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## Gross and net calorific values in fuels

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Finnish Environment Institute SYKE

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## ALKUSANAT

Suomen ympäristökeskus (SYKE) on toiminut ympäristöalan kansallisena vertailulaboratoriona vuodesta 2001 lähtien. Toiminta perustuu ympäristöministeriön määräykseen, mikä on annettu ympäristönsuojelulain (86/2000) nojalla. Vertailulaboratorion tarjoamista palveluista yksi tärkeimmistä on pätevyyskokeiden ja muiden vertailumittausten järjestäminen. Vertailumittausten järjestäminen täyttää kansainvälisten ohjeiden ISO/IEC Guide 43-1 ja ILAC-G13 asettamat vaatimukset. SYKEn laboratoriot on FINAS-akkreditointipalvelun akkreditoima testauslaboratorio T003 ja vertailumittausten järjestäjä PT01 (Proftest SYKE, www.finas.fi).

Tämä pätevyyskoe on toteutettu SYKEn vertailulaboratorion pätevyysalueella ja se antaa tietoa osallistujien pätevyyden lisäksi tulosten vertailukelpoisuudesta myös yleisemmällä tasolla.

Pätevyyskokeen onnistumisen edellytys on järjestäjän ja osallistujien välinen luottamuksellinen yhteistyö.

Parhaat kiitokset yhteistyöstä kaikille osallistujille!

## PREFACE

Finnish Environment Institute (SYKE) has served as the National Reference Laboratory in the environmental sector designated by the Ministry of the Environment under the section 24 of the Environment Protection Act (86/2000) since 2001. The duties of the reference laboratory service include providing proficiency tests and other interlaboratory comparisons for analytical laboratories and other producers of environmental information. The proficiency testing service is a part of the SYKE laboratory management system based on the standard EN ISO/IEC 17025. The SYKE proficiency testing service also conforms to the requirements of ISO/IEC GUIDE 43-1 and ILAC G-13. The SYKE laboratories have been accredited by the Finnish Accreditation service as the testing laboratory T003 and as the proficiency testing provider PT01 (Proftest SYKE, www.finas.fi).

This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides information about performance of the participants as well as comparability of the results at more general level.

The success of the proficiency test requires confidential co-operation between the provider and participants.

Thank you for your co-operation!

Helsingissä 4. Helmikuuta 2011 / Helsinki 4 February 2011

Marja Luotola

Laboratorionjohtaja / Chief of laboratory

# 1 INTRODUCTION

The Finnish Environment Institute (Proftest 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 2010. 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], ISO/IEC 17043 [2], ISO 13528 [3] and IUPAC Recommendations [4]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, www.finas.fi). Proftest SYKE is the accredited proficiency test provider on the field of the present test.

The proficiency test performed as the joint work with the working group (WG) of the European co-operation for Accreditation (EA) for Interlaboratory Comparisons (EA WG ILC in Testing) and the data will be confidentially handled in the work of this WG.

# 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:
The peat sample B1 prepared by Enas in Jyväskylä (Finland) and the coal sample K1 was prepared by Helsinki Energia (Finland). Both samples were homogenized and divided to the sub samples at the laboratory of Water Protection Association of the Kokemäenjoki River in Tampere (Finland, accredited testing laboratory T064 by the Finnish Accreditation Service, www.finas.fi).

The samples were tested at Mibrag mbH in Zeitz (Germany, the accredited testing laboratory DGA-PL-1161.00 by the Deutsche Geselleschaft für Akkreditierung mbH, www.dakks.de). The calorific value of the peat sample was, additionally, tested at the laboratory of Ramboll Analytics in Vantaa (Finland, the accredited testing laboratory T039 by the Finnish Accreditation Service, www.finas.fi).

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

The analytical expert was:
Minna Rantanen, Ramboll Analytics

## 2.2 Participants

In this proficiency test (PT) totally 58 laboratories participated, from which 16 were from Finland and 41 from other European countries and one laboratory from Asia (Appendix 1). The sample testing laboratories Mibrag mbH has the code 60 and Ramboll Analytics has the code 59 in the result tables.

## 2.3 Samples and delivery

The preparation of the samples is presented more detailed 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 crushed coal. The material was air dried and grounded to particle size < 200 µm before homogenization and sample dividing.

The samples were delivered 14 September 2010. They were requested to be analyzed and reported before 7 October 2010.

The samples and the requested measurands were as follows:

| Sample | Sample type | Measurements |
|---|---|---|
| **B1** | Peat | Gross and net calorific value, C, S, N, H, moisture content of the analysis sample ($M_{ad}$), ash content |
| **K1** | Coal | Gross and net calorific value, C, S, N, H, moisture content of the analysis sample ($M_{ad}$), ash content |

In the covering letter with the samples was noted that the moisture content of the analysis had to be measured as the first measurement 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 had the possibility to estimate/calculate the emission factor (as received) for the both samples. For this estimation/calculation the organizer of this PT reported the total moisture contents as received ($M_{ar}$) for peat sample B1 44.3% and for coal sample K1 11.2% in the covering letter of the samples.

## 2.4 Homogeneity studies

Homogeneity of the samples B1 and K1 was tested by analyzing the gross calorific value and the ash content as replicate determinations from fifteen subsamples. The homogeneity of the gross calorific value of the peat sample B1 was tested from eight additional samples by other laboratory due to the somewhat high variability of the first results. After this additional testing the peat sample was considered also as homogenous (Appendix 3). Moreover carbon, nitrogen and hydrogen from fifteen and sulphur from eight subsamples were measured. According to the all 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 show that the samples were appropriate for measurement of calorific value (Appendix 3).

## 2.5 Feedback from the proficiency test

Appendix 4.1 contains the comments sent by the participants. The comments were mainly relating to the data input protocols in the laboratories. The provider gives some comments to the participants considering mainly the reporting of the results in Appendix 4.2.

## 2.6 Analytical methods

### 2.6.1 Gross and net calorific value

The analytical methods based on different standard methods were used for the measurements in the PT. The used analytical methods of the participants are shown in more detail in Appendix 5.1.

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]). A few laboratories were used some national standards (e.g. lab 29, 44). 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 5.1).

The measurements of calorific value were mainly done by IKA, LECO 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 5.1). In the calibration used benzoic acid from 8-10 different 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 5.1). 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 some cases also calculated hydrogen content was used for corrections.

### 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. For example, sulphur was measured using standards: ASTMD 3177 (lab 28), ISO-351, ISO 19579 (lab 51) or DIN51900-1+DIN10304-1 (lab 46). For moisture measurements were used also standard: ASTM D 3173 (lab 28), ISO 11722 (lab 35, 47, 51), ISO 5066-2 or ASTM D 3302 (lab 57). Additionally, one laboratory used infrared moisture analysis (21).

Carbon, hydrogen and nitrogen were also measured using standards: ASTM D 3178 (lab 37), ASTM D5291-10 (lab 46) or ISO 1028 (lab 47). Also some national standards (e.g. lab 29, 37, 38, 4, 42, 44, 48, 49) or in-house methods (EDXRF, lab 57) were used.

Carbon, hydrogen and nitrogen were measured by using different equipments (e.g. VARIOMAX, LECO, ELTRA, ELTRA CHS, Appendix 5.1). Different elemental analyzers (e.g, ELTRA, LECO, Appendix 5.1) were also used for measurements of sulphur. Sulphur was measured also by using $O_2$-combustion and IC-measurement and some other techniques.

Ash content was measured also using some other standards, e.g. ASTMD 3174 (lab 28, 35, 42) and some national standards (e.g. lab 29, 37, 38, 41) or in-house methods were reported as well. Ash content was determined gravimetrically by heating mainly at the temperature 550 °C (Sample B1) or 815 °C (Sample K1). Also some other temperatures were used for ash content measurements (Appendix 5.1).

## 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 measurement of the sample B1 and K1 (Appendix 6). In the calculation of the robust mean outliers were not normally rejected, but they were iterated before the final calculation of the robust mean. However, in this proficiency test some extreme results (at most 1-7 results/measurement) had to be rejected because of rather strict requirements for reproducibility given in the standards for analysis described in the covering letter of the samples. Especially in estimation of the assigned value of gross and net calorific value, the base for extreme value was either the anomalous calorific value or anomalous value in the measured moisture or/and element value used in the calculation or the reported results were not according to the given instructions. 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 near with the assigned values (Table 1). Also the results of homogeneity testing of the samples were used as background information in estimation of the assigned values. Additionally, the calculated assigned values of the calorific values were compared with 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 0.18 % to 0.28 %. For the other measurements the uncertainty varied from 0.34 % to 5.6 % (Appendix 6).

The participants also calculated emission factors (EF) according to the given total moisture contents as received ($M_{ar}$) for the samples and the results were evaluated as well. According to the evaluation of results at least laboratories 34 and 43 were not calculated the emission factor for peat as requested. The case was the same for the emission factor of coal reported by the laboratory 43. These results were excluded from the assigned value calculation. For these laboratories, the performance evaluation of emission factor was not satisfactory, thus weakening the reliability of the performance evaluation of EF as a whole.

After reporting the preliminary results in October 2010 no corrections had done to the assigned values.

### 2.7.3 Standard deviation for proficiency assessment and z score

For the total standard deviation for proficiency assessment used in the calculation of the z score 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 recommended in the standards was mainly fulfilled for the gross calorific values (± 300 J $g^{-1}$). For the net calorific value the reproducibility was increased to ± 368 J $g^{-1}$ for the sample B1 and to ± 374 $Jg^{-1}$ for the sample K1. The reason was partly the variability of the results and the missing of clear reproducibility information for the net caloric value in the standard methods [e.g. 5-8]. In calculation of net calorific value there are more uncertainty sources than in calculation of gross calorific value. Particularly, on the final results of net calorific value uncertainty and errors of other measurements (i.e. moisture, S, H) can affect. For some other measured parameters (i.e. C, H, N, S and ash) the total standard deviation for proficiency assessment had to be increased from the reproducibility presented in the standard methods. However, noticeable was that for H and ash the reproducibility of results were better than in the previous PT and the total standard deviation was able to lower in this PT when compared to the previous PT [22].

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 contents partly due to high variability between the results. The evaluation of emission factor (EF) is only indicative due to the noticed calculation errors for the both sample types.

After reporting the preliminary results in October 2010 no corrections had done to the standard deviations for the proficiency assessment.

# 3 RESULTS AND CONCLUSIONS

## 3.1 Results

The summary of the results is presented in Table1. The reported results and their uncertainties grouped by the measurement methods are presented graphically in Appendix 5.3. Explanations to terms used in the result tables are presented in Appendix 7. The results and the performance of each laboratory are presented in Appendix 8. The summary of z scores is shown in Appendix 9. The measurement uncertainties reported by the laboratories grouped according to the evaluation procedure is reported in Appendix 10. The comparison of z and zeta scores (Appendix 7) is shown in Appendix 11.

Table 1. Summary of the result in the proficiency test 5/2010.

| Analyte | Sample | Unit | Ass. val. | Mean | Mean rob. | Md | SD rob | SD rob, % | Num. of labs | 2*Targ SD% | Accepted z-val% |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ash,d** | B1 | w% | 7,7 | 7.69 | 7.70 | 7.70 | 0.18 | 2,3 | 30 | 6 | 90 |
| | K1 | w% | 10,9 | 10.88 | 10.90 | 10.91 | 0.10 | 0,9 | 48 | 2,5 | 92 |
| **C,d** | B1 | w% | 53,4 | 53.39 | 53.43 | 53.66 | 0.79 | 1,5 | 22 | 3 | 86 |
| | K1 | w% | 73,3 | 73.21 | 73.25 | 73.26 | 0.92 | 1,3 | 38 | 2,5 | 87 |
| **EF** | B1 | t CO2/TJ | 106 | 105.85 | 105.93 | 105.90 | 1.15 | 1,1 | 14 | 4 | 64 |
| | K1 | t CO2/TJ | 93,8 | 93.83 | 93.84 | 93.96 | 1.13 | 1,2 | 23 | 4 | 91 |
| **H,d** | B1 | w% | 5,63 | 5.63 | 5.63 | 5.69 | 0.16 | 2,8 | 20 | 7 | 90 |
| | K1 | w% | 4,6 | 4.60 | 4.60 | 4.57 | 0.18 | 3,8 | 32 | 7 | 91 |
| **Mad,d** | B1 | w% | 2,88 | 2.84 | 2.88 | 2.87 | 0.49 | 17 | 30 | | |
| | K1 | w% | 3,52 | 3.50 | 3.52 | 3.54 | 0.22 | 6,3 | 49 | | |
| **N,d** | B1 | w% | 1,62 | 1.62 | 1.62 | 1.59 | 0.075 | 4,6 | 20 | 15 | 85 |
| | K1 | w% | 2,14 | 2.14 | 2.14 | 2.17 | 0.15 | 7,2 | 30 | 15 | 93 |
| **q-p,net,d** | B1 | J/g | 20460 | 20495.19 | 20460.12 | 20456.00 | 90.31 | 0,4 | 27 | 1,8 | 74 |
| | K1 | J/g | 28810 | 28782.99 | 28806.49 | 28810.00 | 187.57 | 0,7 | 42 | 1,3 | 71 |
| **q-V,gr,d** | B1 | J/g | 21680 | 21696.23 | 21680.50 | 21683.00 | 99.36 | 0,5 | 31 | 1,4 | 77 |
| | K1 | J/g | 29820 | 29805.91 | 29818.50 | 29810.00 | 134.64 | 0,5 | 49 | 1 | 71 |
| **S,d** | B1 | w% | 0,25 | 0.25 | 0.25 | 0.25 | 0.015 | 6,1 | 25 | 15 | 92 |
| | K1 | w% | 0,31 | 0.31 | 0.31 | 0.31 | 0.018 | 5,9 | 45 | 15 | 84 |

| | |
|---|---|
| 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 ($2*s_p$) |
| Accepted z-val% | the satisfactory z scores: the results (%), where $\lvert z \rvert \leq 2$. |

The robust standard deviation of results was lower than 2 % for 50 % of the results and it was lower than 6 % for 78 % 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 7.2 and 6.1 %, respectively. In measurement of moisture the robust standard deviation was 6.3 % in the coal sample and more than duplicated (17 %) in measurement of the peat sample. The standard deviations of the results in this PT were nearly in the same range than in the previous respective PT SYKE 5/2009 [22], where the deviations varied from 0.5 % to 11 %.

In this PT the participants were requested to report the replicate results for all measurements. 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 the 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 0.55 % for the sample B1 and 0.40 % for the sample K1 and in measurement of the net calorific value 0.59 % and 0.42 %, 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 $s_w$ %). The repeatability was mainly acceptable only for carbon C in the elemental measurements (Table 2, the column $s_w$ %).

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 gross calorific value, the ratio $s_b/s_w$, was 2.9 % (the sample B1) and 4.6 % (the sample K1), for the net calorific values 5.3 % and 6.0 %, respectively. The high ratio $s_b/s_w$ for the net calorific value was at least partly resulting from variable procedures used in calculation of the results.

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,d** | B1 | w% | 7,7 | 7,696 | 7,7 | 0,0992 | 0,1463 | 0,1768 | 1,3 | 1,9 | 2,3 | 6 | 30 | 90 |
| | K1 | w% | 10,9 | 10,88 | 10,91 | 0,04347 | 0,1307 | 0,1377 | 0,4 | 1,2 | 1,3 | 2,5 | 48 | 92 |
| **C,d** | B1 | w% | 53,4 | 53,41 | 53,61 | 0,1358 | 0,7927 | 0,8043 | 0,25 | 1,5 | 1,5 | 3 | 22 | 86 |
| | K1 | w% | 73,3 | 73,22 | 73,25 | 0,1307 | 0,9912 | 0,9998 | 0,18 | 1,4 | 1,4 | 2,5 | 38 | 84 |
| **EF** | B1 | t CO2/TJ | 106 | 105,8 | 106,1 | 0,3619 | 2,152 | 2,182 | 0,34 | 2 | 2,1 | 4 | 14 | 64 |
| | K1 | t CO2/TJ | 93,8 | 93,78 | 93,91 | 0,1764 | 1,609 | 1,619 | 0,19 | 1,7 | 1,7 | 4 | 23 | 91 |
| **H,d** | B1 | w% | 5,63 | 5,629 | 5,675 | 0,03594 | 0,1464 | 0,1508 | 0,64 | 2,6 | 2,7 | 7 | 20 | 90 |
| | K1 | w% | 4,6 | 4,596 | 4,57 | 0,03232 | 0,2082 | 0,2107 | 0,7 | 4,5 | 4,6 | 7 | 32 | 88 |
| **Mad,d** | B1 | w% | 2,88 | 2,852 | 2,87 | 0,03728 | 0,49 | 0,4914 | 1,3 | 17 | 17 | | 30 | |
| | K1 | w% | 3,52 | 3,507 | 3,53 | 0,0369 | 0,3003 | 0,3025 | 1,1 | 8,6 | 8,6 | | 49 | |
| **N,d** | B1 | w% | 1,62 | 1,621 | 1,601 | 0,02274 | 0,0727 | 0,07617 | 1,4 | 4,5 | 4,7 | 15 | 20 | 85 |
| | K1 | w% | 2,14 | 2,137 | 2,17 | 0,02053 | 0,1437 | 0,1451 | 0,96 | 6,7 | 6,8 | 15 | 30 | 93 |
| **q-p,net,d** | B1 | J/g | 20460 | 20490 | 20460 | 30,68 | 164,4 | 167,3 | 0,15 | 0,8 | 0,82 | 1,8 | 27 | 74 |
| | K1 | J/g | 28810 | 28790 | 28820 | 35,54 | 211,9 | 214,8 | 0,12 | 0,74 | 0,75 | 1,3 | 42 | 71 |
| **q-V,gr,d** | B1 | J/g | 21680 | 21690 | 21700 | 54,08 | 153,6 | 162,8 | 0,25 | 0,71 | 0,75 | 1,4 | 31 | 77 |
| | K1 | J/g | 29820 | 29810 | 29820 | 35,6 | 162 | 165,8 | 0,12 | 0,54 | 0,56 | 1 | 49 | 71 |
| **S,d** | B1 | w% | 0,25 | 0,2504 | 0,248 | 0,008775 | 0,01508 | 0,01745 | 3,5 | 6 | 7 | 15 | 25 | 92 |
| | K1 | w% | 0,31 | 0,3068 | 0,31 | 0,006946 | 0,02101 | 0,02213 | 2,3 | 6,8 | 7,2 | 15 | 45 | 84 |

Ass. val. - assigned value, Md - median, sw - repeatability standard error, sb - standard error between laboratories, st - reproducibility standard error

Table 3. The robustness ($s_b/s_w$) of the replicate results in the PT5/2010.

| **Analyte** | **Sample** | **$s_b/s_w$** | **Analyte** | **Sample** | **$s_b/s_w$** |
|---|---|---|---|---|---|
| Ash | B1 | 1.5 | S | B1 | 1.7 |
| | K1 | 3.0 | | K1 | 3.0 |
| C | B1 | 5.8 | q-p,net,d | B1 | 5.3 |
| | K1 | 7.6 | | K1 | 6.0 |
| H | B1 | 4.1 | q-V,gr,d | B1 | 2.9 |
| | K1 | 6.4 | | K1 | 4.6 |
| $M_{ad}$ | B1 | 13 | EF | B1 | 5.9 |
| | K1 | 8.1 | | K1 | 9.2 |
| N | B1 | 3.2 | | | |
| | K1 | 7.0 | | | |

## 3.2 Analytical methods and status to the results

In Appendix 5.1 is summarized the used analytical methods in the proficiency test. The difference between the average concentrations of elements measured by different sample preparation methods was tested using the t-test. The results of the t-test are shown in Appendix 5.2. In Appendix 5.3 is presented the results of participated laboratories grouped based on used different standard methods.

### 3.2.1 Ash, moisture and elemental measurements

In measurement of the ash content only a few laboratories reported too high or too low values, and different techniques have not clearly affected the results (Appendix 5.3). In the ash content, no statistically significant difference between the results was noticed.

The analysis moisture ($M_{ad}$) was measured using different standard methods (Appendices 5.1 and 5.3). There was the statistically significant difference between the moisture results in the sample K1 measured by the standards ISO 589 and DIN 51718 and between DIN 51718 and ASTM D 5142 (Appendix 5.2). The differences between the results can be varied from the amounts of used sample amount for analyses, the drying time at an oven and drying atmosphere at an oven or the humidity content of the ambient. The methods ISO 589 and DIN 51718 are based on gravimetric methods and ASTM D 5142 is instrumental procedure. It was difficult to estimate the correct values for analysis moisture at proficiency tests as a result above mentioned reasons. The correct measurement of moisture is important, because it plays a significant role in the calculation of the calorific values.

In measurement of carbon, nitrogen, hydrogen and sulphur different standard methods were used (Appendices 5.1 and 5.3). Only for the results of sulphur in the sample K1 there was the statistically significant difference between the standards ISO 334 and ASTM D 4239 (Appendix 5.3). The difference can be due to the various measuring procedures. ASTM D 4239 is an instrumental procedure using high temperature tube furnace combustion and ISO 334 is Eschka method based on mainly gravimetric technique. ASTM D 4239 is a rapid method and ISO 334 is time consuming containing several analysis steps.

### 3.2.2 Gross and net calorific value

In the Appendices 5.1 and 5.3 are shown the results of the gross calorific values for the samples B1 and K1 with the reported information of the used standard method and the more detail information of the used methods. Basically, there was no clear difference between the gross calorific values obtained using the different standard methods and no statistically significant difference between the results were found. For the laboratories 26 (the sample K1 and B1) and 47 (the sample K1) the deviation of the net calorific value is evident due to the errors in the data reporting (Appendices 4.1, 8). In many cases, the anomalous result was explained by the errors in the data reporting and/ or errors in the measurement. There was some variance between results, but mainly the gross calorific values and net calorific values were between the acceptable variances. The main mistakes might be due to erroneous data handling and calculations.

The reasons for deviated results are fairly complicated to obtain in this PT, because there might be several errors effecting on the final results at the same time.

There are several factors, which have to be taken into account measurement of calorific value:

- Sample should be mixed well before analyses are carried out.
- Analytical moisture and calorific value should be measured at a same time (within a few hours), if the gross calorific value is analyzed from air dried sample. Analytical moisture has a great effect for calculation the gross calorific value as a dry weight basis. The porous fuel material adsorbs moisture very easily and the changes in the moisture content of the laboratory air can cause 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 a laboratory environment. The sample should be analyzed as soon as possible after drying or a dried sample should keep in a small, effectively closed small container until the calorific value analysis is carried out.

- The coal samples can be analyzed in a power form. Usually biomass and peat samples shall be tested in a pellet form or in power form in a closed combustion bag or capsule. In the future, it could be valuable to ask participants report more information from the way of sample handling in the analyzing step as this can be an important issue in the verifying of test results.
- If the sample contains a high amount of sulphur and nitrogen, the correction for sulphur and total acids can affect to a great extent, especially in the case of coal samples.
- The laboratory has to take 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 during 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 the 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.

## 3.3 Uncertainties of the results

Several approaches were used for estimating of measurement uncertainty (Appendix 10). The approach based on X-chart (Meth 2), 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

From 6 to 30 laboratories reported the expanded measurement uncertainties with their results (Table 4, Appendix 11). The estimated uncertainties varied greatly, e.g. for coal (the sample K1) from 0.02 to 30 %. 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, not as percent as the provider of this PT had requested. In many other cases, the reported measurement uncertainties did not meet the requirements presented in the standard methods for the repeatability of the method. On the other hand, almost for each measurement also extremely high measurement uncertainties have been reported (Appendix 11).

As indicative information also the calculated zeta scores are reported in Appendix 11. These have been informed to the participants with the preliminary results as well. In the calculation of zeta score both the uncertainty of assigned value and the measuring uncertainties reported by the laboratories has been taken account (Appendix 7). As there were reported very variable and some cases high measuring uncertainties, no performance evaluation based on the zeta score was performed (see Appendix 4.2). However, as an example there can be seen some cases where the reported high uncertainty of laboratory has really affected the zeta score and improved the performance of the participant comparing with the z score (i.e. lab 20 for C in the sample B1, Appendix 11). On the other hand, very low measuring uncertainties have resulted in poor performance in the use of the zeta score (i.e. lab 51 for q-V,gr,d in the sample B1) and a satisfactory performance based on z score (Appendix 11). The participants can evaluate their performances based on these scores. In the case that the participant provided data of good quality, there is not a large deviation between the z and zeta scores. Thus this information could be useful when laboratories re-evaluate the measurement

uncertainties [23].

Based on the reported measuring uncertainties it is evident that harmonization in the estimating of uncertainties should be continued.

## 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 44.3 % for the peat sample, B1, and 11.2 % for the coal sample, K1, which informed in the covering letter of the samples. In total, 14 laboratories reported the emission factor in measurement of the peat sample, and 23 laboratories reported it for the coal sample (Table 1, Appendix 8).

According to the evaluation of results at least laboratories 34 and 43 had not calculated the emission factor for peat sample B1 as correctly (based on the total moisture as received). The case was the same for the emission factor of coal sample K1 reported by the laboratory 43. These results were excluded from the assigned value calculation. For these laboratories the performance evaluation of emission factor is not satisfactory, and thus weakening the reliability of the performance evaluation of EF as a whole.

The participants were asked to calculate EF-values using the equation presented in the EC directive 2007/589/EC [24]. Mainly the participants informed that the calculation of EF-value was based on the EC directive 2007/589/EC (Appendix 5.1). 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 for fossile fuels. (http://www.energiamarkkinavirasto.fi/files/Paastokerroin11112008.pdf). This is presented in the Appendix 5.1. The one aim has been to harmonized the used equation for the calculation of EF values within the Finnish accredited laboratories.

The emission factors are used in the European emission trading of the energy. 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 9. Additionally, zeta scores have been reported with the preliminary results for those laboratories, which have reported the measuring uncertainties. These sores are only informative and no performance evaluation based on those was done (Appendix 11).

The total number of laboratories participating in this PT was 58. The robust standard deviation of the results was mostly lower than 7.5 %, 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 the calorific values and other determinants. The reproducibility required in the standards was fulfilled for the gross calorific values. For the net calorific value reproducibility was somewhat increased from the value for the gross caloric value partly due to the variability of the results and the missing clear reproducibility information for the net caloric value in the standard methods. For some other measured parameters (i.e. C, H, N, S and ash) total standard deviation for proficiency assessment

had to be increased from the reproducibility of standards (Table 1). The reliability of the performance evaluation of EF was weak due to the errors in the calculation of the emission factor (EF).

**Peat**

Accepting the deviations of 1.4–15 % from the assigned values for the peat sample (B1) 82 % of results were satisfactory (Table 1). In the measurement of ash, H and S at least 90 % of the results were satisfactory. In the measurement of gross and net calorific values 77 % and 74 % of results, respectively, were satisfactory when accepting the deviations 1.4 % and 1.8 % 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 5/2009 [22]. There were more difficulties in the estimation of EF, where less than 64 % of results were satisfactory.

**Coal**

Accepting the deviations of 1–15 % from the assigned values for the coal sample (K1) 85 % of results were satisfactory. For the emission factor, EF, the performance evaluation was somewhat non-reliable probably due to the erroneous calculation. In the measurement of ash, H and N over 90 % of the results were satisfactory. In the measurement of gross and net calorific values 71 % of results were satisfactory, when accepting the deviations 1 and 1.3 % from the assigned values. In this PT the number of satisfactory result of the gross calorific value was higher than in the previous PT/2009 (65 %), while the satisfactory net calorific value was in the same range than in the previous test [22].

This PT showed again that the common procedure for calculation of EF-values is not available at this moment. However, the performance for EF in the peat sample was in the same range than in the previous PT5/2009. Thus, it is urgently needed harmonized equation for the calculation of EF-values within the EU countries.

In total, 84 % from the results were satisfactory when the deviations of 1–15 % from the assigned values were accepted. About 78 % of the participants used the accredited methods and 87 % of their results were satisfactory. SYKE arranged a similar proficiency test in 2009 and then 83 % of the results were satisfactory [22].

# 5 SUMMARY

Proftest 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 2010. One peat sample and one coal sample were delivered to the laboratories for the analysis of each measurement. In total, 58 laboratories participated in the proficiency test. The test performed as the joint work with the working group (WG) of the European co-operation for Accreditation (EA) for Interlaboratory Comparisons (EA WG ILC in Testing) and the data will be confidentially handled in the work of this WG.

The robust means of the reported results by the participants were used as the assigned values for measurements. The uncertainties of the calculated assigned values were mainly less than 0.3 % for calorific values and at maximum 5.6 % for the other measurements.

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. In total, 84 % of the participating laboratories reported the satisfactory results when the deviations of 1–15 % from the assigned values were accepted.

About 78 % of the participants used the accredited methods and 87 % of their results were satisfactory. In measurement of the gross calorific value from the peat sample 77 % of the results were satisfactory and respectively in measurement of the coal sample 71 % from the results were satisfactory. In measurement of the net calorific value from the peat sample 74 % of the results were satisfactory and respectively in measurement of the coal sample 71 % from the results were satisfactory.

This PT showed that the common procedure for calculation of EF-values is not available at this moment. The emission factors are used in the European emission trading of the energy. Thus, it is urgently needed harmonized equation for the calculation of EF-values within the EU countries.

# 6 YHTEENVETO

Suomen ympäristökeskus (Proftest SYKE) järjesti syyskuussa 2010 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin ja kosteuden määrittämiseksi turpeesta ja kivihiilestä. Pätevyyskoe järjestettiin yhteistyössä Euroopan akkreditointielinten yhteistyöjärjestön (EA) testauksen vertailumittaustyöryhmän kanssa (EA WG ILC). Pätevyyskokeen tuloksia käytetään jatkossa luottamuksellisesti akkreditoinnin toiminnan seurantaan kansainvälisellä tasolla.

Pätevyyskokeeseen osallistui yhteensä 58 laboratoriota. Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat määrityksestä riippuen välillä 1–15 %. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa. Tavoitearvon epävarmuus oli lämpöarvon määrityksissä alhaisempi kuin 0.3 % ja muiden määritysten osalta korkeintaan 5.6 %. Tulosten arviointia ei tehty kosteuspitoisuuden määritykselle, koska tulosten hajonta oli suuri. Arviointi on jonkin verran epävarma hiilen päästökertoimelle, koska kaikki laboratoriot eivät olleet laskeneet arvoa tulokosteutta kohti.

Koko tulosaineistossa hyväksyttäviä tuloksia oli 84 %, kun vertailuarvosta sallittiin 1–15 %.n poikkeama. Noin 78 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 87 %. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 77 % (turve) ja 71 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 74 % (turve) ja 71 % (kivihiili).

Pätevyyskokeessa havaittiin, että selvää laskentakaavaa päästökertoimelle ei ole kuvattuna direktiivissä 2007/589/EC [24]. Esimerkiksi Suomessa on tehty kansallinen ohjeistus kiinteiden fossiilisten polttoaineiden päästökertoimen laskentaan. Yhtenäinen ohjeistus päästökertoimen laskennalle eri EU-maissa todettiin puuttuvan, mistä johtuen laskentatapa vaihtelee. Päästökerrointa käytetään Euroopan laajuisessa energian päästökaupassa. Täten yhtenäisen, dokumentoidun, laskentakaavan käyttöönotto EU-laajuisesti on erityisen tärkeä.

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Kuopion Energia Oy, Kuopio, Finland
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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 laboratory of Enas. 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 Water Protection Association of the Kokemäenjoki River. The particle size distribution of peat was measured by the laboratory of Enas using laser diffraction (Malvern).

## Sample K1, steam coal fuel

The sample K1 was a Russian crushed 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 the laboratory of Water Protection Association of the Kokemäenjoki River. The particle size distribution of coal was measured by the Helsinki Energia, Power Plant Chemistry using laser diffraction (Malvern).

# TESTING OF THE SAMPLES

## Homogeneity

Homogeneity was tested from duplicate measurements of calorific value and ash content in fifteen samples, which were homogenised before sampling (Table 1). The gross calorific value in the peat sample B1 was additionally tested from eight samples by other laboratory ($2^{nd}$ test results in Table 1) due to the some variability of the test results of the first analysing laboratory ($1^{st}$ test results in Table 1). In the $2^{nd}$ test the sampling variation ($s_{sam}$) was much smaller than the variation obtained in the $1^{st}$ test. In addition, carbon, hydrogen and nitrogen content from fifteen and sulphur content from eight samples were tested. 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].

Table 1. Results from the homogeneity testing of the peat B1 and coal K1 samples.

| 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, (the $1^{st}$ test)** | 21701 | 0.69 | 150 | 43.5 | 0.29 | yes | 71.4 | 5110 | 5255 | yes |
| **Gross calorific value, J/g, (the $2^{nd}$ test)** | 21649 | 0.69 | 150 | 29.3 | 0.20 | yes | 9.22 | 85 | 5926 | yes |
| **Ash, w-%** | 7.75 | 1.9 | 0.15 | 0.056 | 0.37 | yes | 0.063 | 0.004 | 0.006 | yes |
| **Coal (K1)** | | | | | | | | | | |
| **Gross calorific value, J/g** | 29801 | 0.50 | 150 | 32.9 | 0.22 | yes | 45.2 | 2042 | 4190 | yes |
| **Ash, w-%** | 10.9 | 1.4 | 0.15 | 0.014 | 0.093 | yes | 0.012 | 0.0001 | 0.004 | 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 = 2.01when the number of sub samples is 8, F2 = 1.25 when the number of sub samples is 8

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

F1 = 1.69 when the number of sub samples is 15, F2 = 0.71 when the number of sub samples is 15

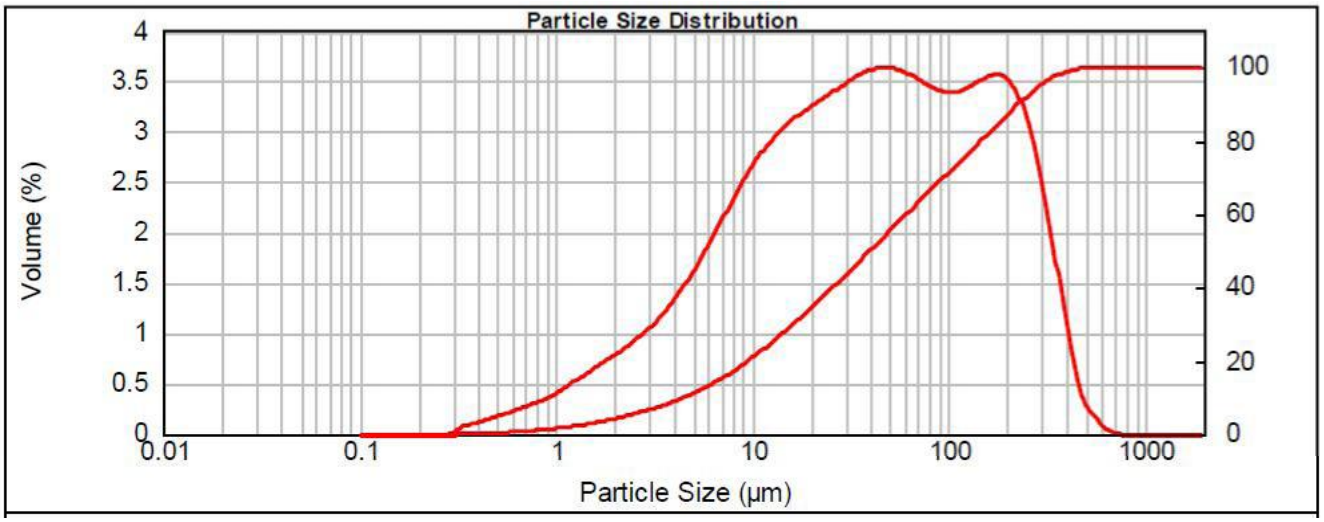
**Conclusion: In each case, the criteria were fulfilled. Additionally, the results of the other tested parameters support the homogeneity of samples. The samples could be regarded as homogenous.**

# TESTING OF THE SAMPLES

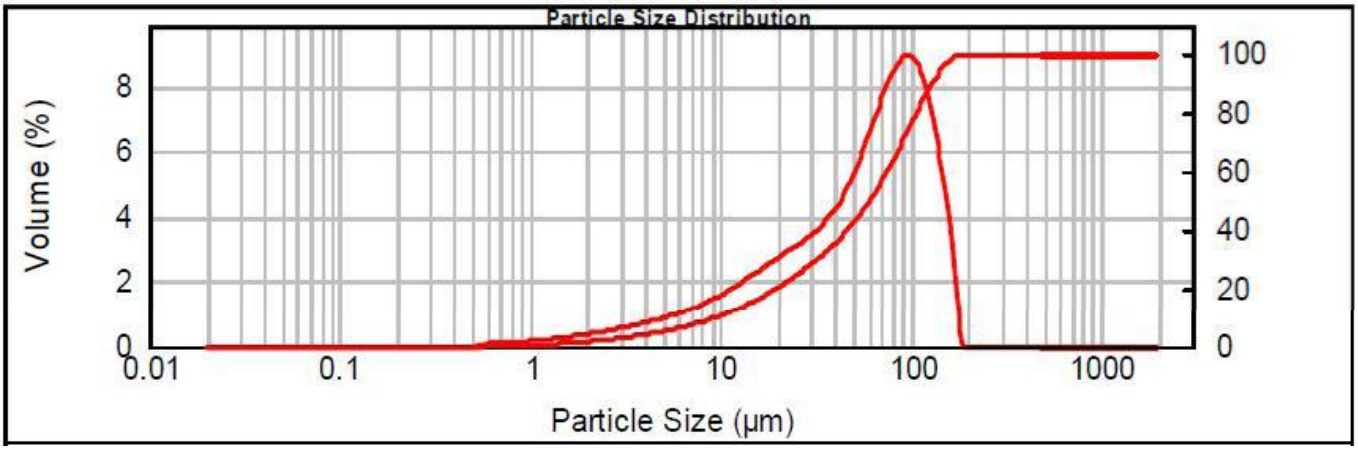
## Particle size

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

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 39.7 µm and 99.8 % of the particles were smaller than 550 µm. For coal sample K1 the mean size of particles was 60.5 µm and 100 % of the particles were smaller than 212 µm. For the both sample material the requirement of particle size given in the international standards was fulfilled [5, 6].




a) The particle size distribution of peat B1.




b) The particle size distribution of coal K1.

Figure 1. The particle size distribution of the fuel samples.

# COMMENTS SENT BY THE PARTICIPANTS

| Lab | Comment to the samples / PT | Action/Proftest |
|---|---|---|
| 13, 16 | The samples were delivered crosswise between the two local offices of the participants. | The local offices changed their samples themselves. The provider will be more carefully in the packing of samples. |
| 23 | The participants ordered both testing samples, but only the sample B1 (peat) delivered. | The sample B1 was unfortunately unpacked and the participant did not want the sample later. The missed sample was not charged. The provider will be more carefully in the packing of samples. |
| 33, 39 | The samples were delayed. | The local, national, post services had difficulties to deliver the packets to the participants. |
| 42 | The samples were delayed due to the incomplete address. | The samples were posted to the address which was informed on the registration form to the provider. |

| Lab | Comment to the results | Action/Proftest |
|---|---|---|
| 26 | The results of q-V,gr,d and q-p,net,d for the samples were reported erroneously.<br><br>The laboratory informed new results for the samples after receiving the preliminary results:<br>B1: q-V,gr,d 21436 and q-p,net,d 20429 J/g,<br>K1: q-V,gr,d 29753 and q-p,net,d 28746 J/g | 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.<br><br>If the results should have been reported rightly they should have been satisfactory.<br><br>The participant can re-calculate z scores according to the guide for participating laboratories in Proftest proficiency testing schemes (www.environment.fi/syke/proftest). |
| 33, 44 | The results of calorific values were reported in MJ/g instead of the requested J/g. | The units were corrected by the provider. However, in the future proficiency tests the unit corrections will be not done. |
| 46 | After sending the preliminary results the participants informed that they were reported $M_{ad}$ in the sample K1 incorrectly.<br>The right results were:<br>1.82 % and 1.74 % | The results were handled as outliers in the statistical treatment. |
| 47 | The laboratory has not reported the results in dry weight basis (as analysed).<br>The laboratory informed new results for the samples after receiving the preliminary results:<br>K1: q-V,gr,d 29920 and q-p,net,d 28970 J/g, Ash% 10.9, S% 0.32 | The results were handled as outliers in the statistical treatment. If the results should have been reported rightly they should have been satisfactory.<br><br>The participant can re-calculate z scores according to the guide for participating laboratories in Proftest proficiency testing schemes (www.environment.fi/syke/proftest). |

# COMMENTS TO THE PARTICIPANTS

| Laboratory | Comments on results |
|---|---|
| 28 | The laboratory provided results several times; new results and corrections to the older ones. The provider recommended that the results will be provided at once and only minor corrections later, if needed. |
| 30, 38, 58 | Laboratories reported only one result, though replicate results were requested. These results were not included in the calculation of assigned values. |
| 16, 31, 28 | Laboratories reported four parallel results, though replicate results were requested. The two first results were included in the final database. |
| 6, 25, 26, 36, 37, 51, 52, 54 | The laboratories reported the measurement uncertainties as ± J/g instead of UC %. The values were corrected by the provider. The provider did not assure that all erroneously reported values have been corrected. No comments to the uncertainty corrections were given from the participants after the preliminary results. The provider strongly recommended that the participants are more carefully to report the uncertainty correctly. The performance evaluation using zeta scores, which based on the measurement uncertainties, is unsure due to the errors in the result reporting by the participants. |
| - | After receiving the preliminary results several participants informed their missing data in the z and zeta score comparison (Appendix 6 in the preliminary results). These participants were not reported their measurement uncertainties with the results. As the zeta score is based on the uncertainties the data of non-reported participants were not reported in this Annex. The provider will more clearly describe the zeta score reporting in the covering letter of preliminary results. |
| - | Fewer errors than the previous test were found in the wrongly reported units, which is a good feedback. In the future wrong unit will be not corrected by the provider, unless a total amount of results is too low for the statistical calculations. |

# ANALYTICAL METHODS

| Analyte | Code | Method |
|---|---|---|
| **q-V,gr,d q-p,net,d** | **1** | CEN/TS 14918 |
| | **2** | ISO 1928 |
| | **3** | DIN 51900 |
| | **4** | ASTM D 5865 |
| | **5** | Other |
| **Ash** | **1** | CEN/TS 14775 |
| | **2** | ISO 1171 |
| | **3** | DIN 51719 |
| | **4** | ASTM D 5142 |
| | **5** | Other |
| **C, H, N** | **1** | CEN/TS 15104 |
| | **2** | ISO/TS 12902 |
| | **3** | ASTM D 5373 |
| | **4** | Other |
| **S** | **1** | CEN/TS 15289 |
| | **2** | ISO 334 |
| | **3** | ASTM D 4239 |
| | **4** | Other |
| **$M_{ad}$** | **1** | CEN/TS 14774 |
| | **2** | ISO 589 |
| | **3** | DIN 51718 |
| | **4** | ASTM D 5142 |
| | **5** | Other |

# ANALYTICAL METHODS

## Measurements:

| Measurement of gross calorific value | Sample B1 | Sample K1 |
|---|---|---|
| **Date of analysis in 2010** | 20.9, 22.9, 21.9, 23.9, 28.9, 30.9, 1.10, 5.10, 6.10, 7.10, 29.9-4.10, 4-7.10, 9-10.10, 13.10 | 29.9/4.10, 27.9, 28.9, 22.9, 24.9, 26.9, 27.9, 29.9, 30.9, 1.10, 4-5.10, 4.10, 5.10, 6.10 29.9-4.10, 4-7.10, 5-7.10, 29-30.9, 30.9-1.10, 13.10 |
| **Sample amount** | Mainly 0.5-1.2 g used<br>< 0.5 g used: 0.3 g (lab 20), 0.2 g (lab 30) | Mainly 0.5-1 g used<br>< 0.5 g used: 0.3 g (lab 20), 0.3-0.4 g (lab 46) |
| **Drying of sample** | Air dried: lab 7, 8, 9, 12, 15, 16, 21, 22, 24, 26, 31, 37, 57<br>At 105 °C dried: lab 4, 14, 27, 34, 38<br>Air dried & at 105 °C dried: lab 58<br>No drying: lab 5, 20, 29, 30, 40, 43, 60 | Air dried: lab 2, 3, 4, 11, 12, 13, 15, 21, 22, 23, 24, 25, 28, 31, 36, 37, 42, 44, 45, 47, 48, 52, 57<br>At 105 °C dried: lab 13, 29, 34, 38, 39, 46, 58<br>Air dried & at 105 °C dried: lab 33, 49, 52<br>No drying: lab 5, 6, 20, 32, 40, 43, 49, 54, 56, 60 |
| **Equipment (manufacturer, volume of bomb and volume of added water)** | 14 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<br>3 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 14, 16)<br>8 labs: LECO (model AC 300 or 350) with bomb volume 260 - 400 ml and with the added water of 1 ml or 5 ml | 17 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<br>10 labs: LECO (model AC 300, 350 or 500) with bomb volume 300 - 400 ml (2000 ml lab 6) and with added water of 1 – 10 ml<br>10 labs: PARR (model 1261, 1281,6200, 6300 or 6400) with bomb volume 250-500 ml (or not given) and with the added water of 1 ml<br>Sanio Gallenkamp with the bomb volume 250 ml and added water 1 ml (lab 3),<br>1 lab: Julius Peters with the bomb volume 301 ml and with the added water 10 ml<br>1 lab: Lagent MS with the bomb volume 300 ml and with the added water 1 ml<br>1 lab: Precizia KL 10 with the bomb volume 350 ml and with the added water 5 ml |

# ANALYTICAL METHODS

## Measurements:

| Measurement of gross calorific value | Sample B1 | Sample K1 |
|---|---|---|
| **Calibration** | **Benzoeacid**<br>4 labs: PARR, 26454, 26434.9 or 26432.1 J/g<br>6 labs: BAS-BCS, 26439,7 J/g<br>3 labs: IKA, 26456, 26460-26470 J/g<br>6 labs: ALPHA, 26564, 26454 or 26457 J/g<br>1 labs: NIST<br>2 lab: Fluka, 26470 J/g<br>4 lab: LECO, 26451, 26440, 28190 J/g<br>1 lab: Federal state unitary enterprise, 26454 J/g<br>1 lab: Sigma-Aldrich<br>7 labs: as weighed<br>9 labs: in air<br>2 labs: in vacuum<br><br>**Correction of the certified value[1]**<br>17 labs: no<br>9 labs: yes (lab 4, 5, 8, 16, 21, 22, 58, 59)[1] | **Benzoeacid**<br>10 labs: PARR, 26454 or 26432.1 J/g<br>8 labs: IKA, 26460, 26456 or 26556 J/g<br>8 labs: BAS-BCS, 26439.7 J/g<br>5 labs: ALPHA, 26434, 26454, 26464 or 26457 J/g<br>3 labs: NIST, 26434 J/g<br>4 lab: LECO, 26451, 26440 J/g<br>1 lab: Fluka, 26470 J/g<br>1 lab: Sigma-Aldrich<br>1 lab: Riedel, 26453 J/g<br>1 lab: BHD, 26434.9 J/g<br>1 lab: Federal state unitary enterprise, 26454 J/g<br>9 labs: as weighed<br>19 labs: in air (lab 3, 11, 13, 15, 24, 28, 33, 34, 37, 38, 40, 41, 42, 45, 46, 48, 58, 60)<br>7 labs: in vacuum<br><br>**Correction of the certified value[1]**<br>32 labs: no<br>12 labs: yes (lab 4, 5, 12, 21, 22, 36, 48, 49, 58)[1] |

**[1]Correction the value given in the certificate**

lab 5: corrected value 26449 J/g (5 ml water)
lab 8: mean has been calculated from the control sample charts (x-charts)
lab 1, 12, 59: volume, temperature, pressure
lab 16: corrected value 26442 J/g
lab 21: It has been used as an input reference value for the calorimeter
lab 36: wire and N in air
lab 4, 22, 48, 49, 58: with factor that is calculated according to the certificate

# ANALYTICAL METHODS

## Calculations:

| Gross calorific value | Sample B1 | Sample K1 |
|---|---|---|
| **Correction taken into account in calculations** | wire, ignition, acid, moisture (lab 60)<br>wire, ignition, S, acid (lab 4)<br>moisture (lab 24)<br>wire, moisture (lab 9)<br>analysis moisture (lab 7)<br>wire, S, acid (lab 30, 57)<br>wire, S, acid, moisture (lab 11, 16, 20, 22, 26, 27, 59)<br>wire, S and N (lab 15)<br>N, S, moisture (lab 31)<br>cotton, wire, moisture, (lab 8)<br>wire, S, moisture (lab 2, 29)<br>wire, moisture, N, S (lab 5)<br>not in detail (lab 34, 37, 43)<br>fixed acid correction (lab 14)<br>wire, cotton, S, combustion aid (dode-cane) (lab 40) | wire, ignition, acid, moisture (lab 60)<br>wire, ignition, S, acid, moisture (lab 4, 5, 41)<br>wire, ignition, S, moisture, acid (lab 2)<br>not in detail (lab 11, 34, 37, 43)<br>S, N, moisture (lab 24, 31)<br>wire, acid (lab 22)<br>wire, S (lab 48)<br>wire (lab 53)<br>wire, S, acid (lab 33, 46, 47, 52, 56, 57)<br>wire, N (lab 36)<br>wire, S, acid, moisture (lab 12, 20, 22, 28, 32, 54)<br>correction 156 J/g (lab 38)<br>wire, S, N (lab 15)<br>wire, acid, moisture (lab 13)<br>wire, N, S, moisture (lab 5, 29)<br>wire, S, moisture (lab 21, 25, 42)<br>wire, cotton, moisture (lab 3, 44)<br>wire, cotton, S, combustion aid (dode-cane) (lab 40)<br>wire, paper, S, acid (lab 45)<br>moisture (lab 49)<br>wire, moisture, paper (lab 50) |
| **Net calorific value** | **Sample B1** | **Sample K1** |
| **Correction taken into account in calculations** | N+O, H/measured (lab 1, 4, 40)<br>H/fixed (lab 7, 8 (5.60%))<br>H/measured (lab 22, 30)<br>N+O (40 lab 24), H (6, lab 24)<br>N+O, H/calculated (lab 27 )<br>[N+O]=100 % -[ash-C-H-S] (lab 21)<br>not in detail (lab 34, 37, 43)<br>S, H measured (lab 9)<br>N+O, H (lab 29, 60)<br>only H (lab 12, 3, 59)<br>N, H fixed (1.22 MJ/kg)<br>N-5.6% (fixed)+N%=35% (lab 16)<br>S, N, acid, wire, moisture (lab 26)<br>moisture, acid, ash, H, N/measured (lab 57) | DIN ( 212 J/% for H, 24.4 J/% for $H_2O$ (lab 2)<br>N+O, H/measured (lab 1, 4, 22, 40)<br>N+O, H/calculated (lab 41)<br>not in detail (lab 5, 6, 11, 34, 37, 43 and 38)<br>H/measured (lab 3, 50, 12)<br>H/calculated (lab 25, 46, 53)<br>H/calculated from volatiles (lab 13)<br>N+O]=100 % -[ash-C-H-S] (lab 21)<br>only H (lab 12, 6:lab 24, lab 31)<br>N+O, H (lab 29, 60)<br>%$H_2O$=8.94*H(%), heat of vaporization of water (25ºC,p) 43985 J/mol (lab 32)<br>N (59 kJ/mol), S (55.45 J/mol), H (lab 36)<br>Fixed H, ash, moisture (lab 42)<br>H, N (lab 45)<br>H, O, moisture (lab 48)<br>H 5.8%, O 32%, N 1.5% use in calcula-tion ISO1928:1995, annex E3.2 (lab 49)<br>N+O, H ISO 1925 (lab 52)<br>H, O (lab 56)<br>moisture, acid, ash, H, N/measured (lab 57) |

# ANALYTICAL METHODS

## Measurements:

| Measurement of C, H and N | Sample B1 | Sample K1 |
|---|---|---|
| **Sample amount** | 1 – 350 mg (depending on an equipment), 1 g (N), 796 mg | 1 – 250 mg (depending on an equipment), 1 g (N) or > 1g, 919 mg |
| **Equipment (manufacturer)** | 3 labs: VarioMAX CHN<br>2 labs: Vario EL<br>6 labs: LECO CHN or CS<br>labs: ELTRA CHS-500<br>1 lab: CE Instruments<br>1 lab: EURO EA<br>1 lab: Skalar Primacs SLC (only C)<br>1 lab: Tru Spe CHN<br>1 lab: Jena multi EA 2000 (only C)<br>1 lab: Dionex ICSS2000 (only N)<br>1 lab: Martinek analyzer (C, H)<br>1 lab: Pramas-Vagner (N)<br>1 lab: Dennstedt oven (C, N) | 3 labs: VarioMAX CHN<br>2 labs: Vario EL<br>10 labs: LECO CHN, CHN/S, TC, CR or CS<br>3 labs: ELTRA CHS<br>4 lab: Vario MACRO<br>1 lab. Bichi, KjellFix<br>1 lab: EURO EA<br>1 lab: CE Instruments<br>1 lab: Skalar Primacs SLC (only C)<br>1 lab: Martinek analyzer (C, H)<br>1 lab: Pramas-Vagner (N)<br>1 lab: Dennstedt oven (C, N)<br>1 lab: TruSpec CHN (N)<br>1 lab: Thermo Finning Flash 1112<br>1 lab: Elemental analyzer Flash EA 1112, Thermo<br>C, H calculated (lab 47) |
| **Measurement of S** | **Sample B1** | **Sample K1** |
| **Sample amount** | Mainly 0.1-0.5 g (depending on an equipment), 6 g (lab 57)<br>Eschka: 1 g (lab 31) | Mainly 0.1-0.4 g (depending on an equipment), 1 mg (lab 3), 1 g (lab 24, 3), 70 mg (lab 52), 6 g (lab 57)<br>Eschka method: 1 g (lab 49) |
| **Equipment (manufacturer)** | 2 labs: ELTRA CS<br>8 labs: LECO SC or S<br>1 lab: IKA AOD<br>1 lab: EURO EA<br>1 lab: LECO CHNS<br>1 lab: Oxidation + ion chromatorgraphy (lab 21)<br>1 lab: Iris Interip thermo elementar (lab 9)<br>1 lab: Jena multi EA 2000<br>1 lab: Mitsubishi TS-100V<br>1 lab: Esche mixture<br>1 lab: EDXRF (lab 57) | 6 labs: ELTRA CS or CHS<br>14 labs: LECO, SC, S or CHN/S<br>1 labs: Vario EL<br>1 lab: EURO EA<br>1 lab: LECO CHNS<br>1 lab: Oxidation + ion chromatorgraphy (lab 21)<br>1 lab: Muffle furnace F6000, Vamstead/Thermolyne Corporation<br>1 lab: S.I.E.<br>1 lab: Esche mixture<br>1 lab: Parr 1261 + ion chromatoraphy<br>1 lab: Elemental analyzer Flash EA 1112 + FDP 1112, Thermo<br>1 lab: EDXRF (lab 57)<br>1 lab: carbolite tube furnace |

# ANALYTICAL METHODS

## Measurements:

| **Measurement of ash content** | **Sample B1** | **Sample K1** |
|---|---|---|
| **Sample amount** | 0.6-4 g (mainly 1 g) | 0.15-5 g (mainly 1 g) |
| **Measurement and temperature** | **Measurement**<br>19 labs: Gravimetric<br>5 labs: TGA (lab 15, 21, 37)<br>1 lab: Tgl (lab 29)<br>**Temperature**<br>14 labs: 550 °C<br>1 lab: 525 °C (lab 9)<br>7 labs: 815 °C (lab 8, 14, 16, 38, 57, 60)<br>1 lab: 925 °C (lab 21)<br>1 lab: 950 °C (lab 26)<br>1 lab: 725 °C (lab 43)<br>1 lab: 740 °C (lab 58, no method) | **Measurement**<br>35 labs: Gravimetric<br>2 labs: TGI (lab 3, 29)<br>5 lab: TGA (lab 15, 21, 36, 45)<br>1 lab. MAC-400 (lab 37)<br>**Temperature**<br>30 labs: 815 °C<br>4 lab: 750 °C (lab 6, 28, 32, 54)<br>2 lab: 550 °C (lab 20, 49)<br>1 lab: 925 °C (lab 21)<br>1 lab: 960 °C (lab 36)<br>1 lab: 820 °C (lab 42)<br>1 lab: 725 °C (lab 43)<br>1 lab: 800 °C (lab 46)<br>1 lab: 740 °C (lab 58, no method) |
| **Measurement of moisture** | **Sample B1** | **Sample K1** |
| | 17 an air (lab 4, 5, 7, 9, 12, 15, 16, 20, 21, 22, 24, 31, 34, 38, 57, 58<br>7 lab an $N_2$ atmosphere (26, 27, 29, 37, 40, 43, 60) | 25 an air (lab 3, 4, 13, 15, 20, 21, 22, 23, 24, 28, 31, 33, 34, 38, 39, 41, 42, 44, 45, 46, 48, 49, 50, 52, 53, 57, 58)<br>14 lab an $N_2$ atmosphere (lab 2, 4, 11, 12, 25, 29, 32, 36, 37, 40, 43, 47, 54, 56, 60) |

## Calculations:

| **Emission factor (EF)[1]** | **Sample B1** | **Sample K1** |
|---|---|---|
| **Equation** according to the decision 2007/589/EC | 9 labs: According to EC decision[1]<br>1 lab: national (lab 40)<br>1 lab (lab 21): based on the equation: 1000*3.664*(C/100)*(1-(50.8/100)/Q(p,net,50,8 %) | 15 labs: According to EC decision<br>1 labs: national (lab 40)<br>1 lab (lab 29): based on the equation: 1000*3.664*(C/100)*(1-(8.27/100)/Q(p,net,8.27 %)<br>1 lab: EU. D. 2003/87/CE<br>1 lab: $F=C(tC/t_{com})*3.664/Pci$ (lab 32) |

[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.

In Finland the Energy Market Authority has made the guideline for the calculation of emission factor for fossile fuels as follows (http://www.energiamarkkinavirasto.fi/files/Paastokerroin11112008.pdf):

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

# SIGNIFICANT DIFFERENCES IN THE RESULTS REPORTED USING DIFFERENT STANDARD METHODS

In the statistical comparison of the methods has included the data, in which the number of the results was ≥ 3.

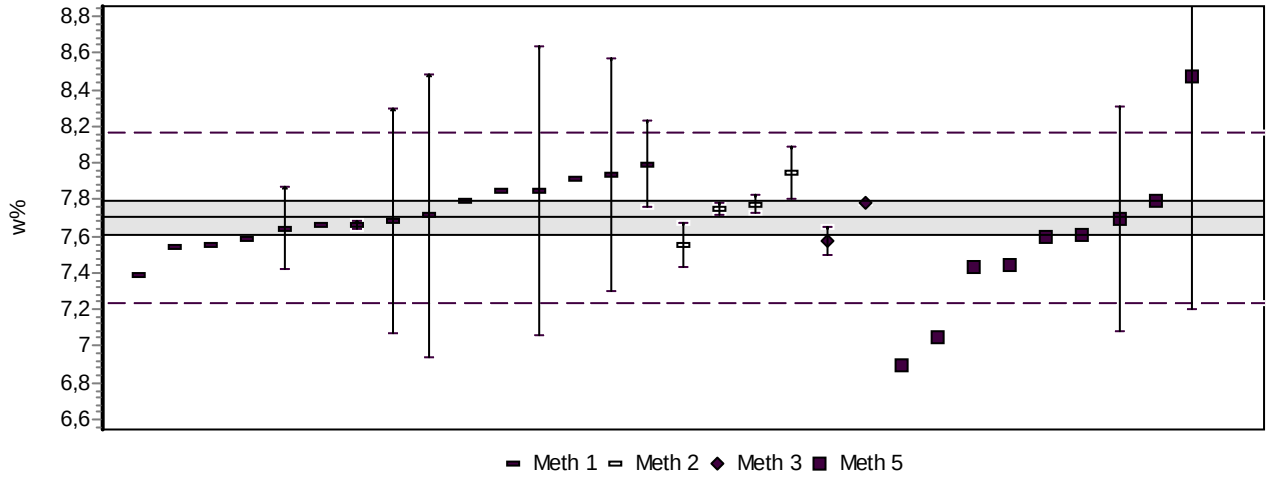
| Analyte | Sample | Method | X | sd | n | Significant difference |
|---|---|---|---|---|---|---|
| **S** | K1 | 2. ISO 334 | 0.25 | 0.06 | 6 | X: meth 2-3 |
| | | 3. ASTM D 4239 | 0.31 | 0.01 | 15 | |
| **$M_{ad}$** | K1 | 2. ISO 589 | 3.43 | 0.19 | 9 | X: meth 2-3, 3-4 |
| | | 3. DIN 51718 | 3.76 | 0.18 | 4 | |
| | | 4. ASTM D 5142 | 3.63 | 0.13 | 7 | |

where, X: the mean value
sd: the standard deviation
n: the number of the result

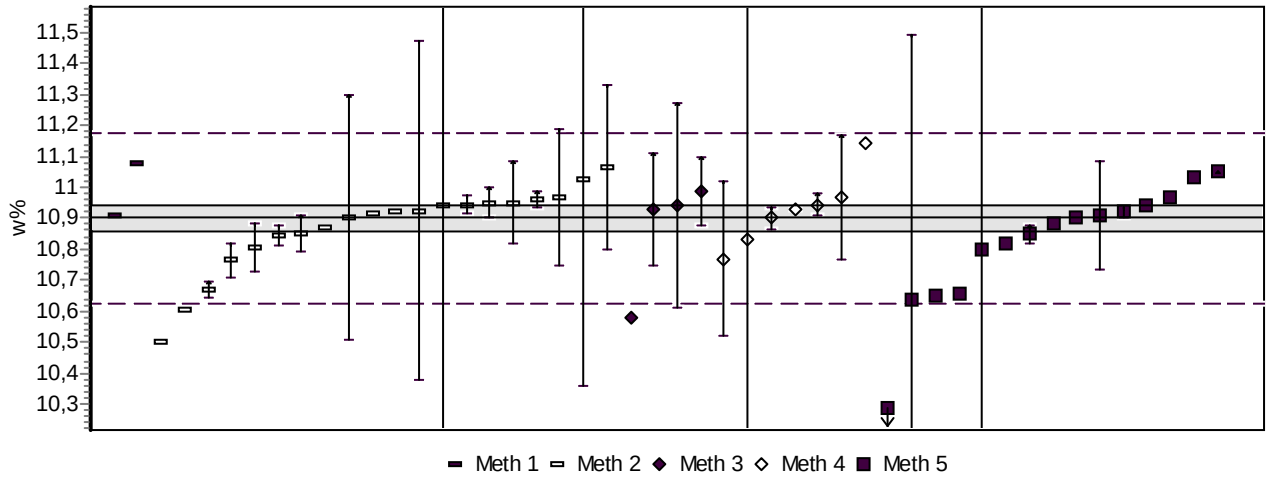
## LIITE 5.3. RESULTS GROUPED ACCORDING TO THE METHODS

APPENDIX 5.3.*Method code - see appendix 5.1*

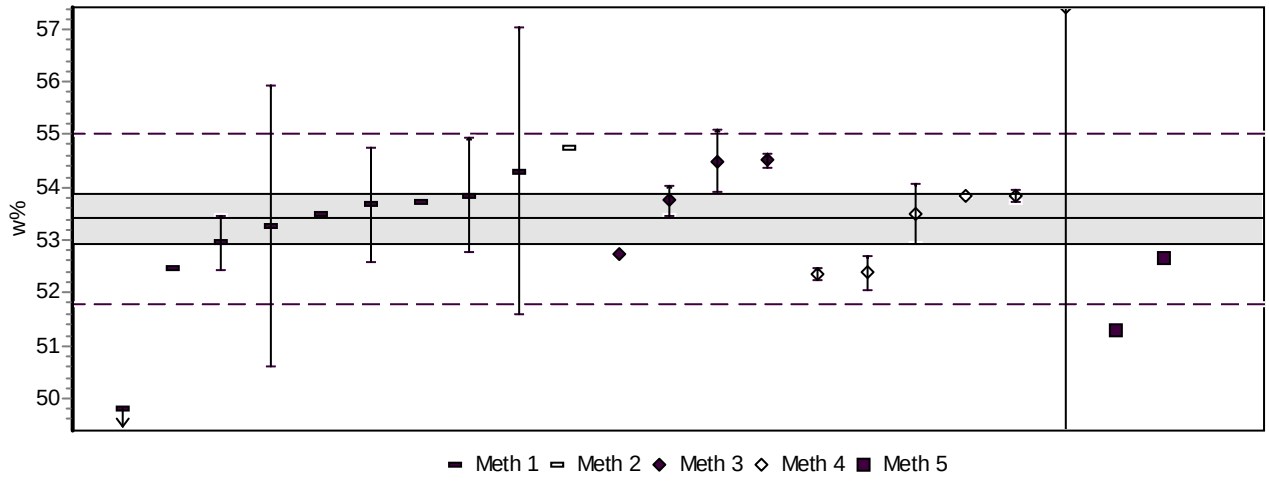
Analyytti *(Analyte)* **Ash,d** Näyte *(Sample)* B1



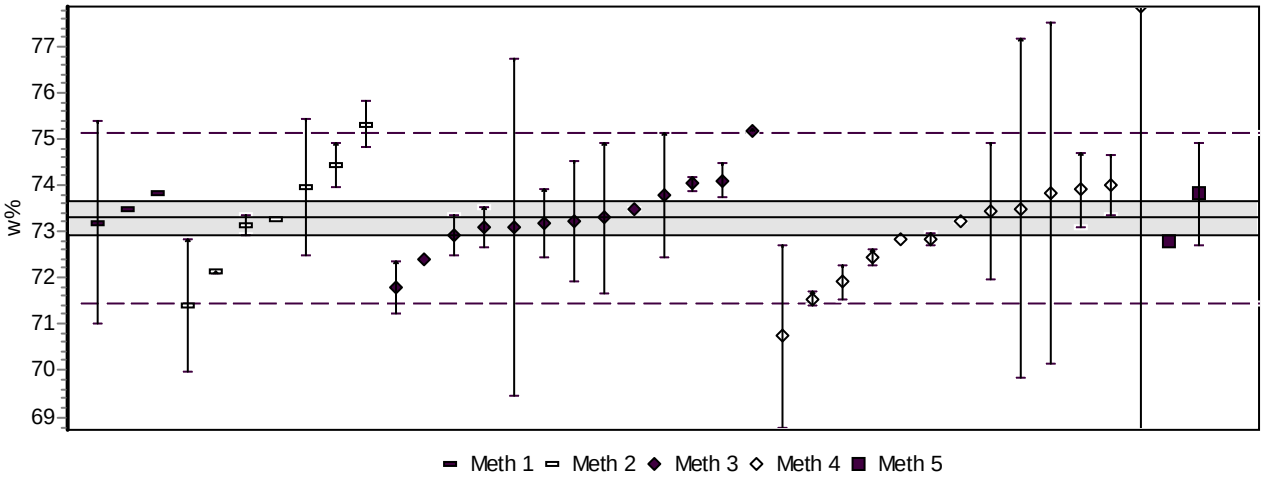

Analyytti *(Analyte)* **Ash,d** Näyte *(Sample)* K1



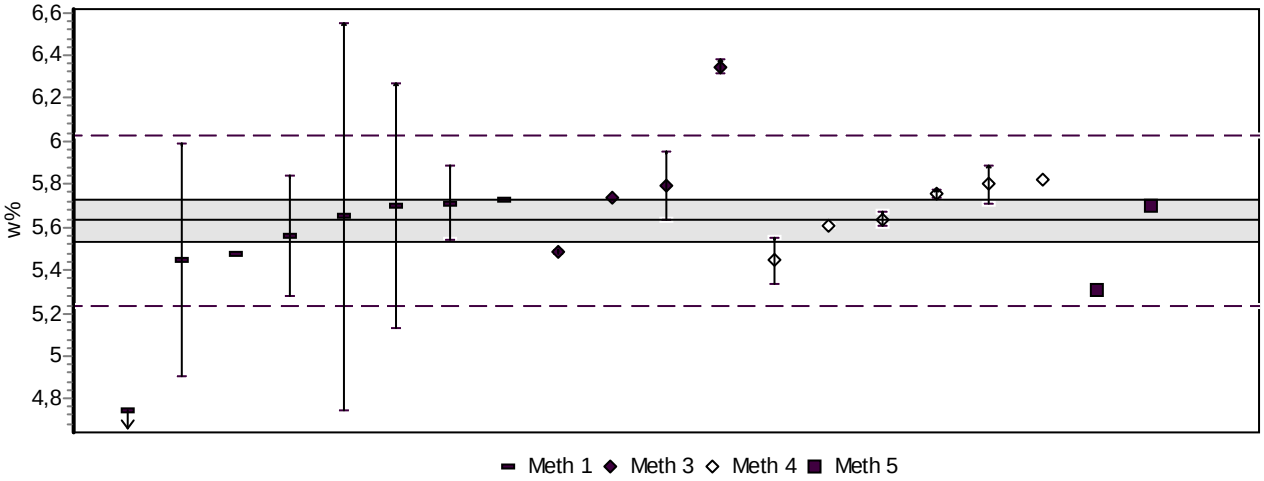

Analyytti *(Analyte)* **C,d** Näyte *(Sample)* B1



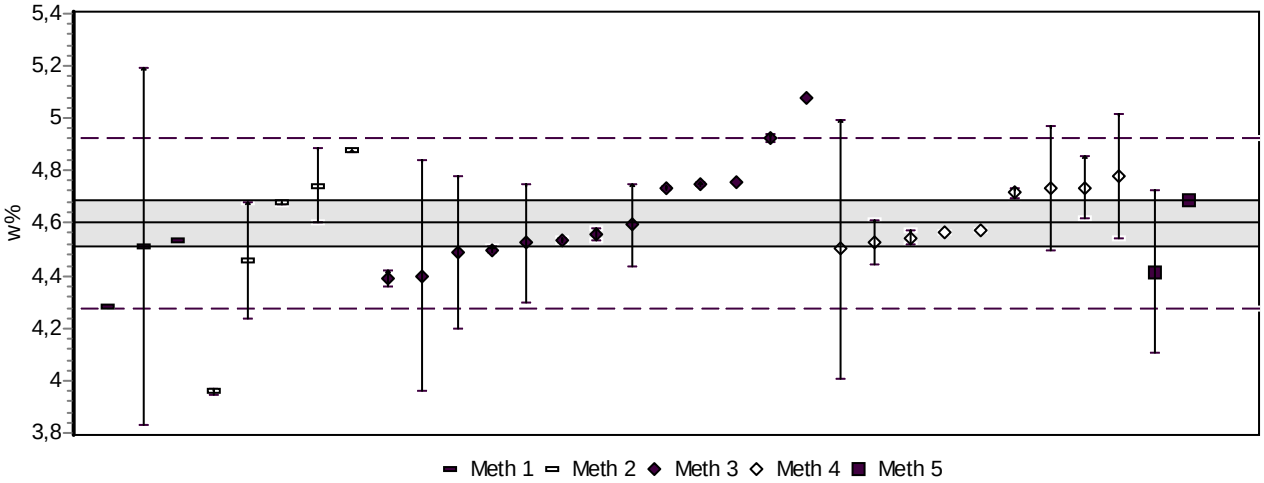
Analyytti *(Analyte)* **C,d** Näyte *(Sample)* K1



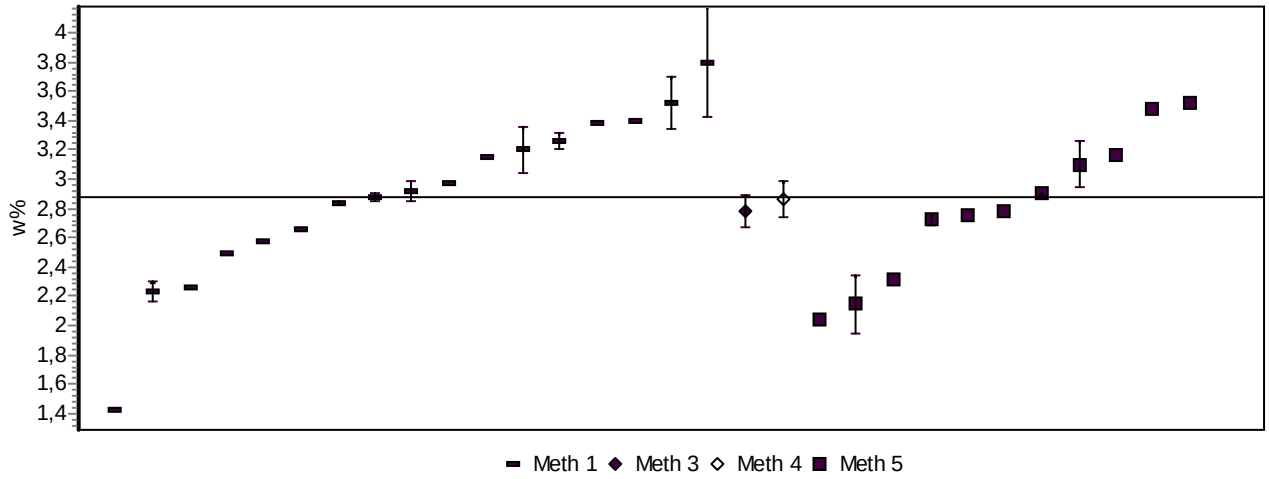

Analyytti *(Analyte)* **H,d** Näyte *(Sample)* B1



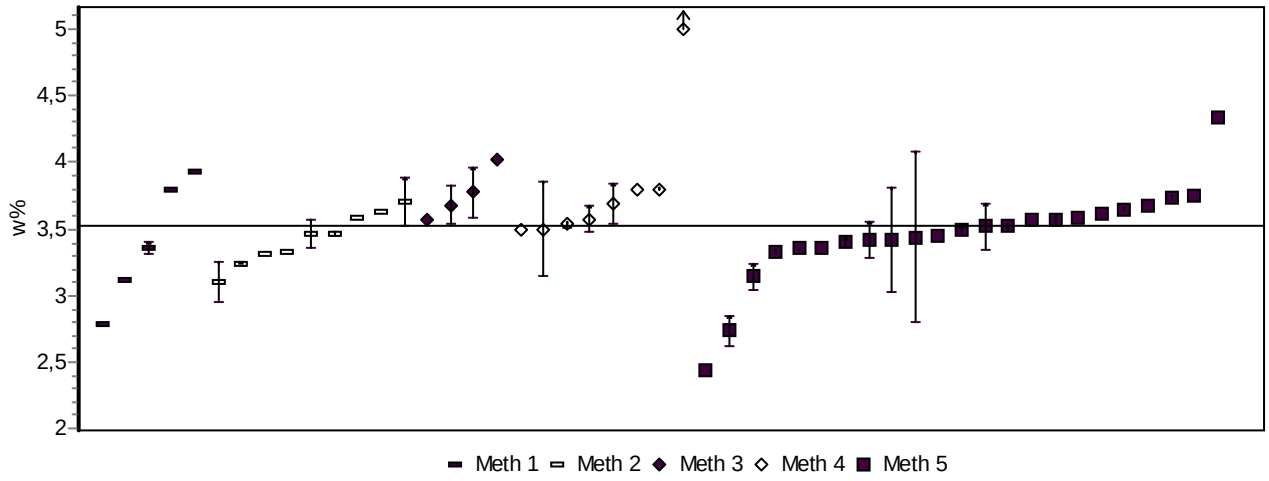

Analyytti *(Analyte)* **H,d** Näyte *(Sample)* K1



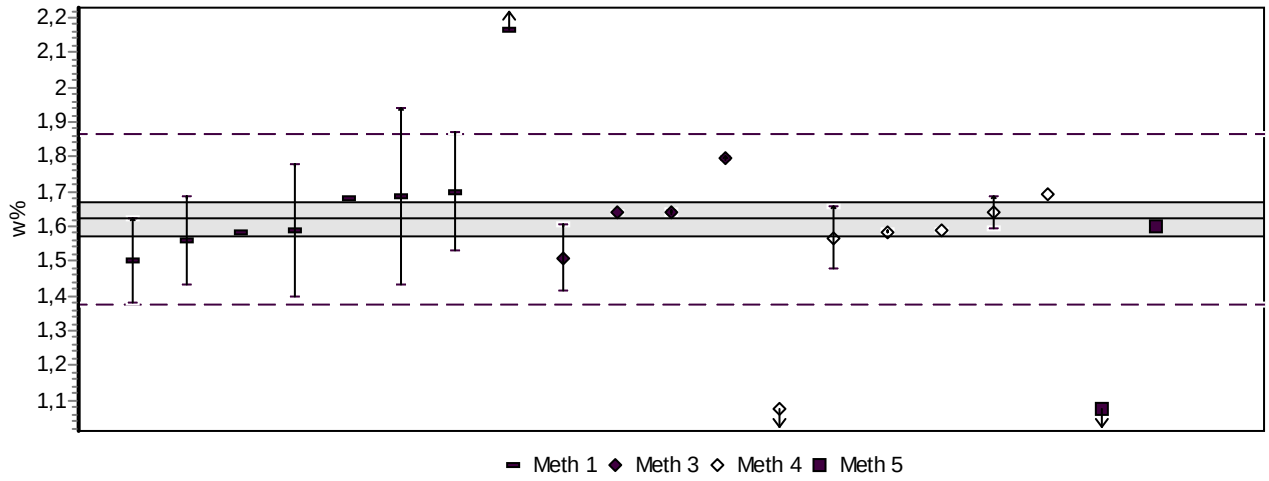
Analyytti *(Analyte)* **Mad,d** Näyte *(Sample)* B1



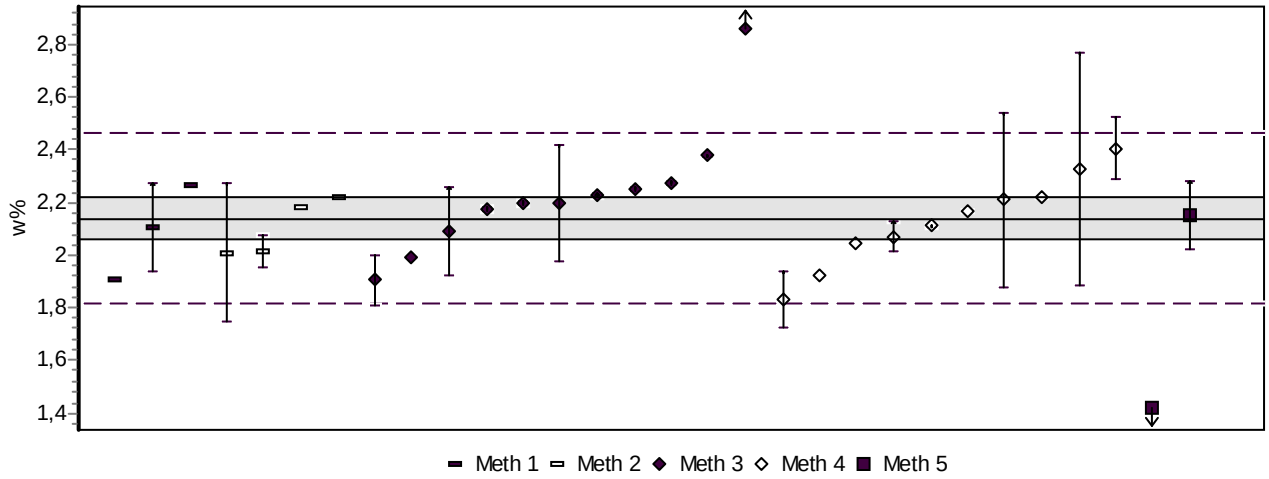

Analyytti *(Analyte)* **Mad,d** Näyte *(Sample)* K1



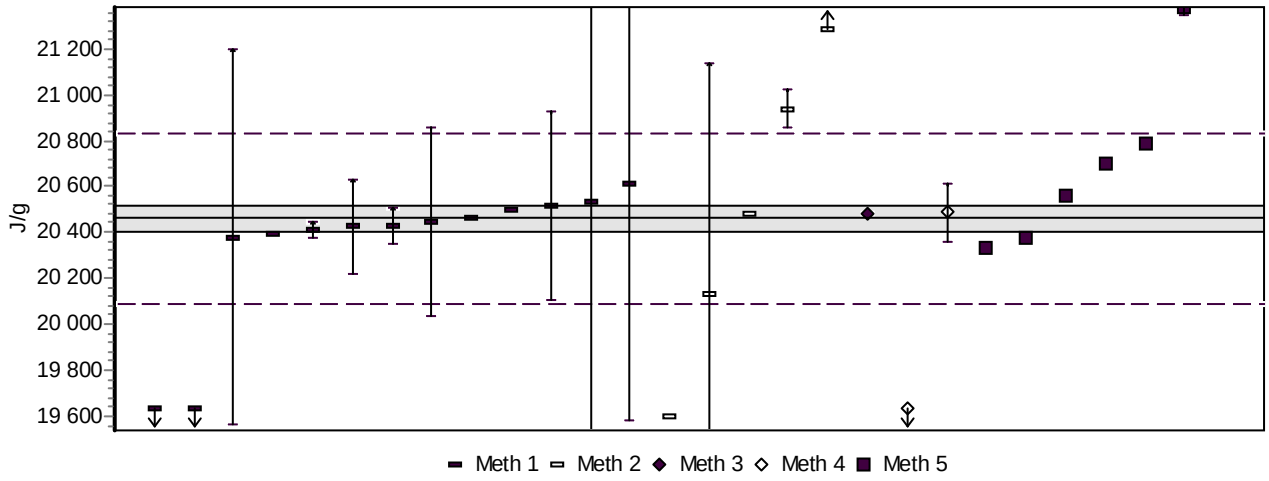

Analyytti *(Analyte)* **N,d** Näyte *(Sample)* B1



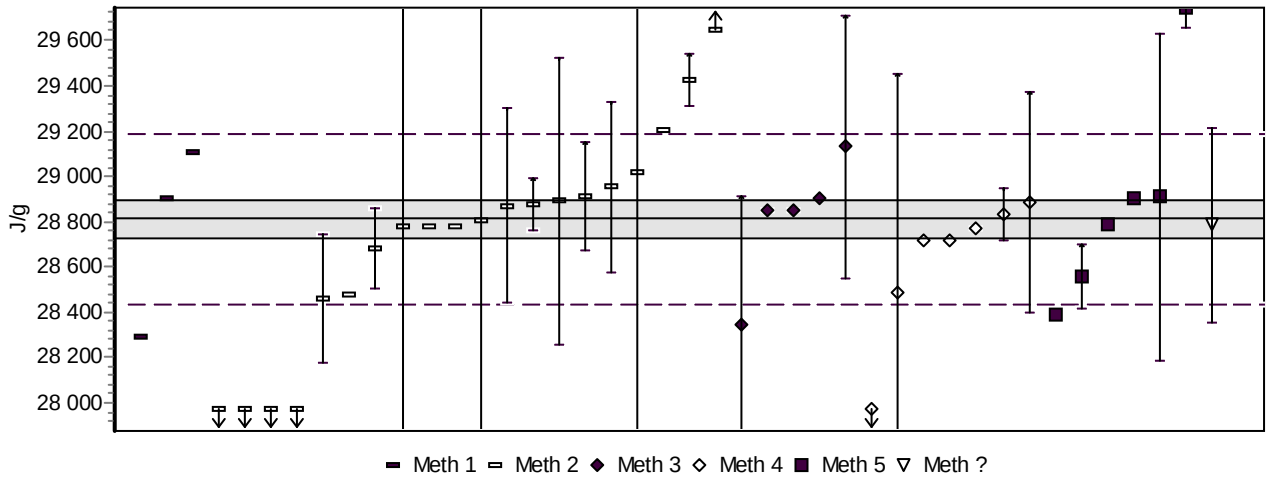
Analyytti *(Analyte)* **N,d** Näyte *(Sample)* K1



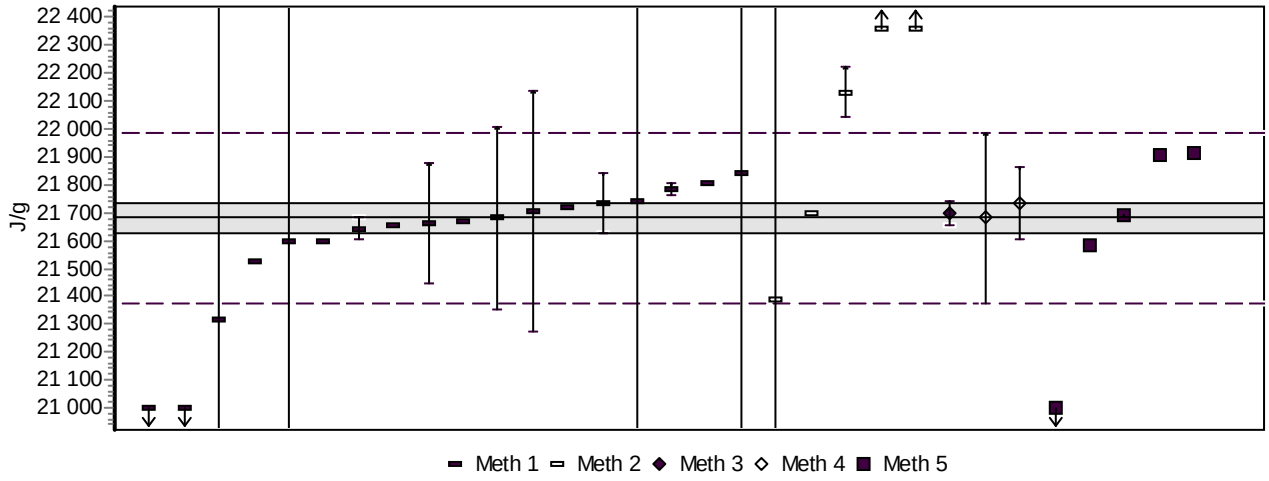

Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* B1



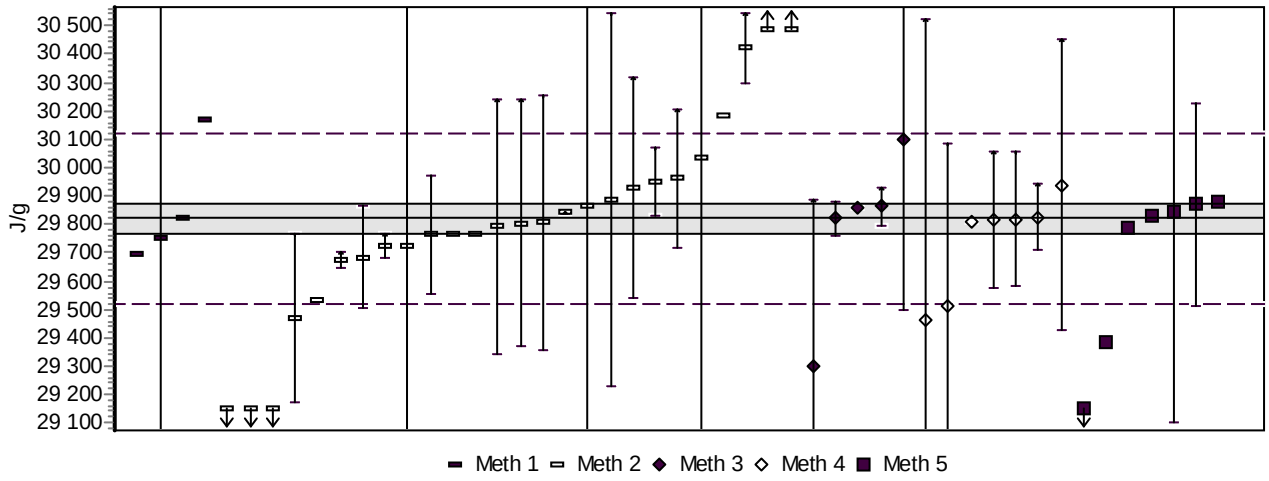

Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* K1



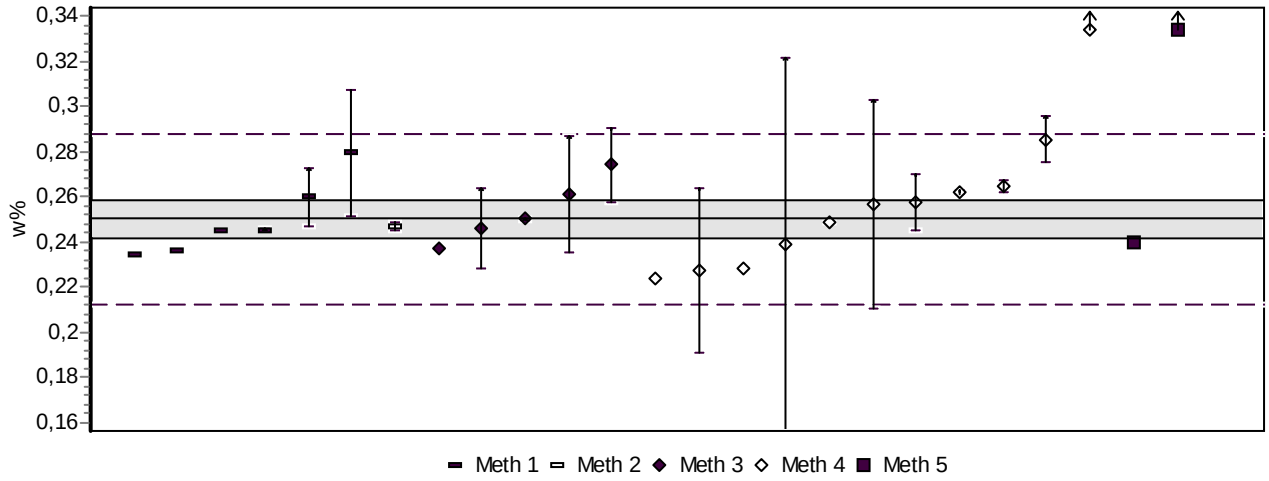
Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* B1



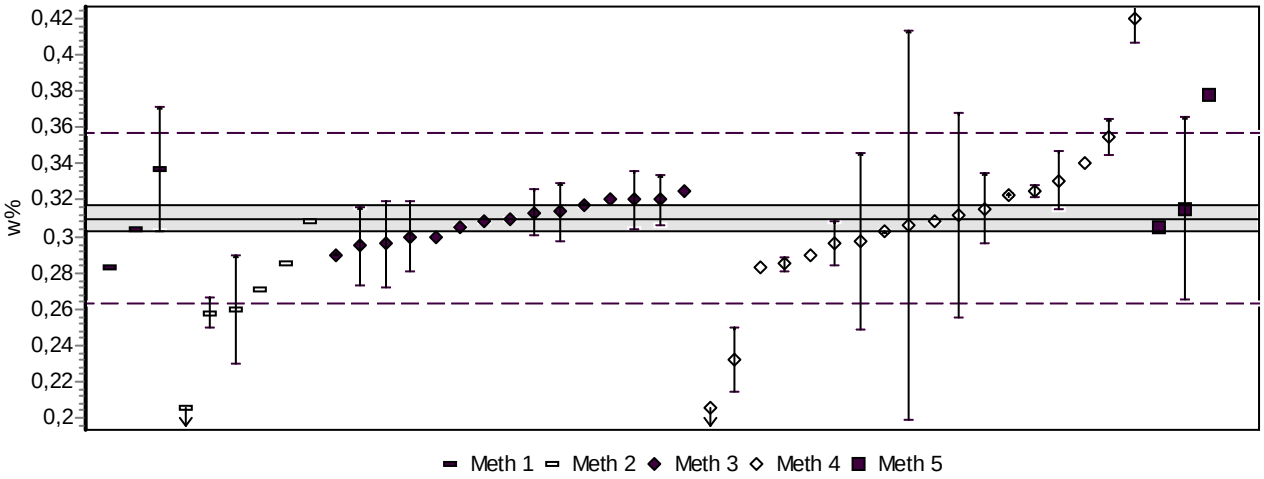

Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* K1




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



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



# EVALUATION OF THE ASSIGNED VALUES AND THEIR UNCERTAINTIES

| Analyte | Sample | Unit | Assigned value | Estimation of assigned value | Uncertainty (U = 2*u)[1)], % | u/$s_p$ [2)] |
|---|---|---|---|---|---|---|
| Ash | B1 | w% | 7.7 | Robust mean | 1.2 | 0.2 |
| | K1 | w% | 10.9 | Robust mean | 0.34 | 0.1 |
| C | B1 | w% | 53.4 | Robust mean | 0.89 | 0.3 |
| | K1 | w% | 73.3 | Robust mean | 0.52 | 0.2 |
| H | B1 | w% | 5.6 | Robust mean | 1.7 | 0.3 |
| | K1 | w% | 4.6 | Robust mean | 1.8 | 0.3 |
| EF | B1 | $tCO_2/TJ$ | 106 | Robust mean | 2.5 | 0.2 |
| | K1 | $tCO_2/TJ$ | 93.8 | Robust mean | 2.3 | 0.2 |
| M | B1 | w% | 7.68 | Robust mean | 3.9 | - |
| | K1 | w% | 3.17 | Robust mean | 5.6 | - |
| N | B1 | w% | 1.62 | Robust mean | 2.8 | 0.2 |
| | K1 | w% | 2.14 | Robust mean | 3.5 | 0.2 |
| q-p,net,d | B1 | J/g | 20460 | Robust mean | 0.25 | 0.1 |
| | K1 | J/g | 28810 | Robust mean | 0.28 | 0.2 |
| q-V,gr,d | B1 | J/g | 21680 | Robust mean | 0.23 | 0.2 |
| | K1 | J/g | 29820 | Robust mean | 0.18 | 0.2 |
| S | B1 | w% | 0.25 | Robust mean | 3.3 | 0.2 |
| | K1 | w% | 0.31 | Robust mean | 2.3 | 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.

# TERMS IN THE RESULT TABLES

| | |
|---|---|
| **Sample** | The code of the sample |
| **z-Graphics** | z score - the graphical presentation |
| **z score** | calculated as follows:<br>$z = (x_i - X)/s_p$, where<br>$x_i$ = the result of the individual laboratory<br>X = the assigned value<br>$s_p$ = the target value of the standard deviation for proficiency assessment. |
| **zeta score** | zeta= $(x_i - X)/\sqrt{u^2_{lab} + u^2 c}$ , $u_{lab}$ = the standard uncertainty of the participant's result<br>$u_c$ = the standard uncertainty of the assigned value |
| **Outl test OK** | yes - the result passed the outlier test<br>H = Hampel test (a test for the mean value) |
| **Assigned value** | the reference value |
| **Assigned value 2*$U_C$** | the expanded uncertainty of the assigned value |
| **2* Targ SD %,**<br>**Targ 2SD%** | 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 |
| **Nr** | the number of the result in the diagram *(Appendix 11)* |

***Summary on the z scores***

S – satisfactory ( $-2 \leq z \leq 2$)
Q – questionable ( $2 < z < 3$), positive error, the result deviates more than 2 * $s_p$ from the assigned value
q – questionable ( $-3 > z < -2$), negative error, the result deviates more than 2 * $s_p$ from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 * $s_p$ from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 * $s_p$ from the assigned 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,…p)
$s^*$ = 1.483 median of $|x_i - x^*|$ (i = 1, 2,…p)
For each $x_i$ (i = 1, 2,…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 [3].

## LIITE 8. RESULTS OF EACH PARTICIPANT

APPENDIX 8.

| 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,d** | w% | B1 | | 0,649 | yes | 7,7 | 6 | 7,85 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,514 | yes | 10,9 | 2,5 | 10,83 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 1,124 | yes | 53,4 | 3 | 54,3 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,218 | yes | 73,3 | 2,5 | 73,1 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | B1 | | 0,355 | yes | 5,63 | 7 | 5,7 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -1,242 | yes | 4,6 | 7 | 4,4 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,8 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,5 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 0,658 | yes | 1,62 | 15 | 1,7 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 0,374 | yes | 2,14 | 15 | 2,2 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,831 | yes | 20460 | 1,8 | 20610 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -0,190 | yes | 28810 | 1,3 | 28770 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 1,064 | yes | 21680 | 1,4 | 21840 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -0,644 | yes | 29820 | 1 | 29720 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,533 | yes | 0,25 | 15 | 0,26 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,430 | yes | 0,31 | 15 | 0,32 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 2** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,220 | yes | 10,9 | 2,5 | 10,93 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 0,005 | yes | 73,3 | 2,5 | 73,31 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | -0,683 | yes | 4,6 | 7 | 4,49 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 4,025 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | 0,491 | yes | 28810 | 1,3 | 28900 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,292 | yes | 29820 | 1 | 29860 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,430 | yes | 0,31 | 15 | 0,3 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 3** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,991 | yes | 10,9 | 2,5 | 11,04 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,93 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | 1,602 | yes | 28810 | 1,3 | 29110 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 2,354 | yes | 29820 | 1 | 30170 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,237 | yes | 0,31 | 15 | 0,3045 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 4** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 1,277 | yes | 7,7 | 6 | 7,995 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,514 | yes | 10,9 | 2,5 | 10,97 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -0,568 | yes | 53,4 | 3 | 52,95 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -2,079 | yes | 73,3 | 2,5 | 71,4 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -0,542 | yes | 106 | 4 | 104,8 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -0,453 | yes | 93,8 | 4 | 92,95 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 0,414 | yes | 5,63 | 7 | 5,712 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | 0,888 | yes | 4,6 | 7 | 4,743 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,235 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 2,735 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,280 | yes | 1,62 | 15 | 1,586 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -0,819 | yes | 2,14 | 15 | 2,008 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -0,179 | yes | 20460 | 1,8 | 20430 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -1,853 | yes | 28810 | 1,3 | 28460 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | -0,112 | yes | 21680 | 1,4 | 21660 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -2,341 | yes | 29820 | 1 | 29470 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 1,280 | yes | 0,25 | 15 | 0,274 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,129 | yes | 0,31 | 15 | 0,313 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 5** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,649 | yes | 7,7 | 6 | 7,85 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,110 | yes | 10,9 | 2,5 | 10,91 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,155 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 2,79 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-V,gr,d** | J/g | B1 | | -0,063 | yes | 21680 | 1,4 | 21670 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -1,915 | yes | 29820 | 1 | 29530 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,693 | yes | 0,25 | 15 | 0,237 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -0,086 | yes | 0,31 | 15 | 0,308 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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,d** | w% | K1 | | 0,330 | yes | 10,9 | 2,5 | 10,95 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,224 | yes | 73,3 | 2,5 | 73,09 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | 0,932 | yes | 4,6 | 7 | 4,75 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,795 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,561 | yes | 2,14 | 15 | 2,23 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,494 | yes | 28810 | 1,3 | 28720 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,010 | yes | 29820 | 1 | 29820 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | 0,645 | yes | 0,31 | 15 | 0,325 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 7** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,411 | yes | 7,7 | 6 | 7,795 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,57 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -0,274 | yes | 20460 | 1,8 | 20410 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | -0,254 | yes | 21680 | 1,4 | 21640 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **Laboratory 8** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,433 | yes | 7,7 | 6 | 7,6 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,31 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -0,445 | yes | 20460 | 1,8 | 20380 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | -0,540 | yes | 21680 | 1,4 | 21600 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **Laboratory 9** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,390 | yes | 7,7 | 6 | 7,61 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **C,d** | w% | B1 | | -0,843 | yes | 53,4 | 3 | 52,72 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| **H,d** | w% | B1 | | 0,553 | yes | 5,63 | 7 | 5,739 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,045 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **N,d** | w% | B1 | | 0,156 | yes | 1,62 | 15 | 1,639 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| **q-p,net,d** | J/g | B1 | | -0,668 | yes | 20460 | 1,8 | 20340 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | -0,659 | yes | 21680 | 1,4 | 21580 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **S,d** | w% | B1 | | -0,080 | yes | 0,25 | 15 | 0,2485 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| **Laboratory 10** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,514 | yes | 10,9 | 2,5 | 10,97 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 2,210 | yes | 73,3 | 2,5 | 75,33 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,575 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | 0,441 | yes | 28810 | 1,3 | 28890 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,466 | yes | 29820 | 1 | 29890 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | 0,430 | yes | 0,31 | 15 | 0,32 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 11** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,147 | yes | 10,9 | 2,5 | 10,92 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,971 | yes | 73,3 | 2,5 | 72,41 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | 2,950 | yes | 4,6 | 7 | 5,075 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,59 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | -1,340 | yes | 2,14 | 15 | 1,925 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,171 | yes | 28810 | 1,3 | 28780 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,335 | yes | 29820 | 1 | 29770 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | 0,000 | yes | 0,31 | 15 | 0,31 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 12** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 1,017 | yes | 7,7 | 6 | 7,935 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,917 | yes | 10,9 | 2,5 | 11,03 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,568 | yes | 53,4 | 3 | 53,86 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,742 | yes | 73,3 | 2,5 | 73,98 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 0,283 | yes | 106 | 4 | 106,6 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 0,426 | yes | 93,8 | 4 | 94,6 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 0,099 | yes | 5,63 | 7 | 5,649 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,867 | yes | 4,6 | 7 | 4,46 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,525 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,774 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,963 | yes | 1,62 | 15 | 1,503 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -0,779 | yes | 2,14 | 15 | 2,015 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -0,065 | yes | 20460 | 1,8 | 20450 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 0,766 | yes | 28810 | 1,3 | 28950 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,721 | yes | 29820 | 1 | 29930 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,587 | yes | 0,25 | 15 | 0,261 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,150 | yes | 0,31 | 15 | 0,3135 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

| 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 13** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -2,349 | yes | 10,9 | 2,5 | 10,58 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,575 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | 0,214 | yes | 28810 | 1,3 | 28850 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,268 | yes | 29820 | 1 | 29860 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -1,699 | yes | 0,31 | 15 | 0,2705 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 14** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,173 | yes | 7,7 | 6 | 7,66 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,265 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,234 | yes | 20460 | 1,8 | 20500 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | 0,283 | yes | 21680 | 1,4 | 21720 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **Laboratory 15** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -1,342 | yes | 7,7 | 6 | 7,39 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,220 | yes | 10,9 | 2,5 | 10,87 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | B1 | | | C | 2,88 | | 2,655 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,33 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-V,gr,d** | J/g | B1 | | -5,288 | H | 21680 | 1,4 | 20880 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -6,190 | H | 29820 | 1 | 28900 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -1,413 | yes | 0,25 | 15 | 0,2235 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -1,161 | yes | 0,31 | 15 | 0,283 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 16** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,368 | yes | 7,7 | 6 | 7,785 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,4 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -0,432 | yes | 20460 | 1,8 | 20380 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | -0,550 | yes | 21680 | 1,4 | 21600 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **Laboratory 17** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -2,165 | yes | 10,9 | 2,5 | 10,61 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,635 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | -1,768 | yes | 28810 | 1,3 | 28480 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,369 | yes | 29820 | 1 | 29770 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **Laboratory 18** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,183 | yes | 10,9 | 2,5 | 10,93 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,126 | yes | 73,3 | 2,5 | 73,19 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | 0,187 | yes | 93,8 | 4 | 94,15 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | -0,472 | yes | 4,6 | 7 | 4,524 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,463 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | -0,327 | yes | 2,14 | 15 | 2,088 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,134 | yes | 28810 | 1,3 | 28790 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,181 | yes | 29820 | 1 | 29790 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,602 | yes | 0,31 | 15 | 0,296 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 19** | | | | | | | | | | | | | | | | |
| **C,d** | w% | K1 | | 0,164 | yes | 73,3 | 2,5 | 73,45 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | 1,118 | yes | 4,6 | 7 | 4,78 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,415 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 1,651 | yes | 2,14 | 15 | 2,405 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **S,d** | w% | K1 | | 0,237 | yes | 0,31 | 15 | 0,3155 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 20** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 3,355 | H | 7,7 | 6 | 8,475 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,734 | yes | 10,9 | 2,5 | 10,8 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 6,055 | H | 53,4 | 3 | 58,25 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 7,040 | H | 73,3 | 2,5 | 79,75 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,1 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,52 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-V,gr,d** | J/g | B1 | | -2,405 | yes | 21680 | 1,4 | 21320 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -0,469 | yes | 29820 | 1 | 29750 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,613 | yes | 0,25 | 15 | 0,2385 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -0,172 | yes | 0,31 | 15 | 0,306 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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 21** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -1,104 | yes | 7,7 | 6 | 7,445 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,587 | yes | 10,9 | 2,5 | 10,82 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,531 | yes | 53,4 | 3 | 53,83 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,513 | yes | 73,3 | 2,5 | 72,83 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 0,189 | yes | 106 | 4 | 106,4 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -0,773 | yes | 93,8 | 4 | 92,35 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -0,140 | yes | 5,63 | 7 | 5,603 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,158 | yes | 4,6 | 7 | 4,575 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,165 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 4,34 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 0,593 | yes | 1,62 | 15 | 1,692 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 0,156 | yes | 2,14 | 15 | 2,165 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,128 | yes | 20460 | 1,8 | 20480 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 2,096 | yes | 28810 | 1,3 | 29200 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,122 | yes | 21680 | 1,4 | 21700 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 2,431 | yes | 29820 | 1 | 30180 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,347 | yes | 0,25 | 15 | 0,2565 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,065 | yes | 0,31 | 15 | 0,3115 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 22** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,065 | yes | 7,7 | 6 | 7,715 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,294 | yes | 10,9 | 2,5 | 10,94 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,337 | yes | 53,4 | 3 | 53,67 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,115 | yes | 73,3 | 2,5 | 73,19 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -0,071 | yes | 106 | 4 | 105,8 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -0,400 | yes | 93,8 | 4 | 93,05 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -0,926 | yes | 5,63 | 7 | 5,447 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,534 | yes | 4,6 | 7 | 4,514 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,2 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,105 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,502 | yes | 1,62 | 15 | 1,559 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -0,209 | yes | 2,14 | 15 | 2,107 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,307 | yes | 20460 | 1,8 | 20520 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 1,709 | yes | 28810 | 1,3 | 29130 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,171 | yes | 21680 | 1,4 | 21710 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 1,858 | yes | 29820 | 1 | 30100 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 1,573 | yes | 0,25 | 15 | 0,2795 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 1,161 | yes | 0,31 | 15 | 0,337 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 23** | | | | | | | | | | | | | | | | |
| **q-V,gr,d** | J/g | K1 | | 0,154 | yes | 29820 | 1 | 29840 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **Laboratory 24** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,238 | yes | 7,7 | 6 | 7,645 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,073 | yes | 10,9 | 2,5 | 10,91 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,92 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,44 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | B1 | | -0,163 | yes | 20460 | 1,8 | 20430 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -1,335 | yes | 28810 | 1,3 | 28560 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,366 | yes | 21680 | 1,4 | 21740 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 0,335 | yes | 29820 | 1 | 29870 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -3,355 | H | 0,31 | 15 | 0,232 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 25** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -0,367 | yes | 10,9 | 2,5 | 10,85 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 1,261 | yes | 73,3 | 2,5 | 74,45 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,65 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | 0,355 | yes | 28810 | 1,3 | 28880 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,892 | yes | 29820 | 1 | 29950 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -1,054 | yes | 0,31 | 15 | 0,2855 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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 26** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,390 | yes | 7,7 | 6 | 7,79 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,514 | yes | 10,9 | 2,5 | 10,97 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,125 | yes | 53,4 | 3 | 53,5 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,682 | yes | 73,3 | 2,5 | 73,92 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | B1 | | 0,634 | yes | 5,63 | 7 | 5,755 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | 0,714 | yes | 4,6 | 7 | 4,715 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,785 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,58 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,288 | yes | 1,62 | 15 | 1,585 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -0,187 | yes | 2,14 | 15 | 2,11 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 5,276 | H | 20460 | 1,8 | 21430 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 5,142 | H | 28810 | 1,3 | 29770 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | -5,598 | H | 21680 | 1,4 | 20830 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -7,495 | H | 29820 | 1 | 28700 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,640 | yes | 0,25 | 15 | 0,262 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,538 | yes | 0,31 | 15 | 0,3225 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 27** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,693 | yes | 7,7 | 6 | 7,54 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **C,d** | w% | B1 | | 0,112 | yes | 53,4 | 3 | 53,49 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| **H,d** | w% | B1 | | 0,964 | yes | 5,63 | 7 | 5,82 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,39 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **N,d** | w% | B1 | | -7,753 | H | 1,62 | 15 | 0,678 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| **q-p,net,d** | J/g | B1 | | -81,380 | H | 20460 | 1,8 | 5476 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | 0,814 | yes | 21680 | 1,4 | 21800 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **S,d** | w% | B1 | | -0,827 | yes | 0,25 | 15 | 0,2345 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| **Laboratory 28** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,147 | yes | 10,9 | 2,5 | 10,92 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,065 | C | 73,3 | 2,5 | 73,24 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | 0,067 | yes | 93,8 | 4 | 93,925 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | -0,404 | yes | 4,6 | 7 | 4,535 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,355 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 13,270 | H | 2,14 | 15 | 4,27 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -1,722 | yes | 28810 | 1,3 | 28490 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -2,384 | yes | 29820 | 1 | 29460 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -5,441 | H | 0,31 | 15 | 0,1835 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 29** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -1,147 | yes | 7,7 | 6 | 7,435 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,037 | yes | 10,9 | 2,5 | 10,91 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -0,911 | yes | 53,4 | 3 | 52,67 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,584 | yes | 73,3 | 2,5 | 73,84 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 0,024 | yes | 106 | 4 | 106,1 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 0,426 | yes | 93,8 | 4 | 94,6 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -1,632 | yes | 5,63 | 7 | 5,309 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -1,149 | yes | 4,6 | 7 | 4,415 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | C | 2,88 | | 3,475 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,675 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,152 | yes | 1,62 | 15 | 1,602 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 0,059 | yes | 2,14 | 15 | 2,149 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 1,773 | yes | 20460 | 1,8 | 20790 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 0,542 | yes | 28810 | 1,3 | 28910 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 1,509 | yes | 21680 | 1,4 | 21910 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 0,178 | yes | 29820 | 1 | 29850 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,560 | yes | 0,25 | 15 | 0,2395 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,237 | yes | 0,31 | 15 | 0,3155 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 30** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,519 | yes | 7,7 | 6 | 7,58 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **C,d** | w% | B1 | | -5,718 | H | 53,4 | 3 | 48,82 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| **H,d** | w% | B1 | | -28,510 | H | 5,63 | 7 | 0,012 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 1,43 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **N,d** | w% | B1 | | 35,230 | H | 1,62 | 15 | 5,90 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| **q-p,net,d** | J/g | B1 | | -6,712 | H | 20460 | 1,8 | 19224 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | -6,128 | H | 21680 | 1,4 | 20750 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **S,d** | w% | B1 | | 60,270 | H | 0,25 | 15 | 1,38 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |

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 31** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,171 | yes | 7,7 | 6 | 7,661 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,451 | yes | 10,9 | 2,5 | 10,96 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -1,292 | yes | 53,4 | 3 | 52,37 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -1,899 | yes | 73,3 | 2,5 | 71,56 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -2,288 | yes | 106 | 4 | 101,2 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -1,972 | yes | 93,8 | 4 | 90,1 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -0,944 | yes | 5,63 | 7 | 5,444 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,453 | C | 4,6 | 7 | 4,527 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,26 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,36 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,428 | yes | 1,62 | 15 | 1,568 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -1,903 | yes | 2,14 | 15 | 1,835 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 2,599 | yes | 20460 | 1,8 | 20940 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 3,300 | H | 28810 | 1,3 | 29430 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 2,982 | yes | 21680 | 1,4 | 22130 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 4,031 | H | 29820 | 1 | 30420 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,400 | yes | 0,25 | 15 | 0,2575 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,882 | yes | 0,31 | 15 | 0,3305 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 32** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 1,798 | yes | 10,9 | 2,5 | 11,14 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 0,235 | yes | 73,3 | 2,5 | 73,52 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | -0,091 | yes | 93,8 | 4 | 93,63 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | 0,994 | yes | 4,6 | 7 | 4,76 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,49 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | -0,903 | yes | 2,14 | 15 | 1,995 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,227 | yes | 28810 | 1,3 | 28770 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,094 | yes | 29820 | 1 | 29810 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,430 | yes | 0,31 | 15 | 0,3 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 33** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,330 | yes | 10,9 | 2,5 | 10,95 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,52 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-V,gr,d** | J/g | K1 | | -0,959 | yes | 29820 | 1 | 29680 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **Laboratory 34** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 1,082 | yes | 7,7 | 6 | 7,95 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,404 | yes | 10,9 | 2,5 | 10,84 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -1,261 | yes | 53,4 | 3 | 52,39 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,928 | yes | 73,3 | 2,5 | 72,45 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -5,755 | H | 106 | 4 | 93,8 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -0,666 | yes | 93,8 | 4 | 92,55 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 0,855 | yes | 5,63 | 7 | 5,799 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | 0,848 | yes | 4,6 | 7 | 4,736 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,84 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,32 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,259 | yes | 1,62 | 15 | 1,589 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -0,586 | yes | 2,14 | 15 | 2,046 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,521 | yes | 20460 | 1,8 | 20560 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -0,123 | yes | 28810 | 1,3 | 28790 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,053 | yes | 21680 | 1,4 | 21690 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 0,080 | yes | 29820 | 1 | 29830 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,160 | yes | 0,25 | 15 | 0,247 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -1,075 | yes | 0,31 | 15 | 0,285 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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 35** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,216 | yes | 7,7 | 6 | 7,75 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,367 | yes | 10,9 | 2,5 | 10,85 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,437 | yes | 53,4 | 3 | 53,75 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,546 | yes | 73,3 | 2,5 | 73,8 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 9,835 | H | 106 | 4 | 126,8 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 8,769 | H | 93,8 | 4 | 110,3 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -0,736 | yes | 5,63 | 7 | 5,485 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,621 | yes | 4,6 | 7 | 4,5 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,9 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,74 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 0,165 | yes | 1,62 | 15 | 1,64 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 0,218 | yes | 2,14 | 15 | 2,175 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -26,820 | H | 20460 | 1,8 | 15520 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -22,950 | H | 28810 | 1,3 | 24510 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,007 | yes | 21680 | 1,4 | 21680 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -2,059 | yes | 29820 | 1 | 29510 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,000 | yes | 0,25 | 15 | 0,25 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,430 | yes | 0,31 | 15 | 0,32 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 36** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -0,954 | yes | 10,9 | 2,5 | 10,77 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 0,819 | yes | 73,3 | 2,5 | 74,05 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | 0,240 | yes | 93,8 | 4 | 94,25 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | -0,280 | yes | 4,6 | 7 | 4,555 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,535 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,685 | yes | 2,14 | 15 | 2,25 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | 0,401 | yes | 28810 | 1,3 | 28890 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,805 | yes | 29820 | 1 | 29940 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,860 | yes | 0,31 | 15 | 0,29 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 37** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,065 | yes | 7,7 | 6 | 7,685 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -1,908 | yes | 10,9 | 2,5 | 10,64 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -0,175 | yes | 53,4 | 3 | 53,26 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,224 | yes | 73,3 | 2,5 | 73,5 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -0,519 | yes | 106 | 4 | 104,9 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 0,000 | yes | 93,8 | 4 | 93,8 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -0,355 | yes | 5,63 | 7 | 5,56 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | 0,807 | yes | 4,6 | 7 | 4,73 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,875 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,57 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 0,535 | yes | 1,62 | 15 | 1,685 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 0,436 | yes | 2,14 | 15 | 2,21 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,410 | yes | 20460 | 1,8 | 20540 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 1,129 | yes | 28810 | 1,3 | 29020 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,399 | yes | 21680 | 1,4 | 21740 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 1,422 | yes | 29820 | 1 | 30030 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,240 | yes | 0,25 | 15 | 0,2455 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -0,323 | yes | 0,31 | 15 | 0,3025 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 38** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -2,814 | H | 7,7 | 6 | 7,05 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -1,761 | yes | 10,9 | 2,5 | 10,66 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 1,699 | yes | 53,4 | 3 | 54,761 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,045 | yes | 73,3 | 2,5 | 73,259 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,75 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,57 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | B1 | | -4,670 | H | 20460 | 1,8 | 19600 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -5,447 | H | 28810 | 1,3 | 27790 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 9,093 | H | 21680 | 1,4 | 23060 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 25,420 | H | 29820 | 1 | 33610 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -1,149 | yes | 0,25 | 15 | 0,22845 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -0,877 | yes | 0,31 | 15 | 0,28962 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 39** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,367 | yes | 10,9 | 2,5 | 10,95 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,325 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-V,gr,d** | J/g | K1 | | -0,654 | yes | 29820 | 1 | 29720 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |

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 40** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,628 | yes | 7,7 | 6 | 7,555 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 1,284 | yes | 10,9 | 2,5 | 11,07 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,424 | yes | 53,4 | 3 | 53,74 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,191 | yes | 73,3 | 2,5 | 73,47 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 0,165 | yes | 106 | 4 | 106,3 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 0,187 | yes | 93,8 | 4 | 94,15 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | -0,771 | yes | 5,63 | 7 | 5,478 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -1,981 | yes | 4,6 | 7 | 4,281 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,98 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,8 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 0,514 | yes | 1,62 | 15 | 1,683 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 0,760 | yes | 2,14 | 15 | 2,262 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,024 | yes | 20460 | 1,8 | 20460 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 0,507 | yes | 28810 | 1,3 | 28910 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | -0,184 | yes | 21680 | 1,4 | 21650 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 0,003 | yes | 29820 | 1 | 29820 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,720 | yes | 0,25 | 15 | 0,2365 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -1,140 | yes | 0,31 | 15 | 0,2835 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 41** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,037 | yes | 10,9 | 2,5 | 10,9 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 0,769 | yes | 73,3 | 2,5 | 74 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | 0,773 | yes | 93,8 | 4 | 95,25 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,42 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | -0,184 | yes | 28810 | 1,3 | 28780 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,107 | yes | 29820 | 1 | 29800 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,538 | yes | 0,31 | 15 | 0,2975 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 42** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -11,050 | H | 10,9 | 2,5 | 9,395 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,145 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | -24,820 | H | 28810 | 1,3 | 24160 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -29,190 | H | 29820 | 1 | 25470 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -2,151 | yes | 0,31 | 15 | 0,26 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 43** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,649 | yes | 7,7 | 6 | 7,55 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,294 | yes | 10,9 | 2,5 | 10,94 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 1,373 | yes | 53,4 | 3 | 54,5 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -1,626 | yes | 73,3 | 2,5 | 71,81 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -4,021 | H | 106 | 4 | 97,47 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -1,364 | yes | 93,8 | 4 | 91,24 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 0,837 | yes | 5,63 | 7 | 5,795 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,031 | yes | 4,6 | 7 | 4,595 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,86 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,695 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,905 | yes | 1,62 | 15 | 1,51 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -1,464 | yes | 2,14 | 15 | 1,905 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,144 | yes | 20460 | 1,8 | 20490 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 0,141 | yes | 28810 | 1,3 | 28840 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,366 | yes | 21680 | 1,4 | 21740 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 0,047 | yes | 29820 | 1 | 29830 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,213 | yes | 0,25 | 15 | 0,246 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -0,645 | yes | 0,31 | 15 | 0,295 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 44** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -0,110 | yes | 10,9 | 2,5 | 10,89 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,615 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-V,gr,d** | J/g | K1 | | -0,218 | yes | 29820 | 1 | 29790 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **Laboratory 45** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,367 | yes | 10,9 | 2,5 | 10,95 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -1,506 | yes | 73,3 | 2,5 | 71,92 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | -0,053 | yes | 93,8 | 4 | 93,7 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | -3,975 | yes | 4,6 | 7 | 3,96 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,705 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | -20,350 | H | 28810 | 1,3 | 25000 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,372 | yes | 29820 | 1 | 29760 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,086 | yes | 0,31 | 15 | 0,308 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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 46** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,220 | yes | 10,9 | 2,5 | 10,93 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 0,611 | yes | 73,3 | 2,5 | 73,86 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | 0,906 | yes | 93,8 | 4 | 95,5 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | -0,615 | yes | 4,6 | 7 | 4,501 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | H | 3,52 | | 98,22 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 1,153 | yes | 2,14 | 15 | 2,325 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -2,480 | yes | 28810 | 1,3 | 28350 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -3,484 | H | 29820 | 1 | 29300 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,602 | yes | 0,31 | 15 | 0,296 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 47** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -2,936 | yes | 10,9 | 2,5 | 10,5 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,75 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | -5,393 | H | 28810 | 1,3 | 27800 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -6,841 | H | 29820 | 1 | 28800 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,215 | yes | 0,31 | 15 | 0,305 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 48** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 1,211 | yes | 10,9 | 2,5 | 11,06 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | 0,884 | yes | 73,3 | 2,5 | 74,11 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | 2,022 | yes | 4,6 | 7 | 4,925 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,5 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,822 | yes | 2,14 | 15 | 2,272 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | 0,539 | yes | 28810 | 1,3 | 28910 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,956 | yes | 29820 | 1 | 29960 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | 1,914 | yes | 0,31 | 15 | 0,3545 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 49** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,022 | yes | 7,7 | 6 | 7,695 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,145 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -1,784 | yes | 20460 | 1,8 | 20130 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| **q-V,gr,d** | J/g | B1 | | -1,918 | yes | 21680 | 1,4 | 21390 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **S,d** | w% | B1 | | -1,200 | yes | 0,25 | 15 | 0,2275 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| **Laboratory 50** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 1,101 | yes | 10,9 | 2,5 | 11,05 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -1,266 | yes | 73,3 | 2,5 | 72,14 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | -0,533 | yes | 93,8 | 4 | 92,8 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | 1,708 | yes | 4,6 | 7 | 4,875 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,245 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,249 | yes | 2,14 | 15 | 2,18 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,027 | yes | 28810 | 1,3 | 28810 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,329 | yes | 29820 | 1 | 29870 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -8,172 | H | 0,31 | 15 | 0,12 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 51** | | | | | | | | | | | | | | | | |
| **q-V,gr,d** | J/g | B1 | | 0,689 | yes | 21680 | 1,4 | 21780 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **Laboratory 52** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -1,688 | yes | 10,9 | 2,5 | 10,67 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,169 | yes | 73,3 | 2,5 | 73,15 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | K1 | | 0,320 | yes | 93,8 | 4 | 94,4 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | K1 | | 0,491 | yes | 4,6 | 7 | 4,679 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,36 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,495 | yes | 2,14 | 15 | 2,22 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,675 | yes | 28810 | 1,3 | 28680 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,902 | yes | 29820 | 1 | 29690 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | 1,312 | yes | 0,31 | 15 | 0,3405 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 53** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | -0,991 | yes | 10,9 | 2,5 | 10,77 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -2,794 | yes | 73,3 | 2,5 | 70,74 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,465 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **q-p,net,d** | J/g | K1 | | 0,323 | yes | 28810 | 1,3 | 28870 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,091 | yes | 29820 | 1 | 29810 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -2,237 | yes | 0,31 | 15 | 0,258 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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 54** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,000 | yes | 10,9 | 2,5 | 10,9 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,398 | yes | 73,3 | 2,5 | 72,94 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | 0,839 | yes | 4,6 | 7 | 4,735 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,8 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,343 | yes | 2,14 | 15 | 2,195 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | -0,481 | yes | 28810 | 1,3 | 28720 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | -0,013 | yes | 29820 | 1 | 29820 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | 0,323 | yes | 0,31 | 15 | 0,3175 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 55** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,909 | yes | 7,7 | 6 | 7,91 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,073 | yes | 10,9 | 2,5 | 10,91 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -1,167 | yes | 53,4 | 3 | 52,47 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 0,610 | yes | 73,3 | 2,5 | 73,86 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | B1 | | 0,507 | yes | 5,63 | 7 | 5,73 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,425 | yes | 4,6 | 7 | 4,532 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,495 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,125 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -0,288 | yes | 1,62 | 15 | 1,585 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -1,464 | yes | 2,14 | 15 | 1,905 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | -0,369 | yes | 20460 | 1,8 | 20390 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -2,787 | yes | 28810 | 1,3 | 28290 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | -1,031 | yes | 21680 | 1,4 | 21520 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -0,825 | yes | 29820 | 1 | 29700 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | -0,267 | yes | 0,25 | 15 | 0,245 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | -0,258 | yes | 0,31 | 15 | 0,304 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 56** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | K1 | | 0,330 | yes | 10,9 | 2,5 | 10,95 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | K1 | | -0,060 | yes | 73,3 | 2,5 | 73,25 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **H,d** | w% | K1 | | -0,230 | yes | 4,6 | 7 | 4,563 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | K1 | | | yes | 3,52 | | 3,45 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | K1 | | 0,489 | yes | 2,14 | 15 | 2,219 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | K1 | | 0,513 | yes | 28810 | 1,3 | 28910 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | K1 | | 0,382 | yes | 29820 | 1 | 29880 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | K1 | | -0,086 | yes | 0,31 | 15 | 0,308 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 57** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | 0,325 | yes | 7,7 | 6 | 7,775 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -0,697 | yes | 10,9 | 2,5 | 10,8 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 1,380 | yes | 53,4 | 3 | 54,5 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | 2,079 | yes | 73,3 | 2,5 | 75,2 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 1,863 | yes | 106 | 4 | 110 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 2,186 | yes | 93,8 | 4 | 97,9 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 3,636 | H | 5,63 | 7 | 6,347 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -1,307 | yes | 4,6 | 7 | 4,389 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,72 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,405 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 1,440 | yes | 1,62 | 15 | 1,795 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | 1,480 | yes | 2,14 | 15 | 2,377 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 7,342 | H | 20460 | 1,8 | 21810 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 16,460 | H | 28810 | 1,3 | 31890 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 11,150 | H | 21680 | 1,4 | 23370 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 21,960 | H | 29820 | 1 | 33090 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 1,893 | yes | 0,25 | 15 | 0,2855 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 4,710 | H | 0,31 | 15 | 0,4195 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

| 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 58** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -3,506 | H | 7,7 | 6 | 6,89 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | -1,835 | yes | 10,9 | 2,5 | 10,65 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | -2,647 | yes | 53,4 | 3 | 51,28 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,524 | yes | 73,3 | 2,5 | 72,82 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | -9,528 | H | 106 | 4 | 85,8 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | 1,066 | yes | 93,8 | 4 | 95,8 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 0,376 | yes | 5,63 | 7 | 5,704 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | 0,534 | yes | 4,6 | 7 | 4,686 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 3,52 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 2,44 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | -6,469 | H | 1,62 | 15 | 0,834 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -10,430 | H | 2,14 | 15 | 0,466 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 1,320 | yes | 20460 | 1,8 | 20703 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | -2,237 | yes | 28810 | 1,3 | 28391 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 1,535 | yes | 21680 | 1,4 | 21913 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | -2,918 | yes | 29820 | 1 | 29385 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 8,640 | H | 0,25 | 15 | 0,412 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 2,925 | yes | 0,31 | 15 | 0,378 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |
| **Laboratory 59** | | | | | | | | | | | | | | | | |
| **q-V,gr,d** | J/g | B1 | | 0,007 | yes | 21680 | 1,4 | 21680 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| **Laboratory 60** | | | | | | | | | | | | | | | | |
| **Ash,d** | w% | B1 | | -0,541 | yes | 7,7 | 6 | 7,575 | 7,7 | 7,696 | 0,1756 | 2,3 | 27 | 3 | 0 | 30 |
| | w% | K1 | | 0,661 | yes | 10,9 | 2,5 | 10,99 | 10,91 | 10,88 | 0,1371 | 1,3 | 47 | 1 | 0 | 48 |
| **C,d** | w% | B1 | | 0,549 | yes | 53,4 | 3 | 53,84 | 53,61 | 53,41 | 0,7942 | 1,5 | 20 | 2 | 0 | 22 |
| | w% | K1 | | -0,497 | yes | 73,3 | 2,5 | 72,84 | 73,25 | 73,22 | 0,9928 | 1,4 | 36 | 2 | 0 | 38 |
| **EF** | t | B1 | | 0,189 | yes | 106 | 4 | 106,4 | 106,1 | 105,9 | 2,125 | 2 | 10 | 4 | 0 | 14 |
| | t | K1 | | -0,133 | yes | 93,8 | 4 | 93,55 | 93,91 | 93,78 | 1,6 | 1,7 | 22 | 1 | 0 | 23 |
| **H,d** | w% | B1 | | 0,036 | yes | 5,63 | 7 | 5,637 | 5,675 | 5,629 | 0,1487 | 2,6 | 18 | 2 | 0 | 20 |
| | w% | K1 | | -0,345 | yes | 4,6 | 7 | 4,544 | 4,57 | 4,596 | 0,209 | 4,5 | 31 | 1 | 0 | 32 |
| **Mad,d** | w% | B1 | | | yes | 2,88 | | 2,785 | 2,87 | 2,852 | 0,4869 | 17,0 | 28 | 2 | 0 | 30 |
| | w% | K1 | | | yes | 3,52 | | 3,68 | 3,53 | 3,507 | 0,301 | 8,6 | 48 | 1 | 0 | 49 |
| **N,d** | w% | B1 | | 0,177 | yes | 1,62 | 15 | 1,642 | 1,601 | 1,621 | 0,07511 | 4,6 | 17 | 3 | 0 | 20 |
| | w% | K1 | | -0,436 | yes | 2,14 | 15 | 2,07 | 2,17 | 2,137 | 0,1439 | 6,7 | 28 | 2 | 0 | 30 |
| **q-p,net,d** | J/g | B1 | | 0,103 | yes | 20460 | 1,8 | 20480 | 20460 | 20490 | 165,3 | 0,8 | 21 | 6 | 0 | 27 |
| | J/g | K1 | | 0,214 | yes | 28810 | 1,3 | 28850 | 28820 | 28790 | 213,3 | 0,7 | 34 | 8 | 0 | 42 |
| **q-V,gr,d** | J/g | B1 | | 0,132 | yes | 21680 | 1,4 | 21700 | 21700 | 21690 | 161,4 | 0,7 | 26 | 5 | 0 | 31 |
| | J/g | K1 | | 0,013 | yes | 29820 | 1 | 29820 | 29820 | 29810 | 164,9 | 0,6 | 41 | 8 | 0 | 49 |
| **S,d** | w% | B1 | | 0,800 | yes | 0,25 | 15 | 0,265 | 0,248 | 0,2504 | 0,0173 | 6,9 | 23 | 2 | 0 | 25 |
| | w% | K1 | | 0,645 | yes | 0,31 | 15 | 0,325 | 0,31 | 0,3068 | 0,022 | 7,2 | 41 | 4 | 0 | 45 |

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

## LIITE 9. SUMMARY OF TEH z SCORES

APPENDIX 9.

| 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,d | B1 | S | . | . | S | S | . | S | S | S | . | . | S | . | S | S | S | . | . | . | U | S | S | . |
| | K1 | S | S | S | S | S | S | . | . | . | S | S | S | q | . | S | . | q | S | . | S | S | S | . |
| C,d | B1 | S | . | . | S | . | . | . | . | S | . | . | S | . | . | . | . | . | . | . | U | S | S | . |
| | K1 | S | S | . | q | . | S | . | . | . | Q | S | S | . | . | . | . | . | S | S | U | S | S | . |
| EF | B1 | . | . | . | S | . | . | . | . | . | . | . | S | . | . | . | . | . | . | . | . | S | S | . |
| | K1 | . | . | . | S | . | . | . | . | . | . | . | S | . | . | . | . | . | S | . | . | S | S | . |
| H,d | B1 | S | . | . | S | . | . | . | . | S | . | . | S | . | . | . | . | . | . | . | . | S | S | . |
| | K1 | S | S | . | S | . | S | . | . | . | . | Q | S | . | . | . | . | . | S | S | . | S | S | . |
| Mad,d | B1 | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . |
| | K1 | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . |
| N,d | B1 | S | . | . | S | . | . | . | . | S | . | . | S | . | . | . | . | . | . | . | . | S | S | . |
| | K1 | S | . | . | S | . | S | . | . | . | . | S | S | . | . | . | . | . | S | S | . | S | S | . |
| q-p,net,d | B1 | S | . | . | S | . | . | S | S | S | . | . | S | . | S | . | S | . | . | . | . | S | S | . |
| | K1 | S | S | S | S | . | S | . | . | . | S | S | S | S | . | . | . | S | S | . | . | Q | S | . |
| q-V,gr,d | B1 | S | . | . | S | S | . | S | S | S | . | . | . | . | S | u | S | . | . | . | q | S | S | . |
| | K1 | S | S | Q | q | S | S | . | . | . | S | S | S | S | . | u | . | S | S | . | S | Q | S | S |
| S,d | B1 | S | . | . | S | S | . | . | . | S | . | . | S | . | . | S | . | . | . | . | S | S | S | . |
| | K1 | S | S | S | S | S | S | . | . | . | S | S | S | S | . | S | . | . | S | S | S | S | S | . |
| % Accredited | | 100 yes | 100 yes | 75 yes | 88 yes | 100 | 100 yes | 100 | 100 | 100 | 80 yes | 86 yes | 100 yes | 75 | 100 | 67 | 100 | 67 | 100 yes | 100 yes | 50 yes | 88 | 100 yes | 100 |

| Analyte | Sample\Lab | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash,d | B1 | S | . | S | S | . | S | S | S | . | . | S | S | . | S | q | . | S | . | . | S | . | . | . |
| | K1 | S | S | S | . | S | S | . | S | S | S | S | S | S | S | S | S | S | S | u | S | S | S | S |
| C,d | B1 | . | . | S | S | . | S | u | S | . | . | S | S | . | S | S | . | S | . | . | S | . | . | . |
| | K1 | . | S | S | . | S | S | . | S | S | . | S | S | S | S | S | . | S | S | . | S | . | S | S |
| EF | B1 | . | . | . | . | . | S | . | q | . | . | u | U | . | S | . | . | S | . | . | u | . | . | . |
| | K1 | . | . | . | . | S | S | . | S | S | . | S | U | S | S | . | . | S | S | . | S | . | S | S |
| H,d | B1 | . | . | S | S | . | S | u | S | . | . | S | S | . | S | . | . | S | . | . | S | . | . | . |
| | K1 | . | . | S | . | S | S | . | S | S | . | S | S | S | S | . | . | S | . | . | S | . | u | S |
| Mad,d | B1 | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . |
| | K1 | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . |
| N,d | B1 | . | . | S | u | . | S | U | S | . | . | S | S | . | S | . | . | S | . | . | S | . | . | . |
| | K1 | . | . | S | . | U | S | . | S | S | . | S | S | S | S | . | . | S | . | . | S | . | . | S |
| q-p,net,d | B1 | S | . | U | u | . | S | u | Q | . | . | S | u | . | S | u | . | S | . | . | S | . | . | . |
| | K1 | S | S | U | . | S | S | . | U | S | . | S | u | S | S | u | . | S | S | u | S | . | u | q |
| q-V,gr,d | B1 | S | . | u | S | . | S | u | Q | . | . | S | S | . | S | U | . | S | . | . | S | . | . | . |
| | K1 | S | S | u | . | q | S | . | U | S | S | S | q | S | S | U | S | S | S | u | S | S | S | u |
| S,d | B1 | . | . | S | S | . | S | U | S | . | . | S | S | . | S | S | . | S | . | . | S | . | . | . |
| | K1 | u | S | S | . | u | S | . | S | S | . | S | S | S | S | S | . | S | S | q | S | . | S | S |
| % Accredited | | 86 yes | 100 yes | 71 yes | 71 yes | 62 yes | 100 yes | 14 | 69 yes | 100 yes | 100 yes | 94 yes | 69 yes | 100 yes | 100 yes | 50 yes | 100 | 100 yes | 100 yes | 0 yes | 94 yes | 100 yes | 71 yes | 75 yes |

| Analyte | Sample\Lab | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash,d | B1 | . | . | S | . | . | . | . | . | S | . | S | u | . | S | 90 |
| | K1 | q | S | . | S | . | S | S | S | S | S | S | S | . | S | 92 |
| C,d | B1 | . | . | . | . | . | . | . | . | S | . | S | q | . | S | 86 |
| | K1 | . | S | . | S | . | S | q | S | S | S | Q | S | . | S | 87 |
| EF | B1 | . | . | . | . | . | . | . | . | . | . | S | u | . | S | 64 |
| | K1 | . | . | . | S | . | S | . | . | . | . | Q | S | . | S | 91 |
| H,d | B1 | . | . | . | . | . | . | . | . | S | . | U | S | . | S | 90 |
| | K1 | . | Q | . | S | . | S | . | S | S | S | S | S | . | S | 91 |
| Mad,d | B1 | . | . | . | . | . | . | . | . | . | . | . | . | . | . | |
| | K1 | . | . | . | . | . | . | . | . | . | . | . | . | . | . | |
| N,d | B1 | . | . | . | . | . | . | . | . | S | . | S | u | . | S | 85 |
| | K1 | . | S | . | S | . | S | . | S | S | S | S | u | . | S | 93 |
| q-p,net,d | B1 | . | . | S | . | . | . | . | . | S | . | U | S | . | S | 74 |
| | K1 | u | S | . | S | . | S | S | S | q | S | U | q | . | S | 71 |
| q-V,gr,d | B1 | . | . | S | . | S | . | . | . | S | . | U | S | S | S | 77 |
| | K1 | u | S | . | S | . | S | S | S | S | S | U | q | . | S | 71 |
| S,d | B1 | . | . | S | . | . | . | . | . | S | . | S | U | . | S | 92 |
| | K1 | S | S | . | u | . | S | q | S | S | S | U | Q | . | S | 84 |
| % Accredited | | 25 yes | 86 yes | 100 yes | 88 yes | 100 yes | 100 yes | 60 yes | 100 yes | 93 yes | 100 yes | 50 | 44 | 100 yes | 100 yes | |

| Analyte | Sample\Lab | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), u - unsatisfactory ($z \leq -3$ )

%* - percentage of satisfactory results

Totally satisfactory, % In all: 84 In accredited: 87 In non-accredited: 70

# MEASUREMENT UNCERTAINTIES REPORTED BY THE LABORATORIES

**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

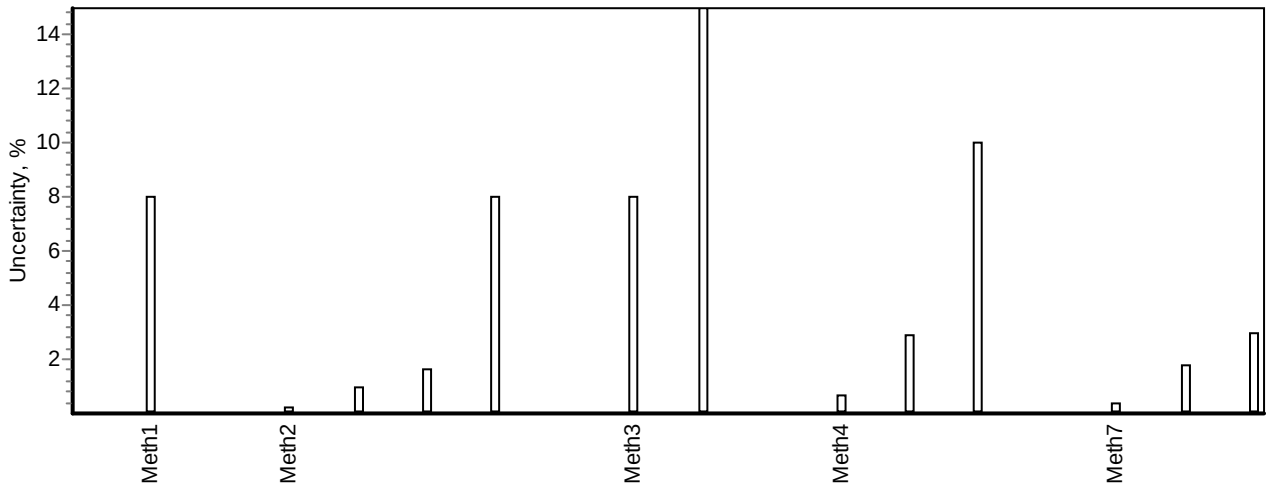
8. no uncertainty estimation

*IQC= internal quality control*

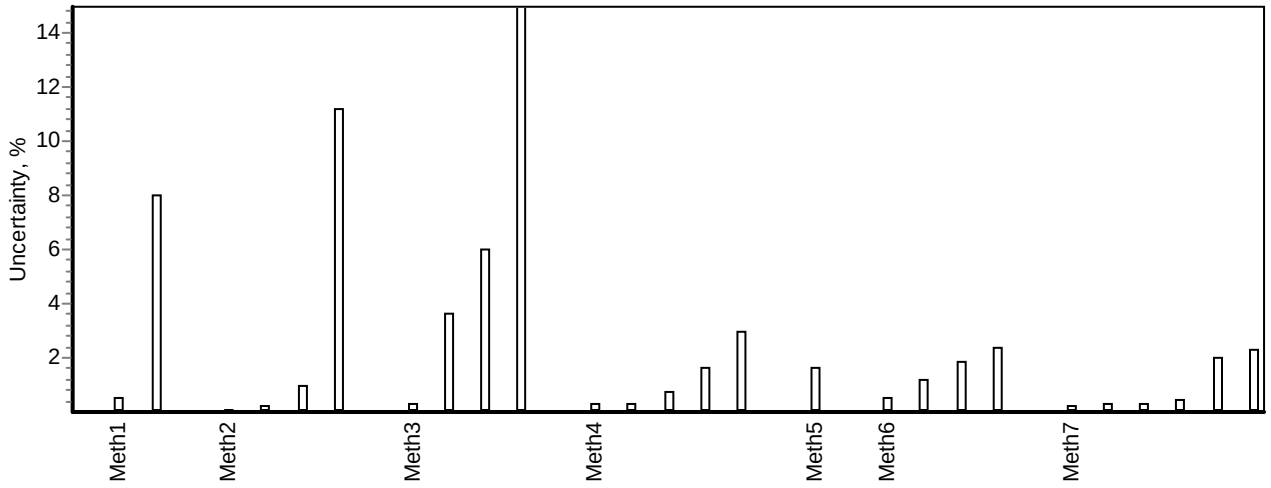
[1)] http://www.nordicinnovation.net
[2)] http://www.eurachem.org

**LIITE 10.**
APPENDIX 10.

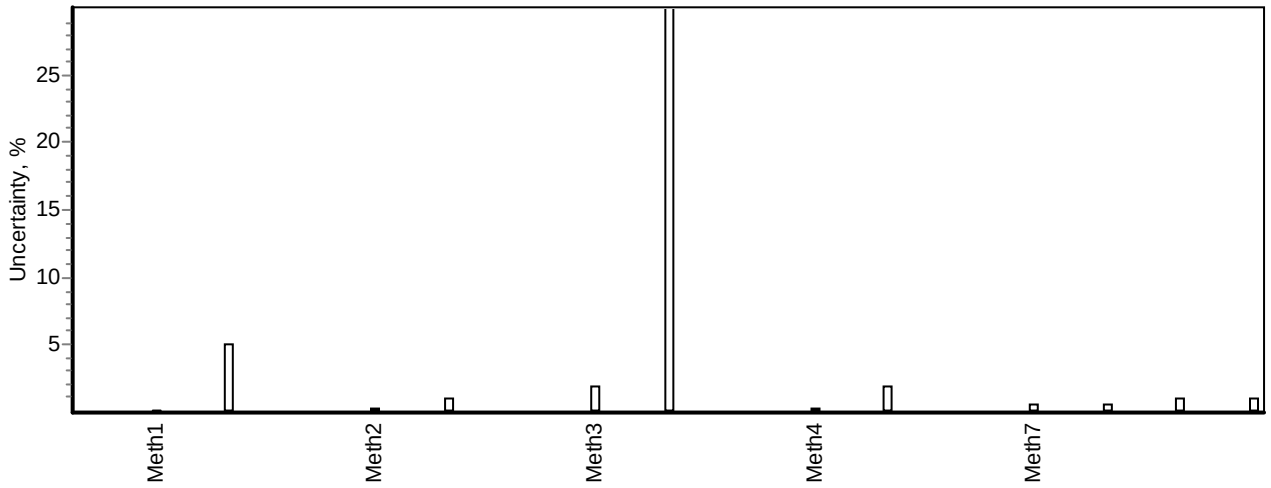
Analyytti *(Analyte)* **Ash,d** Näyte *(Sample)* B1



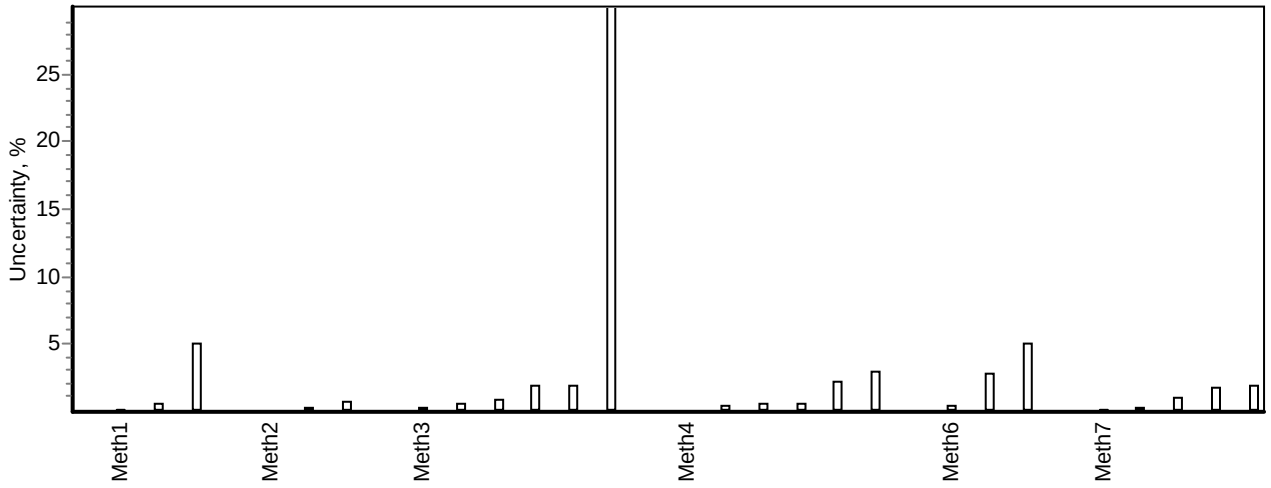

Analyytti *(Analyte)* **Ash,d** Näyte *(Sample)* K1



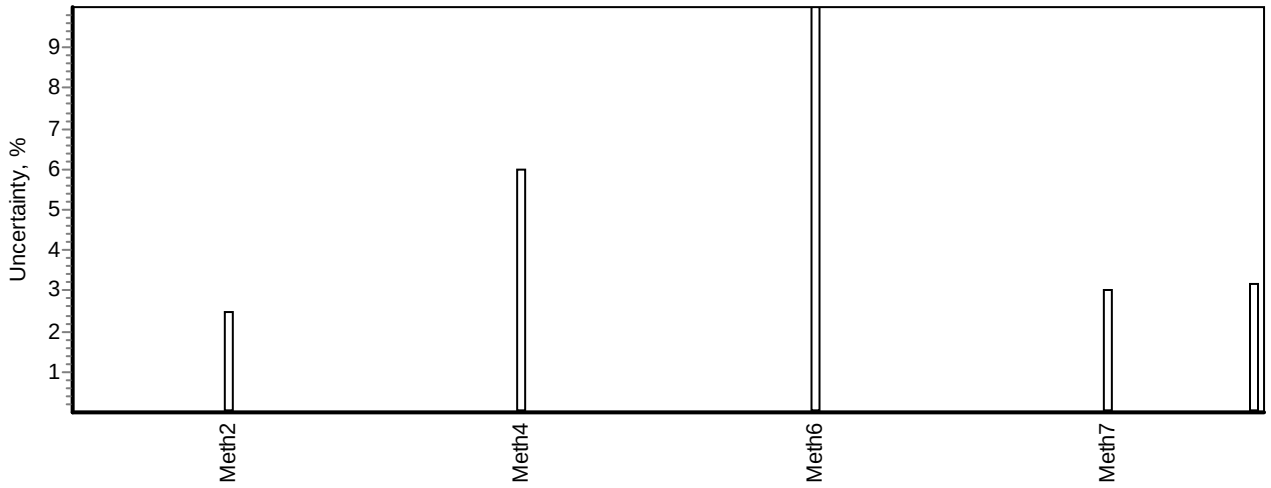

Analyytti *(Analyte)* **C,d** Näyte *(Sample)* B1



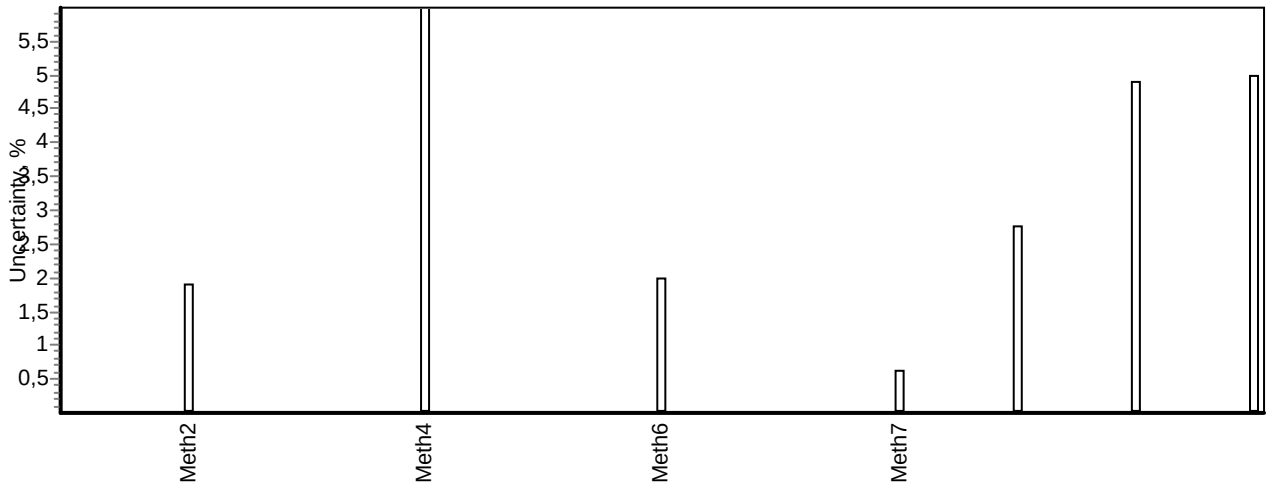
Analyytti *(Analyte)* **C,d** Näyte *(Sample)* K1



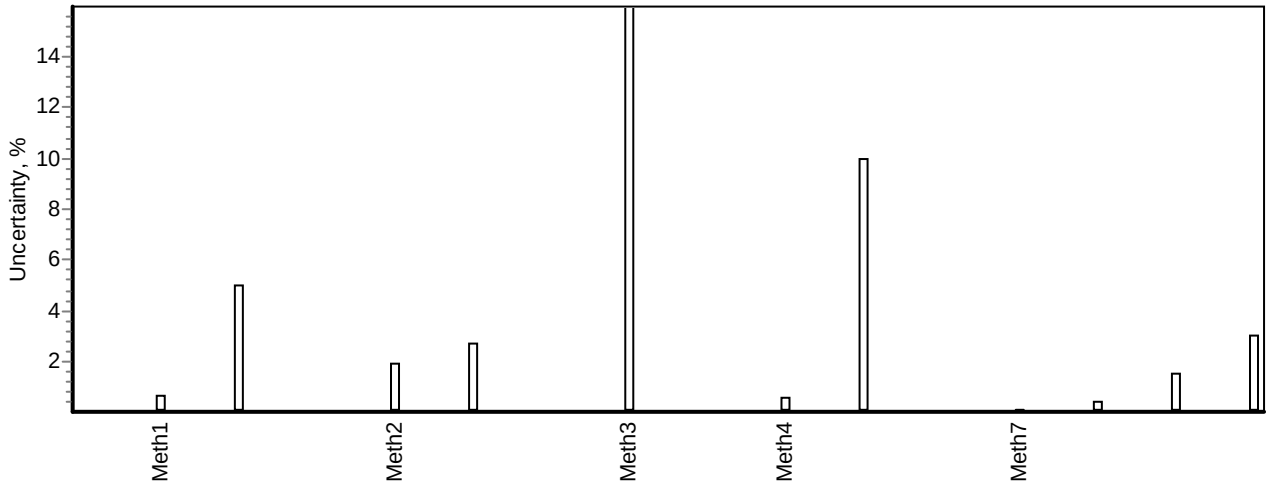

Analyytti *(Analyte)* **EF** Näyte *(Sample)* B1



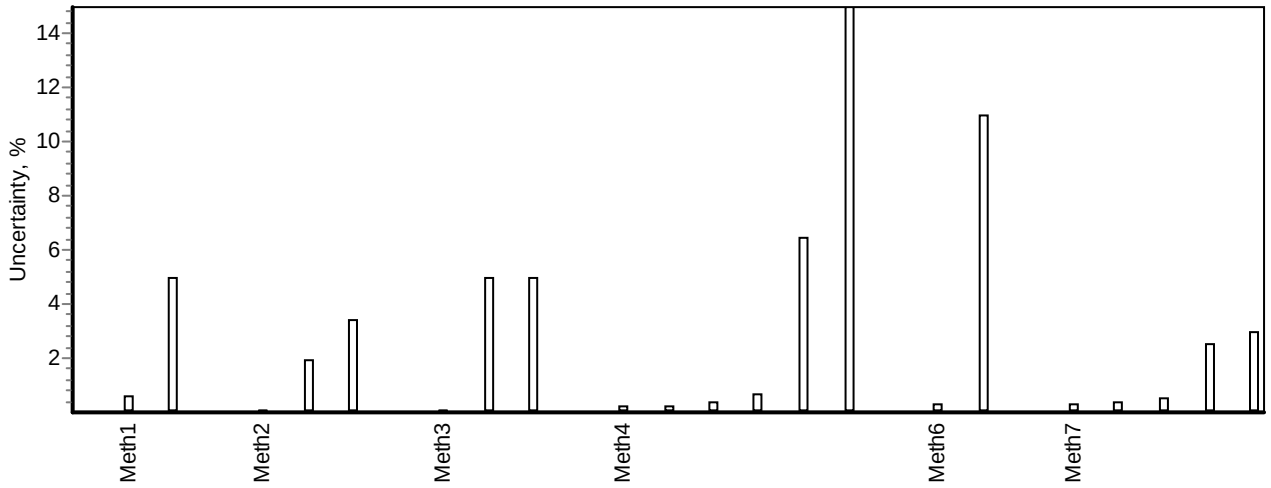

Analyytti *(Analyte)* **EF** Näyte *(Sample)* K1



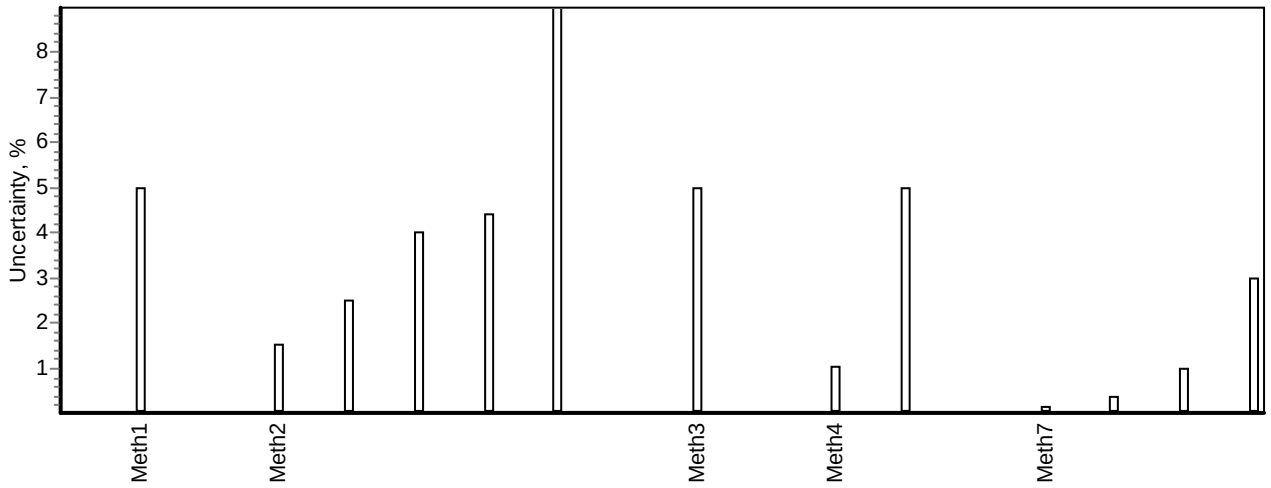
Analyytti *(Analyte)* **H,d** Näyte *(Sample)* B1



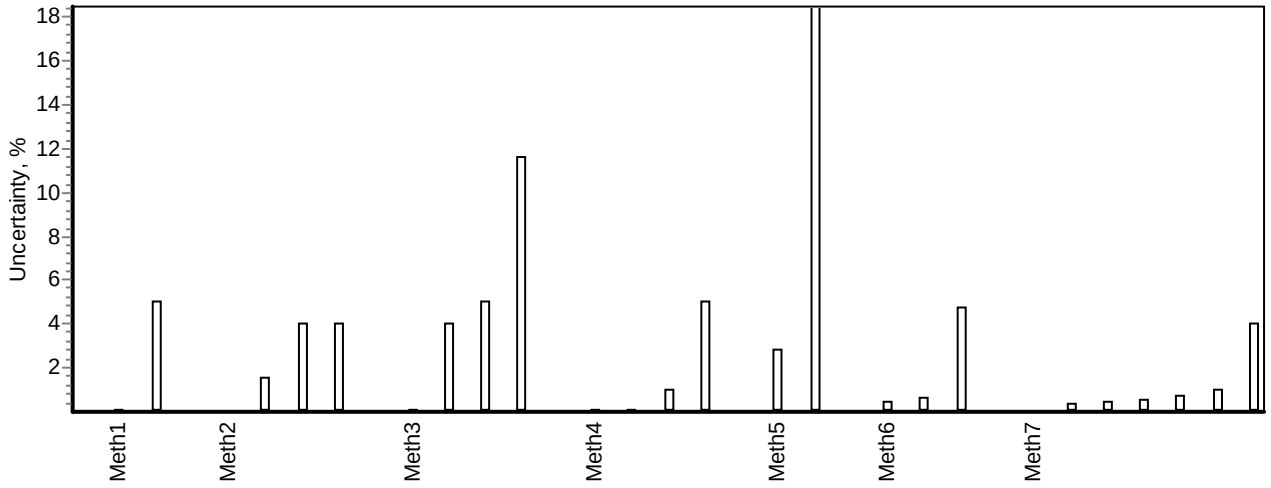

Analyytti *(Analyte)* **H,d** Näyte *(Sample)* K1



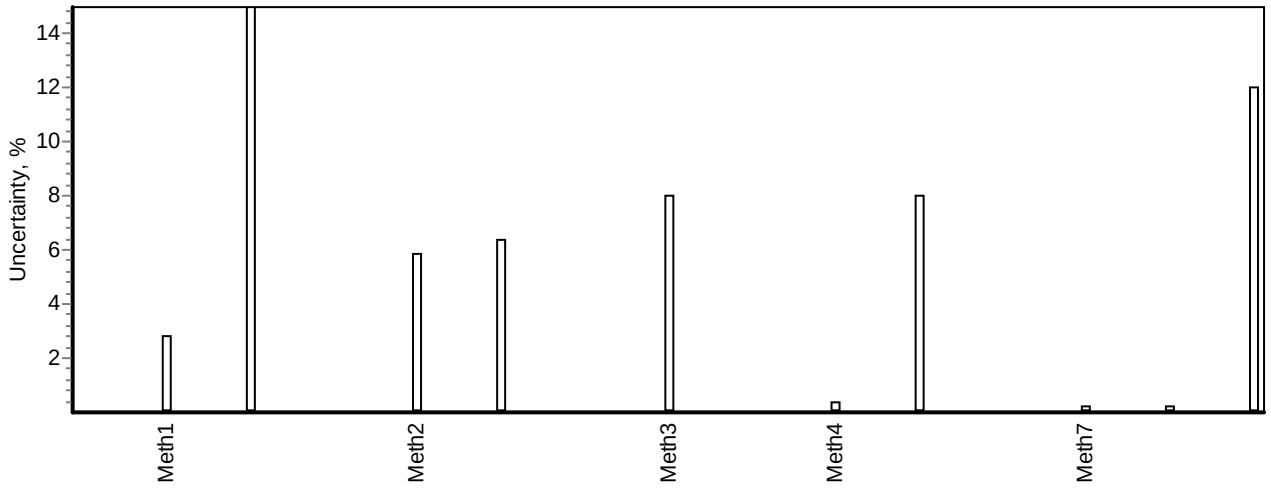

Analyytti *(Analyte)* **Mad,d** Näyte *(Sample)* B1



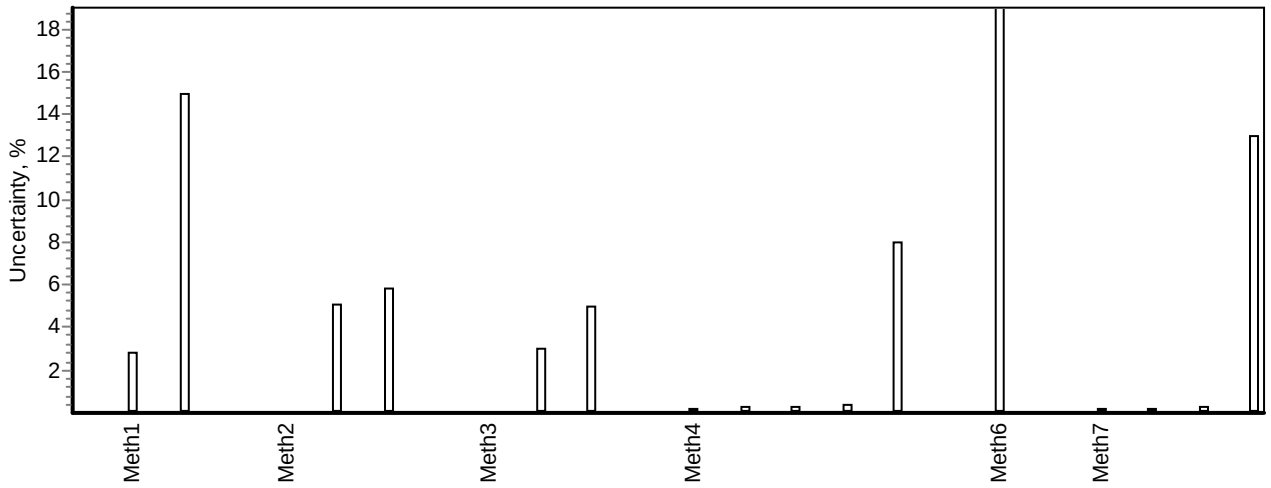
Analyytti *(Analyte)* **Mad,d** Näyte *(Sample)* K1



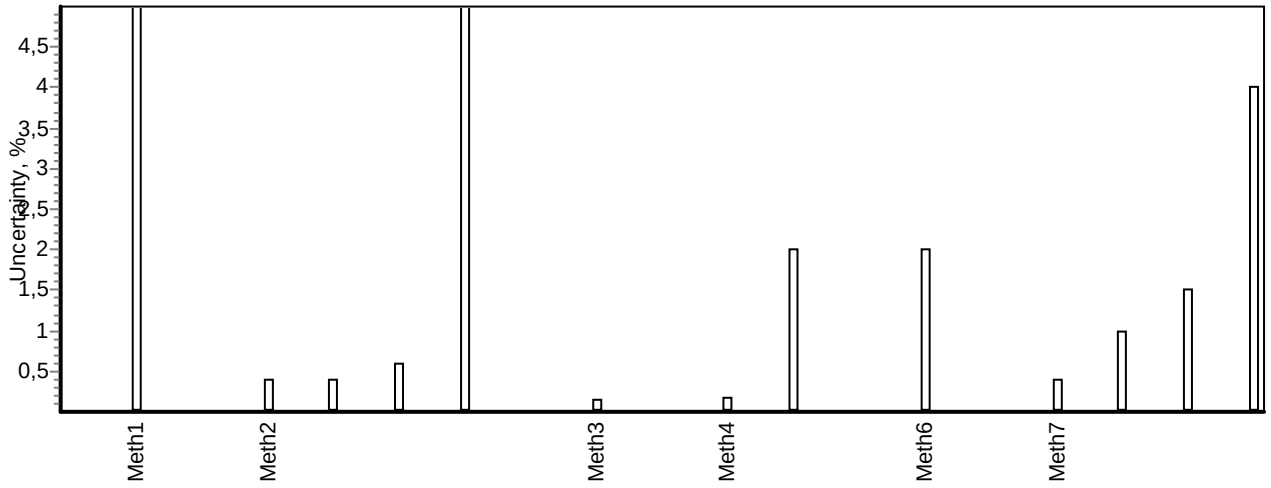

Analyytti *(Analyte)* **N,d** Näyte *(Sample)* B1



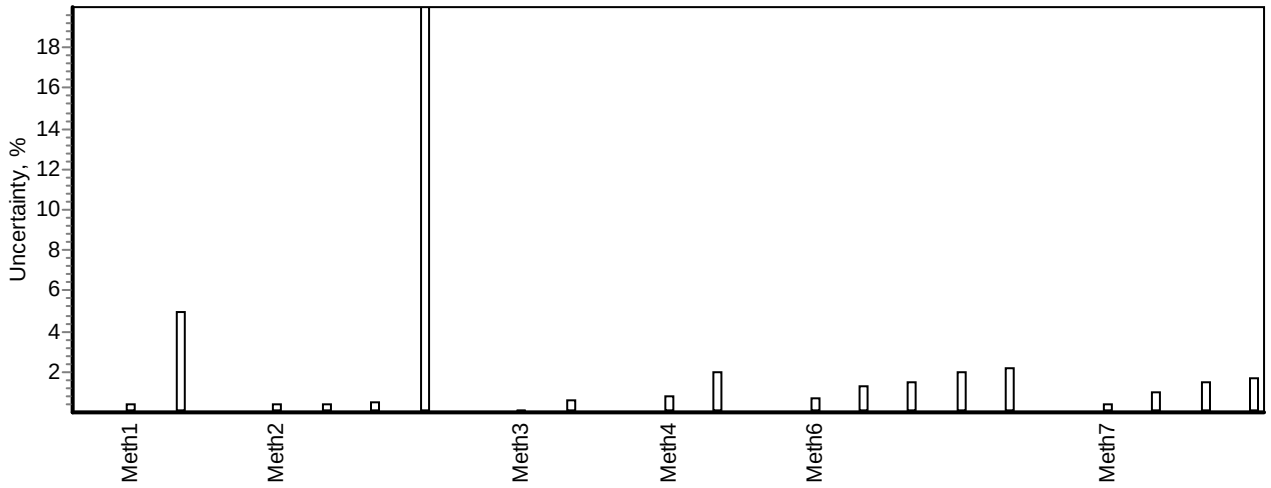

Analyytti *(Analyte)* **N,d** Näyte *(Sample)* K1



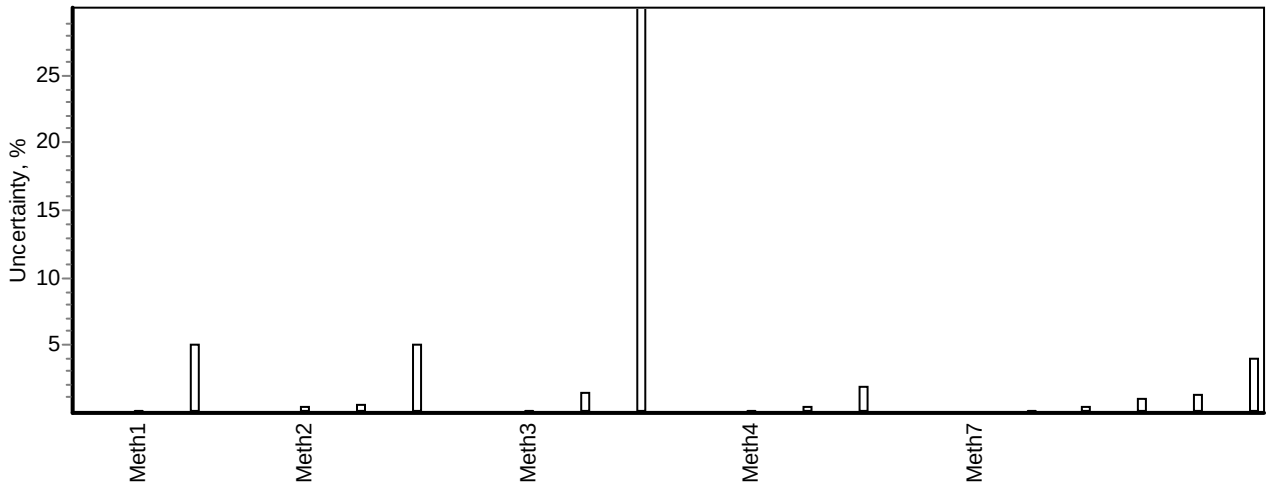
Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* B1



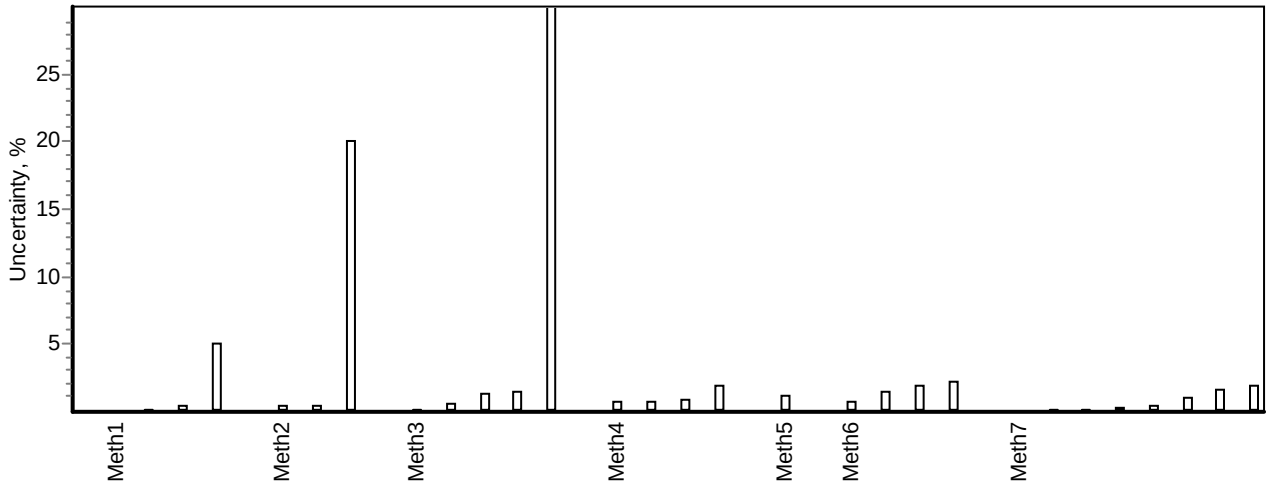

Analyytti *(Analyte)* **q-p,net,d** Näyte *(Sample)* K1



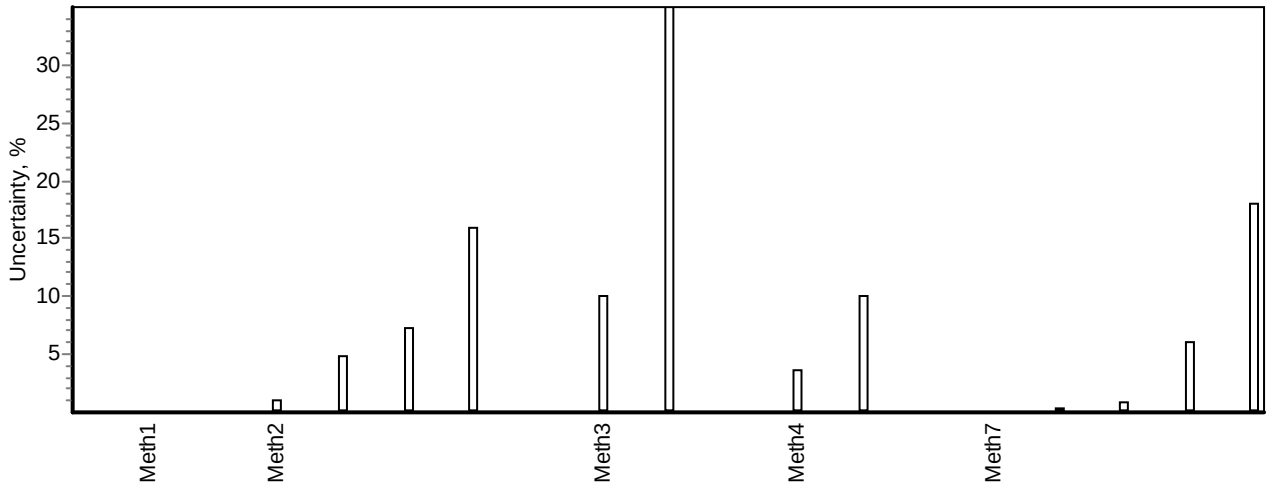

Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* B1



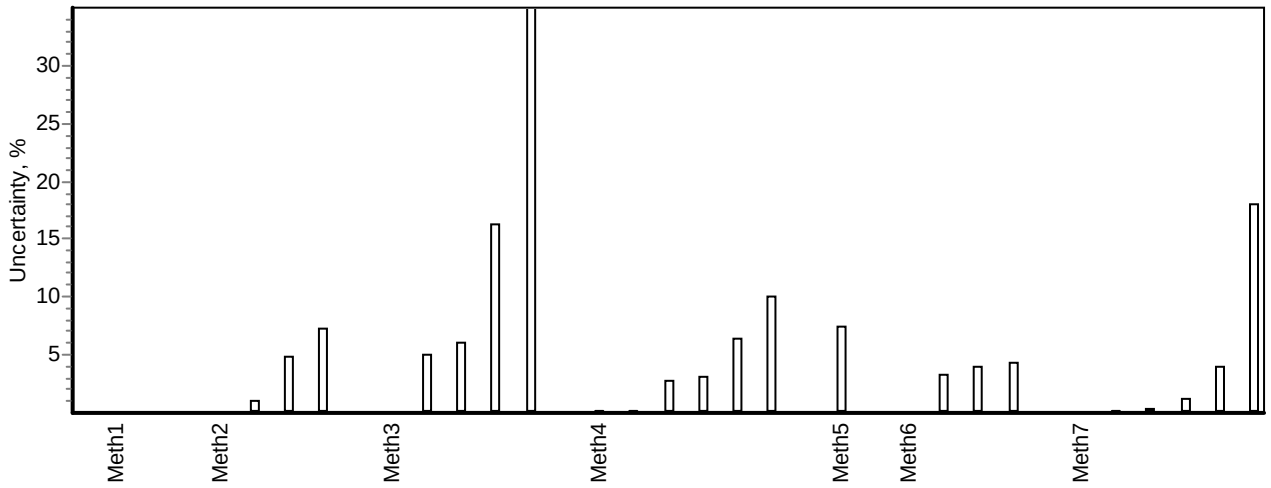
Analyytti *(Analyte)* **q-V,gr,d** Näyte *(Sample)* K1




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




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

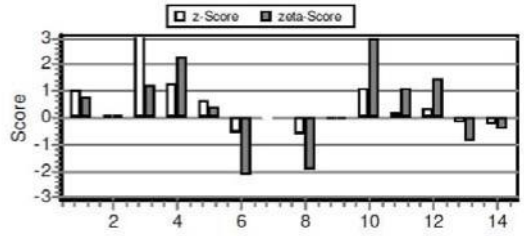


# z AND zeta SCORES OF LABORATORIES

Analyte **Ash,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **7,7** | **0,09** | **6** |

**z&zeta-Score diagram**

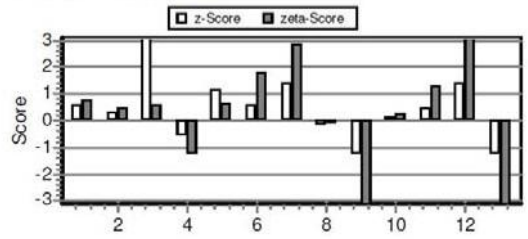



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 7,935 | 8 | 1,02 | 0,73 |
| 2 | 22 | 7,715 | 10 | 0,06 | 0,04 |
| 3 | 20 | 8,475 | 15 | 3,35 | 1,22 |
| 4 | 4 | 7,995 | 3 | 1,28 | 2,30 |
| 5 | 1 | 7,85 | 10 | 0,65 | 0,38 |
| 6 | 60 | 7,575 | 1 | -0,54 | -2,13 |
| 7 | 49 | 7,695 | 8 | -0,02 | -0,02 |
| 8 | 43 | 7,55 | 1,6 | -0,65 | -1,99 |
| 9 | 37 | 7,685 | 8 | -0,06 | -0,05 |
| 10 | 34 | 7,95 | 1,78 | 1,08 | 2,98 |
| 11 | 35 | 7,75 | 0,39 | 0,22 | 1,05 |
| 12 | 57 | 7,775 | 0,637 | 0,32 | 1,46 |
| 13 | 31 | 7,6605 | 0,23848 | -0,17 | -0,86 |
| 14 | 24 | 7,645 | 2,9 | -0,24 | -0,46 |

Analyte **C,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **53,4** | **0,48** | **3** |

**z&zeta-Score diagram**

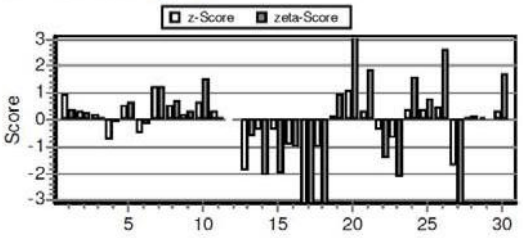



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 53,855 | 2 | 0,57 | 0,77 |
| 2 | 22 | 53,67 | 2 | 0,34 | 0,46 |
| 3 | 20 | 58,25 | 30 | 6,05 | 0,55 |
| 4 | 4 | 52,945 | 1 | -0,57 | -1,27 |
| 5 | 1 | 54,3 | 5 | 1,12 | 0,65 |
| 6 | 60 | 53,84 | 0,2 | 0,55 | 1,79 |
| 7 | 43 | 54,5 | 1,1 | 1,37 | 2,86 |
| 8 | 37 | 53,26 | 5 | -0,17 | -0,10 |
| 9 | 34 | 52,39 | 0,62 | -1,26 | -3,49 |
| 10 | 26 | 53,5 | 1,09 | 0,12 | 0,26 |
| 11 | 35 | 53,75 | 0,53 | 0,44 | 1,25 |
| 12 | 57 | 54,505 | 0,246 | 1,38 | 4,43 |
| 13 | 31 | 52,365 | 0,2364 | -1,29 | -4,18 |

Analyte **Ash,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **10,9** | **0,04** | **2,5** |

**z&zeta-Score diagram**

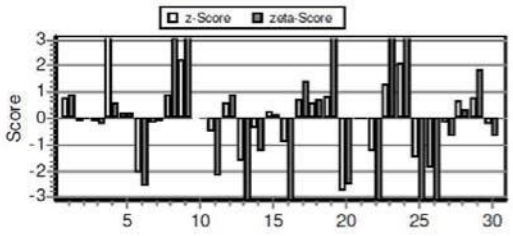



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 11,025 | 6 | 0,92 | 0,38 |
| 2 | 22 | 10,94 | 3 | 0,29 | 0,24 |
| 3 | 18 | 10,925 | 5 | 0,18 | 0,09 |
| 4 | 20 | 10,8 | 15 | -0,73 | -0,12 |
| 5 | 4 | 10,97 | 2 | 0,51 | 0,63 |
| 6 | 1 | 10,83 | 7 | -0,51 | -0,18 |
| 7 | 48 | 11,065 | 2,4 | 1,21 | 1,23 |
| 8 | 10 | 10,97 | 1,82 | 0,51 | 0,69 |
| 9 | 2 | 10,93 | 1,64 | 0,22 | 0,33 |
| 10 | 60 | 10,99 | 1 | 0,66 | 1,54 |
| 11 | 43 | 10,94 | 11,2 | 0,29 | 0,07 |
| 12 | 54 | 10,9 | 0,3 | 0,00 | 0,00 |
| 13 | 37 | 10,64 | 8 | -1,91 | -0,61 |
| 14 | 34 | 10,845 | 0,31 | -0,40 | -2,11 |
| 15 | 35 | 10,85 | 0,27 | -0,37 | -2,02 |
| 16 | 36 | 10,77 | 2,3 | -0,95 | -1,04 |
| 17 | 42 | 9,395 | 1,6 | -11,05 | -19,35 |
| 18 | 53 | 10,765 | 0,51 | -0,99 | -3,97 |
| 19 | 28 | 10,92 | 0,13 | 0,15 | 0,94 |
| 20 | 50 | 11,05 | 0,04 | 1,10 | 7,45 |
| 21 | 33 | 10,945 | 0,25 | 0,33 | 1,86 |
| 22 | 25 | 10,85 | 0,53 | -0,37 | -1,43 |
| 23 | 57 | 10,805 | 0,72 | -0,70 | -2,17 |
| 24 | 39 | 10,95 | 0,45 | 0,37 | 1,58 |
| 25 | 45 | 10,95 | 1,2 | 0,37 | 0,73 |
| 26 | 31 | 10,9615 | 0,23848 | 0,45 | 2,57 |
| 27 | 52 | 10,67 | 0,26 | -1,69 | -9,45 |
| 28 | 24 | 10,91 | 1,6 | 0,07 | 0,11 |
| 29 | 41 | 10,905 | 3,62 | 0,04 | 0,03 |
| 30 | 6 | 10,945 | 0,3 | 0,33 | 1,74 |

Analyte **C,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **73,3** | **0,38** | **2,5** |

**z&zeta-Score diagram**

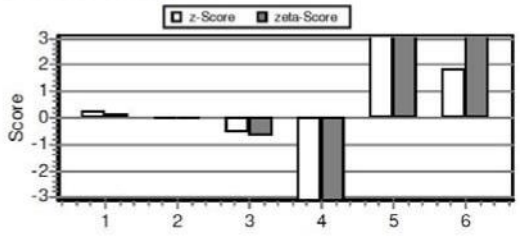



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 73,98 | 2 | 0,74 | 0,89 |
| 2 | 22 | 73,195 | 3 | -0,11 | -0,09 |
| 3 | 18 | 73,185 | 1 | -0,13 | -0,28 |
| 4 | 20 | 79,75 | 30 | 7,04 | 0,54 |
| 5 | 19 | 73,45 | 2 | 0,16 | 0,20 |
| 6 | 4 | 71,395 | 2 | -2,08 | -2,58 |
| 7 | 1 | 73,1 | 5 | -0,22 | -0,11 |
| 8 | 48 | 74,11 | 0,5 | 0,88 | 3,05 |
| 9 | 10 | 75,325 | 0,66 | 2,21 | 6,47 |
| 10 | 2 | 73,305 | 2,22 | 0,01 | 0,01 |
| 11 | 60 | 72,845 | 0,2 | -0,50 | -2,24 |
| 12 | 29 | 73,835 | 1,5 | 0,58 | 0,91 |
| 13 | 43 | 71,81 | 0,8 | -1,63 | -4,33 |
| 14 | 54 | 72,935 | 0,6 | -0,40 | -1,26 |
| 15 | 37 | 73,505 | 5 | 0,22 | 0,11 |
| 16 | 34 | 72,45 | 0,23 | -0,93 | -4,10 |
| 17 | 26 | 73,925 | 1,09 | 0,68 | 1,40 |
| 18 | 35 | 73,8 | 1,85 | 0,55 | 0,71 |
| 19 | 36 | 74,05 | 0,2 | 0,82 | 3,68 |
| 20 | 53 | 70,74 | 2,81 | -2,79 | -2,53 |
| 21 | 28 | 73,24 | 1,8 | -0,07 | -0,09 |
| 22 | 50 | 72,14 | 0,04 | -1,27 | -6,09 |
| 23 | 25 | 74,455 | 0,63 | 1,26 | 3,83 |
| 24 | 57 | 75,205 | 0,028 | 2,08 | 10,01 |
| 25 | 45 | 71,92 | 0,5 | -1,51 | -5,28 |
| 26 | 31 | 71,56 | 0,2364 | -1,90 | -8,37 |
| 27 | 52 | 73,145 | 0,32 | -0,17 | -0,69 |
| 28 | 46 | 73,86 | 5 | 0,61 | 0,30 |
| 29 | 41 | 74,005 | 0,89 | 0,77 | 1,85 |
| 30 | 6 | 73,095 | 0,6 | -0,22 | -0,71 |

Analyte **EF** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **106** | **0,91** | **4** |

**z&zeta-Score diagram**

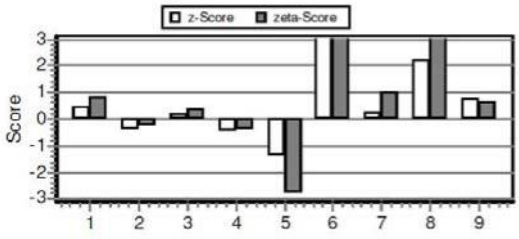



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 106,6 | 10 | 0,28 | 0,11 |
| 2 | 22 | 105,85 | 6 | -0,07 | -0,05 |
| 3 | 4 | 104,85 | 3 | -0,54 | -0,70 |
| 4 | 43 | 97,475 | 2,5 | -4,02 | -6,55 |
| 5 | 35 | 126,85 | 3,16 | 9,83 | 10,14 |
| 6 | 57 | 109,95 | 0,579 | 1,86 | 7,11 |

Analyte **EF** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **93,8** | **0,63** | **4** |

**z&zeta-Score diagram**

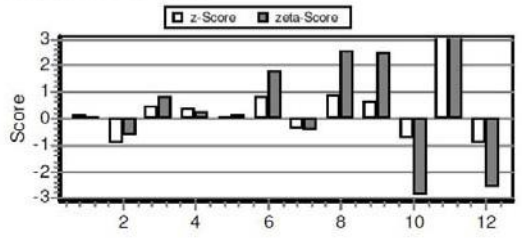



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 94,6 | 2 | 0,43 | 0,80 |
| 2 | 22 | 93.05 | 6 | -0.40 | -0.27 |
| 3 | 18 | 94,15 | 2 | 0,19 | 0,35 |
| 4 | 4 | 92,95 | 5 | -0,45 | -0,36 |
| 5 | 43 | 91,242 | 1,9 | -1,36 | -2,77 |
| 6 | 35 | 110,25 | 2,76 | 8,77 | 10,59 |
| 7 | 36 | 94,25 | 0,63 | 0,24 | 1,04 |
| 8 | 57 | 97,9 | 0 | 2,19 | 13,02 |
| 9 | 41 | 95,25 | 4,9 | 0,77 | 0,62 |

Analyte **H,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **5,63** | **0,1** | **7** |

**z&zeta-Score diagram**

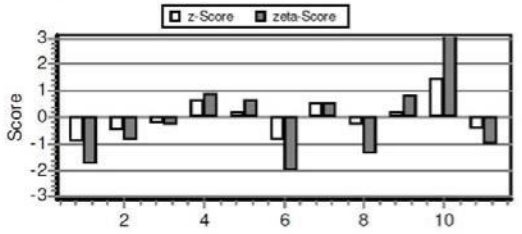



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 5,6495 | 16 | 0,10 | 0,04 |
| 2 | 22 | 5,4475 | 10 | -0,93 | -0,66 |
| 3 | 4 | 5,7115 | 3 | 0,41 | 0,82 |
| 4 | 1 | 5,7 | 10 | 0,36 | 0,24 |
| 5 | 60 | 5,637 | 0,6 | 0,04 | 0,13 |
| 6 | 43 | 5,795 | 2,7 | 0,84 | 1,78 |
| 7 | 37 | 5,56 | 5 | -0,36 | -0,47 |
| 8 | 34 | 5,7985 | 1,52 | 0,86 | 2,53 |
| 9 | 26 | 5,755 | 0,36 | 0,63 | 2,45 |
| 10 | 35 | 5,485 | 0,11 | -0,74 | -2,89 |
| 11 | 57 | 6,3465 | 0,546 | 3,64 | 13,54 |
| 12 | 31 | 5,444 | 1,9212 | -0,94 | -2,57 |

Analyte **N,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **1,62** | **0,05** | **15** |

**z&zeta-Score diagram**

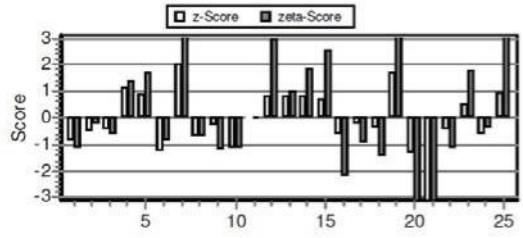



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 1,503 | 8 | -0,96 | -1,80 |
| 2 | 22 | 1,559 | 8 | -0,50 | -0,91 |
| 3 | 4 | 1,586 | 12 | -0,28 | -0,35 |
| 4 | 1 | 1,7 | 10 | 0,66 | 0,90 |
| 5 | 60 | 1,6415 | 2,8 | 0,18 | 0,63 |
| 6 | 43 | 1,51 | 6,4 | -0,91 | -2,02 |
| 7 | 37 | 1,685 | 15 | 0,53 | 0,50 |
| 8 | 26 | 1,585 | 0,22 | -0,29 | -1,40 |
| 9 | 35 | 1,64 | 0,24 | 0,16 | 0,80 |
| 10 | 57 | 1,795 | 0,394 | 1,44 | 6,93 |
| 11 | 31 | 1,568 | 5,8478 | -0,43 | -1,00 |

Analyte **H,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **4,6** | **0,09** | **7** |

**z&zeta-Score diagram**

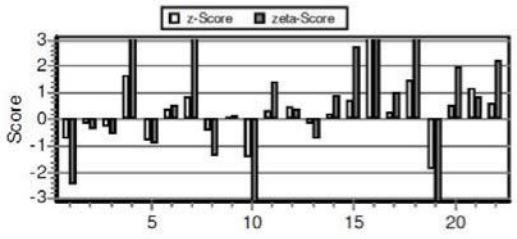



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 4,4605 | 5 | -0,87 | -1,16 |
| 2 | 22 | 4,514 | 15 | -0,53 | -0,25 |
| 3 | 18 | 4,524 | 5 | -0,47 | -0,62 |
| 4 | 19 | 4,78 | 5 | 1,12 | 1,41 |
| 5 | 4 | 4,743 | 3 | 0,89 | 1,70 |
| 6 | 1 | 4,4 | 10 | -1,24 | -0,89 |
| 7 | 48 | 4,9255 | 0,36 | 2,02 | 7,10 |
| 8 | 2 | 4,49 | 6,44 | -0,68 | -0,73 |
| 9 | 60 | 4,5445 | 0,6 | -0,34 | -1,18 |
| 10 | 29 | 4,415 | 7 | -1,15 | -1,15 |
| 11 | 43 | 4,595 | 3,4 | -0,03 | -0,06 |
| 12 | 54 | 4,735 | 0,2 | 0,84 | 2,98 |
| 13 | 37 | 4,73 | 5 | 0,81 | 1,03 |
| 14 | 34 | 4,7365 | 2,52 | 0,85 | 1,83 |
| 15 | 26 | 4,715 | 0,36 | 0,71 | 2,51 |
| 16 | 35 | 4,5 | 0,29 | -0,62 | -2,20 |
| 17 | 36 | 4,555 | 0,5 | -0,28 | -0,97 |
| 18 | 28 | 4,535 | 0,2 | -0,40 | -1,44 |
| 19 | 50 | 4,875 | 0,04 | 1,71 | 6,11 |
| 20 | 57 | 4,3895 | 0,693 | -1,31 | -4,43 |
| 21 | 45 | 3,96 | 0,3 | -3,98 | -14,10 |
| 22 | 31 | 4,527 | 1,9212 | -0,45 | -1,17 |
| 23 | 52 | 4,679 | 0,06 | 0,49 | 1,75 |
| 24 | 46 | 4,501 | 11 | -0,61 | -0,39 |
| 25 | 6 | 4,75 | 0,2 | 0,93 | 3,31 |

Analyte **N,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **2,14** | **0,08** | **15** |

**z&zeta-Score diagram**

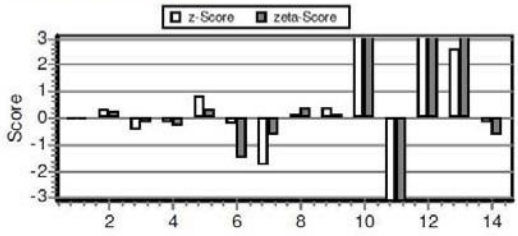



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 2,015 | 3 | -0,78 | -2,49 |
| 2 | 22 | 2,1065 | 8 | -0,21 | -0,36 |
| 3 | 18 | 2,0875 | 8 | -0,33 | -0,57 |
| 4 | 19 | 2,405 | 5 | 1,65 | 3,67 |
| 5 | 4 | 2,0085 | 13 | -0,82 | -0,96 |
| 6 | 1 | 2,2 | 10 | 0,37 | 0,51 |
| 7 | 48 | 2,272 | 0,36 | 0,82 | 3,28 |
| 8 | 60 | 2,07 | 2,8 | -0,44 | -1,42 |
| 9 | 29 | 2,1495 | 6 | 0,06 | 0,13 |
| 10 | 43 | 1,905 | 5,1 | -1,46 | -3,73 |
| 11 | 54 | 2,195 | 0,3 | 0,34 | 1,37 |
| 12 | 37 | 2,21 | 15 | 0,44 | 0,41 |
| 13 | 26 | 2,11 | 0,22 | -0,19 | -0,75 |
| 14 | 35 | 2,175 | 0,22 | 0,22 | 0,87 |
| 15 | 36 | 2,25 | 0,3 | 0,69 | 2,74 |
| 16 | 28 | 4,27 | 0,1 | 13,27 | 53,17 |
| 17 | 50 | 2,18 | 0,04 | 0,25 | 1,00 |
| 18 | 57 | 2,3775 | 0,149 | 1,48 | 5,93 |
| 19 | 31 | 1,8345 | 5,8478 | -1,90 | -4,57 |
| 20 | 52 | 2,2195 | 0,04 | 0,50 | 1,99 |
| 21 | 46 | 2,325 | 19 | 1,15 | 0,82 |
| 22 | 6 | 2,23 | 0,3 | 0,56 | 2,24 |

Analyte **q-p,net,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **20460** | **55** | **1,8** |

**z&zeta-Score diagram**

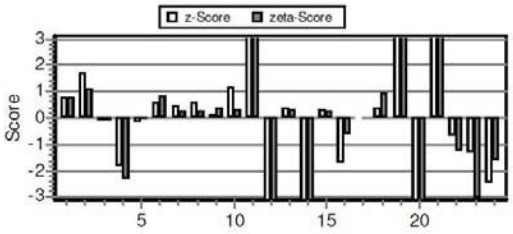



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 20448 | 2 | -0,07 | -0,06 |
| 2 | 22 | 20516,5 | 2 | 0,31 | 0,27 |
| 3 | 16 | 20380,5 | 4 | -0,43 | -0,19 |
| 4 | 4 | 20427 | 1 | -0,18 | -0,31 |
| 5 | 1 | 20613 | 5 | 0,83 | 0,30 |
| 6 | 7 | 20409,5 | 0,18 | -0,27 | -1,53 |
| 7 | 49 | 20131,5 | 5 | -1,78 | -0,65 |
| 8 | 43 | 20486,5 | 0,6 | 0,14 | 0,39 |
| 9 | 37 | 20535,5 | 5 | 0,41 | 0,15 |
| 10 | 26 | 21431,5 | 0,4 | 5,28 | 19,08 |
| 11 | 35 | 15521 | 1,5 | -26,82 | -41,29 |
| 12 | 57 | 21812 | 0,156 | 7,34 | 41,81 |
| 13 | 31 | 20938,5 | 0,40233 | 2,60 | 9,51 |
| 14 | 24 | 20430 | 0,4 | -0,16 | -0,61 |

Analyte **q-p,net,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **28810** | **82** | **1,3** |

**z&zeta-Score diagram**

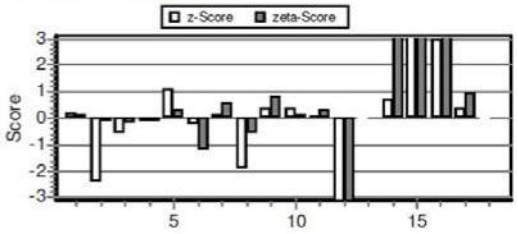



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 28953,5 | 1,3 | 0,77 | 0,75 |
| 2 | 22 | 29130 | 2 | 1,71 | 1,09 |
| 3 | 18 | 28785 | 1,5 | -0,13 | -0,11 |
| 4 | 4 | 28463 | 1 | -1,85 | -2,34 |
| 5 | 1 | 28774,5 | 5 | -0,19 | -0,05 |
| 6 | 48 | 28911 | 0,82 | 0,54 | 0,81 |
| 7 | 10 | 28892,5 | 2,2 | 0,44 | 0,26 |
| 8 | 29 | 28911,5 | 2,5 | 0,54 | 0,28 |
| 9 | 43 | 28836,5 | 0,4 | 0,14 | 0,37 |
| 10 | 37 | 29021,5 | 5 | 1,13 | 0,29 |
| 11 | 26 | 29773 | 0,4 | 5,14 | 13,32 |
| 12 | 35 | 24513 | 1,5 | -22,95 | -22,81 |
| 13 | 36 | 28885 | 1,7 | 0,40 | 0,30 |
| 14 | 42 | 24162 | 1 | -24,82 | -36,43 |
| 15 | 53 | 28870,5 | 1,5 | 0,32 | 0,27 |
| 16 | 28 | 28487,5 | 3,4 | -1,72 | -0,66 |
| 17 | 50 | 28805 | 20 | -0,03 | 0,00 |
| 18 | 25 | 28876,5 | 0,4 | 0,36 | 0,94 |
| 19 | 57 | 31893 | 0,146 | 16,46 | 65,39 |
| 20 | 45 | 24999 | 0,7 | -20,35 | -39,44 |
| 21 | 31 | 29428 | 0,40233 | 3,30 | 8,58 |
| 22 | 52 | 28683,5 | 0,62 | -0,68 | -1,29 |
| 23 | 24 | 28560 | 0,5 | -1,34 | -3,04 |
| 24 | 46 | 28345,5 | 2 | -2,48 | -1,62 |

Analyte **q-V,gr,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **21680** | **51** | **1,4** |

**z&zeta-Score diagram**

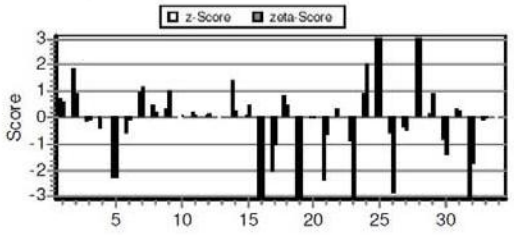



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 22 | 21706 | 2 | 0,17 | 0,12 |
| 2 | 20 | 21315 | 30 | -2,41 | -0,11 |
| 3 | 16 | 21596,5 | 4 | -0,55 | -0,19 |
| 4 | 4 | 21663 | 1 | -0,11 | -0,15 |
| 5 | 1 | 21841,5 | 5 | 1,06 | 0,30 |
| 6 | 7 | 21641,5 | 0,18 | -0,25 | -1,20 |
| 7 | 60 | 21700 | 0,2 | 0,13 | 0,60 |
| 8 | 49 | 21389 | 5 | -1,92 | -0,54 |
| 9 | 43 | 21735,5 | 0,6 | 0,37 | 0,79 |
| 10 | 37 | 21740,5 | 5 | 0,40 | 0,11 |
| 11 | 34 | 21688 | 0,02 | 0,05 | 0,31 |
| 12 | 26 | 20830,5 | 0,4 | -5,60 | -17,39 |
| 13 | 35 | 21681 | 1,4 | 0,01 | 0,01 |
| 14 | 51 | 21784,5 | 0,09 | 0,69 | 3,83 |
| 15 | 57 | 23371,5 | 0,076 | 11,15 | 62,64 |
| 16 | 31 | 22132,5 | 0,40233 | 2,98 | 8,82 |
| 17 | 24 | 21735,5 | 0,5 | 0,37 | 0,92 |
| 18 | 59 | 21681 | 1,5 | 0,01 | 0,01 |

Analyte **q-V,gr,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **29820** | **52** | **1** |

**z&zeta-Score diagram**

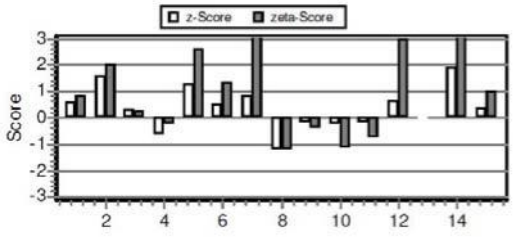



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 29927,5 | 1,3 | 0,72 | 0,55 |
| 2 | 22 | 30097 | 2 | 1,86 | 0,92 |
| 3 | 18 | 29793 | 1,5 | -0,18 | -0,12 |
| 4 | 20 | 29750 | 30 | -0,47 | -0,02 |
| 5 | 4 | 29471 | 1 | -2,34 | -2,33 |
| 6 | 1 | 29724 | 5 | -0,64 | -0,13 |
| 7 | 48 | 29962,5 | 0,82 | 0,96 | 1,13 |
| 8 | 10 | 29889,5 | 2,2 | 0,47 | 0,21 |
| 9 | 2 | 29863,5 | 0,23 | 0,29 | 1,01 |
| 10 | 60 | 29822 | 0,2 | 0,01 | 0,05 |
| 11 | 29 | 29846,5 | 2,5 | 0,18 | 0,07 |
| 12 | 43 | 29827 | 0,4 | 0,05 | 0,11 |
| 13 | 54 | 29818 | 0,8 | -0,01 | -0,02 |
| 14 | 37 | 30032 | 5 | 1,42 | 0,28 |
| 15 | 34 | 29832 | 0,007 | 0,08 | 0,46 |
| 16 | 26 | 28702,5 | 0,4 | -7,49 | -17,73 |
| 17 | 35 | 29513 | 1,95 | -2,06 | -1,06 |
| 18 | 36 | 29940 | 1,7 | 0,80 | 0,47 |
| 19 | 42 | 25468,5 | 1 | -29,19 | -33,48 |
| 20 | 53 | 29806,5 | 1,5 | -0,09 | -0,06 |
| 21 | 28 | 29464,5 | 3,6 | -2,38 | -0,67 |
| 22 | 50 | 29869 | 20 | 0,33 | 0,02 |
| 23 | 33 | 29677 | 0,1 | -0,96 | -4,78 |
| 24 | 25 | 29953 | 0,4 | 0,89 | 2,04 |
| 25 | 57 | 33094 | 0,171 | 21,96 | 85,20 |
| 26 | 39 | 29722,5 | 0,14 | -0,65 | -2,93 |
| 27 | 45 | 29764,5 | 0,7 | -0,37 | -0,52 |
| 28 | 31 | 30421 | 0,40233 | 4,03 | 9,04 |
| 29 | 23 | 29843 | 0,013 | 0,15 | 0,88 |
| 30 | 52 | 29685,5 | 0,6 | -0,90 | -1,45 |
| 31 | 24 | 29870 | 1,2 | 0,34 | 0,28 |
| 32 | 46 | 29300,5 | 2 | -3,48 | -1,77 |
| 33 | 41 | 29804 | 1,46 | -0,11 | -0,07 |
| 34 | 6 | 29818,5 | 0,8 | -0,01 | -0,01 |

Analyte **S,d** Sample **B1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **0,25** | **0,008** | **15** |

**z&zeta-Score diagram**

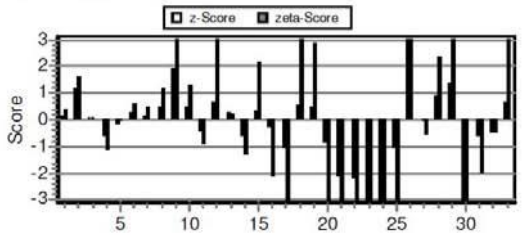



| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 0,261 | 10 | 0,59 | 0,81 |
| 2 | 22 | 0,2795 | 10 | 1,57 | 2,03 |
| 3 | 21 | 0,2565 | 18 | 0,35 | 0,28 |
| 4 | 20 | 0,2385 | 35 | -0,61 | -0,27 |
| 5 | 4 | 0,274 | 6 | 1,28 | 2,63 |
| 6 | 1 | 0,26 | 5 | 0,53 | 1,31 |
| 7 | 60 | 0,265 | 1 | 0,80 | 3,56 |
| 8 | 49 | 0,2275 | 16 | -1,20 | -1,21 |
| 9 | 43 | 0,246 | 7,3 | -0,21 | -0,41 |
| 10 | 37 | 0,2455 | 0,08 | -0,24 | -1,12 |
| 11 | 34 | 0,247 | 0,78 | -0,16 | -0,73 |
| 12 | 26 | 0,262 | 0,41 | 0,64 | 2,97 |
| 13 | 35 | 0,25 | 0,04 | 0,00 | 0,00 |
| 14 | 57 | 0,2855 | 3,715 | 1,89 | 5,34 |
| 15 | 31 | 0,2575 | 4,83762 | 0,40 | 1,01 |

Analyte **S,d** Sample **K1**

| Assigned value | Assigned 2*UC | Targ 2SD, % |
|---|---|---|
| **0,31** | **0,007** | **15** |

**z&zeta-Score diagram**




| Nr | Lab | Mean | Reported UC,% | z | zeta |
|---|---|---|---|---|---|
| 1 | 12 | 0,3135 | 5 | 0,15 | 0,41 |
| 2 | 22 | 0,337 | 10 | 1,16 | 1,57 |
| 3 | 21 | 0,3115 | 18 | 0,06 | 0,05 |
| 4 | 18 | 0,296 | 8 | -0,60 | -1,13 |
| 5 | 20 | 0,306 | 35 | -0,17 | -0,07 |
| 6 | 19 | 0,3155 | 6 | 0,24 | 0,55 |
| 7 | 4 | 0,313 | 4 | 0,13 | 0,42 |
| 8 | 1 | 0,32 | 5 | 0,43 | 1,15 |
| 9 | 48 | 0,3545 | 2,8 | 1,91 | 7,33 |
| 10 | 10 | 0,32 | 4,38 | 0,43 | 1,28 |
| 11 | 2 | 0,3 | 6,47 | -0,43 | -0,97 |
| 12 | 60 | 0,325 | 1 | 0,65 | 3,89 |
| 13 | 29 | 0,3155 | 16 | 0,24 | 0,22 |
| 14 | 43 | 0,295 | 7,3 | -0,65 | -1,32 |
| 15 | 54 | 0,3175 | 0,1 | 0,32 | 2,14 |
| 16 | 37 | 0,3025 | 0,08 | -0,32 | -2,14 |
| 17 | 34 | 0,285 | 1,29 | -1,08 | -6,32 |
| 18 | 26 | 0,3225 | 0,41 | 0,54 | 3,51 |
| 19 | 35 | 0,32 | 0,009 | 0,43 | 2,86 |
| 20 | 36 | 0,29 | 0,09 | -0,86 | -5,71 |
| 21 | 42 | 0,26 | 11,5 | -2,15 | -3,26 |
| 22 | 53 | 0,258 | 3,27 | -2,24 | -9,49 |
| 23 | 28 | 0,1835 | 0,12 | -5,44 | -36,12 |
| 24 | 50 | 0,12 | 0,04 | -8,17 | -54,28 |
| 25 | 25 | 0,2855 | 0,08 | -1,05 | -7,00 |
| 26 | 57 | 0,4195 | 3,203 | 4,71 | 14,45 |
| 27 | 45 | 0,308 | 0,06 | -0,09 | -0,57 |
| 28 | 31 | 0,3305 | 4,83762 | 0,88 | 2,35 |
| 29 | 52 | 0,3405 | 0,03 | 1,31 | 8,71 |
| 30 | 24 | 0,232 | 7,5 | -3,35 | -8,32 |
| 31 | 46 | 0,296 | 4 | -0,60 | -2,04 |
| 32 | 41 | 0,2975 | 16,205 | -0,54 | -0,51 |
| 33 | 6 | 0,325 | 0,1 | 0,65 | 4,28 |

# Documentation page

| | | |
|---|---|---|
| Publisher | Finnish Environment Institute (SYKE) | Date<br>February 2011 |
| Author(s) | Mirja Leivuori, Minna Rantanen, Kaija Korhonen-Ylönen ja Markku Ilmakunnas | |
| Title of publication | Proficiency test 5/2010<br>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 (Proftest 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 2010. One peat sample and one coal sample were delivered to the laboratories for the analysis of each measurement. In total, 58 laboratories participated in the proficiency test. The test performed in collaboration with the working group (WG) of the European co-operation for Accreditation (EA) for Interlaboratory Comparisons (EA WG ILC in Testing).<br><br>The robust means of the reported results by the participants were used as the assigned values for measurements. 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, 84 % of the participating laboratories reported the satisfactory results. About 78 % of the participants used accredited methods and 87 % of their results were satisfactory. In measurement of the gross calorific value from the peat sample 77 % of the results were satisfactory and respectively in measurement of the coal sample 71 % from the results were satisfactory. In measurement of the net calorific value from the peat sample 74 % of the results were satisfactory and respectively in measurement of the coal sample 71 % from the results were satisfactory. | |
| Keywords | Proficiency test, interlaboratory comparison, Proftest, SYKE, 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 4/2011 | |
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| Printing place and year | Helsinki 2011 | |
| Other information | | |

# Kuvailulehti

| | | |
|---|---|---|
| Julkaisija | Suomen ympäristökeskus (SYKE) | Julkaisuaika<br>Helmikuu 2011 |
| Tekijä(t) | Mirja Leivuori, Minna Rantanen, Kaija Korhonen-Ylönen ja Markku Ilmakunnas | |
| Julkaisun nimi | Laboratorioiden välinen pätevyyskoe 5/2010<br>Kalorimetrinen ja tehollinen lämpöarvo polttoaineista | |
| Julkaisun osat/<br>muut saman projektin tuottamat julkaisut | Julkaisu on saatavana myös internetistä: http://www.ymparisto.fi/julkaisut | |
| Tiivistelmä | Suomen ympäristökeskus (Proftest SYKE) järjesti syyskuussa 2011 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin ja kosteuden määrittämiseksi turpeesta ja kivihiilestä. Pätevyyskoe järjestettiin yhteistyössä Euroopan akkreditointielinten yhteistyöjärjestön (EA) testauksen vertailumittaustyöryhmän kanssa (EA WG ILC in testing).<br><br>Pätevyyskokeeseen osallistui yhteensä 58 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 0.3 % ja muiden testisuureiden osalta korkeintaan 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.<br><br>Koko tulosaineistossa hyväksyttäviä tuloksia oli 84 %, kun vertailuarvosta sallittiin 1-15 %.n poikkeama. Noin 78 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 87 %. Kalorimetrisen lämpöarvon tuloksista oli tyydyttäviä 77 % (turve) ja 71 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat tyydyttävien tulosten osuudet olivat 74 % (turve) ja 71 % (kivihiili). | |
| Asiasanat | Pätevyyskoe, vertailumittaus, Proftest, SYKE, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, päästökerroin, tuhkan, kosteuden, hiilen, rikin, typen ja vedyn määritys, turve, hiili, ympäristölaboratoriot | |
| Julkaisusarjan nimi<br>ja numero | Suomen ympäristökeskuksen moniste 4/2011 | |
| Julkaisun teema | | |
| Projektihankkeen nimi<br>ja projektinumero | | |
| Rahoittaja/<br>toimeksiantaja | | |
| Projektiryhmään<br>kuuluvat organisaatiot | | |
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| | Sivuja<br>70 | Kieli<br>englanti |
| | Luottamuksellisuus<br>Julkinen | Hinta |
| Julkaisun myynti/<br>jakaja | Suomen ympäristökeskus, Asiakaspalvelu<br>E-mail: neuvonta.syke@ymparisto.fi<br>Puh. 020 610 183<br>Telefax. 020 490 2190 | |
| Julkaisun kustantaja | Suomen ympäristökeskus, PL 140, 00251 Helsinki | |
| Painopaikka ja -aika | Helsinki 2011 | |
| Muut tiedot | | |

# Presentationsblad

| | | |
|---|---|---|
| Utgivare | Finlands Miljöcentral (SYKE) | Datum<br>Februari 2011 |
| Författare | Mirja Leivuori, Minna Rantanen, Kaija Korhonen-Ylönen och Markku Ilmakunnas | |
| Publikationens titel | Provningsjämförelse 5/2010<br>Kalorimetriskt och effektivt värmevärde i bränsle | |
| Publikationens delar/ andra publikationer inom samma projekt | Publikationen finns tillgänglig på internet<br>www.ymparisto.fi/julkaisut | |
| Sammandrag | Under September 2010 genomförde Finlands Miljöcentral (Proftest SYKE) en provningsjämförelse, som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, svavel, väte, kol, nitrogen, aska och fuktighet i torv och stenkol. Tillsammans 58 laboratorier deltog i jämförelsen. Testet utfördes in samarbete med arbetsgruppen för arbetsgruppen (WG) för Europeiska samarbetet för ackreditering (EA) för Provningsjämförelser (EA WG ILC i Testing).<br><br>Som referensvärde av analytens koncentration användes mest det robust medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 84 % av alla resultaten acceptabelt, när total deviation på 1–15 % från referensvärdet accepterades. | |
| Nyckelord | provningsjämförelse, Proftest, SYKE, kalorimetriskt och effektivt värmevärde, utsläppskoefficient, svavel, väte, kol, nitrogen, aska och fuktighet, stenkol, torv, miljölaboratorier | |
| Publikationsserie och nummer | Suomen ympäristökeskuksen raportteja 4/2011 | |
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| Projektets namn och nummer | | |
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