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Mervi Pajula, Mirja Leivuori, Minna Salonen, Riitta Koivikko,  
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Finnish Environment Institute  
Research Infrastructure

Author(s): Mervi Pajula<sup>1)</sup>, Mirja Leivuori<sup>1)</sup>, Minna Salonen<sup>2)</sup>, Riitta Koivikko<sup>1)</sup>, Keijo Tervonen<sup>1)</sup>,  
Sari Lanteri<sup>1)</sup> and Markku Ilmakunnas<sup>1)</sup>

1) Finnish Environment Institute

2) Eurofins Environmental Testing Finland Oy, Jyväskylä

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## Abstract

### Proficiency test 06/2025:

### Gross and net calorific values of solid fuels

Proftest Syke carried out the proficiency test (PT) for the measurements of gross and net calorific value, the content of ash and moisture content of the analysis sample, chlorine, fluorine, sulphur, carbon, hydrogen, nitrogen, and volatile matter in wood pellet (not Cl, F, S), biofuel (not F), and coal samples in September 2025. The participants could also estimate the emission factor for the coal sample. In total, there were 34 participants in the PT.

The robust mean, the median, or the mean of the results reported by the participants was used as the assigned value for the measurements. The performance evaluation was based on the  $z$  and  $E_n$  scores. In total, 80 % of the reported results were satisfactory based on  $z$  scores, when the deviation of 1–35 % from the assigned value was accepted. Of the results evaluated with the  $E_n$  scores, 90 % were satisfactory. For the gross calorific value 68 % (wood pellet sample), 78 % (biofuel sample), and 83 % (coal sample) of the results evaluated by  $z$  scores were satisfactory. For the net calorific value 63 % (wood pellet), 67 % (biofuel), and 78 % (coal) of the results evaluated by  $z$  scores were satisfactory. Warm thanks to all participants in this proficiency test!

**Keywords:** Proficiency test, interlaboratory comparison, coal, biofuel, wood pellet, calorific value, emission factor, ash, carbon, chlorine, fluorine, hydrogen, moisture, nitrogen, sulphur, volatile matter

## Tiivistelmä

### Pätevyyskoe 06/2025: Kalorimetrinen ja tehollinen

### lämpöarvo kiinteistä polttoaineista

Proftest Syke järjesti syyskuussa 2025 pätevyyskokeen kalorimetrinen ja tehollisen lämpöarvon sekä analyysikosteuden, tuhkan, rikin, hiilen, typen, vedyn ja haihtuvien aineiden määrittämiseksi puupelletistä (ei Cl, F, S), biopolttoaineesta (ei F) ja kivihiilestä. Osallistujilla oli myös mahdollisuus laskea päästökerroin kivihiilinäytteestä. Pätevyyskokeessa oli 34 osallistujaa.

Testisuureiden vertailuarvoina käytettiin osallistujatulosten robustia keskiarvoa, mediaania tai keskiarvoa. Pätevyyden arviointi tehtiin  $z$ - ja  $E_n$ -arvojen avulla. Tuloksista, jotka arvioitiin  $z$ -arvoilla, oli hyväksyttäviä 80 %, kun sallittiin 1–35 % poikkeama vertailuarvosta. Tuloksista, jotka arvioitiin  $E_n$ -arvoilla 90 % oli hyväksyttäviä. Kalorimetrinen lämpöarvon  $z$ -arvolla arvioituista tuloksista oli hyväksyttäviä 68 % (puupellettinäyte), 78 % (biopolttoainenäyte) ja 83 % (kivihiilinäyte). Tehollisen lämpöarvon tuloksista hyväksyttäviä oli 63 % (puupellettinäyte), 67 % (biopolttoainenäyte) ja 78 % (kivihiilinäyte). Kiitos pätevyyskokeen osallistujille!

**Asiasanat:** pätevyyskoe, vertailumittaus, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, fluori, hiili, päästökerroin, haihtuvat aineet, kloori, kosteus, tuhka, rikki, typi, vety, biopolttoaine, kivihiili, puupelletti

## Sammandrag

# Kompetensprövning 06/2025: Kalorimetriskt och effektivt värmevärde från fasta bränslen

Under september 2025 genomförde Profitest Syke en kompetensprövning, som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, askhalt, fukthalten i analysprovet, fluor, klor, svavel, kol, kväve, väte och flyktiga föreningar i trädpellet (inte Cl, F, S), biobränsle (inte F) och stenkol. Det var en möjlighet att beräkna emissionsfaktor i stenkol prov. Denna kompetensprövning hade totalt 34 deltagare.

Som referensvärde för analytens koncentration användes det robusta medelvärdet, medianen eller medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z- och  $E_n$ -värden. I denna kompetensprövning var 80 % av resultaten värderades med z-värden acceptabla, när en total deviation på 1–35 % från referensvärdet tilläts. 90 % av resultaten som utvärderades med  $E_n$ -värdet var acceptabla. Av de kalorimetriska värmevärdesresultaten som bedömdes med z-värden 68 % (trädpellet), 78 % (biobränsle) och 83 % (stenkol) acceptabla. Av de effektiva värmevärdesresultaten var 63 % (trädpellet), 67 % (biobränsle) och 78 % (stenkol) acceptabla. Ett varmt tack till alla deltagare i testet!

**Nyckelord:** kompetensprövning, kalorimetriskt och effektivt värmevärde, emissionsfaktor, askhalt, fluor, flyktiga föreningar, fukthalt, klor, kol, nitrogen, svavel, väte, biobränsle, stenkol, träd pellet

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# 1 Introduction

Proftest Syke carried out the proficiency test (PT) for the analysis of gross and net calorific values in solid fuels in September 2025 (CAL 06/2025). In the PT, gross and net calorific values,  $C_d$ ,  $S_d$ ,  $H_d$ ,  $N_d$ , moisture content of the analysis sample ( $M_{ad}$ ), ash content ( $Ash_d$ ) as well as volatile matter ( $V_d$ ) were tested in wood pellet (spruce sawdust, not S), biofuel (logging residues, coniferous 1.1.4: EN ISO 17225-1), and coal samples. In this PT also  $Cl_d$  and  $F_d$  were tested in the coal sample and  $Cl_d$  in the biofuel sample. Further, for the coal sample it was possible to estimate the emission factor (EF).

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, [finas.fi/sites/en](https://finas.fi/sites/en)). The measurands and samples of this proficiency test are included in the Calorific value scheme of the accreditation scope.

## 2 Organising the proficiency test

### 2.1 Responsibilities

#### Organiser

ProfTest Syke, Finnish Environment Institute (Syke)  
Mustialankatu 3, FI 00790 Helsinki, Finland  
Phone: +358 295 251 000, Email: [profTest@syke.fi](mailto:profTest@syke.fi)

#### The responsibilities in organising the proficiency test

Mirja Leivuori	coordinator
Mervi Pajula	substitute for coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

**Cooperation partner** Eurofins Environmental Testing Finland Oy, Jyväskylä

**Analytical expert** Minna Salonen, Eurofins Environmental Testing Finland Oy, Jyväskylä  
email: [firstname.lastname@etn.eurofins.com](mailto:firstname.lastname@etn.eurofins.com)

**Subcontracting** KVVY Tutkimus Oy, Tampere (T064, [finas.fi/sites/en](https://finas.fi/sites/en)):  
Sample material homogenisation and dividing into subsamples  
(wood pellet and biofuel)

Homogeneity testing of the samples: Eurofins Environmental Testing Finland Oy, Jyväskylä (T039, [finas.fi/sites/en](https://finas.fi/sites/en))

### 2.2 Participants

In total 34 laboratories participated in this PT (Appendix 1), of which 11 were from Finland and 23 from abroad. 68 % of the participants reported that they have accredited quality management system based on ISO/IEC 17025, and one participant has quality management system based on ISO 9000 series, while 10 participants did not report their accreditation status. 74 % of the participants used accredited analytical methods at least for a part of the measurements. For this PT, the cooperation partner has code 4 in the result tables.

## 2.3 Samples and their timetable

Three types of samples were delivered to the participants: wood pellet (B2, spruce sawdust), biofuel (B3, logging residues, coniferous, 1.1.4: EN ISO 17225-1), and coal (K1) samples.

In the PT, gross and net calorific values,  $C_d$ ,  $S_d$ ,  $H_d$ ,  $N_d$ , moisture content of the analysis sample ( $M_{ad}$ ), ash content ( $Ash_d$ ) as well as volatile matter ( $V_d$ ) were tested in wood pellet (not  $S_d$ ), biofuel, and coal samples. In this PT  $Cl_d$  and  $F_d$  were tested also in the coal sample and  $Cl_d$  in the biofuel sample.

Participants could also estimate or calculate the emission factor (as received, EF) for the coal sample. For this estimation or calculation, the total moisture content of the sample as received ( $M_{ar}$ ) was given for the sample  $M_{ar}$  (K1) = 9.5 %.

In this PT the raw materials from previous similar PTs were used. The wood pellet sample B2 was naked softwood (spruce) sawdust shavings prepared from the same sample batch as in PTs CAL 07/2017 and CAL 08/2023 [4, 5], and the coal sample K1 was from the PT CAL 04/2011 [6]. The biofuel (B3, logging residues) sample material was prepared by Enersense Oy. The wood pellet B2 and biofuel B3 sample materials were homogenised and divided into subsamples at KVVY Tutkimus Oy. The coal sample (K1) was re-homogenised and divided into subsamples by the organiser. All the samples were tested at the laboratory of Eurofins Environment Testing Finland Oy.

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 homogenised before the measurements and to be stored in a dry place at room temperature. Further, the moisture content of the analysis sample was instructed to be analysed on every measurement day. This was important as it eliminates the influence of humidity on the measurements.

The samples were dispatched to the participants abroad mainly on 20 August 2025. For one participant abroad the samples were resent on 10 September 2025 (Appendix 4). For the national participants samples were dispatched on 2 September 2025. The samples arrived to the participants mainly on 3-4 September 2025. For one participant abroad the samples arrived on 11 September 2025.

The results were requested to be reported at the latest on 30 September 2025. Participants delivered the results mainly accordingly except for one participant, who reported the results on 1 October 2025. The preliminary results report was delivered to the participants via ProfTestWEB on 14 October 2025.

## 2.4 Homogeneity and stability studies

To assess sample homogeneity, the gross and net calorific values and the ash content were determined for samples B2 and K1 as duplicate measurements from three subsamples, and for sample B3 from six subsamples. The remaining measurands were tested as duplicate measurements from two subsamples (Appendix 3). According to the homogeneity test results, wood pellet (B2) and biofuel (B3) samples were considered homogenous. Homogeneity test was not passed for the sample K1 for calorific values, but the homogeneity was confirmed based on the participant results. Based on the previous experience of the provider, the samples are known to be stable over the given time period of the test.

## 2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants were mainly related to difficulties in performance. The comment from the provider focused on the missing sample arrival information and background survey answers. Additionally, other background information was missing, such as the used methods, their accreditation status, and the measurement uncertainty when accredited methods were applied. 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 more than  $5 \times s_{\text{rob}}$  or 50 % from the robust mean, were rejected before the statistical results handling. If the result had been reported as below the limit of reporting, it was not included in the statistical calculations. If a participant reported a zero result, it was excluded from the data processing.

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 in 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 participants [7].

### 2.6.2 Assigned values

Either the robust mean, the median, or the mean of the results reported by the participants was used as the assigned value for measurands of the test samples. Robust mean was used when in the statistical data processing there were at least 12 results ( $n_{\text{stat}} \geq 12$ , B2:  $Ash_d, M_{ad}, q_{V,gr,d}$ ; B3:  $Ash_d, M_{ad}, q_{V,gr,d}$ ; K1:  $Ash_d, C_d, H_d, M_{ad}, N_d, q_{V,gr,d}$ ). In cases, where the number of results in the statistical data processing was lower than 12 ( $n_{\text{stat}} < 12$ ) or the deviation of the results was large, the mean or the median of the results reported by the participants was used as the assigned value. No assigned value was set for volatile matter ( $V_d$ ) of biofuel sample (B3) due to the large deviation of the results. Detailed information of the assigned values, their uncertainties, and reliability are shown in Appendix 5.

The assigned values based on the robust mean, the median, or the mean 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 median, or the mean 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, 7]. The uncertainties of the assigned values varied between 0.2 % and 0.5 % for the calorific values. For the other evaluated measurands the uncertainties varied from 0.7 % to 64 % (Appendix 5). **After reporting the preliminary results report no changes have been made for the assigned values.**

### 2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated both with the z and  $E_n$  scores.

The standard deviation for proficiency assessment was estimated based on the measurand concentration, the results of homogeneity tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. Additionally, the requirements of the reproducibility of the used international standard methods were considered for the gross calorific values of the different sample types. The standard deviation for proficiency assessment ( $2 \times s_{pt}$  at the 95 % confidence level) was set to 1–35 % depending on the measurands. Standard deviation for proficiency assessment was not given for the moisture content of analysis sample  $M_{ad}$  (all samples), and thus the results were not evaluated. Further, due to the high deviation of the results, no evaluation was given for nitrogen ( $N_d$ ) for the sample B2 and volatile matter ( $V_d$ ) in the sample B3. **After reporting the preliminary results report no changes have been made for the standard deviations of the proficiency assessment values.**

When the number of reported results was low ( $n_{stat} < 6$ ) and the uncertainty was set for the assigned value, the performance was estimated by means of  $E_n$  scores ('Error, normalised', K1:  $Cl_d$  and EF, Appendix 10).  $E_n$  scores were calculated for the results for which the measurement uncertainty was given.

When using the robust mean, the median, or the mean as the assigned value, the reliability was tested according to the criterion  $u_{pt} / s_{pt} \leq 0.3$ , where  $u_{pt}$  is the standard uncertainty of the assigned value and  $s_{pt}$  is the standard deviation for proficiency assessment [2, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled, and the assigned values were considered reliable (Table 1).

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 fulfilled for all samples and measurands.

**Table 1. Uncertainty of the performance evaluation: deviations from the criteria when evaluating the results.**

Measurand	Sample	Reliability of the assigned value
$F_d$	K1	x
$H_d$	K1	x

## 3 Results and conclusions

### 3.1 Results

The summary of the results is presented in Table 2. The terms in the results table are explained in Appendix 6. The results and the performance of each participant are presented in Appendix 7 and the reported results with their expanded uncertainties ( $k=2$ ) are presented in Appendix 8. The summaries of the  $z$  and  $E_n$  scores are shown in Appendices 9 and 10 and the  $z$  scores in the ascending order in Appendix 11.

The robust standard deviations of the results varied from 0.5 to 19 % (Table 2). The highest robust standard deviation (19 %) was for low  $S_d$  concentration in the sample B3. The robust standard deviation was lower than 2 % for 46 % of the results and lower than 6 % for 77 % of the results. The robust standard deviations were somewhat lower than in the previous similar proficiency test CAL 08/2024, where the deviations varied from 0.3 % to 38 % [8].

**Table 2. The summary of the results in the proficiency test CAL 06/2025.**

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	$s_{rob}$	$s_{rob}$ %	$2 \times s_{pt}$ %	$n_{all}$	Acc $z$ %	Acc $E_n$ %
Ash <sub>d</sub>	B2	w%	0.29	0.30	0.29	0.30	0.04	14.9	30	16	81	
	B3	w%	4.06	4.07	4.06	4.05	0.19	4.6	15	17	94	
	K1	w%	9.65	9.64	9.65	9.67	0.11	1.2	2.5	18	78	
C <sub>d</sub>	B2	w%	50.5	50.5	50.5	50.7	0.6	1.3	2.5	14	79	
	B3	w%	51.2	51.2	51.2	51.2	1.0	1.9	3	15	87	
	K1	w%	70.1	70.1	70.1	69.9	1.2	1.6	3	18	89	
Cl <sub>d</sub>	B3	mg/kg	144	144	144	145	12	8.5	20	12	64	
	K1	mg/kg	137	137	-	134	-	-	-	11	80	
EF	K1	t CO <sub>2</sub> /TJ	95.5	95.5	-	95.4	-	-	-	7	100	
F <sub>d</sub>	K1	mg/kg	91.2	91.2	-	93.4	-	-	30	8	75	
H <sub>d</sub>	B2	w%	6.15	6.15	6.15	6.16	0.27	4.5	8	14	93	
	B3	w%	6.00	6.00	6.01	5.98	0.21	3.4	6	14	79	
	K1	w%	4.56	4.54	4.56	4.50	0.19	4.1	7	16	88	
M <sub>ad</sub>	B2	w%	7.51	7.51	7.51	7.58	0.31	4.1	-	15	-	
	B3	w%	6.12	6.10	6.12	6.25	0.40	6.5	-	16	-	
	K1	w%	5.33	5.33	5.33	5.37	0.28	5.2	-	19	-	
N <sub>d</sub>	B2	w%	0.066	0.059	-	0.066	-	-	-	14	-	
	B3	w%	0.53	0.53	0.53	0.52	0.07	14.2	25	14	92	
	K1	w%	1.91	1.89	1.91	1.91	0.07	3.8	10	15	87	
Q <sub>p,net,d</sub>	B2	J/g	18800	18800	18773	18805	147	0.8	1.6	16	63	
	B3	J/g	19112	19112	19140	19130	187	1.0	1.7	15	67	
	K1	J/g	27250	27250	27241	27223	212	0.8	1.3	18	78	

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	$s_{rob}$	$s_{rob} \%$	$2 \times s_{pt} \%$	$n_{all}$	Acc z %	Acc $E_n$ %
$q_{V,gr,d}$	B2	J/g	20085	20077	20085	20075	109	0.5	1.5	19	68	
	B3	J/g	20405	20417	20405	20432	146	0.7	1.7	18	78	
	K1	J/g	28185	28188	28185	28143	182	0.6	1.2	18	83	
$S_d$	B3	w%	0.042	0.042	0.042	0.045	0.008	18.7	35	14	75	
	K1	w%	0.35	0.35	0.35	0.35	0.03	9.1	15	19	74	
$V_d$	B2	w%	85.6	85.6	85.6	85.7	1.4	1.6	3	9	89	
	B3	w%	-	77.3	77.3	77.1	1.5	2.0	-	10	-	
	K1	w%	36.4	36.4	36.4	36.5	0.7	1.9	5	14	71	

Rob. mean: the robust mean,  $s_{rob}$ : the robust standard deviation,  $s_{rob} \%$ : the robust standard deviation as percent,  $2 \times s_{pt} \%$ : the standard deviation for proficiency assessment at the 95 % confidence level,  $n_{all}$ : the number of the participants, Acc z %: the share of results (%), where  $|z| \leq 2$ , Acc.  $E_n$  %: The share of results (%), where  $|E_n| \leq 1$ .

In this PT the participants were to report replicate results for all measurements. The repeatability ( $s_w$ ) and reproducibility ( $s_t$ ) of the replicate results was tested using ANOVA statistical handling (Table 3). The targets for the repeatability and reproducibility are the ones recommended in the international standards or in the technical specifications related to the measurements of fuels.

For the gross calorific value measurements of wood pellets and coal, the repeatability and reproducibility limits are 120 J/g and 300 J/g, respectively [9, 10]. For biofuels, the corresponding limits are 140 J/g and 400 J/g [9, 10]. When converted to repeatability standard deviation ( $s_r$ ) and reproducibility standard deviation ( $s_R$ ) in accordance with ISO 5725-2, the corresponding values are  $s_r = 42.9$  J/g and  $s_R = 107$  J/g for wood pellets and coal, and  $s_r = 50.0$  J/g and  $s_R = 143$  J/g for biofuels [11].

According to the ANOVA results for the gross calorific value,  $s_w < s_r$  for sample B2, while  $s_w > s_r$  for samples B3 and K1 (Table 3). This indicates that, on average, the participants' internal precision is consistent with the expected method performance for sample B2, whereas for samples B3 and K1, the internal variation exceeds the expected repeatability of the method. In addition, for samples B2, B3 and K1,  $s_t > s_R$ . This indicates that, on average, the overall variation between participants is higher than expected, suggesting that some participants may have systematic deviations or inconsistent performance relative to the method's reproducibility limit. The participants are encouraged to verify that the within-laboratory precision meets the expected repeatability of the method. A summary of the comparison between ANOVA-derived standard deviations and the method specific limits is presented in Table 4.

The estimation of the robustness of the methods could be done by the ratio  $s_b/s_w$ . For the robust methods the ratio  $s_b/s_w$  should not exceed 3. Here, however, the robustness exceeded the value 3 for ca. 67 % of the results (Table 3). For the gross calorific value, the ratio  $s_b/s_w$ , was 3.9 in the sample B2, 1.9 in the sample B3 and 1.5 in the sample K1. For the net calorific values 5.3, 4.1 and 2.0, respectively. For the calorific values the ratio  $s_b/s_w$  was almost in the same range than in the previous similar PT CAL 08/2024 [8].

**Table 3. The summary of repeatability based on replicate determinations (ANOVA statistics).**

Measurand	Sample	Unit	Assigned value	Mean	S <sub>w</sub>	S <sub>b</sub>	S <sub>t</sub>	S <sub>w</sub> %	S <sub>b</sub> %	S <sub>t</sub> %	S <sub>b</sub> /S <sub>w</sub>
Ash <sub>d</sub>	B2	w%	0.29	0.30	0.01	0.06	0.06	5.0	21	22	4.2
	B3	w%	4.06	4.07	0.12	0.16	0.20	3.0	4.0	5.0	1.4
	K1	w%	9.65	9.64	0.05	0.14	0.15	0.51	1.4	1.5	2.8
C <sub>d</sub>	B2	w%	50.5	50.5	0.14	0.61	0.63	0.28	1.2	1.2	4.4
	B3	w%	51.2	51.2	0.14	0.84	0.85	0.27	1.6	1.7	6.1
	K1	w%	70.1	70.1	0.25	1.10	1.13	0.35	1.6	1.6	4.5
Cl <sub>d</sub>	B3	mg/kg	144	144	6.28	9.85	11.7	4.4	6.8	8.1	1.6
	K1	mg/kg	137	137	11.6	58.3	59.5	9.9	50	50	5.0
EF	K1	t CO <sub>2</sub> /TJ	95.5	95.5	0.21	0.70	0.73	0.22	0.73	0.76	3.4
F <sub>d</sub>	K1	mg/kg	91.2	91.2	3.04	11.4	11.8	3.3	12	13	3.7
H <sub>d</sub>	B2	w%	6.15	6.15	0.06	0.24	0.25	0.93	4.0	4.1	4.3
	B3	w%	6.00	6.00	0.15	0.16	0.22	2.5	2.6	3.6	1.1
	K1	w%	4.56	4.54	0.05	0.25	0.26	1.1	5.5	5.6	5.1
M <sub>ad</sub>	B2	w%	7.51	7.51	0.08	0.27	0.28	1.1	3.5	3.7	3.2
	B3	w%	6.12	6.10	0.09	0.37	0.38	1.4	6.1	6.3	4.4
	K1	w%	5.33	5.33	0.08	0.25	0.26	1.5	4.6	4.8	3.1
N <sub>d</sub>	B2	w%	0.066	0.059	0.01	0.05	0.05	25	110	110	4.3
	B3	w%	0.53	0.53	0.05	0.06	0.07	8.7	11	14	1.3
	K1	w%	1.91	1.89	0.02	0.11	0.11	1.1	5.5	5.6	5.1
q <sub>p,net,d</sub>	B2	J/g	18800	18800	30.5	160	163	0.16	0.85	0.87	5.3
	B3	J/g	19112	19112	43.7	178	183	0.23	0.93	0.96	4.1
	K1	J/g	27250	27250	95.1	194	216	0.35	0.71	0.79	2.0
q <sub>v,gr,d</sub>	B2	J/g	20085	20077	32.5	128	132	0.16	0.64	0.66	3.9
	B3	J/g	20405	20417	80.9	156	176	0.40	0.76	0.86	1.9
	K1	J/g	28185	28188	99.1	152	182	0.35	0.54	0.64	1.5
S <sub>d</sub>	B3	w%	0.042	0.042	0.01	0.01	0.02	14	38	40	2.6
	K1	w%	0.35	0.35	0.02	0.03	0.03	4.4	7.9	9.1	1.8
V <sub>d</sub>	B2	w%	85.6	85.6	0.33	1.18	1.22	0.39	1.4	1.4	3.5
	B3	w%	-	77.3	0.37	1.34	1.39	0.48	1.7	1.8	3.6
	K1	w%	36.4	36.4	0.11	0.72	0.73	0.29	2.0	2.0	6.7

Ass.val.: assigned value; s<sub>w</sub>: repeatability standard error; s<sub>b</sub>: between participant's standard error; s<sub>t</sub>: reproducibility standard error.

**Table 4. Comparison of ANOVA-derived standard deviations with method repeatability and reproducibility limits for gross calorific value**

Sample	$s_r$	$s_w$	Repeatability requirement	$s_R$	$s_t$	Reproducibility requirement
B2, wood pellet	42.9	32.5	✓	107	132	X
B3, biofuel	50.0	80.9	X	143	176	X
K1, coal	42.9	99.1	X	107	182	X

$s_r$ : repeatability standard deviation (J/g, requirement);  $s_R$ : reproducibility standard deviation (J/g, requirement);  
 $s_w$ : repeatability standard deviation (J/g, ANOVA);  $s_t$ : reproducibility standard deviation (J/g, ANOVA);  
 ✓: requirement fulfilled; X: requirement un-fulfilled.

## 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 12. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 13. The statistical comparison of the analytical methods was possible for the data where the number of the results was  $\geq 5$  ( $C_d$ ,  $H_d$  and  $M_{ad}$  in the sample K1).

### 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 12 and 13.

Mostly standard methods EN ISO 18125 [9], ISO 1928 [10], and EN ISO 21654 [12] were used for the measurement of calorific values ( $q_{v,gr,d}$  and  $q_{p,net,d}$ , Appendix 13). Three participants used standard method EN 15400 (withdrawn) [13] and three participants used standard method ASTM D5865 [14]. Reported other methods were national translations or withdrawn versions of the former mentioned international standard methods or internal methods. Also, standard methods designed for waste materials were used.

For the measurements of gross calorific values ( $q_{v,gr,d}$ ), various analytical instruments were used. The used instruments were mainly Parr, IKA, and LECO with various model numbers (Appendix 12). For the samples B3 and K1, a statistically significant difference was observed between the  $q_{v,gr,d}$  results obtained with IKA ( $n=8$ ) and LECO ( $n=6$ ) instruments (Appendix 14). However, the interpretation involves some uncertainty due to the limited number of results. Despite these statistical differences, all three instrument types produced results that were within the acceptable deviation from the assigned value.

## 3.2.2 Measurement of the additional measurands

In the PT mainly the following standard methods or technical specifications were used for the measurements of different parameters (Table 5).

**Table 5. Used international standards in the measurements of the additional measurands.**

Measurand	Method
Ash <sub>d</sub>	EN ISO 18122 [15], EN ISO 21656 [16], ISO 1171 [17], ASTM D7582 [18]
C <sub>d</sub> , H <sub>d</sub> and N <sub>d</sub>	ISO 29541 [19], EN ISO 16948 [20], EN ISO 21663 [21], ASTM D5373 [22]
M <sub>ad</sub> (the moisture content of analysis sample)	ISO 589 [23], ASTM D7582 [18], EN ISO 18134-3 [24], ISO 11722 [25], EN ISO 21660-3 [26]
S <sub>d</sub>	EN ISO 16994 [27], ASTM D4239 [28], ISO 334 [29], ISO 19579 [30], EN ISO 21663 [21], EN 15408 [34]
V <sub>d</sub> , (volatile matter)	ISO 562 [31], EN ISO 18123 [32]
Cl <sub>d</sub>	EN ISO 16994 [27], EN 15408 [34], ASTM D8247 [35], ASTM D4208 [36]
F <sub>d</sub>	EN ISO 16994 [27], EN 15408 [34], ASTM D8247 [35]

However, in some cases also other international and national standards or technical specifications e.g. ASTM D1552, ASTM D3173, ASTM D3174, ASTM D3175, ASTM D5291, ASTM D6376, ASTM E776, ISO 10304, ISO 11724, ISO 17813, ISO 22036, ISO 29541, or internal/inhouse methods were used. Also, other standard methods designed for solid waste or solid recovered fuels was used as well as some withdrawn methods.

The moisture content of analysis sample was determined by heating at the temperatures 40 °C (samples B2 and K1), 105 °C (all samples), and 107 °C (all samples, Appendix 12). Statistical comparison of the methods ISO 11722 and other methods was possible for the sample K1. However, no statistically significant differences were observed between the methods.

The ash content was determined by heating at the temperature 105 °C (sample B2), 550 °C (all samples), 750 °C (sample B3, K1), or at the temperature 815 °C (sample B2, K1, Appendix 12). 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 [14, 16]. Ash content and volatile matter were measured using various furnaces or thermogravimetries (TGAs, Appendix 12). Due to the low number of results, the statistical comparison of the used methods was not possible.

Most of the participants measured CHN and S using various elemental analysers or ICP-OES instruments e.g. LECO, CHNS Elementar, Eltra, Metrohm, Perkin Elmer, Skalar, Thermo Scientific, Analytic Jena, and CkiC (Appendix 12). Statistical comparison of the methods ISO 29541 and ASTM D5373 was possible for carbon and hydrogen in sample K1. However, no statistically significant differences were observed between the methods. Due to the low number of results, the statistical comparison of the used methods was not possible for nitrogen and sulphur.

Halogens, Cl and F, were measured using various ion chromatography analysers after oxygen bomb digestion, combustion ion chromatography, and coulometric titrator (e.g. Thermo Scientific, Metrohm, Sherwood, Appendix 12). Mostly international standards were used (Table 5, Appendix 13), but also some other methods were reported (e.g. potentiometric, Mohr's method). Due to the low number of results, the statistical comparison of the used methods was not possible.

### 3.3 Uncertainties of the reported results

Together with their results, the participants were to report the expanded uncertainties ( $k=2$ ) as percentage. Altogether 76 % of the participants reported the measurement uncertainty with at least some of their results (Table 6, Appendix 15). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for evaluating the measurement uncertainty (Appendix 15). The most used approach to evaluate the measurement uncertainty was evaluation using method validation data. Other approaches were using the internal quality control data (X, R, and/or R% chart, Appendix 15). Other approaches were using the internal quality control data and the results obtained from proficiency tests as well as using the modelling approach. Depending on the sample and measurand, up to four participants used MUKIT measurement uncertainty software for the evaluation of their uncertainties, which is available on the webpage: [syke.fi/envical/en](http://syke.fi/envical/en) [37, 38]. Generally, the used approach for evaluating the measurement uncertainty did not make definite impact on the uncertainty evaluations. Nearly all the participants reported the measurement uncertainty for all the results obtained with accredited methods.

The evaluated measurement uncertainties varied highly for all the tested measurands (Table 6). Especially, very low ( $< 1\%$ ) or high ( $\geq 50\%$ ) uncertainties can be considered very questionable. **It was evident, that some uncertainties have been reported erroneously as absolute values** (bolded numbers in Table 6, Appendices 8 and 15), **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 organiser. When reporting measurement uncertainties, the accuracy of the numeric values should correlate with the accuracy of the result. Harmonisation of the uncertainties' estimation should be continued.

**Table 6. The ranges of the reported expanded uncertainties by participants as percent in the samples (U:%,  $k=2$ ).**

Measurand	Uncertainty % B2	Uncertainty % B3	Uncertainty % K1
Ash <sub>d</sub>	<i>0.05-30</i>	<i>0.198-30</i>	<i>0.05-30</i>
C <sub>d</sub>	<i>0.04-30</i>	<i>0.04-35</i>	<i>0.04-30</i>
Cl <sub>d</sub>	-	18.11-50	8.71-50
EF	-	-	8-24
F <sub>d</sub>	-	-	3.66-45
H <sub>d</sub>	<i>0.038-30</i>	<i>0.037-30</i>	<i>0.036-30</i>
M <sub>ad</sub>	<i>0.04-15</i>	<i>0.07-15</i>	<i>0.02-36.3</i>
N <sub>d</sub>	<i>0.052-57</i>	<i>0.038-57</i>	<i>0.044-30</i>
Q <sub>p,net,d</sub>	<b>1-614</b>	<b>1-1592</b>	<b>1-513</b>
Q <sub>V,gr,d</sub>	<b>1-614</b>	<b>1-1592</b>	<b>1-513</b>
S <sub>d</sub>	-	<i>0.002-37</i>	<i>0.029-30</i>
V <sub>d</sub>	<i>1.02-15</i>	<i>1.02-15</i>	<i>0.36-6</i>

In table with bold the values of expanded measurement uncertainty over 50 % and with italic the values lower than 1 %.

### 3.4 Estimation of emission factor

The participants had the opportunity to estimate the emission factor (EF) [33, 34] for the coal sample in the PT, using their measured net calorific value and the total moisture content 'as received', as specified in the sample cover letter. For CO<sub>2</sub> neutral fuels (B2, B3) the estimation of the emission factor was not done. In this PT, seven participants reported their results for the emission factor (Table 2, Appendices 8 and 13). The estimation of the emission factor was partly based on the given guidelines, but also various internal procedures were used (Appendix 12). It is recommended to validate the estimation of the emission factor to use total moisture content as received given by the provider. Harmonisation of the estimation of emission factor should be continued.

## 4 Evaluation of the results

The performance evaluation of the participants was based on the z and E<sub>n</sub> scores (Table 7 and Appendix 7).

**Table 7. Assessment of the z and E<sub>n</sub> scores.**

Criteria for z scores	Criteria for E <sub>n</sub> scores	Assessment
$ z  \leq 2.0$	$ E_n  \leq 1.0$	Satisfactory
$2.0 <  z  < 3.0$		Questionable
$ z  \geq 3.0$	$ E_n  > 1.0$	Unsatisfactory

In total, 80 % of the results evaluated with the z scores were satisfactory when accepting the deviation of 1–35 % from the assigned value (Appendix 9). About 74 % of the participants used accredited methods and 82 % of their results were satisfactory based on z score evaluation. Of the results evaluated with the E<sub>n</sub> scores, 90 % were satisfactory.

Based on the z score evaluation for the gross calorific value 68 % of the wood pellet results, 78 % of the biofuel results, and 83 % of the coal results were satisfactory. For the net calorific value 63 % of the wood pellet results, 67 % of the biofuel results, and 78 % of the coal results were satisfactory (Table 2).

In the previous similar proficiency test CAL 08/2024, 84 % of the results evaluated with z scores were satisfactory when a deviation of 1–25 % from the assigned value was accepted, and 89 % of the results evaluated with E<sub>n</sub> scores were satisfactory [8].

The summary of the performance evaluation is shown in Table 8. The percentage of the satisfactory results based on z score evaluation varied between 77 % and 82 % for the tested sample types. For E<sub>n</sub> scores the satisfactory result percentages varied between 80 % and 100 % (Appendix 10).

The results of the moisture content of the analysis sample (M<sub>ad</sub>) were not evaluated, but the assigned values were given. Due to the large deviation of the reported results or the low number of results in the statistical data processing, no evaluation was given for nitrogen (N<sub>d</sub>) in sample B2 and volatile matter (V<sub>d</sub>) in sample B3.

**Table 8. Summary of the performance evaluation in the proficiency test CAL 06/2025.**

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
Wood pellet, B2	z score: 77	1.5–30	Difficulties in measurements for $C_d$ , $q_{p,net,d}$ and $q_{v,gr,d}$ : < 80 % satisfactory results. In the CAL 08/2024 the performance was satisfactory based on z scores for 81 % of the results, when accepting deviation of 1.4–25 % from the assigned value [8].
Biofuel, B3	z score: 80	1.7–35	Difficulties in measurements for $Cl_d$ , $H_d$ , $q_{p,net,d}$ , $q_{v,gr,d}$ and $S_d$ : < 80 % satisfactory results. In the PT CAL 08/2024, 87 % of the results evaluated with z scores were satisfactory when accepting deviation of 1.7–15 % from the assigned value, and 80 % of the results ( $Cl_d$ , $H_d$ , $N_d$ , $V_d$ ) evaluated with $E_n$ scores [8].
Coal, K1	z score: 82 $E_n$ score: 90	1.2–30	Difficulties in measurements for $Ash_d$ , $F_d$ , $q_{p,net,d}$ , $S_d$ and $V_d$ : < 80 % satisfactory results. The evaluation is informative for $F_d$ and $H_d$ since the reliability of assigned value criterion was not met (2.6.3). In the PT CAL 08/2024, 89 % of the results evaluated with z scores were satisfactory when accepting deviation 1-10 % from the assigned value, and 75 % of the results ( $Cl_d$ ) evaluated with $E_n$ scores [8].

### Wood pellet (B2)

For wood pellet sample 77 % of the results were satisfactory based on z scores, which is slightly lower proportion than in the previous similar PT CAL 08/2024 (Table 8, [8]). The percentage of satisfactory results based on z scores ranged from 63 % to 93 % (Table 2).

The percentage of satisfactory results for the gross and net calorific values was 68 % and 63 %, respectively (Table 2). In the previous similar PT CAL 08/2024, the percentage of satisfactory results for the gross and the net calorific values was 86 % and 83 %, respectively. Thus, the performance was considerably lower for the calorific values in this PT. The results of the moisture content of the analysis sample ( $M_{ad}$ ) and nitrogen ( $N_d$ ) were not evaluated, but the assigned values are given (Table 2).

### Biofuel (B3)

For biofuel sample 80 % of the results evaluated with z scores were satisfactory, which is lower proportion than in the previous PT CAL 08/2024 (Table 8, [8]). The percentage of satisfactory results based on z scores ranged from 64 % to 94 % (Table 2).

The percentage of satisfactory results for the gross and net calorific values based on z score evaluation was 78 % and 67 %, respectively (Table 2). In the previous similar PT CAL 08/2024, the percentage of satisfactory results for the gross and the net calorific values was 89 % and 86 % of the results, respectively [8]. Thus, the performance was considerably lower in this PT. The results of the moisture content of the analysis sample ( $M_{ad}$ ) and volatile matter ( $V_d$ ) were not evaluated, but the assigned values are given for  $M_{ad}$  (Table 2).

### Coal (K1)

For coal sample 82 % of the results evaluated with z scores were satisfactory, which is somewhat lower proportion than in the previous similar PT CAL 08/2024 (Table 8, [8]). The percentage of satisfactory results varied between 71 % and 89 % (Table 2). Based on the  $E_n$  score evaluation for the coal sample 90 % of the results were satisfactory (Table 8, Appendix 10). The percentage of satisfactory  $E_n$  scores varied between 80-100 % (Appendix 10).

The percentage of satisfactory results for the gross and net calorific values was 83 % and 78 %, respectively (Table 2). In the previous similar PT CAL 08/2024, the percentage of satisfactory results for the gross and net calorific values was 89 % and 80 %, respectively [8]. Thus, the performance was somewhat lower for the calorific values in this PT. The results of the moisture content of analysis sample ( $M_{ad}$ ) were not evaluated, but the assigned values are given (Table 2).

## 5 Summary

ProfTest Syke carried out the proficiency test (PT) of gross and net calorific value in solid fuels in September 2025 (CAL 06/2025). In the PT, gross and net calorific values,  $C_d$ ,  $S_d$ ,  $H_d$ ,  $N_d$ , moisture content of the analysis sample ( $M_{ad}$ ), ash content ( $Ash_d$ ) as well as volatile matter ( $V_d$ ) were tested in wood pellet (spruce sawdust, not  $S_d$ ), biofuel, and coal samples. In this PT,  $Cl_d$  and  $F_d$  were tested also in the coal sample and  $Cl_d$  in the biofuel sample. Further, for the coal sample it was possible to estimate the emission factor (EF). In total 34 participants took part in the PT.

The robust mean, the median, or the mean of the results reported by the participants were used as the assigned value for measurands. The uncertainties of the assigned values varied between 0.2 % and 0.5 % for calorific values. For the other evaluated measurands the uncertainties varied from 0.7 % to 64 %.

The evaluation of the performance was based on the  $z$  and  $E_n$  scores. The performance evaluation was not done for the moisture content of analysis sample ( $M_{ad}$ ) in all samples, nitrogen ( $N_d$ ) in the wood pellet (B2), and volatile matter ( $V_d$ ) in the biofuel (B3).

In the PT 80 % of the results evaluated with the  $z$  scores were satisfactory, when accepting the deviation of 1–35 % from the assigned value. About 74 % of the participants used the accredited methods and 82 % of their results based on  $z$  score evaluation was satisfactory. Of the results evaluated with the  $E_n$  scores, 90 % were satisfactory.

Based on the  $z$  score evaluation for the gross calorific value 68 % of the wood pellet results, 78 % of the biofuel results, and 83 % of the coal results were satisfactory. For the net calorific value 63 % of the wood pellet results, 67 % of the biofuel results, and 78 % of the coal results were satisfactory.

## 6 Summary in Finnish

Profstest Syke järjesti pätevyyskokeen kalorimetrista ja tehollista lämpöarvoa kiinteistä polttoaineista analysoiville laboratorioille syyskuussa 2025 (CAL 06/2025). Pätevyyskokeessa testattiin kalorimetrinen ja tehollinen lämpöarvo ( $q_{p,net,d}$ ,  $q_{v,gr,d}$ ),  $C_d$ ,  $S_d$ ,  $H_d$ ,  $N_d$ , analyysikosteus ( $M_{ad}$ )- ja tuhkapitoisuus ( $Ash_d$ ) sekä haihtuvat aineet ( $V_d$ ) puupelletistä (ei S), biopolttoaineesta ja kivihiilestä. Lisäksi testattiin  $Cl_d$  ja  $F_d$  kivihiilestä sekä  $Cl_d$  biopolttoaineesta. Osallistujilla oli mahdollisuus myös arvioida päästökerroin kivihiilinäytteelle. Pätevyyskokeessa oli 34 osallistujaa.

Testisuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai niiden keskiarvoa tai mediaania. Vertailuarvon epävarmuus oli lämpöarvomäärityksissä 0,2–0,5 %. Muille testisuureille vertailuarvon epävarmuus oli 0,7–64 %.

Osallistujien pätevyyden arviointi tehtiin z- ja  $E_n$ -arvojen avulla. Tulosten arviointia ei tehty näytteiden analyysikosteuspitoisuudelle ( $M_{ad}$ ), typen ( $N_d$ ) määritykselle puupelletistä (B2) ja haihtuville aineille ( $V_d$ ) biopolttoaineesta (B3). Koko tulosaineistossa oli hyväksyttäviä, z-arvoilla arvioituja tuloksia 80 %, kun vertailuarvosta sallittiin 1–35 % poikkeama. Noin 74 % osallistujista käytti akkreditoituja määrittämenetelmiä ja näistä tuloksista oli hyväksyttäviä 82 % z-arvoilla arvioituna. Tuloksista, jotka arvoitiin  $E_n$ -arvoilla oli 90 % hyväksyttäviä.

Kalorimetrinen lämpöarvon määrityksissä z-arvolla arvioituna 68 % puupelletin, 78 % biopolttoaineen ja 83 % kivihiilen tuloksista oli hyväksyttäviä. Vastaavasti tehollisen lämpöarvon määrittämisessä z-arvolla arvioiduista tuloksista 63 % puupelletin, 67 % biopolttoaineen ja 78 % kivihiilen tuloksista oli hyväksyttäviä.

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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](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
<b>Bulgaria</b>	AES-3C Maritza East 1 EOOD; Testing Laboratory "Energy Materials"
<b>Finland</b>	Enersense Oy Eurofins Environment Testing Finland Oy, Energy & Water Jyväskylä Finnsementti Oy FTF Fuel Testing Finland Oy Kaakkois-Suomen ammattikorkeakoulu Oy / KymiLabs Kymen Ympäristölaboratorio Oy NG Nordic Finland Oy, Riihimäki Savo-Karjalan Ympäristötutkimus Oy, Joensuu Savo-Karjalan Ympäristötutkimus Oy, Kuopio SSAB Europe Raahe, Raahe UPM Tutkimuskeskus, Lappeenranta
<b>France</b>	ALS France ArcelorMittal Fos sur Mer Eurofins Analyses des Matériaux et Combustibles France SOCOR Dechy France
<b>Latvia</b>	Environmental Consultation Office
<b>Lithuania</b>	AB "Siauliai Energija" chemijos laboratorija, Siauliai, Lithuania Axioma servisas, Biofuel research laboratory Cement testing laboratory Co Akmenes cementas Lithuania Vilniaus kogeneracine jėgainė
<b>Republic of Korea</b>	Daedeok Analytical Research Institute Intertek KIMSCO Ulsan Testing Center, South Korea Korea East-West Power
<b>Romania</b>	ICSI Ramnicu Valcea Laborator analize fizico-chimice apa si carbune, Romania Romcim SA -Punct de lucru Hoghiz S.C. TUV Austria Romania S.R.L. SC Eurototal Comp SRL
<b>Slovenia</b>	Premogovnik Velenje d.o.o
<b>Spain</b>	Laboratorio Central de Calidad - LCC
<b>Sweden</b>	Eurofins Water Testing Sweden AB SGS Analytics Sweden AB
<b>Thailand</b>	INSEE Ecocycle Co.,Ltd

## Appendix 2. Sample preparation

### **Sample B3, biofuel (conifer bark, biomass, EN ISO 17225-1; 1 Wood biomass)**

Sample B3 was wood biomass, conifer bark, collected from Finnish wood. The logging residues were air dried (105 °C), ground with grinding mill and sieved with 1 mm sieve at the laboratory of Enersense. (Finland). The dried and sieved sample was mixed by a mechanised sample mixer and distributed to sub-samples using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of KVVY Tutkimus Oy (Tampere).

## Appendix 3. Homogeneity of the samples

### Criteria for homogeneity:

$S_{\text{analytical}} / S_{\text{pt}} < 0.5$  and  $S_{\text{sam}}^2 < c$ , where

$S_{\text{analytical}}$  = analytical deviation, standard deviation of the results in a sub sample

$S_{\text{pt}}$  = standard deviation for proficiency assessment

$S_{\text{sam}}$  = between-sample deviation, standard deviation of results between sub samples

$c = F1 \times S_{\text{all}}^2 + F2 \times S_{\text{analytical}}^2$ , where

$S_{\text{all}}^2 = (0.3 \times S_{\text{pt}})^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

**Table 1. Homogeneity test results of samples.**

Measurements	n	Mean	S <sub>pt</sub> %	S <sub>pt</sub>	S <sub>analytical</sub>	S <sub>analytical</sub> / S <sub>pt</sub>	S <sub>analytical</sub> / S <sub>pt</sub> < 0.5?	S <sub>sam</sub>	S <sub>sam</sub> <sup>2</sup>	c	Is S <sub>sam</sub> <sup>2</sup> < c?
<b>Wood pellet (B2)</b>											
Gross calorific value, J/g	3	20192	0.75	151	39.5	0.28	Yes	27.5	758	12840	Yes
Net calorific value, J/g	3	18876	0.80	151	39.5	0.26	Yes	27.5	758	12800	Yes
Ash %, d	3	0.31	15	0.05	0.02	0.46	Yes	0.01	< 0.001	0.003	Yes
<b>Biofuel (B3)</b>											
Gross calorific value, J/g	6	20448	0.85	174	66.1	0.38	Yes	40.8	1660	13260	Yes
Net calorific value, J/g	6	19182	0.85	163	47.5	0.29	Yes	63.5	4030	9120	Yes
Ash %, d	5	4.24	7.5	0.32	0.15	0.46	Yes	0.14	0.02	0.07	Yes
<b>Coal (K1)</b>											
Gross calorific value, J/g	3	28094	0.60	169	14.5	0.09	Yes	96.5	9309	8562	No
Net calorific value, J/g	3	27124	0.65	176	14.5	0.08	Yes	96.5	9309	9282	No
Ash %, d	3	9.71	1.25	0.12	0.03	0.29	Yes	< 0.01	< 0.001	0.009	Yes

**Conclusion:** The samples could be considered as homogenous because most of the criteria of the homogeneity test were met. In those two cases where the homogeneity criteria were not met, the results from the participants confirm the homogeneity compared to the standard deviation for the proficiency test.

## Appendix 4. Feedback from the proficiency test

### Feedback from the participants

Participant	Comments on technical execution	Action / Proftest Syke
10	The participant did not receive sample B2.	The missing sample was delivered to the participant. The organizer apologized for the missing sample.

Participant	Comments to the results	Action / Proftest Syke
5	The participant asked more information on the analytical methods used in determination of the assigned values for K1: $N_d$ and $V_d$	The provider informed the participant of the mostly used standard methods by participants for the determination of K1: $N_d$ and $V_d$ . In addition, the procedure used for setting the assigned values was clarified.
20	The participant requested assistance in investigating the reasons for the questionable results for $q_{v,gr,d}$ and $q_{p,net,d}$ of the samples B2 and B3.	To investigate the problem the provider recommended the participant to re-analyse the PT samples. The provider doesn't have detailed description of participant methods or environmental conditions; therefore, it is difficult to assess possible sources for error.
24	The participant requested clarification on the discrepancy between $q_{v,gr,d}$ and $q_{p,net,d}$ Z scores on samples B2 and B3.	The provider gave an example on how to calculate $q_{p,net,d}$ from $q_{v,gr,d}$ values for samples B2 and B3 according to the international standards.

### Feedback to the participants

Participant	Comments
5, 6, 7, 11, 18, 19, 20, 21, 22, 23, 24, 27, 28, 31, 33, 34	The participants did not return the sample arrival information to the organiser. The participants should follow the instructions of the organiser.
7, 11, 19, 22, 23, 29	The participants did not answer the background survey. The participants should follow the instructions of the organiser.
7	The samples were returned to the organiser due to incorrect address. The organiser kindly reminds all participants to keep their contact information updated.
1, 3, 7, 11, 12, 14, 20, 25, 26	The participants did not inform the accreditation status of their method for some measurands. The participants should follow the instructions of the organiser.
17	The participants did not report the results of replicate measurements for some measurands. The participants should follow the instructions of the organiser.
3, 28, 32	The participant did not inform the used method for some measurand. The participants should follow the instructions of the organiser.
7, 22, 28	The bottle numbers of sample containers were missing from the result form.
22, 32, 33	The measurement uncertainty should be reported with the results obtained by accredited methods.
1, 2, 5, 7, 12, 14, 15, 17, 20, 28, 33	Some of the participants' results were Cochran outliers (Part. 1: B2: $H_d$ ; B3: $q_{v,gr,d}$ , $q_{p,net,d}$ ; K1: $C_d$ , $H_d$ , $q_{v,gr,d}$ , $q_{p,net,d}$ . Part. 2: B2: $H_d$ . Part. 5: K1: $H_d$ ; $M_{ad}$ . Part. 7: K1: $q_{v,gr,d}$ , $q_{p,net,d}$ . Part. 12: B3: $Cl_d$ ; K1: $Cl_d$ . Part. 14: B3: $C_d$ , $q_{v,gr,d}$ . Part. 15: B2: $H_d$ ; B3: $C_d$ , $N_d$ . Part. 17: B2: $V_d$ ; B3: $Cl_d$ . Part. 20: B3: $q_{v,gr,d}$ ; K1: $M_{ad}$ . Part. 28: B2: $V_d$ ; K1: $C_d$ , $N_d$ . Part. 33: K1: $EF$ , $S_d$ ). The participants are recommended to check the allowed difference for the parallel results.
1, 15, 32	The participants reported a zero-value result for some measurand/sample. Those results were not included in the statistical results handling and no performance evaluation was given.
20	The participant has not used the total moisture as received ( $M_{ar}$ ) value given by the provider in the calculation of K1: EF. The equation for the emission factor calculation is based on the decision EU 2018/2066 [39]. The participants should follow the instructions of the organiser.
All	Some participants have used withdrawn standard methods. The organiser recommends using the latest version of the standard method.
All	Some participants presumably reported absolute measurement uncertainty together with their results, but the request from the organizer was to report the relative measurement uncertainty. The participants should follow the instructions of the organiser.

## Appendix 5. Assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	$U_{pt}$	$U_{pt}, \%$	Determination of assigned value	$U_{pt}/s_{pt}$
Ash <sub>d</sub>	B2	w%	0.29	0.03	9.3	Robust mean	0.31
	B3	w%	4.06	0.12	2.9	Robust mean	0.19
	K1	w%	9.65	0.07	0.7	Robust mean	0.28
C <sub>d</sub>	B2	w%	50.5	0.4	0.7	Mean	0.28
	B3	w%	51.2	0.5	1.0	Mean	0.33
	K1	w%	70.1	0.7	1.0	Robust mean	0.33
Cl <sub>d</sub>	B3	mg/kg	144	8	5.7	Mean	0.29
	K1	mg/kg	137	25	18.1	Mean	-
EF	K1	t CO <sub>2</sub> /TJ	95.5	0.7	0.7	Mean	-
F <sub>d</sub>	K1	mg/kg	91.2	9.5	10.4	Mean	0.35*
H <sub>d</sub>	B2	w%	6.15	0.14	2.2	Mean	0.28
	B3	w%	6.00	0.11	1.9	Mean	0.32
	K1	w%	4.56	0.12	2.7	Robust mean	0.39*
M <sub>ad</sub>	B2	w%	7.51	0.23	3.0	Robust mean	-
	B3	w%	6.12	0.27	4.4	Robust mean	-
	K1	w%	5.33	0.17	3.2	Robust mean	-
N <sub>d</sub>	B2	w%	0.066	0.04	63.6	Median	-
	B3	w%	0.53	0.04	7.2	Mean	0.29
	K1	w%	1.91	0.05	2.4	Robust mean	0.24
q <sub>p,net,d</sub>	B2	J/g	18800	38	0.2	Mean	0.13
	B3	J/g	19112	96	0.5	Mean	0.29
	K1	J/g	27250	109	0.4	Mean	0.31
q <sub>v,gr,d</sub>	B2	J/g	20085	80	0.4	Robust mean	0.27
	B3	J/g	20405	102	0.5	Robust mean	0.29
	K1	J/g	28185	113	0.4	Robust mean	0.33
S <sub>d</sub>	B3	w%	0.042	0.01	11.0	Mean	0.31
	K1	w%	0.35	0.02	4.4	Mean	0.29
V <sub>d</sub>	B2	w%	85.6	0.9	1.0	Mean	0.33
	B3	w%	-	-	-	Mean	-
	K1	w%	36.4	0.5	1.3	Mean	0.26

\* All results acceptable, or the majority were within in the acceptable level.

$U_{pt}$  = Expanded uncertainty of the assigned value

Criterion for reliability of the assigned value  $u_{pt}/s_{pt} \leq 0.3$ , where

$s_{pt}$  = target value of the standard deviation for proficiency assessment

$u_{pt}$  = 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.

<b>Measurand</b>	The tested parameter
<b>Sample</b>	The code of the sample
<b>Assigned value</b>	The value attributed to a particular property of a proficiency test item
<b>Participant's result</b>	The result reported by the participant (when replicate results are reported, the mean value)
<b><math>2 \times s_{pt} \%</math></b>	The standard deviation for proficiency assessment ( $s_{pt}$ ) at the 95 % confidence level
<b>z score</b>	Used for the participant's performance 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

### Assessment of the z scores

$ z  \leq 2.0$	Satisfactory
$2.0 <  z  < 3.0$	Questionable (warning signal), the result deviates more than $2 \times s_{pt}$ from the assigned value.
$ z  \geq 3.0$	Unsatisfactory (action signal), the result deviates more than $3 \times s_{pt}$ from the assigned value.

<b><math>E_n</math> score</b>	Error, normalised – 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

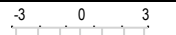













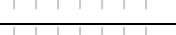










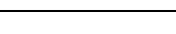
### Assessment of the $E_n$ scores

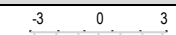















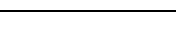
$ E_n  \leq 1.0$	Satisfactory, should be taken as an indicator of successful performance when the uncertainties are valid.
$ E_n  > 1.0$	Unsatisfactory (action signal), could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

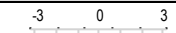













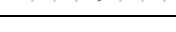
<b>Md</b>	Median
<b>s</b>	Standard deviation
<b>s %</b>	Standard deviation, %
<b><math>n_{stat}</math></b>	Number of results in statistical processing

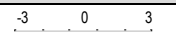









More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in ProfTest Syke Guide for participants [1, 2, 7].

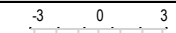


















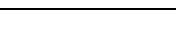
## Appendix 7. Results of each participant

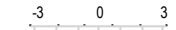











Participant 1													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		0.52	0.29	30	0.31	0.30	0.30	0.04	12.8	16	
	w%	B3		0.34	4.06	15	4.17	4.05	4.07	0.19	4.6	16	
	w%	K1		2.28	9.65	2.5	9.93	9.67	9.64	0.14	1.5	17	
C <sub>d</sub>	w%	B2		-4.28	50.5	2.5	47.8	50.7	50.5	0.6	1.2	12	
	w%	B3		-4.43	51.2	3	47.8	51.2	51.2	0.8	1.6	12	
	w%	K1		-2.52	70.1	3	67.5	69.9	70.1	1.1	1.6	17	
Cl <sub>d</sub>	mg/kg	B3		1.11	144	20	160	145	144	11	7.5	7	
	mg/kg	K1			137		163	134	137	30	22.1	6	
H <sub>d</sub>	w%	B2		2.24	6.15	8	6.70	6.16	6.15	0.25	4.0	13	
	w%	B3		1.78	6.00	6	6.32	5.98	6.00	0.19	3.2	11	
	w%	K1		3.60	4.56	7	5.14	4.50	4.54	0.15	3.4	15	
M <sub>ad</sub>	w%	B2			7.51		7.25	7.58	7.51	0.27	3.6	12	
	w%	B3			6.12		5.64	6.25	6.10	0.38	6.2	14	
	w%	K1			5.33		4.97	5.37	5.33	0.25	4.7	17	
N <sub>d</sub>	w%	B2			0.066		0	0.066	0.059	0.046	77.8	6	
	w%	B3		-0.75	0.53	25	0.48	0.52	0.53	0.07	12.5	12	
	w%	K1		-1.15	1.91	10	1.80	1.91	1.89	0.05	2.6	15	
q <sub>p,net,d</sub>	J/g	B2		-4.65	18800	1.6	18100	18805	18800	48	0.3	8	
	J/g	B3		-5.00	19112	1.7	18300	19130	19112	143	0.8	10	
	J/g	K1		-4.52	27250	1.3	26450	27223	27250	206	0.8	15	
q <sub>v,gr,d</sub>	J/g	B2		-3.22	20085	1.5	19600	20075	20077	130	0.6	13	
	J/g	B3		-4.06	20405	1.7	19700	20432	20417	166	0.8	15	
	J/g	K1		-3.75	28185	1.2	27550	28143	28188	168	0.6	15	
S <sub>d</sub>	w%	B3		0.82	0.042	35	0.048	0.045	0.042	0.007	16.5	9	
	w%	K1		4.76	0.35	15	0.48	0.35	0.35	0.03	8.5	15	

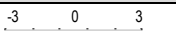



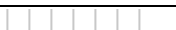





Participant 2													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		0.31	0.29	30	0.30	0.30	0.30	0.04	12.8	16	
	w%	B3		0.89	4.06	15	4.33	4.05	4.07	0.19	4.6	16	
	w%	K1		0.87	9.65	2.5	9.76	9.67	9.64	0.14	1.5	17	
C <sub>d</sub>	w%	B2		0.42	50.5	2.5	50.8	50.7	50.5	0.6	1.2	12	
	w%	B3		0.21	51.2	3	51.4	51.2	51.2	0.8	1.6	12	
	w%	K1		-0.18	70.1	3	69.9	69.9	70.1	1.1	1.6	17	
Cl <sub>d</sub>	mg/kg	B3		-0.80	144	20	133	145	144	11	7.5	7	
	mg/kg	K1			137		113	134	137	30	22.1	6	
EF	t CO2/TJ	K1			95.5		94.9	95.4	95.5	0.7	0.7	5	
F <sub>d</sub>	mg/kg	K1		-2.91	91.2	30	51.4	93.4	91.2	11.6	12.7	6	
H <sub>d</sub>	w%	B2		-1.60	6.15	8	5.76	6.16	6.15	0.25	4.0	13	
	w%	B3		-1.91	6.00	6	5.66	5.98	6.00	0.19	3.2	11	
	w%	K1		-0.74	4.56	7	4.44	4.50	4.54	0.15	3.4	15	
M <sub>ad</sub>	w%	B2			7.51		7.58	7.58	7.51	0.27	3.6	12	
	w%	B3			6.12		6.28	6.25	6.10	0.38	6.2	14	
	w%	K1			5.33		5.42	5.37	5.33	0.25	4.7	17	

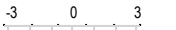



Participant 2												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
N <sub>d</sub>	w%	B2		0.066	0.066		0.014	0.066	0.059	0.046	77.8	6
	w%	B3		-0.04	0.53	25	0.53	0.52	0.53	0.07	12.5	12
	w%	K1		0.00	1.91	10	1.91	1.91	1.89	0.05	2.6	15
q <sub>p.net,d</sub>	J/g	B2		0.09	18800	1.6	18814	18805	18800	48	0.3	8
	J/g	B3		1.32	19112	1.7	19326	19130	19112	143	0.8	10
	J/g	K1		0.02	27250	1.3	27254	27223	27250	206	0.8	15
q <sub>V.gr,d</sub>	J/g	B2		-0.09	20085	1.5	20071	20075	20077	130	0.6	13
	J/g	B3		0.90	20405	1.7	20561	20432	20417	166	0.8	15
	J/g	K1		0.23	28185	1.2	28224	28143	28188	168	0.6	15
S <sub>d</sub>	w%	B3		-0.97	0.042	35	0.035	0.045	0.042	0.007	16.5	9
	w%	K1		0.63	0.35	15	0.37	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	B2		-0.42	85.6	3	85.1	85.7	85.6	1.2	1.4	8
	w%	B3		0.01	36.4	5	36.4	36.5	36.4	0.7	2.0	10
	w%	K1		0.01	36.4	5	36.4	36.5	36.4	0.7	2.0	10

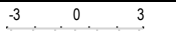




Participant 3												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		0.83	9.65	2.5	9.75	9.67	9.64	0.14	1.5	17
Cl <sub>d</sub>	mg/kg	K1			137		78	134	137	30	22.1	6
H <sub>d</sub>	w%	K1		0.25	4.56	7	4.60	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	K1			5.33		5.55	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	K1		2.83	1.91	10	2.18	1.91	1.89	0.05	2.6	15
q <sub>p.net,d</sub>	J/g	K1		-0.49	27250	1.3	27163	27223	27250	206	0.8	15
q <sub>V.gr,d</sub>	J/g	K1		-0.25	28185	1.2	28143	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		1.90	0.35	15	0.40	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	K1		0.33	36.4	5	36.7	36.5	36.4	0.7	2.0	10

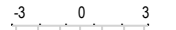








Participant 4												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		-0.34	0.29	30	0.28	0.30	0.30	0.04	12.8	16
	w%	B3		0.39	4.06	15	4.18	4.05	4.07	0.19	4.6	16
	w%	K1		0.46	9.65	2.5	9.71	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	B2		-0.08	50.5	2.5	50.5	50.7	50.5	0.6	1.2	12
	w%	B3		-0.56	51.2	3	50.8	51.2	51.2	0.8	1.6	12
	w%	K1		-0.19	70.1	3	69.9	69.9	70.1	1.1	1.6	17
Cl <sub>d</sub>	mg/kg	B3		0.03	144	20	145	145	144	11	7.5	7
	mg/kg	K1			137		129	134	137	30	22.1	6
EF	t CO <sub>2</sub> /TJ	K1			95.5		94.7	95.4	95.5	0.7	0.7	5
F <sub>d</sub>	mg/kg	K1		0.75	91.2	30	101.5	93.4	91.2	11.6	12.7	6
H <sub>d</sub>	w%	B2		-0.16	6.15	8	6.11	6.16	6.15	0.25	4.0	13
	w%	B3		-0.67	6.00	6	5.88	5.98	6.00	0.19	3.2	11
	w%	K1		0.19	4.56	7	4.59	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	B2			7.51		7.59	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		5.81	6.25	6.10	0.38	6.2	14
	w%	K1			5.33		5.31	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	B2		0.066	0.066		<0.2	0.066	0.059	0.046	77.8	6
	w%	B3		1.28	0.53	25	0.62	0.52	0.53	0.07	12.5	12
	w%	K1		0.31	1.91	10	1.94	1.91	1.89	0.05	2.6	15

Participant 4												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
q <sub>p,net,d</sub>	J/g	B2		-0.38	18800	1.6	18744	18805	18800	48	0.3	8
	J/g	B3		-0.05	19112	1.7	19104	19130	19112	143	0.8	10
	J/g	K1		0.23	27250	1.3	27290	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	B2		-0.08	20085	1.5	20073	20075	20077	130	0.6	13
	J/g	B3		-0.11	20405	1.7	20387	20432	20417	166	0.8	15
	J/g	K1		0.55	28185	1.2	28278	28143	28188	168	0.6	15
S <sub>d</sub>	w%	B3		0.41	0.042	35	0.045	0.045	0.042	0.007	16.5	9
	w%	K1		0.38	0.35	15	0.36	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	B2		0.04	85.6	3	85.7	85.7	85.6	1.2	1.4	8
	w%	B3		0.04	85.6	3	76.1	77.1	77.3	1.4	1.8	8
	w%	K1		0.29	36.4	5	36.7	36.5	36.4	0.7	2.0	10

Participant 5												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		0.21	9.65	2.5	9.68	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	K1		-0.66	70.1	3	69.4	69.9	70.1	1.1	1.6	17
H <sub>d</sub>	w%	K1		-0.88	4.56	7	4.42	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	K1			5.33		5.31	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	K1		2.52	1.91	10	2.15	1.91	1.89	0.05	2.6	15
q <sub>p,net,d</sub>	J/g	K1		-0.68	27250	1.3	27129	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	K1		-0.62	28185	1.2	28080	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		0.63	0.35	15	0.37	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	K1		2.97	36.4	5	39.1	36.5	36.4	0.7	2.0	10

Participant 6												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		-2.22	0.29	30	0.19	0.30	0.30	0.04	12.8	16
M <sub>ad</sub>	w%	B2			7.51		7.79	7.58	7.51	0.27	3.6	12
q <sub>V,gr,d</sub>	J/g	B2		1.49	20085	1.5	20310	20075	20077	130	0.6	13

Participant 7												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
q <sub>p,net,d</sub>	J/g	B2		6.10	18800	1.6	19718	18805	18800	48	0.3	8
	J/g	K1		-0.10	27250	1.3	27233	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	B2		8.06	20085	1.5	21300	20075	20077	130	0.6	13
	J/g	K1		0.60	28185	1.2	28286	28143	28188	168	0.6	15

Participant 8												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		-1.26	0.29	30	0.24	0.30	0.30	0.04	12.8	16
	w%	K1		-0.41	9.65	2.5	9.60	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	B2		-0.40	50.5	2.5	50.3	50.7	50.5	0.6	1.2	12
	w%	K1		-1.43	70.1	3	68.6	69.9	70.1	1.1	1.6	17
Cl <sub>d</sub>	mg/kg	K1			137		231	134	137	30	22.1	6
F <sub>d</sub>	mg/kg	K1		-1.14	91.2	30	75.6	93.4	91.2	11.6	12.7	6
H <sub>d</sub>	w%	B2		0.55	6.15	8	6.29	6.16	6.15	0.25	4.0	13
	w%	K1		0.69	4.56	7	4.67	4.50	4.54	0.15	3.4	15

Participant 8												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
M <sub>ad</sub>	w%	B2			7.51		6.75	7.58	7.51	0.27	3.6	12
	w%	K1			5.33		4.05	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	B2			0.066		<0.2	0.066	0.059	0.046	77.8	6
	w%	K1		0.10	1.91	10	1.92	1.91	1.89	0.05	2.6	15
q <sub>p.net,d</sub>	J/g	B2		-16.66	18800	1.6	16295	18805	18800	48	0.3	8
	J/g	K1		-12.31	27250	1.3	25070	27223	27250	206	0.8	15
q <sub>V.gr,d</sub>	J/g	B2		-7.70	20085	1.5	18925	20075	20077	130	0.6	13
	J/g	K1		-5.88	28185	1.2	27190	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		-5.69	0.35	15	0.20	0.35	0.35	0.03	8.5	15

Participant 9												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
C <sub>d</sub>	w%	B2		-1.03	50.5	2.5	49.9	50.7	50.5	0.6	1.2	12
	w%	B3		-1.26	51.2	3	50.2	51.2	51.2	0.8	1.6	12
	w%	K1		-1.46	70.1	3	68.6	69.9	70.1	1.1	1.6	17
H <sub>d</sub>	w%	B2		0.72	6.15	8	6.33	6.16	6.15	0.25	4.0	13
	w%	B3		-0.05	6.00	6	5.99	5.98	6.00	0.19	3.2	11
	w%	K1		-0.93	4.56	7	4.41	4.50	4.54	0.15	3.4	15
N <sub>d</sub>	w%	B2			0.066		0.091	0.066	0.059	0.046	77.8	6
	w%	B3		0.49	0.53	25	0.56	0.52	0.53	0.07	12.5	12
	w%	K1		0.05	1.91	10	1.91	1.91	1.89	0.05	2.6	15

Participant 10												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
S <sub>d</sub>	w%	B3		-1.50	0.042	35	0.031	0.045	0.042	0.007	16.5	9
	w%	K1		-2.50	0.35	15	0.28	0.35	0.35	0.03	8.5	15

Participant 11												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
C <sub>d</sub>	w%	K1		-0.31	70.1	3	69.8	69.9	70.1	1.1	1.6	17
H <sub>d</sub>	w%	K1		-1.28	4.56	7	4.36	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	K1			5.33		5.73	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	K1		0.55	1.91	10	1.96	1.91	1.89	0.05	2.6	15
S <sub>d</sub>	w%	K1		-2.57	0.35	15	0.28	0.35	0.35	0.03	8.5	15

Participant 12												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B3		-0.26	4.06	15	3.98	4.05	4.07	0.19	4.6	16
	w%	K1		0.95	9.65	2.5	9.77	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	B3		0.20	51.2	3	51.4	51.2	51.2	0.8	1.6	12
	w%	K1		-0.08	70.1	3	70.0	69.9	70.1	1.1	1.6	17
Cl <sub>d</sub>	mg/kg	B3		20.72	144	20	442	145	144	11	7.5	7
	mg/kg	K1			137		291	134	137	30	22.1	6
EF	t CO <sub>2</sub> /TJ	K1			95.5		96.0	95.4	95.5	0.7	0.7	5
H <sub>d</sub>	w%	B3		3.43	6.00	6	6.62	5.98	6.00	0.19	3.2	11
	w%	K1		4.97	4.56	7	5.35	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	B3			6.12		6.31	6.25	6.10	0.38	6.2	14
	w%	K1			5.33		5.37	5.37	5.33	0.25	4.7	17

Participant 12												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
N <sub>d</sub>	w%	B3		1.49	0.53	25	0.63	0.52	0.53	0.07	12.5	12
	w%	K1		-0.17	1.91	10	1.89	1.91	1.89	0.05	2.6	15
q <sub>p,net,d</sub>	J/g	B3		-1.52	19112	1.7	18865	19130	19112	143	0.8	10
	J/g	K1		-1.52	27250	1.3	26980	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	B3		-0.62	20405	1.7	20297	20432	20417	166	0.8	15
	J/g	K1		-0.27	28185	1.2	28140	28143	28188	168	0.6	15
S <sub>d</sub>	w%	B3		6.60	0.042	35	0.091	0.045	0.042	0.007	16.5	9
	w%	K1		-0.69	0.35	15	0.33	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	B3		3.98			81.2	77.1	77.3	1.4	1.8	8
	w%	K1		3.98	36.4	5	40.0	36.5	36.4	0.7	2.0	10

Participant 13												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		-0.08	9.65	2.5	9.64	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	K1		-0.38	70.1	3	69.7	69.9	70.1	1.1	1.6	17
M <sub>ad</sub>	w%	K1			5.33		5.34	5.37	5.33	0.25	4.7	17
S <sub>d</sub>	w%	K1		-0.13	0.35	15	0.35	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	K1		2.80	36.4	5	39.0	36.5	36.4	0.7	2.0	10

Participant 14												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B3		-0.03	4.06	15	4.05	4.05	4.07	0.19	4.6	16
C <sub>d</sub>	w%	B3		6.58	51.2	3	56.3	51.2	51.2	0.8	1.6	12
Cl <sub>d</sub>	mg/kg	B3			144	20	<750	145	144	11	7.5	7
M <sub>ad</sub>	w%	B3			6.12		6.45	6.25	6.10	0.38	6.2	14
q <sub>V,gr,d</sub>	J/g	B3		-0.78	20405	1.7	20270	20432	20417	166	0.8	15
S <sub>d</sub>	w%	B3			0.042	35	<1175	0.045	0.042	0.007	16.5	9

Participant 15												
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		2.53	0.29	30	0.40	0.30	0.30	0.04	12.8	16
	w%	B3		0.05	4.06	15	4.08	4.05	4.07	0.19	4.6	16
C <sub>d</sub>	w%	B2		-1.08	50.5	2.5	49.8	50.7	50.5	0.6	1.2	12
	w%	B3		1.89	51.2	3	52.7	51.2	51.2	0.8	1.6	12
Cl <sub>d</sub>	mg/kg	B3		-1.00	144	20	130	145	144	11	7.5	7
H <sub>d</sub>	w%	B2		1.51	6.15	8	6.52	6.16	6.15	0.25	4.0	13
	w%	B3		2.48	6.00	6	6.45	5.98	6.00	0.19	3.2	11
M <sub>ad</sub>	w%	B2			7.51		5.47	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		3.99	6.25	6.10	0.38	6.2	14
N <sub>d</sub>	w%	B2			0.066		0.013	0.066	0.059	0.046	77.8	6
	w%	B3		-0.91	0.53	25	0.47	0.52	0.53	0.07	12.5	12
q <sub>p,net,d</sub>	J/g	B2		-3.72	18800	1.6	18240	18805	18800	48	0.3	8
	J/g	B3		-3.09	19112	1.7	18610	19130	19112	143	0.8	10
q <sub>V,gr,d</sub>	J/g	B2		-2.95	20085	1.5	19640	20075	20077	130	0.6	13
	J/g	B3		-2.71	20405	1.7	19935	20432	20417	166	0.8	15
S <sub>d</sub>	w%	B3			0.042	35	0	0.045	0.042	0.007	16.5	9

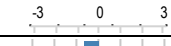














Participant 16												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
q <sub>V,gr,d</sub>	J/g	B2		-0.41	20085	1.5	20023	20075	20077	130	0.6	13

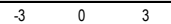










Participant 17												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		-0.62	0.29	30	0.26	0.30	0.30	0.04	12.8	16
	w%	B3		-0.64	4.06	15	3.87	4.05	4.07	0.19	4.6	16
Cl <sub>d</sub>	mg/kg	B3		729	144	20	10635	145	144	11	7.5	7
M <sub>ad</sub>	w%	B2		7.51			7.87	7.58	7.51	0.27	3.6	12
	w%	B3		6.12			6.46	6.25	6.10	0.38	6.2	14
N <sub>d</sub>	w%	B2		0.066			0.054	0.066	0.059	0.046	77.8	6
	w%	B3		0.53		25	0.546	0.52	0.53	0.07	12.5	12
q <sub>V,gr,d</sub>	J/g	B2		-0.28	20085	1.5	20043	20075	20077	130	0.6	13
	J/g	B3		0.80	20405	1.7	20544	20432	20417	166	0.8	15
S <sub>d</sub>	w%	B3		-0.03	0.042	35	0.042	0.045	0.042	0.007	16.5	9
V <sub>d</sub>	w%	B2		0.92	85.6	3	86.8	85.7	85.6	1.2	1.4	8
	w%	B3		76.7			76.7	77.1	77.3	1.4	1.8	8

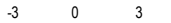






Participant 18												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		-2.03	9.65	2.5	9.41	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	K1		2.35	70.1	3	72.6	69.9	70.1	1.1	1.6	17
M <sub>ad</sub>	w%	K1		5.33			5.24	5.37	5.33	0.25	4.7	17
q <sub>p,net,d</sub>	J/g	K1		-0.15	27250	1.3	27223	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	K1		-0.18	28185	1.2	28155	28143	28188	168	0.6	15

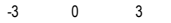




Participant 19												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
C <sub>d</sub>	w%	B2		0.33	50.5	2.5	50.7	50.7	50.5	0.6	1.2	12
	w%	B3		0.80	51.2	3	51.8	51.2	51.2	0.8	1.6	12
H <sub>d</sub>	w%	B2		-0.96	6.15	8	5.92	6.16	6.15	0.25	4.0	13
	w%	B3		-2.33	6.00	6	5.58	5.98	6.00	0.19	3.2	11
N <sub>d</sub>	w%	B2		0.066			0.105	0.066	0.059	0.046	77.8	6
	w%	B3		-0.08	0.53	25	0.53	0.52	0.53	0.07	12.5	12
q <sub>p,net,d</sub>	J/g	B2		0.30	18800	1.6	18845	18805	18800	48	0.3	8
	J/g	B3		0.70	19112	1.7	19225	19130	19112	143	0.8	10
q <sub>V,gr,d</sub>	J/g	B2		0.33	20085	1.5	20135	20075	20077	130	0.6	13
	J/g	B3		0.20	20405	1.7	20440	20432	20417	166	0.8	15

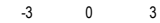


























Participant 20												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		0.80	0.29	30	0.33	0.30	0.30	0.04	12.8	16
	w%	B3		-0.26	4.06	15	3.98	4.05	4.07	0.19	4.6	16
	w%	K1		-2.78	9.65	2.5	9.32	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	B2		0.40	50.5	2.5	50.8	50.7	50.5	0.6	1.2	12
	w%	B3		-0.23	51.2	3	51.0	51.2	51.2	0.8	1.6	12
	w%	K1		0.37	70.1	3	70.5	69.9	70.1	1.1	1.6	17
EF	t CO <sub>2</sub> /TJ	K1			95.5		93.4	95.4	95.5	0.7	0.7	5

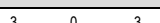











Participant 20												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
H <sub>d</sub>	w%	B2		-0.63	6.15	8	6.00	6.16	6.15	0.25	4.0	13
	w%	B3		-0.67	6.00	6	5.88	5.98	6.00	0.19	3.2	11
	w%	K1		-0.34	4.56	7	4.51	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	B2			7.51		7.21	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		4.78	6.25	6.10	0.38	6.2	14
	w%	K1			5.33		4.86	5.37	5.33	0.25	4.7	17
q <sub>p,net,d</sub>	J/g	B2		2.68	18800	1.6	19204	18805	18800	48	0.3	8
	J/g	B3		2.43	19112	1.7	19507	19130	19112	143	0.8	10
	J/g	K1		1.65	27250	1.3	27543	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	B2		2.80	20085	1.5	20507	20075	20077	130	0.6	13
	J/g	B3		2.49	20405	1.7	20837	20432	20417	166	0.8	15
	J/g	K1		1.93	28185	1.2	28511	28143	28188	168	0.6	15
S <sub>d</sub>	w%	B3		1.43	0.042	35	0.053	0.045	0.042	0.007	16.5	9
	w%	K1		0.76	0.35	15	0.37	0.35	0.35	0.03	8.5	15

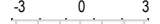





























Participant 21												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B3		-4.45	4.06	15	2.71	4.05	4.07	0.19	4.6	16
C <sub>d</sub>	w%	B3		-1.60	51.2	3	50.0	51.2	51.2	0.8	1.6	12
Cl <sub>d</sub>	mg/kg	B3		16.50	144	20	382	145	144	11	7.5	7
H <sub>d</sub>	w%	B3		0.81	6.00	6	6.15	5.98	6.00	0.19	3.2	11
M <sub>ad</sub>	w%	B3			6.12		5.33	6.25	6.10	0.38	6.2	14
N <sub>d</sub>	w%	B3		-1.36	0.53	25	0.44	0.52	0.53	0.07	12.5	12
q <sub>p,net,d</sub>	J/g	B3		-3.94	19112	1.7	18472	19130	19112	143	0.8	10
q <sub>V,gr,d</sub>	J/g	B3		-3.66	20405	1.7	19771	20432	20417	166	0.8	15
S <sub>d</sub>	w%	B3		5.71	0.042	35	0.084	0.045	0.042	0.007	16.5	9
V <sub>d</sub>	w%	B3					78.8	77.1	77.3	1.4	1.8	8

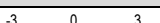






Participant 22												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		79.88	9.65	2.5	19.29	9.67	9.64	0.14	1.5	17
M <sub>ad</sub>	w%	K1			5.33		4.49	5.37	5.33	0.25	4.7	17
q <sub>p,net,d</sub>	J/g	K1		-7.77	27250	1.3	25874	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	K1		-7.78	28185	1.2	26870	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		-1.52	0.35	15	0.31	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	K1		-1.18	36.4	5	35.3	36.5	36.4	0.7	2.0	10





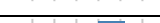


Participant 23												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B3		1.41	4.06	15	4.49	4.05	4.07	0.19	4.6	16
M <sub>ad</sub>	w%	B3			6.12		6.18	6.25	6.10	0.38	6.2	14
q <sub>p,net,d</sub>	J/g	B3		-0.06	19112	1.7	19103	19130	19112	143	0.8	10
q <sub>V,gr,d</sub>	J/g	B3		-0.19	20405	1.7	20372	20432	20417	166	0.8	15

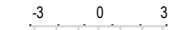







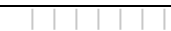
















Participant 24												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		0.80	0.29	30	0.33	0.30	0.30	0.04	12.8	16
	w%	B3		-0.26	4.06	15	3.98	4.05	4.07	0.19	4.6	16
	w%	K1		-0.08	9.65	2.5	9.64	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	B2		0.29	50.5	2.5	50.7	50.7	50.5	0.6	1.2	12
	w%	B3		-0.41	51.2	3	50.9	51.2	51.2	0.8	1.6	12
	w%	K1		-0.91	70.1	3	69.1	69.9	70.1	1.1	1.6	17
EF	t CO2/TJ	K1			95.5		0.1	95.4	95.5	0.7	0.7	5
H <sub>d</sub>	w%	B2		1.81	6.15	8	6.60	6.16	6.15	0.25	4.0	13
	w%	B3		1.58	6.00	6	6.29	5.98	6.00	0.19	3.2	11
	w%	K1		1.69	4.56	7	4.83	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	B2			7.51		7.12	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		6.39	6.25	6.10	0.38	6.2	14
	w%	K1			5.33		5.42	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	B2			0.066		0.310	0.066	0.059	0.046	77.8	6
	w%	B3		4.15	0.53	25	0.81	0.52	0.53	0.07	12.5	12
	w%	K1		0.16	1.91	10	1.93	1.91	1.89	0.05	2.6	15
q <sub>p,net,d</sub>	J/g	B2		1.89	18800	1.6	19084	18805	18800	48	0.3	8
	J/g	B3		4.08	19112	1.7	19775	19130	19112	143	0.8	10
	J/g	K1		2.50	27250	1.3	27694	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	B2		-4.06	20085	1.5	19474	20075	20077	130	0.6	13
	J/g	B3		-1.50	20405	1.7	20145	20432	20417	166	0.8	15
	J/g	K1		-1.21	28185	1.2	27980	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		-1.33	0.35	15	0.32	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	B2		6.92	85.6	3	94.5	85.7	85.6	1.2	1.4	8
	w%	B3			84.1		84.1	77.1	77.3	1.4	1.8	8
	w%	K1		0.54	36.4	5	36.9	36.5	36.4	0.7	2.0	10

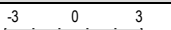







Participant 25												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		0.33	9.65	2.5	9.69	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	K1		0.80	70.1	3	70.9	69.9	70.1	1.1	1.6	17
Cl <sub>d</sub>	mg/kg	K1			137		181	134	137	30	22.1	6
F <sub>d</sub>	mg/kg	K1		0.92	91.2	30	103.8	93.4	91.2	11.6	12.7	6
H <sub>d</sub>	w%	K1		-0.76	4.56	7	4.44	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	K1			5.33		5.47	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	K1		-0.67	1.91	10	1.85	1.91	1.89	0.05	2.6	15
q <sub>p,net,d</sub>	J/g	K1		-1.11	27250	1.3	27054	27223	27250	206	0.8	15
q <sub>V,gr,d</sub>	J/g	K1		-1.28	28185	1.2	27969	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		-0.59	0.35	15	0.33	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	K1		-0.36	36.4	5	36.1	36.5	36.4	0.7	2.0	10

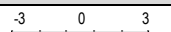







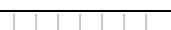

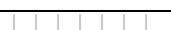

Participant 26													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		0.57	0.29	30	0.32	0.30	0.30	0.04	12.8	16	
	w%	B3		-0.76	4.06	15	3.83	4.05	4.07	0.19	4.6	16	
	w%	K1		0.54	9.65	2.5	9.72	9.67	9.64	0.14	1.5	17	
C <sub>d</sub>	w%	B2		-2.02	50.5	2.5	49.2	50.7	50.5	0.6	1.2	12	
	w%	B3		-1.18	51.2	3	50.3	51.2	51.2	0.8	1.6	12	
	w%	K1		-0.93	70.1	3	69.1	69.9	70.1	1.1	1.6	17	
Cl <sub>d</sub>	mg/kg	B3		0.04	144	20	145	145	144	11	7.5	7	
	mg/kg	K1			137		139	134	137	30	22.1	6	
F <sub>d</sub>	mg/kg	K1		-0.85	91.2	30	79.6	93.4	91.2	11.6	12.7	6	
H <sub>d</sub>	w%	B2		0.23	6.15	8	6.21	6.16	6.15	0.25	4.0	13	
	w%	B3		-0.09	6.00	6	5.98	5.98	6.00	0.19	3.2	11	
	w%	K1		-0.42	4.56	7	4.49	4.50	4.54	0.15	3.4	15	
M <sub>ad</sub>	w%	B2			7.51		7.35	7.58	7.51	0.27	3.6	12	
	w%	B3			6.12		5.67	6.25	6.10	0.38	6.2	14	
	w%	K1			5.33		4.93	5.37	5.33	0.25	4.7	17	
N <sub>d</sub>	w%	B2			0.066		0.042	0.066	0.059	0.046	77.8	6	
	w%	B3		-0.86	0.53	25	0.47	0.52	0.53	0.07	12.5	12	
	w%	K1		-0.50	1.91	10	1.86	1.91	1.89	0.05	2.6	15	
q <sub>p,net,d</sub>	J/g	B2		-0.30	18800	1.6	18756	18805	18800	48	0.3	8	
	J/g	B3		-0.77	19112	1.7	18987	19130	19112	143	0.8	10	
	J/g	K1		-1.05	27250	1.3	27065	27223	27250	206	0.8	15	
q <sub>v,gr,d</sub>	J/g	B2		0.16	20085	1.5	20109	20075	20077	130	0.6	13	
	J/g	B3		-0.67	20405	1.7	20289	20432	20417	166	0.8	15	
	J/g	K1		-0.91	28185	1.2	28031	28143	28188	168	0.6	15	
S <sub>d</sub>	w%	B3		0.34	0.042	35	0.045	0.045	0.042	0.007	16.5	9	
	w%	K1		-0.34	0.35	15	0.34	0.35	0.35	0.03	8.5	15	
V <sub>d</sub>	w%	B2		1.54	85.6	3	87.6	85.7	85.6	1.2	1.4	8	
	w%	B3					78.6	77.1	77.3	1.4	1.8	8	
	w%	K1		0.17	36.4	5	36.6	36.5	36.4	0.7	2.0	10	

Participant 27													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		-0.23	0.29	30	0.28	0.30	0.30	0.04	12.8	16	
	w%	B3		0.67	4.06	15	4.27	4.05	4.07	0.19	4.6	16	
q <sub>p,net,d</sub>	J/g	B2		0.10	18800	1.6	18816	18805	18800	48	0.3	8	
	J/g	B3		0.69	19112	1.7	19224	19130	19112	143	0.8	10	
q <sub>v,gr,d</sub>	J/g	B2		0.50	20085	1.5	20160	20075	20077	130	0.6	13	
	J/g	B3		0.40	20405	1.7	20475	20432	20417	166	0.8	15	

Participant 28													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		0.46	0.29	30	0.31	0.30	0.30	0.04	12.8	16	
	w%	B3		-0.69	4.06	15	3.85	4.05	4.07	0.19	4.6	16	
	w%	K1		-1.08	9.65	2.5	9.52	9.67	9.64	0.14	1.5	17	
C <sub>d</sub>	w%	B2		1.20	50.5	2.5	51.3	50.7	50.5	0.6	1.2	12	
	w%	B3		1.78	51.2	3	52.6	51.2	51.2	0.8	1.6	12	
	w%	K1		1.54	70.1	3	71.7	69.9	70.1	1.1	1.6	17	

Participant 28												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Cl <sub>d</sub>	mg/kg	B3		-10.00	144	20	0	145	144	11	7.5	7
	mg/kg	K1			137		0	134	137	30	22.1	6
EF	t CO <sub>2</sub> /TJ	K1			95.5		96.4	95.4	95.5	0.7	0.7	5
F <sub>d</sub>	mg/kg	K1		0.37	91.2	30	96.3	93.4	91.2	11.6	12.7	6
H <sub>d</sub>	w%	B2		-0.32	6.15	8	6.07	6.16	6.15	0.25	4.0	13
	w%	B3		0.04	6.00	6	6.01	5.98	6.00	0.19	3.2	11
	w%	K1		0.34	4.56	7	4.61	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	B2			7.51		7.63	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		6.23	6.25	6.10	0.38	6.2	14
	w%	K1			5.33		5.48	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	B2			0.066		0.101	0.066	0.059	0.046	77.8	6
	w%	B3		1.33	0.53	25	0.62	0.52	0.53	0.07	12.5	12
	w%	K1		-0.48	1.91	10	1.86	1.91	1.89	0.05	2.6	15
Q <sub>p,net,d</sub>	J/g	B2		-0.31	18800	1.6	18753	18805	18800	48	0.3	8
	J/g	B3		-1.06	19112	1.7	18940	19130	19112	143	0.8	10
	J/g	K1		-0.59	27250	1.3	27146	27223	27250	206	0.8	15
Q <sub>V,gr,d</sub>	J/g	B2		-0.07	20085	1.5	20075	20075	20077	130	0.6	13
	J/g	B3		-0.93	20405	1.7	20244	20432	20417	166	0.8	15
	J/g	K1		-0.29	28185	1.2	28136	28143	28188	168	0.6	15
S <sub>d</sub>	w%	B3		-0.89	0.042	35	0.035	0.045	0.042	0.007	16.5	9
	w%	K1		-2.23	0.35	15	0.29	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	B2		-0.98	85.6	3	84.3	85.7	85.6	1.2	1.4	8
	w%	B3					77.6	77.1	77.3	1.4	1.8	8
	w%	K1		1.68	36.4	5	37.9	36.5	36.4	0.7	2.0	10

Participant 29												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	K1		0.12	9.65	2.5	9.67	9.67	9.64	0.14	1.5	17
C <sub>d</sub>	w%	K1		0.95	70.1	3	71.1	69.9	70.1	1.1	1.6	17
M <sub>ad</sub>	w%	K1			5.33		5.41	5.37	5.33	0.25	4.7	17
Q <sub>p,net,d</sub>	J/g	K1		-1.08	27250	1.3	27059	27223	27250	206	0.8	15
Q <sub>V,gr,d</sub>	J/g	K1		-0.84	28185	1.2	28043	28143	28188	168	0.6	15
S <sub>d</sub>	w%	K1		-0.02	0.35	15	0.35	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	K1		-0.35	36.4	5	36.1	36.5	36.4	0.7	2.0	10

Participant 30												
Measurand	Unit	Sample		z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		0.26	0.29	30	0.30	0.30	0.30	0.04	12.8	16
	w%	B3		-0.61	4.06	15	3.87	4.05	4.07	0.19	4.6	16
C <sub>d</sub>	w%	B2		1.37	50.5	2.5	51.4	50.7	50.5	0.6	1.2	12
	w%	B3		1.79	51.2	3	52.6	51.2	51.2	0.8	1.6	12
Cl <sub>d</sub>	mg/kg	B3		-0.12	144	20	142	145	144	11	7.5	7
H <sub>d</sub>	w%	B2		0.06	6.15	8	6.17	6.16	6.15	0.25	4.0	13
	w%	B3		-0.19	6.00	6	5.97	5.98	6.00	0.19	3.2	11
M <sub>ad</sub>	w%	B2			7.51		7.81	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		6.46	6.25	6.10	0.38	6.2	14
N <sub>d</sub>	w%	B2			0.066		0.001	0.066	0.059	0.046	77.8	6
	w%	B3		-0.96	0.53	25	0.47	0.52	0.53	0.07	12.5	12

Participant 30													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
q <sub>p,net,d</sub>	J/g	B2		0.52	18800	1.6	18879	18805	18800	48	0.3	8	
	J/g	B3		0.47	19112	1.7	19189	19130	19112	143	0.8	10	
q <sub>V,gr,d</sub>	J/g	B2		0.81	20085	1.5	20207	20075	20077	130	0.6	13	
	J/g	B3		0.65	20405	1.7	20517	20432	20417	166	0.8	15	
S <sub>d</sub>	w%	B3		-2.30	0.042	35	0.025	0.045	0.042	0.007	16.5	9	
V <sub>d</sub>	w%	B2		0.09	85.6	3	85.7	85.7	85.6	1.2	1.4	8	
	w%	B3		0.09	85.6	3	78.7	77.1	77.3	1.4	1.8	8	

Participant 31													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B3		-0.03	4.06	15	4.05	4.05	4.07	0.19	4.6	16	
M <sub>ad</sub>	w%	B3		0.16	6.12		6.45	6.25	6.10	0.38	6.2	14	
q <sub>V,gr,d</sub>	J/g	B3		0.16	20405	1.7	20432	20432	20417	166	0.8	15	

Participant 32													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		-3.68	0.29	30	0.13	0.30	0.30	0.04	12.8	16	
	w%	K1		-0.87	9.65	2.5	9.55	9.67	9.64	0.14	1.5	17	
C <sub>d</sub>	w%	B2		-5.03	50.5	2.5	47.3	50.7	50.5	0.6	1.2	12	
	w%	K1		-0.47	70.1	3	69.6	69.9	70.1	1.1	1.6	17	
Cl <sub>d</sub>	mg/kg	K1		0.69	137		0	134	137	30	22.1	6	
F <sub>d</sub>	mg/kg	K1		-3.30	91.2	30	46.0	93.4	91.2	11.6	12.7	6	
H <sub>d</sub>	w%	B2		-1.32	6.15	8	5.83	6.16	6.15	0.25	4.0	13	
	w%	K1		1.54	4.56	7	4.81	4.50	4.54	0.15	3.4	15	
M <sub>ad</sub>	w%	B2		0.23	7.51		5.47	7.58	7.51	0.27	3.6	12	
	w%	K1		0.23	5.33		5.73	5.37	5.33	0.25	4.7	17	
N <sub>d</sub>	w%	B2		-1.03	0.066		0	0.066	0.059	0.046	77.8	6	
	w%	K1		-1.03	1.91	10	1.81	1.91	1.89	0.05	2.6	15	
q <sub>p,net,d</sub>	J/g	B2		-2.11	18800	1.6	18483	18805	18800	48	0.3	8	
	J/g	K1		0.96	27250	1.3	27419	27223	27250	206	0.8	15	
q <sub>V,gr,d</sub>	J/g	B2		-1.81	20085	1.5	19812	20075	20077	130	0.6	13	
	J/g	K1		1.34	28185	1.2	28412	28143	28188	168	0.6	15	
S <sub>d</sub>	w%	K1		-0.65	0.35	15	0.33	0.35	0.35	0.03	8.5	15	
V <sub>d</sub>	w%	B2		0.10	85.6	3	85.7	85.7	85.6	1.2	1.4	8	
	w%	K1		2.48	36.4	5	38.7	36.5	36.4	0.7	2.0	10	

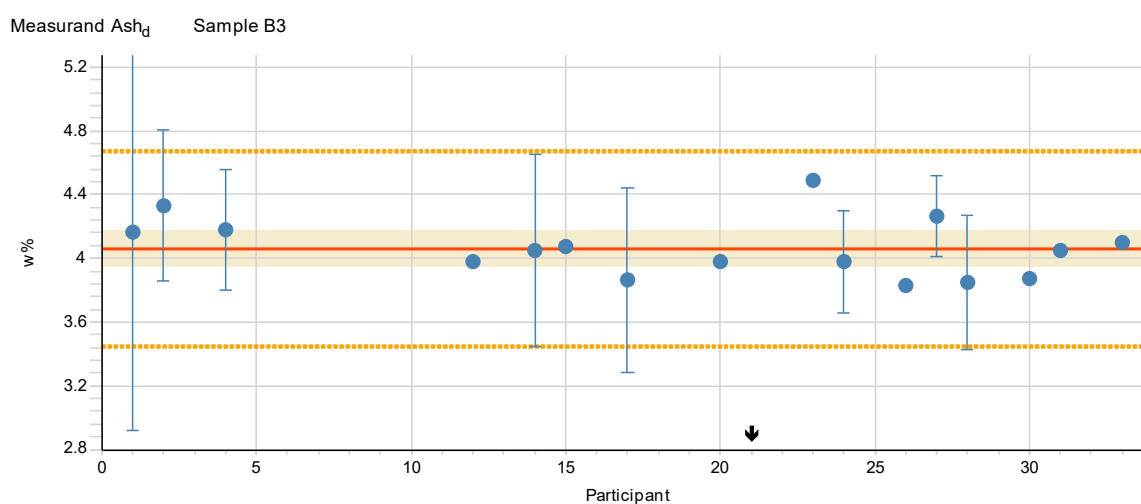
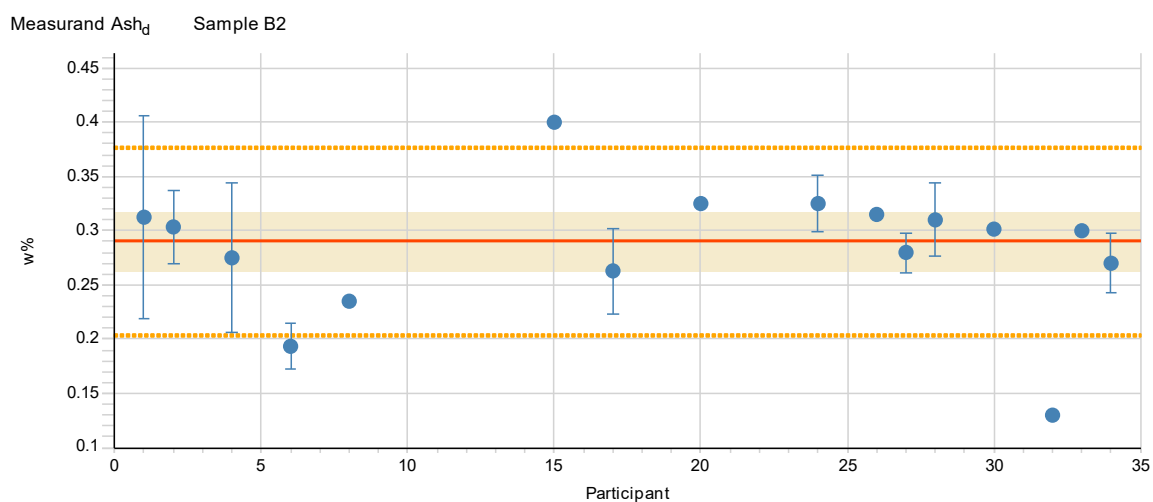
Participant 33													
Measurand	Unit	Sample		z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>	
Ash <sub>d</sub>	w%	B2		0.23	0.29	30	0.30	0.30	0.30	0.04	12.8	16	
	w%	B3		0.13	4.06	15	4.10	4.05	4.07	0.19	4.6	16	
	w%	K1		0.00	9.65	2.5	9.65	9.67	9.64	0.14	1.5	17	
C <sub>d</sub>	w%	B2		0.48	50.5	2.5	50.8	50.7	50.5	0.6	1.2	12	
	w%	B3		0.33	51.2	3	51.5	51.2	51.2	0.8	1.6	12	
	w%	K1		1.24	70.1	3	71.4	69.9	70.1	1.1	1.6	17	
Cl <sub>d</sub>	mg/kg	B3		0.69	144	20	154	145	144	11	7.5	7	
	mg/kg	K1		0.69	137		100	134	137	30	22.1	6	
EF	t CO <sub>2</sub> /TJ	K1		0.00	95.5		95.4	95.4	95.5	0.7	0.7	5	

Participant 33												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
F <sub>d</sub>	mg/kg	K1		-0.05	91.2	30	90.5	93.4	91.2	11.6	12.7	6
H <sub>d</sub>	w%	B2		0.02	6.15	8	6.16	6.16	6.15	0.25	4.0	13
	w%	B3		-0.47	6.00	6	5.92	5.98	6.00	0.19	3.2	11
	w%	K1		-1.22	4.56	7	4.37	4.50	4.54	0.15	3.4	15
M <sub>ad</sub>	w%	B2			7.51		7.20	7.58	7.51	0.27	3.6	12
	w%	B3			6.12		5.80	6.25	6.10	0.38	6.2	14
	w%	K1			5.33		5.10	5.37	5.33	0.25	4.7	17
N <sub>d</sub>	w%	B2			0.066		<0.1	0.066	0.059	0.046	77.8	6
	w%	B3		-0.38	0.53	25	0.51	0.52	0.53	0.07	12.5	12
	w%	K1		0.10	1.91	10	1.92	1.91	1.89	0.05	2.6	15
Q <sub>p,net,d</sub>	J/g	B2		-1.80	18800	1.6	18530	18805	18800	48	0.3	8
	J/g	B3		0.27	19112	1.7	19156	19130	19112	143	0.8	10
	J/g	K1		1.42	27250	1.3	27502	27223	27250	206	0.8	15
Q <sub>V,gr,d</sub>	J/g	B2		-1.44	20085	1.5	19869	20075	20077	130	0.6	13
	J/g	B3		0.22	20405	1.7	20444	20432	20417	166	0.8	15
	J/g	K1		1.50	28185	1.2	28439	28143	28188	168	0.6	15
S <sub>d</sub>	w%	B3		0.34	0.042	35	0.045	0.045	0.042	0.007	16.5	9
	w%	K1		1.52	0.35	15	0.39	0.35	0.35	0.03	8.5	15
V <sub>d</sub>	w%	B2		-1.32	85.6	3	83.9	85.7	85.6	1.2	1.4	8
	w%	B3					75.4	77.1	77.3	1.4	1.8	8
	w%	K1		-0.82	36.4	5	35.7	36.5	36.4	0.7	2.0	10

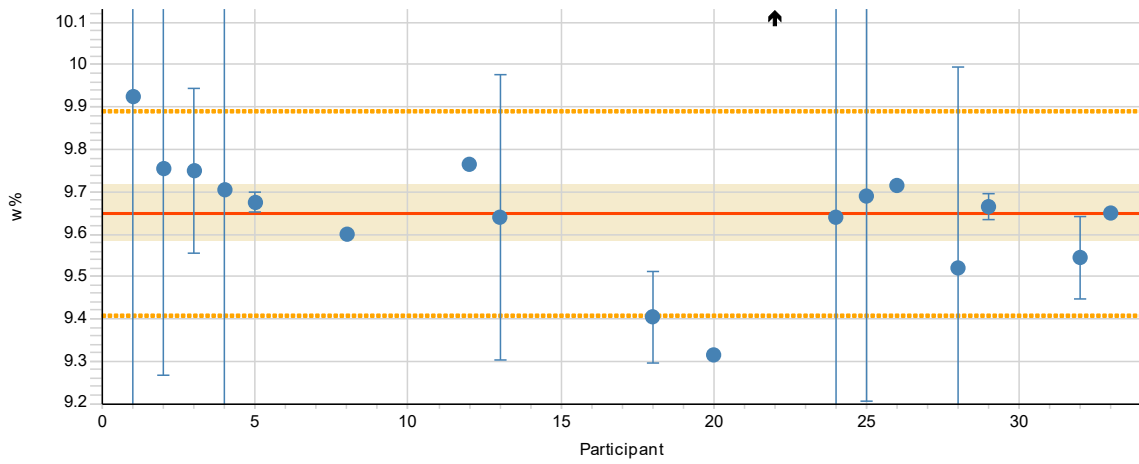
Participant 34												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2*s <sub>pt</sub> %	Participant's result	Md	Mean	s	s %	n <sub>stat</sub>
Ash <sub>d</sub>	w%	B2		-0.46	0.29	30	0.27	0.30	0.30	0.04	12.8	16
M <sub>ad</sub>	w%	B2			7.51		7.74	7.58	7.51	0.27	3.6	12
Q <sub>p,net,d</sub>	J/g	B2		-0.03	18800	1.6	18796	18805	18800	48	0.3	8
Q <sub>V,gr,d</sub>	J/g	B2		0.21	20085	1.5	20117	20075	20077	130	0.6	13

## Appendix 8. Results of participants and their uncertainties

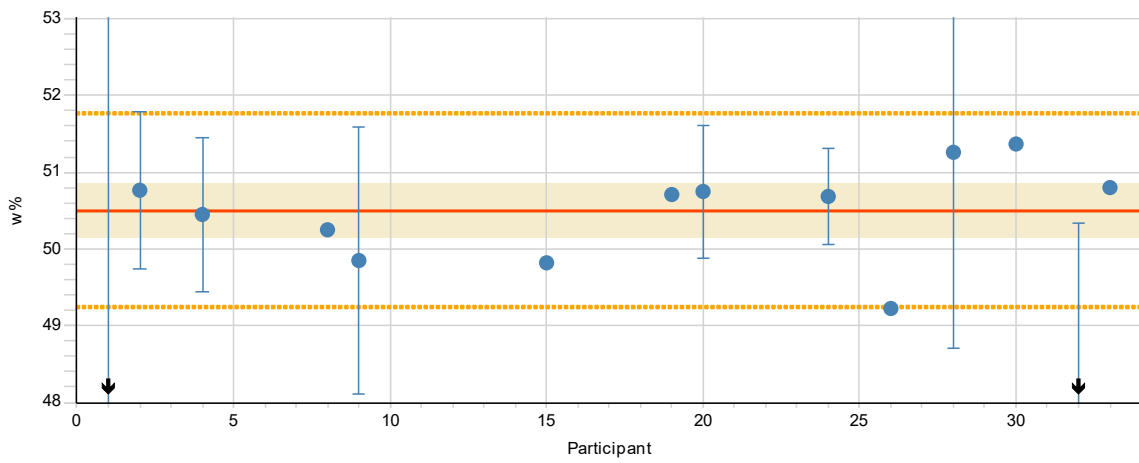
The dashed lines in figures describe the standard deviation for the proficiency assessment, red solid line shows the assigned value, shaded area describes the expanded uncertainty of the assigned value, and arrow describes the value outside the scale.



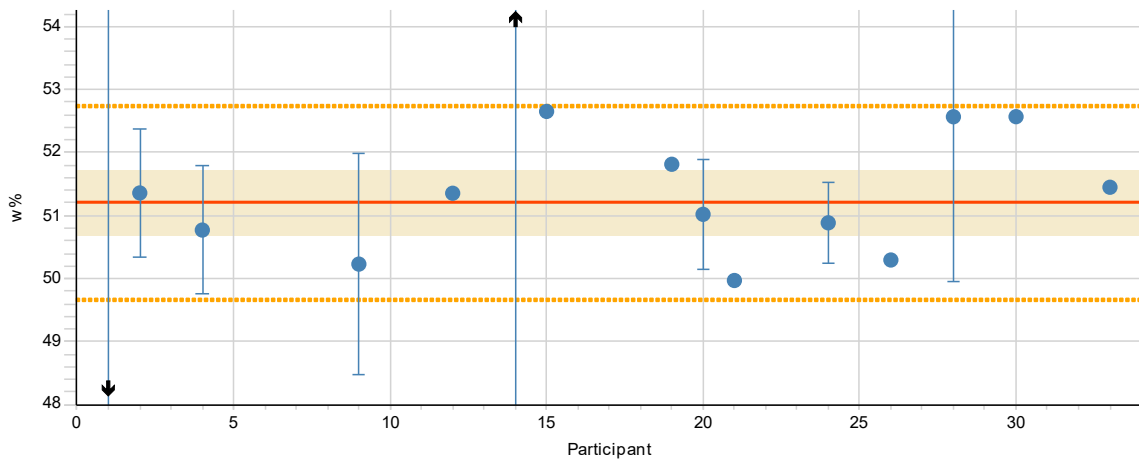
Measurand Ash<sub>d</sub> Sample K1



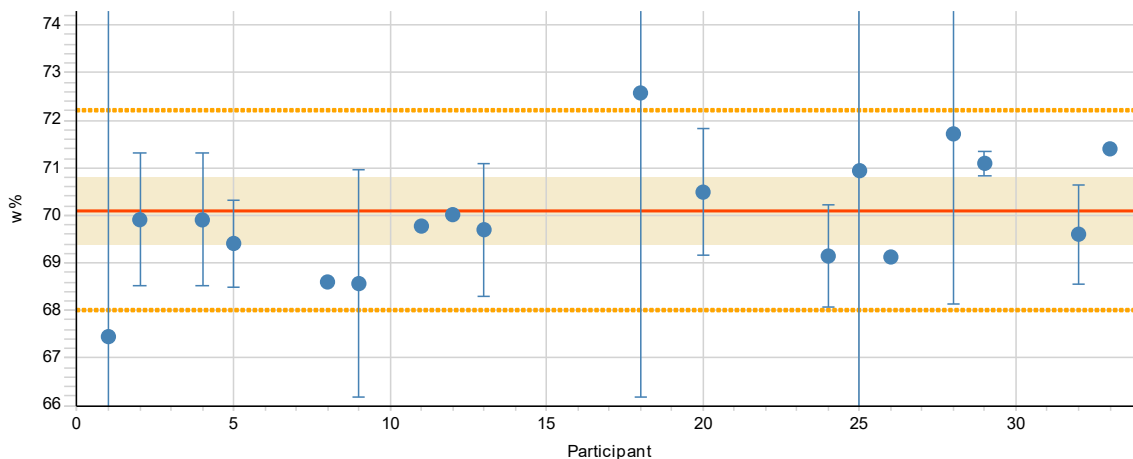
Measurand C<sub>d</sub> Sample B2



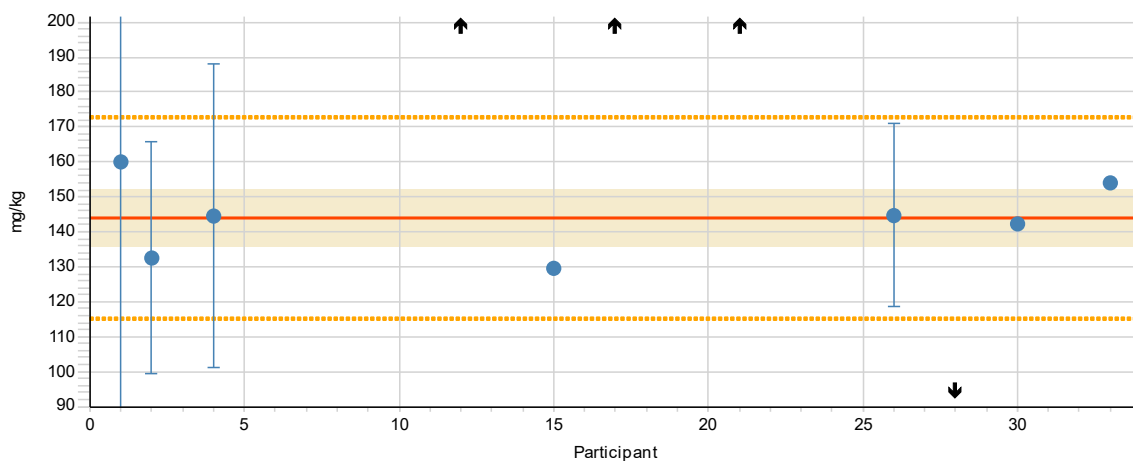
Measurand C<sub>d</sub> Sample B3



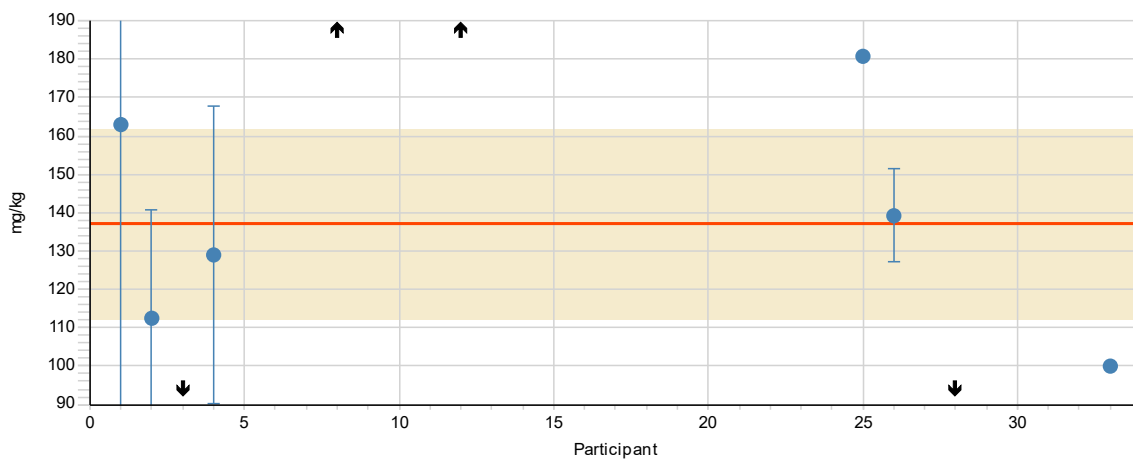
Measurand  $C_d$  Sample K1

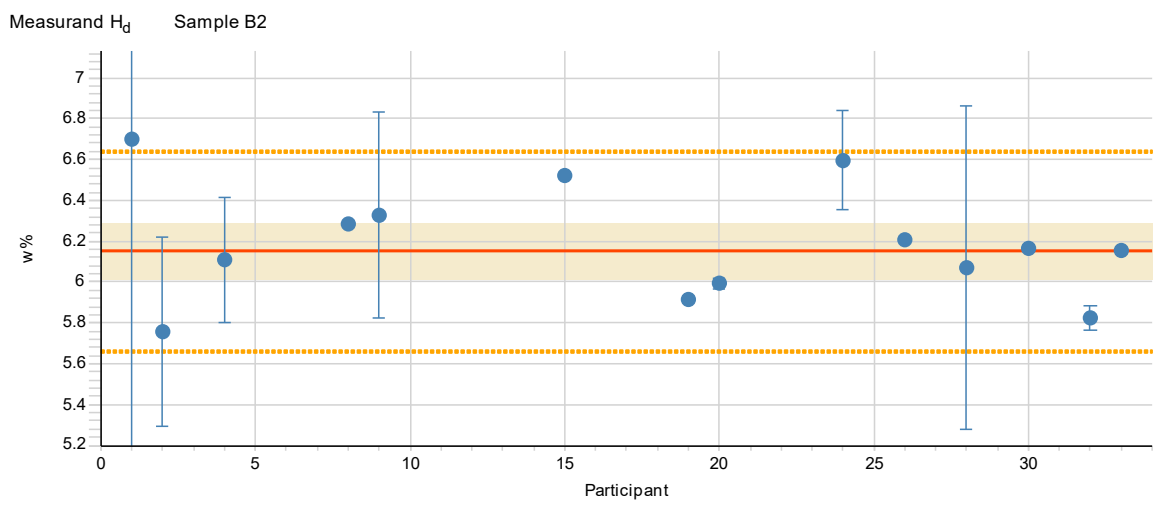
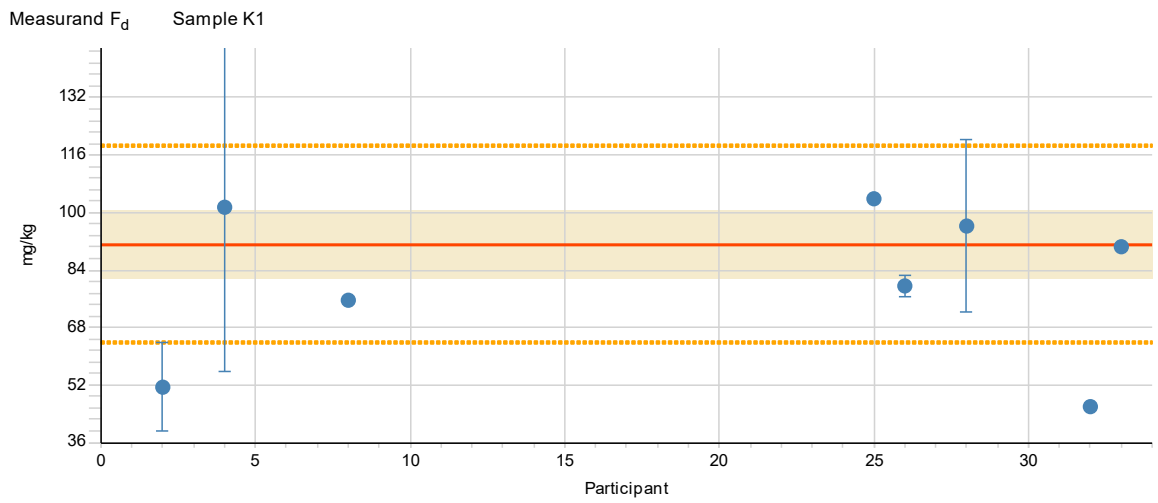
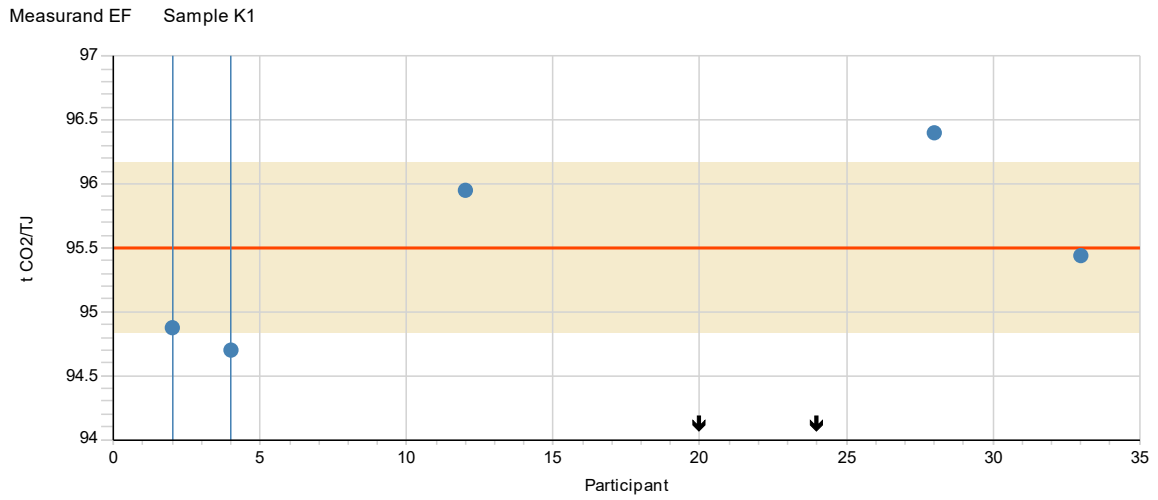


Measurand  $Cl_d$  Sample B3

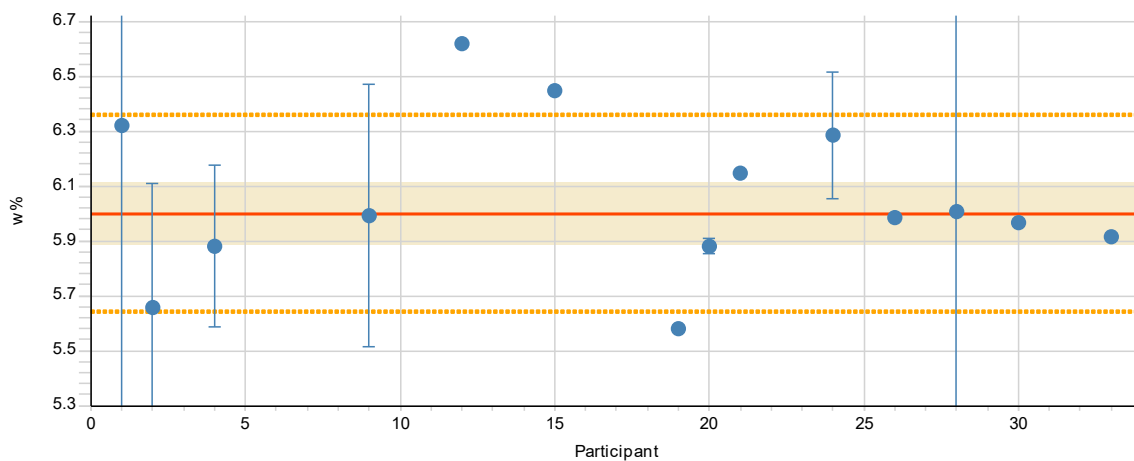


Measurand  $Cl_d$  Sample K1

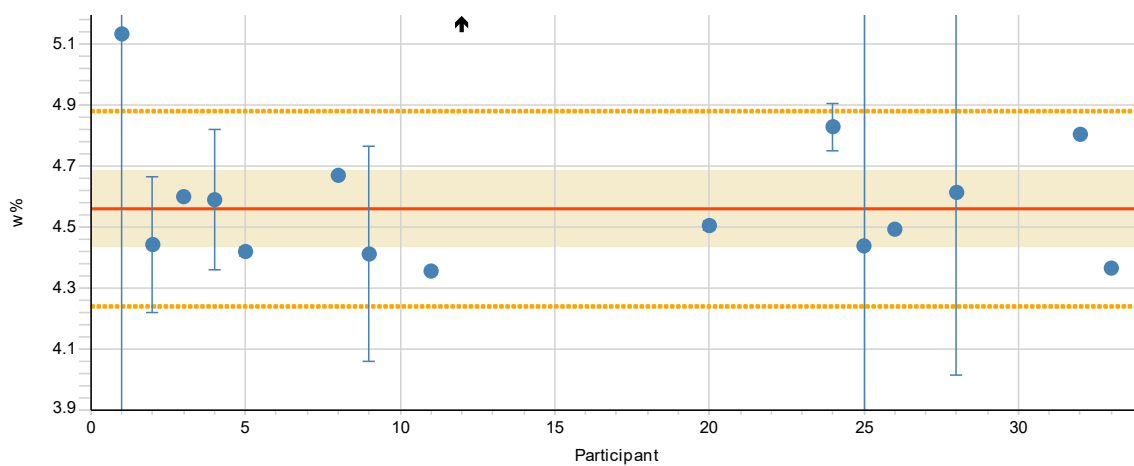




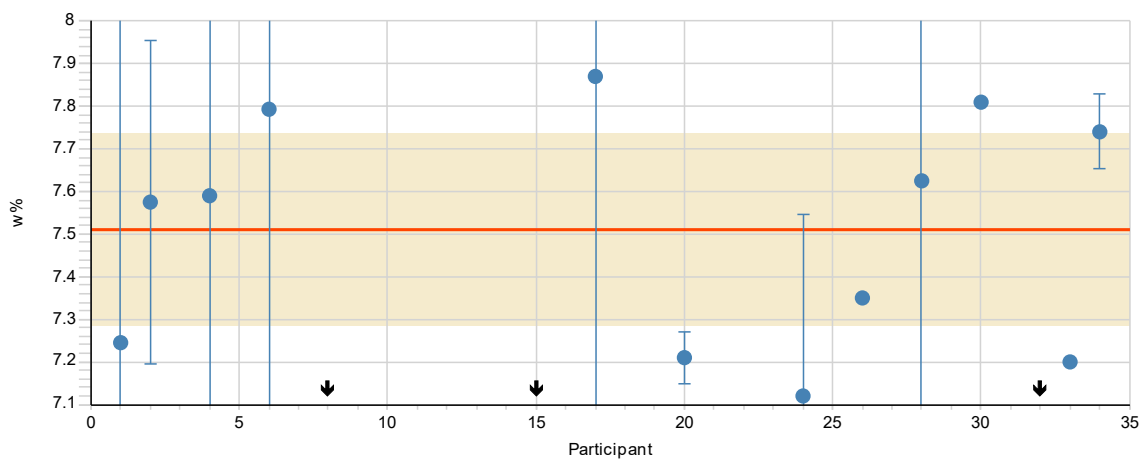
Measurand  $H_d$  Sample B3



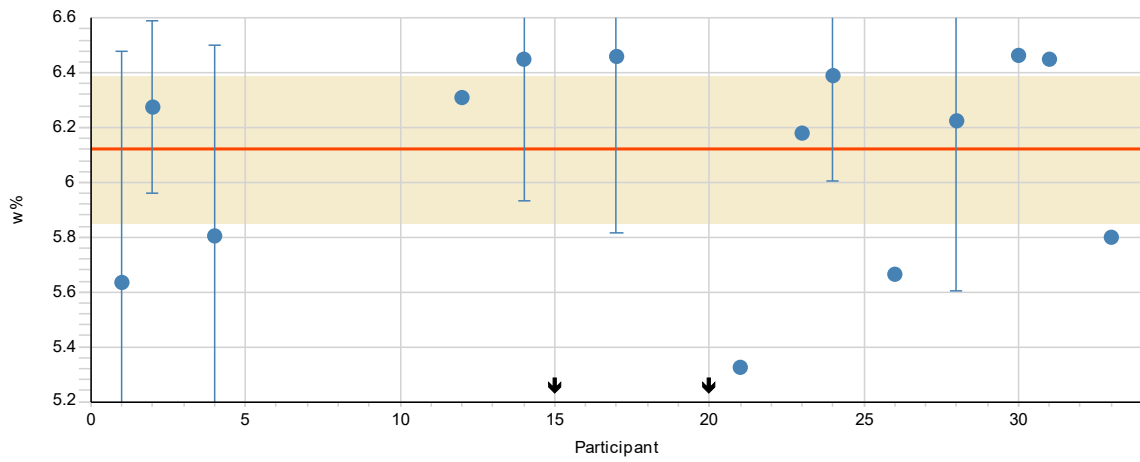
Measurand  $H_d$  Sample K1



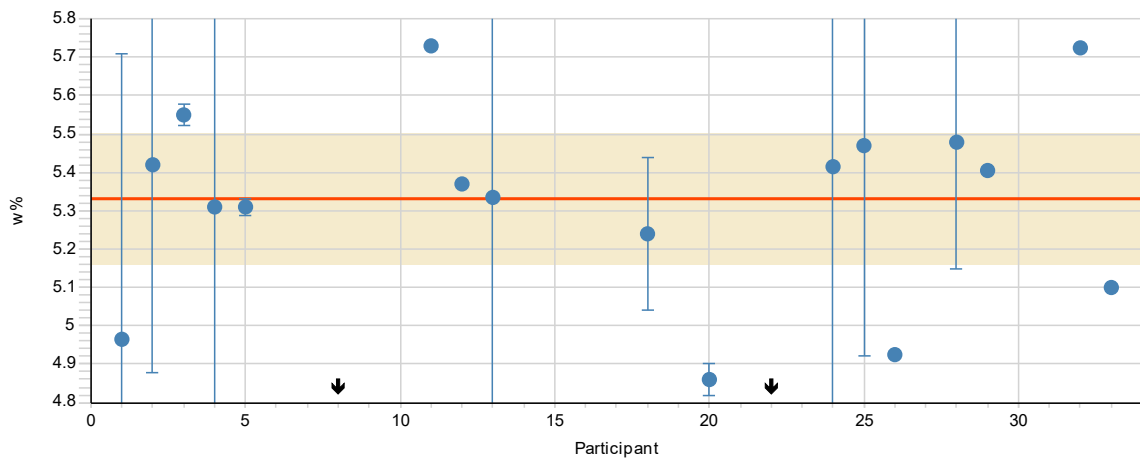
Measurand  $M_{ad}$  Sample B2



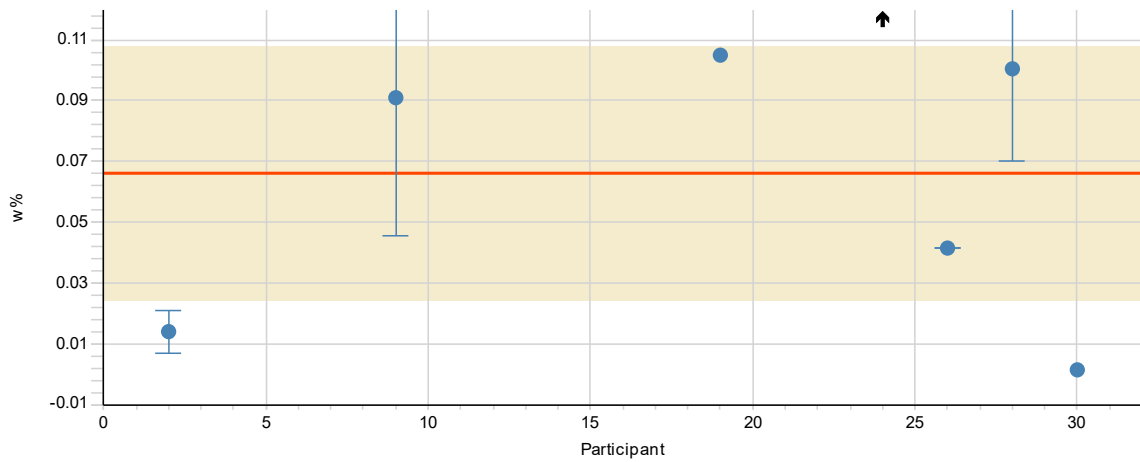
Measurand  $M_{ad}$  Sample B3



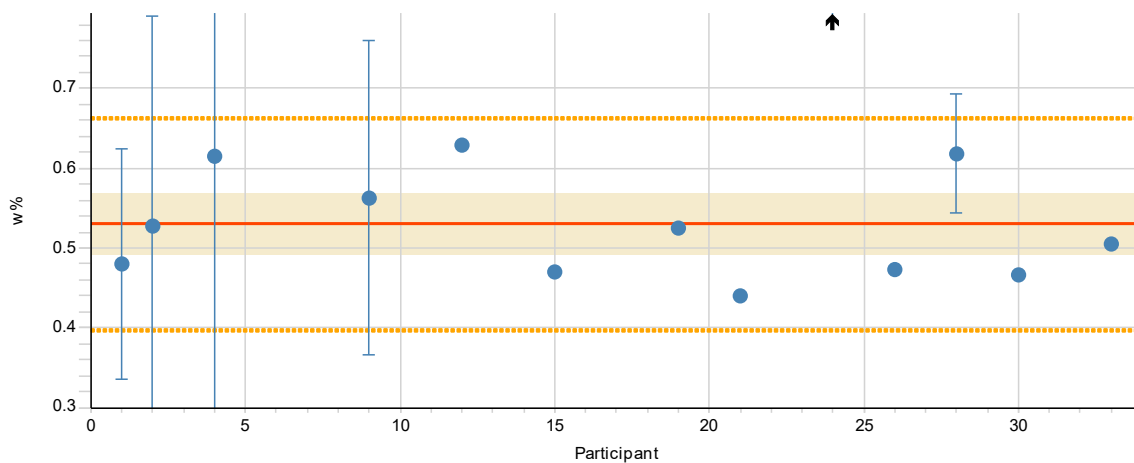
Measurand  $M_{ad}$  Sample K1



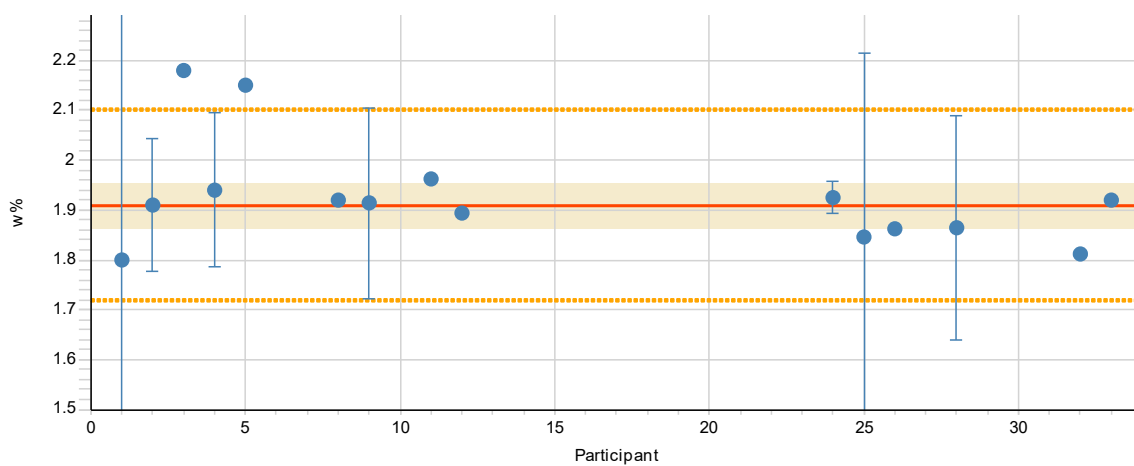
Measurand  $N_d$  Sample B2



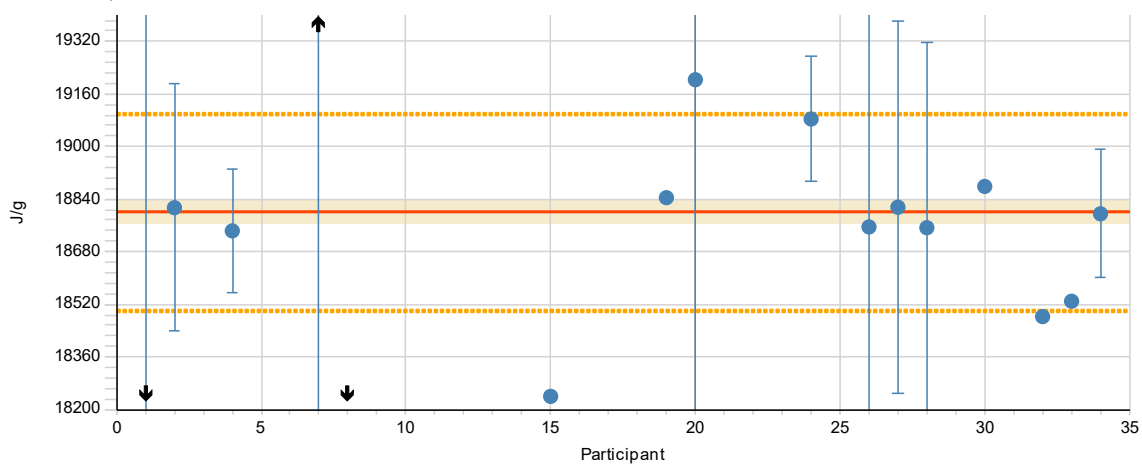
Measurand  $N_d$  Sample B3

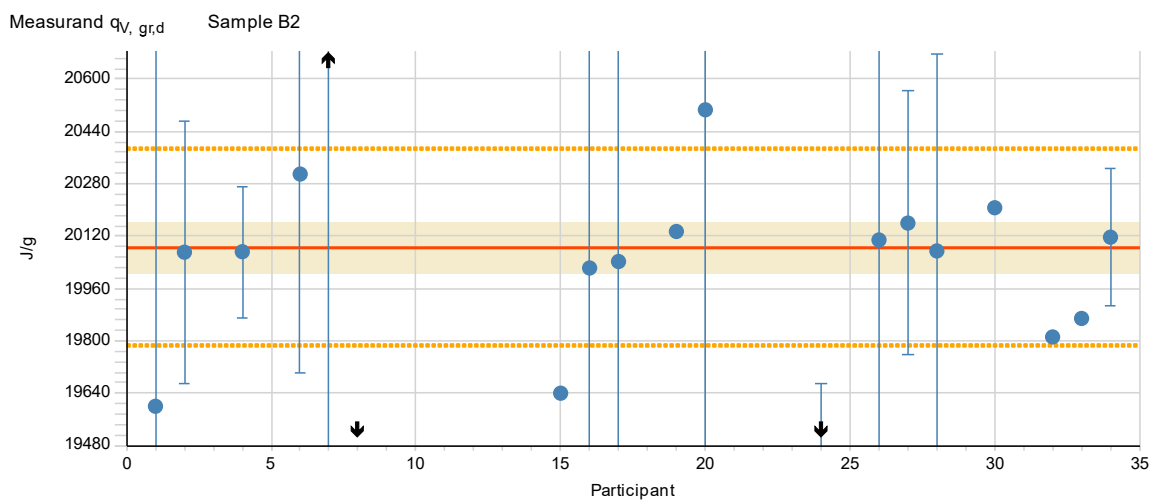
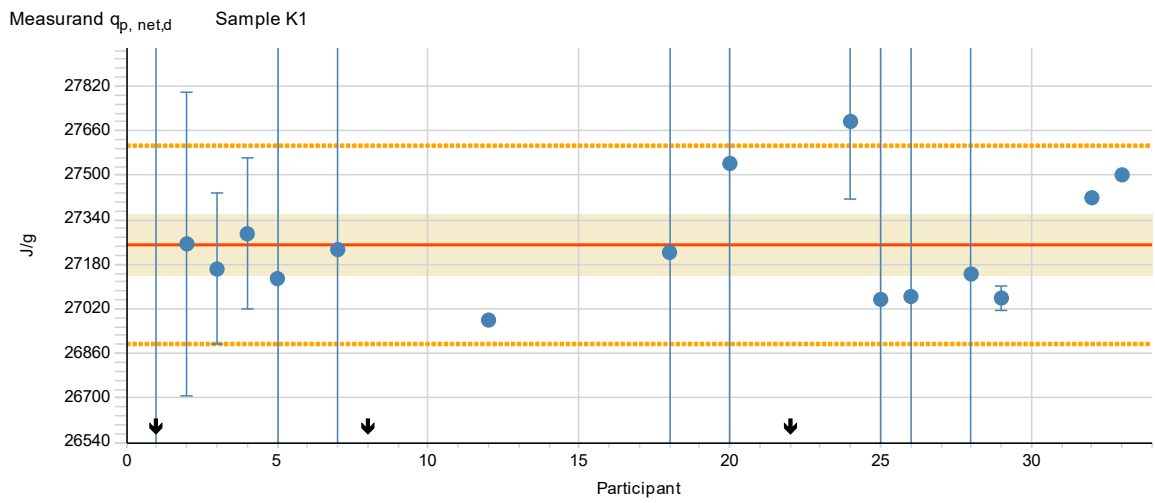
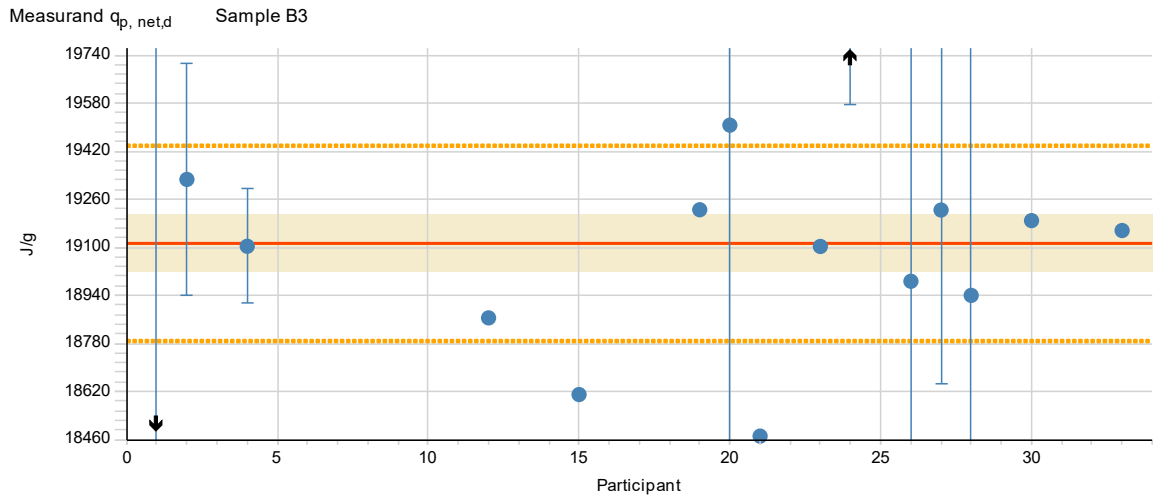


Measurand  $N_d$  Sample K1

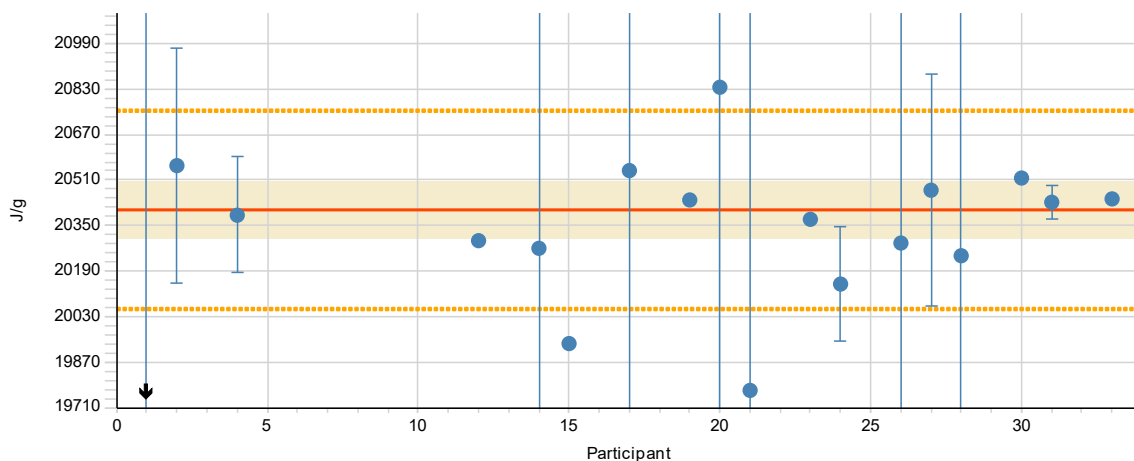


Measurand  $q_{p, net,d}$  Sample B2

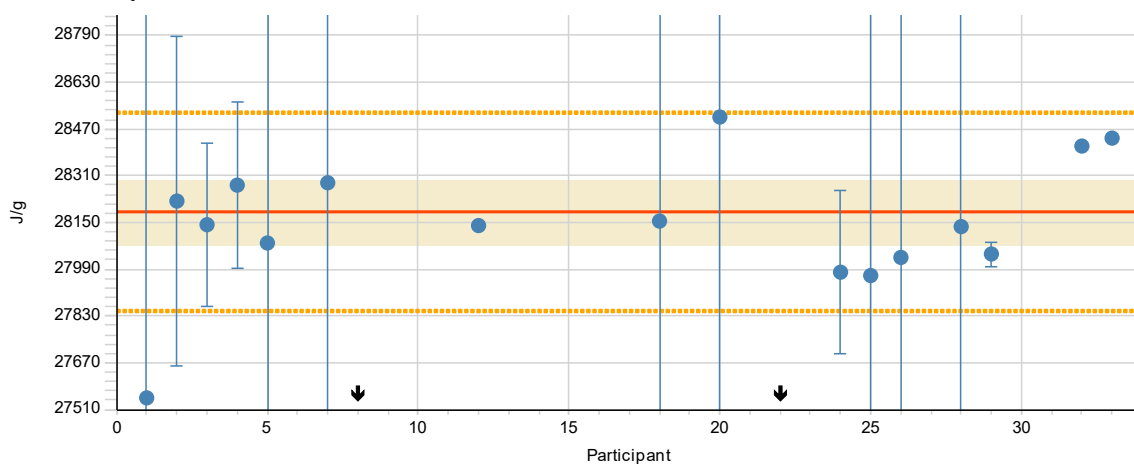




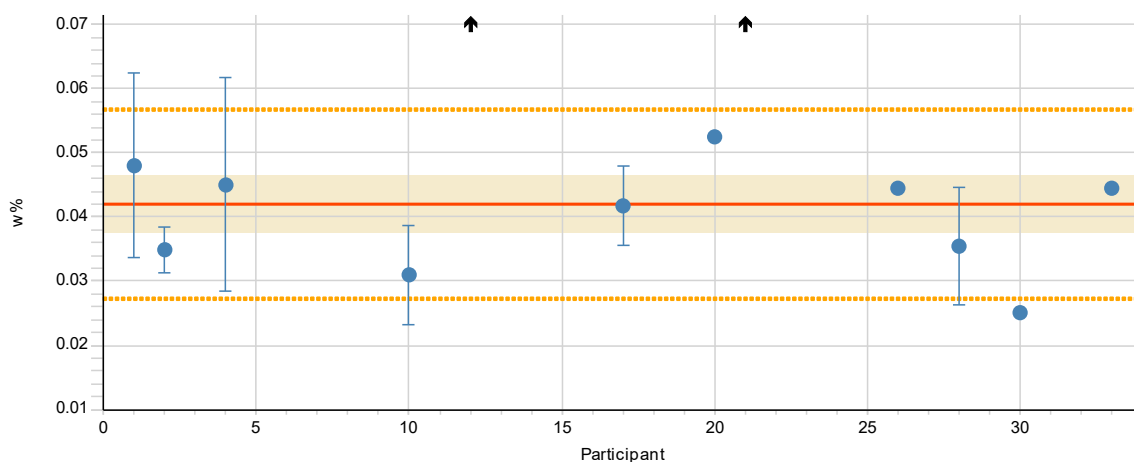
Measurand  $q_{V, gr,d}$  Sample B3

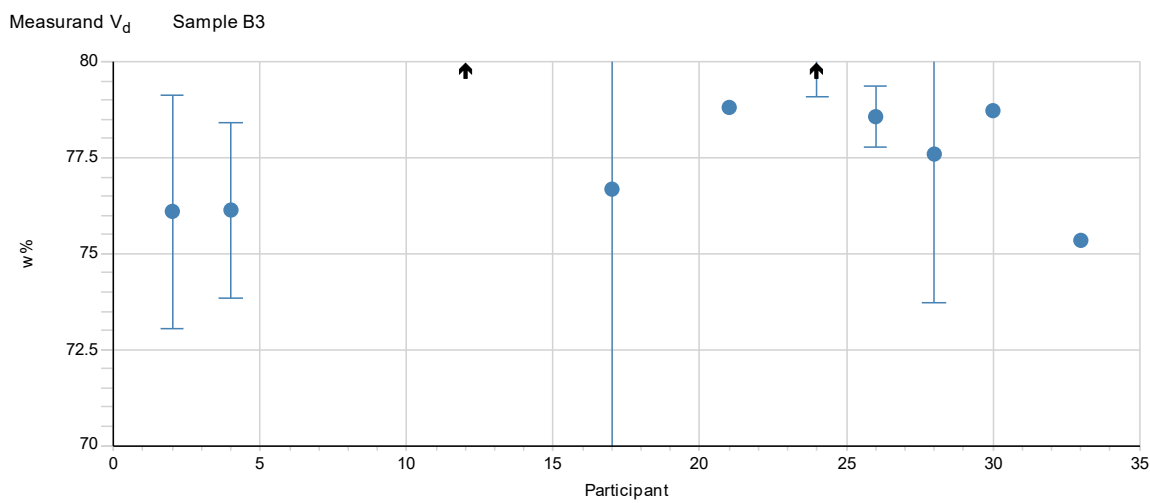
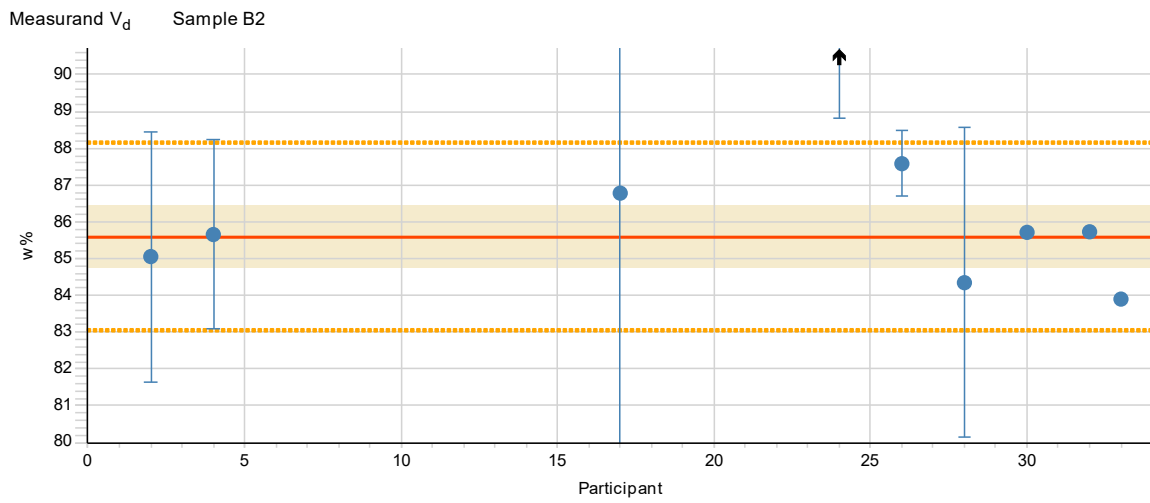
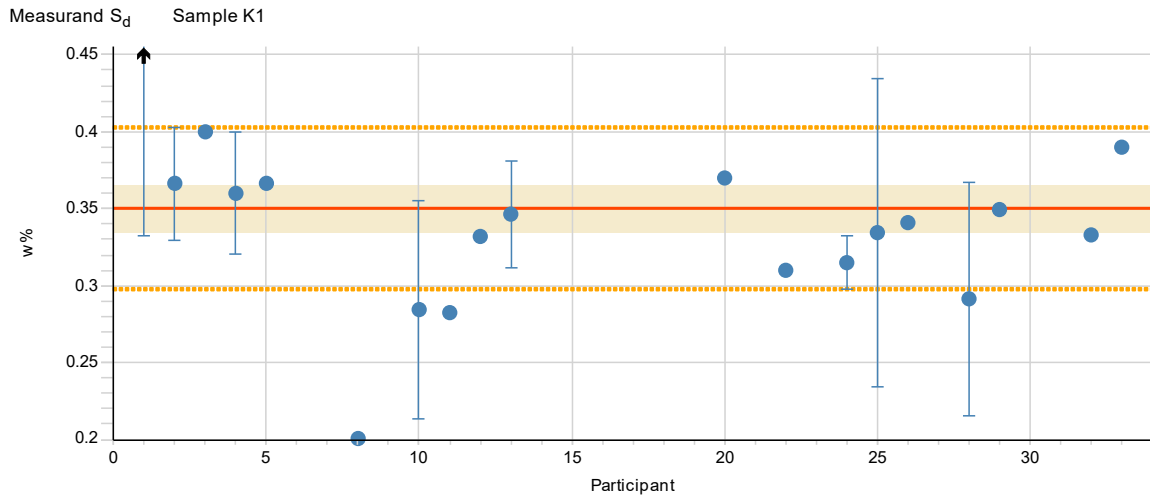


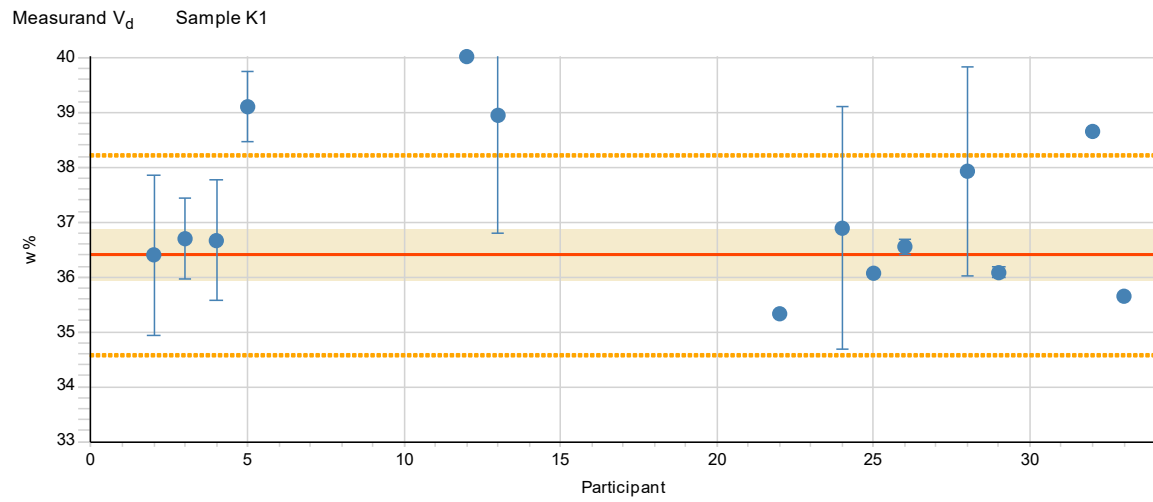
Measurand  $q_{V, gr,d}$  Sample K1



Measurand  $S_d$  Sample B3







## Appendix 9. Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	%	
Ash <sub>d</sub>	B2	S	S	.	S	.	q	.	S	.	.	.	.	.	.	Q	.	S	81.3	
	B3	S	S	.	S	.	.	.	.	.	.	.	S	.	S	S	.	S	94.1	
	K1	Q	S	S	S	S	.	.	S	.	.	.	S	S	.	.	.	.	77.8	
C <sub>d</sub>	B2	u	S	.	S	.	.	.	S	S	.	.	.	.	.	S	.	.	78.6	
	B3	u	S	.	S	.	.	.	.	S	.	.	S	.	U	S	.	.	86.7	
	K1	q	S	.	S	S	.	.	S	S	.	S	S	S	.	.	.	.	88.9	
Cl <sub>d</sub>	B3	S	S	.	S	.	.	.	.	.	.	.	U	.	.	S	.	U	63.6	
F <sub>d</sub>	K1	.	q	.	S	.	.	.	S	.	.	.	.	.	.	.	.	.	75.0	
H <sub>d</sub>	B2	Q	S	.	S	.	.	.	S	S	.	.	.	.	.	S	.	.	92.9	
	B3	S	S	.	S	.	.	.	.	S	.	.	U	.	.	Q	.	.	78.6	
	K1	U	S	S	S	S	.	.	S	S	.	S	U	.	.	.	.	.	87.5	
N <sub>d</sub>	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.		
	B3	S	S	.	S	.	.	.	.	S	.	.	S	.	.	S	.	.	92.3	
	K1	S	S	Q	S	Q	.	.	S	S	.	S	S	.	.	.	.	.	86.7	
q <sub>p,net,d</sub>	B2	u	S	.	S	.	.	U	u	.	.	.	.	.	.	u	.	.	62.5	
	B3	u	S	.	S	.	.	.	.	.	.	.	S	.	.	u	.	.	66.7	
	K1	u	S	S	S	S	.	S	u	.	.	.	S	.	.	.	.	.	77.8	
q <sub>V,gr,d</sub>	B2	u	S	.	S	.	S	U	u	.	.	.	.	.	.	q	S	S	68.4	
	B3	u	S	.	S	.	.	.	.	.	.	.	S	.	S	q	.	S	77.8	
	K1	u	S	S	S	S	.	S	u	.	.	.	S	.	.	.	.	.	83.3	
S <sub>d</sub>	B3	S	S	.	S	.	.	.	.	.	S	.	U	.	.	.	.	S	75.0	
	K1	U	S	S	S	S	.	.	u	.	q	q	S	S	.	.	.	.	73.7	
V <sub>d</sub>	B2	.	S	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	S	88.9
	K1	.	S	S	S	Q	.	.	.	.	.	.	U	Q	.	.	.	.	71.4	
%		35	96	86	100	75	50	50	62	100	50	75	69	75	67	50	100	86		
accredited		20	22	2	22	7	2	3		3	2			1	1		1			

Measurand	Sample	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	%
Ash <sub>d</sub>	B2	.	.	<i>S</i>	.	.	.	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<i>S</i>	.	<b>u</b>	<b>S</b>	<b>S</b>	81.3
	B3	.	.	<i>S</i>	<i>u</i>	.	<i>S</i>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<i>S</i>	<b>S</b>	.	<b>S</b>	.	94.1
	K1	<b>q</b>	.	<i>q</i>	.	<b>U</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<i>S</i>	.	.	<b>S</b>	<b>S</b>	.	77.8
C <sub>d</sub>	B2	.	<i>S</i>	<b>S</b>	.	.	.	<b>S</b>	.	<b>q</b>	.	<b>S</b>	.	<i>S</i>	.	<b>u</b>	<b>S</b>	.	78.6
	B3	.	<i>S</i>	<b>S</b>	<i>S</i>	.	.	<b>S</b>	.	<b>S</b>	.	<b>S</b>	.	<i>S</i>	.	.	<b>S</b>	.	86.7
	K1	<b>Q</b>	.	<b>S</b>	.	.	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<i>S</i>	.	.	<b>S</b>	<b>S</b>	.	88.9
Cl <sub>d</sub>	B3	.	.	.	<i>U</i>	.	.	.	.	<b>S</b>	.	<b>u</b>	.	<i>S</i>	.	.	<b>S</b>	.	63.6
F <sub>d</sub>	K1	.	.	.	.	.	.	.	<i>S</i>	<i>S</i>	.	<i>S</i>	.	.	.	<i>u</i>	<i>S</i>	.	75.0
H <sub>d</sub>	B2	.	<i>S</i>	<b>S</b>	.	.	.	<b>S</b>	.	<b>S</b>	.	<b>S</b>	.	<i>S</i>	.	<b>S</b>	<b>S</b>	.	92.9
	B3	.	<i>q</i>	<b>S</b>	<i>S</i>	.	.	<b>S</b>	.	<b>S</b>	.	<b>S</b>	.	<i>S</i>	.	.	<b>S</b>	.	78.6
	K1	.	.	<b>S</b>	.	.	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	.	.	.	<b>S</b>	<b>S</b>	.	87.5
N <sub>d</sub>	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B3	.	<i>S</i>	.	<i>S</i>	.	.	<b>U</b>	.	<b>S</b>	.	<b>S</b>	.	<i>S</i>	.	.	<b>S</b>	.	92.3
	K1	.	.	.	.	.	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	.	.	.	<b>S</b>	<b>S</b>	.	86.7
Q <sub>p,net,d</sub>	B2	.	<i>S</i>	<b>Q</b>	.	.	.	<b>S</b>	.	<i>S</i>	<b>S</b>	<b>S</b>	.	<i>S</i>	.	<b>q</b>	<b>S</b>	<b>S</b>	62.5
	B3	.	<i>S</i>	<b>Q</b>	<i>u</i>	.	<i>S</i>	<b>U</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<i>S</i>	.	.	<b>S</b>	.	66.7
	K1	<b>S</b>	.	<b>S</b>	.	<b>u</b>	.	<b>Q</b>	<b>S</b>	<b>S</b>	.	<b>S</b>	<i>S</i>	.	.	<b>S</b>	<b>S</b>	.	77.8
Q <sub>V,gr,d</sub>	B2	.	<i>S</i>	<b>Q</b>	.	.	.	<b>u</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<i>S</i>	.	<b>S</b>	<b>S</b>	<b>S</b>	68.4
	B3	.	<i>S</i>	<b>Q</b>	<b>u</b>	.	<i>S</i>	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<i>S</i>	<b>S</b>	.	<b>S</b>	.	77.8
	K1	<b>S</b>	.	<b>S</b>	.	<b>u</b>	.	<b>S</b>	<i>S</i>	<i>S</i>	.	<b>S</b>	<i>S</i>	.	.	<b>S</b>	<b>S</b>	.	83.3
S <sub>d</sub>	B3	.	.	<b>S</b>	<i>U</i>	.	.	.	.	<b>S</b>	.	<b>S</b>	.	<i>q</i>	.	.	<b>S</b>	.	75.0
	K1	.	.	<b>S</b>	.	<b>S</b>	.	<b>S</b>	<b>S</b>	<b>S</b>	.	<b>q</b>	<i>S</i>	.	.	<b>S</b>	<b>S</b>	.	73.7
V <sub>d</sub>	B2	.	.	.	.	.	.	<i>U</i>	.	<i>S</i>	.	<b>S</b>	.	<i>S</i>	.	<i>S</i>	<b>S</b>	.	88.9
	K1	.	.	.	.	<b>S</b>	.	<i>S</i>	<i>S</i>	<b>S</b>	.	<b>S</b>	<i>S</i>	.	.	<i>Q</i>	<b>S</b>	.	71.4
%		50	89	71	38	40	100	75	100	96	100	91	100	93	100	67	100	100	
accredited		4		14	1	5		18	6	19	6	22			2	12	22	3	

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

% - percentage of satisfactory results

Satisfactory results, in total %: 80      in accredited %: 82      in non-accredited %: 74

## Appendix 10. Summary of the $E_n$ scores

Measurand	Sample	1	2	4	26	28	%
Cl <sub>d</sub>	K1	0.3	-0.7	-0.2	0.1	-5.5	80.0
EF	K1	.	0.0	-0.1	.	.	100
%		100	100	100	100	0	

$-1.0 \leq E_n \leq 1.0$  - satisfactory

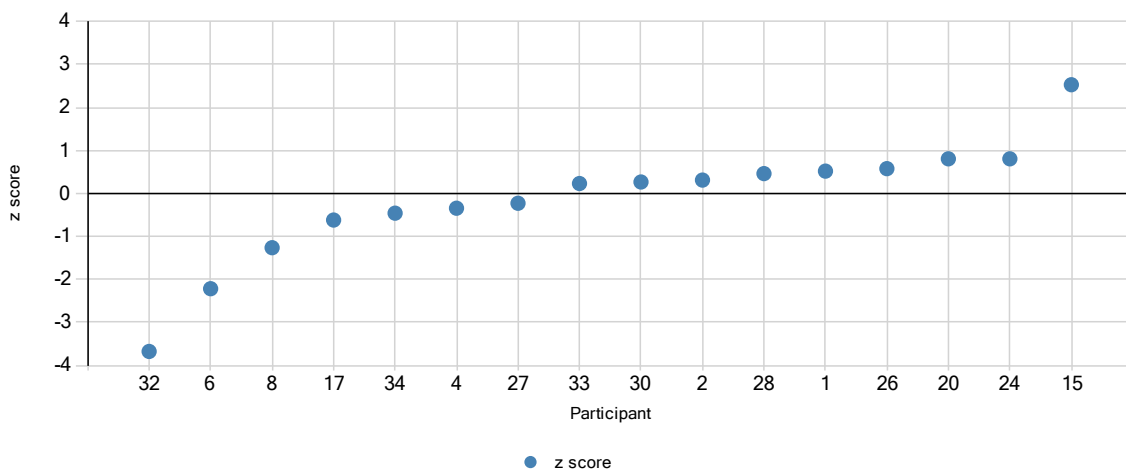
$E_n > 1.0$  or  $E_n < -1.0$  - unsatisfactory

% - percentage of satisfactory results

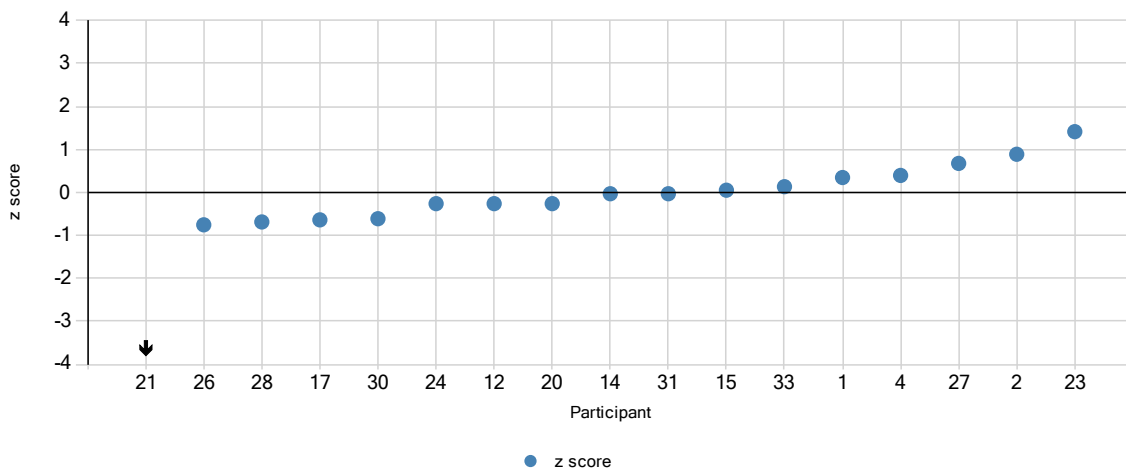
Satisfactory results, in total %: 90

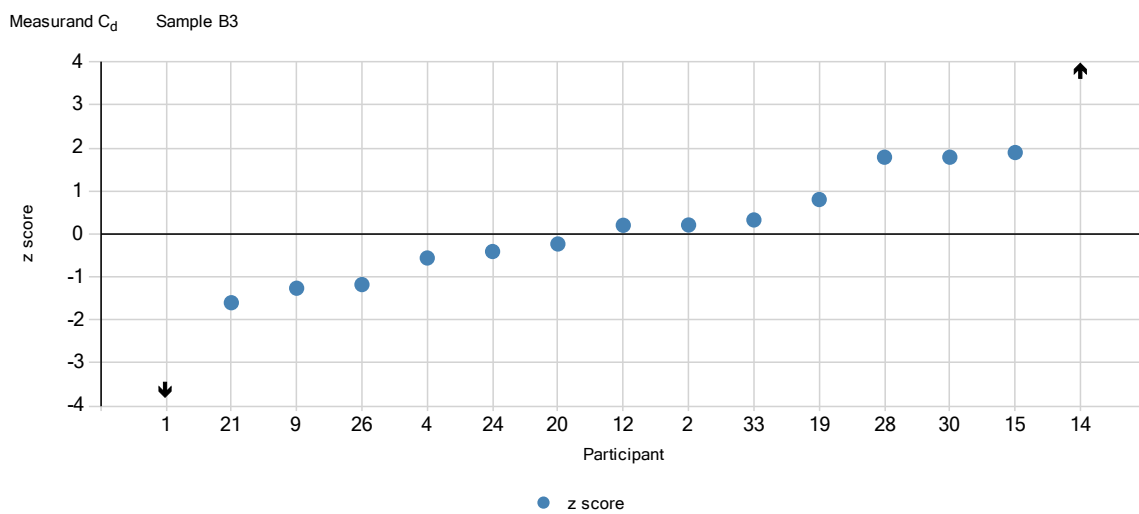
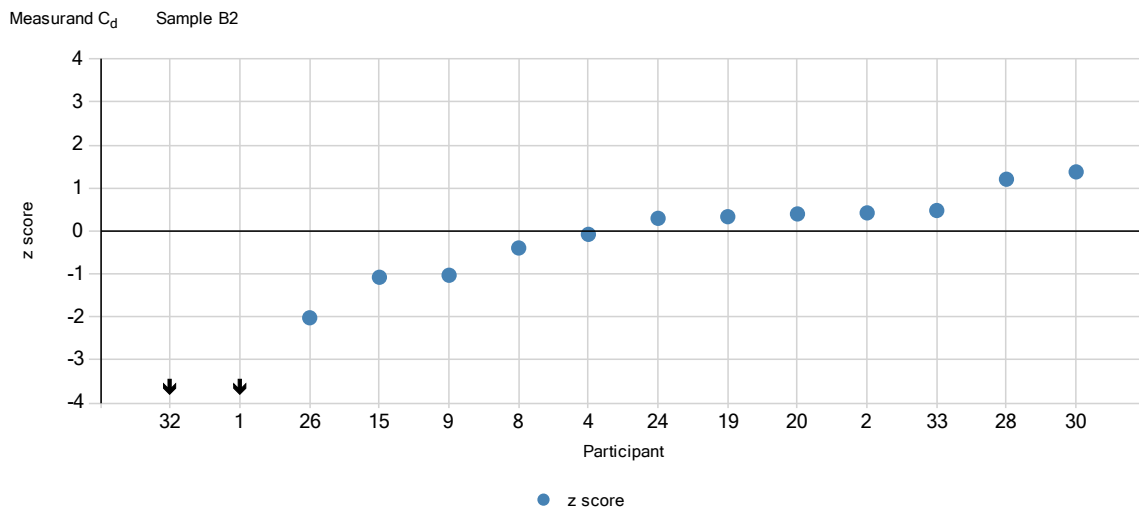
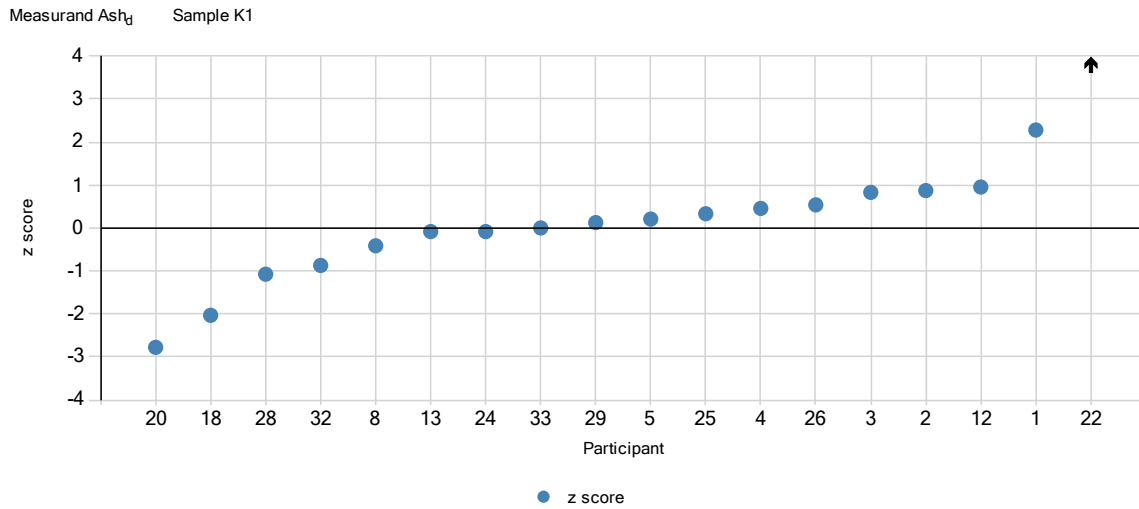
## Appendix 11. z scores in ascending order

Measurand Ash<sub>d</sub> Sample B2

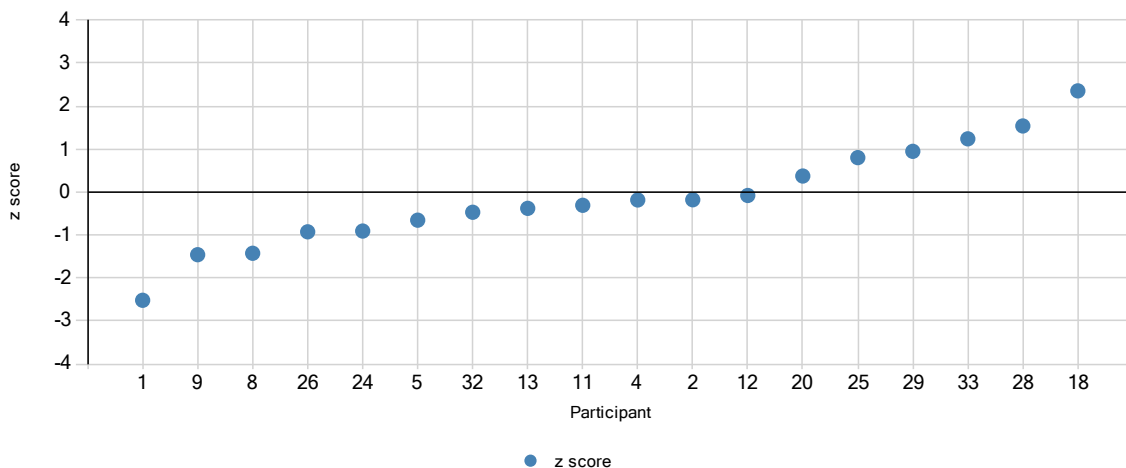


Measurand Ash<sub>d</sub> Sample B3

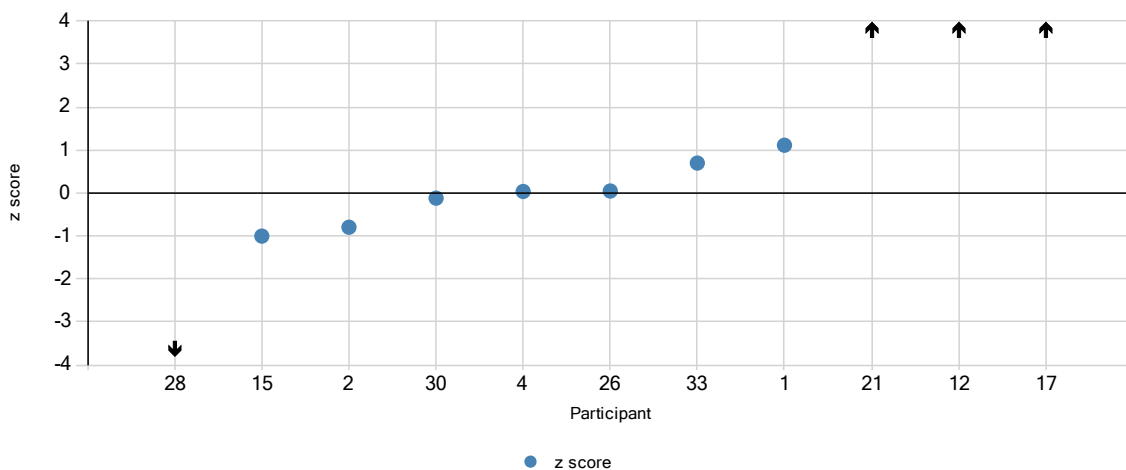




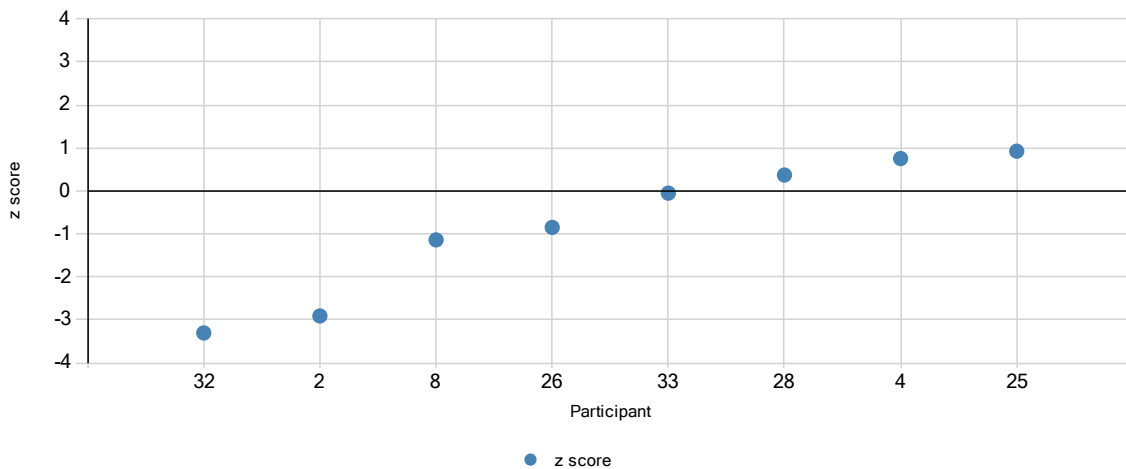
Measurand C<sub>d</sub> Sample K1



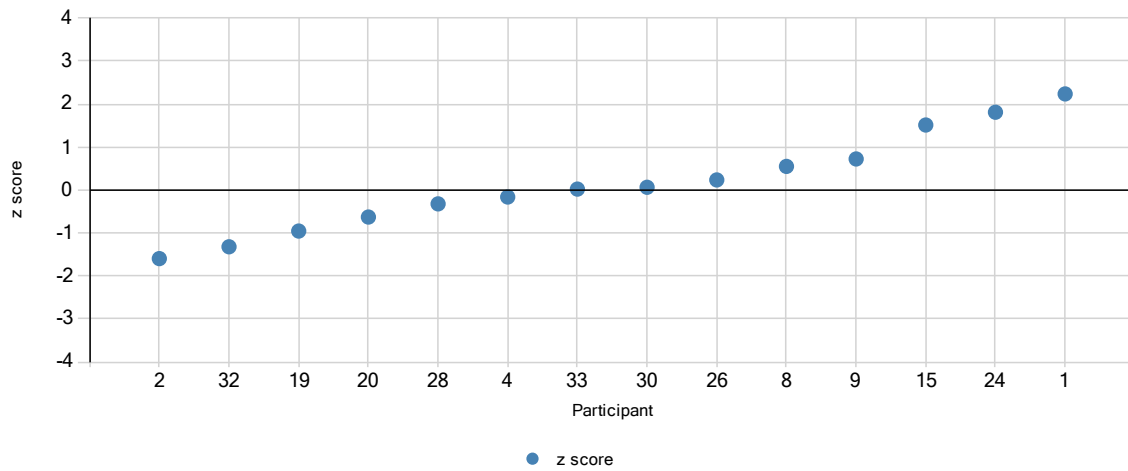
Measurand C<sub>l</sub> Sample B3



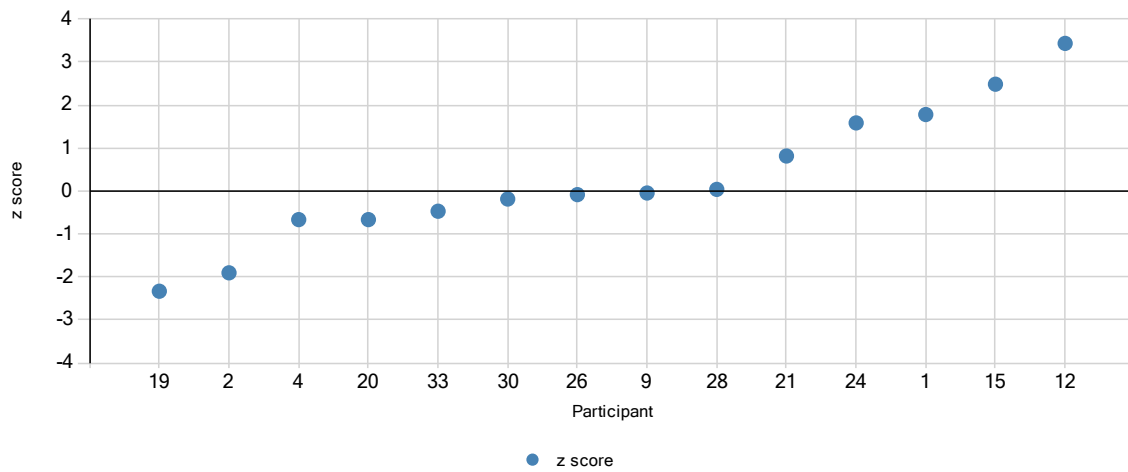
Measurand F<sub>d</sub> Sample K1



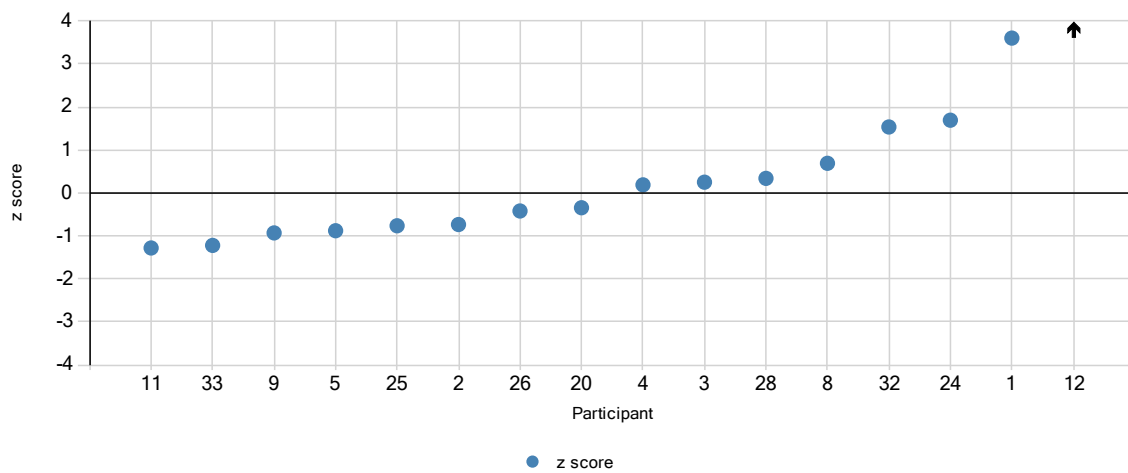
Measurand H<sub>d</sub> Sample B2



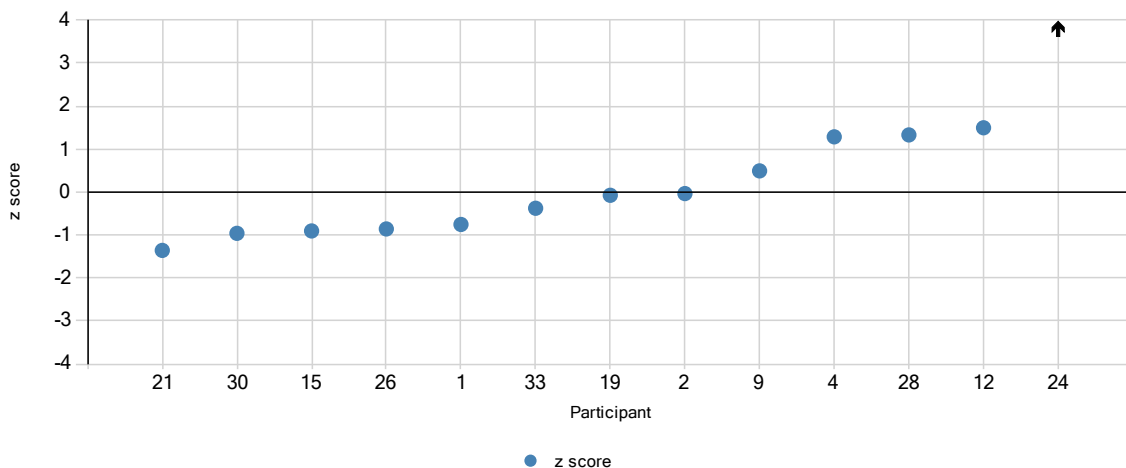
Measurand H<sub>d</sub> Sample B3



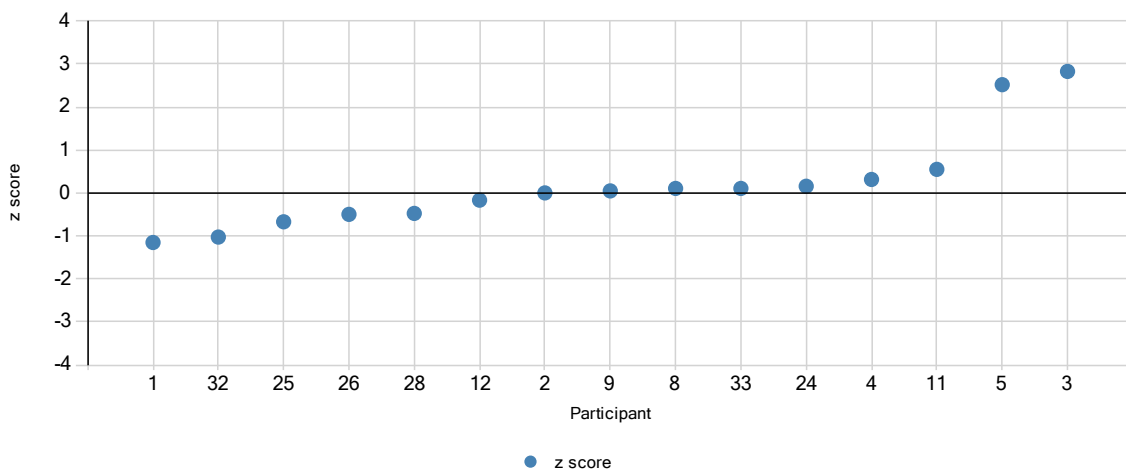
Measurand H<sub>d</sub> Sample K1



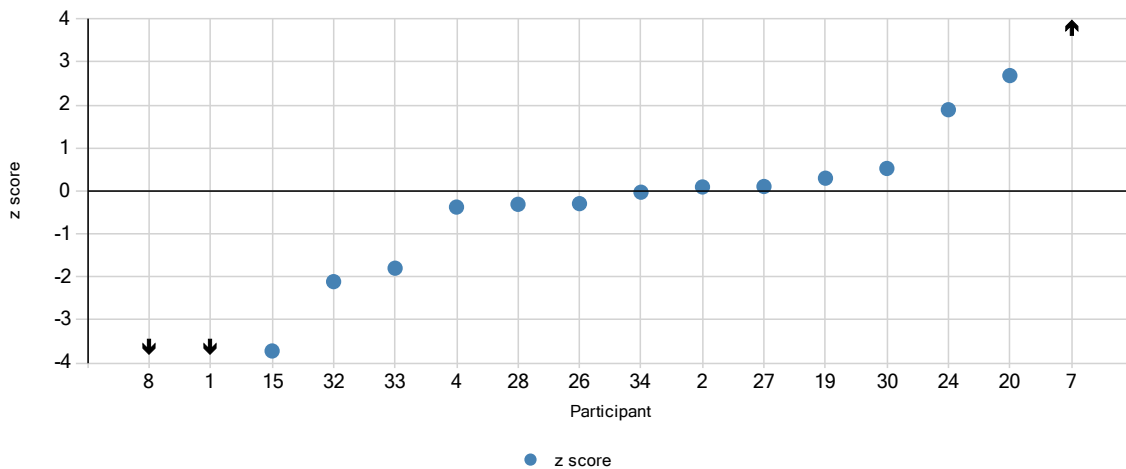
Measurand  $N_d$  Sample B3

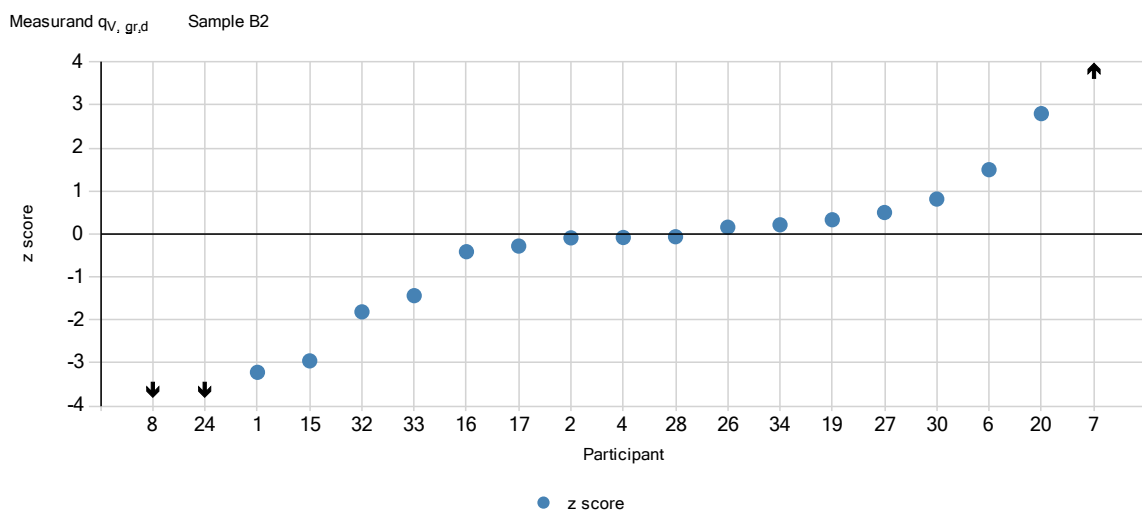
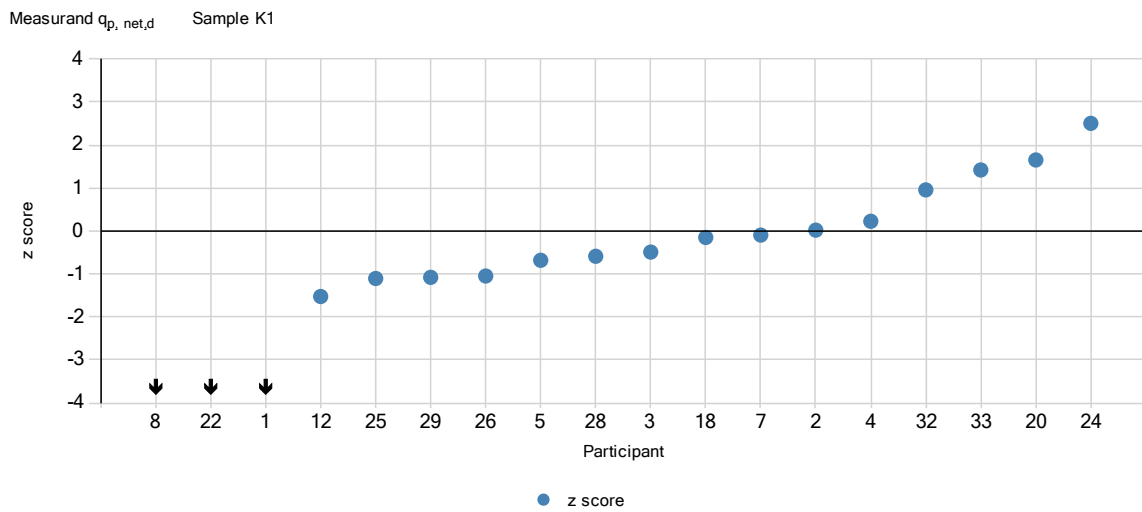
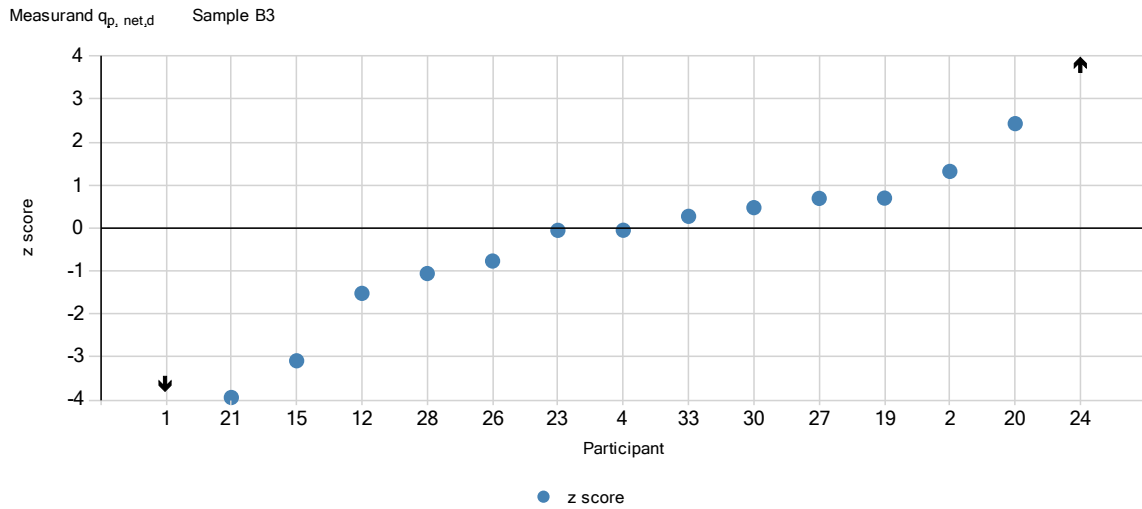


Measurand  $N_d$  Sample K1

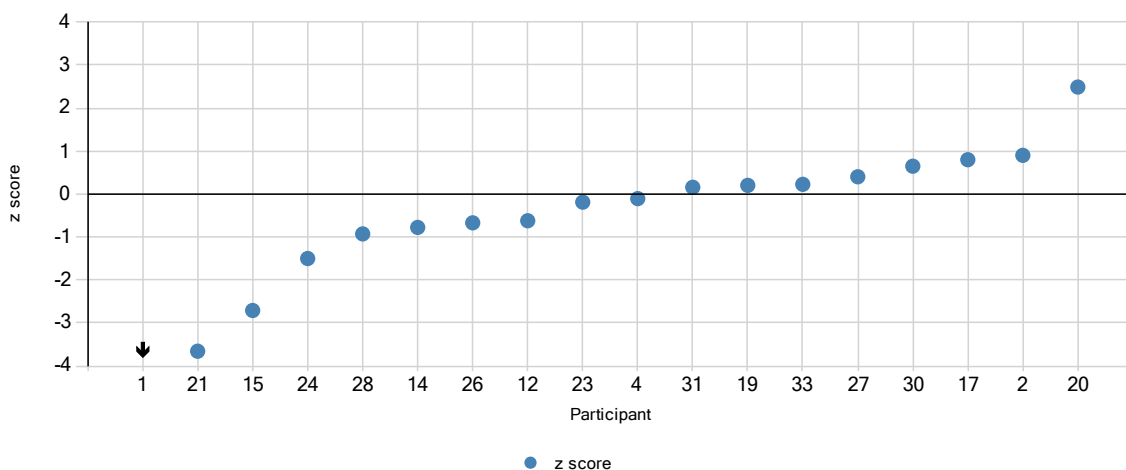


Measurand  $q_{p, net,d}$  Sample B2

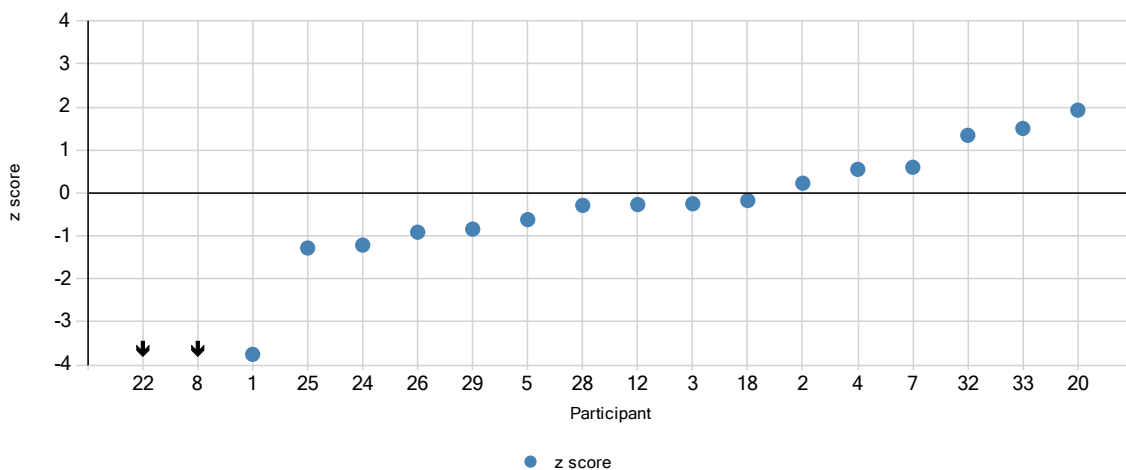




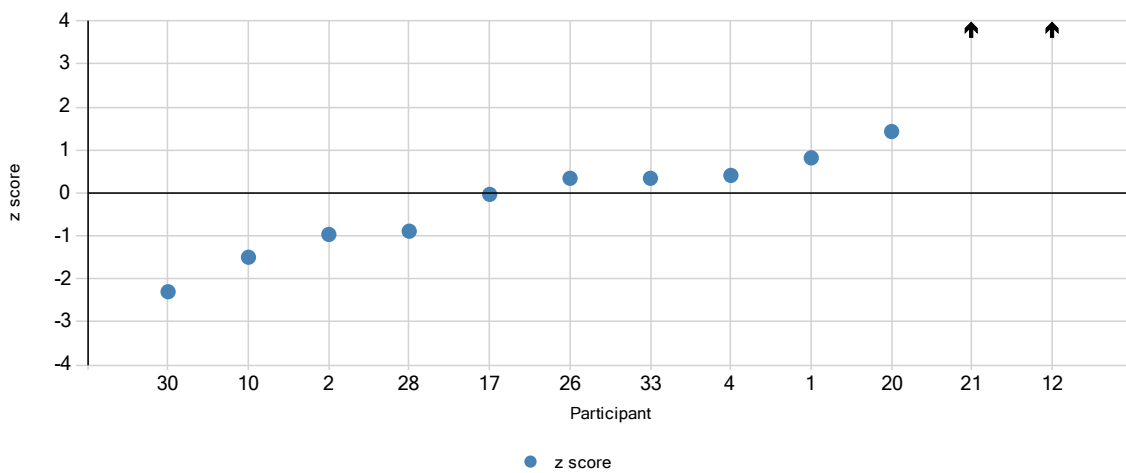
Measurand  $q_{V,gr,d}$  Sample B3



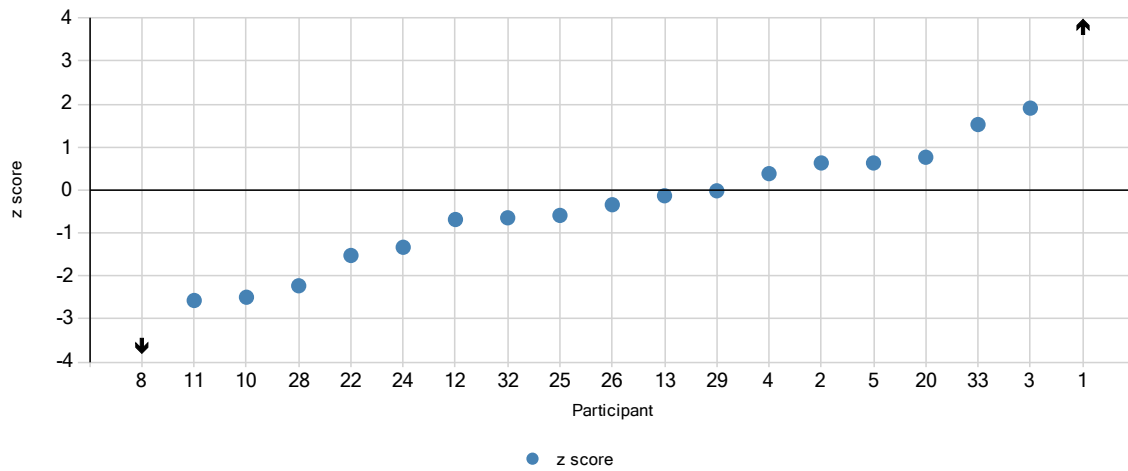
Measurand  $q_{V,gr,d}$  Sample K1



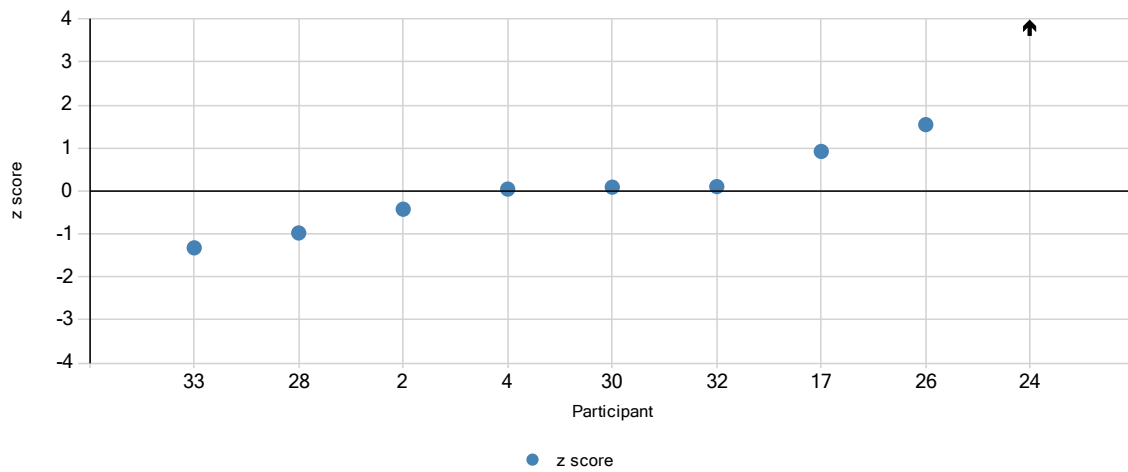
Measurand  $S_d$  Sample B3



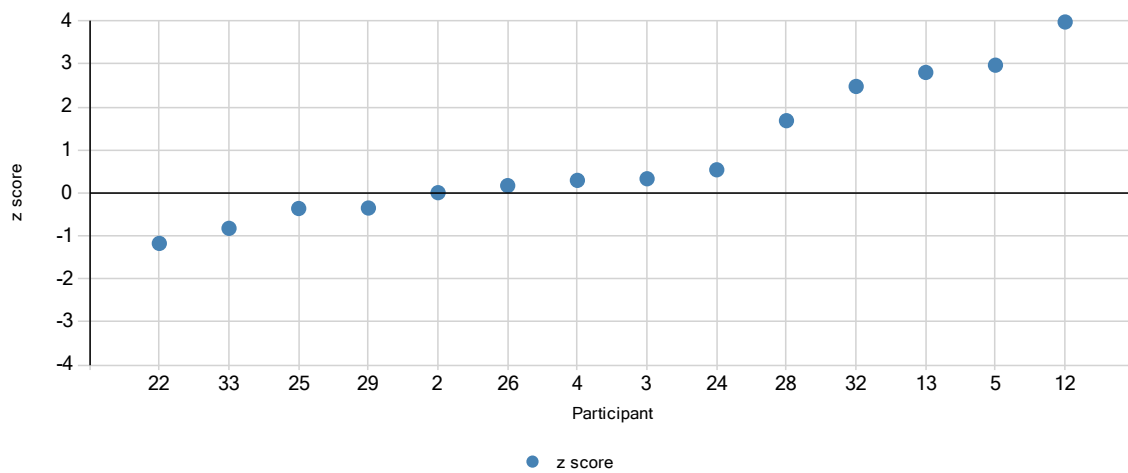
Measurand  $S_d$  Sample K1



Measurand  $V_d$  Sample B2



Measurand  $V_d$  Sample K1



## Appendix 12. Background survey for analytical methods

### Are all the results expressed on a dry basis?

Option	Participants
Yes	1, 2, 3, 5, 6, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 20, 24, 25, 26, 27, 28, 30, 31, 32, 33, 34
No, which results are not?	4: $M_{ad}$ , EF 21: Moisture ( $M_{ad}$ ), EF

### Methods used in $Ash_d$ and the moisture content of analysis sample ( $M_{ad}$ ) measurements:

Measurement	°C	Sample B2 (wood pellet)	Sample B3 (recycle wood)	Sample K1 (coal)
Ash content (ashing temperature °C)	105	part 8		part 8
	550	parts 1, 2, 4, 6, 15, 17, 20, 24, 26, 27, 28, 30, 33, 34	parts 1, 2, 4, 12, 14, 15, 17, 20, 24, 26, 27, 28, 30, 31, 33	part 1
	750		part 21	parts 5, 13, 26
	815	part 32		parts 2, 3, 4, 12, 18, 20, 24, 25, 28, 32, 33
Moisture content of analysis sample, $M_{ad}$ (temperature °C)	40 and 105	part 8		part 8
	105	parts 1, 2, 4, 6, 15, 17, 20, 24, 26, 28, 32, 34	parts 1, 2, 4, 12, 14, 15, 17, 20, 21, 24, 26, 28, 31	parts 1, 2, 3, 12, 18, 20, 24, 26, 28, 32
	107	parts 30, 33	parts 30, 33	parts 4, 5, 13, 25, 33

## Calculations of Emission Factor (EF)

We have used the equation based on the decision EU 2018/2066 [33].

Participant	Answer
2	Emission factor $d/ar = (3.664 * C_d / ar * 10) / Q_{net,d} / ar$
4	Based on national guide
12	Based on national guide
20	Commission Regulation (EU) No 601/2012
21	$EF = ((\%C * Mw_{CO_2}) / MwC) / GCV$
28	Emission factor = $(C (\%) * 36.64) / \text{net calorific value at standard pressure and dry state}$
33	$EF = (8751.3 \times C_d) / PCI_d$

In the cover letter the provider gave the participants the possibility to calculate the EF value using the procedure presented in the EC directive [39, 40] 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 fossil 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 <sub>2</sub> /MJ
C	carbon content as dry, %
M <sub>ar</sub>	total moisture as received, %
Q <sub>net,ar</sub>	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>

## Did you use the total moisture contents as received (M<sub>ar</sub>) mentioned in the covering letter?

Answer	Participants
Yes	2, 3, 4, 8, 12, 28
No, what moisture contents did you use?	1: - 6: - 21: 5.33 33: -

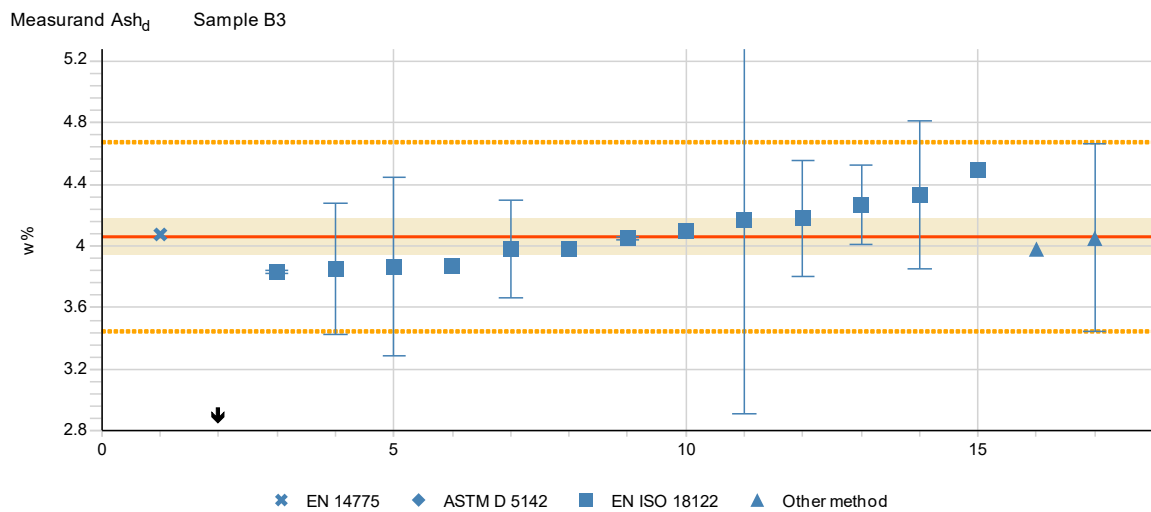
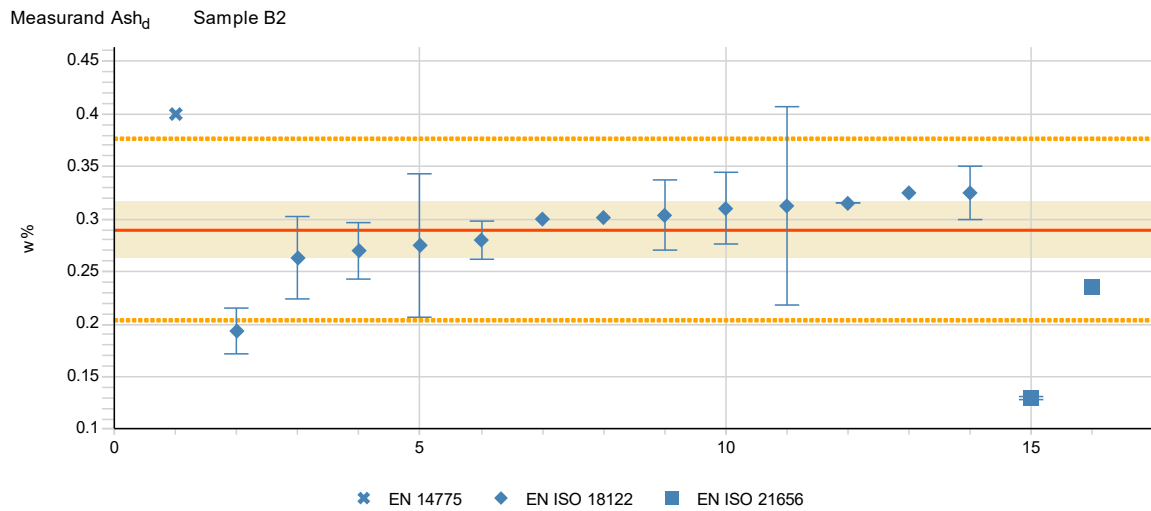
### Which instruments were used for the analyses (name and model)?

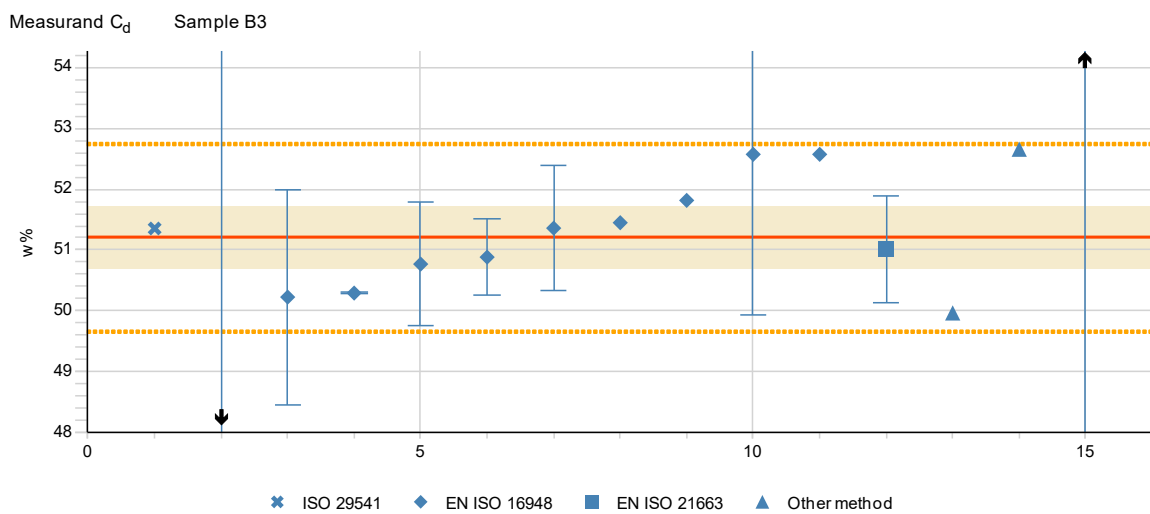
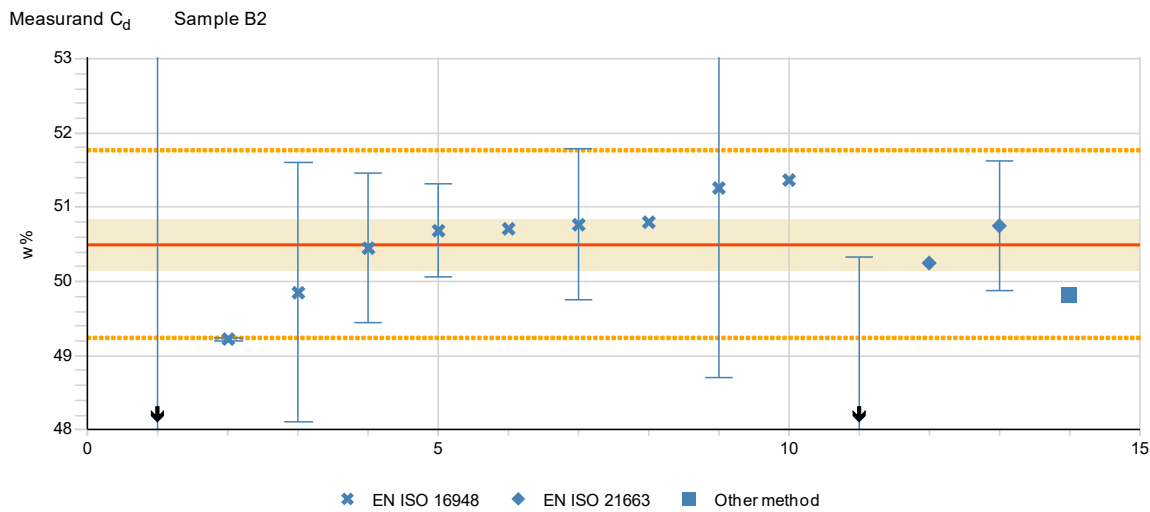
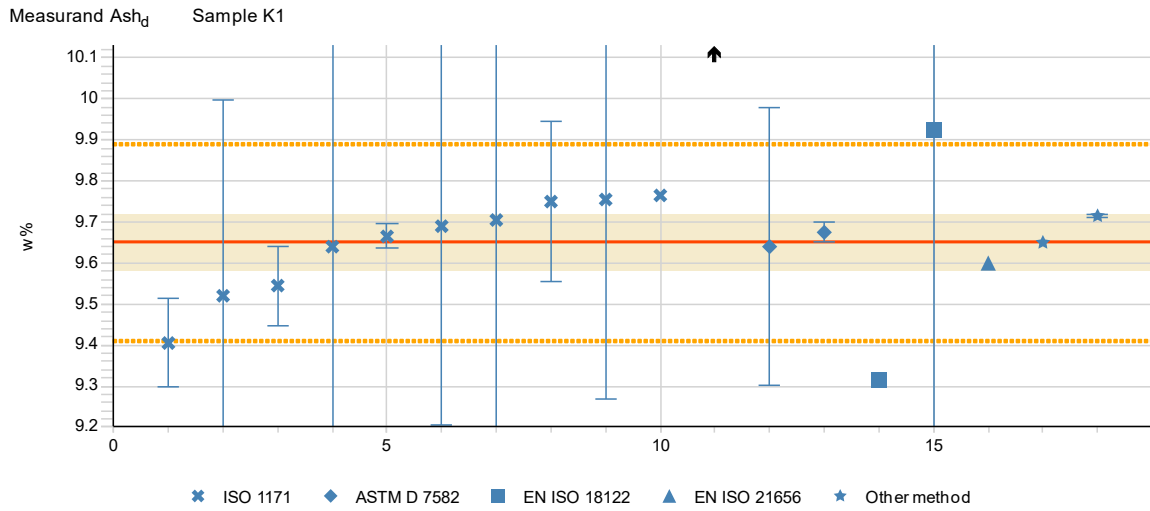
Participant	Calorific value	Ash	Volatiles	Sulphur	CHN	Halogens
1	AC600 Semi-Automatic Isoperibol Calorimeter Gross Calorific Content	Thermolyne tabletop muffle furnace	-	S832 sulphur analyzer	CHN828 Carbon, Hydrogen, and Nitrogen Analyzer	-
2	LECO AC600	Nabertherm N7/H	Carbolite VMF 10/6	LECO S832	LECO CHN828	Dionex Aquion
3	Parr, IKA	Vulcan	Snol	Eschka		
4	LECO AC600	LECO TGA701	Nabertherm C450	Leco SC832DR	Leco CHN628	Metrohm IC Flex 930
5	IKA C6000 Global Standard (isoperibol)	LECO Thermogravimetric analyzer TGA 701	LECO Thermogravimetric analyzer TGA 701	LECO CHN628 series sulfur	LECO CHN628 Carbon/Hydrogen/Nitrogen determinator	-
6	Calorimeter with Parr thermometer, PLAIN mod.6772	Muffle furnace SNOL-7.2	-	-	-	-
8	Calorimeter IKA C6000 isoperibol	CARBOLITE Gero 30-3000°C	-	Halogen Ion Chromatography Methrom 930 IC Compact Flex	Vario MACRO cube	Halogen Ion Chromatography Methrom 930 IC Compact Flex
9	-	-	-		Perkin Elmer 2400 Series II	-
10	-	-	-	ICP-OES 8300		
12	IKA C6000	TGA 701	TGA 701	LECO 628S	LECO CHN628	Sherwood Chloride Analyser 926
13		LECO TGA701	LECO TGA701	Eltra CS-580A	Eltra CS-580A	
14	IKA C6000	Nabertherm LT9/11/P330	-	-	Skalar PRI-MACS ATC 100 - IC-E	
15	Leco AC 600	Nabertherm N11/HR	-	Thermo Scientific Flash 2000	Thermo Scientific Flash 2000	Leco AC 600 and Thermo Scientific Dionex ICS-6000
16	Parr6400, MKPARR	-	-	-	-	-

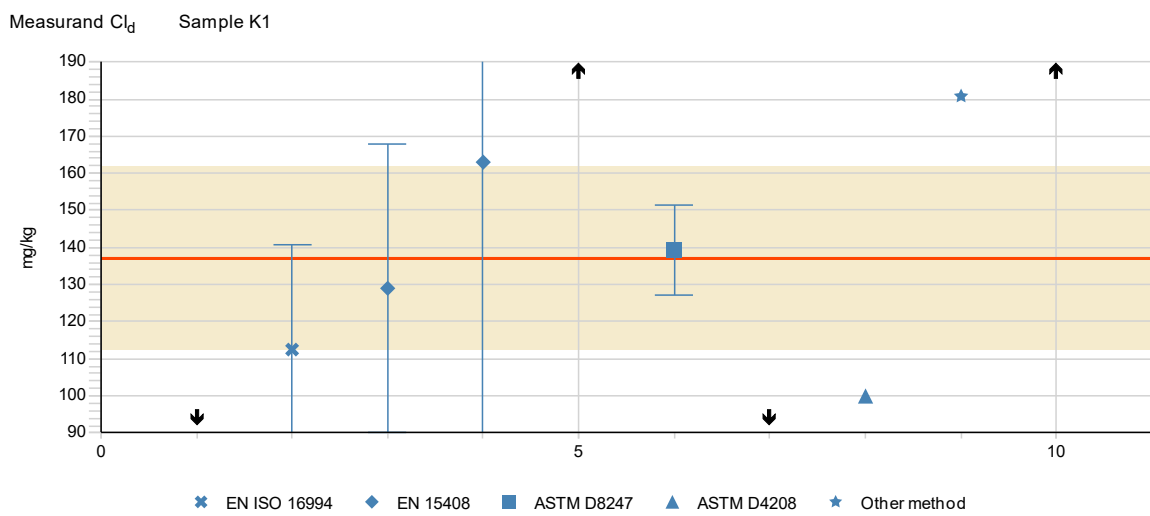
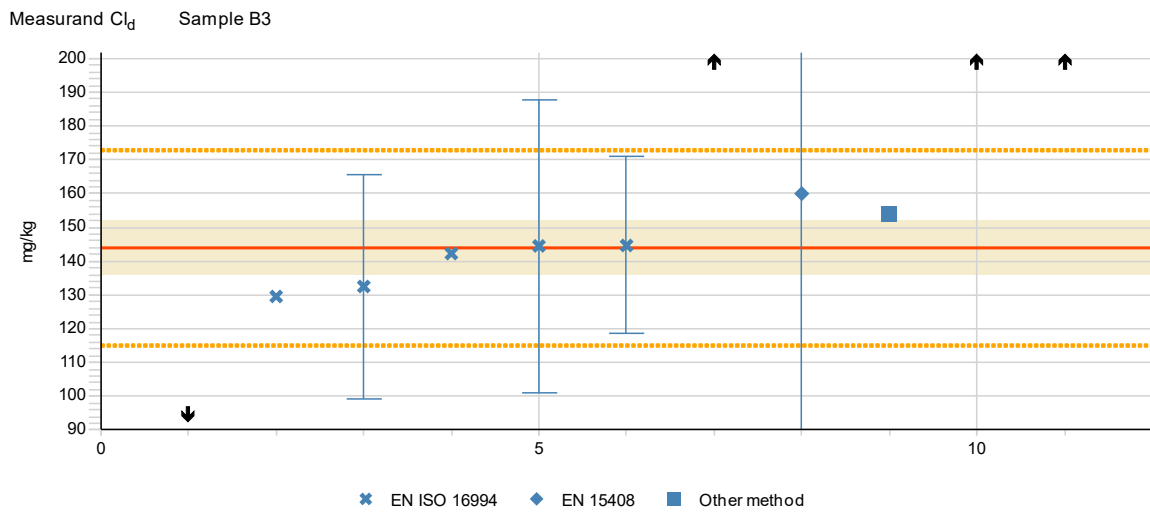
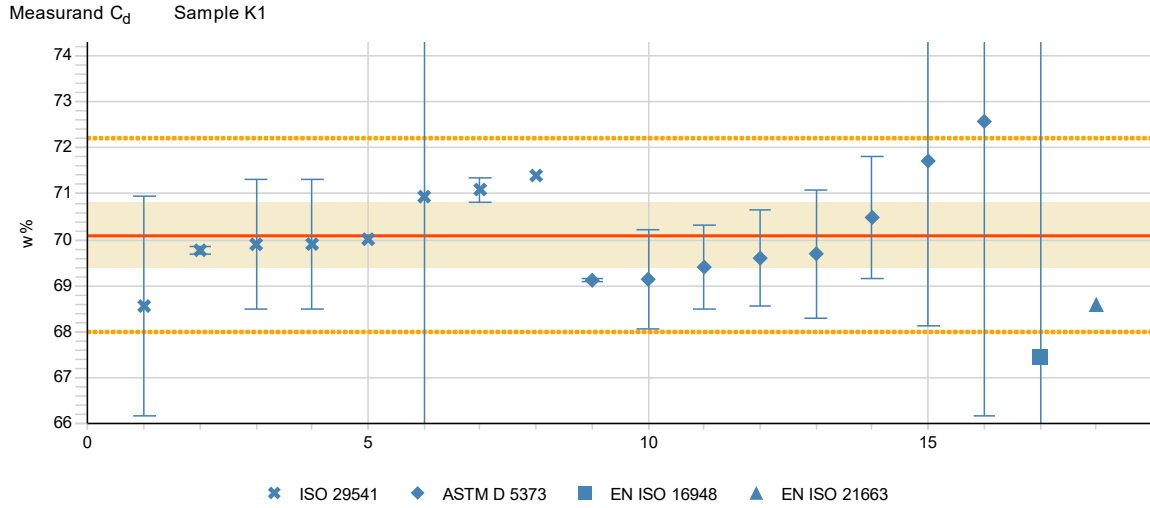
Participant	Calorific value	Ash	Volatiles	Sulphur	CHN	Halogens
17	LECO AC-250	Annealing furnace Nabertherm	Annealing furnace Nabertherm	ICP-OES Thermo Scientific iCAP Pro	-	IC, Dionex ICS-1600 ionikromatografi Thermo Scientific
18	Calorimetric system adiabatic IKA C 5000	Furnance LAC	-	-	Instrumental NDIR Analyzer Multi EA 2000	-
20	Parr 6200	Nabertherm L9	-	Leco SC 832	Leco SC 832, Eltra CHS 580	-
21	Automatics Bomb Calorimeter, Model: AC 600	Furnace, Model: New-2	Furnace, Model: New-2	Sulfur Analyzer, Model: S632	CHN Analyzer, Model: Truspec	-
24	Calorimeter IKA C5000	Snol oven 8,2/1100	Snol oven 8,2/1100	Elemental Analyzer FlashSmart	Elemental Analyzer FlashSmart	-
25	Calorimeter C6400 Parr	Four Carbolite AAF 18	Four Carbolite AAF 18	Vario MACRO - Elementar with TCD and infrared	Vario MACRO - Elementar with TCD and infrared	C-IC Metrohm
26	Parr 6400	Electric furnace	Electric furnace	5E-IRS3600	Thermo Scientific flash2000 series	ICS-2100/AQF-2100H
27	Parr 6300	-	-	-	-	-
28	Parr	TGA for coal and muffle furnace for biofuel	TGA	ELTRA Helios	LECO 628	IC
30	IKA C6000	Eltra Thermostep TGA	Eltra Thermostep TGA	Dionex ICS-1100	Leco CHN828	-
31	Parr 6400	Nabertherm LVT 15/11 B180	-	-	-	-
32	LECO AC 600	Carbolite	Carbolite	CHN Truspec	CHN Truspec	Methrom pH/ion meter
33	Parr 6400	oven Nabert-herm LV15	oven Nabert-herm LV15	CHNS Elementar Vario Cube	CHNS Elementar Vario Cube	Metrohm 930
34	Parr 6400	Nabertherm LV9/11C550	-	-	-	-

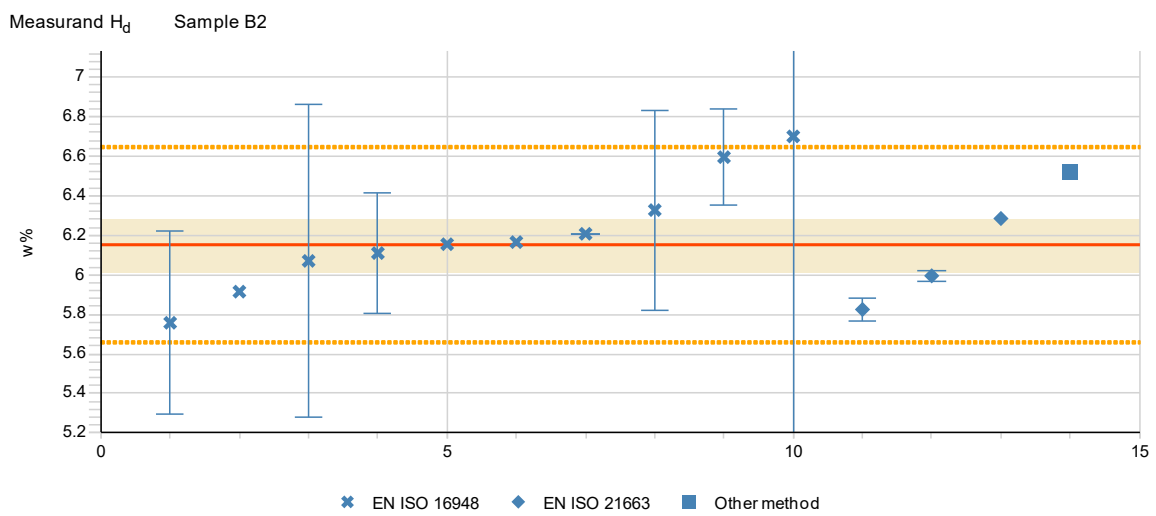
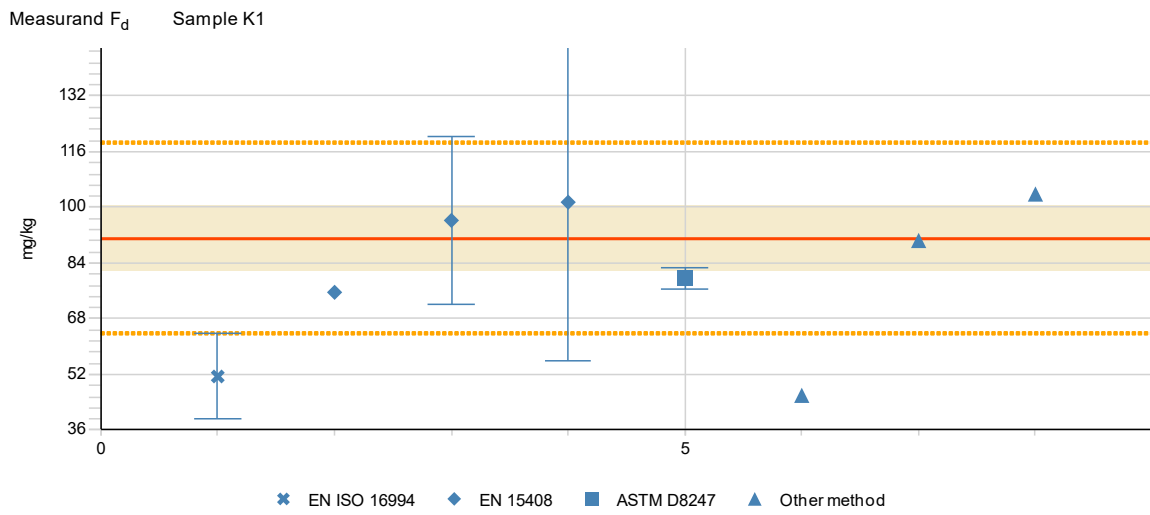
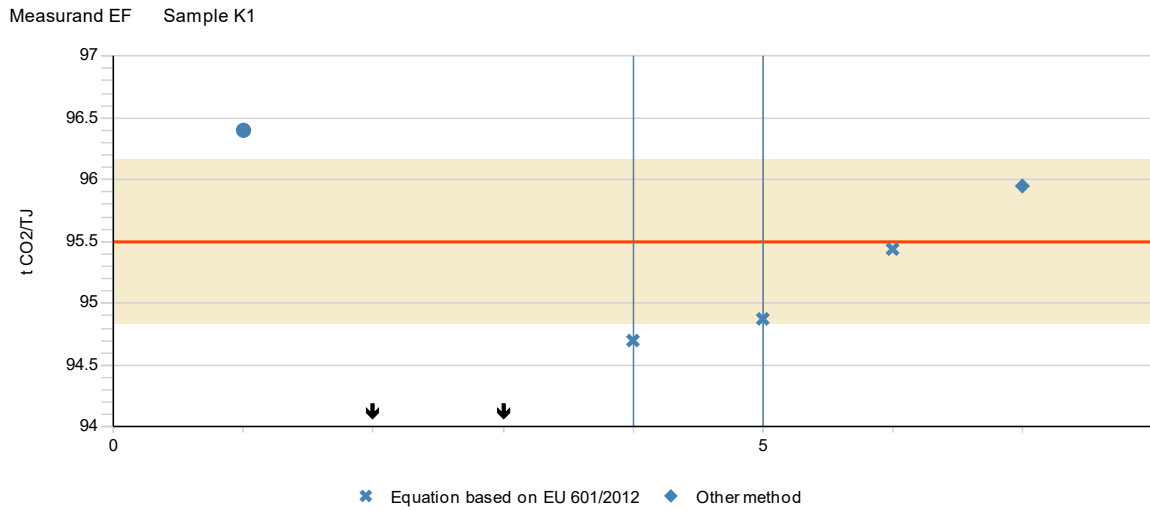
## Appendix 13. Results grouped according to the methods

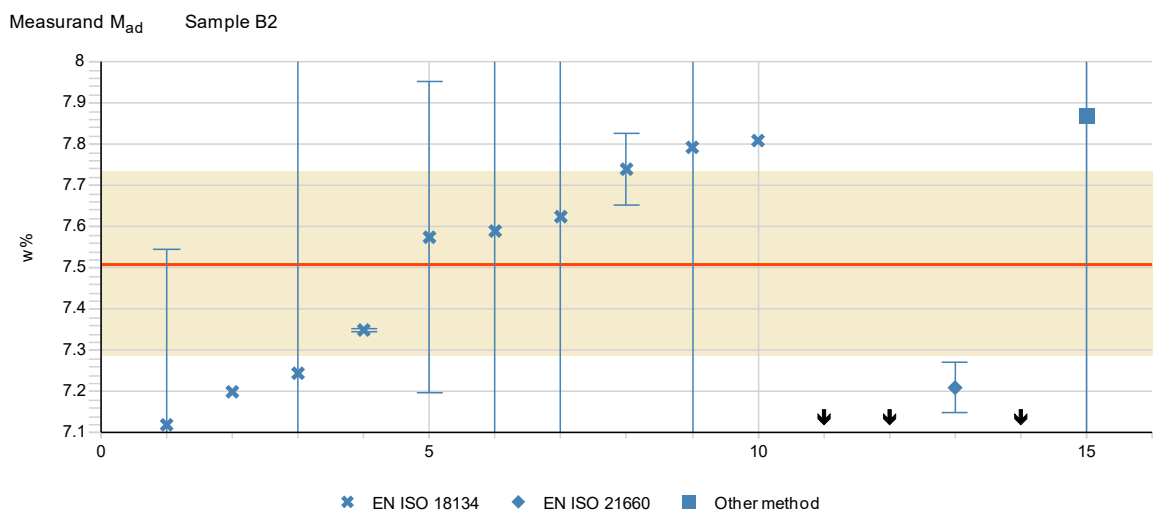
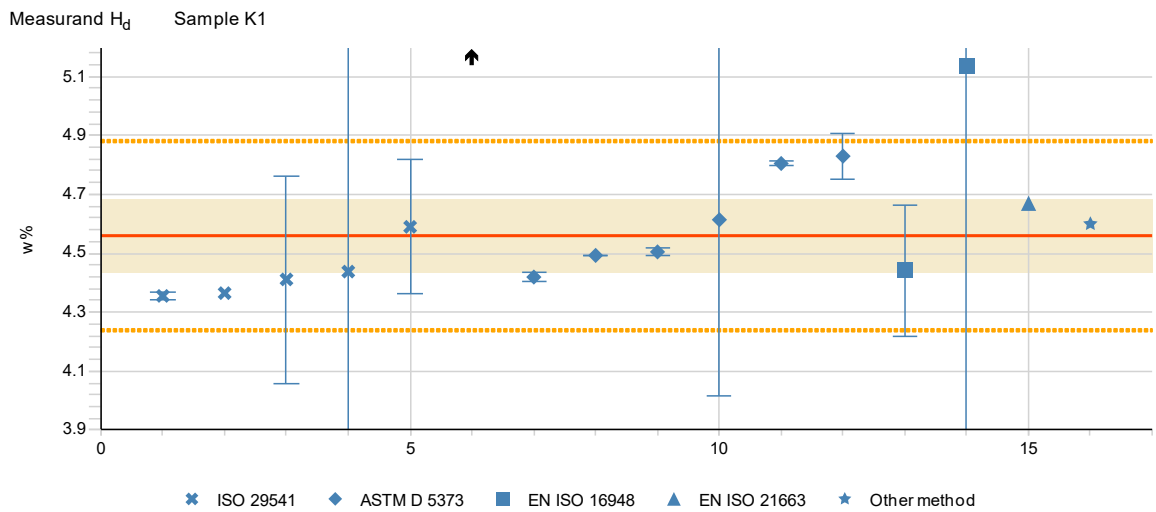
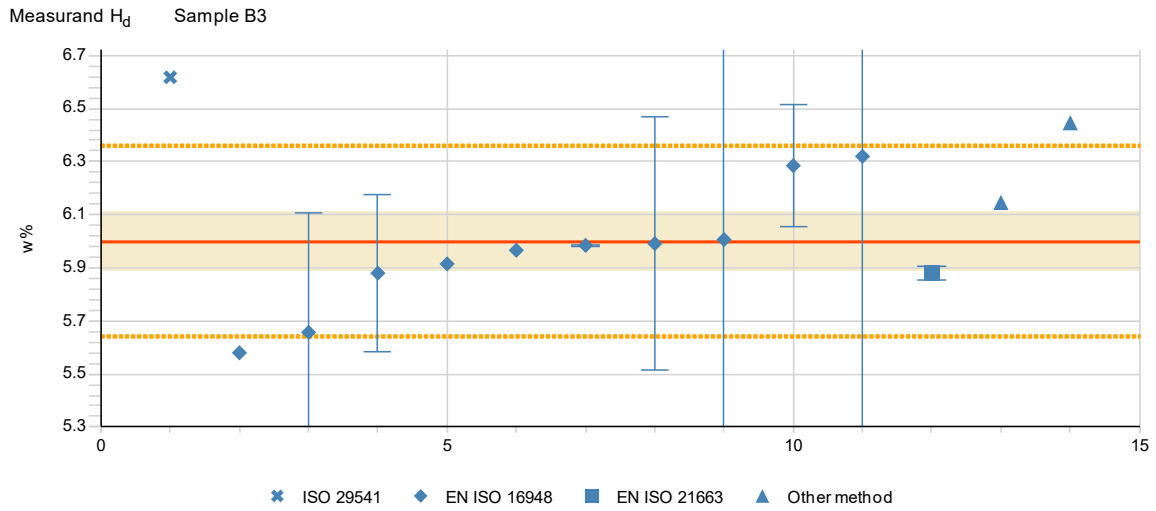
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



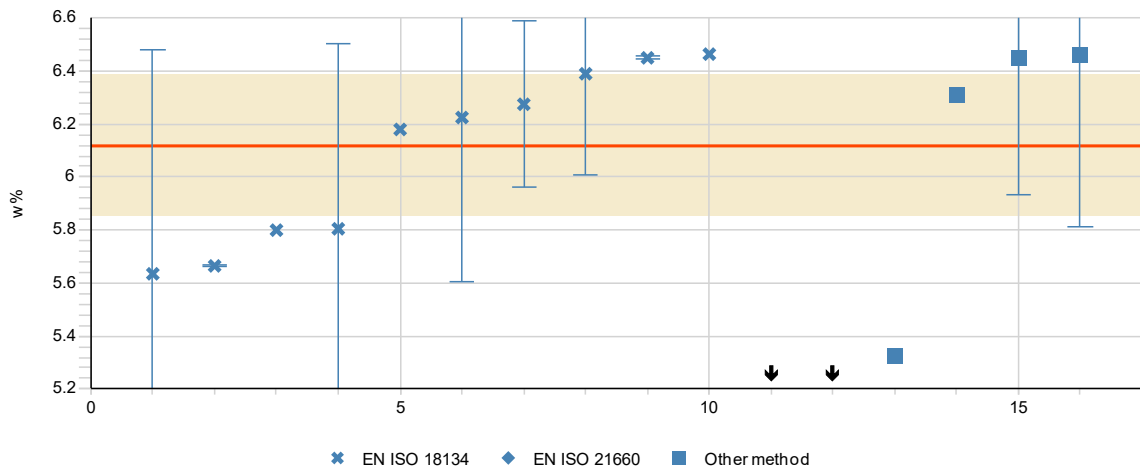




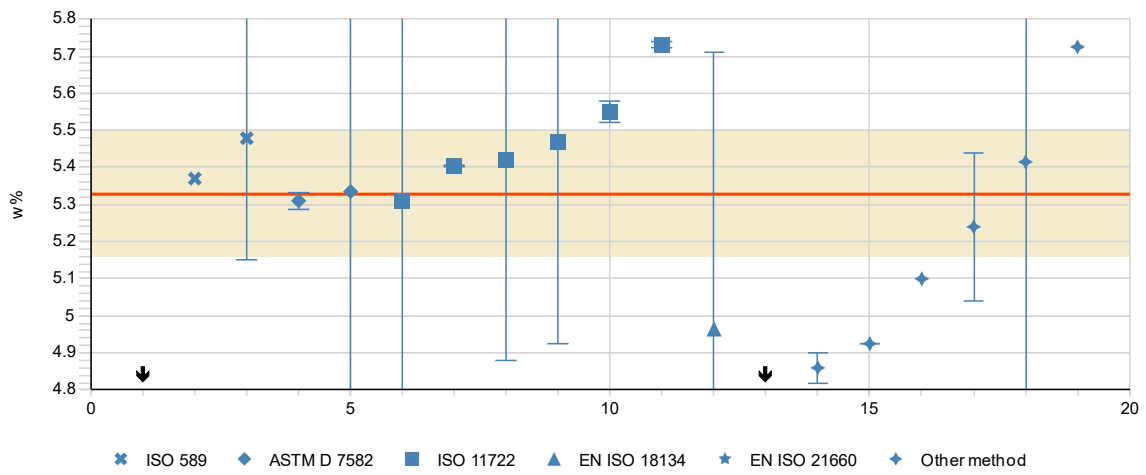




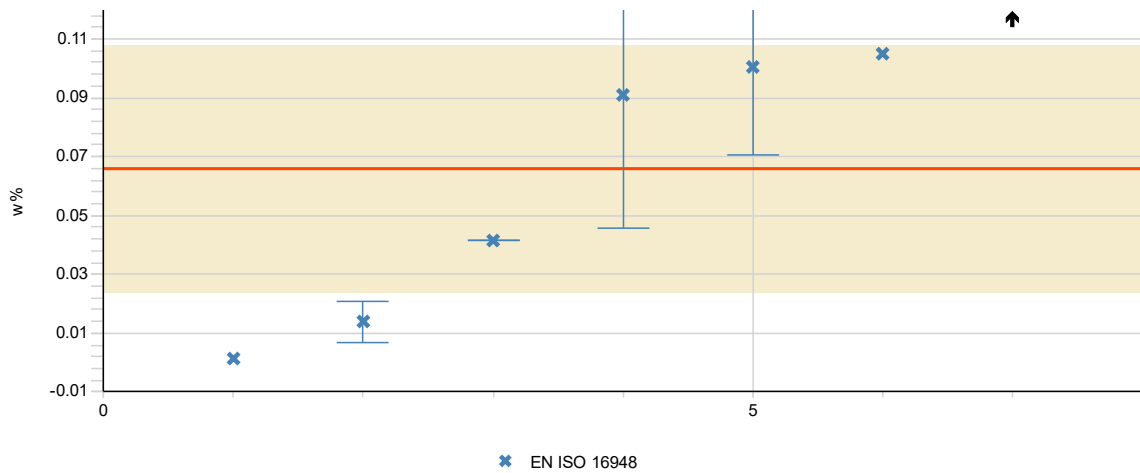
Measurand  $M_{ad}$  Sample B3

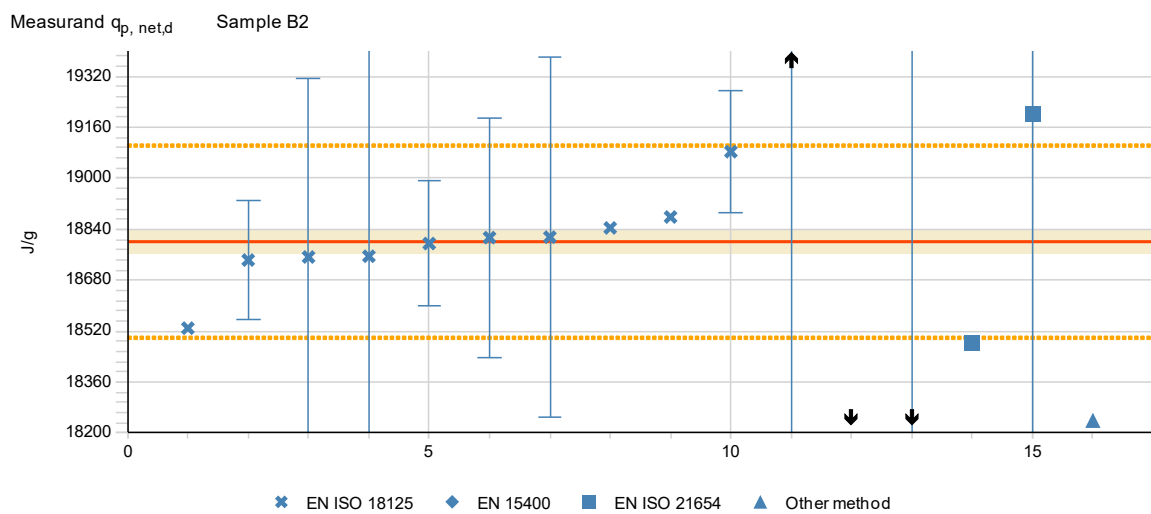
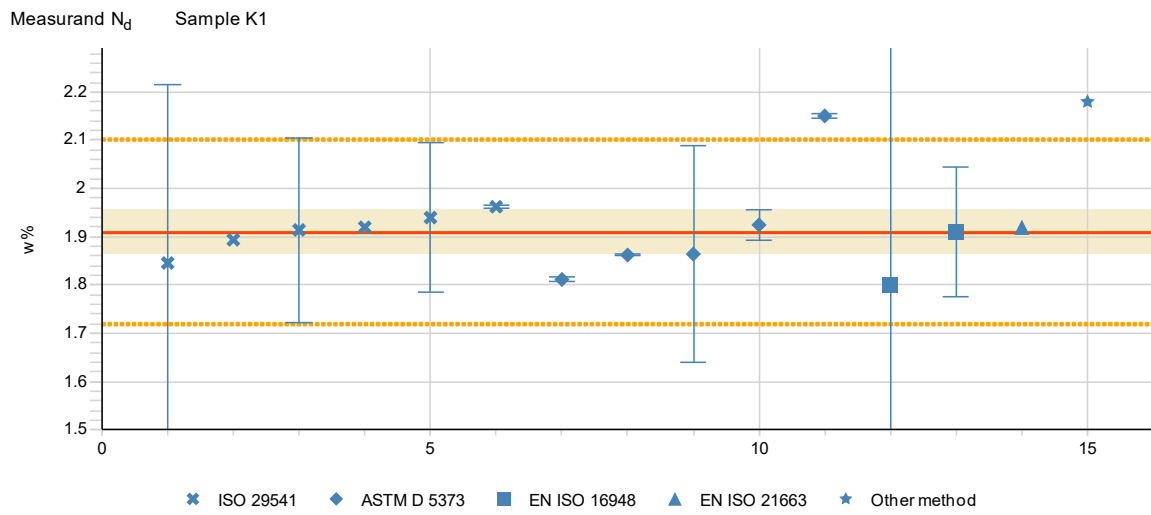
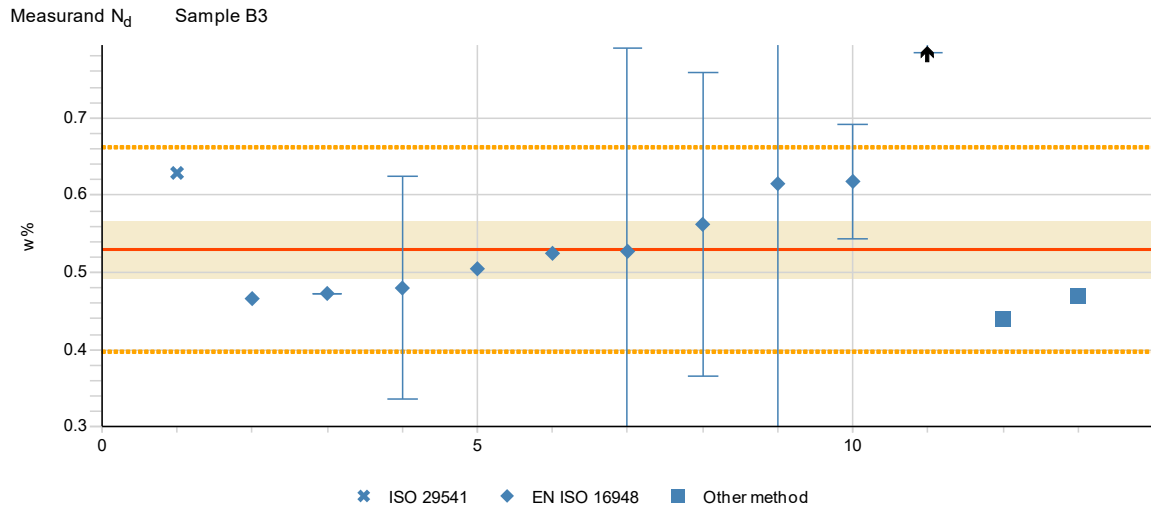


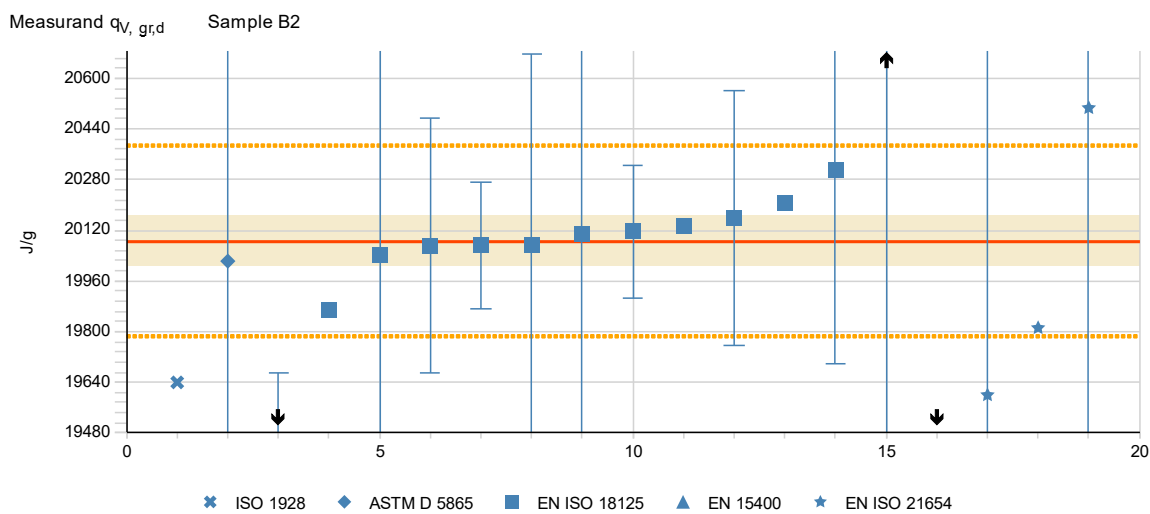
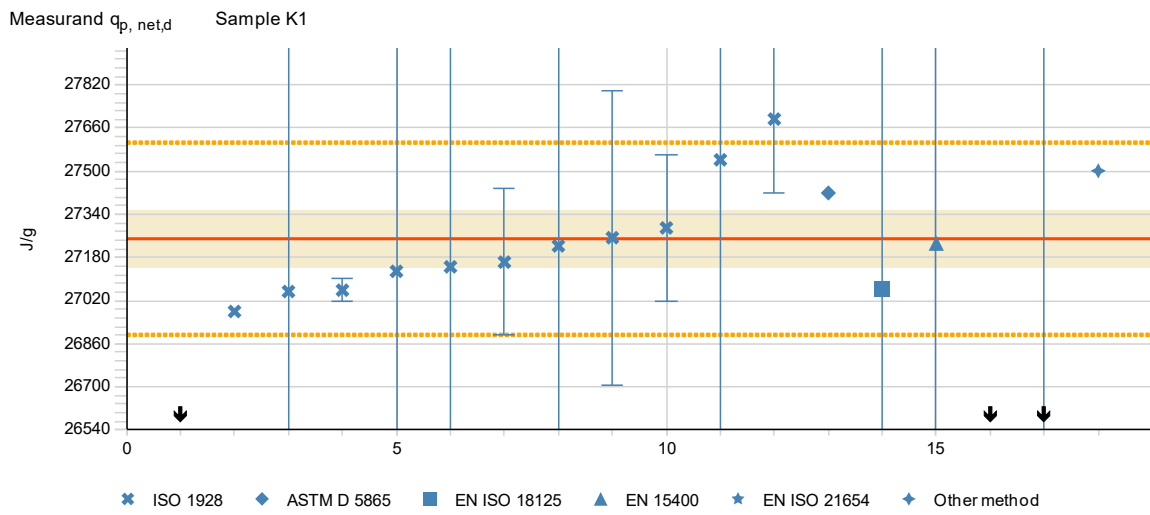
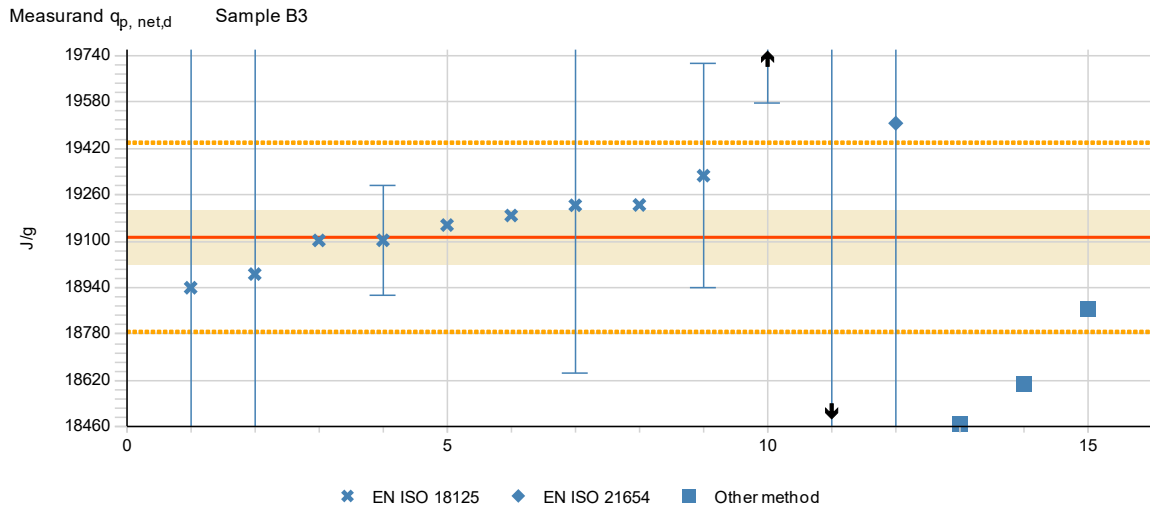
Measurand  $M_{ad}$  Sample K1

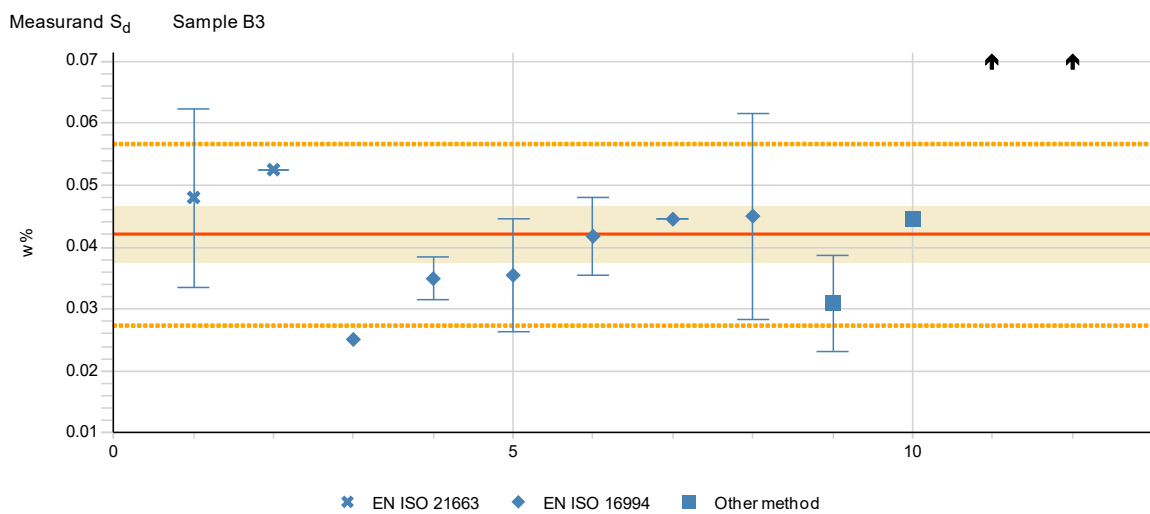
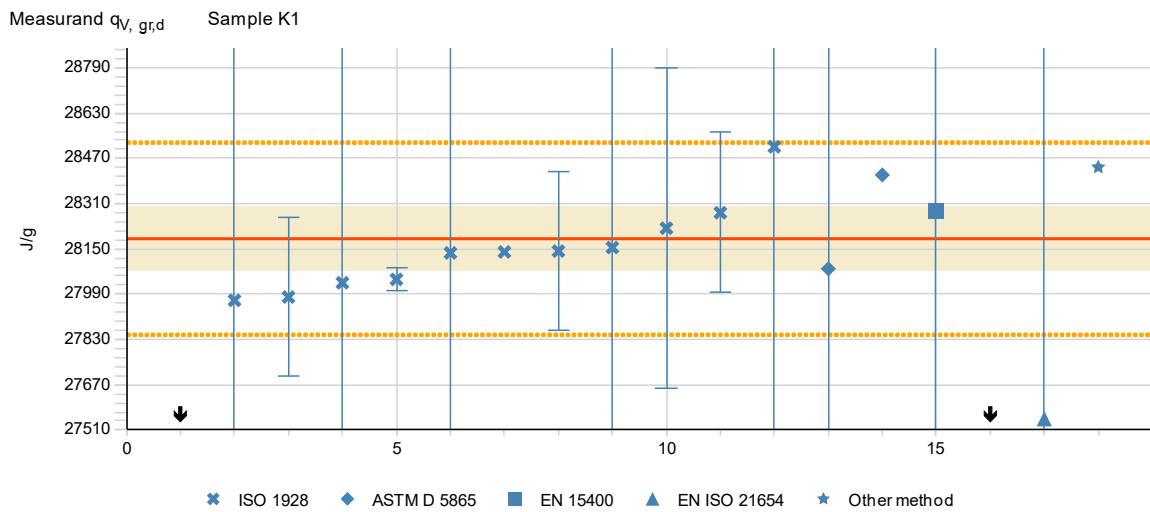
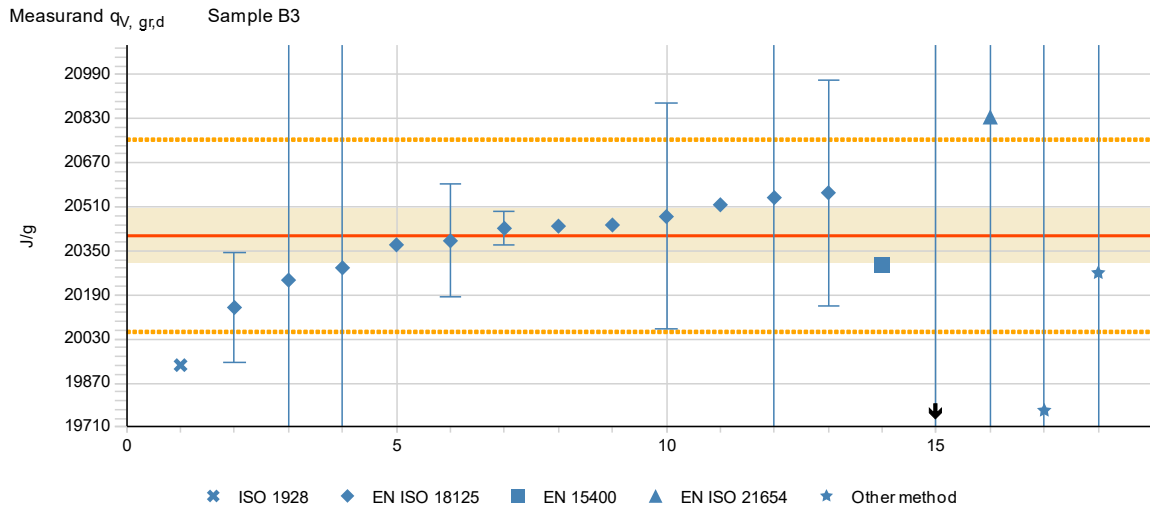


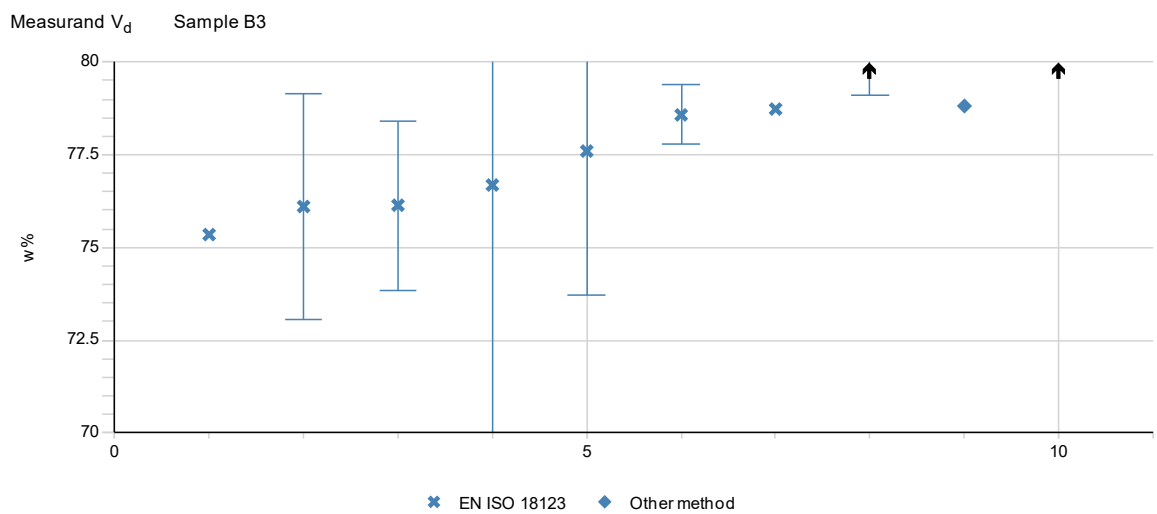
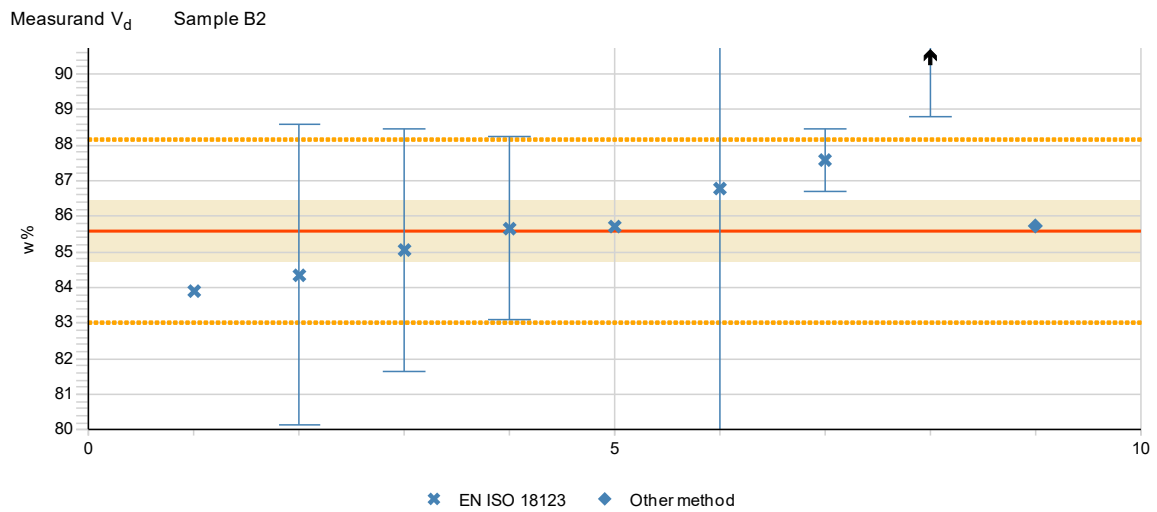
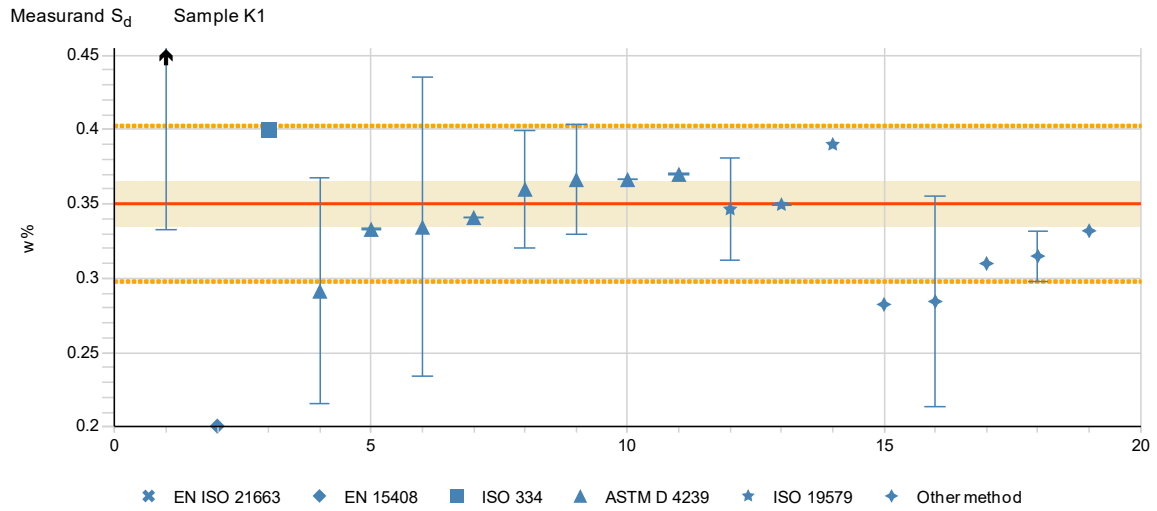
Measurand  $N_d$  Sample B2

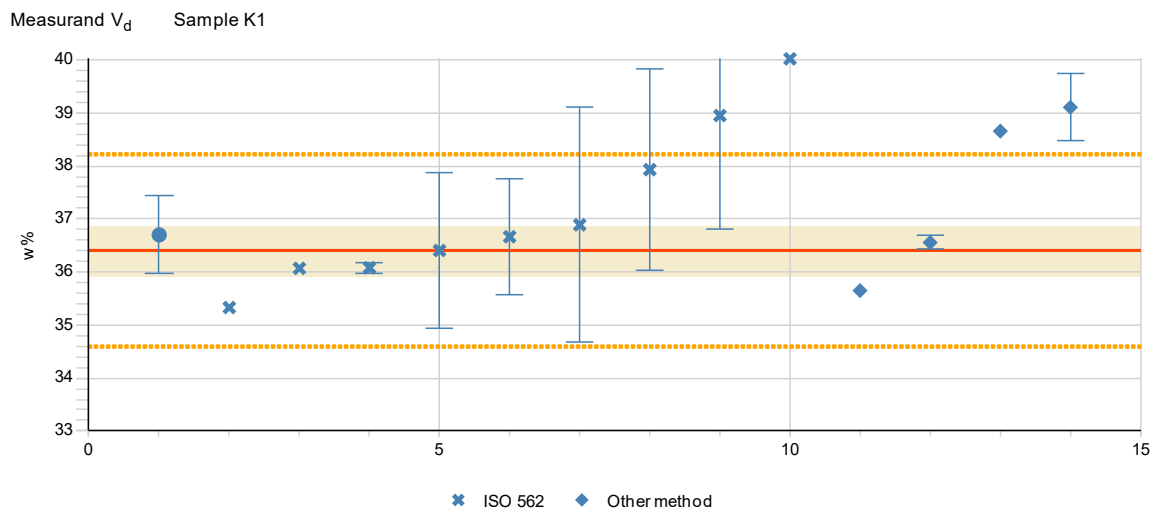






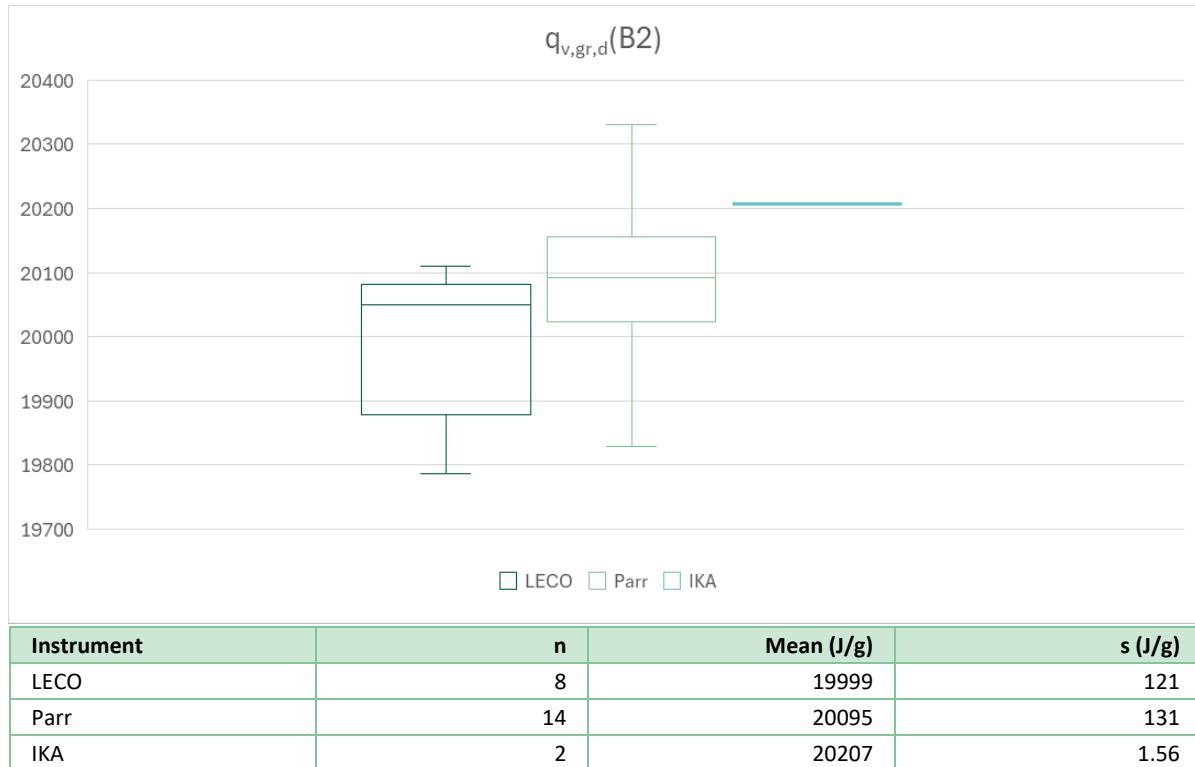




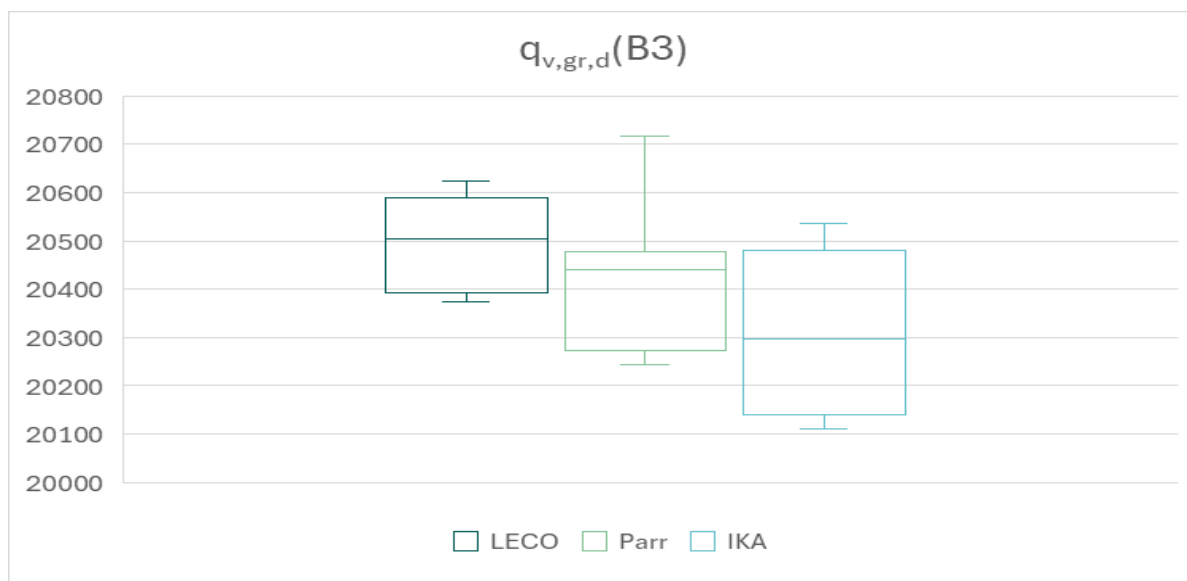


## Appendix 14. Significant differences in the gross calorific value results between instruments

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The horizontal line in the middle of the box is the median of the results. The horizontal lines above and under the box include majority of the results.

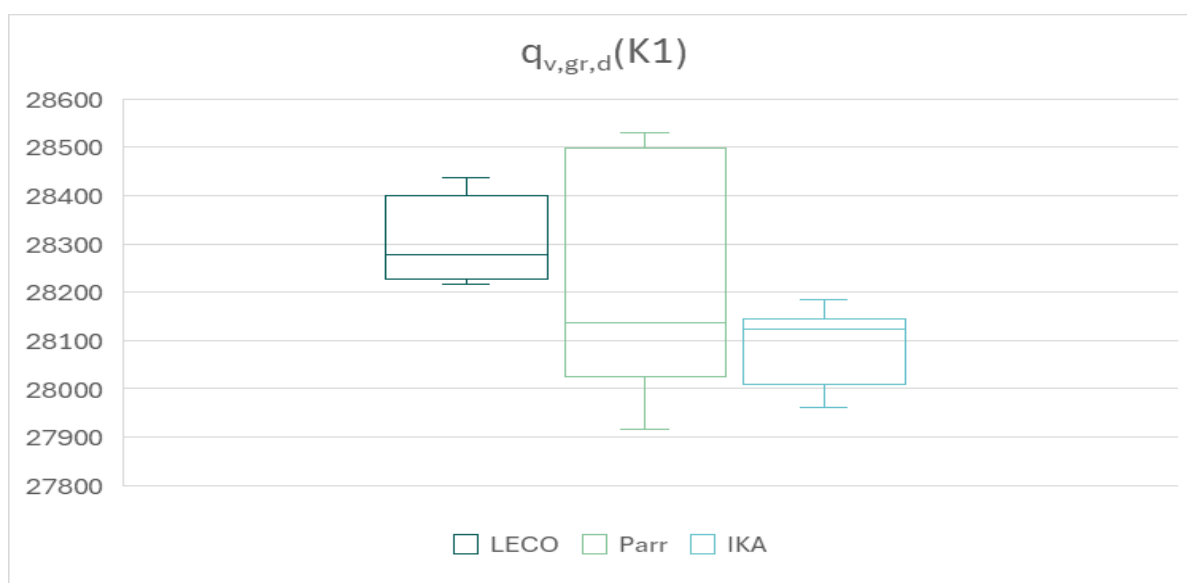


n = number of results; s = standard deviation



Instrument	n	Mean (J/g)	s (J/g)
LECO	6	20497	97.7
Parr	12	20453	207
IKA	8	20307	167

n = number of results; s = standard deviation

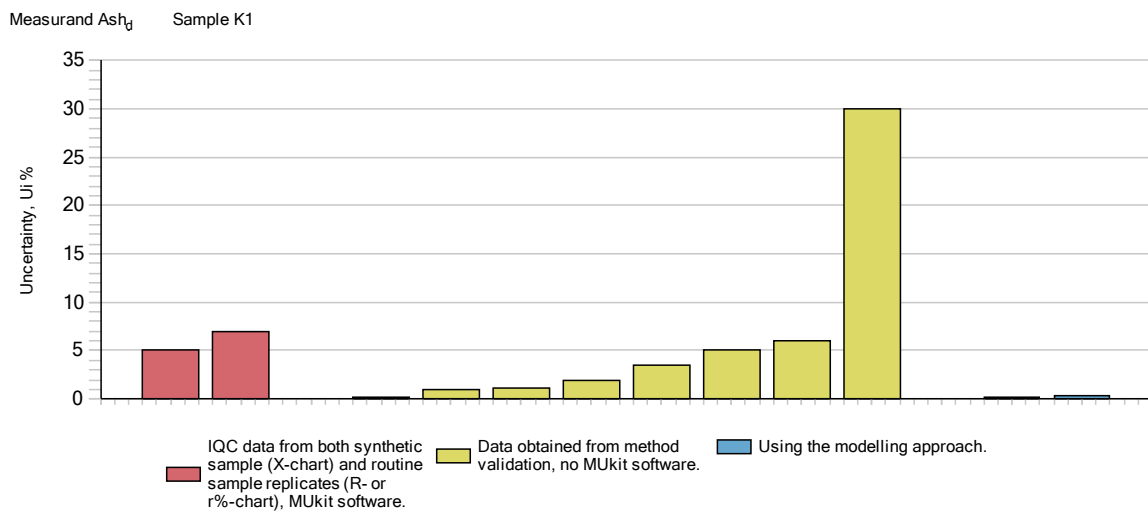
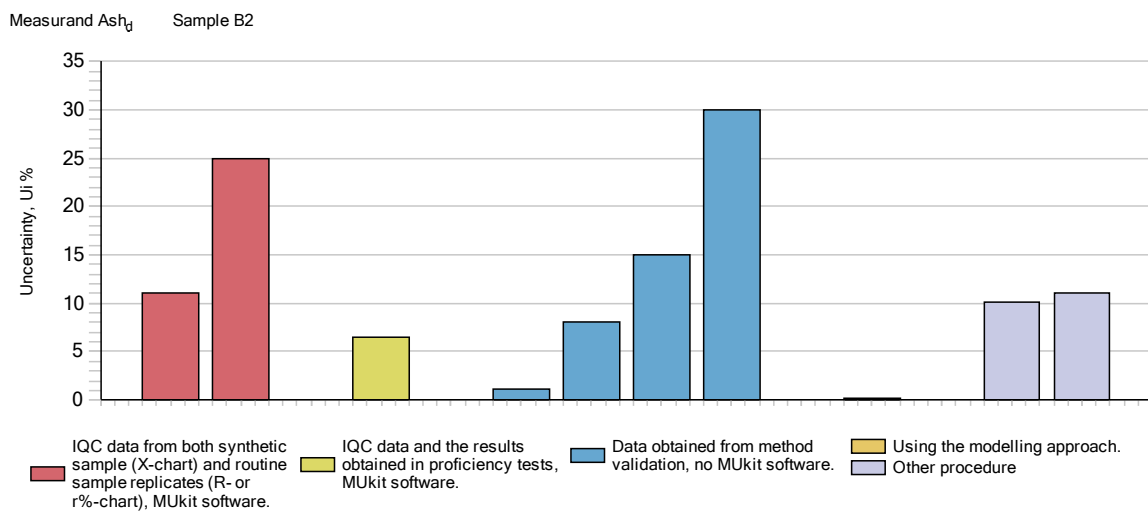


Instrument	n	Mean (J/g)	s (J/g)
LECO	6	28304	89.9
Parr	10	28217	235
IKA	8	28089	79.3

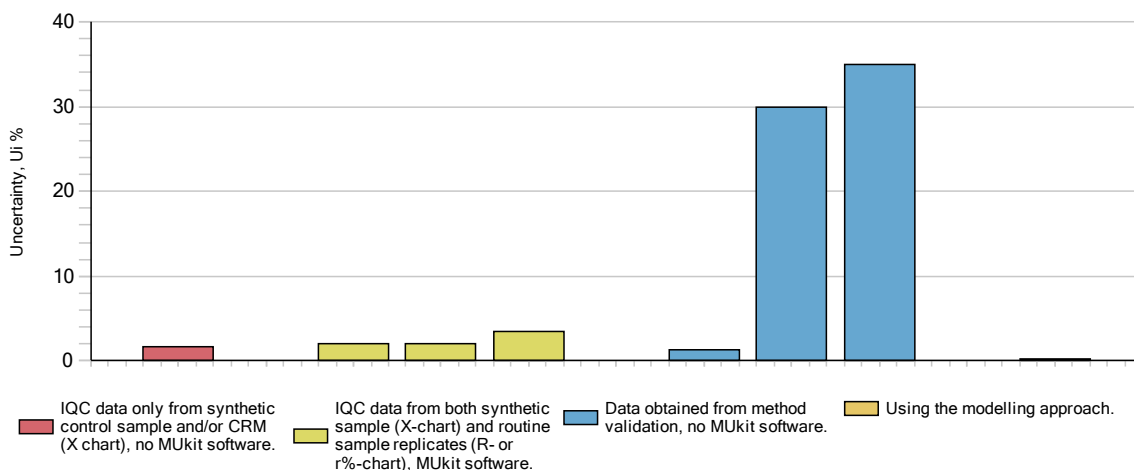
n = number of results; s = standard deviation

## Appendix 15. Examples of measurement uncertainties reported by the participants

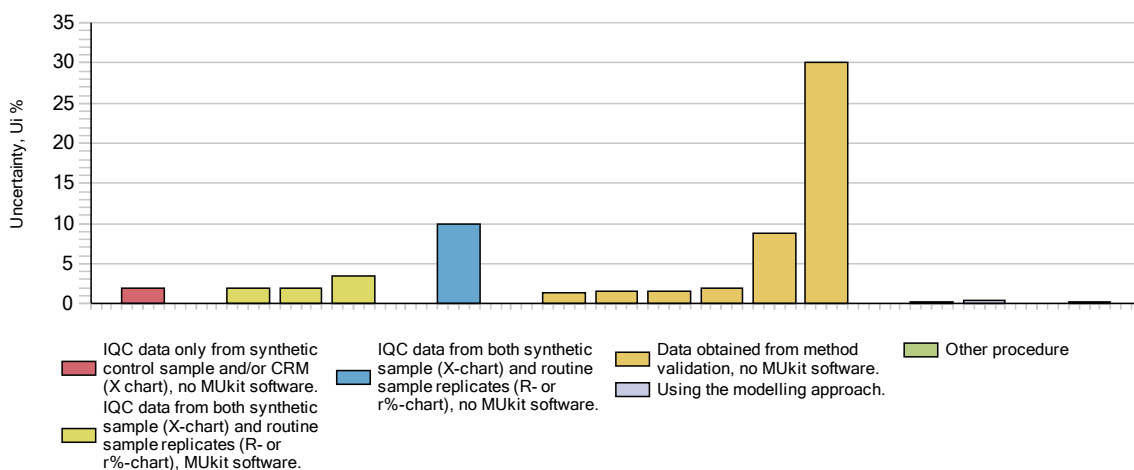
In figures, the presented expanded measurement uncertainties are grouped according to the method of evaluation at 95 % confidence level ( $k=2$ ). The expanded uncertainties were evaluated mainly by using the internal quality control (IQC) data and data obtained from method validation. The used procedures in figures below are distinguished e.g. between using or not using the MUKIT software for uncertainty evaluation [37, 38] or using a modelling approach based [41, 42].



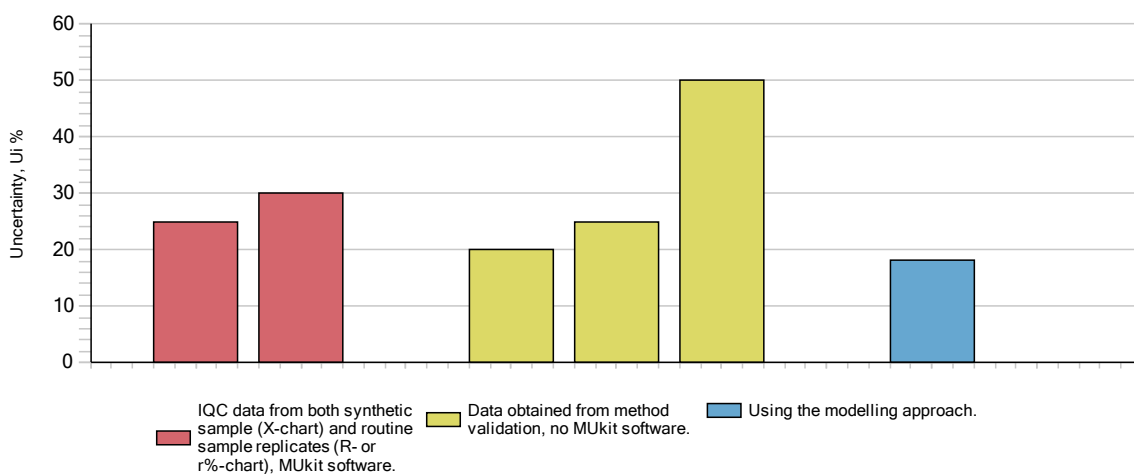
Measurand C<sub>d</sub> Sample B3

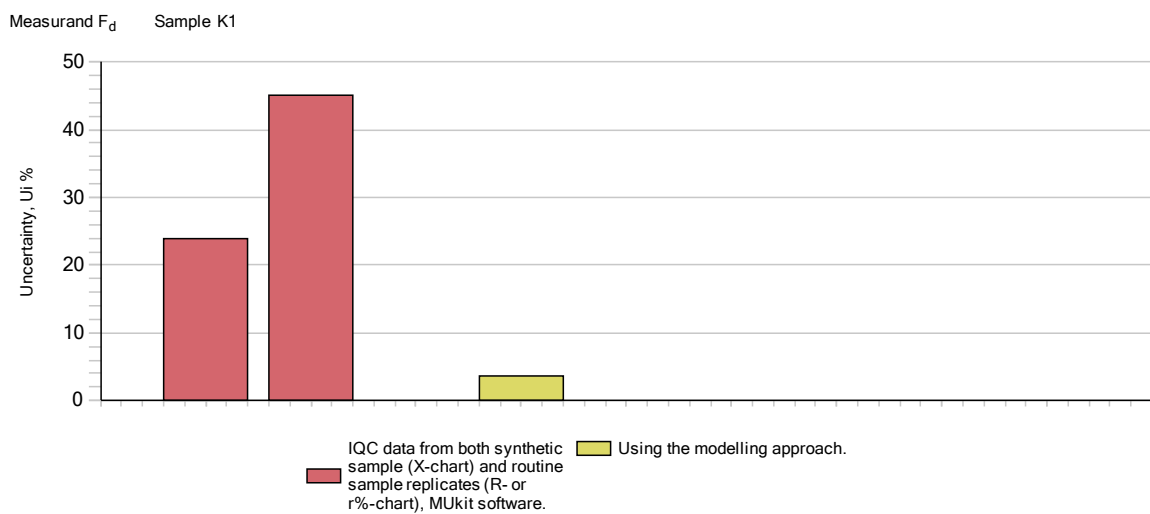
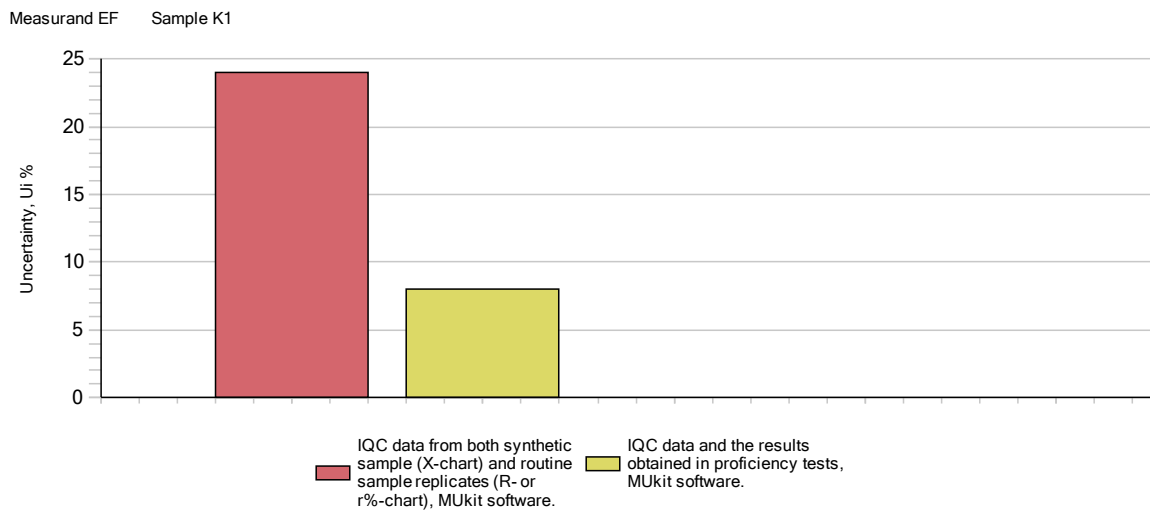
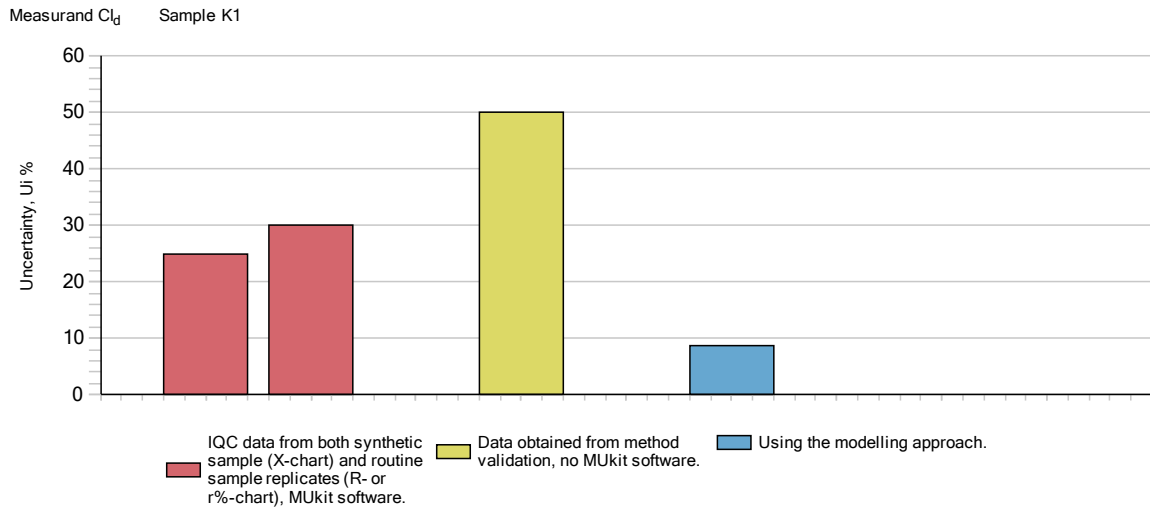


Measurand C<sub>d</sub> Sample K1

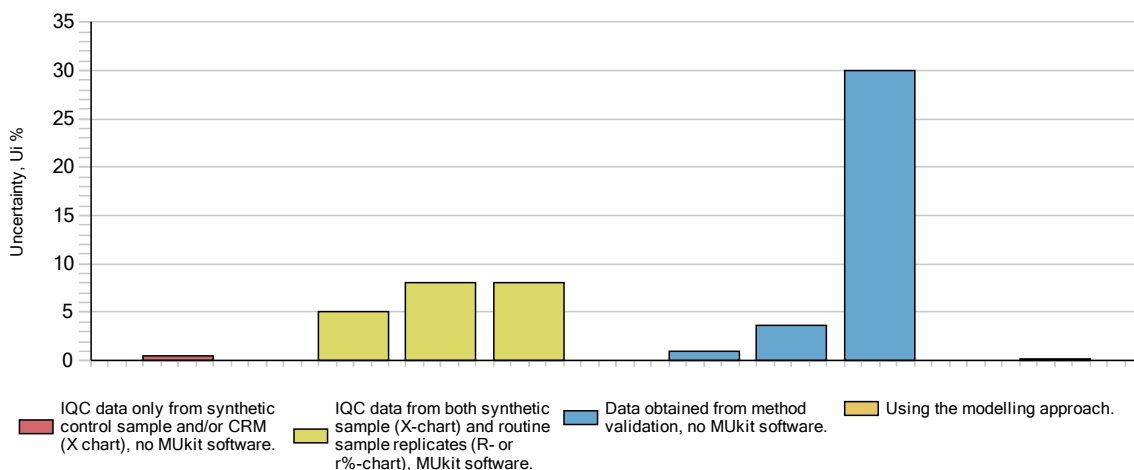


Measurand Cl<sub>d</sub> Sample B3

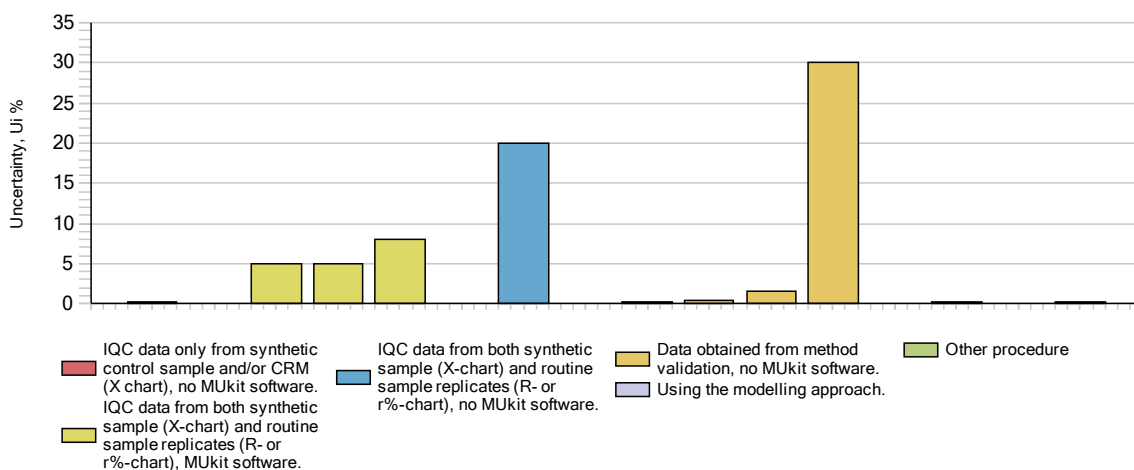




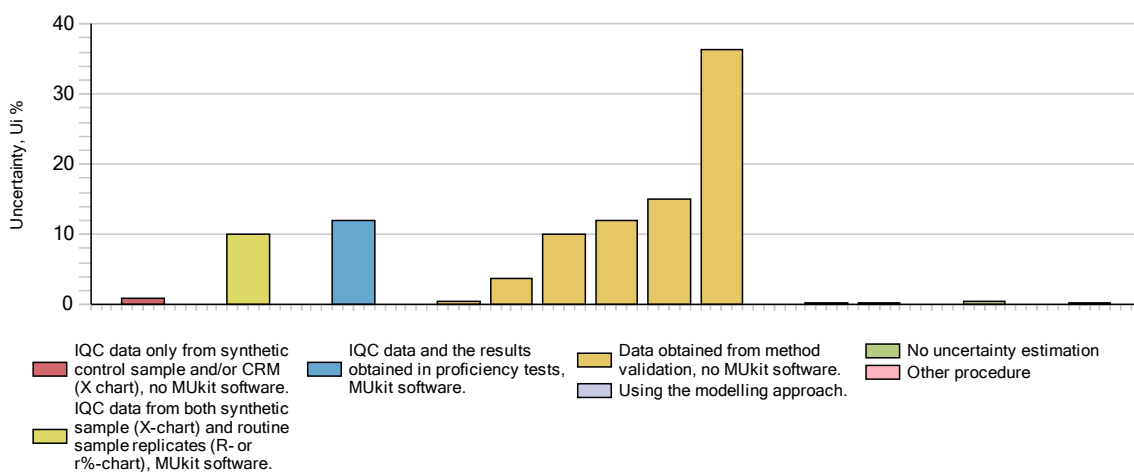
Measurand H<sub>d</sub> Sample B2



Measurand H<sub>d</sub> Sample K1

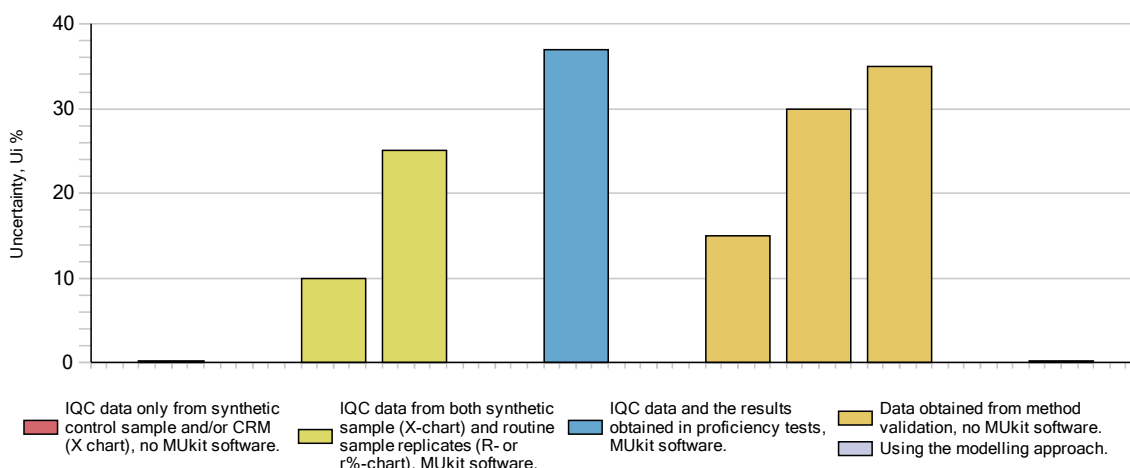


Measurand M<sub>ad</sub> Sample K1

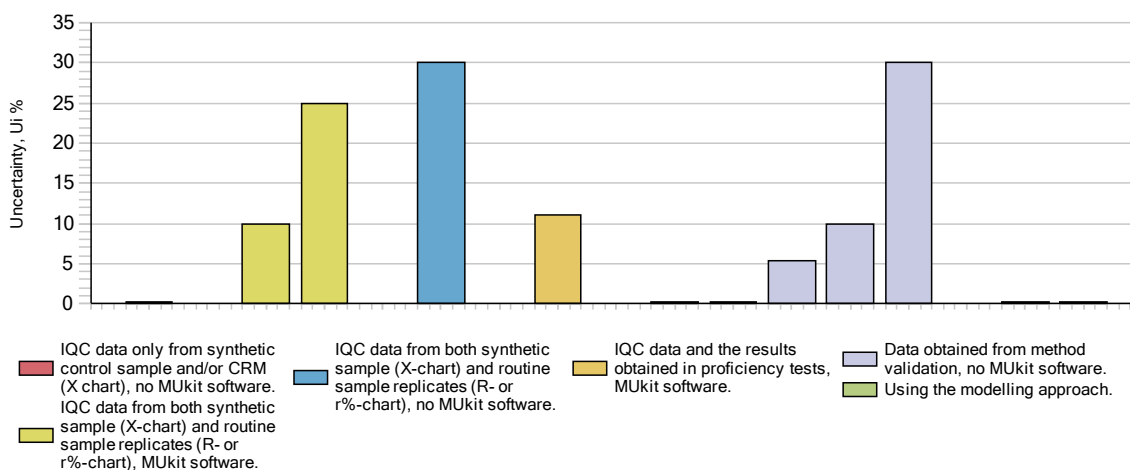




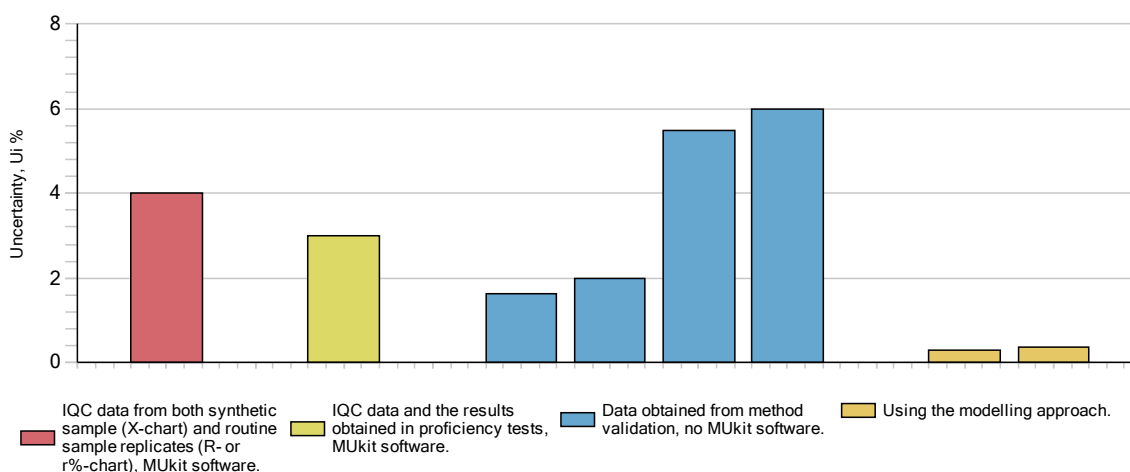
Measurand  $S_d$  Sample B3



Measurand  $S_d$  Sample K1



Measurand  $V_d$  Sample K1



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## Gross and net calorific values of solid fuels



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Finnish Environment Institute

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