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APPENDICES

1 INTRODUCTION

The Finnish Environment Institute (SYKE) carried out the proficiency test for the analysis of the gross and the net calorific value as well as for content of ash, carbon, hydrogen, nitrogen, sulphur and analytical moisture content in fuels in September 2009. The samples were prepared from peat (B1) and coal (K1). Additionally, the participants were asked to estimate/calculate the emission factor for both samples.

The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43-1 [1], ILAC Requirements [2], ISO 13528 [3] and IUPAC Recommendations [4]. SYKE is the Proficiency Testing Provider No. PT01 accredited by the Finnish Accreditation Service (www.finas.fi). The proficiency testing service in SYKE conforms to the requirements of the Guide ISO/IEC 43-1:1997. However, the organizing of tests for measurements in fuels was not yet included in the accredited scope on the time of the PT5/2009, but it will be accredited in the future PTs.

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratories
Hakuninmaantie 6, 00430 Helsinki
tel. +358 20 610 123, fax +358 9 448 320

Subcontractors: Helsingin Energia (the preparation of coal sample)
Pirkanmaa Environment Centre (the final preparation of the samples including mixing, homogenisation and distribution of the samples; the accredited testing laboratory T186 by the Finnish Accreditation Service for the requested sample pretreatments www.finas.fi)
Enas LTD in Jyväskylä (the preparation and testing of peat sample, the accredited testing laboratory T241 by the Finnish Accreditation Service for the requested sample pretreatments www.finas.fi)
Ramboll Analytics LTD in Vantaa (testing of the coal sample, the accredited testing laboratory T039 by the Finnish Accreditation Service for the requested measurements www.finas.fi)

The responsibilities in organizing the proficiency test were as follows:
Mirja Leivuori, coordinator
Kaija Korhonen, substitute of coordinator
Irma Mäkinen as coordinator consultant
Keijo Tervonen, technical assistance
Sari Lanteri, technical assistance
Markku Ilmakunnas, technical assistance and layout of the report.

The analytical experts were:
Minna Rantanen (coal), Ramboll Analytics LTD
Minna Salonen (peat), Enas LTD

2.2 Participants

In this proficiency test (PT) totally 39 laboratories participated, from which 19 were from Finland and 20 from other European countries (Appendix 1).

2.3 Samples and delivery

The more detail preparation of the samples is presented in Appendix 2.

The sample B1 was the peat sample from the Finnish marshland. The material was air dried and grounded by the mill with 500 µm sieve before homogenization and sample dividing.

The coal sample (K1) was prepared from a Russian steam coal. The material was air dried and grounded to particle size < 200 µm before homogenization and sample dividing.

The samples were delivered 1 September 2009. They were requested to be analyzed and reported before 23 September 2009.

The samples and the requested measurands were as follows:

Sample material and sample code	**Analytes (both samples)**
B1 (peat) K1 (coal)	Gross calorific value, q-V,gr,d Net calorific value, q-p,net,d Carbon, C Sulphur, S Nitrogen, N Hydrogen, H Analysis moisture, M_{ad} (marked as M forward) Ash content, Ash

In the letter with the samples was noted that the moisture content of the analysis had to be measured first after storing samples closed one day on the measuring laboratory. The samples were asked to homogenate before measurements and to store in dry place at room temperature.

Additionally, the participants were asked to calculate the emission factor for the both samples. For this calculation the total moisture contents as received (M_{ar}) for peat sample **B1** was 50.8 % and for coal sample **K1** 8.27 %, which were informed to the participant beforehand in sending the samples.

2.4 Homogeneity studies

Homogeneity of the samples B1 and K1 was tested by analyzing the gross and net calorific value and ash content with parallel determinations from twelve subsamples. Additionally carbon, hydrogen and sulphur were measured from six subsamples (Appendix 3). According to the homogeneity test results the both samples B1 and K1 were considered homogenous.

Particle size distribution was also tested from one sub sample of peat (B1) and coal (K1). The results shown, that the samples were appropriate for measurement of calorific value (Appendix 3).

2.5 Comments sent by the participants

Appendix 4 contains the comments sent by the participants. The comments were mainly relating to the data input protocols in the laboratories. However the changes were minor and they contributed very little on the performance evaluation.

2.6 Analytical methods

2.6.1 Gross and net calorific value

The analytical methods based on different standard method were used for the measurements in the PT. The used analytical methods of the participants are shown in more detail in Appendix 5.

Mostly, the standard methods or the CEN/technical specification were used for measurement of calorific value (CEN/TS 14918 [5], ISO 1928 [6], DIN 51900 [7], ASTM D 5865-07 [8]). The participants used mainly the sample amount 0.5–1 g for measurement of the calorific value. Generally, the analyses were carried out from air dried samples (Appendix 5).

The measurements of calorific value were mainly done by LECO, IKA and PARR equipments. The volume of water added into a reaction bomb varied mainly from 1 to 10 ml depending on the type of measuring equipment (Appendix 5). In the calibration used benzoeacid from eight producers. Mainly, the calibration standard was used without correction to the value given in the certificate.

In the calculation of gross calorific value (q-V,gr,d) various correction methods were used. Basically, fuse wire, ignition, acid, cotton, moisture, nitrogen and sulphur corrections were used. However, the participants used several combinations of them (Appendix 5). In the calculation of net calorific value (q-p,net,d) different combinations of correction factors were used as well. Mainly, the measured hydrogen content with or without nitrogen and oxygen corrections was used. However, in many cases also calculated hydrogen content was used for corrections. Many participants were taken into account the analytical moisture of the samples in their calculations.

2.6.2 Measurement of carbon, hydrogen, nitrogen, sulphur, moisture and ash

In the PT several standard methods or technical specifications were used mainly for measurement of different parameters as follows:

- C, H and N: CEN/TS 15104 [9], ISO/TS 12902 [10], ASTM D 5373 [11]
- S: ASTM D 4239 [12], CEN/TS 15289 [13], ISO 334 [14]
- Analytical moisture content: CEN/TS 14774 [15], ISO 589 [16], DIN 51718 [17], ASTM D 5142 [18]
- Ash content: CEN/TS 14775 [19], ISO 1171 [20], DIN 51719 [21], ASTM D 5142 [18]

However, in some cases other international standards or national standards were used (Appendix 5).

Carbon and hydrogen were measured by using different equipments (e.g. VARIOMAX, LECO, ELTRA, ELTRA CHS, Appendix 5). Different elemental analyzers (e.g, ELTRA, LECO, Appendix 5) were also used for measurements of sulphur. Sulphur was measured also by using O_2-combustion and IC-measurement.

Ash content was determined by heating mainly at the temperature 550 ^{o}C (Sample B1) or 815 ^{o}C (Sample K1). Also some other temperatures were used for ash content measurements (Appendix 5).

2.7 Processing of the data

2.7.1 Testing of normality of data, outliers and replicate results

Before the statistical treatment, the data was tested according to the Kolmogorov-Smirnov normality test and the outliers were rejected according to the Hampel test for calculation of the mean value (H in the results sheets). Also before the robust calculation some extreme outliers were rejected in case that the results deviated from the robust mean more than 50 %. The replicate results were tested using the Cochran-test (C in the result sheets). If the result was reported < DL (detection limit), it has not been included in calculation of the results (H in the results sheets).

2.7.2 Assigned values and uncertainties

The robust mean was used as the assigned value for each analyte of the sample B1 and K1 (Appendix 6). In the calculation of the robust mean outliers are not normally rejected, but they are iterated before the final calculation of the robust mean. However, in this proficiency test some extreme results (at most 1–6 results/analyte) had to be rejected because of rather strict requirements for reproducibility given in the standards for analysis described in the sample letter. Especially in the estimation of the assigned value of gross and net calorific value, the base for extreme value was either the anomalous calorific value or the anomalous value in the measured moisture or/and element value used in the calculation. In addition, a few laboratories reported the anomalous values in measurement of the gross and net calorific value, which may indicate systematic errors in measurement. Also the mean value (after using the Hampel outlier test) and the median value of the data were calculated, which were quite similar with the assigned values. Also the results of the homogeneity testing of the samples were used in the estimation of the assigned values. Additionally, the calculated assigned values of the calorific values were compared the results obtained in the kernel density plots [4].

When using the robust mean of the participant results as the assigned value, the uncertainties of the assigned values for calorific values varied from 0.26 % to 0.44 %. For the other measurands the uncertainty varied from 1.0 % to 5.6 % (Appendix 6).

After reporting the preliminary results in October 2009 the assigned values have been slightly modified. Due to one additional dataset and corrected results after the participants' comments (Appendix 4) the statistical data treatment was renewed. The minor changes have not significantly affected the performance of the laboratories in the final evaluation of performance. After the reporting the preliminary results the performance evaluation for emission factor EF was added to the PT's evaluation. The preliminary result for EF evaluation was informed to the laboratories reported the EF result on 11 January 2010 for commenting.

There were some problems in estimation of the assigned value for the calculated emission factors (EF). In particular, some participants did not use the moisture contents informed to the participants in sending the samples. In the sample letter the total moisture contents 50.8 % (the sample B1) and 8.27 % (the sample K1) were asked to use in calculation the EF-values. For the peat sample B1 the erroneously calculated EF results were clear outliers and the performance evaluation was performed. For the coal sample the same calculation error for the same laboratories was evident, but the results were not outliers. For this reason, the assigned value for EF in the coal sample was not estimated in the final data treatment.

2.7.3 Standard deviation for proficiency assessment and z score

For the total standard deviation for proficiency assessment used in calculation of the z scores was used the target value for reproducibility recommended in the international standards or technical specifications for measurement of calorific values and other determinants [5, 6, 9, 10, 12, 19, 20, 21].

The reproducibility required in the standards was fulfilled for net and gross calorific values. For some other measured parameters (i.e. H, S) total standard deviation for proficiency assessment had to be increased from the reproducibility of standards.

The results of analysis moisture (M) have not been evaluated because of rather great variation of the results, but the assigned values for both sample types are presented.

The performance evaluation was carried out by using z scores (Appendix 7).
In the performance evaluation z scores were interpreted as follows:

$\lvert z \rvert \leq 2$	satisfactory results
$2 < \lvert z \rvert < 3$	questionable results
$\lvert z \rvert \geq 3$	unsatisfactory results

The performance evaluation of participants using calculated z scores are presented in Appendix 8.

The reliability of the assigned value was tested according to the criterion:

$u/s_p \leq 0.3$, where

u is the standard uncertainty of the assigned value (the uncertainty of the assigned value (U) divided by 2) and
s_p the standard deviation for proficiency assessment (total standard deviation divided by 2).

The test criterion for the reliability of the assigned value was fulfilled in every case, which indicated that the assigned values were very reliable.

The reliability of the target value for the total deviation and the reliability of the corresponding z score were estimated by comparing the deviation for proficiency assessment (s_p) with the robust standard deviation of the reported results (s_{rob}). The criterion $s_{rob} < 1.2^* s_p$ was fulfilled in every case.

Due to this the evaluation of performance is reliable for this proficiency test. The performance was not evaluated for moisture values partly due to high variability between the results. The performance was not evaluated for emission factor (EF) in the coal sample due to the some calculation errors in the results.

After reporting the preliminary results in October 2009 the standard deviation for proficiency assessment for hydrogen (H) in the sample B1 was increased from value 8.2 to value 9. The minor change has not significantly affected the performance of the laboratories in the final evaluation of performance.

3 RESULTS AND CONCLUSIONS

3.1 Results

The results and the performance of each laboratory are presented in Appendix 8 and the summary of the results in Table 1. Explanations to terms used in the result tables are presented in Appendix 7. The data of replicate measurements are shown in Appendix 9. The results of participated laboratories and their uncertainties are presented graphically in Appendix 10. The summary of z scores is shown in Appendix 11.

Table 1. Summary of the result in the proficiency test 5/2009.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Ac-cepted z-val%
Ash	B1	w%	5,31	5.26	5.31	5.30	0.19	3,5	26	7	88
	K1	w%	8,71	8.72	8.71	8.71	0.15	1,7	29	3,5	79
C	B1	w%	54,62	54.58	54.62	54.60	0.88	1,6	18	3	83
	K1	w%	72,62	72.64	72.62	72.78	1.21	1,7	25	3	92
EF	B1	tCO2/TJ	108	107.54	107.55	106.42	1.95	1,8	16	4	69
	K1	tCO2/TJ		92.84	93.13	92.90	1.21	1,3	17		
H	B1	w%	6,07	6.07	6.07	6.05	0.28	4,5	15	9	93
	K1	w%	5,17	5.20	5.17	5.13	0.28	5,4	21	9	86
M	B1	w%	7,68	7.63	7.68	7.59	0.59	7,7	27		
	K1	w%	3,17	3.03	3.15	3.12	0.35	11	29		
N	B1	w%	2,73	2.73	2.73	2.72	0.15	5,4	15	15	100
	K1	w%	2,26	2.23	2.26	2.27	0.18	7,8	19	15	95
q-p,net,d	B1	J/g	21218	21210.16	21217.85	21184.00	160.76	0,8	24	1,4	75
	K1	J/g	28878	28835.97	28877.88	28839.50	157.61	0,5	26	1	65
q-V,gr,d	B1	J/g	22505	22511.50	22505.25	22502.00	184.45	0,8	28	1,4	75
	K1	J/g	29962	29928.16	29962.17	29932.00	157.80	0,5	29	1	76
S	B1	w%	0,21	0.22	0.21	0.21	0.014	6,5	21	15	90
	K1	w%	0,21	0.21	0.21	0.21	0.012	5,6	29	15	93

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

The robust standard deviation of results was lower than 2 % for 50 % of the results and mostly it was lower than 6 % for 77 % of the results (Table 1). For nitrogen (N) in the sample K1 and for sulphur (S) in the sample B1 the robust standard deviation was 7.8 and 5.6 %, respectively. In measurement of moisture the robust standard deviation was 11 % in the coal sample and 7.7 % in the peat sample. The standard deviations of the results in this PT were lower than in the previous respective PT SYKE 2/2008 [22], where the deviations varied from 0.2 % to 15.4 %.

In this PT the participants were requested to report the replicate results for all measurements. (Appendix 9). The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2. The international standards or technical specifications relating to measurements in fuels recommend targets for the repeatability.

In particular, in measurement of the calorific values, the requirement for the repeatability is ± 120 J/g. In this PT the requirements for the repeatability in measurement of the gross calorific value are 0.57 % for the sample B1 and 0.42 % for the sample K1 and in measurement of the net calorific value 0.53 % and 0.40 %, respectively. In each case the obtained repeatability in measurement of the gross calorific value and the net calorific value was lower than the repeatability requirement (Table 2, the column s_w %). However, some laboratories (lab 14, 20, 21, 29, 31 and

36/the sample B1; lab 6, 7, 11 and 33/the sample K1) have reported higher differences of duplicate determinations than the requirements for the repeatability in measurement of the calorific value (Appendix 9). The repeatability was mainly acceptable only for carbon (C) in the elemental measurements (Table 2, the column s_w %).

Table 2. Summary of repeatability on the basis of duplicate determinations (ANOVA statistics)

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Ac-cepted. z-val %
Ash	B1	w%	5,31	5,258	5,28	0,06403	0,2368	0,2454	1,2	4,5	4,7	7	26	88
	K1	w%	8,71	8,716	8,705	0,05418	0,1411	0,1511	0,62	1,6	1,7	3,5	29	76
C	B1	w%	54,62	54,61	54,6	0,191	0,7926	0,8153	0,35	1,5	1,5	3	18	83
	K1	w%	72,62	72,64	72,75	0,1872	1,272	1,286	0,26	1,8	1,8	3	25	88
EF	B1	tCO2/TJ	108	107,5	107,3	0,2743	1,711	1,733	0,26	1,6	1,6	4	16	69
	K1	tCO2/TJ		92,9	92,9	0,3954	1,33	1,387	0,43	1,4	1,5		17	
H	B1	w%	6,07	6,065	6,05	0,1023	0,2645	0,2836	1,7	4,4	4,7	9	15	93
	K1	w%	5,17	5,196	5,127	0,0327	0,2831	0,2849	0,63	5,4	5,5	9	21	81
M	B1	w%	7,68	7,609	7,6	0,08479	0,5146	0,5215	1,1	6,8	6,9		27	
	K1	w%	3,17	3,034	3,145	0,05281	0,4901	0,493	1,7	16	16		29	
N	B1	w%	2,73	2,73	2,716	0,04985	0,1714	0,1785	1,8	6,3	6,5	15	15	100
	K1	w%	2,26	2,234	2,274	0,03221	0,1862	0,189	1,4	8,3	8,5	15	19	95
q-p,net,d	B1	J/g	21220	21210	21180	32,35	156,9	160,2	0,15	0,74	0,76	1,4	24	75
	K1	J/g	28880	28840	28850	40,05	194,5	198,6	0,14	0,67	0,69	1	26	65
q-V,gr,d	B1	J/g	22510	22520	22500	47,98	225,1	230,2	0,21	1	1	1,4	28	71
	K1	J/g	29960	29930	29940	44,66	180,7	186,2	0,15	0,6	0,62	1	29	76
S	B1	w%	0,21	0,2149	0,214	0,006778	0,01481	0,01628	3,2	6,9	7,6	15	20	90
	K1	w%	0,21	0,2075	0,2075	0,003195	0,01086	0,01132	1,5	5,2	5,5	15	27	89

The summary of the robustness of the methods, the ratio s_b/s_w, is presented in Table 3. The ratio s_b/s_w should not be exceeded 3 for robust methods. However in Table 3 is seen that in many cases the robustness exceed the value 3. For the calorific value, the ratio s_b/s_w, was around 5 for both fuel material.

Table 3. The robustness (s_b/s_w) of the replicate results in the PT5/2009.

Analyte	Sample	s_b/s_w	Analyte	Sample	s_b/s_w
Ash	B1	3.7	S	B1	2.2
	K1	2.6		K1	3.4
C	B1	4.1	q-p,net,d	B1	4.9
	K1	6.8		K1	4.9
H	B1	2.6	q-V,gr,d	B1	4.7
	K1	8.7		K1	4.0
M	B1	6.1	EF	B1	6.2
	K1	9.3		K1	2.7
N	B1	3.4			

3.2 Analytical methods and status to the results

3.2.1 Gross and net calorific value

In the figures 1 and 2 are shown the results of the gross calorific values for the samples B1 and K1 with the reported information of the used standard method (the results reported without method information is not shown, see more Appendix 5). Basically, there was no clear difference between the gross calorific values obtained using the different standard methods. For the laboratories 7 (the sample K1), 14 (the sample B1) and 27 (the sample B1) the deviation of the result is evident due to the errors in the data reporting (Appendix 4). In many cases the anomalous result was explained by the errors in the data reporting and/or errors in the measurement. The laboratory 36 used only one a capsule of acetobutyrate in the measurement of gross calorific value, which might have affected to the unsatisfactory results of the laboratory (Appendix 8).

In the calculation of the net calorific value some inaccuracy might have caused the questionable results for the laboratories 34 (the sample B1 and K1) and 10 (the sample K1). However, their results for the gross calorific value were satisfactory (Appendix 8).

There are several factors, which can cause anomalous results in measurement of calorific value:

- Analytical moisture and calorific value should be measured at same time (at least within 24 h). The porous fuel material adsorbs moisture very easily and the changes in the moisture content of the laboratory air, caused inaccuracies to the calorific value reported as a dry weight basis.
- In measurement of calorific value from the dried sample, moisture can absorb into a sample very easily from environment.
- If the sample contains high amount of sulphur and nitrogen, the correction for sulphur and total acids can affect to great extent.
- The laboratory has to taken into account the calibration conditions, whether benzoic acid has been weighed in air or in vacuum (on the basis of a certificate). Further, in the measurement of the sample the conditions should be similar as in the calibration process (e.g, a pressure, an amount of calorimeter water, a correction for total acids).
- The mass of the sample (g) has to been adequate to meet the valid temperature rise and the linear calibration range.
- Stability of the calorimeter has to been checked before sample measurements with certified benzoic acid.
- The calculation of gross and net calorific value should be based on the formulas of the international standards. If in the calculation any literature values for the parameters needed are used, those should be reported with the calorific values. To get more accurate results the measured parameters for the correction parameters are recommended to use.

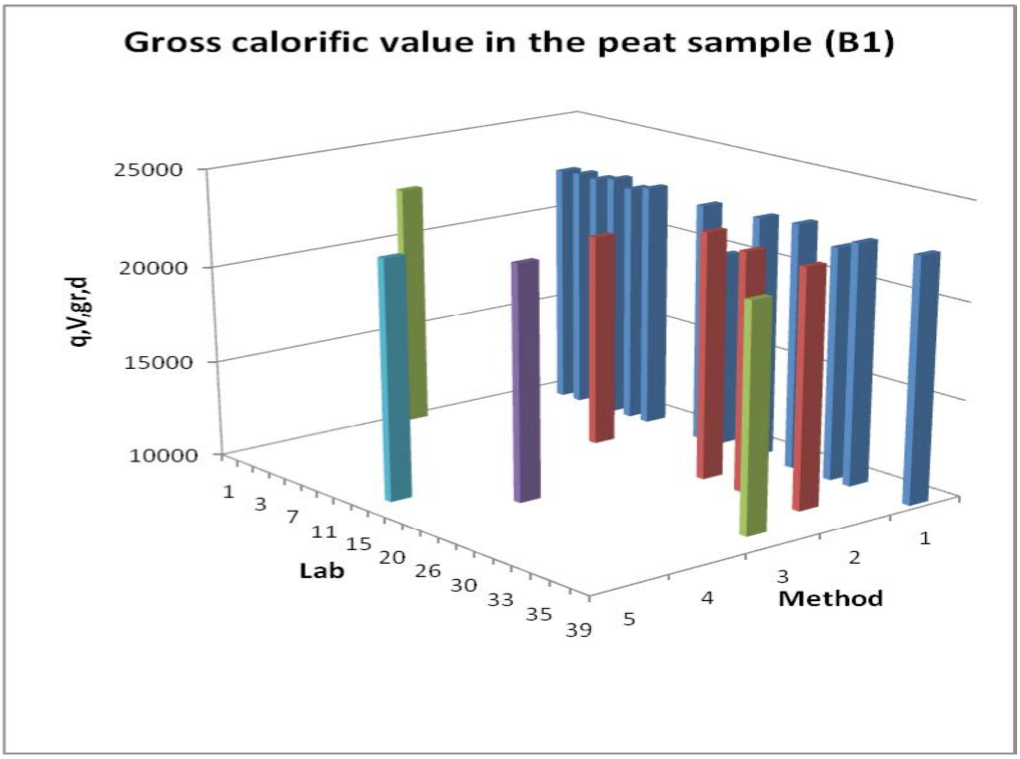

Figure 1. The reported gross calorific value (J/g) in the sample B1by the laboratories and the used method. Method 1: CEN/TS 14918, Method 2: ISO 1924, Method 3: DIN 5190, Method 4: CEN/ TS 14918 & CEN/TS 1540, Method 5: Other/national.

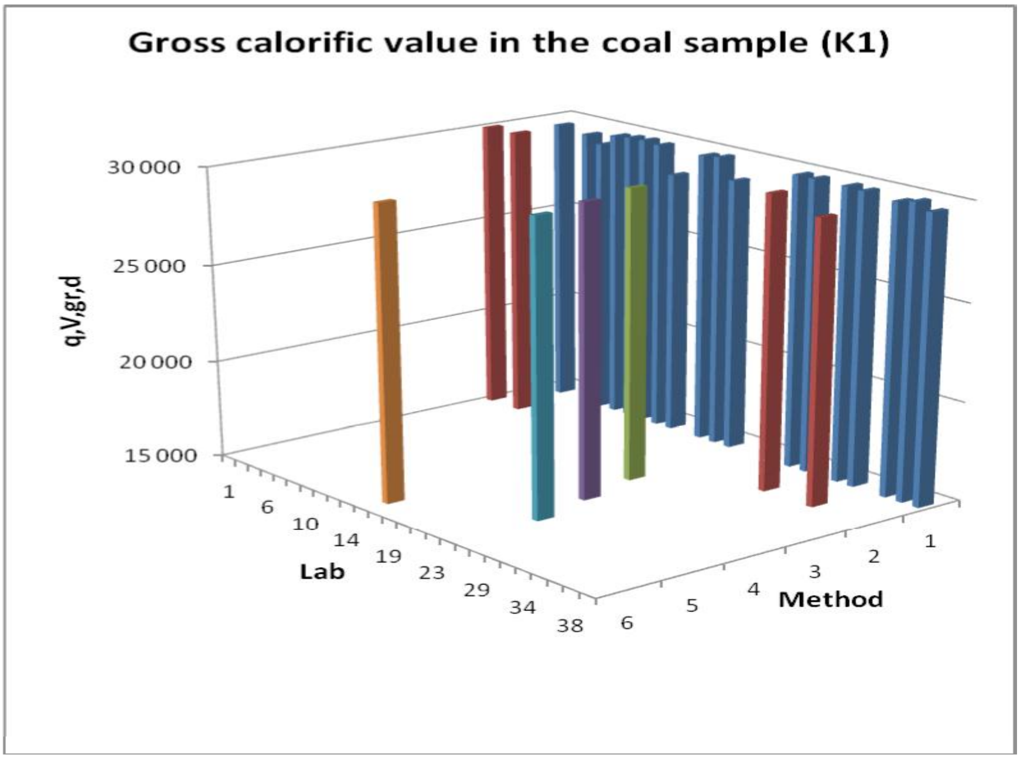

Figure 2. The reported gross calorific value (J/g) in the sample K1by the laboratories and the used method. Method 1: CEN/TS 14918, Method 2: DIN 51900, Method 3: CEN/TS 14918 / CEN/ TS 5400, Method 4: C ISO 1928 & DIN 51900, Method 5: ASTM D 5865-07, Method 6: Other/ national.

3.2.2 Other measurands

In measurement of ash content only a few laboratories reported too high or too low values and different techniques have not clearly affect the results.

In measurement of moisture different standard methods were used. However, correct measurement of moisture is important, because it plays an important role in calculation of the calorific values.

For elemental measurements (C, N, H) the laboratories used different equipment and the results varied most in measurement of nitrogen (N) partly due to the low content of N.

3.3 Uncertainties of the results

From 9 to 18 laboratories reported the expanded measurement uncertainties with their results (Table 4, Appendix 10). The estimated uncertainties varied greatly, e.g. for sulphur from 0.01 to 35 %. For the calorific value the uncertainty variation was also very large. Typically, about a half of the reported calorific value uncertainties were higher than the requirements for repeatability presented in the standard methods [5, 6].

Particularly, very low uncertainties (around 0.01 %) can be considered as questionable. Possibly, some uncertainties have been wrongly reported. In many other cases, the reported measurement uncertainties did not met the requirements presented in the standard methods for the repeatability of the method. On the other hand, almost for each measurand also extremely high measurement uncertainties have been reported in particular in measurement of the calorific value (Appendix 10).

Several approaches were used for estimating of measurement uncertainty (Appendix 12). The approach based on existing IQC and validation data (Meth 3) or CRM data (Meth 4) were most common. Generally, the approach for estimating measurement uncertainty has not made a definite impact on the uncertainty estimates. It is evident that harmonization in the estimating of uncertainties should be continued.

Table 4. The range of the expanded measuring uncertainties reported by the participants in the PT 5/2009.

Sample	Ash, %	C, %	H, %	M, %	N, %	q-V,gr,d, %	q-p,net,d, %	S, %
B1	0.21–16	0.2–10	0.6–16	0.14–10	0.14–12	0.2–30	0.71–5	0.01–35
K1	0.02–15	0.2–10	0.3–10	0.02–10	0.11–13.9	0.2–30	0.32–5	0.01–35

3.4 Estimation of emission factor

Additionally, the laboratories were asked to estimate the emission factors for the samples distributed in the PT by taking into account their own net calorific values and the total moisture values as received 50.8 % for the peat sample, B1, and 8.27 % for the coal sample, K1, which informed in the letter with the samples. Totally 16 laboratories reported the emission factor in measurement of the peat sample and 17 laboratories reported it for the coal sample (Table 1, Appendix 8). In the proficiency test also evaluated the performance of the emission factor after the sending the preliminary results of PT in October 2009.

Also the performance was evaluated for EF-values due to the requirements of some participants, which their presented after report of the preliminary results. By evaluating the performance the provider also wanted the participants to take into account the calculation of EF-values correctly. However, later the provider obtained, that some participants had not used the total moisture content as received (e.g. 50.8 % for the sample B1, 8.27 % for the sample K1), which the provider reported in the sample letter.

In the statistical evaluation (robust average) of the EF results several laboratories (i.e. 1, 11, 14 and 35) were outliers for the sample B1. The reason seems to be, that in the EF calculation the informed total moisture content as received (M_{ar}) was not taken account. This was confirmed from laboratories 1 and 14 (see Appendix 4). It could be concluded, that the same error in the calculation is most probable for the EF result in the sample K1, though the results of the laboratories are not outliers. Thus, in the final performance evaluation the emission factor for the sample K1 was not evaluated.

The participants were asked to calculate EF-values using the equation presented in the EC directive 2007/589/EC [23]. Later has been obtained, that in this EC directive has not been given the detailed equation for calculation of EF-values. Mainly the participants informed that the calculation of EF-value was based on the EC directive 2007/589/EC (Appendix 5). Some national guides of the equation for the calculation of EF-value are available (e.g. in Finland).

In Finland the Energy Market Authority has made the guideline for the calculation of emission factor (http://www.energiamarkkinavirasto.fi/files/Paastokerroin11112008.pdf). The one aim has been to harmonised the used equation for the calculation of EF-values within the Finnish accredited laboratories.

The Finnish formula for calculating the emission factor is as follows:

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

where

EF	emission factor, g CO_2/MJ
C	carbon content as dry, %
M_{ar}	total moisture as received, %
$Q_{net,ar}$	net calorific value as received, MJ/kg

This PT showed that the common procedure for calculation of EF-values within the different EU countries is urgently needed.

4 EVALUATION OF PERFORMANCE

The evaluation of the participants was based on z scores, which were calculated using the estimated target values for the total deviation. The calculated z scores are presented with the results of each participant (Appendix 8) and the summary of z scores is presented in Appendix 11.

The total number of laboratories participating in this PT was 39. The robust standard deviation of the results was mostly lower than 6 %, while for the calorific values it was lower than 1 %.

The criteria for performance had been mainly set according to the target value for reproducibility recommended in the international standards or technical specifications for measurement of calorific values and other determinants. The reproducibility required in the standards was fulfilled for net and gross calorific values. For some other measured parameters (i.e. C, H, N) total standard deviation for proficiency assessment had to be increased from the reproducibility of standards (Table 1).

The evaluation of performance was not done for the measurement of moisture and for the emission factor of the coal sample.

Peat

Accepting the deviations of 1–15 % from the assigned values for the peat sample (B1) 84 % of results were satisfactory. In the measurement of S and N over 90 % of the results were satisfactory. In the measurement of gross and net calorific values 75 % of results were satisfactory when accepting the deviations of 1–1.4% from the assigned values. In this PT the number of satisfactory results of the calorific values for the peat sample was in the same range than in the previous PT 2/2008 [22]. There were more difficulties in the estimation of EF, where less than 69 % of results were satisfactory.

Coal

Accepting the deviations of 1–15 % from the assigned values for the coal sample (K1) 84 % of results were satisfactory. In the measurement of C, S and N over 90 % of the results were satisfactory. In the measurement of gross and net calorific values 65 % and 76 % of results were satisfactory, respectively, when accepting the deviations of 1–1.4 % from the assigned values. In this PT the number of satisfactory results of the gross and net calorific values for the coal sample was lower than in the previous PT 2/2008 [22], in which 75 % and 83 % of results were satisfactory, respectively. However, it should be noticed that the number of participating laboratories in this PT were double to the previous year.

This PT showed that the common procedure for calculation of EF-values is not available at this moment. However, it is urgently needed harmonized equation for the calculation of EF-values within the EU countries.

In total, 83 % from the results were satisfactory when the deviations of 1–15 % from the assigned values were accepted. About 65 % of the participants used accredited methods and 87 % of their results were satisfactory. SYKE arranged a similar proficiency test in 2008 [22] and then 80 % of the results were satisfactory.

5 SUMMARY

The Finnish Environment Institute (SYKE) carried out the proficiency test for measurement the gross and the net calorific value, the content of ash, carbon, nitrogen, hydrogen, moisture and sulfur in fuels in September 2009. One peat sample and one coal sample were delivered to the laboratories for the analysis of each measurand. In total, 39 laboratories participated in the proficiency test.

The robust means of the reported results by the participants were used as the assigned values for measurands. The uncertainties of the calculated assigned values were mainly less than 0.44 % for calorific values and less than 5.6 % for the other measurands.

The evaluation of performance was based on the z score which was calculated using the standard deviation for proficiency assessment at 95 % confidence level. The evaluation of performance was not done for the measurement of moisture and for the emission factor of the coal sample. In total, 84 % of the participating laboratories reported the satisfactory results when the deviations of 1–15 % from the assigned values were accepted. About 65 % of the participants used accredited methods and 87 % of their results were satisfactory. In measurement of the gross calorific value from the peat sample 71 % of the results were satisfactory and respectively in measurement of the coal sample 76 % from the results were satisfactory. In measurement of the net calorific value from the peat sample 75 % of the results were satisfactory and respectively in measurement of the coal sample 65 % from the results were satisfactory.

This PT showed that the common procedure for calculation of EF-values is not available at this moment. However, it is urgently needed harmonized equation for the calculation of EF-values within the EU countries.

6 YHTEENVETO

Suomen ympäristökeskus (SYKE) järjesti syyskuussa 2010 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin ja kosteuden määrittämiseksi turpeesta ja kivihiilestä.

Pätevyyskokeeseen osallistui yhteensä 39 laboratoriota. Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat välillä1–15 %. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa. Tavoitearvon epävarmuus oli lämpöarvon määrityksissä alhaisempi kuin 0.44 % ja muiden testisuureiden osalta alhaisempi kuin 5.6 %. Tulosten arviointia ei tehty kosteuspitoisuuden määritykselle, koska osallistujien välinen hajonta oli suuri. Arviointia ei myöskään tehty päästökertoimelle hiilen osalta, koska kaikki laboratoriot eivät olleet laskeneet arvoa tulokosteutta kohti.

Koko tulosaineistossa hyväksyttäviä tuloksia oli 83 %, kun vertailuarvosta sallittiin 1–15 %.n poikkeama. Noin 65 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 87 %. Kalorimetrisen lämpöarvon tuloksista oli tyydyttäviä 71 % (turve) ja 76 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat tyydyttävien tulosten osuudet olivat 75 % (turve) ja 65 % (kivihiili).

Pätevyyskokeessa havaittiin, että selvää laskentakaavaa päästökertoimelle ei ole kuvattuna direktiivissä 2007/589/EC [23]. Kansallisia ohjeistuksia päästökertoimelle on tehty mm. Suomessa, mutta yhtenäinen ohjeistus päästökertoimen laskennalle eri EU-maissa todettiin puuttuvan. Yhtenäisen, dokumentoidun, laskentakaavan käyttöönotto EU-laajuisesti on kuitenkin erityisen tärkeä.

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PARTICIPANTS IN THE PROFICIENCY TEST SYKE 5/2009

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PREPARATION OF THE SAMPLES

Sample B1, peat

The sample B1 was prepared from the sample material taken from the Finnish marshal.
The peat was dried at room temperature and grounded by a mill with 500 µm sieve at the Enas LTD. The dried and sieved sample was mixed by a mechanized sample mixer and distributed in sub samples of 50 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of Pirkanmaa Environment Centre. The particle size distribution of peat was measured by Enas LTD using laser diffraction and sieving.

Sample K1, steam coal fuel

The sample K1 was a Russian steam coal. The coal was dried at room temperature and grounded to particle size < 200 µm at the Helsinki Energy. The dried and sieved sample was mixed by a mechanized sample mixer and distributed in sub samples of 50 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of Pirkanmaa Environment Centre. The particle size distribution of coal was measured by the Helsinki Energy, Power Plant Chemistry using laser diffraction.

TESTING OF THE SAMPLES

Homogeneity

Homogeneity was tested from duplicate measurements of calorific value and ash content in twelve samples, which were homogenised before sampling. In addition, carbon, hydrogen, nitrogen and sulphur content were tested in six samples. The analytical variation s_{an} and the sampling variation s_{sam} was calculated using one-way variance analysis. For this proficiency test, the analytical results were statistically handled according to the IUPAC guidelines for the treatment of homogeneity testing data and the total standard deviation for proficiency assessment [4].

Meaurements	Value	s_p%	s_p	s_{an}	s_{an}/s_p	Is $s_a/s_p<0.5$?	s_{sam}	s_{sam}^2	c	Is $s_{sam}^2<c$?
Peat (B1)										
Gross calorific value, J/g	22563	0.66	150	16.4	0.11	yes	34.9	1215	3855	yes
Net calorific value, J/g	21261	0.70	149	17.8	0.12	yes	34.2	1169	3842	yes
Ash, w-%	5.34	2.8	0.15	0.017	0.11	yes	0.042	0.002	0.004	yes
Coal (K1)										
Gross calorific value, J/g	29078	0.50	145	23.9	0.17	yes	0	0	3899	yes
Net calorific value, J/g	30229	0.50	150	24.8	0.17	yes	0	0	4155	yes
Ash, w-%	9.16	1.64	0.15	0.064	0.43	yes	0.054	0.003	0.007	yes

where,

s_p = standard deviation for proficiency assessment, (total standard deviation divided by 2)

s_p% = standard deviation for proficiency assessment as percent, (total standard deviation divided by 2)

s_{an} = analytical deviation, mean standard deviation of results in a sub sample

s_{sam} = sampling deviation, standard deviation of results between sub samples

$c = F1 \bullet s_{all}^2 + F2 \bullet s_a^2$

where:

$s_{all}^2 = (0.3 \bullet s_t)^2$

F1 = 1.79 when the number of sub samples is 12, F2 = 0.86 when the number of sub samples is 12

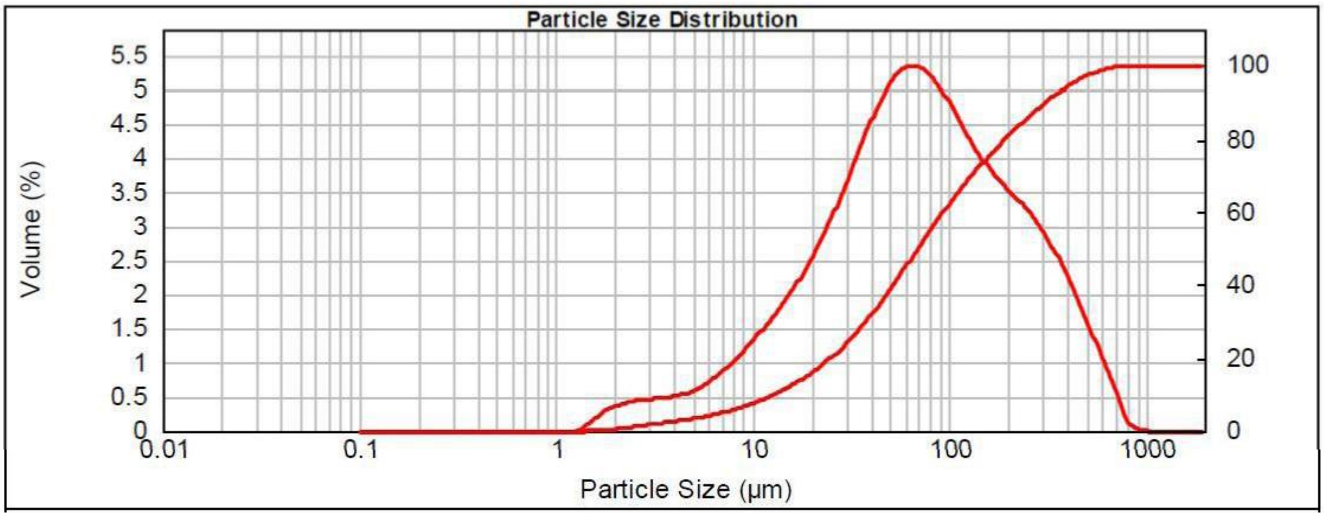
Conclusion: In each case, the criteria were fulfilled. Additionally, the results of the other tested parameters support the homogeneity of samples. The samples could be regarded as homogenous.

Particle size

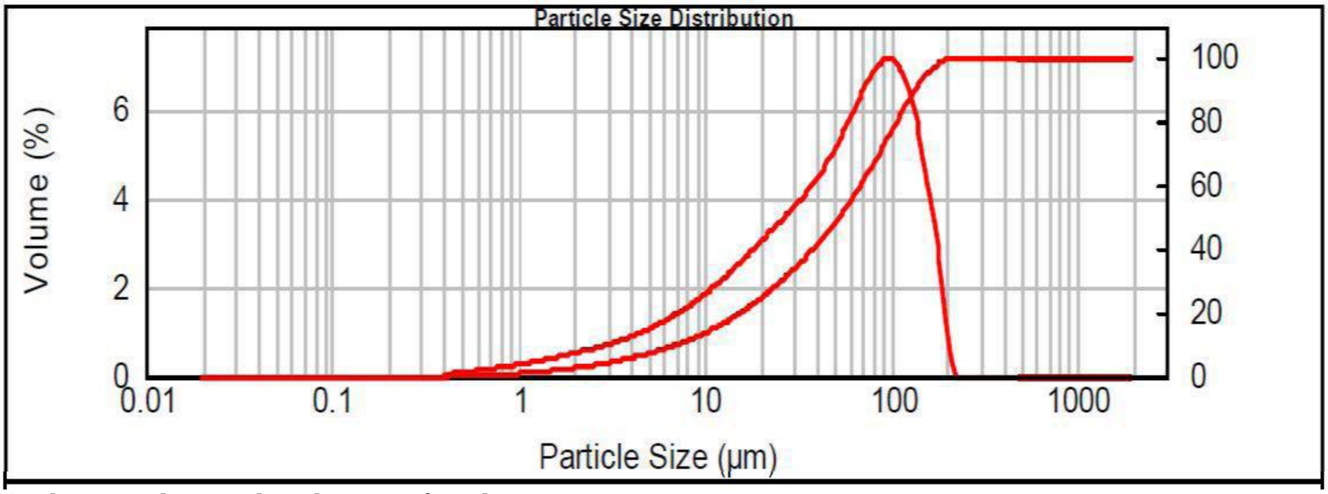
To test the particle size of samples one sample of each sample type was tested using laser diffraction.

In Figure 1 is showing the distribution of particle size for the samples B1 and K1. For peat sample B1 the mean size of particles was 69.6 µm and 98.5 % of the particles were smaller than 550 µm. The particle size distribution of peat sample B1 was tested also by sieving and the results were comparable with laser diffraction measured. For coal sample K1 the mean size of particles was 52.5 µm and 100 % of the particles were smaller than 212 µm.

TESTING OF THE SAMPLES (continue)



a) The particle size distribution of peat B1.



b) The particle size distribution of coal K1.

COMMENTS SENT BY THE PARTICIPANTS

Lab	Comment to the samples / PT	Action/SYKE
9	The laboratory was received the both sample, but ordered only the coal sample.	The provider was sent the both samples. The peat sample was not charged from the laboratory.
29	The moisture content to be measured should be indicated more detail: total moisture as received or analysis moisture.	In the sample letter the provider has been asked to measure analysis moisture. However, in the next PT moisture content to measured will be marked more detailed.
29	In the sample letter has not been clearly indicated the different possibilities to report results (i.e. not possible to report in the internet).	The provider will clear up the description of result reporting in the sample letter.

Lab	Comment to the results	Action/SYKE
1	The laboratory has not reported the EF-value in dry matter (i.e. to take account the given total moisture as received, M_{ar}).	The results were handled as outliers in the statistical treatment. If the results should have been reported rightly they should have been satisfactory. The participant can re-calculate z scores according to the guide for participating laboratories in SYKE proficiency testing schemes (www.environment.fi/syke/proftest).
7	The replicate results of q-V,gr,d and q-p,net,d for the sample K1 was reported erroneously.	The results were not corrected into the final data. They were outliers in the statistical treatment, and so they have not affected the performance evaluation. If the results should have been reported rightly they should have been satisfactory. The participant can re-calculate z scores according to the guide for participating laboratories in SYKE proficiency testing schemes (www.environment.fi/syke/proftest).
11	The laboratory has sent original data by e-mail for B1 and K1, but the provider received only a part of it before the sending of preliminary data.	The original data was sent on time, but due to one erroneously worked cc-mail address the provider has not received the e-mail. The e-mail address has been corrected. The data was included in the final data and in the final statistical treatment.

COMMENTS SENT BY THE PARTICIPANTS (continue)

Lab	Comment to the results	Action/SYKE
14	The laboratory has not noticed that the EF-value should be reported in dry matter (i.e. to take account the given total moisture as received, M_{ar}). The laboratory informed new results for the peat sample after receiving the preliminary results B1: q-V,gr,d 22420 and q-p,net,d 21070 J/g.	The results were handled as outliers in the statistical treatment. The corrected results reported by the laboratory were: 107.20 tCO_2/TJ for B1 and 94.45 tCO_2/TJ for K1. If the results should have been reported rightly, they should have been satisfactory. The new results have not included in the PT. The participant can re-calculate z scores according to the guide for participating laboratories in SYKE proficiency testing schemes (www.environment.fi/syke/proftest).
18	The laboratory informed that they have erroneously reported the result of internal quality control sample for the sample K1. The laboratory did not participate in the test for coal.	The data has deleted from the final data.
20	The laboratory has reported erroneously the ash and analysis moisture results for the sample K1.	The results were not corrected into the final data. They were outliers in the statistical handling, and so they have not affected the performance evaluation. The corrected values for K1 were: ash 8.80 and 8.77 w%, M 3.22 and 3.21. If the results should have been reported rightly, the result should been satisfactory. The participant can re-calculate z scores according to the guide for participating laboratories in SYKE proficiency testing schemes (www.environment.fi/syke/proftest).
24	The laboratory informed that they have not reported EF-value in dry for the sample K1.	The result was not corrected, but the assigned value for EF in the sample K1 was not calculated and the performance was not evaluated.
27	The laboratory was erroneously reported the result for the sample B1, although they have measured the sample K1.	The results were not corrected into the final data. They were outliers in the statistical handling, and so they have not affected the statistical handling of data. If the results should have been reported rightly, the result of q-V,gr,d and ash should have been satisfactory, while q-p, net,d should have been unsatisfactory.
37	The data of laboratory was for the sample K1, but it was handled as for the sample B1 in the preliminary data treatment.	The PT provider has transported erroneously the data of the laboratory from the reported result by the paper version: the order of the results B1 and K1 had been changed. In the future PTs the provider will increase the quality checks for the manually transported data. However, the PT provider recommends strongly the electronic data reporting.

METHOD DESCRIPTIONS

Measurements:

Measurement of gross calorific value	**Sample B1**	**Sample K1**
Date of analysis	Mainly 4 – 20 Sept. 2009 Later than 20 Sept: lab 2, 7, 13, 34, 35 and 39	Mainly 3 – 20 Sept. 2009 Later than 20 Sept: lab 7, 16, 28, 34 and 39
Standard method	13 labs: CEN/TS 14918 4 labs: ISO 1928 (lab 14, 29, 31 and 35) 2 labs: DIN 51900 1 lab: CEN/TS 14918 & CEN/TS 1540 (lab 21) 1 lab: IB/TL-method	18 labs: ISO 1928 4 labs: DIN 51900 (lab 2, 5, 30 and 36) 1 lab: CEN/TS 14918 & CEN/TS 15400 (lab 21) 1 lab: ISO 1928 & DIN 51900 (lab 23) 1 lab: ASTM D5865-07 (lab 24) 1 lab: IB/TL-method (lab 15)
Sample amount	Mainly 0.5-1 g used < 0.5 g used: 0.2 g (lab 36), 0.4 g (lab 33), 0.4 g + 0.4 g of spike (lab 14)	Mainly 0.5-1 g used < 0.5 g used: 0.3 g (lab 21), 0.4 g (lab 33), 0.4 g + 0.4 g of spike (lab 14)
Drying of sample	Air dried: lab 3, 11, 15, 17, 20, 21, 29, 30, 33 and 34 At 105 ^{o}C dried: lab 2, 4, 7, 13, 14, 25, 26 and 36 Air dried & at 105 ^{o}C dried: lab 20 No drying: lab 1, 10, 31,35 and 39	Air dried: lab 4, 11, 15, 16, 17, 20, 21, 24, 28, 29, 30, 33, 34 and 37 At 105 ^{o}C dried: lab 5, 6, 9, 12, 13 36 and 38 Air dried & at 105 ^{o}C dried: lab 5, 19, 23 and 26 No drying: lab 1, 10, 31, 35 and 39
Equipment (manufacturer, volume of bomb and volume of added water)	10 labs: IKA (model C2000, C5000, C5003 or C7000) with different bomb volumes (200 – 260 ml) and with the added water of 1 or 5 ml 8 labs: PARR (model 1261, 1281, 6300 or 6400) with bomb volume 250 ml (or not given) and with the added water of 0 ml (lab 2 and 26), 1 ml, 5 ml, 65 ml (lab 21) or not given 5 labs: LECO (model AC 300 or 350) with bomb volume 300 - 400 ml and with the added water of 1 ml or 5 ml 1 lab: Other models (lab 3)	14 labs: IKA (model 2000, 5000, 5003 or 7000) with different bomb volumes (200 – 260 ml) and with the added water of 1 or 5 ml 7 labs: LECO (model AC 300, 350 or 500) with bomb volume 300 - 400 ml and with added water of 1 – 10 ml 5 labs: PARR (model 1281,6200, 6300 or 6400) with bomb volume 250 ml (or not given) and with the added water of 1 ml, 65 ml (lab 21), or not given 2 labs: Other models (lab 12 and 37)

METHOD DESCRIPTIONS (continue)

Measurements:

Measurement of gross calorific value	**Sample B1**	**Sample K1**
Calibration	**Benzoeacid** 7 labs: PARR, 26454, 26434.9 or 26432.1 J/g 4 labs: BAS-BCS, 26439,7 J/g 3 labs: IKA , 26456 J/g 3 labs: ALPHA, 26564, 26454 or 26457J/g 2 labs: NIST, 26434 J/g 1 lab: Fluka, 26470 J/g 1 lab: LECO, 26 451 J/g 1 lab: POCH, 26450 J/g 8 labs: as weighed 6 labs: in air 3 labs: in vacuum 1 lab: keep in P_2O_5 **Correction of the certified value[1]** 16 labs: no 6 labs: yes (lab 4, 10, 17, 26, 30 and 39)[1]	**Benzoeacid** 6 labs: PARR, 26454 or 26432.1 J/g 6 labs: IKA , 26460, 26456 or 26556 J/g 4 labs: BAS-BCS, 26439,7 J/g 3 labs: ALPHA, 26454, 26464 or 26457J/g 2 labs: NIST, 26434 J/g 2 lab: LECO, 26 451 J/g 1 lab: Fluka, 26470 J/g 1 lab: POCH, 26450 J/g 10 labs: as weighed 5 labs: in air 5 labs: in vacuum 1 lab: keep in P_2O_5 1 lab: in oxygen (lab 6) **Correction of the certified value[1]** 21 labs: no 5 labs: yes (lab 4, 10, 17, 30 and 39)[1]

[1]Correction the value given in the certificate
lab 4: weight in air, pressure in bomb, room temperature, mass of b tablet, water in bomb volume
lab 10: + 35 J/g acid correction
lab 17: according to the certificate
lab 26: according to DIN 51900
lab 30: by multiplying the certified value with f (determined at the laboratory)
lab 39: the corrected value 26 449 J/g (5ml of water)

METHOD DESCRIPTIONS (continue)

Measurements:

Measurement of C, H and N	**Sample B1**	**Sample K1**
Standard method	9 labs: CEN/TS 15104 1 lab: ISO/TS 12902 1 lab: ASTM D5373 1 lab: CEN/TS 15289 1 lab: DIN 51732 1 lab: IB/TL method	8 lab: ASTM D5373 or/and 5291 5 labs: CEN/TS 15104 4 lab: ISO/TS 12902 1 lab: CEN/TS 15289 1 lab: DIN 51732 1 lab: IB/TL method 1 lab: PN-G-04571 1 lab: C, H- conductivity measurement (lab 22) 1 lab C, H- calculated, N- ASTM D3179 (lab 16)
Sample amount	1 – 350 mg (depending on an equipment)	1 – 250 mg (depending on an equipment)
Equipment (manufacturer)	6 labs: VarioMAX CHN 2 labs: Vario EL 4 labs: LECO CHN 2 labs: ELTRA CHS 1 lab: CE Instruments 1 lab: EURO EA	6 labs: VarioMAX CHN 2 labs: Vario EL 6 labs: LECO CHN, TC or CS 3 labs: ELTRA CHS 1 lab: Vario MACRO 1 lab: Instruments EA 1 lab: KJELFLEX 1 lab: COSTEC (Only C)
Measurement of S	**Sample B1**	**Sample K1**
Standard method	3 labs: CEN/TS 15289 3 labs: ASTM D4239 1 lab: DIN 51724 1 lab: ESV 664 1 lab: ISO 334 1 lab: SS 187177 1 lab: IB/TL method 1 lab: EN 14582 1 lab: CEN/TS 15289 1 lab: NFM 03-038 1 lab: in-house method	10 labs: ASTM D4239 4 labs: ISO 334 (Eschka method) 1 lab: DIN 51724 1 lab: SS 187177 1 lab: IB/TL method 1 lab: PN-6- 04584 1 lab: EN 14582 3 labs: in-house method
Sample amount	Mainly 0.1-0.5 g (depending on an equipment), 1-2 mg (lab 36) ESV method: 1 g	Mainly 0.1-0.4 g (depending on an equipment), 1-2 mg (lab 36) ISO 334 /Eschka method: 1 g
Equipment (manufacturer)	5 labs: ELTRA CS 4 labs: LECO SC or S 1 lab: IKA AOD 1 lab: SYLAB-IRF 1 lab: EURO EA 1 lab: ASC PIE 1 lab: Oxidation + ion chromatorgraphy (lab 29)	8 labs: ELTRA CS or CHS 8 labs: LECO SC or S 1 lab: IKA AOD 1 lab: EURO EA 1 lab: ASL PIE 1 lab: Vario MACRO 1 lab: Oxidation + ion chromatorgraphy (lab 29)

METHOD DESCRIPTIONS (continue)

Measurements:

Measurement of ash content	**Sample B1**	**Sample K1**
Standard method	12 labs: CEN/TS 14775 3 labs: DIN 51719 1 lab: SS187171 1 lab: PN-6-04560 1 lab: EN 15169 1 lab: NFM 03-003	12 labs: ISO 1171 5 labs: DIN 51719 4 labs: ASTM D5142 1 lab: SS187157 1 lab: ASTM D3174 1 lab: PN-6-04560 1 lab: EN 15169
Sample amount	0.6-4 g (mainly 1 g)	0.15-5 g (mainly 1 g)
Measurement and temperature	**Measurement** 15 labs: Gravimetric 4 labs: TGA (lab 10, 15, 20 and 29) 1 lab: Tgl (lab 3) **Temperature** 12 labs: 550 ^{o}C 3 labs: 815 ^{o}C (lab 1, 35 and 36) 1 lab: 500 ^{o}C (lab 34) 1 lab: 600 ^{o}C (lab 15)	**Measurement** 19 labs: Gravimetric 8 labs: TGA (lab 9, 10, 11, 15, 20, 24, 28 and 29) **Temperature** 22 labs: 815 ^{o}C 2 lab: 750 ^{o}C (lab 28 and 37)
Measurement of moisture	**Sample B1**	**Sample K1**
Standard method	10 labs: CEN/TS 14774 1 lab: DIN 51718 1 lab: DIN 38414 1 lab: ISO 589 1 lab: EN 14346 1 lab: SS 187184 1 lab: PN-6-04560 1 NFM 03-002 1 lab: IR-scale	7 labs: ISO 589 4 labs: DIN 51718 3 labs: ASTM D5142 1 lab: DIN 38414 1 lab: EN 14346 1 lab: STN 441377 1 lab: ISO 11722 1 lab/ CEN/TS 14774 1 lab GOST 11014 1 lab: IR-scale 1 lab: PN-6-05460

METHOD DESCRIPTIONS (continue)

Calculations:

Gross calorific value	**Sample B1**	**Sample K1**
Correction taken into account in calculations	wire, ignition, acid, moisture (lab 1) cotton, acid, moisture (lab 2) wire, cotton, moisture (lab 3) wire, ignition, S, acid (lab 4) wire (lab 7) wire, cotton, S, acid, moisture (lab 10) S, moisture (lab 11) moisture (lab 13 and 31) wire, S, acid (lab 14) correction 138.48 J/g (lab 15) wire, ignition, S, acid, moisture (lab 17) wire, S, acid, moisture (lab 19 and 21) wire, S and N (lab 20) ignition, S, acid (lab 25) wire, moisture,d (lab 26) wire, S moisture (lab 29 and 30) wire, moisture, N, S (lab 33) not in detail (lab 34) acid (lab 35) wire, cotton, ignition, capsule of acetobutyrate (lab 36) wire, S, moisture (lab 39)	wire, ignition, acid, moisture (lab 1) wire, ignition, S, moisture, acid (lab 4 and 17) not in detail (lab 5, 16, 34 and 38) wire, S, acid (lab 6 and 14) wire (lab 7) wire, S (lab 9) cotton (lab 10) S, moisture (lab 11 and 24) wire, S, acid, moisture (lab 12, 19 and 21) correction 138.48 J/g (lab 15) wire, S, N (lab 20) wire, acid, moisture (lab 23) wire, N, S, moisture (lab 27 and 33) wire, ignition, S (lab 28) wire, S, moisture (lab 29, 30 and 39) wire, cotton, ignition, capsule of acetobutyrate (lab 36) wire, cotton, S, acid (lab 37)
Net calorific value	**Sample B1**	**Sample K1**
Correction taken into account in calculations	N+O, H/measured (lab 1, 4, 7, 11, 36 and 39) H/fixed (lab 2, 3 and 17) H/measured (lab 14, 15, 19, 30 and 35) N+O, HHV (lab 10) H/calculated (lab 25) N+O, H/fixed (lab 26) [N+O]=100 % -[ash-C-H-S] (lab 29) CEN/TS 14918, cap. 12.2 (lab 33) not in detail (lab 34 and 38)	N+O, H/measured (lab 1, 4, 7, 9, 11, 36 and 39) not in detail (lab 5, 16, 34 and 38) H/measured (lab 7, 9, 14, 15, 19 and 28) N+O, HHV (lab 10) H/fixed (lab 12) H/calculated from volatiles (lab 23) H/calculated using Nanlin equation (lab 24) ISO 1928 constant pressure (lab 27) N+O]=100 % -[ash-C-H-S] (lab 29) N+O, H/measured, ash (lab 30) CEN/TS 14918, cap. 12.2 (lab 33) N+O, H/measured (lab 37)

METHOD DESCRIPTIONS (continue)

Calculations:

Emission factor (EF)	Sample B1	Sample K1
Equation according to the decision 2007/589/EC	11 labs: According to EC decision[1] 1 lab: national (lab 14) 1 lab (lab 29): based on the equation: 1000*3.664*(C/100)*(1-(50.8/100)/Q(p,net,50,8 %)	11 labs: According to EC decision 3 labs: national (lab 5,14,24) 1 lab (lab 29): based on the equation: 1000*3.664*(C/100)*(1-(8.27/100)/Q(p,net,8.27 %)

[1]In the sample letter the provider gave a possibility to the participants to calculate the EF-value using the procedure presented in the EC directive and using the total moisture content as received presented in the letter. Later has been obtained, that in the EC directives has not been given the detailed equation for calculation of EF-values. However, a written description has been given. Due to this some national guides for the equation of EF-value calculation has been produced.

ASSIGNED VALUES AND THEIR UNCERTAINTIES

Analyte	Sample	Unit	Assigned value	Estimation of assigned value	n	Uncertainty (U = 2*u)[1)], %	u/s_p [2)]
Ash	B1	w%	5.31	Robust mean	23	1.9	0.3
	K1	w%	8.71	Robust mean	27	0.83	0.2
C	B1	w%	54.62	Robust mean	17	0.98	0.3
	K1	w%	72.62	Robust mean	24	2.5	0.3
H	B1	w%	6.07	Robust mean	14	3.1	0,3
	K1	w%	5.20	Robust mean	20	3.0	0.3
EF	B1	tCO_2/TJ	108	Robust mean	11	1.4	0.3
	K1	tCO_2/TJ	-	Robust mean	-	-	-
M	B1	w%	7.68	Robust mean	24	3.9	-
	K1	w%	3.17	Robust mean	24	5.6	-
N	B1	w%	2.73	Robust mean	15	3.5	0.2
	K1	w%	2.26	Robust mean	19	4.7	0.3
q-p,net,d	B1	J/g	21218	Robust mean	19	0.44	0.3
	K1	J/g	28878	Robust mean	20	0.31	0.3
q-V,gr,d	B1	J/g	22505	Robust mean	25	0.41	0.3
	K1	J/g	29962	Robust mean	25	0.26	0.3
S	B1	w%	0.21	Robust mean	21	3.6	0.2
	K1	w%	0.21	Robust mean	25	2.9	0.2

The expanded uncertainty of the assigned value[1)] was estimated according to the equation [3]:

$$U\% = \frac{100 \times \left(\frac{2 \times 1.25 \times s_{rob}}{\sqrt{n}} \right)}{AV}$$

where,
U% = the expanded uncertainty of the assigned value
n = the number of the results
s_{rob} = the robust standard deviation
AV= the assigned value

To test the reliability of uncertainty of assigned value the ratio, u/s_p [2)], was calculated [4], where:

s_p = the total standard deviation for proficiency assessment divided by 2
u = the standard uncertainty of the assigned value

If $u/s_p \leq 0.3$ the assigned value is reliable and the z scores are qualified.

EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant

Sample	The code of the sample
z-Graphics	z score - the graphical presentation
z score	calculated as follows: $z = (x_i - X)/s_p$, where x_i = the result of the individual laboratory X = the reference value (*the assigned value*) s_p = the target value of the standard deviation for proficiency assessment.
Outl test OK	yes - the result passed the outlier test H = Hampel test (a test for the mean value) In addition, in robust statistics some results deviating from the original robust mean have been rejected.
Assigned value	the reference value
2* Targ SD %	the target value of total standard deviation for proficiency assessment (s_p) at 95 % confidence level
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
Robust mean	Robust mean
SD	Standard deviation
SD%	Standard deviation, %
SD %rob	Robust standard deviation, %
Passed	The results passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores

A - accepted ($-2 \le z \le 2$)
p - questionable ($2 < z \le 3$), positive error, the result > X
n - questionable ($-3 \le z < -2$), negative error, the result < X
P - non- accepted ($z > 3$), positive error, the result >>> X
N - non- accepted ($z < -3$), negative error, the result <<< X (X = the reference value)

Robust analysis

The items of data is sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.

Initial values for x^* and s^* are calculated as:

X^* = median of x_i $(i = 1, 2, \ldots p)$
s^* = 1.483 median of $|x_i - x^*|$ $(i = 1, 2, \ldots p)$

For each x_i $(i = 1, 2, \ldots p)$ is calculated:

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

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

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

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

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

Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons, Annex C ISO 13528 2005 [3].

LIITE 8.

Appendix 8. *RESULTS OF EACH LABORATORY*

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig- ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl. fai- led	Mis- sing	Num of labs
Laboratory 1																
Ash	w%	B1		-0,646	yes	5,31	7	5,19	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		0,164	yes	8,71	3,5	8,735	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-0,311	yes	54,62	3	54,36	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-0,041	yes	72,62	3	72,58	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-6,551	H	108	4	93,85	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			92,15	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,018	yes	6,07	9	6,065	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		0,000	yes	5,17	9	5,17	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,375	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,4	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-0,464	yes	2,73	15	2,635	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		-0,796	yes	2,26	15	2,125	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		0,017	yes	21220	1,4	21220	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-0,166	yes	28880	1	28850	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		0,187	yes	22510	1,4	22530	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-0,017	yes	29960	1	29960	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,635	yes	0,21	15	0,22	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,000	yes	0,21	15	0,21	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 2																
Ash	w%	B1		0,457	yes	5,31	7	5,395	5,28	5,258	0,243	4,6	25	1	0	26
M	w%	B1			yes	7,68		7,975	7,6	7,609	0,5159	6,8	23	4	0	27
q-p,net,d	J/g	B1		0,377	yes	21220	1,4	21270	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		-0,057	yes	22510	1,4	22500	22500	22520	227,7	1	23	5	0	28
Laboratory 3																
Ash	w%	B1		1,614	yes	5,31	7	5,61	5,28	5,258	0,243	4,6	25	1	0	26
M	w%	B1			yes	7,68		8,36	7,6	7,609	0,5159	6,8	23	4	0	27
q-p,net,d	J/g	B1		0,616	yes	21220	1,4	21310	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		0,257	yes	22510	1,4	22550	22500	22520	227,7	1	23	5	0	28
S	w%	B1		-1,270	yes	0,21	15	0,19	0,214	0,2149	0,01611	7,5	19	1	1	21
Laboratory 4																
Ash	w%	B1		1,533	yes	5,31	7	5,595	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		0,656	yes	8,71	3,5	8,81	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-0,049	yes	54,62	3	54,58	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		0,161	yes	72,62	3	72,8	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-0,370	yes	108	4	107,2	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			93,75	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		0,139	yes	6,07	9	6,108	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		0,258	yes	5,17	9	5,23	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,51	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		2,85	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		0,137	yes	2,73	15	2,758	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		0,534	yes	2,26	15	2,351	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-0,259	yes	21220	1,4	21180	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-1,506	yes	28880	1	28660	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-0,016	yes	22510	1,4	22500	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-1,212	yes	29960	1	29780	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,191	yes	0,21	15	0,213	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,444	yes	0,21	15	0,217	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 5																
Ash	w%	K1		-0,262	yes	8,71	3,5	8,67	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		0,537	yes	72,62	3	73,21	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	K1			yes			93,3	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	K1		-0,236	yes	5,17	9	5,115	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		3,635	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	K1		0,807	yes	28880	1	28990	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		0,844	yes	29960	1	30090	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		-0,635	yes	0,21	15	0,2	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 6																
Ash	w%	K1		-0,853	yes	8,71	3,5	8,58	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		1,864	yes	72,62	3	74,65	72,75	72,64	1,272	1,8	23	2	0	25
H	w%	K1		7,675	H	5,17	9	6,955	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		2,29	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	K1		1,000	yes	2,26	15	2,429	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	K1		-4,806	H	28880	1	28180	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		-2,313	yes	29960	1	29620	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		21,330	H	0,21	15	0,546	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 7																
Ash	w%	B1		0,484	yes	5,31	7	5,4	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-0,426	yes	8,71	3,5	8,645	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-1,593	yes	54,62	3	53,31	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-1,744	yes	72,62	3	70,72	72,75	72,64	1,272	1,8	23	2	0	25
H	w%	B1		1,223	yes	6,07	9	6,404	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		2,257	yes	5,17	9	5,695	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,555	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,145	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-0,103	yes	2,73	15	2,709	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		-0,817	yes	2,26	15	2,122	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		0,757	yes	21220	1,4	21330	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		2,649	C	28880	1	29260	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		1,349	yes	22510	1,4	22720	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-4,649	H	29960	1	29270	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		-0,127	yes	0,21	15	0,208	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,540	yes	0,21	15	0,2185	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 8																
Ash	w%	B1		-0,323	yes	5,31	7	5,25	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		0,623	yes	8,71	3,5	8,805	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		3,198	H	54,62	3	57,24	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		3,475	yes	72,62	3	76,41	72,75	72,64	1,272	1,8	23	2	0	25
M	w%	B1			yes	7,68		7,82	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,25	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	B1		-0,832	yes	21220	1,4	21090	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		0,679	yes	28880	1	28980	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-0,746	yes	22510	1,4	22390	22500	22520	227,7	1	23	5	0	28
	J/g	K1		0,654	yes	29960	1	30060	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,254	yes	0,21	15	0,214	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,032	yes	0,21	15	0,2105	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 9																
Ash	w%	K1		-0,197	yes	8,71	3,5	8,68	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		4,517	H	72,62	3	77,54	72,75	72,64	1,272	1,8	23	2	0	25
H	w%	K1		-0,462	C	5,17	9	5,063	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		3,205	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	K1		1,602	yes	2,26	15	2,532	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	K1		-0,326	yes	28880	1	28830	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		-0,551	yes	29960	1	29880	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		-0,381	yes	0,21	15	0,204	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 10																
Ash	w%	B1		-0,780	yes	5,31	7	5,165	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-1,440	yes	8,71	3,5	8,491	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-0,647	yes	54,62	3	54,09	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-1,397	yes	72,62	3	71,1	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-0,749	yes	108	4	106,4	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			H			99,17	92,9	92,9	1,367	1,5	16	1	0	17
M	w%	B1			yes	7,68		6,745	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,475	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	B1		-0,448	yes	21220	1,4	21150	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-7,597	H	28880	1	27780	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-0,467	yes	22510	1,4	22430	22500	22520	227,7	1	23	5	0	28
	J/g	K1		0,010	yes	29960	1	29960	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		2,895	yes	0,21	15	0,2556	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-0,254	yes	0,21	15	0,206	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 11																
Ash	w%	B1		0,484	yes	5,31	7	5,4	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-0,361	yes	8,71	3,5	8,655	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		0,281	yes	54,62	3	54,85	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		0,073	yes	72,62	3	72,7	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-6,574	H	108	4	93,8	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			90,65	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,622	yes	6,07	9	5,9	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-0,731	yes	5,17	9	5	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		8,15	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,2	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		0,830	yes	2,73	15	2,9	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		0,236	yes	2,26	15	2,3	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		1,431	yes	21220	1,4	21430	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		2,618	C	28880	1	29260	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		1,317	yes	22510	1,4	22710	22500	22520	227,7	1	23	5	0	28
	J/g	K1		2,460	C	29960	1	30330	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,000	yes	0,21	15	0,21	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,000	yes	0,21	15	0,21	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 12																
Ash	w%	K1		0,066	yes	8,71	3,5	8,72	8,705	8,716	0,1498	1,7	25	4	0	29
M	w%	K1			yes	3,17		3,035	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	K1		-0,526	yes	28880	1	28800	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		-0,274	yes	29960	1	29920	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		1,587	yes	0,21	15	0,235	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 13																
Ash	w%	B1		-0,215	yes	5,31	7	5,27	5,28	5,258	0,243	4,6	25	1	0	26
M	w%	B1			H	7,68		10,05	7,6	7,609	0,5159	6,8	23	4	0	27
q-p,net,d	J/g	B1		4,952	H	21220	1,4	21950	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		4,256	yes	22510	1,4	23180	22500	22520	227,7	1	23	5	0	28
Laboratory 14																
Ash	w%	B1		1,264	yes	5,31	7	5,545	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-2,165	yes	8,71	3,5	8,38	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		0,207	yes	54,62	3	54,79	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-1,244	yes	72,62	3	71,27	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-5,880	H	108	4	95,3	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			94,85	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		1,208	yes	6,07	9	6,4	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-1,676	yes	5,17	9	4,78	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		6,86	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		1,79	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		1,514	yes	2,73	15	3,04	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		-0,738	yes	2,26	15	2,135	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		8,093	H	21220	1,4	22420	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-9,370	H	28880	1	27530	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-9,141	H	22510	1,4	21070	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-9,459	H	29960	1	28550	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,318	yes	0,21	15	0,215	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-0,413	yes	0,21	15	0,2035	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 15																
Ash	w%	B1		-0,511	yes	5,31	7	5,215	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		0,722	yes	8,71	3,5	8,82	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		0,500	yes	54,62	3	55,03	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		0,941	yes	72,62	3	73,64	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		0,255	yes	108	4	108,5	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			94,05	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,696	yes	6,07	9	5,88	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		2,708	yes	5,17	9	5,8	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,75	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,225	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		0,220	yes	2,73	15	2,775	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		0,088	yes	2,26	15	2,275	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-0,848	yes	21220	1,4	21090	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		0,312	yes	28880	1	28920	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-0,825	yes	22510	1,4	22380	22500	22520	227,7	1	23	5	0	28
	J/g	K1		1,509	yes	29960	1	30190	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		-0,286	yes	0,21	15	0,2055	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-1,143	yes	0,21	15	0,192	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 16																
Ash	w%	K1		-0,394	yes	8,71	3,5	8,65	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		0,294	yes	72,62	3	72,94	72,75	72,64	1,272	1,8	23	2	0	25
H	w%	K1		-0,150	yes	5,17	9	5,135	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		3,05	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	K1		-1,416	yes	2,26	15	2,02	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	K1		-0,229	yes	28880	1	28850	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		-0,384	yes	29960	1	29900	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		-4,444	H	0,21	15	0,14	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 17																
Ash	w%	B1		0,404	yes	5,31	7	5,385	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-0,558	yes	8,71	3,5	8,625	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-1,037	yes	54,62	3	53,77	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-1,111	yes	72,62	3	71,41	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-0,880	yes	108	4	106,1	107,3	107,5	1,692	1,6	11	5	0	16
M	w%	B1			yes	7,68		6,49	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		1,875	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		0,193	yes	2,73	15	2,769	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		0,466	yes	2,26	15	2,339	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-0,842	yes	21220	1,4	21090	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		-1,219	yes	22510	1,4	22310	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-1,225	yes	29960	1	29780	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		1,460	yes	0,21	15	0,233	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,286	yes	0,21	15	0,2145	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 18																
q-V,gr,d	J/g	B1		0,778	yes	22510	1,4	22630	22500	22520	227,7	1	23	5	0	28
Laboratory 19																
Ash	w%	B1		0,511	yes	5,31	7	5,405	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		3,280	H	8,71	3,5	9,21	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-0,049	yes	54,62	3	54,58	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		0,262	yes	72,62	3	72,91	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-0,301	yes	108	4	107,3	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			92,9	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,071	yes	6,07	9	6,05	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-0,217	yes	5,17	9	5,12	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,565	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,49	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-0,882	yes	2,73	15	2,55	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		0,012	yes	2,26	15	2,262	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-0,421	yes	21220	1,4	21160	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		0,717	yes	28880	1	28980	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-0,181	yes	22510	1,4	22480	22500	22520	227,7	1	23	5	0	28
	J/g	K1		0,918	yes	29960	1	30100	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		1,016	yes	0,21	15	0,226	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-0,667	yes	0,21	15	0,1995	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig- ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl. fai- led	Mis- sing	Num of labs
Laboratory 20																
Ash	w%	B1		-3,309	yes	5,31	7	4,695	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		66,290	H	8,71	3,5	18,82	8,705	8,716	0,1498	1,7	25	4	0	29
M	w%	B1			yes	7,68		7,535	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			H	3,17		1,57	3,145	3,034	0,4882	16,0	26	3	0	29
q-V,gr,d	J/g	B1		-14,960	H	22510	1,4	20150	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-6,562	H	29960	1	28980	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		-0,762	yes	0,21	15	0,198	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-0,825	yes	0,21	15	0,197	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 21																
Ash	w%	B1		0,054	yes	5,31	7	5,32	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		268,600	H	8,71	3,5	49,65	8,705	8,716	0,1498	1,7	25	4	0	29
M	w%	B1			yes	7,68		8,3	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		2,77	3,145	3,034	0,4882	16,0	26	3	0	29
q-V,gr,d	J/g	B1		-2,158	yes	22510	1,4	22170	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-0,681	yes	29960	1	29860	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		-0,063	yes	0,21	15	0,209	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-1,143	C	0,21	15	0,192	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 22																
C	w%	K1		0,789	yes	72,62	3	73,48	72,75	72,64	1,272	1,8	23	2	0	25
H	w%	K1		-0,967	yes	5,17	9	4,945	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		2,965	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	K1		-2,773	yes	2,26	15	1,79	2,274	2,234	0,1865	8,3	19	0	0	19
S	w%	K1		0,254	yes	0,21	15	0,214	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 23																
Ash	w%	K1		-0,197	yes	8,71	3,5	8,68	8,705	8,716	0,1498	1,7	25	4	0	29
M	w%	K1			yes	3,17		3,16	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	K1		-0,436	yes	28880	1	28820	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		-0,344	yes	29960	1	29910	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		-0,222	yes	0,21	15	0,2065	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 24																
Ash	w%	K1		0,230	yes	8,71	3,5	8,745	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		-0,464	yes	72,62	3	72,12	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	K1			yes			92,24	92,9	92,9	1,367	1,5	16	1	0	17
M	w%	K1			yes	3,17		3,426	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	K1		-0,069	yes	28880	1	28870	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		0,234	yes	29960	1	30000	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		0,921	yes	0,21	15	0,2245	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 25																
Ash	w%	B1		-0,915	yes	5,31	7	5,14	5,28	5,258	0,243	4,6	25	1	0	26
M	w%	B1			yes	7,68		7,83	7,6	7,609	0,5159	6,8	23	4	0	27
q-p,net,d	J/g	B1		1,330	yes	21220	1,4	21420	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		0,828	yes	22510	1,4	22640	22500	22520	227,7	1	23	5	0	28
Laboratory 26																
Ash	w%	B1		-3,390	yes	5,31	7	4,68	5,28	5,258	0,243	4,6	25	1	0	26
M	w%	B1			yes	7,68		7,61	7,6	7,609	0,5159	6,8	23	4	0	27
q-p,net,d	J/g	B1		0,929	yes	21220	1,4	21360	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		0,428	yes	22510	1,4	22570	22500	22520	227,7	1	23	5	0	28
Laboratory 27																
Ash	w%	B1		17,730	H	5,31	7	8,605	5,28	5,258	0,243	4,6	25	1	0	26
M	w%	B1			H	7,68		3,325	7,6	7,609	0,5159	6,8	23	4	0	27
q-p,net,d	J/g	B1		55,210	H	21220	1,4	29420	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		48,280	H	22510	1,4	30110	22500	22520	227,7	1	23	5	0	28
Laboratory 28																
Ash	w%	K1		0,131	yes	8,71	3,5	8,73	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		0,138	yes	72,62	3	72,77	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	K1			yes			92,75	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	K1		-0,322	yes	5,17	9	5,095	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		3,19	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	K1		-0,979	yes	2,26	15	2,094	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	K1		0,599	yes	28880	1	28960	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		0,681	yes	29960	1	30060	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1			H	0,21	15	n.a.	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 29																
Ash	w%	B1		-1,883	yes	5,31	7	4,96	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-1,509	C	8,71	3,5	8,48	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-1,135	yes	54,62	3	53,69	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-0,748	yes	72,62	3	71,81	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-1,574	yes	108	4	104,6	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			90,75	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,800	yes	6,07	9	5,851	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-0,898	yes	5,17	9	4,961	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			H	7,68		92,67	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			H	3,17		97,87	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-0,002	yes	2,73	15	2,729	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		0,112	yes	2,26	15	2,279	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		0,751	yes	21220	1,4	21330	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		2,324	yes	28880	1	29210	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		1,742	C	22510	1,4	22780	22500	22520	227,7	1	23	5	0	28
	J/g	K1		2,109	yes	29960	1	30280	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,191	yes	0,21	15	0,213	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,000	yes	0,21	15	0,21	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 30																
Ash	w%	B1		1,157	yes	5,31	7	5,525	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		2,067	yes	8,71	3,5	9,025	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		0,140	yes	54,62	3	54,73	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-0,331	yes	72,62	3	72,26	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-0,949	yes	108	4	106	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			92,2	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,659	yes	6,07	9	5,89	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-0,393	yes	5,17	9	5,079	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,5	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		2,95	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-0,254	yes	2,73	15	2,678	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		-0,094	yes	2,26	15	2,244	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		1,586	yes	21220	1,4	21450	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		0,471	yes	28880	1	28950	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		1,482	yes	22510	1,4	22740	22500	22520	227,7	1	23	5	0	28
	J/g	K1		0,481	yes	29960	1	30030	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,667	yes	0,21	15	0,2205	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-1,333	yes	0,21	15	0,189	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 31																
M	w%	B1			yes	7,68		6,795	7,6	7,609	0,5159	6,8	23	4	0	27
q-V,gr,d	J/g	B1		-1,247	yes	22510	1,4	22310	22500	22520	227,7	1	23	5	0	28
Laboratory 32																
Ash	w%	B1		-0,915	yes	5,31	7	5,14	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-0,262	yes	8,71	3,5	8,67	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		1,398	yes	54,62	3	55,77	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		0,978	yes	72,62	3	73,69	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		0,976	yes	108	4	110,1	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			94,72	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		1,863	yes	6,07	9	6,579	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		1,343	yes	5,17	9	5,482	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,995	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,075	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-1,934	yes	2,73	15	2,334	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		-1,678	yes	2,26	15	1,976	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-0,963	yes	21220	1,4	21080	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-1,060	yes	28880	1	28730	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-0,060	yes	22510	1,4	22500	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-0,437	yes	29960	1	29900	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,667	yes	0,21	15	0,2205	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		0,635	yes	0,21	15	0,22	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 33																
Ash	w%	B1		-0,027	yes	5,31	7	5,305	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		1,607	yes	8,71	3,5	8,955	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-0,037	yes	54,62	3	54,59	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		0,110	yes	72,62	3	72,74	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		0,579	yes	108	4	109,3	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			92,55	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-1,867	yes	6,07	9	5,56	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-1,590	yes	5,17	9	4,8	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,49	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		3,47	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		1,319	yes	2,73	15	3	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		1,298	yes	2,26	15	2,48	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-2,609	yes	21220	1,4	20830	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		0,918	yes	28880	1	29010	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-2,952	yes	22510	1,4	22040	22500	22520	227,7	1	23	5	0	28
	J/g	K1		0,517	yes	29960	1	30040	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		0,444	yes	0,21	15	0,217	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-0,254	yes	0,21	15	0,206	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 34																
Ash	w%	B1		0,619	yes	5,31	7	5,425	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		0,066	yes	8,71	3,5	8,72	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		2,356	yes	54,62	3	56,55	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		1,405	C	72,62	3	74,15	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		0,741	yes	108	4	109,6	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			94,9	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		-0,650	yes	6,07	9	5,893	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		0,499	yes	5,17	9	5,286	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		7,55	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		2,6	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	B1		-80,200	H	21220	1,4	9306	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-17,970	H	28880	1	26280	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		0,159	yes	22510	1,4	22530	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-0,077	yes	29960	1	29950	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		-0,476	yes	0,21	15	0,2025	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-1,111	yes	0,21	15	0,1925	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 35																
Ash	w%	B1		-0,538	yes	5,31	7	5,21	5,28	5,258	0,243	4,6	25	1	0	26
C	w%	B1		-1,106	yes	54,62	3	53,714	54,6	54,61	0,8028	1,5	16	2	0	18
EF	tCO2/TJ	B1		-6,713	H	108	4	93,5	107,3	107,5	1,692	1,6	11	5	0	16
H	w%	B1		0,242	yes	6,07	9	6,136	6,05	6,065	0,279	4,6	14	1	0	15
M	w%	B1			yes	7,68		8,4	7,6	7,609	0,5159	6,8	23	4	0	27
N	w%	B1		-0,352	yes	2,73	15	2,658	2,716	2,73	0,1757	6,4	15	0	0	15
q-p,net,d	J/g	B1		-1,084	yes	21220	1,4	21057	21180	21210	158,1	0,7	19	5	0	24
q-V,gr,d	J/g	B1		-1,168	yes	22510	1,4	22321	22500	22520	227,7	1	23	5	0	28
S	w%	B1		2,540	yes	0,21	15	0,25	0,214	0,2149	0,01611	7,5	19	1	1	21
Laboratory 36																
Ash	w%	B1		-1,560	yes	5,31	7	5,02	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		-0,886	yes	8,71	3,5	8,575	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		-5,078	H	54,62	3	50,46	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-1,515	yes	72,62	3	70,97	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-8,472	H	108	4	89,7	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			90,8	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		0,568	yes	6,07	9	6,225	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		-0,580	yes	5,17	9	5,035	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			H	7,68		5,65	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			H	3,17		1,35	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		-0,440	yes	2,73	15	2,64	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		1,150	yes	2,26	15	2,455	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-5,642	H	21220	1,4	20380	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-3,899	yes	28880	1	28320	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		-4,856	H	22510	1,4	21740	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-3,685	yes	29960	1	29410	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1			H	0,21	15	<0,1	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1			H	0,21	15	<0,1	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 37																
Ash	w%	K1		0,328	yes	8,71	3,5	8,76	8,705	8,716	0,1498	1,7	25	4	0	29
q-p,net,d	J/g	K1		-1,503	yes	28880	1	28660	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		-1,011	yes	29960	1	29810	29940	29930	184,4	0,6	25	4	0	29
Laboratory 38																
Ash	w%	K1		0,197	yes	8,71	3,5	8,74	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	K1		0,353	yes	72,62	3	73	72,75	72,64	1,272	1,8	23	2	0	25
H	w%	K1		1,163	yes	5,17	9	5,441	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	K1			yes	3,17		3,82	3,145	3,034	0,4882	16,0	26	3	0	29
q-p,net,d	J/g	K1		-0,332	yes	28880	1	28830	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	K1		0,387	yes	29960	1	30020	29940	29930	184,4	0,6	25	4	0	29
S	w%	K1		-0,127	yes	0,21	15	0,208	0,2075	0,2075	0,01121	5,4	22	5	2	29
Laboratory 39																
Ash	w%	B1		-0,673	yes	5,31	7	5,185	5,28	5,258	0,243	4,6	25	1	0	26
	w%	K1		2,099	yes	8,71	3,5	9,03	8,705	8,716	0,1498	1,7	25	4	0	29
C	w%	B1		0,262	yes	54,62	3	54,84	54,6	54,61	0,8028	1,5	16	2	0	18
	w%	K1		-0,872	yes	72,62	3	71,67	72,75	72,64	1,272	1,8	23	2	0	25
EF	tCO2/TJ	B1		-0,046	yes	108	4	107,9	107,3	107,5	1,692	1,6	11	5	0	16
	tCO2/TJ	K1			yes			92,85	92,9	92,9	1,367	1,5	16	1	0	17
H	w%	B1		3,513	H	6,07	9	7,03	6,05	6,065	0,279	4,6	14	1	0	15
	w%	K1		1,683	yes	5,17	9	5,562	5,127	5,196	0,2811	5,4	19	2	0	21
M	w%	B1			yes	7,68		8,245	7,6	7,609	0,5159	6,8	23	4	0	27
	w%	K1			yes	3,17		2,545	3,145	3,034	0,4882	16,0	26	3	0	29
N	w%	B1		0,027	yes	2,73	15	2,736	2,716	2,73	0,1757	6,4	15	0	0	15
	w%	K1		-0,077	yes	2,26	15	2,247	2,274	2,234	0,1865	8,3	19	0	0	19
q-p,net,d	J/g	B1		-0,491	yes	21220	1,4	21150	21180	21210	158,1	0,7	19	5	0	24
	J/g	K1		-2,594	yes	28880	1	28500	28850	28840	196,1	0,7	20	6	0	26
q-V,gr,d	J/g	B1		1,003	yes	22510	1,4	22660	22500	22520	227,7	1	23	5	0	28
	J/g	K1		-1,782	yes	29960	1	29700	29940	29930	184,4	0,6	25	4	0	29
S	w%	B1		-0,984	yes	0,21	15	0,1945	0,214	0,2149	0,01611	7,5	19	1	1	21
	w%	K1		-1,111	yes	0,21	15	0,1925	0,2075	0,2075	0,01121	5,4	22	5	2	29

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

RESULTS OF DUPLICATE DETERMINATIONS

Sample B1

Ash (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	5,27	5,11	5,19	0,16	3,08
2	5,43	5,36	5,40	0,07	1,30
3	5,62	5,60	5,61	0,02	0,36
4	5,55	5,64	5,60	-0,09	-1,61
7	5,40	5,40	5,40	0,00	0,00
8	5,23	5,27	5,25	-0,04	-0,76
10	5,14	5,19	5,17	-0,05	-0,97
11	5,40	5,40	5,40	0,00	0,00
13	5,24	5,30	5,27	-0,06	-1,14
14	5,56	5,53	5,55	0,03	0,54
15	5,15	5,28	5,22	-0,13	-2,49
17	5,37	5,40	5,39	-0,03	-0,56
19	5,40	5,41	5,41	-0,01	-0,19
20	4,70	4,69	4,70	0,01	0,21
21	5,32	5,32	5,32	0,00	0,00
25	5,14	5,14	5,14	0,00	0,00
26	4,70	4,66	4,68	0,04	0,85
27	8,56	8,65	8,61	-0,09	-1,05
29	5,09	4,83	4,96	0,26	5,24
30	5,56	5,49	5,53	0,07	1,27
32	5,15	5,13	5,14	0,02	0,39
33	5,27	5,34	5,31	-0,07	-1,32
34	5,34	5,51	5,43	-0,17	-3,13
35	5,21		5,21		
36	5,01	5,03	5,02	-0,02	-0,40
39	5,26	5,11	5,19	0,15	2,89

C (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	54,36	54,37	54,37	-0,01	-0,02
4	54,57	54,59	54,58	-0,02	-0,04
7	53,10	53,53	53,32	-0,43	-0,81
8	57,09	57,39	57,24	-0,30	-0,52
10	53,94	54,24	54,09	-0,30	-0,55
11	54,90	54,80	54,90	0,10	0,18
14	54,70	54,88	54,79	-0,18	-0,33
15	54,79	55,27	55,03	-0,48	-0,87
17	53,84	53,70	53,77	0,14	0,26
19	54,56	54,60	54,58	-0,04	-0,07
29	53,75	53,63	53,69	0,12	0,22
30	54,76	54,71	54,74	0,05	0,09
32	55,72	55,81	55,77	-0,09	-0,16
33	54,64	54,54	54,59	0,10	0,18
34	56,90	56,20	56,55	0,70	1,24
35	53,71		53,71		
36	51,68	49,24	50,46	2,44	4,84
39	54,83	54,84	54,84	-0,01	-0,02

H (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	6,050	6,080	6,065	-0,030	-0,49
4	6,055	6,161	6,108	-0,106	-1,74
7	6,494	6,314	6,404	0,180	2,81
11	5,900	5,900	5,900	0,000	0,00
14	6,460	6,340	6,400	0,120	1,88
15	5,860	5,900	5,880	-0,040	-0,68
19	6,026	6,075	6,051	-0,049	-0,81
29	5,841	5,862	5,852	-0,021	-0,36
30	5,914	5,866	5,890	0,048	0,81
32	6,596	6,562	6,579	0,034	0,52
33	5,660	5,460	5,560	0,200	3,60
34	5,996	5,789	5,893	0,207	3,51
35	6,136		6,136		
36	6,400	6,050	6,225	0,350	5,62
39	7,040	7,019	7,030	0,021	0,30

N (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	2,650	2,620	2,635	0,030	1,14
4	2,821	2,695	2,758	0,126	4,57
7	2,702	2,716	2,709	-0,014	-0,52
11	2,800	3,000	2,900	-0,200	-6,90
14	3,040	3,040	3,040	0,000	0,00
15	2,740	2,810	2,775	-0,070	-2,52
17	2,776	2,763	2,770	0,013	0,47
19	2,569	2,530	2,550	0,039	1,53
29	2,719	2,740	2,730	-0,021	-0,77
30	2,661	2,695	2,678	-0,034	-1,27
32	2,327	2,341	2,334	-0,014	-0,60
33	3,000	3,000	3,000	0,000	0,00
35	2,658		2,658		
36	2,640	2,640	2,640	0,000	0,00
39	2,768	2,703	2,736	0,065	2,38

q-p,net,d (J/g)

Lab	R1	R2	Mean	Difference	Difference%
1	21271	21170	21221	101	0,48
2	21293	21255	21274	38	0,18
3	21344	21275	21310	69	0,32
4	21175	21184	21180	-9	-0,04
7	21318	21343	21331	-25	-0,12
8	21103	21086	21095	17	0,08
10	21168	21135	21152	33	0,16
11	21409	21452	21409	-43	-0,20
13	21956	21951	21954	5	0,02
14	22350	22490	22420	-140	-0,62
15	21051	21133	21092	-82	-0,39
17	21117	21069	21093	48	0,23
19	21182	21129	21156	53	0,25
25	21395	21436	21416	-41	-0,19
26	21356	21356	21356	0	0,00
27	29418	29417	29418	1	0,00
29	21335	21324	21330	11	0,05
30	21470	21437	21454	33	0,15
32	21065	21085	21075	-20	-0,09
33	20811	20850	20831	-39	-0,19
34	9326	9286	9306	40	0,43
35	21057		21057		
36	20430	20330	20380	100	0,49
39	21132	21158	21145	-26	-0,12

q-V,gr,d (J/g)

Lab	R1	R2	Mean	Difference	Difference%
1	22585	22484	22535	101	0,45
2	22515	22477	22496	38	0,17
3	22580	22511	22546	69	0,31
4	22498	22507	22503	-9	-0,04
7	22705	22730	22718	-25	-0,11
8	22396	22379	22388	17	0,08
10	22448	22415	22432	33	0,15
11	22692	22733	22692	-41	-0,18
13	23178	23173	23176	5	0,02
14	20980	21150	21065	-170	-0,81
15	22335	22415	22375	-80	-0,36
17	22337	22289	22313	48	0,22
18	22630	22625	22628	5	0,02
19	22503	22450	22477	53	0,24
20	20256	20042	20149	214	1,06
21	22250	22080	22165	170	0,77
25	22615	22656	22636	-41	-0,18
26	22573	22572	22573	1	0,00
27	30111	30110	30111	1	0,00
29	22605	22954	22780	-349	-1,53
30	22755	22722	22739	33	0,15
31	22224	22393	22309	-169	-0,76
32	22489	22502	22496	-13	-0,06
33	22018	22062	22040	-44	-0,20
34	22571	22489	22530	82	0,36
35	22321		22321		
36	21830	21650	21740	180	0,83
39	22652	22674	22663	-22	-0,10

S (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	0,220	0,220	0,220	0,000	0,00
3	0,184	0,196	0,190	-0,012	-6,32
4	0,214	0,212	0,213	0,002	0,94
7	0,206	0,210	0,208	-0,004	-1,92
8	0,214	0,214	0,214	0,000	0,00
10	0,257	0,255	0,256	0,002	0,86
11	0,210	0,210	0,210	0,000	0,00
14	0,215	0,215	0,215	0,000	0,00
15	0,197	0,214	0,206	-0,017	-8,27
17	0,247	0,219	0,233	0,028	12,02
19	0,224	0,228	0,226	-0,004	-1,77
20	0,202	0,194	0,198	0,008	4,04
21	0,202	0,216	0,209	-0,014	-6,70
29	0,211	0,215	0,213	-0,004	-1,88
30	0,217	0,224	0,221	-0,007	-3,17
32	0,216	0,225	0,221	-0,009	-4,08
33	0,217	0,217	0,217	0,000	0,00
34	0,198	0,207	0,203	-0,009	-4,44
35	0,250		0,250		
36	-1,000	-1,000	-1,000	0,000	0,00
39	0,194	0,195	0,195	-0,001	-0,51

M (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	7,37	7,38	7,38	-0,01	-0,14
2	8,00	7,95	7,98	0,05	0,63
3	8,26	8,46	8,36	-0,20	-2,39
4	7,53	7,49	7,51	0,04	0,53
7	7,56	7,55	7,56	0,01	0,13
8	7,85	7,79	7,82	0,06	0,77
10	6,56	6,93	6,74	-0,36	-5,35
11	8,20	8,10	8,20	0,10	1,22
13	10,05		10,05		
14	6,96	6,76	6,86	0,20	2,92
15	7,74	7,76	7,75	-0,02	-0,26
17	6,50	6,48	6,49	0,02	0,31
19	7,52	7,61	7,57	-0,09	-1,19
20	7,58	7,49	7,54	0,09	1,19
21	8,28	8,32	8,30	-0,04	-0,48
25	7,83	7,83	7,83	0,00	0,00
26	7,62	7,60	7,61	0,02	0,26
27	3,27	3,38	3,33	-0,11	-3,31
29	92,63	92,72	92,68	-0,09	-0,10
30	7,54	7,46	7,50	0,08	1,07
31	6,77	6,82	6,80	-0,05	-0,74
32	7,95	8,04	8,00	-0,09	-1,13
33	7,56	7,42	7,49	0,14	1,87
34	7,46	7,64	7,55	-0,18	-2,38
35	8,40		8,40		
36	5,70	5,60	5,65	0,10	1,77
39	8,25	8,24	8,25	0,01	0,12

EF (tCO2/TJ)

Lab	R1	R2	Mean	Difference	Difference%
1	93,6	94,1	93,9	-0,50	-0,53
4	107,2	107,2	107,2	0,00	0,00
10	106,3	106,4	106,4	-0,12	-0,11
11	94,0	93,6	93,8	0,40	0,43
14	95,5	95,1	95,3	0,40	0,42
15	108,3	108,8	108,6	-0,50	-0,46
17	105,8	106,4	106,1	-0,60	-0,57
19	107,2	107,5	107,4	-0,30	-0,28
29	104,6	104,6	104,6	0,00	0,00
30	105,9	106,0	106,0	-0,10	-0,09
32	110,1	110,1	110,1	-0,05	-0,04
33	109,5	109,0	109,3	0,50	0,46
34	110,0	109,2	109,6	0,80	0,73
35	93,5	89,7	91,6	3,80	4,15
39	108,0	107,8	107,9	0,20	0,19

RESULTS OF DUPLICATE DETERMINATIONS (continue)

Sample K1

Ash (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	8,73	8,74	8,74	-0,01	-0,11
4	8,81	8,81	8,81	0,00	0,00
5	8,66	8,68	8,67	-0,02	-0,23
6	8,57	8,59	8,58	-0,02	-0,23
7	8,65	8,64	8,65	0,01	0,12
8	8,82	8,79	8,81	0,03	0,34
9	8,66	8,70	8,68	-0,04	-0,46
10	8,47	8,51	8,49	-0,03	-0,39
11	8,65	8,66	8,66	-0,01	-0,12
12	8,71	8,73	8,72	-0,02	-0,23
14	8,31	8,45	8,38	-0,14	-1,67
15	8,85	8,79	8,82	0,06	0,68
16	8,63	8,67	8,65	-0,04	-0,46
17	8,61	8,64	8,63	-0,03	-0,35
19	9,22	9,20	9,21	0,02	0,22
20	18,67	18,96	18,82	-0,29	-1,54
21	50,22	49,08	49,65	1,14	2,30
23	8,72	8,64	8,68	0,08	0,92
24	8,75	8,74	8,75	0,01	0,11
28	8,69	8,77	8,73	-0,08	-0,92
29	8,32	8,64	8,48	-0,32	-3,77
30	9,07	8,98	9,03	0,09	1,00
32	8,68	8,66	8,67	0,02	0,23
33	8,87	9,04	8,96	-0,17	-1,90
34	8,69	8,75	8,72	-0,06	-0,69
36	8,59	8,56	8,58	0,03	0,35
37	8,76	8,76	8,76	0,00	0,00
38	8,77	8,71	8,74	0,06	0,69
39	9,15	8,91	9,03	0,24	2,66

C (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	72,39	72,76	72,58	-0,37	-0,51
4	72,75	72,84	72,80	-0,09	-0,12
5	73,12	73,29	73,21	-0,17	-0,23
6	74,51	74,79	74,65	-0,28	-0,38
7	70,82	70,62	70,72	0,20	0,28
8	76,44	76,37	76,41	0,07	0,09
9	77,18	77,90	77,54	-0,72	-0,93
10	70,92	71,28	71,10	-0,37	-0,51
11	72,70	72,70	72,70	0,00	0,00
14	71,38	71,15	71,27	0,23	0,32
15	73,47	73,82	73,65	-0,35	-0,48
16	72,93	72,95	72,94	-0,02	-0,03
17	71,40	71,42	71,41	-0,02	-0,03
19	72,96	72,85	72,91	0,11	0,15
22	73,76	73,20	73,48	0,56	0,76
24	72,04	72,19	72,12	-0,15	-0,21
28	72,79	72,75	72,77	0,04	0,05
29	72,03	71,58	71,81	0,45	0,63
30	72,35	72,17	72,26	0,18	0,25
32	73,61	73,76	73,69	-0,15	-0,20
33	72,95	72,53	72,74	0,42	0,58
34	74,80	73,50	74,15	1,30	1,75
36	71,17	70,77	70,97	0,40	0,56
38	72,88	73,13	73,0	-0,25	-0,34
39	71,67	71,67	71,7	0,00	0,00

H (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	5,160	5,180	5,170	-0,020	-0,39
4	5,178	5,282	5,230	-0,104	-1,99
5	5,100	5,130	5,115	-0,030	-0,59
6	6,989	6,922	6,956	0,067	0,96
7	5,705	5,685	5,695	0,020	0,35
9	5,166	4,959	5,063	0,207	4,09
11	5,000	5,000	5,000	0,000	0,00
14	4,790	4,770	4,780	0,020	0,42
15	5,820	5,780	5,800	0,040	0,69
16	5,130	5,140	5,135	-0,010	-0,19
19	5,115	5,124	5,120	-0,009	-0,18
22	4,970	4,920	4,945	0,050	1,01
28	5,105	5,085	5,095	0,020	0,39
29	4,987	4,935	4,961	0,052	1,05
30	5,090	5,067	5,079	0,023	0,45
32	5,477	5,488	5,483	-0,011	-0,20
33	4,860	4,740	4,800	0,120	2,50
34	5,270	5,302	5,286	-0,032	-0,61
36	5,020	5,050	5,035	-0,030	-0,60
38	5,461	5,420	5,441	0,041	0,75
39	5,541	5,582	5,562	-0,041	-0,74

N (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	2,120	2,130	2,125	-0,010	-0,47
4	2,331	2,370	2,351	-0,039	-1,66
6	2,415	2,444	2,430	-0,029	-1,19
7	2,104	2,139	2,122	-0,035	-1,65
9	2,480	2,583	2,532	-0,103	-4,07
11	2,300	2,300	2,300	0,000	0,00
14	2,140	2,130	2,135	0,010	0,47
15	2,270	2,280	2,275	-0,010	-0,44
16	1,990	2,050	2,020	-0,060	-2,97
17	2,326	2,352	2,339	-0,026	-1,11
19	2,293	2,231	2,262	0,062	2,74
22	1,770	1,810	1,790	-0,040	-2,23
28	2,115	2,073	2,094	0,042	2,01
29	2,279	2,279	2,279	0,000	0,00
30	2,251	2,237	2,244	0,014	0,62
32	1,973	1,978	1,976	-0,005	-0,25
33	2,440	2,520	2,480	-0,080	-3,23
36	2,460	2,450	2,455	0,010	0,41
39	2,288	2,206	2,247	0,082	3,65

q-p,net,d (J/g)

Lab	R1	R2	Mean	Difference	Difference%
1	28840	28868	28854	-28	-0,10
4	28674	28647	28661	27	0,09
5	29010	28979	28995	31	0,11
6	28118	28250	28184	-132	-0,47
7	29871	28650	29261	1221	4,17
8	28984	28968	28976	16	0,06
9	28813	28849	28831	-36	-0,12
10	27799	27763	27781	36	0,13
11	29116	29396	29256	-280	-0,96
12	28782	28822	28802	-40	-0,14
14	27580	27470	27525	110	0,40
15	28895	28951	28923	-56	-0,19
16	28839	28851	28845	-12	-0,04
19	28975	28988	28982	-13	-0,04
23	28850	28780	28815	70	0,24
24	28904	28832	28868	72	0,25
28	28957	28972	28965	-15	-0,05
29	29172	29255	29214	-83	-0,28
30	28923	28969	28946	-46	-0,16
32	28704	28746	28725	-42	-0,15
33	28923	29098	29011	-175	-0,60
34	26313	26255	26284	58	0,22
36	28320	28310	28315	10	0,04
37	28641	28681	28661	-40	-0,14
38	28850	28810	28830	40	0,14
39	28508	28499	28504	9	0,03

q-V,gr,d (J/g)

Lab	R1	R2	Mean	Difference	Difference%
1	29945	29974	29960	-29	-0,10
4	29794	29767	29781	27	0,09
5	30101	30076	30089	25	0,08
6	29549	29682	29616	-133	-0,45
7	29876	28655	29266	1221	4,17
8	30068	30052	30060	16	0,05
9	29862	29897	29880	-35	-0,12
10	29983	29944	29964	39	0,13
11	30187	30474	30331	-287	-0,95
12	29900	29942	29921	-42	-0,14
14	28600	28490	28545	110	0,39
15	30160	30216	30188	-56	-0,19
16	29898	29911	29905	-13	-0,04
17	29784	29773	29779	11	0,04
19	30093	30106	30100	-13	-0,04
20	28998	28960	28979	38	0,13
21	29920	29800	29860	120	0,40
23	29944	29877	29911	67	0,22
24	30033	29961	29997	72	0,24
28	30056	30072	30064	-16	-0,05
29	30236	30320	30278	-84	-0,28
30	30011	30057	30034	-46	-0,15
32	29875	29918	29897	-43	-0,14
33	29953	30126	30040	-173	-0,58
34	29979	29922	29951	57	0,19
36	29410	29410	29410	0	0,00
37	29792	29829	29811	-37	-0,12
38	30040	30000	30020	40	0,13
39	29695	29695	29695	0	0,00

S (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	0,210	0,210	0,210	0,000	0,00
4	0,221	0,213	0,217	0,008	3,69
5	0,200	0,200	0,200	0,000	0,00
6	0,520	0,572	0,546	-0,052	-9,52
7	0,220	0,217	0,219	0,003	1,37
8	0,214	0,207	0,211	0,007	3,33
9	0,201	0,207	0,204	-0,006	-2,94
10	0,206	0,207	0,206	-0,001	-0,49
11	0,210	0,210	0,210	0,000	0,00
12	0,230	0,240	0,235	-0,010	-4,26
14	0,203	0,204	0,204	-0,001	-0,49
15	0,195	0,189	0,192	0,006	3,13
16	0,140	0,140	0,140	0,000	0,00
17	0,213	0,216	0,215	-0,003	-1,40
19	0,202	0,197	0,200	0,005	2,51
20	0,196	0,198	0,197	-0,002	-1,02
21	0,208	0,176	0,192	0,032	16,67
22	0,214	0,214	0,214	0,000	0,00
23	0,201	0,212	0,207	-0,011	-5,33
24	0,223	0,226	0,225	-0,003	-1,34
28	-1,000	-1,000			
29	0,210	0,210	0,210	0,000	0,00
30	0,191	0,187	0,189	0,004	2,12
32	0,220	0,220	0,220	0,000	0,00
33	0,206	0,206	0,206	0,000	0,00
34	0,194	0,191	0,193	0,003	1,56
36	-1,000	-1,000			
38	0,208	0,208	0,208	0,000	0,00
39	0,193	0,192	0,193	0,001	0,52

M (w%)

Lab	R1	R2	Mean	Difference	Difference%
1	3,42	3,38	3,40	0,04	1,18
4	2,88	2,82	2,85	0,06	2,11
5	3,63	3,64	3,64	-0,01	-0,28
6	2,33	2,25	2,29	0,08	3,49
7	3,14	3,15	3,15	-0,01	-0,32
8	3,26	3,24	3,25	0,02	0,62
9	3,22	3,19	3,21	0,03	0,94
10	3,48	3,47	3,48	0,00	0,07
11	3,20	3,20	3,20	0,00	0,00
12	3,03	3,04	3,04	-0,01	-0,33
14	1,79	1,79	1,79	0,00	0,00
15	3,23	3,22	3,23	0,01	0,31
16	3,03	3,07	3,05	-0,04	-1,31
17	1,86	1,89	1,88	-0,03	-1,60
19	3,47	3,51	3,49	-0,04	-1,15
20	1,55	1,59	1,57	-0,04	-2,55
21	2,86	2,68	2,77	0,18	6,50
22	2,96	2,97	2,97	-0,01	-0,34
23	3,22	3,10	3,16	0,12	3,80
24	3,39	3,46	3,43	-0,07	-2,04
28	3,19	3,19	3,19	0,00	0,00
29	97,84	97,90	97,87	-0,06	-0,06
30	2,94	2,96	2,95	-0,02	-0,68
32	3,07	3,08	3,08	-0,01	-0,33
33	3,38	3,56	3,47	-0,18	-5,19
34	2,64	2,56	2,60	0,08	3,08
36	1,30	1,40	1,35	-0,10	-7,41
38	3,89	3,75	3,82	0,14	3,66
39	2,61	2,48	2,55	0,13	5,11

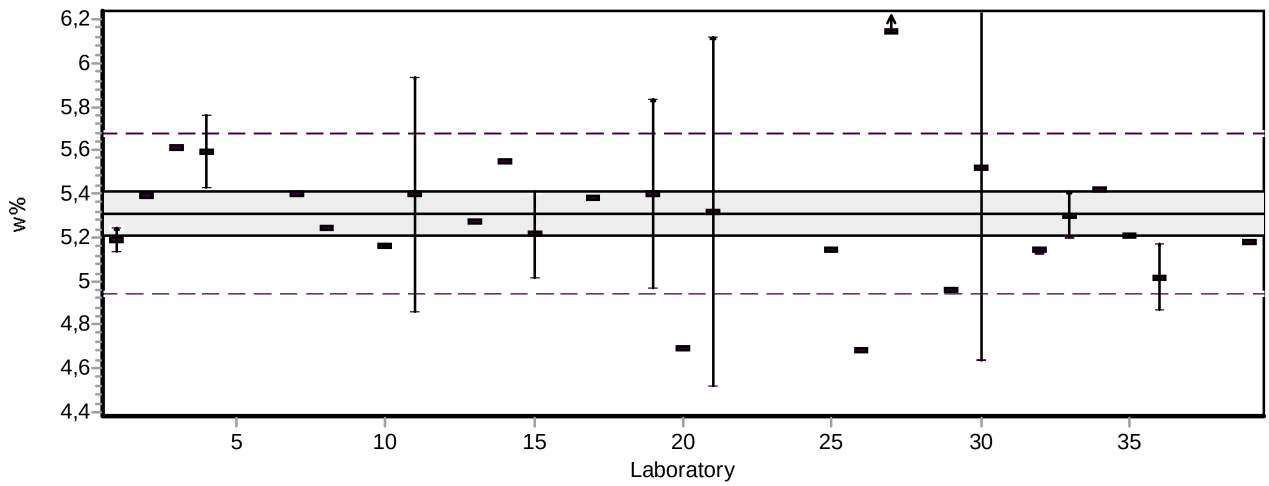
EF (tCO2/TJ)

Lab	R1	R2	Mean	Difference	Difference%
1	92,0	92,3	92,2	-0,30	-0,33
4	93,7	93,8	93,8	-0,10	-0,11
5	93,1	93,5	93,3	-0,40	-0,43
10	99,1	99,3	99,2	-0,15	-0,15
11	91,0	90,3	90,7	0,70	0,77
14	94,8	94,9	94,9	-0,10	-0,11
15	93,8	94,3	94,1	-0,50	-0,53
19	92,9	92,9	92,9	0,00	0,00
24	92,0	92,5	92,2	-0,42	-0,46
28	92,8	92,7	92,8	0,10	0,11
29	90,9	90,6	90,8	0,30	0,33
30	92,4	92,0	92,2	0,40	0,43
32	94,7	94,8	94,7	-0,08	-0,08
33	93,1	92,0	92,6	1,10	1,19
34	95,6	94,2	94,9	1,42	1,50
36	90,8		90,8		
39	92,8	92,9	90,8	-0,10	-0,11

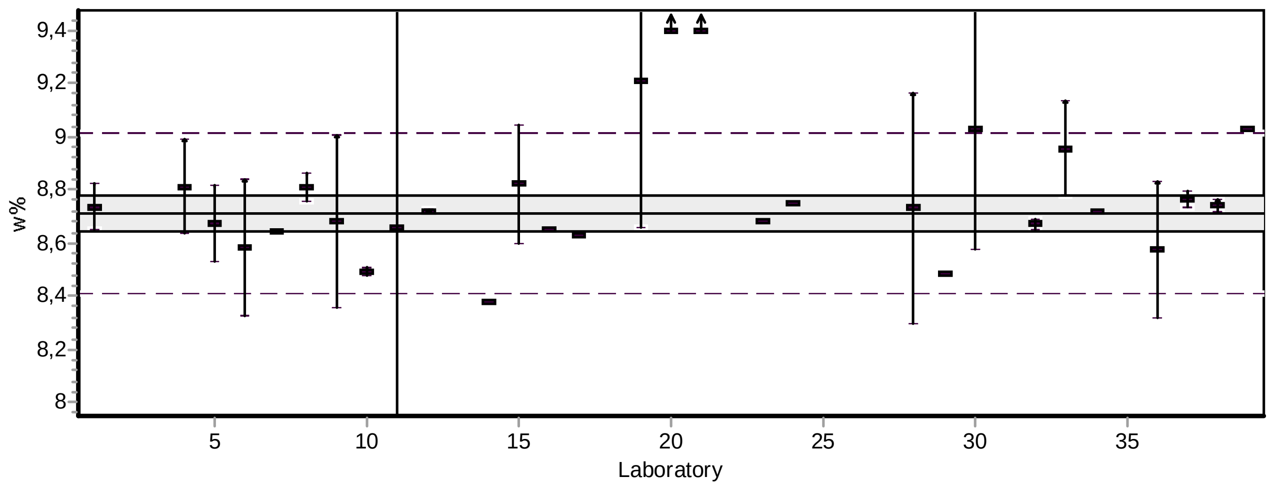
LIITE 10.

Appendix 10. *GRAPHICAL PRESENTATION OF THE RESULTS AND THEIR UNCERTANTIES*

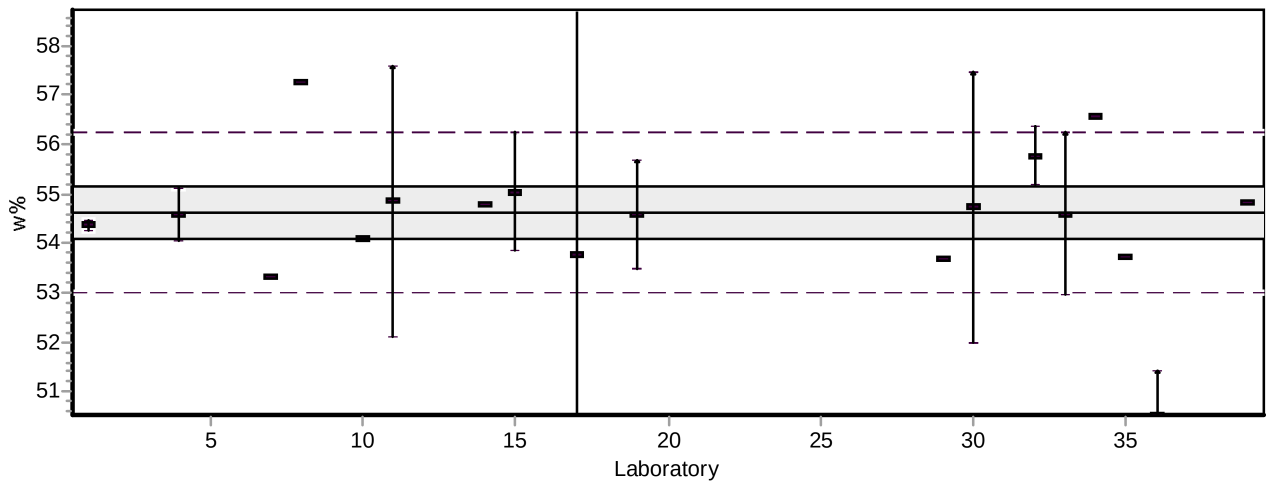
Analyytti *(Analyte)* **Ash** Näyte *(Sample)* B1



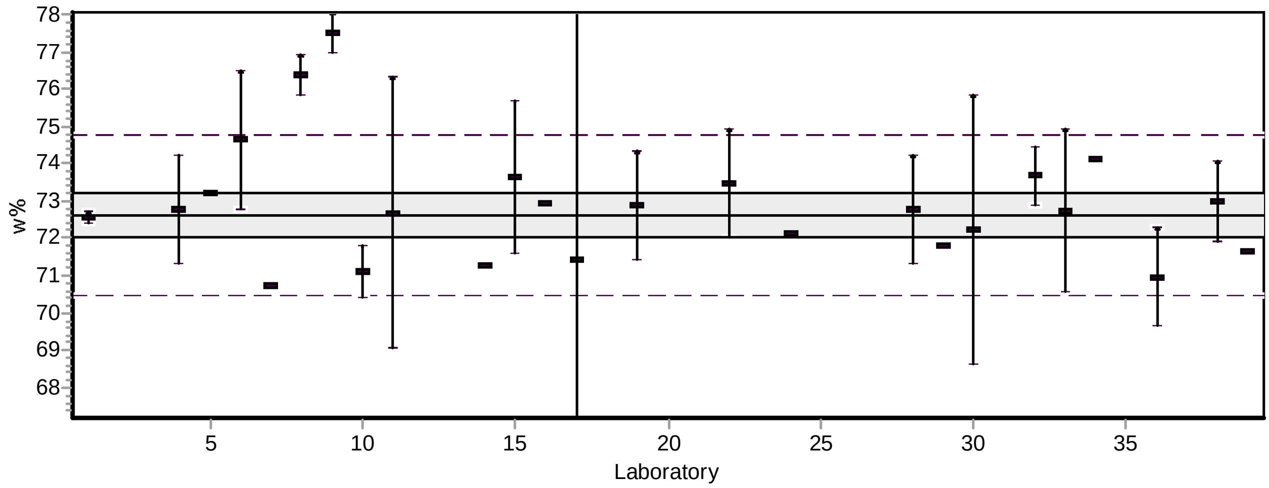
Analyytti *(Analyte)* **Ash** Näyte *(Sample)* K1



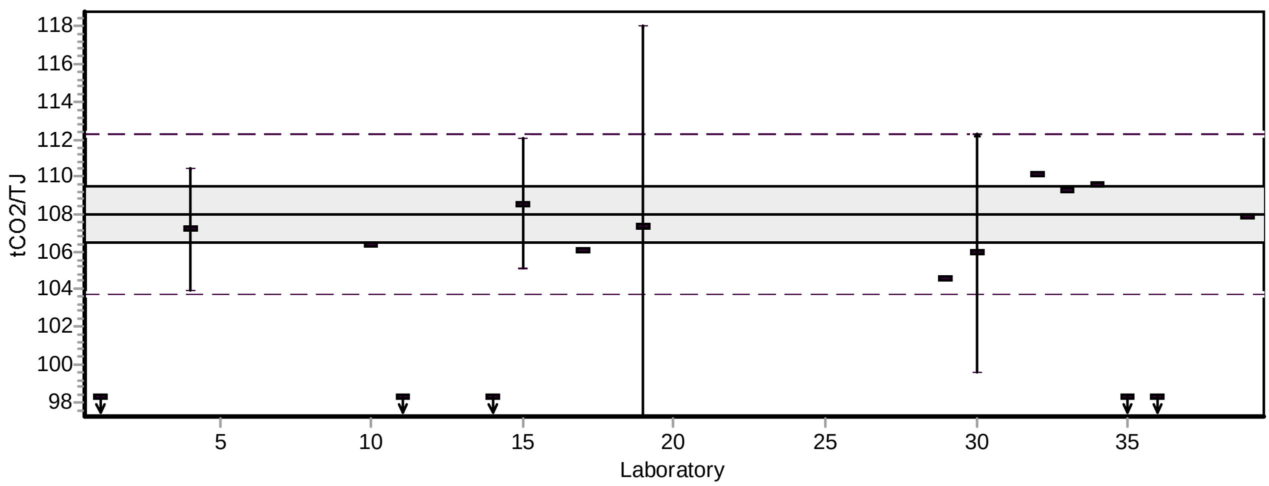
Analyytti *(Analyte)* **C** Näyte *(Sample)* B1



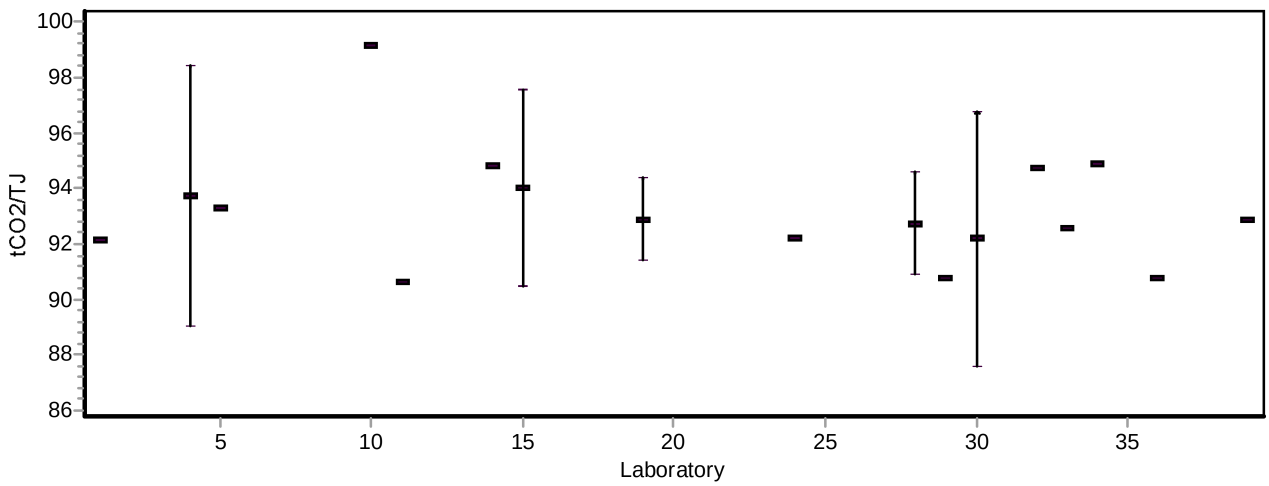
Analyytti *(Analyte)* **C** Näyte *(Sample)* K1



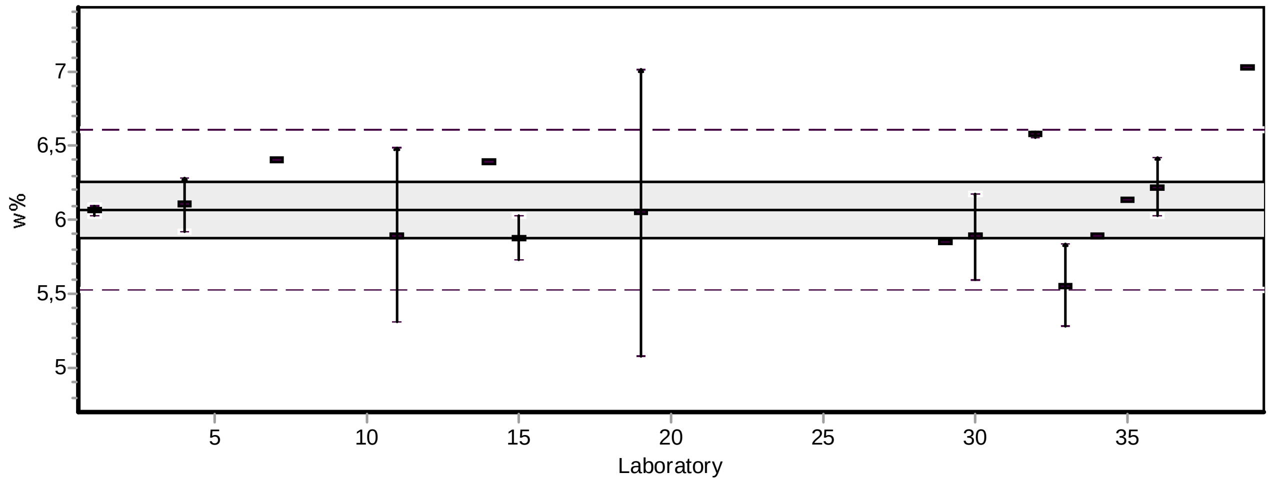
Analyytti *(Analyte)* **EF** Näyte *(Sample)* B1



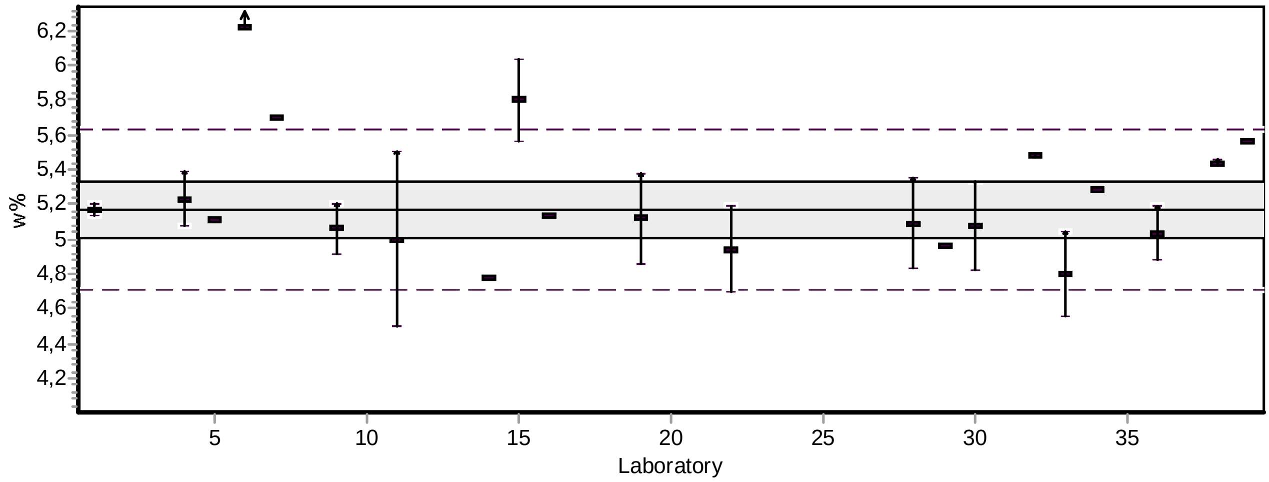
Analyytti *(Analyte)* **EF** Näyte *(Sample)* K1



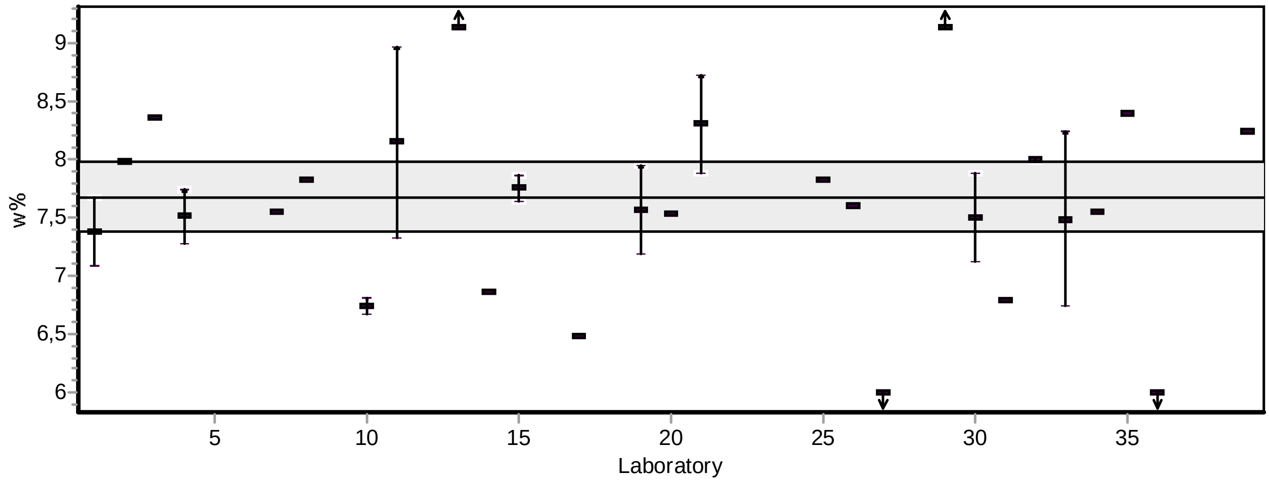
Analyytti *(Analyte)* **H** Näyte *(Sample)* B1



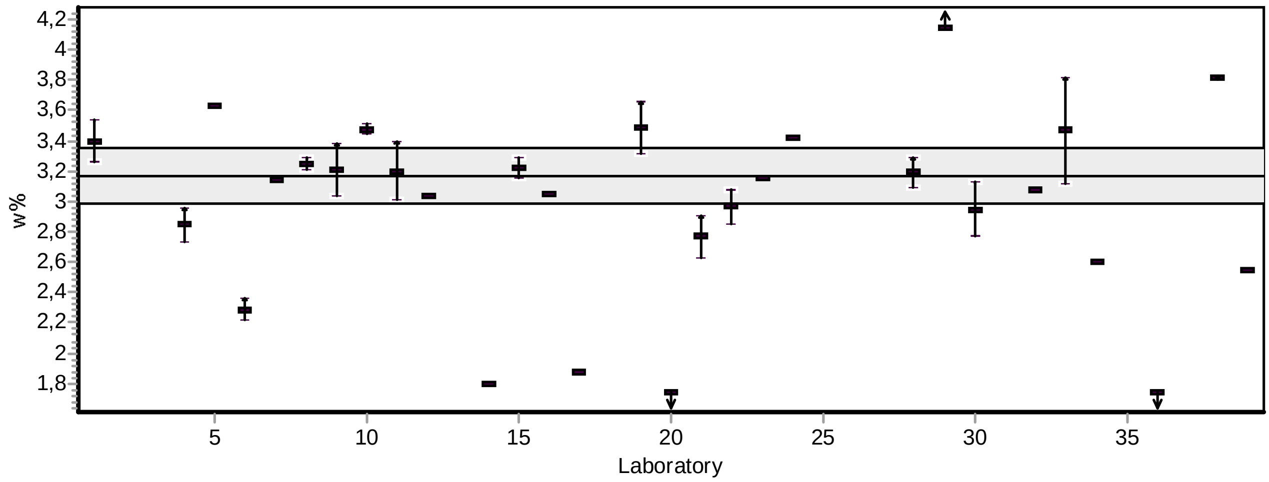
Analyytti *(Analyte)* **H** Näyte *(Sample)* K1



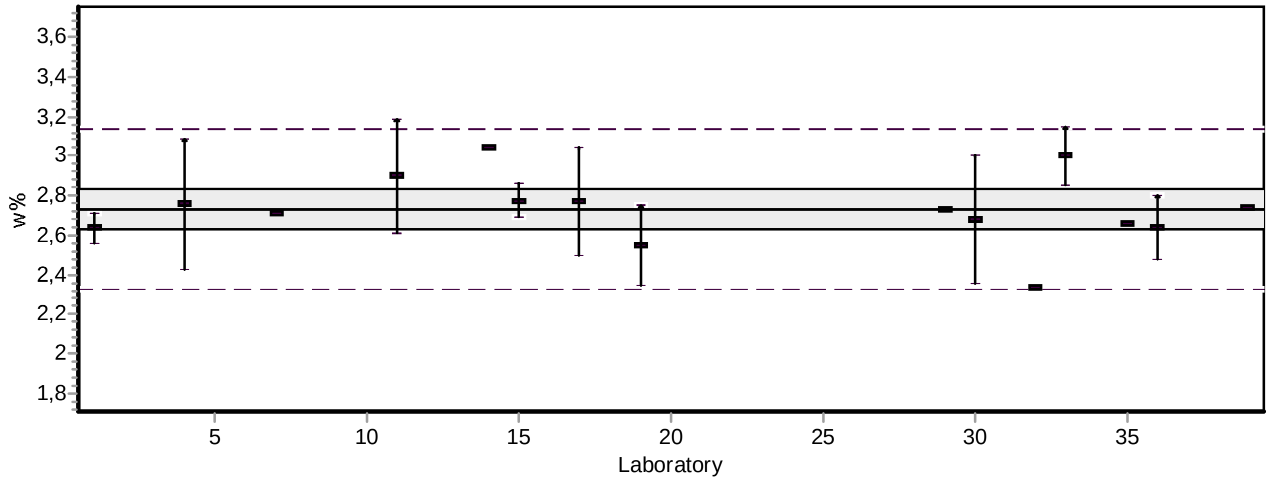
Analyytti *(Analyte)* **M** Näyte *(Sample)* B1



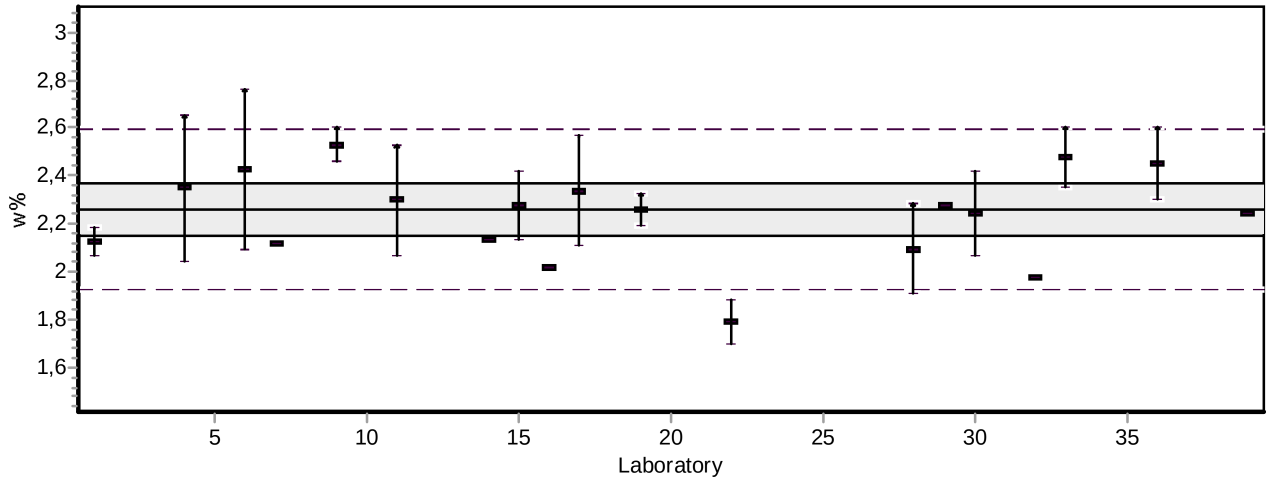
Analyytti *(Analyte)* **M** Näyte *(Sample)* K1



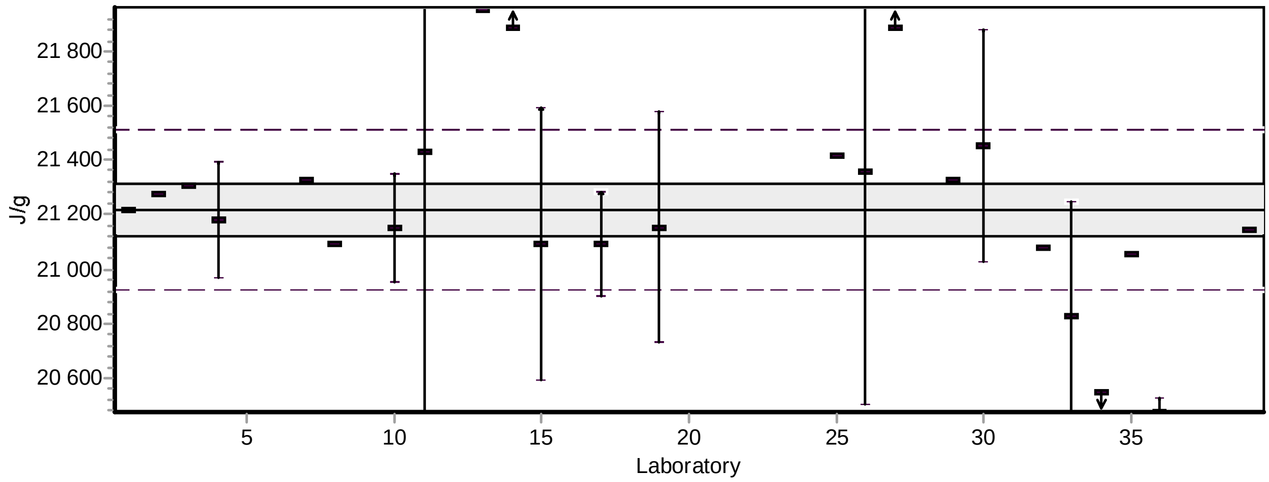
Analyytti *(Analyte)* **N** Näyte *(Sample)* B1



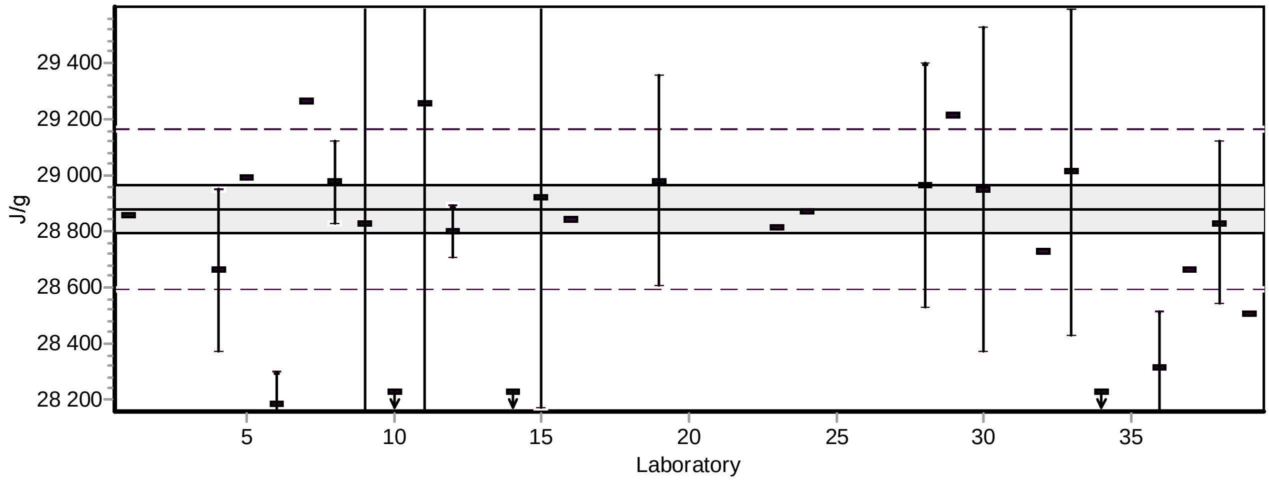
Analyytti *(Analyte)* **N** Näyte *(Sample)* K1



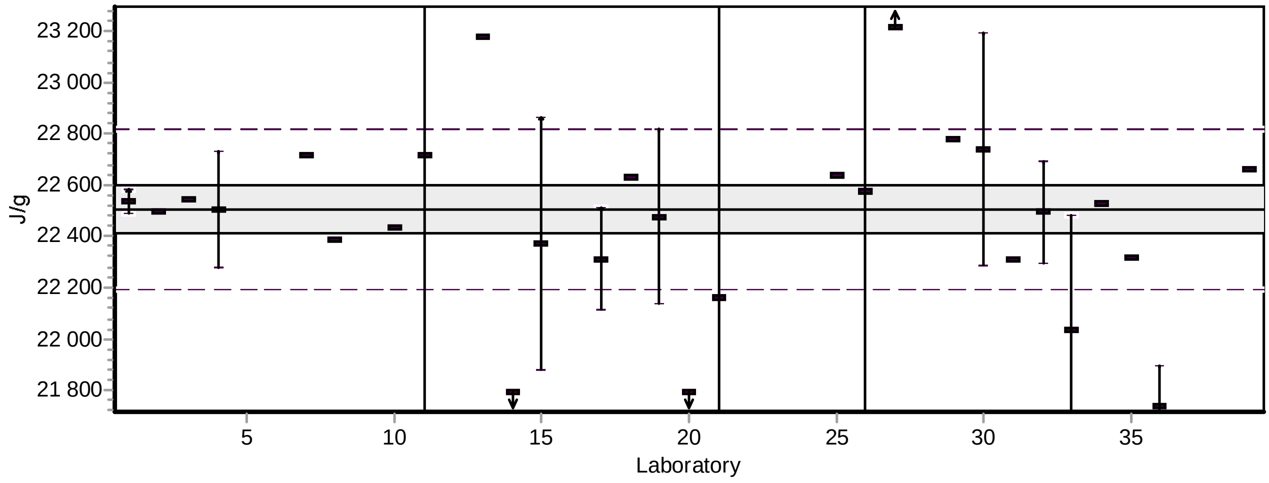
Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* B1



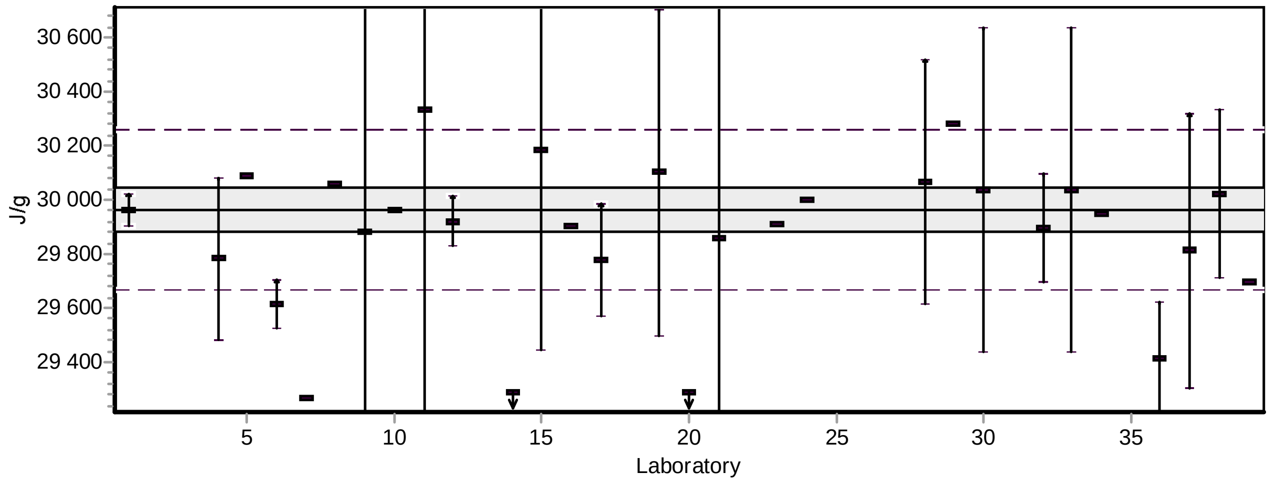
Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* K1



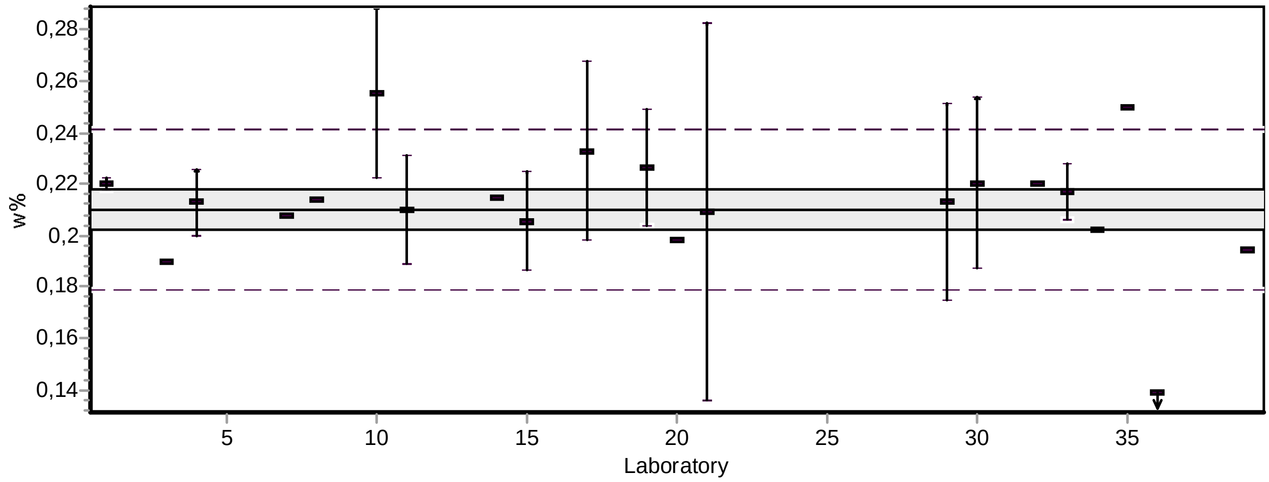
Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* B1



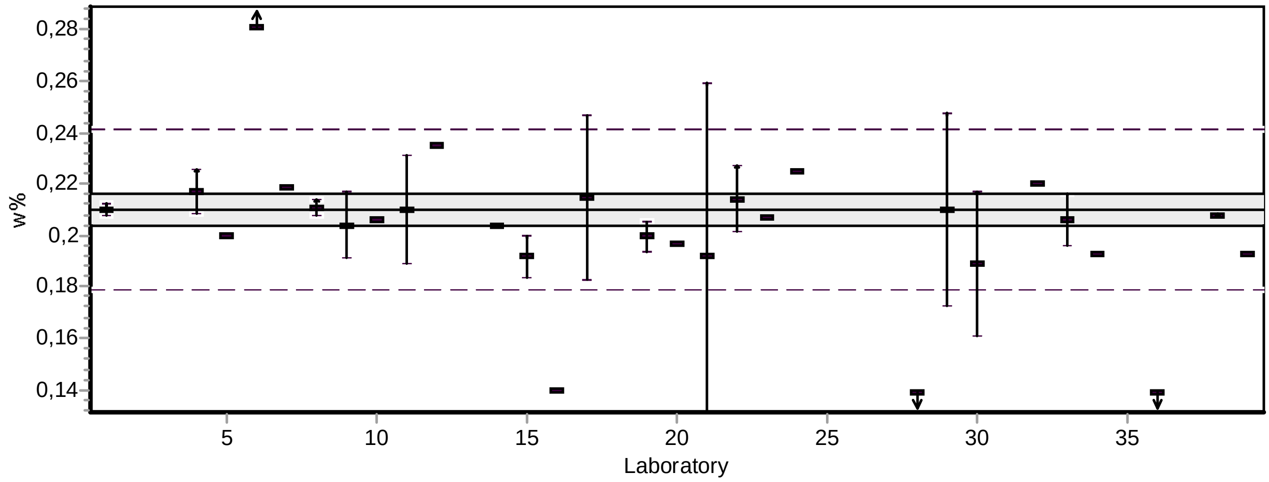
Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* K1



Analyytti *(Analyte)* **S** Näyte *(Sample)* B1



Analyytti *(Analyte)* **S** Näyte *(Sample)* K1



LIITE 11.

Appendix 11.SUMMARY OF z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Ash	B1	A	A	A	A	.	.	A	A	.	A	A	.	A	A	A	.	A	.	A	**N**	A	.	.
	K1	A	.	.	A	A	A	A	A	A	A	A	A	.	n	A	A	A	.	**P**	**P**	**P**	.	A
C	B1	A	.	.	A	.	.	A	**P**	.	A	A	.	.	A	A	.	A	.	A	.	.	.	.
	K1	A	.	.	A	A	A	A	**P**	**P**	A	A	.	.	A	A	A	A	.	A	.	.	A	.
EF	B1	**N**	.	.	A	.	.	.	.	.	A	**N**	.	.	**N**	A	.	A	.	A	.	.	.	.
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
H	B1	A	.	.	A	.	.	A	.	.	.	A	.	.	A	A	.	.	.	A	.	.	.	.
	K1	A	.	.	A	A	**P**	p	.	A	.	A	.	.	A	p	A	.	.	A	.	.	A	.
M	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
N	B1	A	.	.	A	.	.	A	.	.	.	A	.	.	A	A	.	A	.	A	.	.	.	.
	K1	A	.	.	A	.	A	A	.	A	.	A	.	.	A	A	A	A	.	A	.	.	n	.
q-p,net,d	B1	A	A	A	A	.	.	A	A	.	A	A	.	**P**	**P**	A	.	A	.	A	.	.	.	.
	K1	A	.	.	A	A	**N**	p	A	A	**N**	p	A	.	**N**	A	A	.	.	A	.	.	.	A
q-V,gr,d	B1	A	A	A	A	.	.	A	A	.	A	A	.	**P**	**N**	A	.	A	A	A	**N**	n	.	.
	K1	A	.	.	A	A	n	**N**	A	A	A	p	A	.	**N**	A	A	A	.	A	**N**	A	.	A
S	B1	A	.	A	A	.	.	A	A	.	p	A	.	.	A	A	.	A	.	A	A	A	.	.
	K1	A	.	.	A	A	**P**	A	A	A	A	A	A	.	A	A	**N**	A	.	A	A	A	A	A
%		93	100	100	100	100	43	79	80	86	82	80	100	33	60	93	86	100	100	93	33	67	75	100
Accredited		yes		yes	yes	yes	yes	yes	yes	yes	yes	yes	yes			yes	yes	yes		yes		yes	yes	

Analyte	Sample\Lab	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	%
Ash	B1	.	A	**N**	**P**	.	A	A	.	A	A	A	A	A	.	.	A	88
	K1	A	.	.	.	A	A	p	.	A	A	A	.	A	A	A	p	79
C	B1	.	.	.	.	.	A	A	.	A	A	p	A	**N**	.	.	A	83
	K1	A	.	.	.	A	A	A	.	A	A	A	.	A	.	A	A	92
EF	B1	.	.	.	.	.	A	A	.	A	A	A	**N**	**N**	.	.	A	69
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
H	B1	.	.	.	.	.	A	A	.	A	A	A	A	A	.	.	**P**	93
	K1	.	.	.	.	A	A	A	.	A	A	A	.	A	.	A	A	86
M	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
N	B1	.	.	.	.	.	A	A	.	A	A	.	A	A	.	.	A	100
	K1	.	.	.	.	A	A	A	.	A	A	.	.	A	.	.	A	95
q-p,net,d	B1	.	A	A	**P**	.	A	A	.	A	n	**N**	A	**N**	.	.	A	75
	K1	A	.	.	.	A	p	A	.	A	A	**N**	.	**N**	A	A	n	65
q-V,gr,d	B1	.	A	A	**P**	.	A	A	A	A	n	A	A	**N**	.	.	A	75
	K1	A	.	.	.	A	p	A	.	A	A	A	.	**N**	A	A	A	76
S	B1	.	.	.	.	.	A	A	.	A	A	A	p	.	.	.	A	90
	K1	A	.	.	.	.	A	A	.	A	A	A	.	.	.	A	A	93
%		100	100	67	0	100	87	93	100	100	87	77	75	54	100	100	80	
Accredited		yes				yes		yes		yes		yes		yes	yes	yes		

A - accepted (-2 ≤ Z ≤ 2), p - questionable (2 < Z ≤ 3), n - questionable (-3 ≤ Z < -2), P - non-accepted (Z > 3), N - non-accepted (Z < -3),

%* - percentage of accepted results

Totally accepted, % In all: 83 In accredited: 87

MEASUREMENT UNCERTAINTIES REPORTED BY THE LABORATORIES GROUPED ACCORDING TO THE EVALUATION PROCEDURE

For evaluation of the measurement uncertainty the participants have used the procedures as follows: In the figures the procedures have been presented using the same code number.

1. using the variation of the results in X chart (for the artificial samples)

2. using the variation of the results in X chart and the variation of the replicates (r%- or R- chart for real samples)

3. using the data obtained in method validation and IQC, see e.g. NORDTEST TR 537[1)]

4. using the data obtained in the analysis of CRM (besides IQC data). see e.g.NORDTEST TR 537[1)]

5. using the IQC data and the results obtained in proficiency tests. see e.g. NORDTEST TR 537[1)]

6. using the "modelling approach" (GUM Guide or EURACHEM Guide Quantifying Uncertainty in Analytical Measurements[2)]

7. other procedure

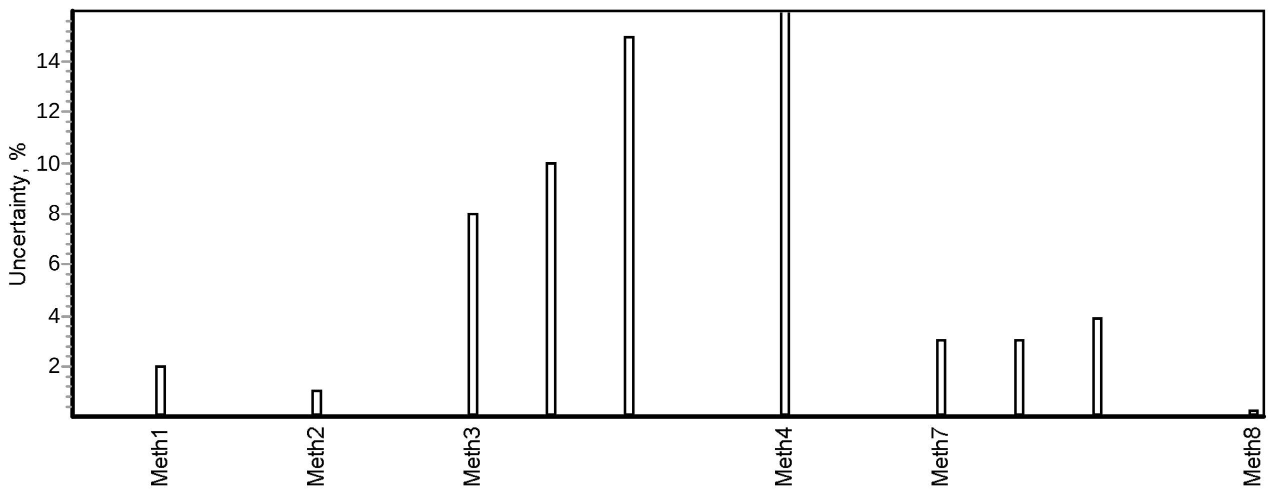
8. no uncertainty estimation

IQC= internal quality control

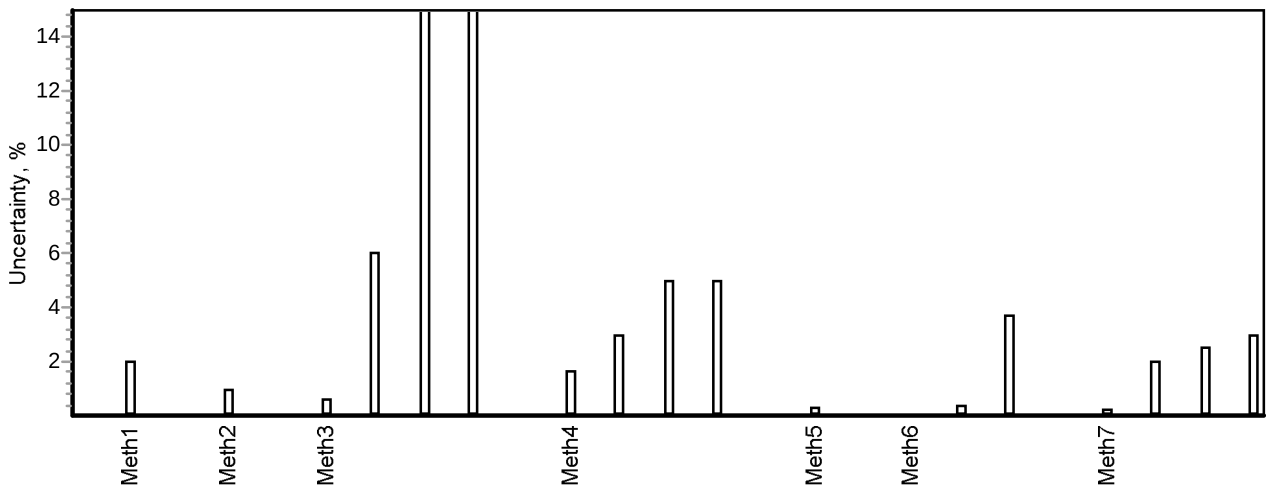
[1)] http://www.nordicinnovation.net/nordtestfiler/tec537.pdf (NORDTEST guide for estimation of measurement uncertainty)
[2)] http://www.eurachem.ul.pt/guides/QUAM2000-1.pdf

LIITE 12.
Appendix 12.

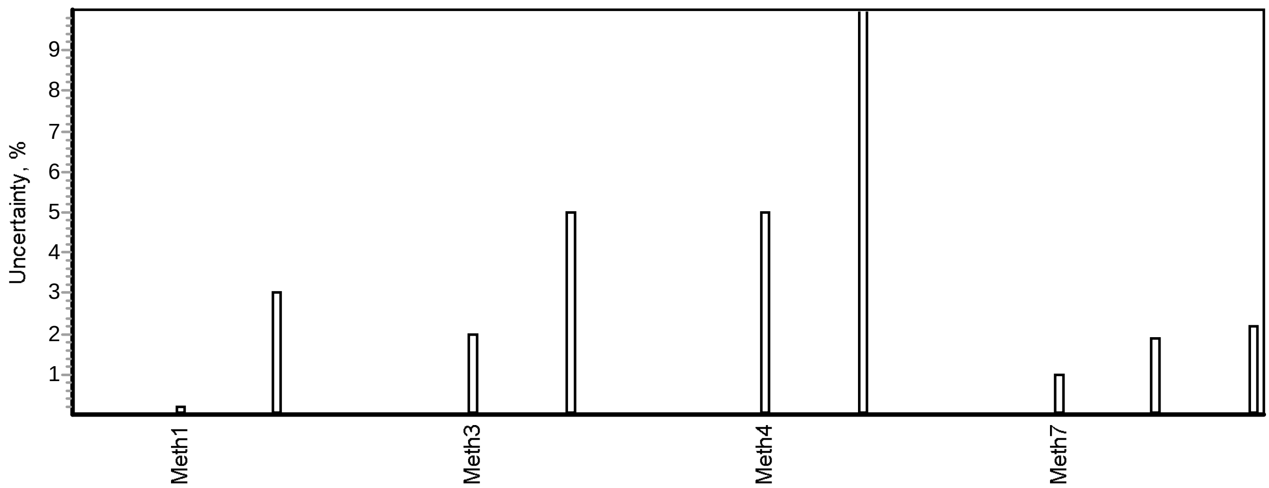
Analyytti *(Analyte)* **Ash** Näyte *(Sample)* B1



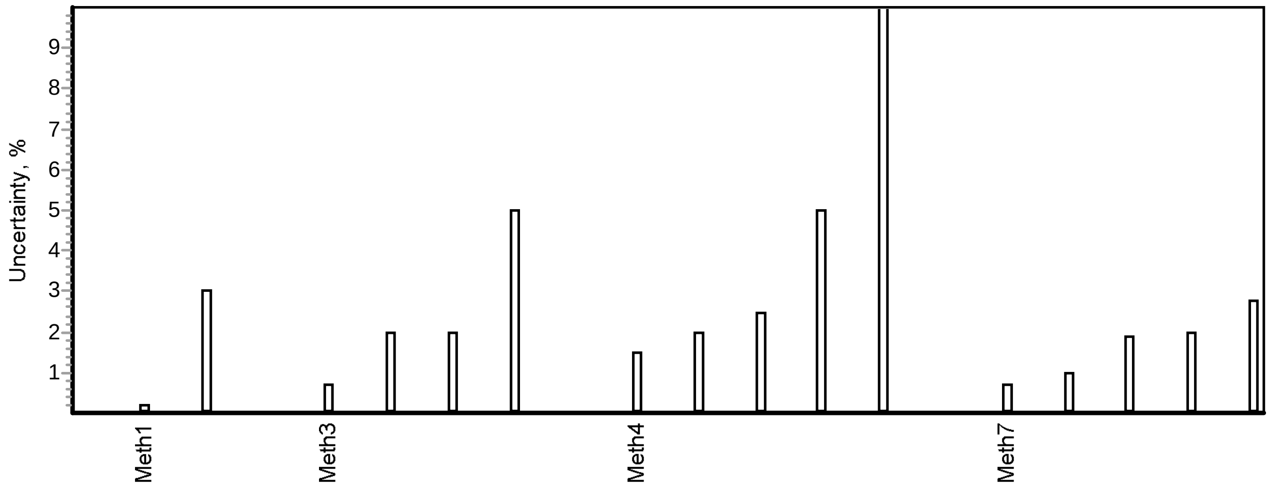
Analyytti *(Analyte)* **Ash** Näyte *(Sample)* K1



Analyytti *(Analyte)* **C** Näyte *(Sample)* B1

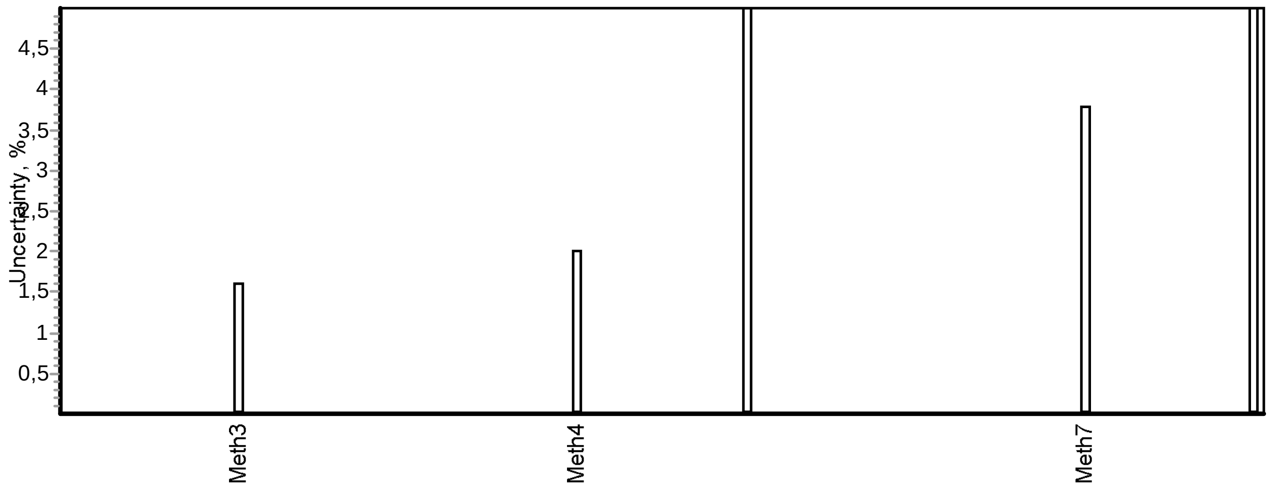


Analyytti *(Analyte)* **C** Näyte *(Sample)* K1

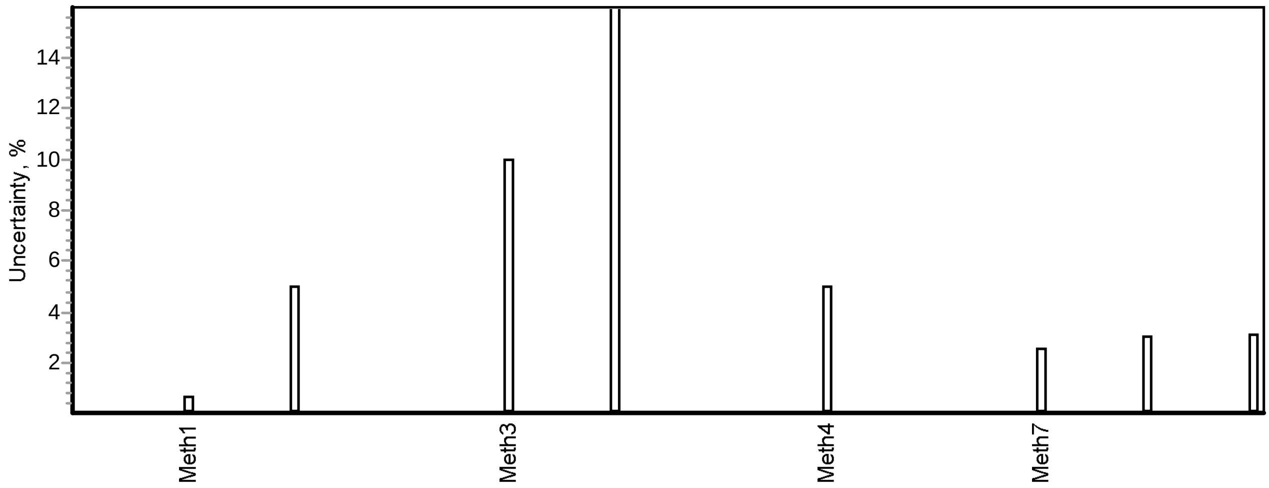


Analyytti *(Analyte)* **EF** Näyte *(Sample)* B1

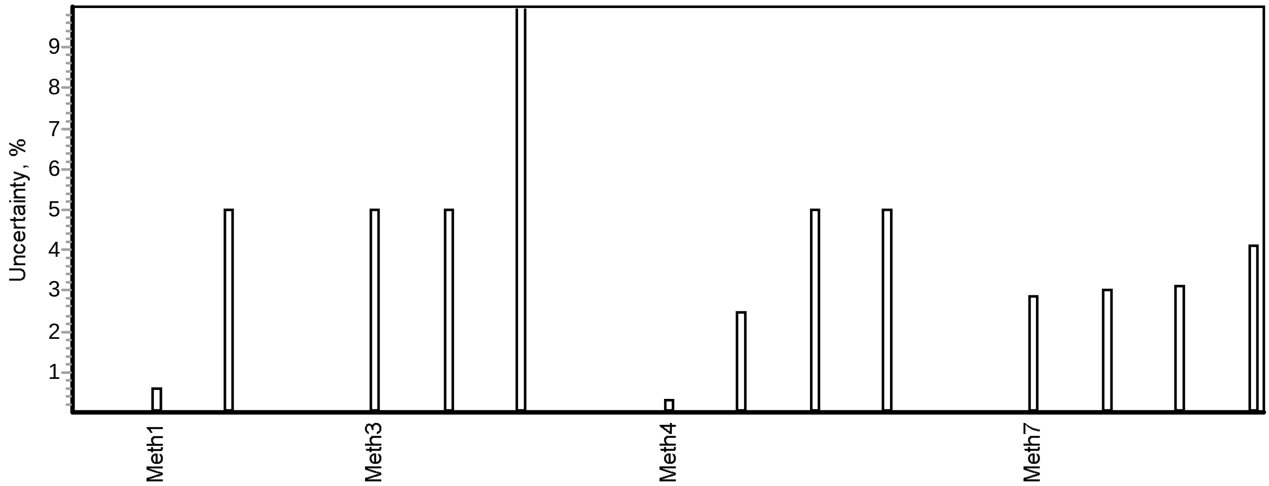
Analyytti *(Analyte)* **EF** Näyte *(Sample)* K1



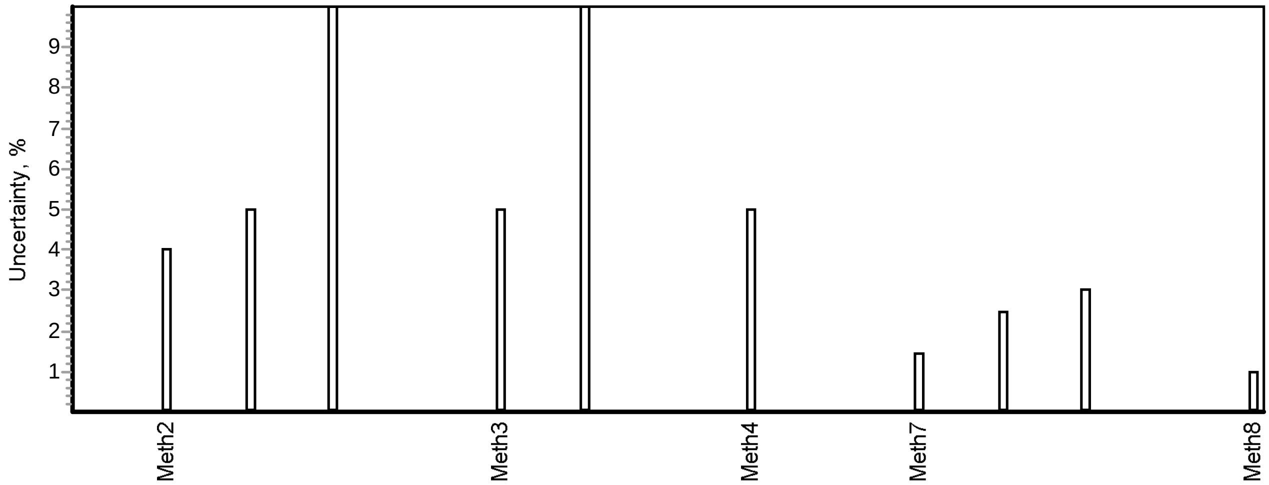
Analyytti *(Analyte)* **H** Näyte *(Sample)* B1



Analyytti *(Analyte)* **H** Näyte *(Sample)* K1



Analyytti *(Analyte)* **M** Näyte *(Sample)* B1



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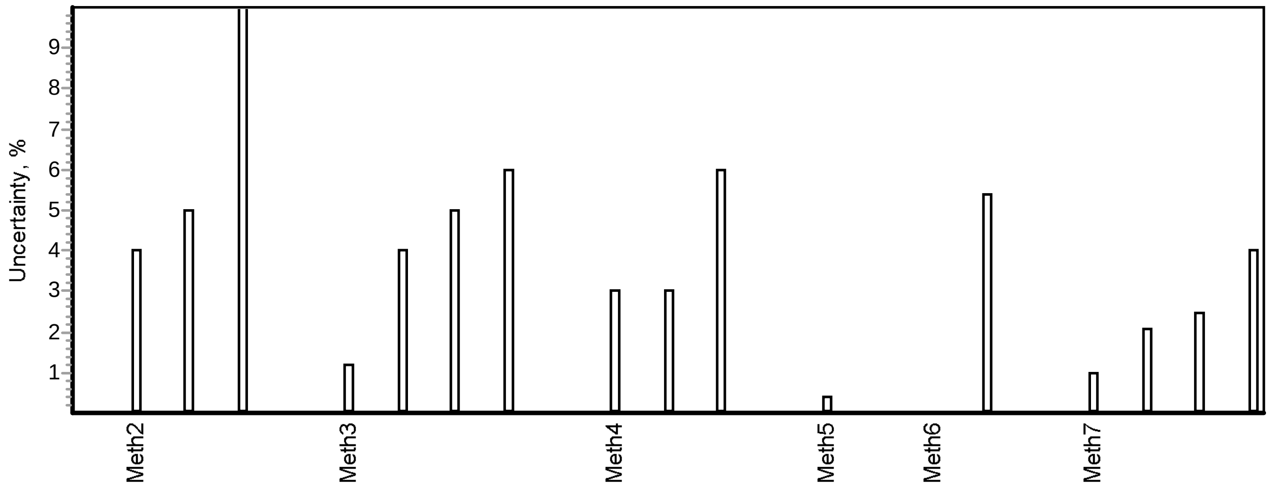

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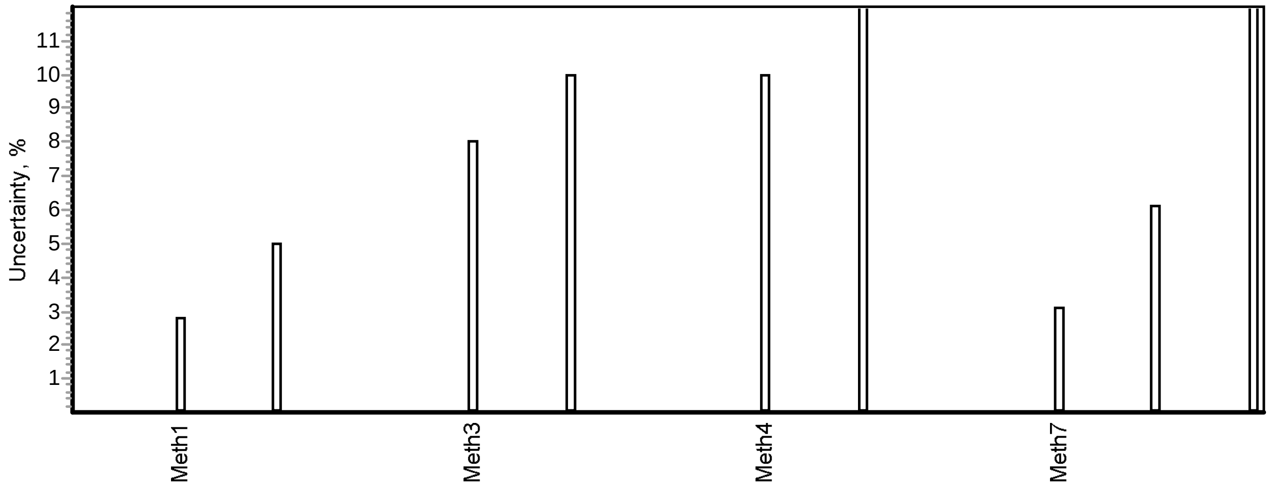

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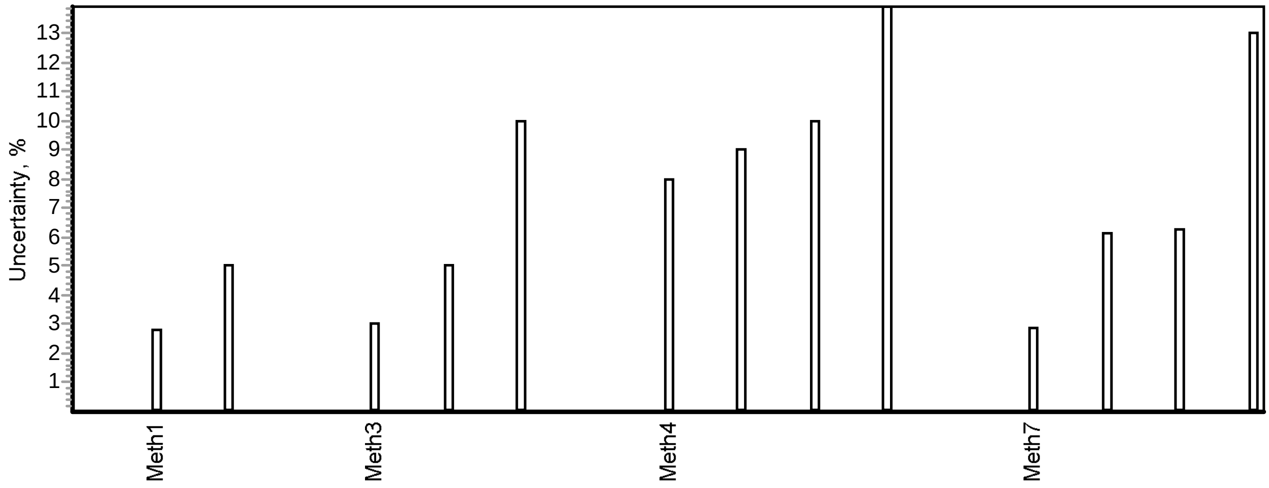
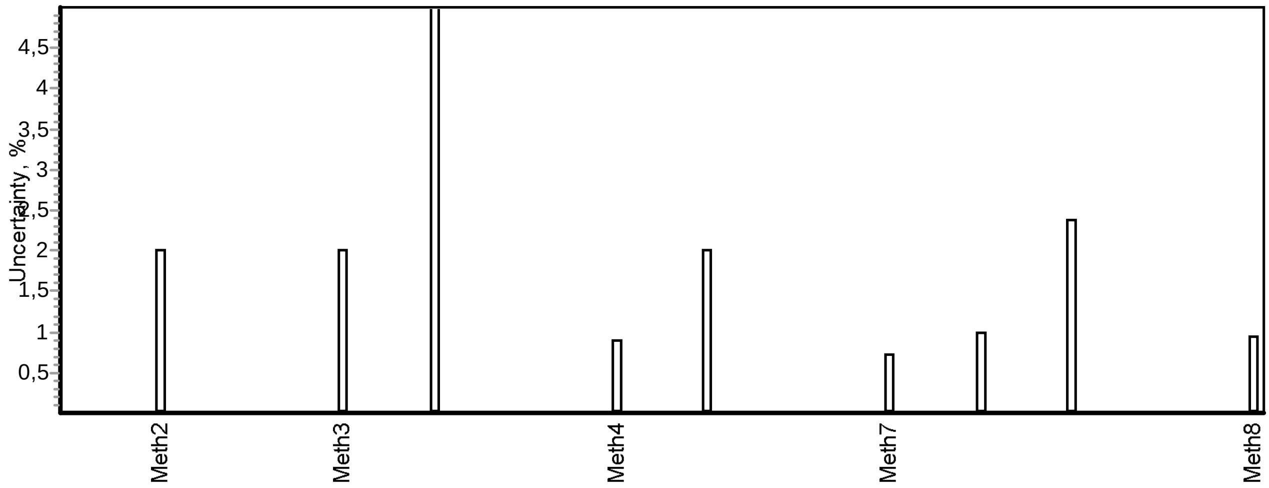
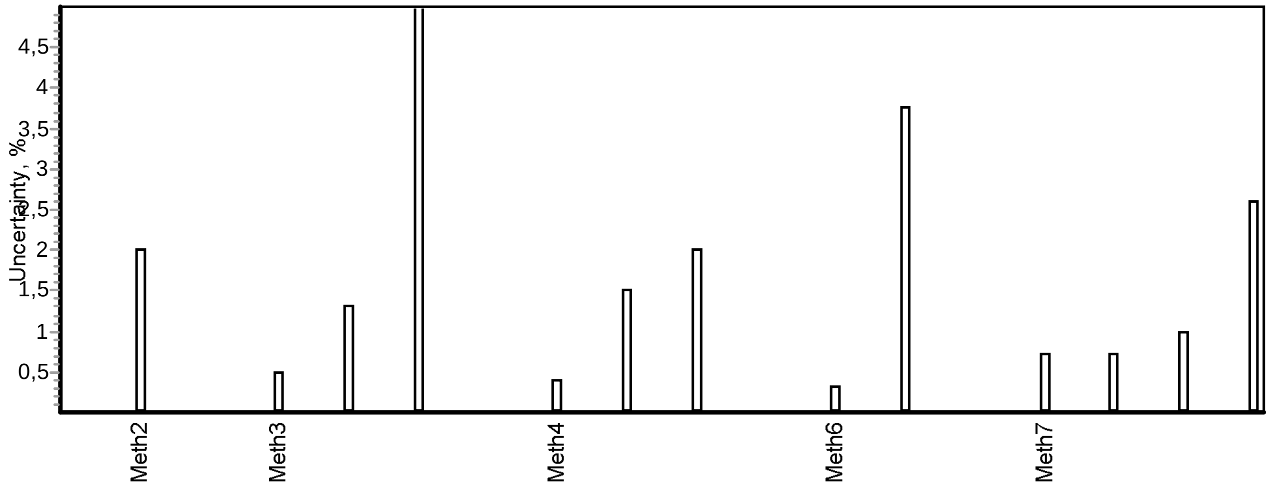


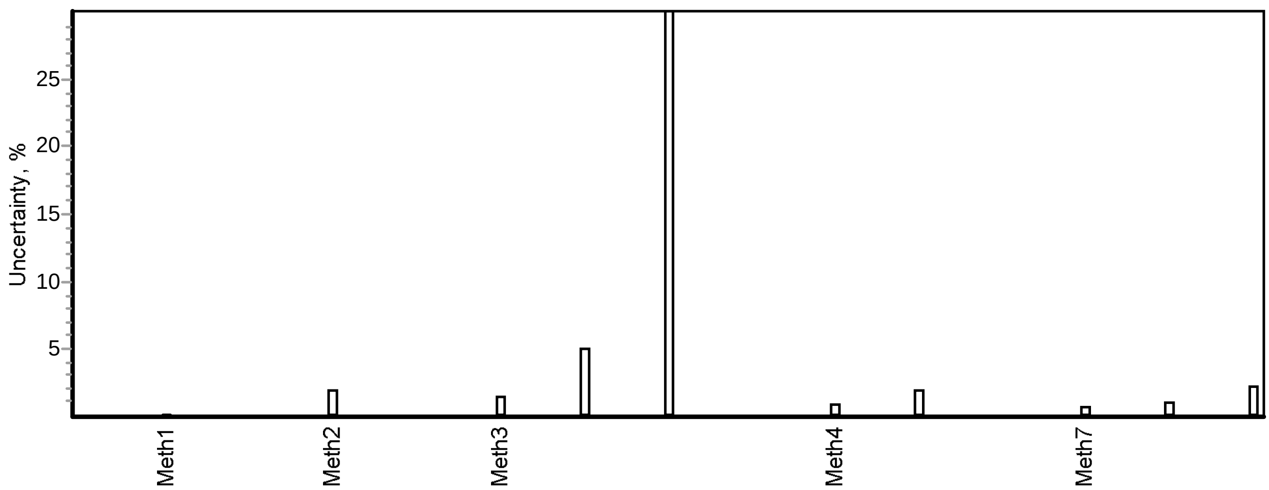
Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* B1



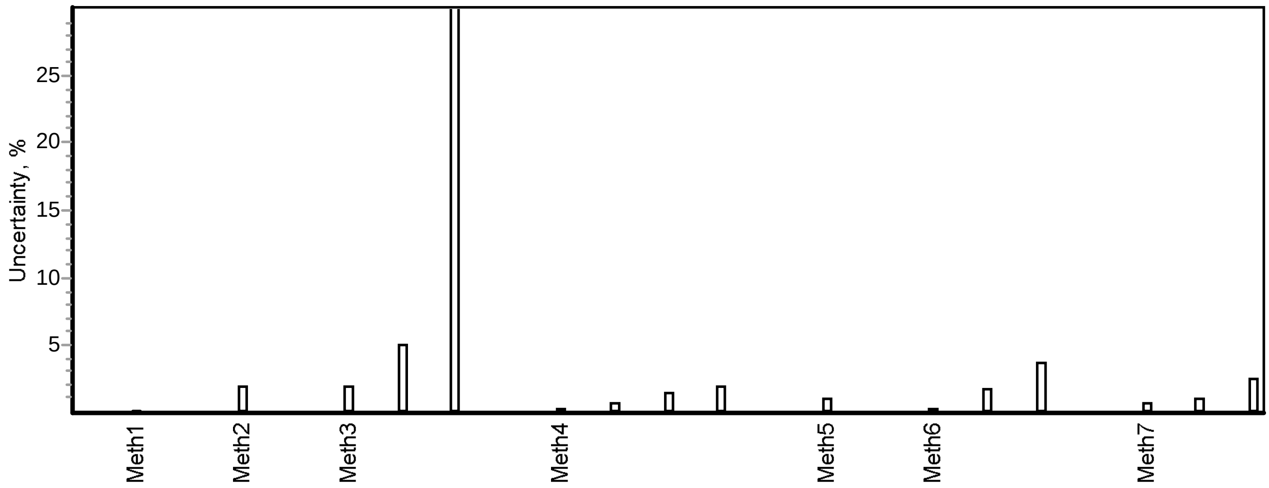
Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* K1



Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* B1



Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* K1



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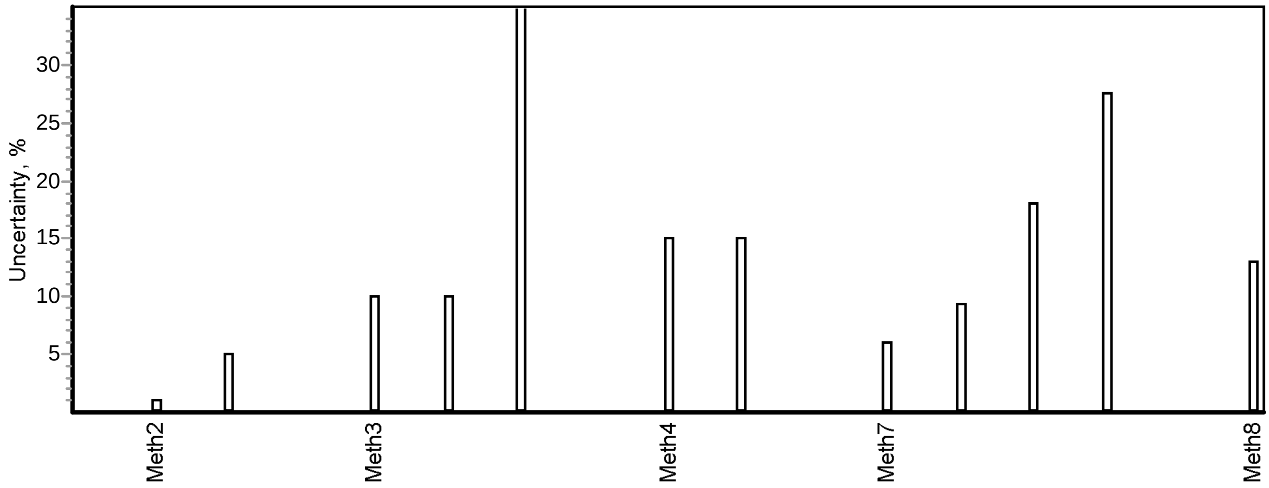

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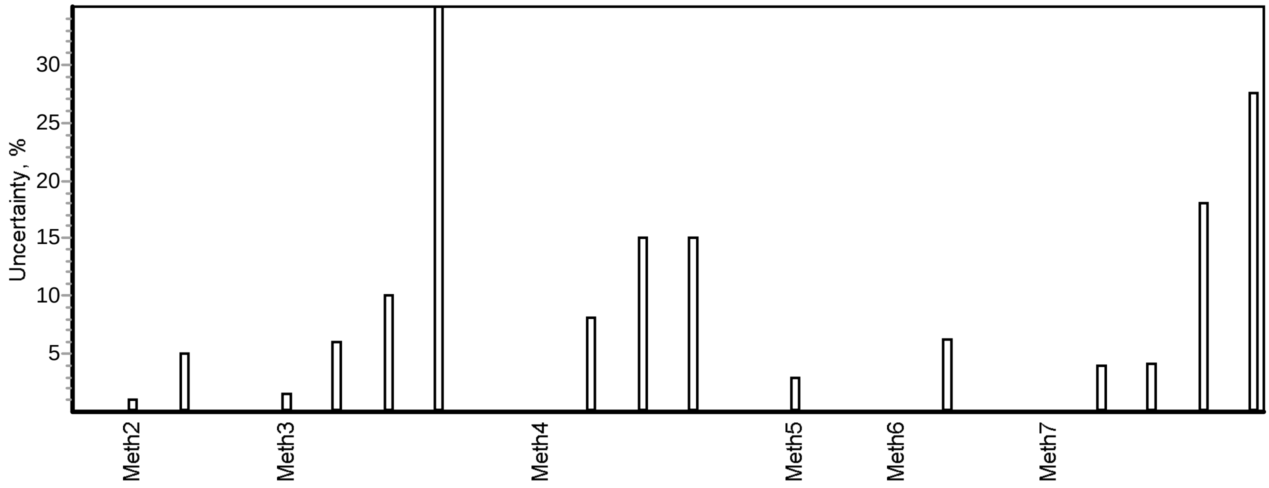

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date February 2010
Author(s)	Mirja Leivuori, Irma Mäkinen, Minna Rantanen, Minna Salonen, Kaija Korhonen ja Markku Ilmakunnas	
Title of publication	Proficiency test 5/2009 Gross and net calorific value in fuels	
Parts of publication/ other project publications	The publication is available on the internet: www.ymparisto.fi/julkaisut	
Abstract	The Finnish Environment Institute (SYKE) carried out the proficiency test for measurement the gross and the net calorific value, the content of ash, carbon, nitrogen, hydrogen, moisture and sulfur in fuels in September 2009. One peat sample and one coal sample were delivered to the laboratories for the analysis of each measurand. In total, 39 laboratories participated in the proficiency test. The robust means of the reported results by the participants were used as the assigned values for measurands. The evaluation of performance was based on the z score which was calculated using the standard deviation for proficiency assessment at 95 % confidence level. The total standard deviation for performance assessment was mainly set on the basis of the reproducibility requirements presented the standard methods. The evaluation of performance was not done for the measurement of moisture and for the emission factor of the coal sample. In total, 83 % of the participating laboratories reported the satisfactory results. About 65 % of the participants used accredited methods and 87 % of their results were satisfactory. In measurement of the gross calorific value from the peat sample 71 % of the results were satisfactory and respectively in measurement of the coal sample 76 % from the results were satisfactory. In measurement of the net calorific value from the peat sample 75 % of the results were satisfactory and respectively in measurement of the coal sample 65 % from the results were satisfactory.	
Keywords	Proficiency test, interlaboratory comparison, coal, peat, measurement of calorific value, emission factor, measurement of ash, moisture, carbon, sulphur, nitrogen and hydrogen, environmental laboratories	
Publication series and number	Suomen ympäristökeskuksen raportteja 2/2010	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
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	No. of pages 59	Language English
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For sale at/ distributor	Finnish Environment Institute, Customer service E-mail: neuvonta.syke@ymparisto.fi Tel. + 358 20 610 183 Telefax. + 358 20 490 2190	
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Printing place and year	Helsinki 2010	
Other information		

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Helmikuu 2010
Tekijä(t)	Mirja Leivuori, Irma Mäkinen, Minna Rantanen, Minna Salonen, Kaija Korhonen ja Markku Ilmakunnas	
Julkaisun nimi	Laboratorioiden välinen pätevyyskoe 5/2009 Kalorimetrinen ja tehollinen lämpöarvo polttoaineista	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana myös internetistä: http://www.ymparisto.fi/julkaisut	
Tiivistelmä	Suomen ympäristökeskus (SYKE) järjesti syyskuussa 2010 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin ja kosteuden määrittämiseksi turpeesta ja kivihiilestä. Pätevyyskokeeseen osallistui yhteensä 39 laboratoriota. Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat välillä 1-15 %. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa. Tavoitearvon epävarmuus oli lämpöarvon määrityksissä alhaisempi kuin 0.44 % ja muiden testisuureiden osalta alhaisempi kuin 5.6 %. Tulosten arviointia ei tehty kosteuspitoisuuden määritykselle, koska osallistujien välinen hajonta oli suuri. Arviointia ei myöskään tehty päästökertoimelle hiilen osalta, koska kaikki laboratoriot eivät olleet laskeneet arvoa tulokosteutta kohti. Koko tulosaineistossa hyväksyttäviä tuloksia oli 83 %, kun vertailuarvosta sallittiin 1-15 %.n poikkeama. Noin 65 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 87 %. Kalorimetrisen lämpöarvon tuloksista oli tyydyttäviä 71 % (turve) ja 76 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat tyydyttävien tulosten osuudet olivat 75 % (turve) ja 65 % (kivihiili).	
Asiasanat	Pätevyyskoe, vertailumittaus, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, päästökerroin, tuhkan, kosteuden, hiilen, rikin, typen ja vedyn määritys, turve, hiili, ympäristölaboratoriot	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen moniste 2/2010	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
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Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2010	
Muut tiedot		

Presentationsblad

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Författare	Mirja Leivuori, Irma Mäkinen, Minna Rantanen, Minna Salonen, Kaija Korhonen och Markku Ilmakunnas	
Publikationens titel	Provningsjämförelse 5/2009 Kalorimetriskt och effektivt värmevärde i bränsle	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under September 2009 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, svavel, väte, kol, nitrogen, aska och fuktighet i torv och stenkol. Tillsammans 39 laboratorier deltog i jämförelsen. Som referensvärde av analytens koncentration användes mest det robust medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 83 % av alla resultaten tillfredsställande, när total deviation på 1–15 % från referensvärdet accepterades.	
Nyckelord	provningsjämförelse, kalorimetriskt och effektivt värmevärde, utsläppskoefficient, svavel, väte, kol, nitrogen, aska och fuktighet, stenkol, torv, miljölaboratorier	
Publikationsserie och nummer	Suomen ympäristökeskuksen raportteja 2/2010	
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