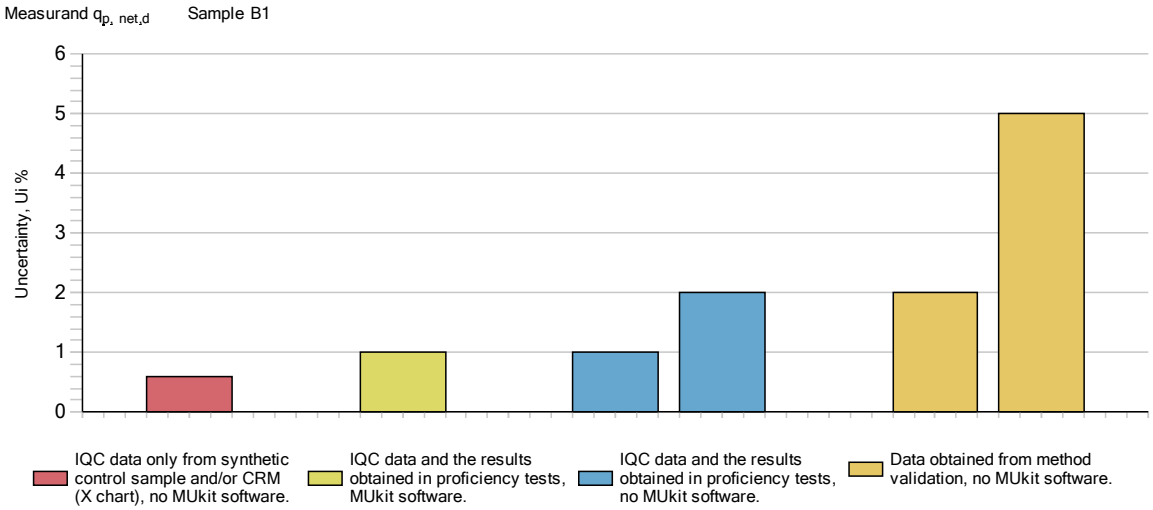


Measurand M_{ad} Sample K1

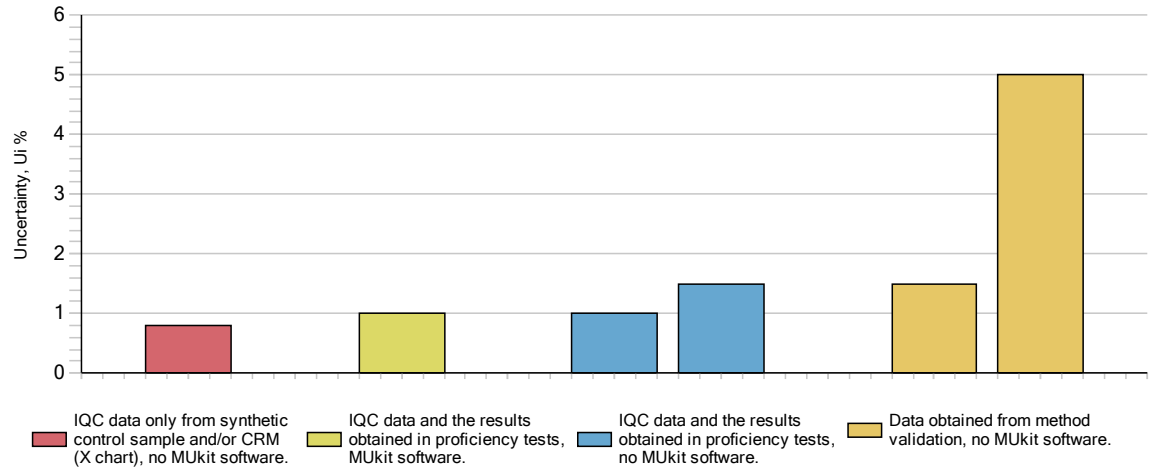



Measurand N_d Sample B2
Uncertainty, Ui %
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

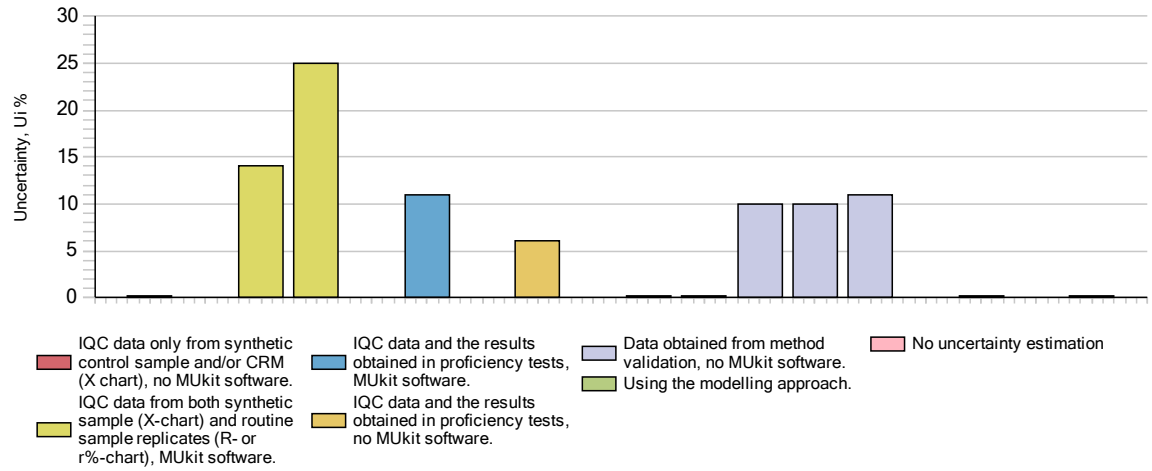

Measurand N_d Sample B3
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand $q_{p,\ net,d}$ Sample B1
Uncertainty, Ui %
6
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.

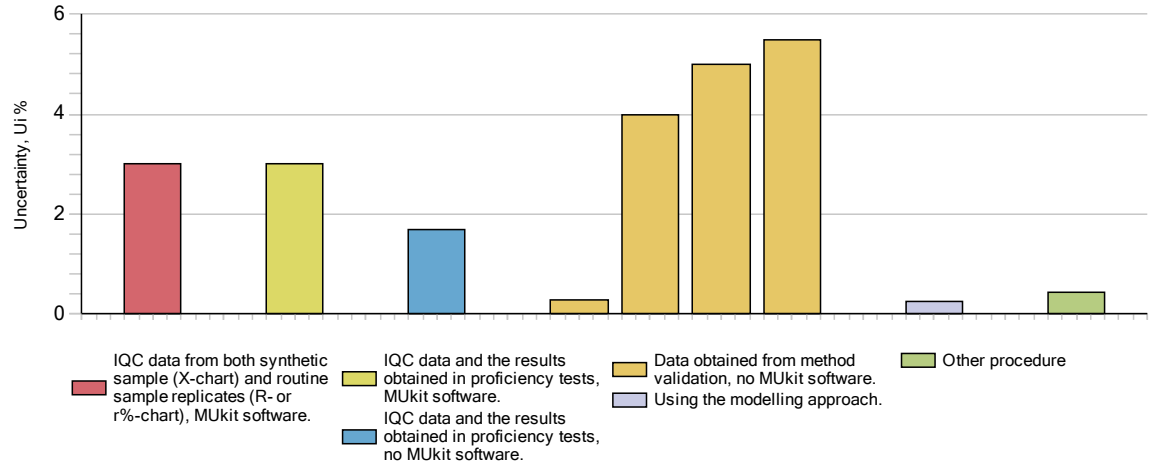
Measurand $q_{V,\ gr,d}$ Sample B1



Measurand S_d Sample K1



Measurand V_d Sample K1



Interlaboratory Proficiency Test 07/2021: Gross and net calorific values in fuels

SYKE

PROF TEST SYKE

ISBN 978-952-11-5463-8 (PDF)
ISSN 1796-1726 (online)

Finnish Environment Institute