



GA no 282826

## Report Round Robin I Validation of “standard” test methods

---

Deliverable no. D8.1

### Report Round Robin I – Validation of “standard” test methods

Dissemination Level		
<b>PU</b>	Public	X
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	

Nature		
<b>R</b>	Report	X
<b>O</b>	Other	

Deliverable Details	
Due date:	31.12.2012
Submission date:	28.02.2013
Authors:	Magdalena Wojcik and Martin Englisch, <i>ofi</i>
Involved participants:	See list chapter 3
WP no. and title:	WP 8 Fuel specification, lab analysis and quality assurance
WP leader:	<i>ofi</i>
Task no. and title:	8.1 Fuel properties & investigation of “standard” parameters
Task leader:	<i>ofi</i>
Draft/Final:	FINAL
Keywords:	

## Table of Contents

<b>1</b>	<b><i>Introduction</i></b> .....	<b>3</b>
<b>2</b>	<b><i>Organization of Round Robin</i></b> .....	<b>3</b>
<b>3</b>	<b><i>Participants</i></b> .....	<b>5</b>
<b>4</b>	<b><i>Terminology and performance parameters</i></b> .....	<b>5</b>
<b>5</b>	<b><i>Evaluation procedure</i></b> .....	<b>9</b>
<b>6</b>	<b><i>Summary and conclusions</i></b> .....	<b>45</b>
<b>7</b>	<b><i>References</i></b> .....	<b>48</b>

---

## 1 Introduction

For parameters listed in EN 14961 “Solid biofuels — Fuel specifications and classes — Part 1: General requirements” a complete set of analytical methods was developed. They include the determination of most frequently required chemical and physical parameters in solid biofuel characterization like moisture content, bulk density, ash content, C, H, N, major and minor elements, Cl, S, content of volatile matter etc.. Analytical methods listed in EN 14961 are optimised for solid biofuels but not for torrefied biomass. Since torrefied biomass gains increasing interest a proper characterisation of these new fuels seems important. Extending the applicability of methods for solid biofuel to torrefied materials would be a fast and economic option if the applicability of the methods and a respective validation based on an international round robin is successfully proven.

Before including torrefied biofuels in international standards for solid biofuels a validation exercise is required to obtain necessary data on the performance of the methods with respect to accuracy, reliability and applicability. This validation round robin was one goal of the SECTOR project. It furthermore should address doubts if the methods deliver reasonable accurate results for torrefied biofuels.

Due to many analytical possibilities and freedom of selection of equipment given in some of the existing standards the results represent a picture of the performance of the participating laboratories, the majority accredited or otherwise qualified with experience in solid biofuel analysis. A final evaluation of the chemical test methods themselves should be done with care due to this wide variation in equipment and execution of analysis and due to different level of experience of participating laboratories.

The present report summarises the results of the round robin and provides a statistical evaluation of these tests, which were carried out in accordance with the provisions of ISO 5725.

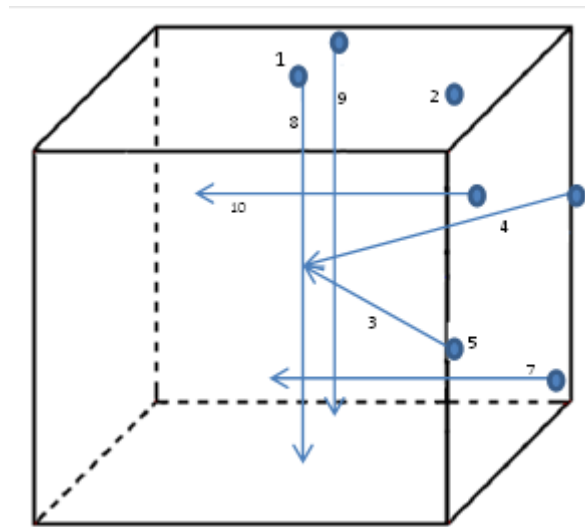
## 2 Organization of Round Robin

For the present round robin a sample from an industrial plant was taken to represent typical conditions. A torrefied wood pellets sample (6mm) was provided by the company Topell Nederland BV. The sample was produced from wood chips and forest residues containing usual mineral contaminations. The sample was delivered in one big bag to **ofi** for homogeneity testing.

Homogeneity testing was based on ash content and content of volatile matter to check for distribution of minerals and the homogeneity of torrefaction. Two independent test series

were performed. One series with 10 mixed samples (each about 0,5kg) taken from the big bag and one series with 46 mixed samples (each 0,1kg) taken from each sample send to the single participants of the round robin.

Figure 1: Sampling points for homogeneity test of torrefied sample big bag.



Each participant received a homogeneous sample of 4-8kg, depending on the methods registered. All samples sent to participants were sampled and checked by **ofi** before dispatch.

Methods included in the round robin are listed in table 1.

Table 1: methods provided

Parameter	Method/ Standard
Bulk density	acc. EN 15103
Mechanical durability	acc. EN 15210-1
Moisture content	acc. EN 14774-1 or 2
Ash content	acc. EN 14775
Calorific value	acc. EN 14918
Content of chlorine and sulphur	acc. EN 15289
Content of volatile matter	acc. EN 15148
Content of carbon, hydrogen, nitrogen	acc. EN 15104
Content of major elements	acc. EN 15290
Content of minor elements	acc. EN 15297
Ash melting behaviour	acc. CEN/TS 15370

### 3 Participants

A total of 43 laboratories from 17 countries and from 4 different continents participated in this round robin. The participation was open for all (experienced) laboratories worldwide. The number of individual tests by a particular participant was not limited. The number of participants in different countries and the tested methods are given table 2.

The **anonymity** of test results is ensured for all participants due to an appropriate encoding procedure.

Table 2: participating laboratories and methods provided

PARTICIPANTES	Country	EN 15103	EN 15210-1	EN 14774 1 or 2	EN 14775	EN 14918	EN 15289	EN 15148	EN 15104	EN 15290	EN 15297	CEN/TS 15370-1
BBRG, University of British Columbia	Can	x	x	x	x	x						
Belab AB	Se	x	x	x	x	x	x	x	x			x
Bioenergy 2020+ GmbH	A			x	x	x	x	x	x	x	x	
Biomass Energy Lab	USA	x	x	x	x	x	x	x	x			
BLT	A	x	x	x	x	x		x				
Bränselaboratoriet Umeå AB	Se	x	x	x	x	x	x	x	x			x
CENER	Es	x	x	x	x	x		x	x			
CRA-W U13	Be	x	x	x	x	x		x				
Danish Technological Institute	DK	x	x	x	x							
DBFZ Deutsches Biomasse Forschungszentrum GmbH	D	x	x	x	x	x	x	x	x	x	x	
Dong Energy, ENV Lab.	DK	x	x	x	x	x	x	x	x	x	x	
ECN	Nl			x	x	x	x	x	x	x	x	
ENAS	Fi	x	x	x	x	x	x	x	x	x	x	x
Energie AG Oberösterreich Kraftwerke GmbH	A			x	x	x	x	x	x			
EON	Uk			x	x	x	x	x	x	x	x	
Eskom Holdings SOC Limited	SA	x	x	x	x	x	x	x	x	x	x	x
Eurofins Environment Sweden AB	Se	x	x	x	x	x	x	x	x	x	x	x
Eurofins Umwelt Ost GmbH, Ndl. Freiberg	D	x	x	x	x	x	x	x	x	x	x	x
Force	DK	x	x	x	x	x	x	x	x	x	x	x
HAWK Hochschule für Angewandte Wissenschaft und Kunst	D	x	x	x	x	x	x		x			
HFA	A	x	x	x		x				x	x	
IEN, Poland	Pl			x	x	x		x	x			
Laboratório Nacional de Energia e Geologia, I.P.	Pt	x	x	x	x	x	x	x	x	x	x	x
LCB	Es	x	x	x	x	x	x	x	x	x		x
NUON	Nl			x	x	x	x	x	x			
OFI	A	x	x	x	x	x	x	x	x	x	x	x
Ramboll	Fi	x	x	x	x	x	x	x	x	x	x	x
RWE	D	x		x	x	x	x	x	x	x	x	x
SGS Institut Fresenius GmbH	D	x	x	x	x	x	x	x	x	x	x	x
SGS Minerals Services	Can	x	x	x	x	x		x	x			x
SP	Se	x	x	x	x	x	x	x	x	x	x	x
Suez	Be	x	x	x	x	x	x	x	x	x	x	x
TES	Uk	x	x	x	x	x	x	x	x	x	x	x
TE-Tol	Sl			x	x	x			x			
TFZ	D	x	x	x	x	x						
TLR International Laboratories	Nl	x	x	x	x	x	x	x	x	x	x	x
TNB Research Lab	My			x	x	x	x	x	x	x	x	x
TU-Wien	A			x	x	x	x	x	x			x
Unidad de Desarrollo	Chile	x	x	x	x	x				x		
University Teknologi Petronas	My	x		x	x	x		x	x	x		
Vattenfall	DK	x	x	x	x	x	x	x	x	x		
Verbund	A			x	x	x	x	x	x			x
VTT	Fi	x		x	x	x	x	x	x			

### 4 Terminology and performance parameters

The terms specified below, which are used in the statistical evaluation of the validation round robin are generally known or are defined, among other sources, in ISO 5725-1:1994 and

previous issues of this standard, in ISO Guide 43-1:1997 and in CEN Guide 13:2008 as follows:

### Arithmetic mean, average ( $\bar{x}$ ):

Quotient of the sum of independently identified individual values  $x_i$  and their number  $n$ :

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i$$

**Note:** In the evaluation of the comparison test  $m$  is used for  $x$  and it is calculated as an overall mean of  $x_i$  ( $x_i$  = test result of a particulate participant = mean value of an particulate number of individual measurements in one laboratory), after removal of outliers

### Variance ( $s^2$ ):

Quotient of the sum of squares of deviations of the individual values from the arithmetic mean and  $(n - 1)$ , i.e. number of degrees of freedom:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2$$

### Standard deviation ( $s$ ):

Positive value of the root of the variance of a series of measured values:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

### Coefficient of variation:

Dispersion of individual results expressed as quotient of the standard deviation and arithmetic mean in percent.

### Repeatability conditions:

Conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.

**Reproducibility conditions:**

Conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

**Between-laboratory standard deviation ( $s_L$ ):**

Term including between-operator and between-equipment variability.

**Repeatability standard deviation ( $s_r$ ):**

Standard deviation of test results obtained under repeatability conditions:

$$s_r = \sqrt{\frac{\sum_{i=1}^n (a_i - 1) s_i^2}{(\sum_{i=1}^n a_i) - n}}$$

$a_i$  = number of test results per participant

$s_i$  = standard deviation of a particulate test result

$n$  = number of participants

**Reproducibility standard deviation ( $s_R = (s_r^2 + s_L^2)^{0,5}$ ):**

The standard deviation of test results obtained under reproducibility conditions.

**Repeatability limit ( $r$ ):**

A value less than or equal to what the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95%:

$$r = 2,8 * s_r$$

**Reproducibility limit ( $R$ ):**

A value less than or equal to what the absolute difference between two test results obtained under reproducibility conditions may be expected to be with a probability of 95%:

$$R = 2,8 * s_R$$

**Outlier according to Cochran:**

With this test, the within-laboratory variances are tested for homogeneity ("outliers regarding standard deviations"):

$$\text{Cochran criterion } C = \frac{s_{\max}^2}{\sum_{i=1}^n s_i^2}$$

$s_{\max}$  = highest value of all  $s_i$

C-values for statistical (probability 99%) and possible (probability 95%) outliers are listed in relevant literature

**Outlier according to Grubbs:**

With this test, the extreme values of  $x_i$  ( $x_{\text{extr}} = x_{\text{max}}$  or  $x_{\text{min}}$ ) are tested to be an outlier ("outlier regarding the mean value")

$$\text{Grubbs criterion } G = \left| \bar{x}_p - \bar{x}_{\text{extr}} \right| / s_p$$

$x_p$  = general mean incl. test result which is tested according to Grubbs ( $x_{\text{extr}}$ )

$x_{\text{extr}}$  = extreme value of  $x_i$

$s_p$  = general standard deviation (tested result is taken into account as in  $x_p$ )

G-values for statistical (probability 99%) and possible (probability 95%) outliers from literature



## 5 Evaluation procedure

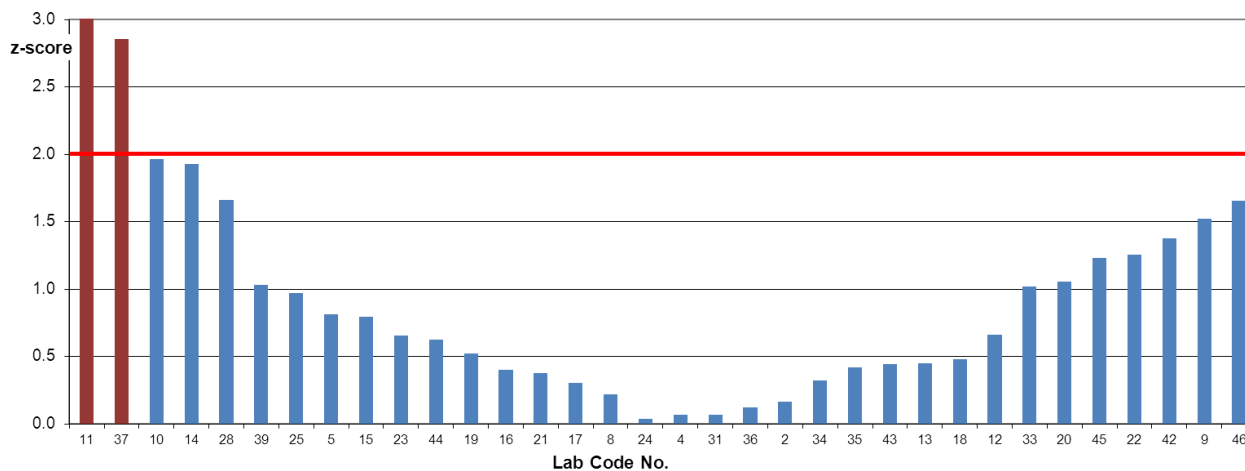
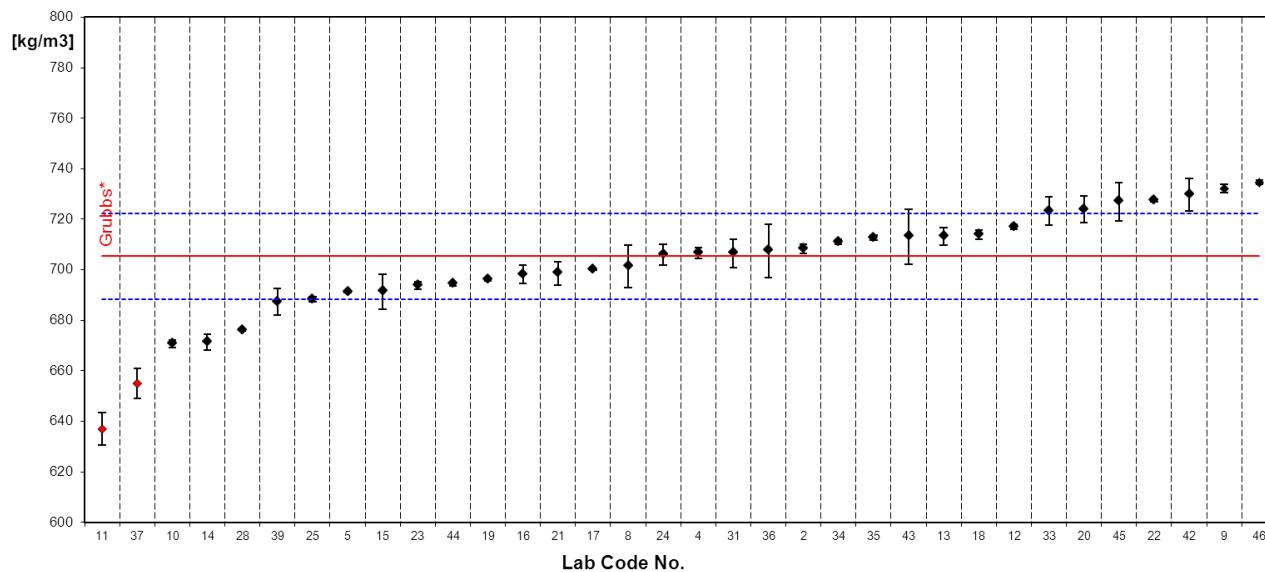
The test results provided by the individual participants were subjected to a statistical evaluation in accordance with the provisions of ISO 5725-2:2002 ("Accuracy [trueness and precision] of measurement methods and results" - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method"). This was done independent of the fact of how many participants attended the individual tests. In all cases the raw data provided by the participants served as a basis for this evaluation (individual test results).

After the calculation of **means** and **standard deviations** for the individual testing labs, **outlier tests according to Cochran and Grubbs** were conducted in order to identify *possible outliers* in this way (95% probability; marked with "\*\*") and/or *statistical outliers* (99% probability; marked with "\*\*\*").

**Statistical outliers** according to *Cochran* and according to *Grubbs* were, **in general, not taken into account in the calculation of the validation results**. Statistical stranglers were only taken into account if necessary to assure enough results for evaluation. The elimination of outliers and stranglers is iterative. By eliminating outliers, new outliers and stranglers may pop up. After each iteration outliers are eliminated, the statistical analysis is repeated to study the distribution in order to trace new outliers or stranglers. This iterative procedure will continue until no new outliers are found or, if the process brings the calculation to instability or senseless results, the number of iterations is limited manually. In a few cases, multiple outliers mask each other. In these cases, when results are not reliable, they were excluded on basis of the experience of the authors.

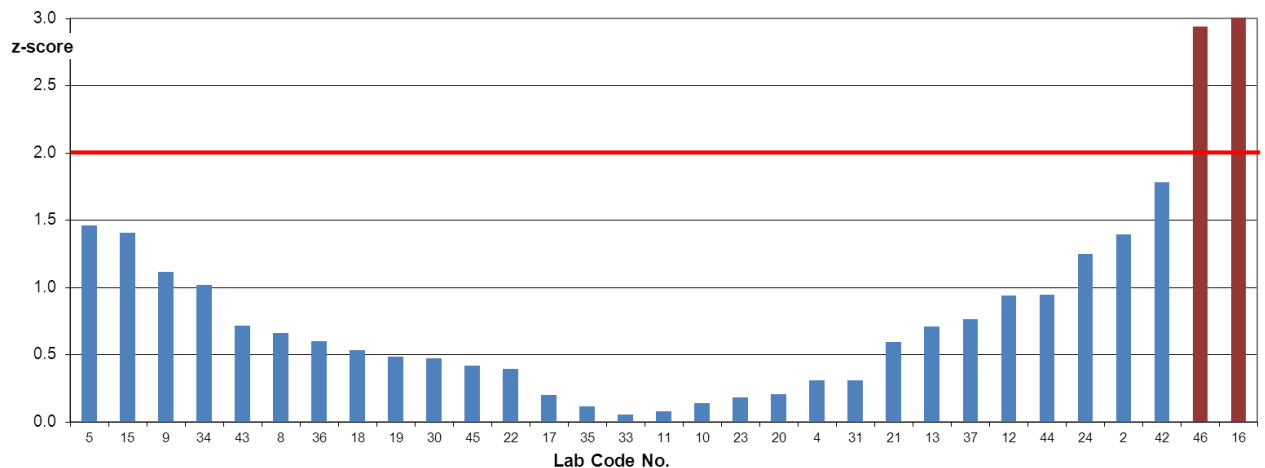
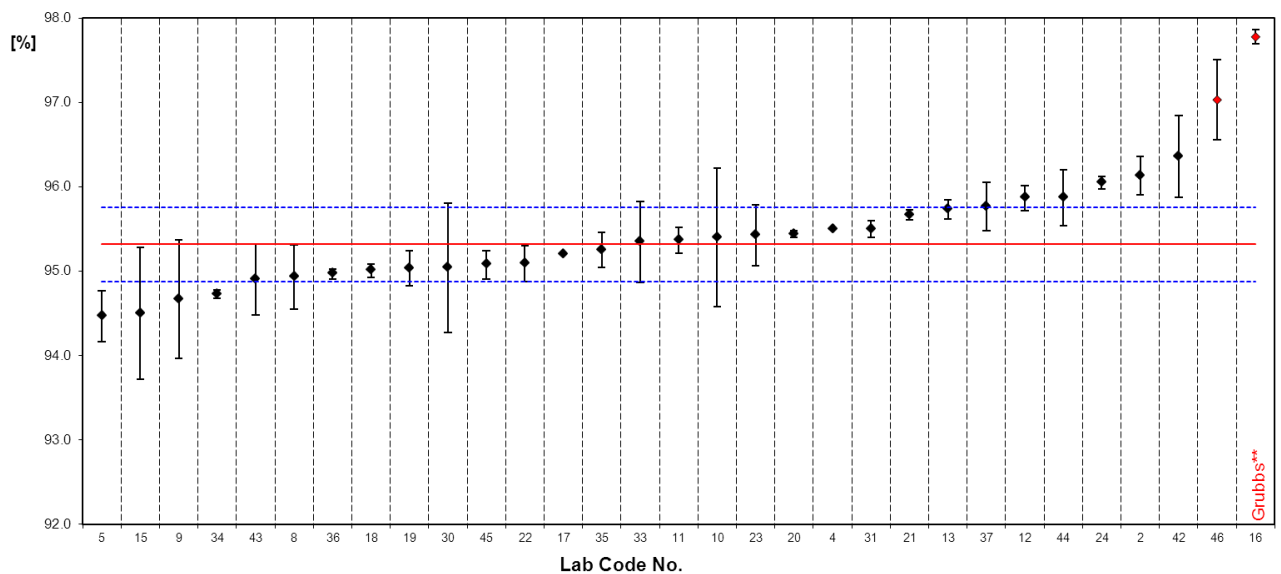
The mean value in the graph, the Z-score and the respective standard deviation given in the **graphic representation of the results** of a particular test includes just the participants after outlier correction. Those participants which were identified as outliers by the tests according to Cochran and Grubbs and that were not taken for calculation of the statistical parameters have been marked red in tables and figures. **Values marked in red in the diagrams are not used for the calculation of the statistical data!** For number of participants only labs not identified as outliers were counted.

### Results for the determination of bulk density according to EN 15103



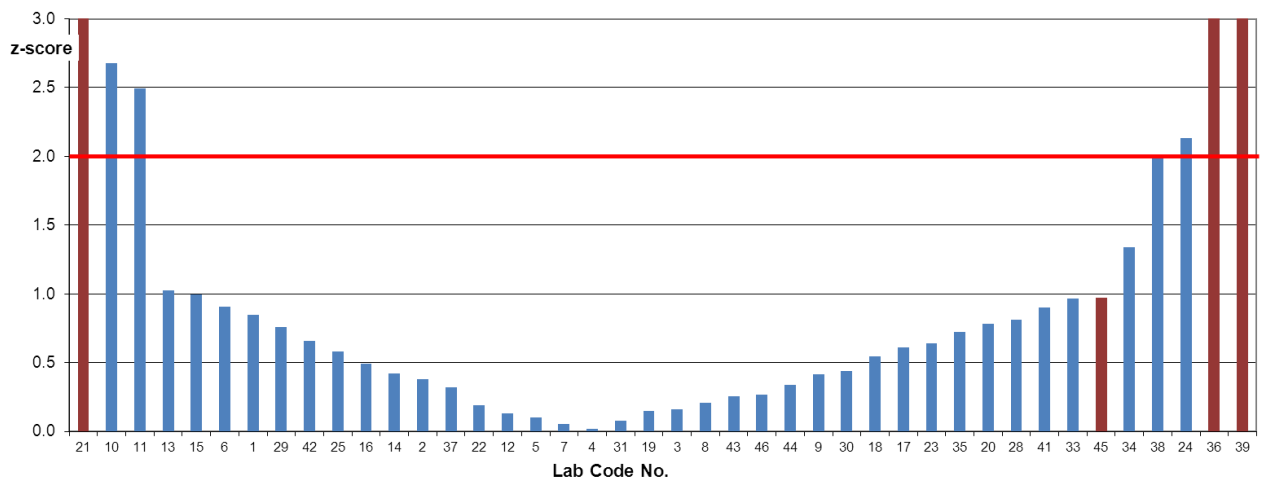
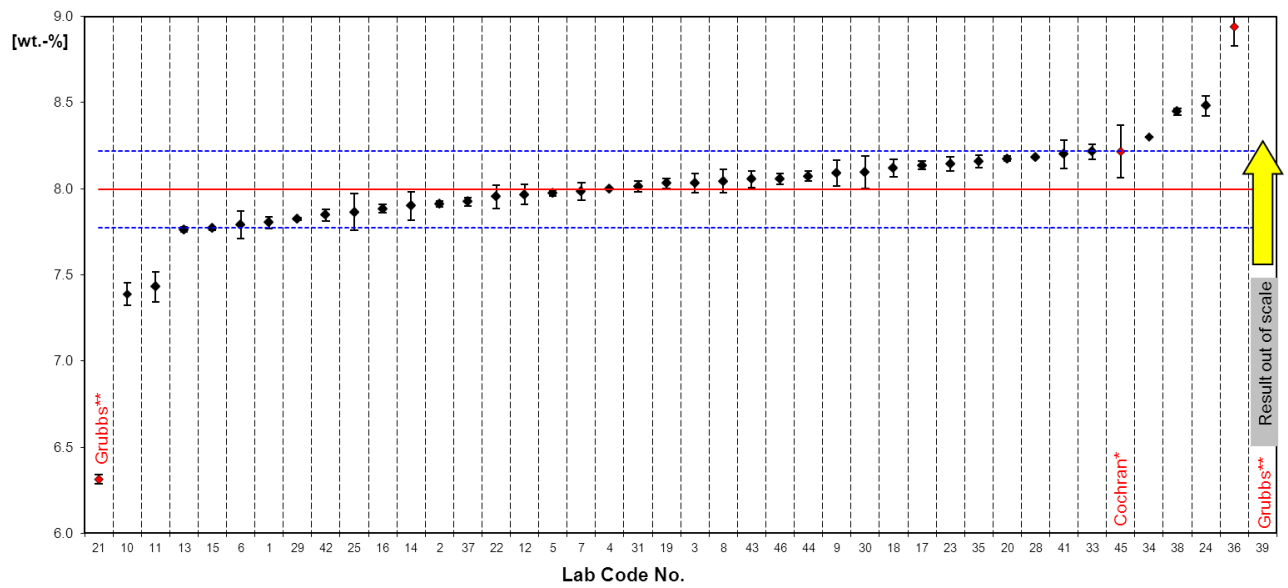
<b>General mean = assigned value</b>	<b>m</b>	<b>705</b>	<b>[kg/m3]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>20</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>4.43</b>	<b>[kg/m3]</b>
<b>Repeatability coefficient of variation</b>		<b>0.63</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>291</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>17.0</b>	<b>[kg/m3]</b>
<b>Between-laboratory coefficient of variation</b>		<b>2.42</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>310</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>17.6</b>	<b>[kg/m3]</b>
<b>Reproducibility coefficient of variation</b>		<b>2.50</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>12.4</b>	<b>[kg/m3]</b>
		<b>1.76</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>49.3</b>	<b>[kg/m3]</b>
		<b>6.99</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>32</b>	

### Results for the determination of mechanical durability according to EN 15210-1



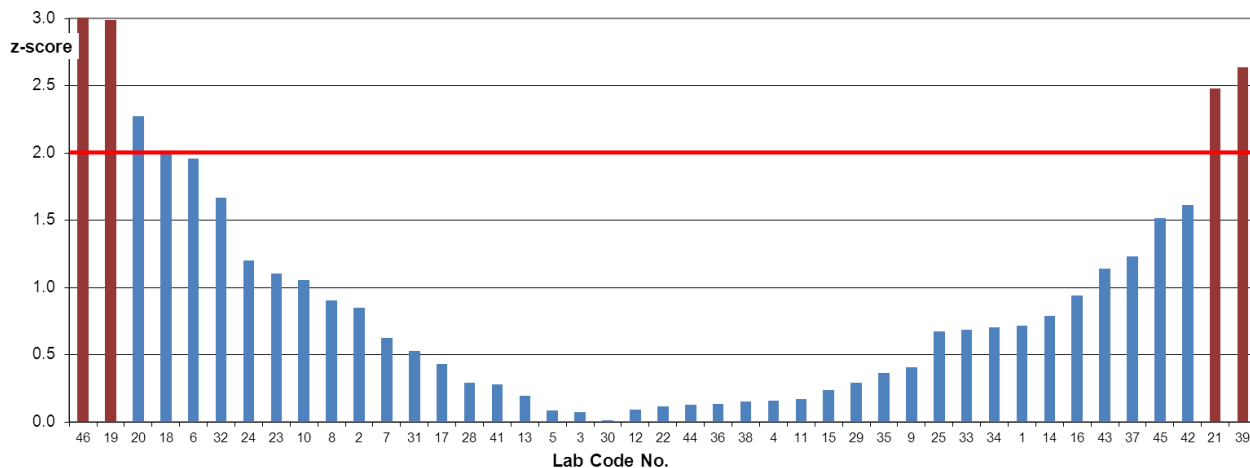
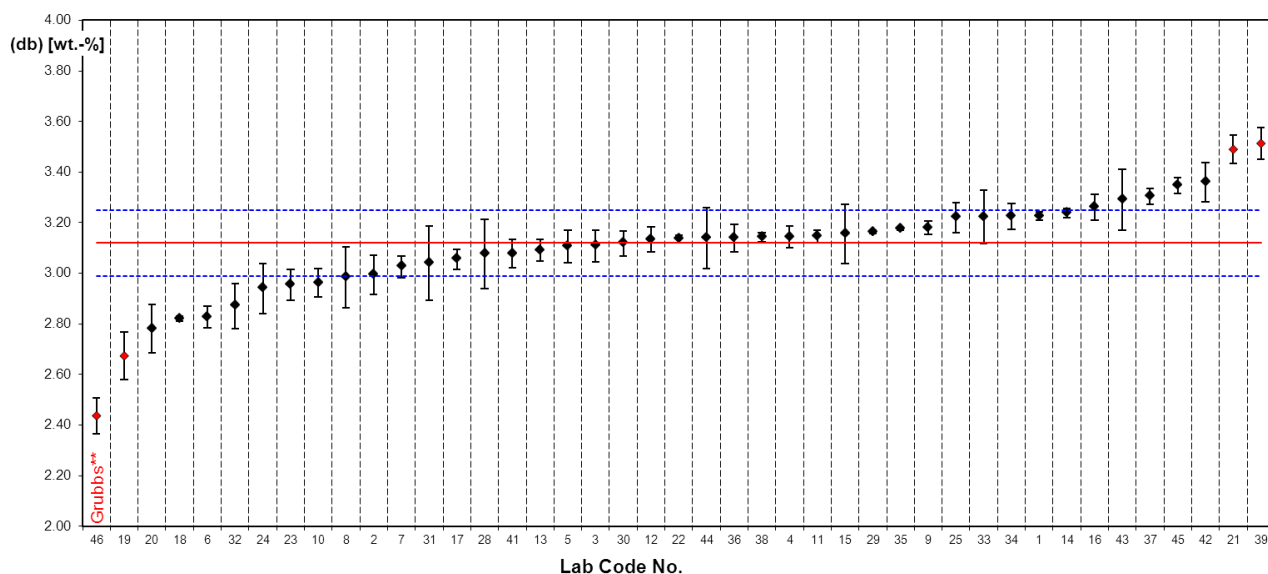
<b>General mean = assigned value</b>	<b>m</b>	<b>95.3</b>	<b>[%]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.15</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.38</b>	<b>[%]</b>
<b>Repeatability coefficient of variation</b>		<b>0.40</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.19</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.44</b>	<b>[%]</b>
<b>Between-laboratory coefficient of variation</b>		<b>0.46</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.34</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.58</b>	<b>[%]</b>
<b>Reproducibility coefficient of variation</b>		<b>0.61</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>1.08</b>	<b>[%]</b>
		<b>1.13</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>1.63</b>	<b>[%]</b>
		<b>1.72</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>29</b>	

**Results for the determination of moisture content according EN 14774-1 or 2**



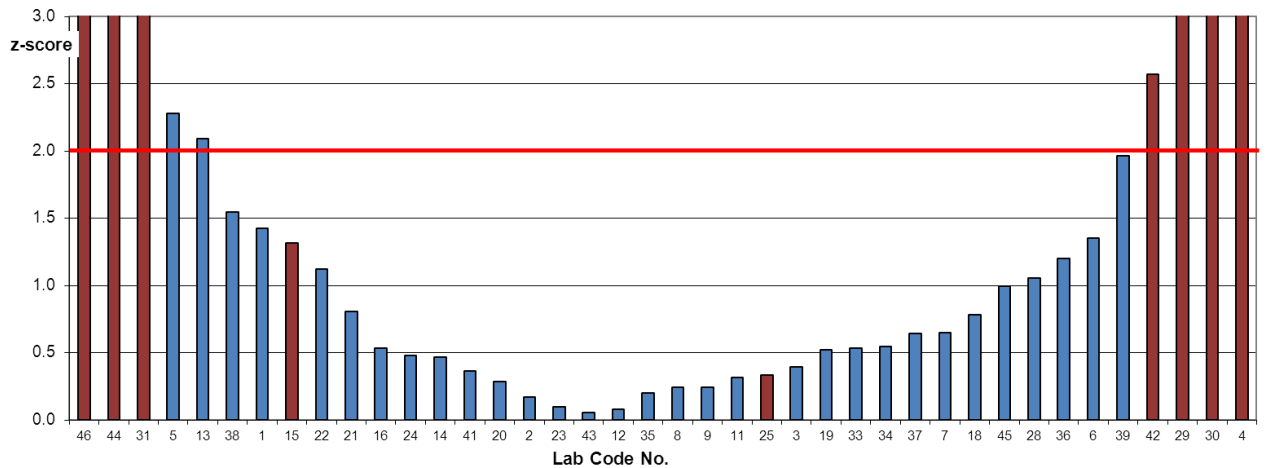
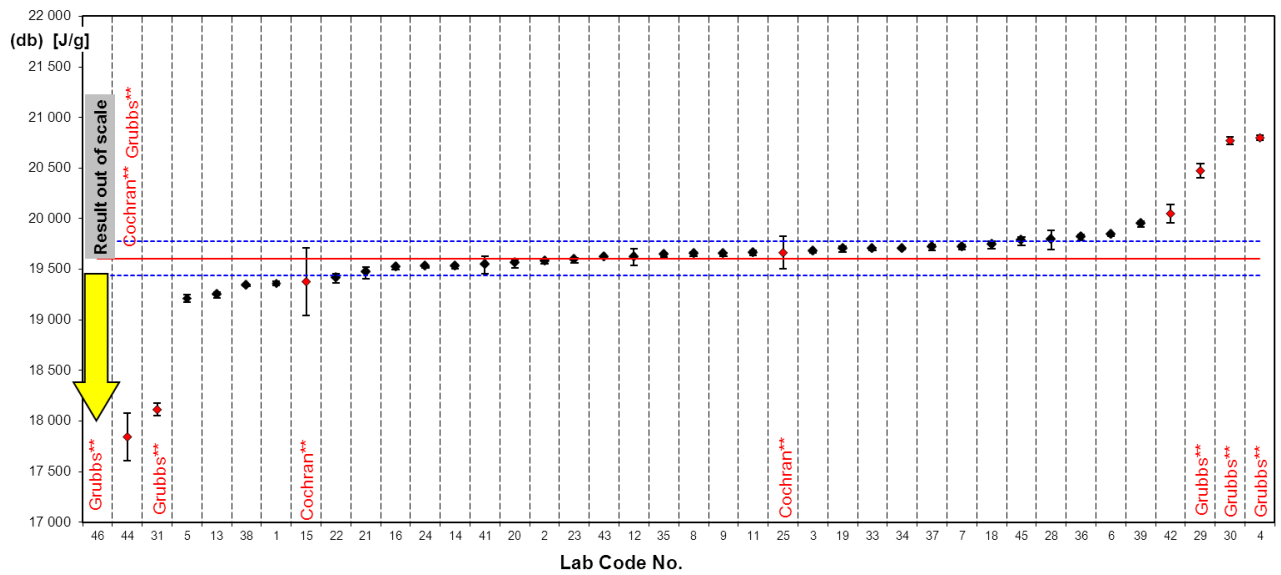
General mean = assigned value	m	8.00	[wt.-%]
Repeatability variance	$s_r^2$	0.0027	
Repeatability standard deviation	$s_r$	0.05	[wt.-%]
Repeatability coefficient of variation		0.65	%
Between-laboratory variance	$s_L^2$	0.049	
Between-laboratory standard deviation	$s_L$	0.22	[wt.-%]
Between-laboratory coefficient of variation		2.76	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.052	
Reproducibility standard deviation	$s_R$	0.23	[wt.-%]
Reproducibility coefficient of variation		2.84	%
Repeatability limit	r	0.15	[wt.-%]
		1.83	%
Reproducibility limit	R	0.64	[wt.-%]
		7.95	%
Number of participants	n	38	

### Results for the determination of ash content according to EN 14775



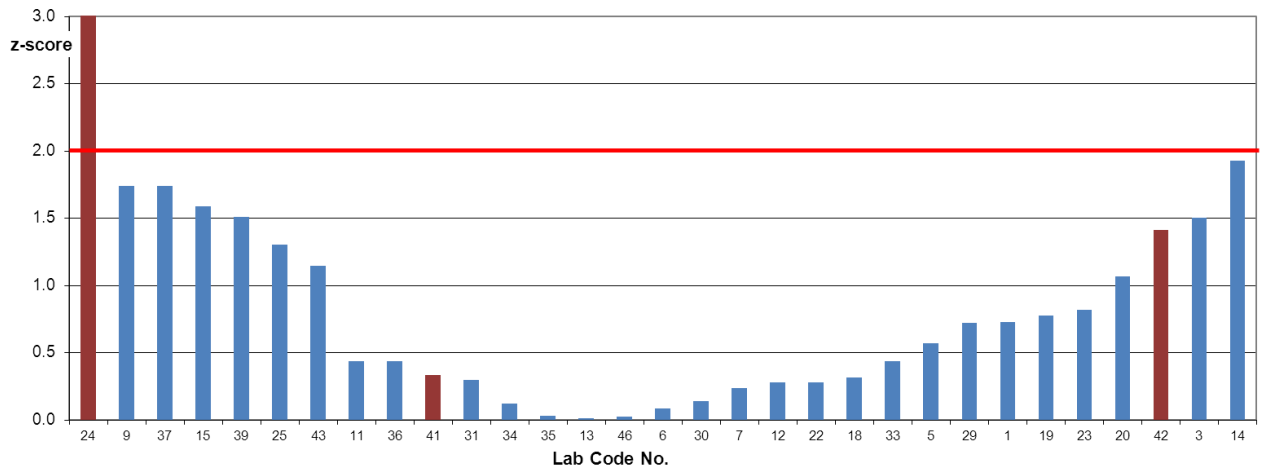
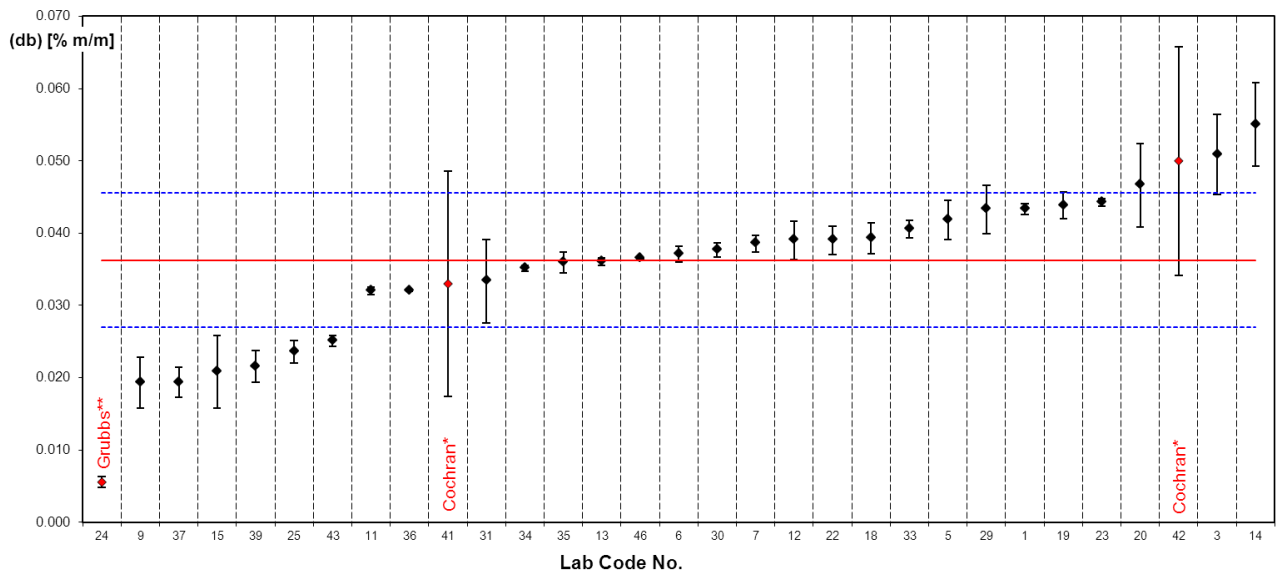
<b>General mean = assigned value</b>	<b>m</b>	<b>3.12</b>	<b>(db) [wt.-%]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.0051</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.07</b>	<b>(db) [wt.-%]</b>
<b>Repeatability coefficient of variation</b>		<b>2.29</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.017</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.13</b>	<b>(db) [wt.-%]</b>
<b>Between-laboratory coefficient of variation</b>		<b>4.21</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.022</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.15</b>	<b>(db) [wt.-%]</b>
<b>Reproducibility coefficient of variation</b>		<b>4.79</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.20</b>	<b>(db) [wt.-%]</b>
		<b>6.40</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>0.42</b>	<b>(db) [wt.-%]</b>
		<b>13.4</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>39</b>	

### Results for the determination of net calorific value according to EN 14918



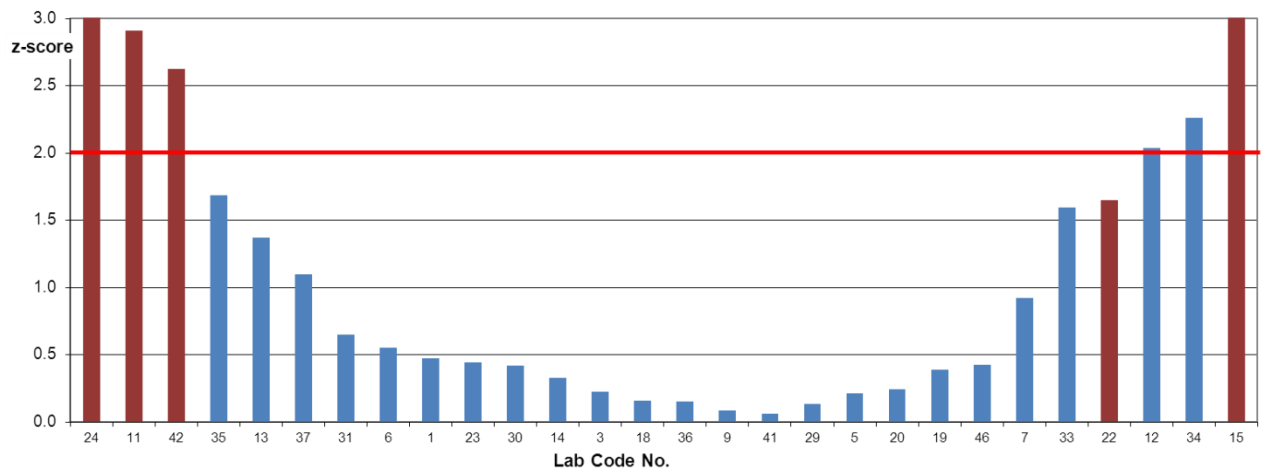
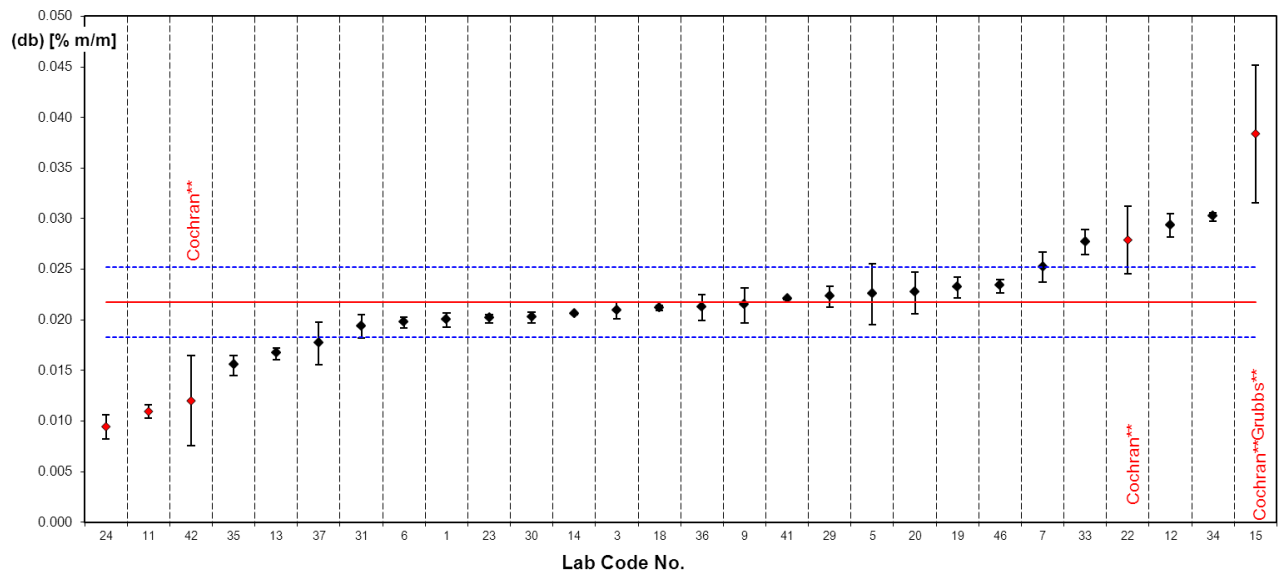
General mean = assigned value	m	19606	(db) [J/g]
Repeatability variance	$s_r^2$	1355	
Repeatability standard deviation	$s_r$	37	(db) [J/g]
Repeatability coefficient of variation		0.2	%
Between-laboratory variance	$s_L^2$	28517	
Between-laboratory standard deviation	$s_L$	169	(db) [J/g]
Between-laboratory coefficient of variation		0.86	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	29872	
Reproducibility standard deviation	$s_R$	173	(db) [J/g]
Reproducibility coefficient of variation		0.88	%
Repeatability limit	r	103	(db) [J/g]
		0.53	%
Reproducibility limit	R	484	(db) [J/g]
		2.47	%
Number of participants	n	31	

### Results for the determination of sulphur content according to EN 15289



<b>General mean = assigned value</b>	<b>m</b>	<b>0.036</b>	<b>(db) [% m/m]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.0000</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.003</b>	<b>(db) [% m/m]</b>
<b>Repeatability coefficient of variation</b>		<b>7.7</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.0001</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.009</b>	<b>(db) [% m/m]</b>
<b>Between-laboratory coefficient of variation</b>		<b>25.7</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.0001</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.010</b>	<b>(db) [% m/m]</b>
<b>Reproducibility coefficient of variation</b>		<b>26.8</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.008</b>	<b>(db) [% m/m]</b>
		<b>21.66</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>0.027</b>	<b>(db) [% m/m]</b>
		<b>75.16</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>28</b>	

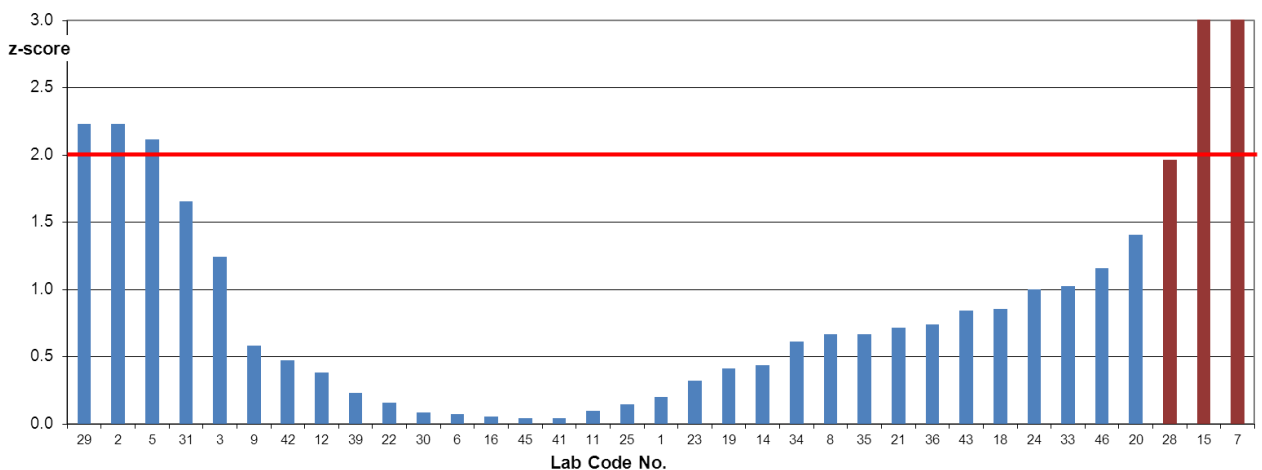
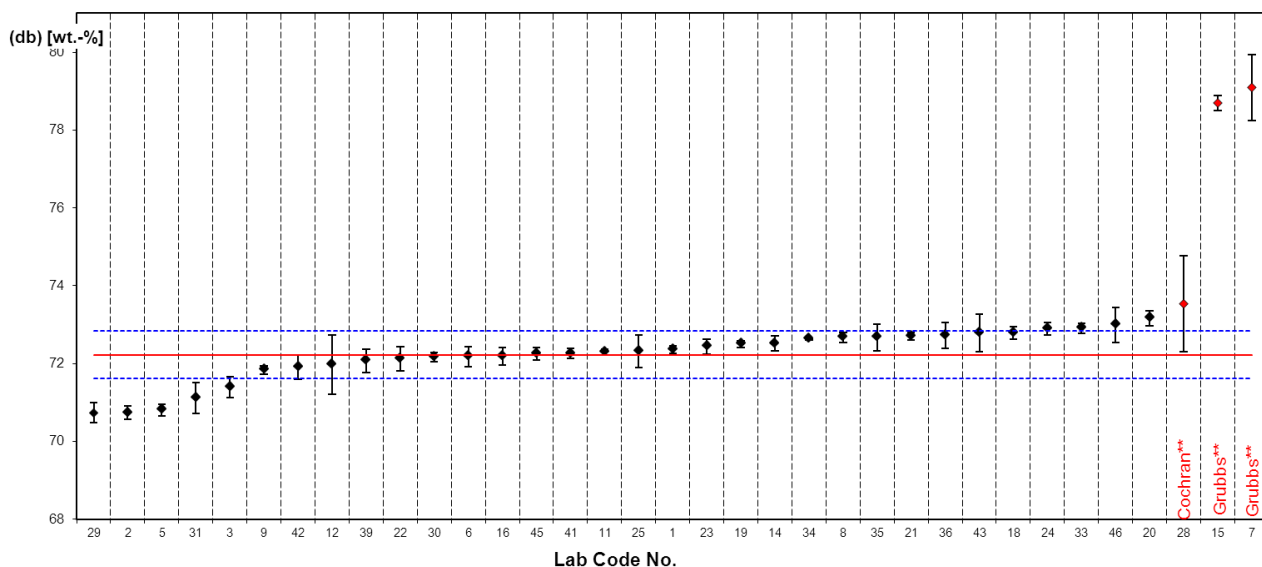
### Results for the determination of chlorine content according to EN 15289



<b>General mean = assigned value</b>	<b>m</b>	<b>0.022</b>	<b>(db) [% m/m]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.0000</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.00</b>	<b>(db) [% m/m]</b>
<b>Repeatability coefficient of variation</b>		<b>5.9</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.000</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.00</b>	<b>(db) [% m/m]</b>
<b>Between-laboratory coefficient of variation</b>		<b>16.1</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.000</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.00</b>	<b>(db) [% m/m]</b>
<b>Reproducibility coefficient of variation</b>		<b>17.1</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.004</b>	<b>(db) [% m/m]</b>
		<b>16.43</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>0.010</b>	<b>(db) [% m/m]</b>
		<b>47.86</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>23</b>	

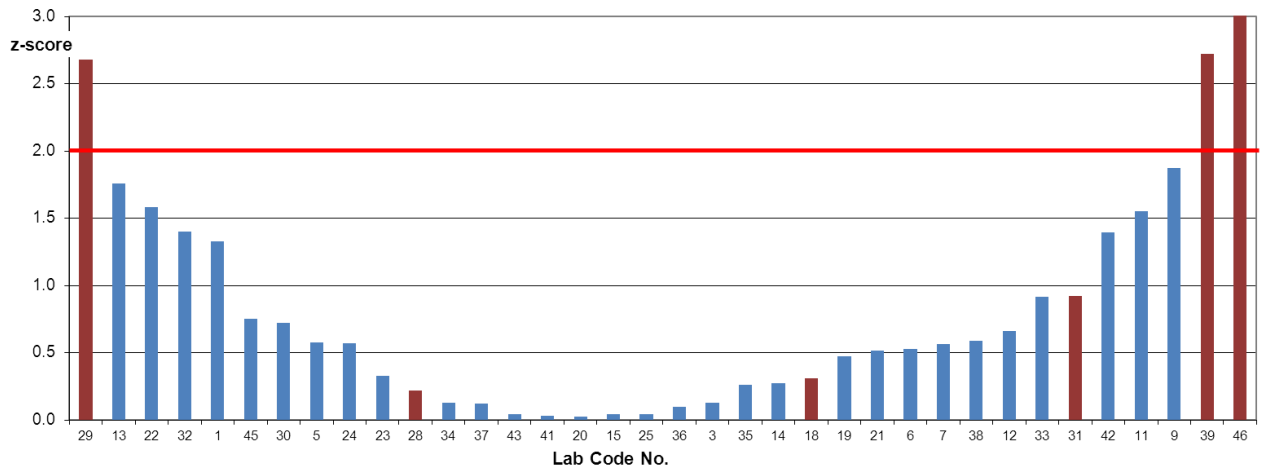
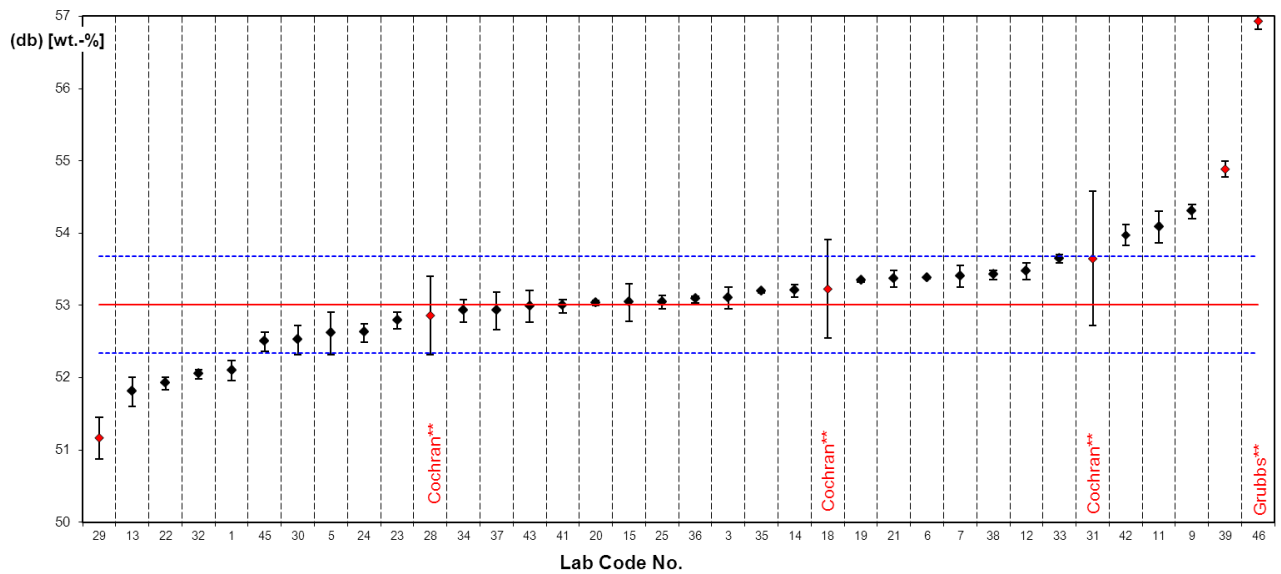


### Results for the determination of volatile matter according to EN 15148



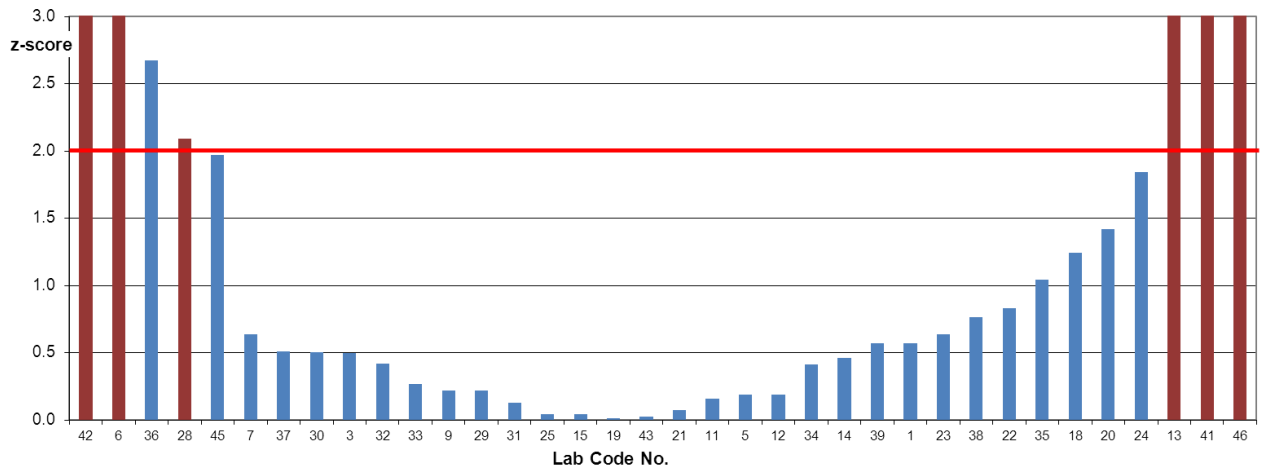
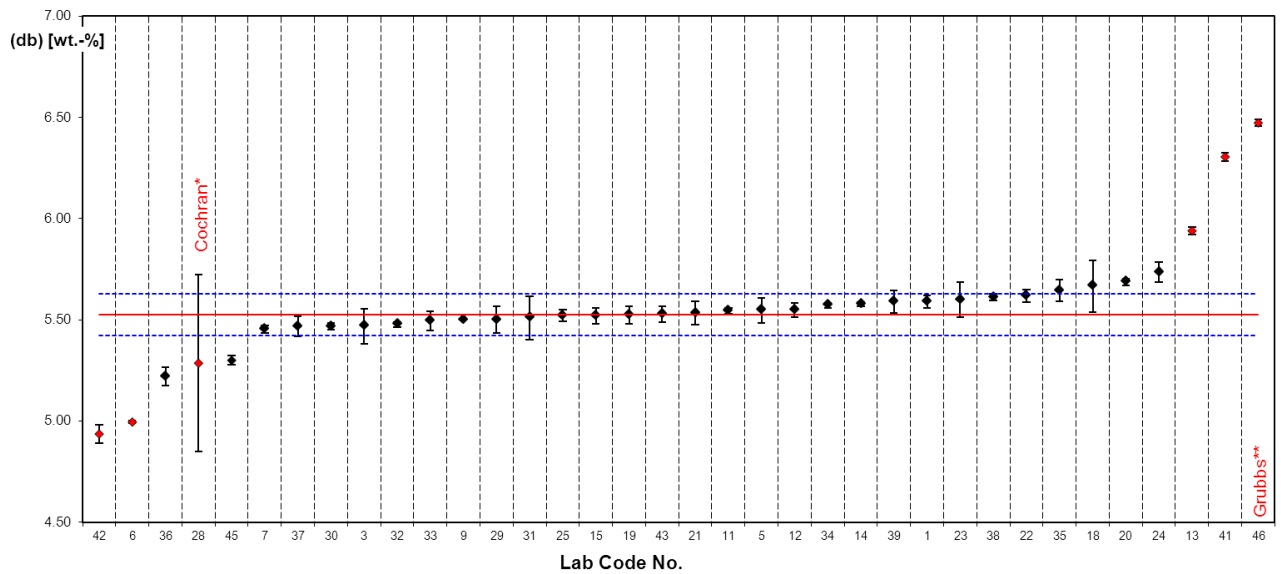
<b>General mean = assigned value</b>	<b>m</b>	<b>72.2</b>	<b>(db) [wt.-%]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.075</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.27</b>	<b>(db) [wt.-%]</b>
<b>Repeatability coefficient of variation</b>		<b>0.38</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.371</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.61</b>	<b>(db) [wt.-%]</b>
<b>Between-laboratory coefficient of variation</b>		<b>0.84</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.446</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.67</b>	<b>(db) [wt.-%]</b>
<b>Reproducibility coefficient of variation</b>		<b>0.92</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.77</b>	<b>(db) [wt.-%]</b>
		<b>1.06</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>1.87</b>	<b>(db) [wt.-%]</b>
		<b>2.59</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>32</b>	

### Results for the determination of carbon content according to EN 15104



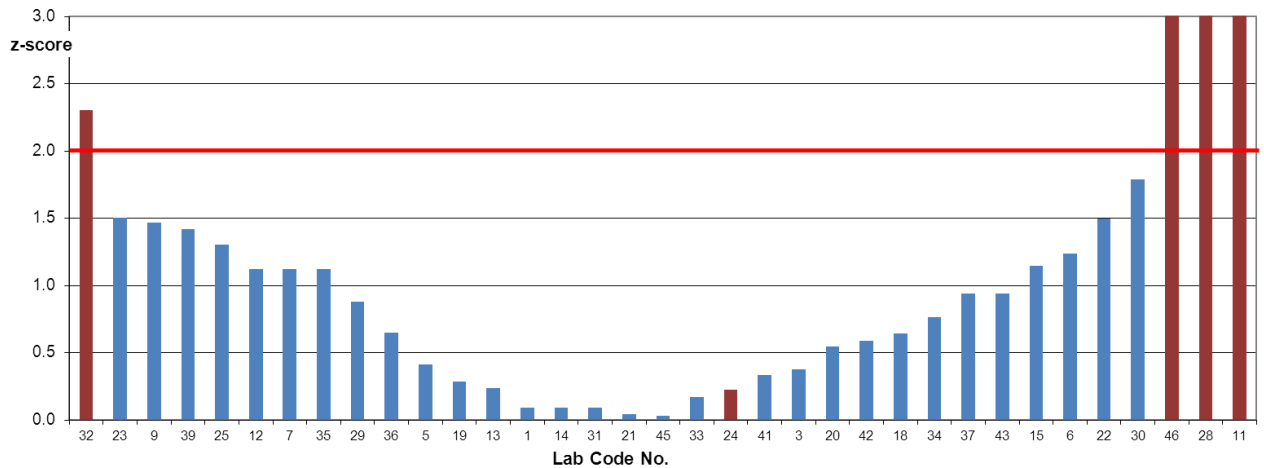
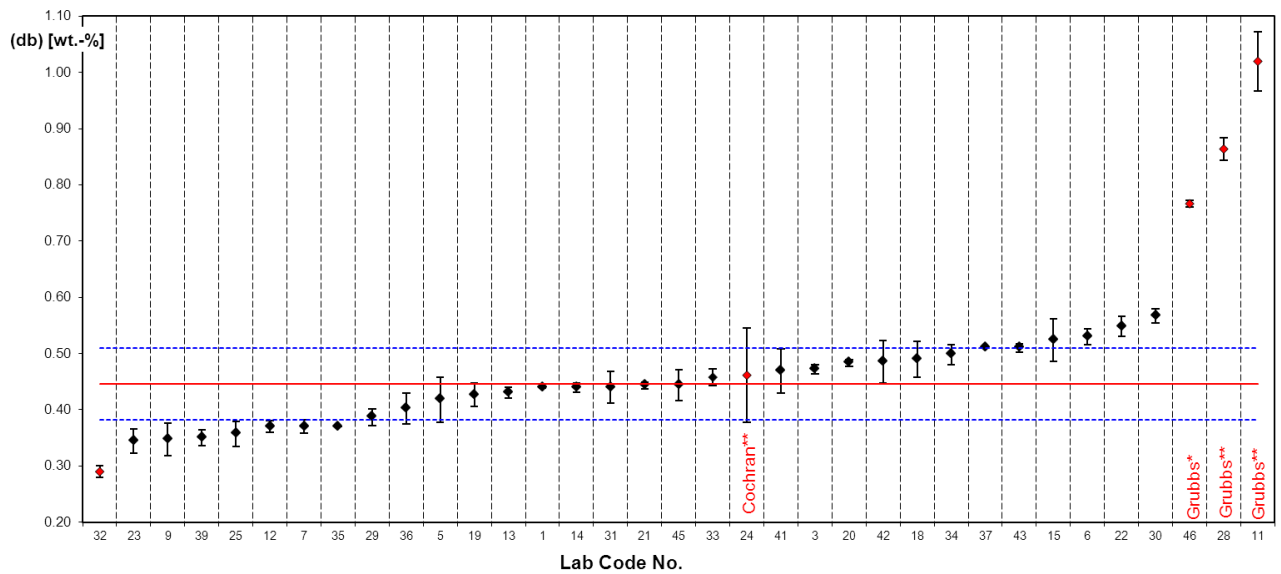
<b>General mean = assigned value</b>	<b>m</b>	<b>53.0</b>	<b>(db) [wt.-%]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.0236</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.15</b>	<b>(db) [wt.-%]</b>
<b>Repeatability coefficient of variation</b>		<b>0.29</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.451</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.67</b>	<b>(db) [wt.-%]</b>
<b>Between-laboratory coefficient of variation</b>		<b>1.27</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.474</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.69</b>	<b>(db) [wt.-%]</b>
<b>Reproducibility coefficient of variation</b>		<b>1.30</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.43</b>	<b>(db) [wt.-%]</b>
		<b>0.81</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>1.93</b>	<b>(db) [wt.-%]</b>
		<b>3.64</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>32</b>	

### Results for the determination of hydrogen content according to EN 15104



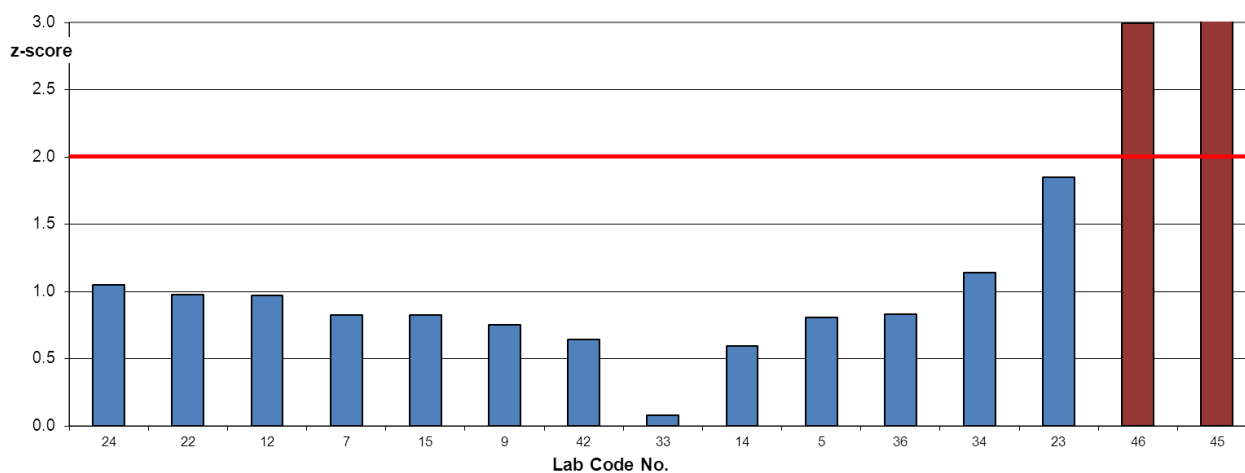
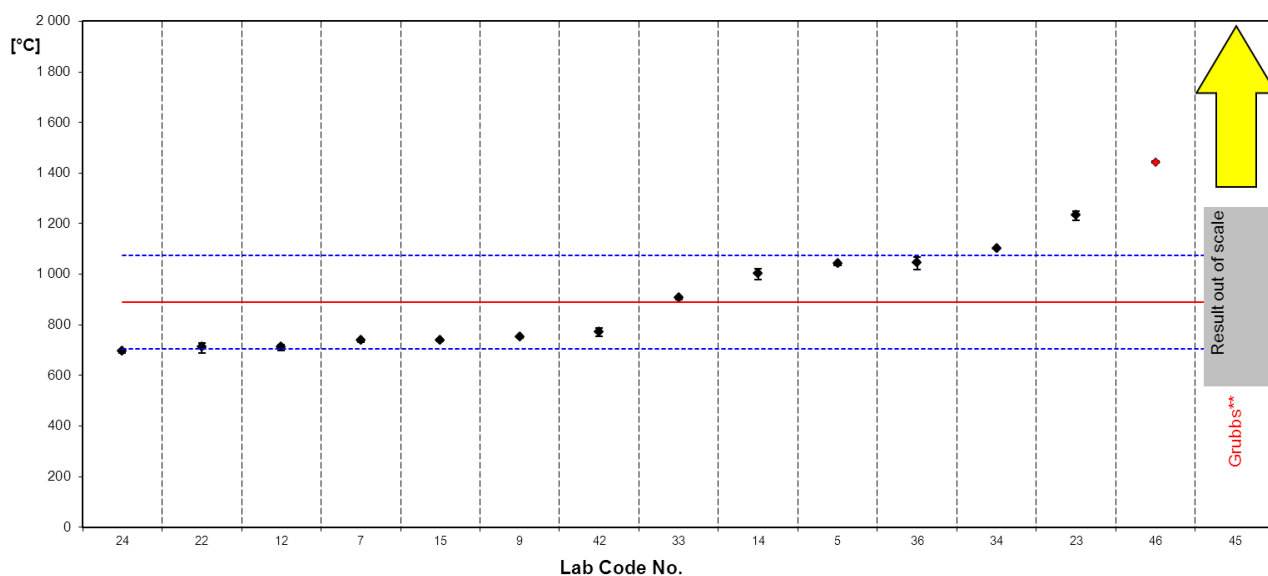
<b>General mean = assigned value</b>	<b>m</b>	<b>5.52</b>	<b>(db) [wt.-%]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.003</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.05</b>	<b>(db) [wt.-%]</b>
<b>Repeatability coefficient of variation</b>		<b>0.91</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.010</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.10</b>	<b>(db) [wt.-%]</b>
<b>Between-laboratory coefficient of variation</b>		<b>1.85</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.013</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.11</b>	<b>(db) [wt.-%]</b>
<b>Reproducibility coefficient of variation</b>		<b>2.06</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.14</b>	<b>(db) [wt.-%]</b>
		<b>2.55</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>0.32</b>	<b>(db) [wt.-%]</b>
		<b>5.78</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>30</b>	

### Results for the determination of nitrogen content according to EN 15104



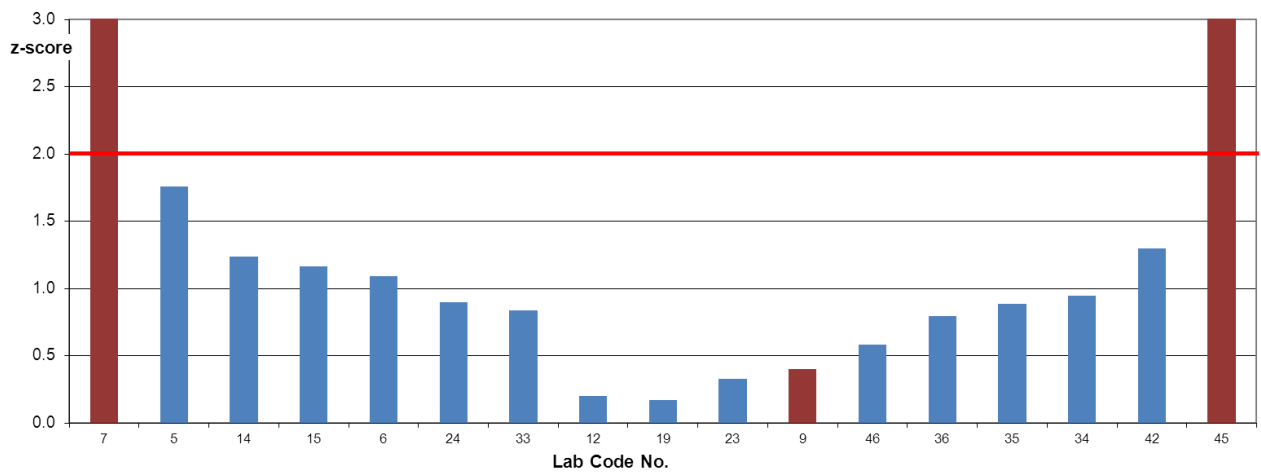
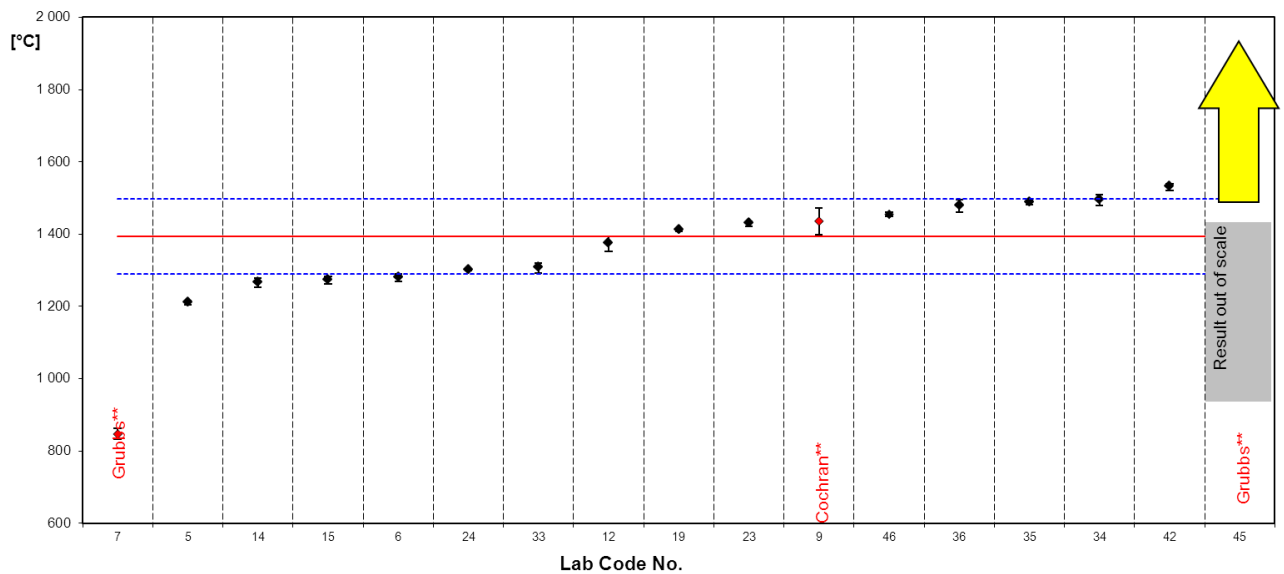
<b>General mean = assigned value</b>	<b>m</b>	<b>0.45</b>	<b>(db) [wt.-%]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.001</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.023</b>	<b>(db) [wt.-%]</b>
<b>Repeatability coefficient of variation</b>		<b>5.16</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.004</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.064</b>	<b>(db) [wt.-%]</b>
<b>Between-laboratory coefficient of variation</b>		<b>14.31</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.005</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.068</b>	<b>(db) [wt.-%]</b>
<b>Reproducibility coefficient of variation</b>		<b>15.21</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.06</b>	<b>(db) [wt.-%]</b>
		<b>14.45</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>0.19</b>	<b>(db) [wt.-%]</b>
		<b>42.58</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>29</b>	

### Results for the determination of shrinking temperature according to CEN /TS 15370-1



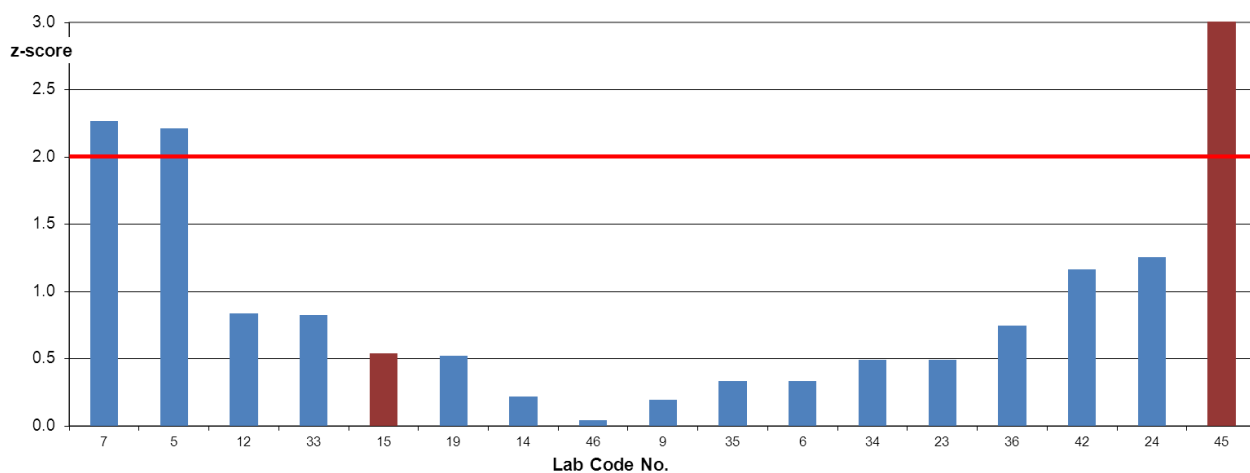
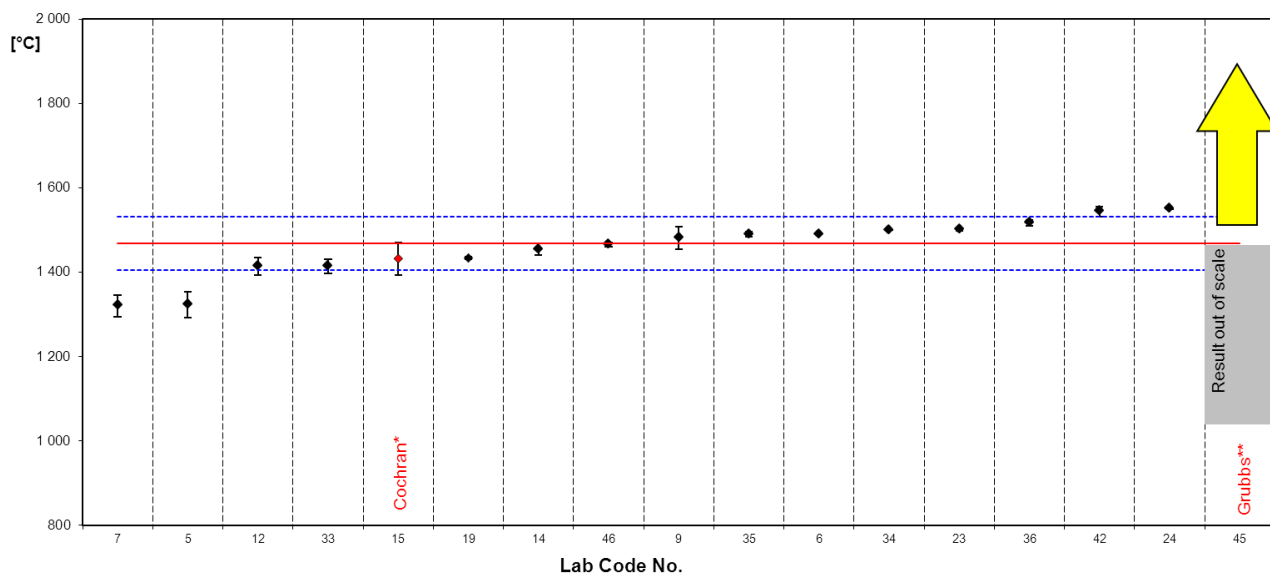
General mean = assigned value	m	889	[°C]
Repeatability variance	$s_r^2$	227	
Repeatability standard deviation	$s_r$	15.1	[°C]
Repeatability coefficient of variation		1.7	%
Between-laboratory variance	$s_L^2$	33988	
Between-laboratory standard deviation	$s_L$	184	[°C]
Between-laboratory coefficient of variation		20.7	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	34214	
Reproducibility standard deviation	$s_R$	185	[°C]
Reproducibility coefficient of variation		20.8	%
Repeatability limit	r	42 4.7	[°C] %
Reproducibility limit	R	518 58.2	[°C] %
Number of participants	n	13	

## Results for the determination of deformation temperature according to CEN /TS 15370-1



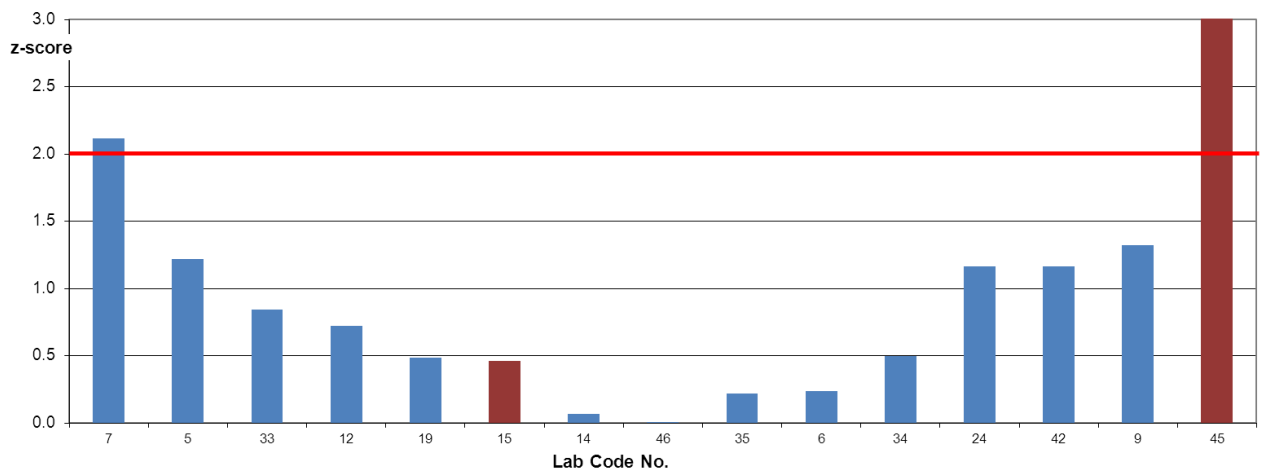
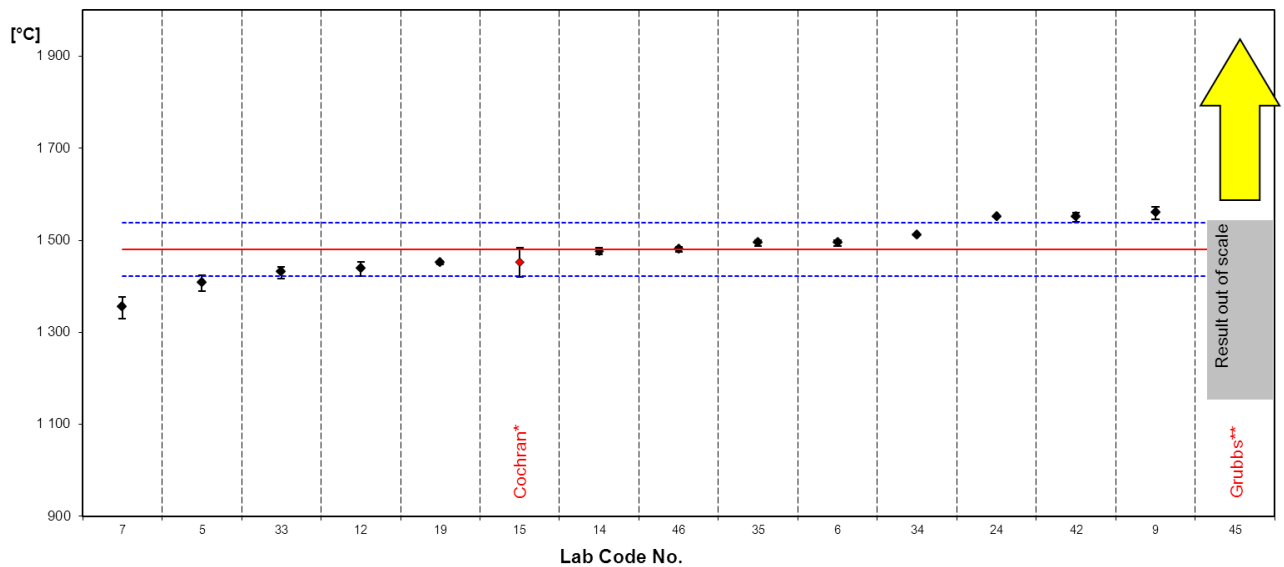
General mean = assigned value	m	1394	[°C]
Repeatability variance	$s_r^2$	134	
Repeatability standard deviation	$s_r$	11.59	[°C]
Repeatability coefficient of variation		0.8	%
Between-laboratory variance	$s_L^2$	10805	
Between-laboratory standard deviation	$s_L$	104	[°C]
Between-laboratory coefficient of variation		7.5	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	10939	
Reproducibility standard deviation	$s_R$	105	[°C]
Reproducibility coefficient of variation		7.5	%
Repeatability limit	r	32	[°C]
		2.3	%
Reproducibility limit	R	293	[°C]
		21.0	%
Number of participants	n	14	

### Results for the determination of hemisphere temperature according to CEN /TS 15370-1



General mean = assigned value	m	1468	[°C]
Repeatability variance	$s_r^2$	185	
Repeatability standard deviation	$s_r$	13.62	[°C]
Repeatability coefficient of variation		0.9	%
Between-laboratory variance	$s_L^2$	4069	
Between-laboratory standard deviation	$s_L$	64	[°C]
Between-laboratory coefficient of variation		4.3	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	4254	
Reproducibility standard deviation	$s_R$	65	[°C]
Reproducibility coefficient of variation		4.4	%
Repeatability limit	r	38	[°C]
		2.6	%
Reproducibility limit	R	183	[°C]
		12.4	%
Number of participants	n	15	

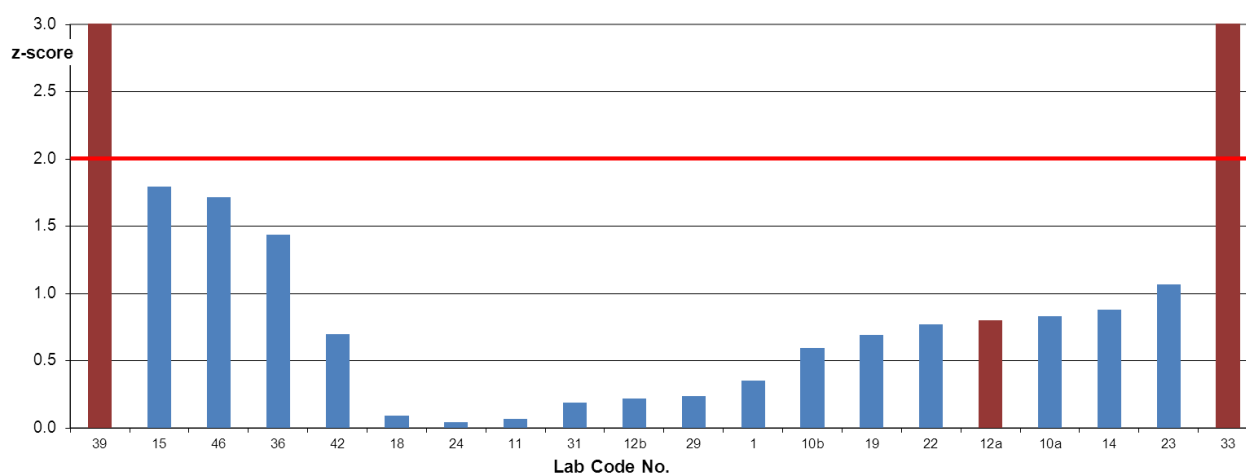
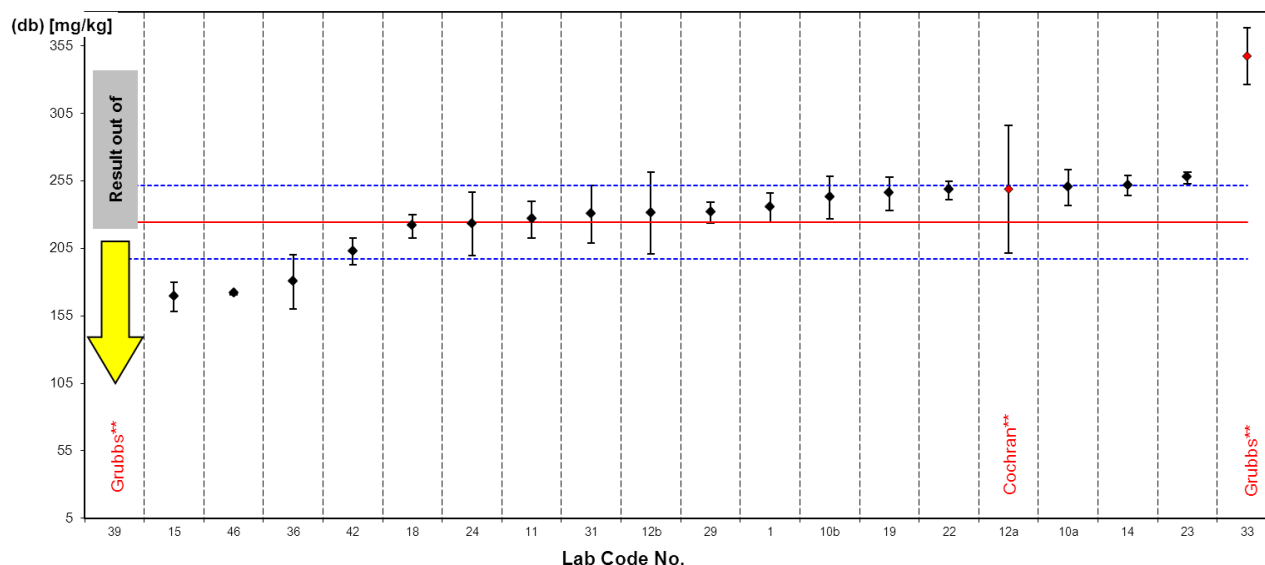
### Results for the determination of flow temperature according to CEN /TS 15370-1



General mean = assigned value	m	1480	[°C]
Repeatability variance	$s_r^2$	120	
Repeatability standard deviation	$s_r$	11	[°C]
Repeatability coefficient of variation		0.7	%
Between-laboratory variance	$s_L^2$	3474	
Between-laboratory standard deviation	$s_L$	59	[°C]
Between-laboratory coefficient of variation		4.0	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	3594	
Reproducibility standard deviation	$s_R$	60	[°C]
Reproducibility coefficient of variation		4.1	%
Repeatability limit	r	31	[°C]
		2.1	%
Reproducibility limit	R	168	[°C]
		11.3	%
Number of participants	n	13	

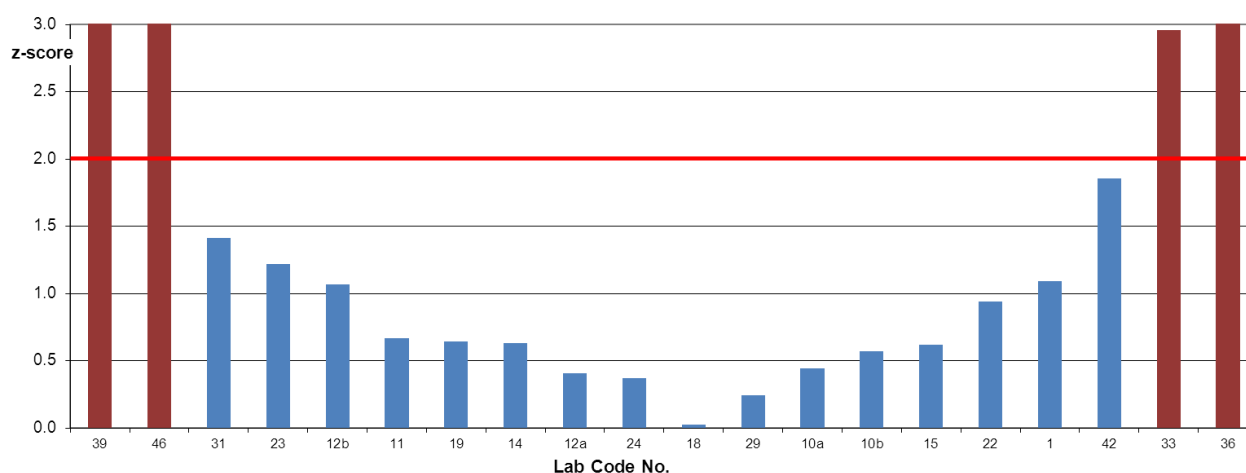
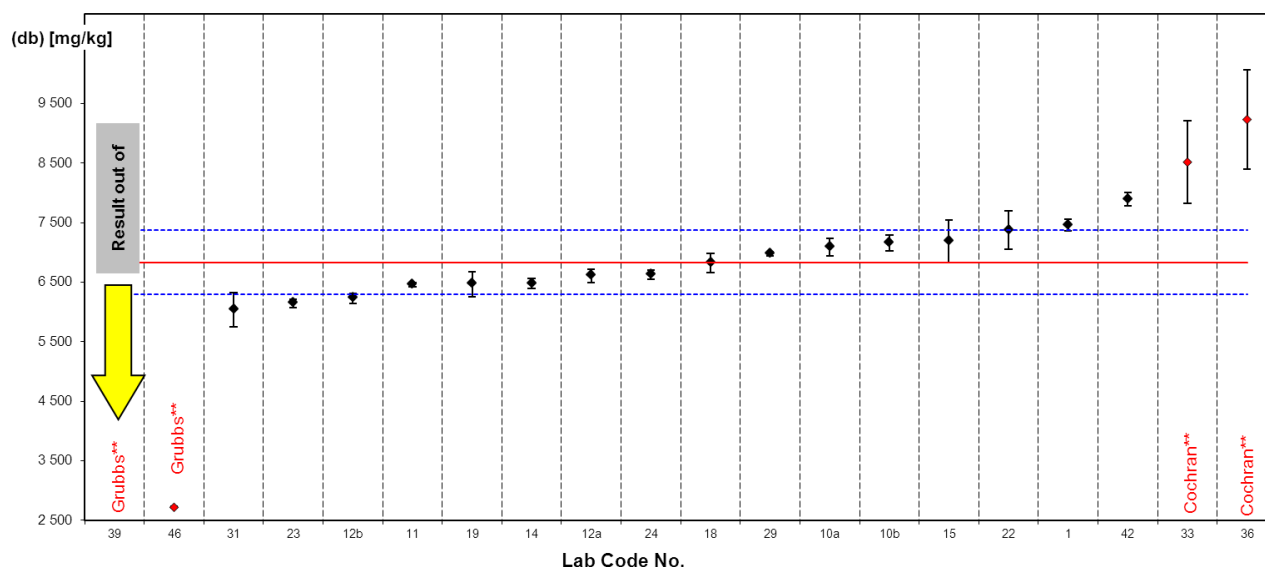


### Results for the determination of content of the major element Al according to EN 15290



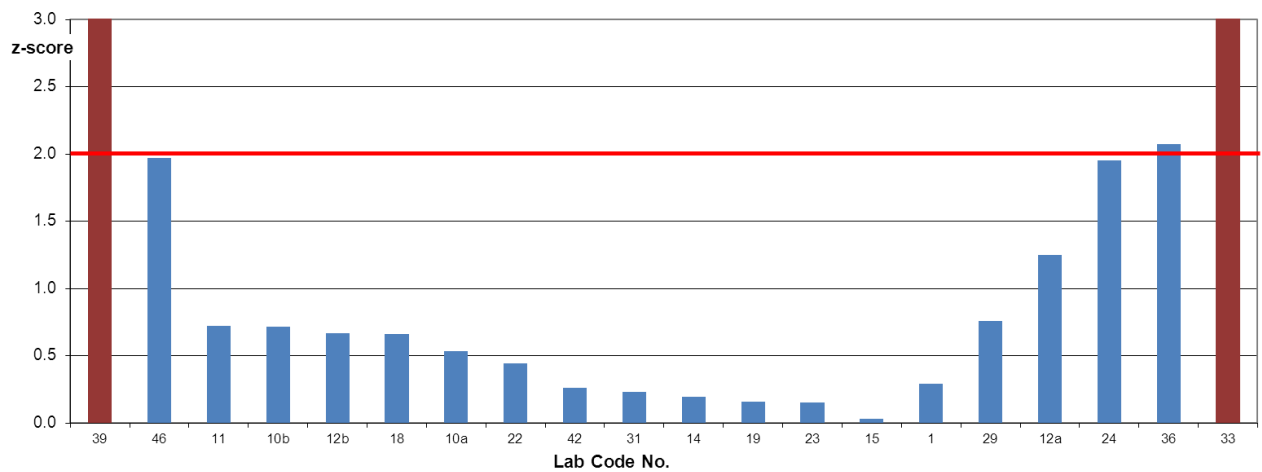
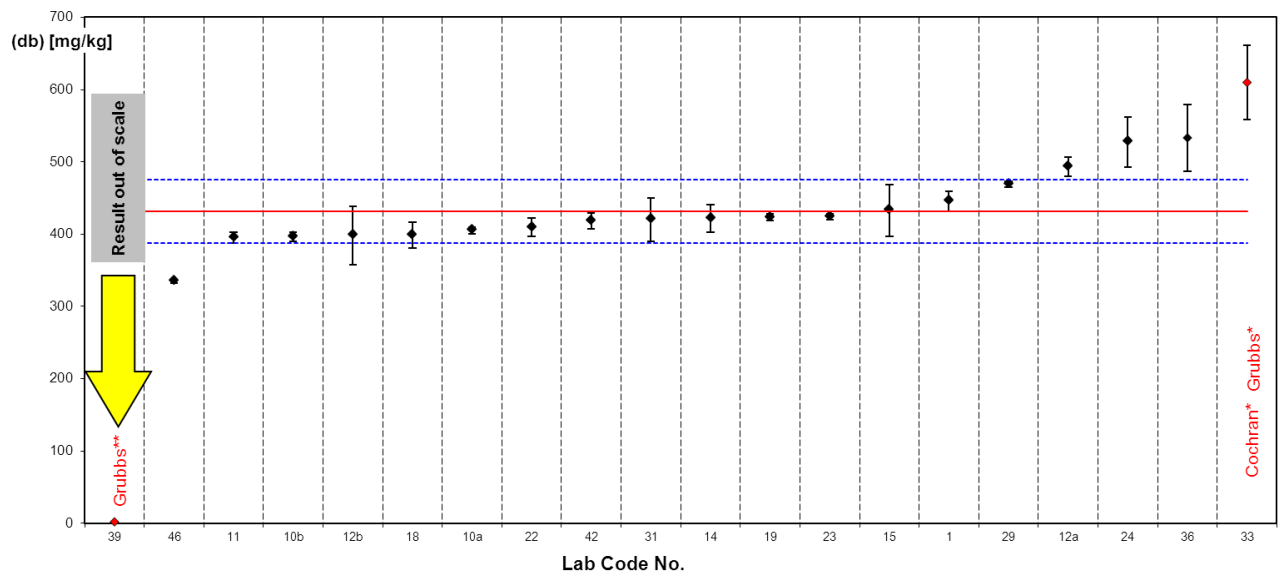
General mean = assigned value	m	224	(db) [mg/kg]
Repeatability variance	$s_r^2$	214	
Repeatability standard deviation	$s_r$	15	(db) [mg/kg]
Repeatability coefficient of variation		6.5	%
Between-laboratory variance	$s_L^2$	734	
Between-laboratory standard deviation	$s_L$	27	(db) [mg/kg]
Between-laboratory coefficient of variation		12.1	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	948	
Reproducibility standard deviation	$s_R$	31	(db) [mg/kg]
Reproducibility coefficient of variation		13.7	%
Repeatability limit	r	41	(db) [mg/kg]
		18.2	%
Reproducibility limit	R	86	(db) [mg/kg]
		38.4	%
Number of participants	n	17	

### Results for the determination of content of the major element Ca according to EN 15290



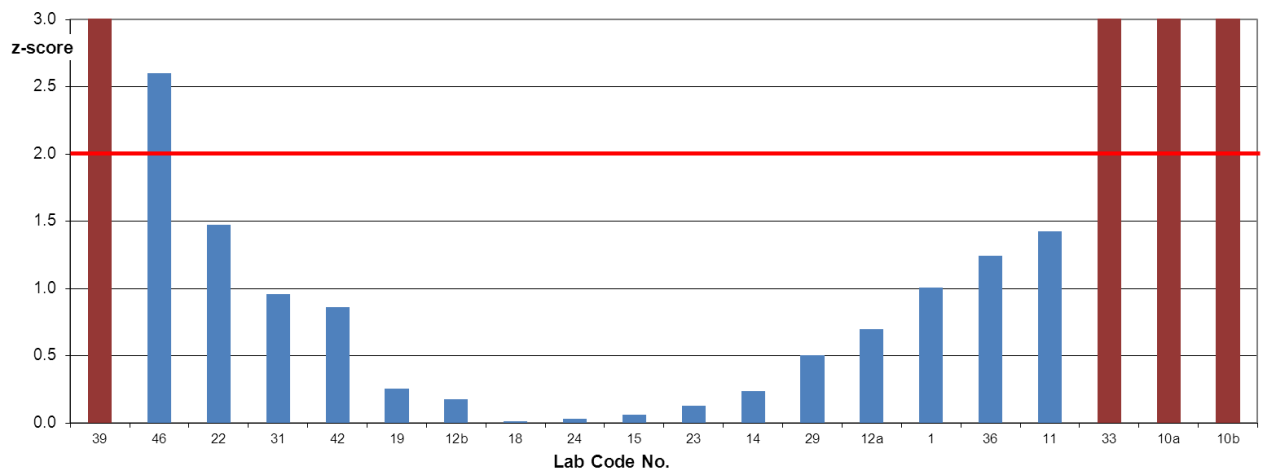
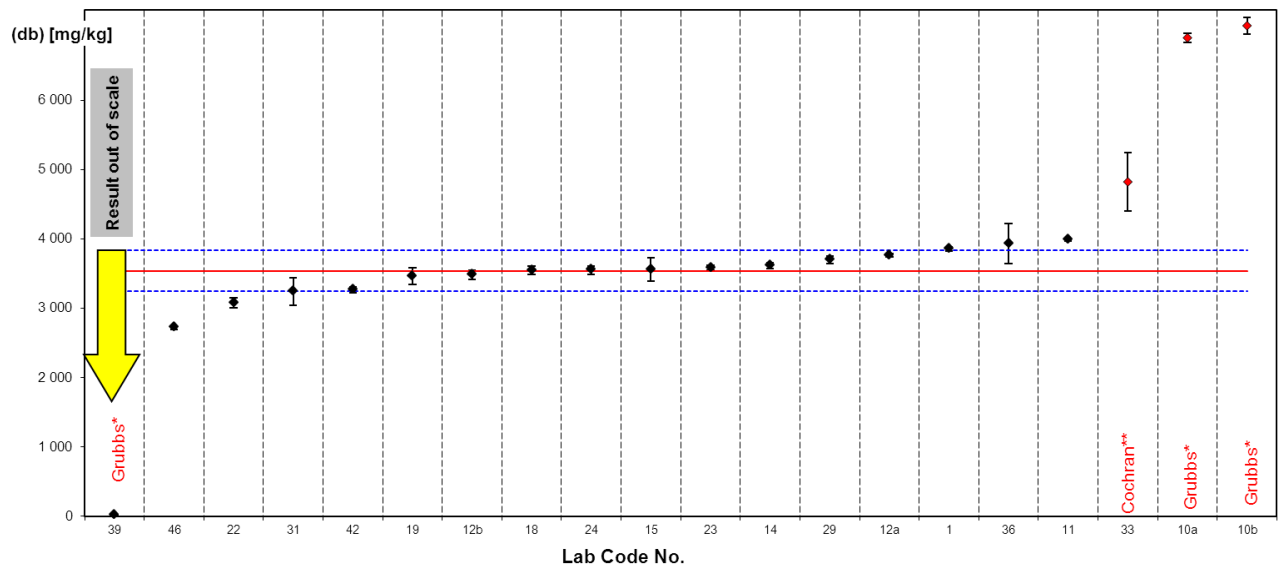
General mean = assigned value	m	6835	(db) [mg/kg]
Repeatability variance	$s_r^2$	28730	
Repeatability standard deviation	$s_r$	169.50	(db) [mg/kg]
Repeatability coefficient of variation		2.5	%
Between-laboratory variance	$s_L^2$	294945	
Between-laboratory standard deviation	$s_L$	543	(db) [mg/kg]
Between-laboratory coefficient of variation		7.9	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	323675	
Reproducibility standard deviation	$s_R$	569	(db) [mg/kg]
Reproducibility coefficient of variation		8.3	%
Repeatability limit	r	475 6.9	(db) [mg/kg] %
Reproducibility limit	R	1593 23.3	(db) [mg/kg] %
Number of participants	n	16	

### Results for the determination of content of the major element Fe according to EN 15290



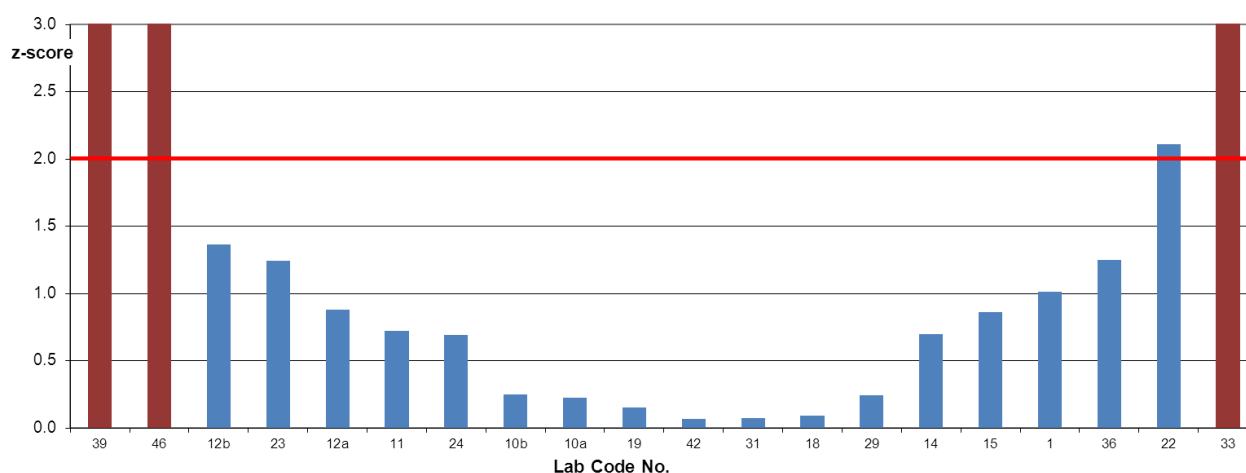
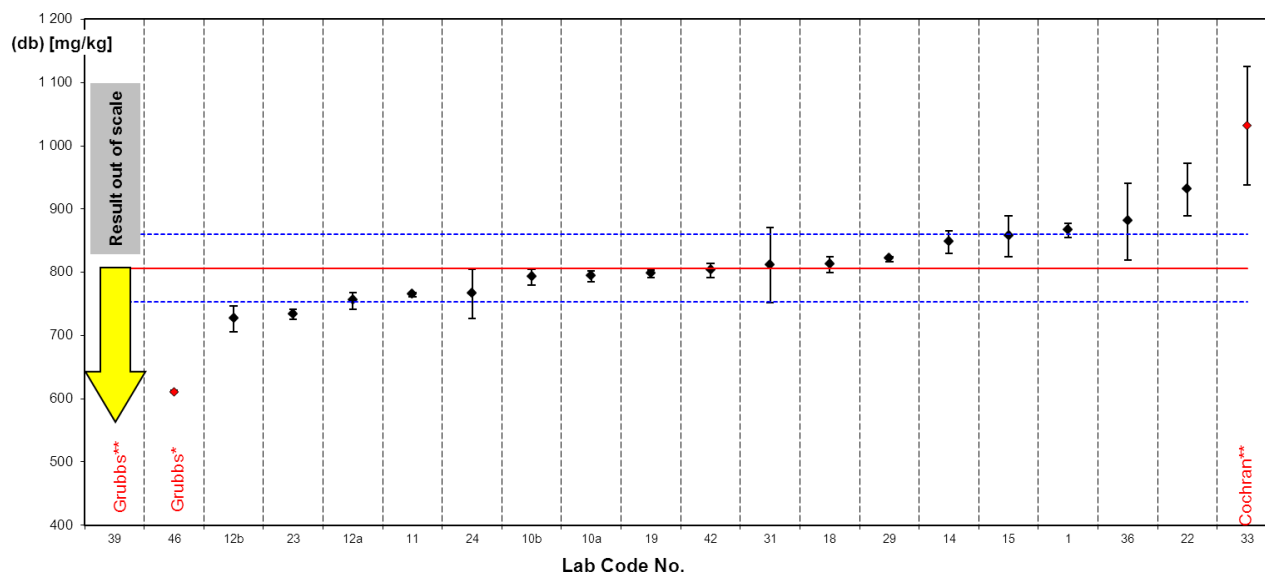
General mean = assigned value	m	431	(db) [mg/kg]
Repeatability variance	$s_r^2$	486	
Repeatability standard deviation	$s_r$	22	(db) [mg/kg]
Repeatability coefficient of variation		5.1	%
Between-laboratory variance	$s_L^2$	1930	
Between-laboratory standard deviation	$s_L$	44	(db) [mg/kg]
Between-laboratory coefficient of variation		10.2	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	2416	
Reproducibility standard deviation	$s_R$	49	(db) [mg/kg]
Reproducibility coefficient of variation		11.4	%
Repeatability limit	r	62	(db) [mg/kg]
		14.3	%
Reproducibility limit	R	138	(db) [mg/kg]
		31.9	%
Number of participants	n	18	

### Results for the determination of content of the major Element K according to EN 15290



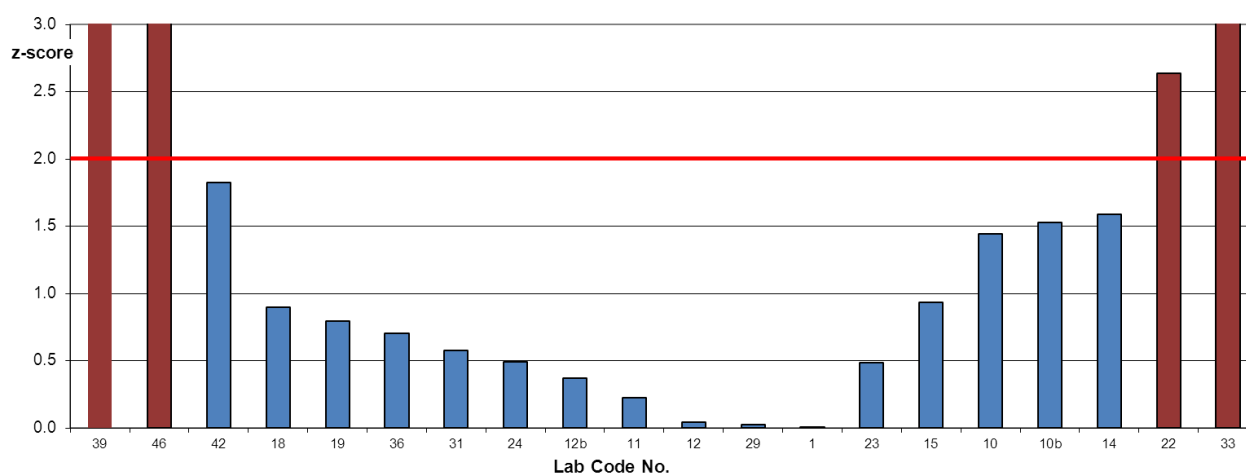
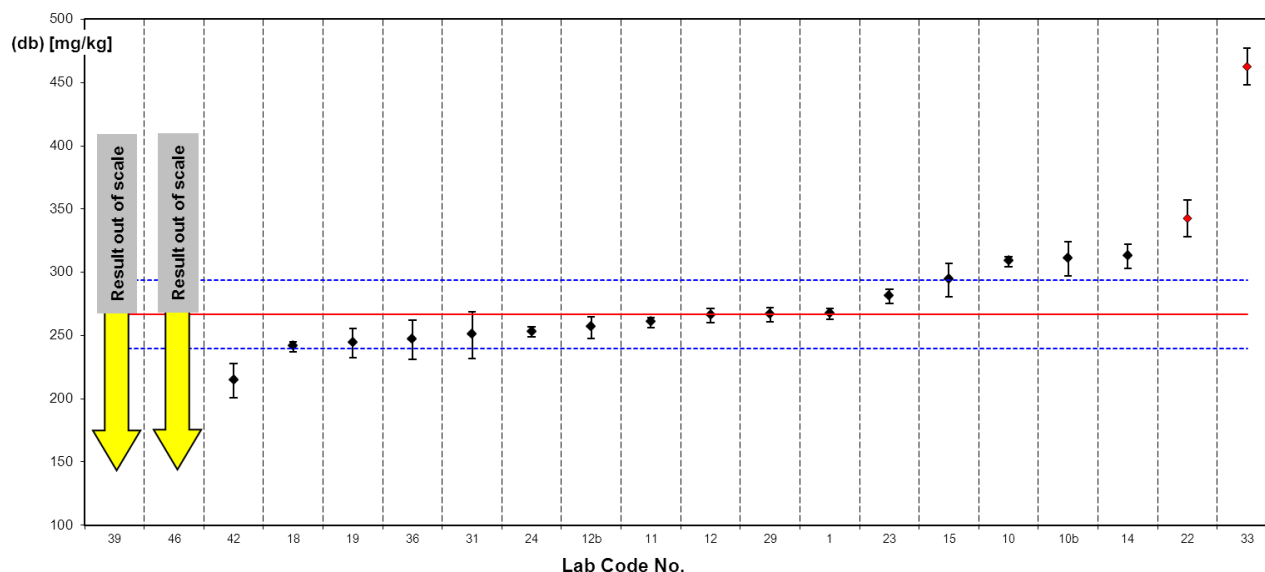
General mean = assigned value	m	3541	(db) [mg/kg]
Repeatability variance	$s_r^2$	10134	
Repeatability standard deviation	$s_r$	101	(db) [mg/kg]
Repeatability coefficient of variation		3	%
Between-laboratory variance	$s_L^2$	89219	
Between-laboratory standard deviation	$s_L$	299	(db) [mg/kg]
Between-laboratory coefficient of variation		8	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	99353	
Reproducibility standard deviation	$s_R$	315	(db) [mg/kg]
Reproducibility coefficient of variation		9	%
Repeatability limit	r	282	(db) [mg/kg]
		8.0	%
Reproducibility limit	R	883	(db) [mg/kg]
		24.9	%
Number of participants	n	16	

### Results for the determination of content of the major Element Mg according to EN 15290



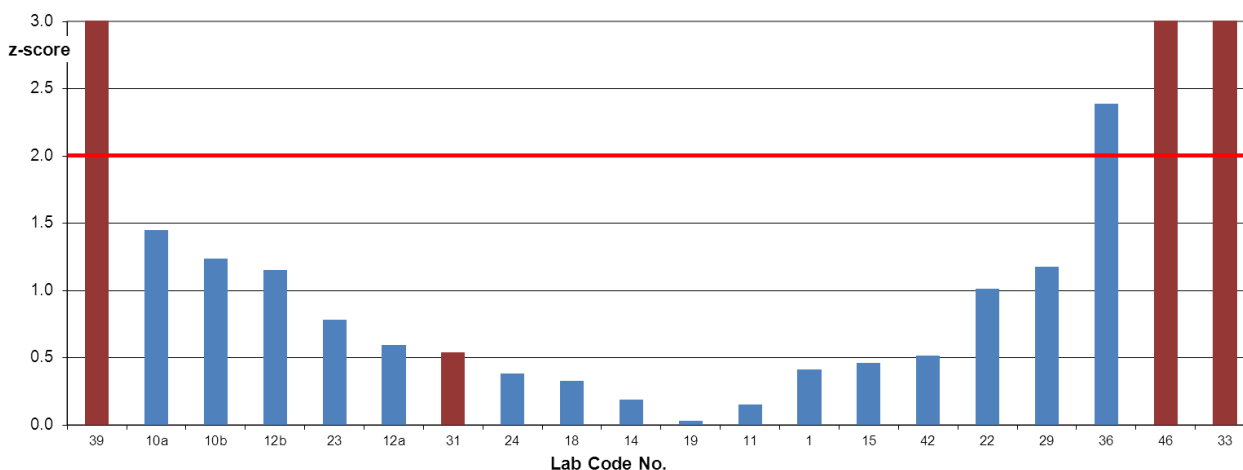
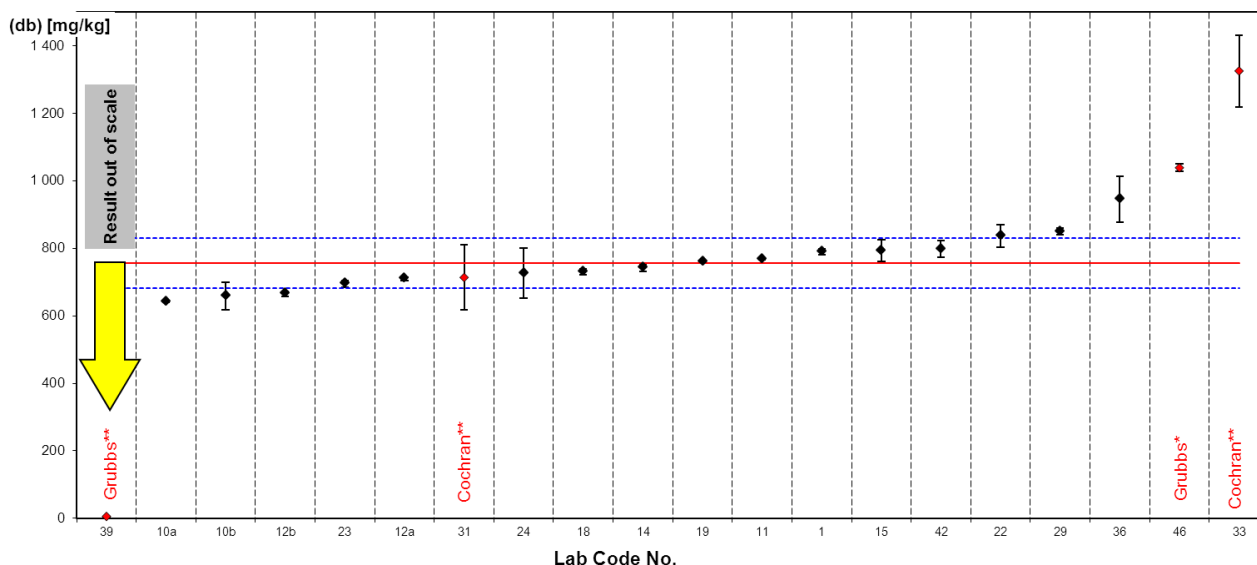
General mean = assigned value	m	806	(db) [mg/kg]
Repeatability variance	$s_r^2$	628	
Repeatability standard deviation	$s_r$	25	(db) [mg/kg]
Repeatability coefficient of variation		3.1	%
Between-laboratory variance	$s_L^2$	2830	
Between-laboratory standard deviation	$s_L$	53	(db) [mg/kg]
Between-laboratory coefficient of variation		6.6	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	3458	
Reproducibility standard deviation	$s_R$	59	(db) [mg/kg]
Reproducibility coefficient of variation		7.3	%
Repeatability limit	r	70 8.7	(db) [mg/kg] %
Reproducibility limit	R	165 20.4	(db) [mg/kg] %
Number of participants	n	17	

### Results for the determination of content of the major Element Na according to EN 15290



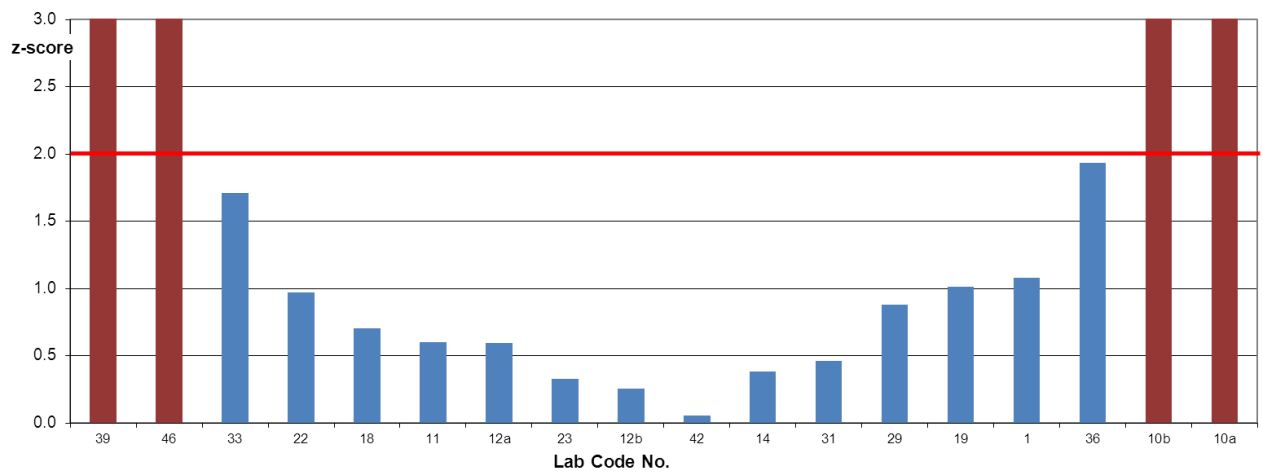
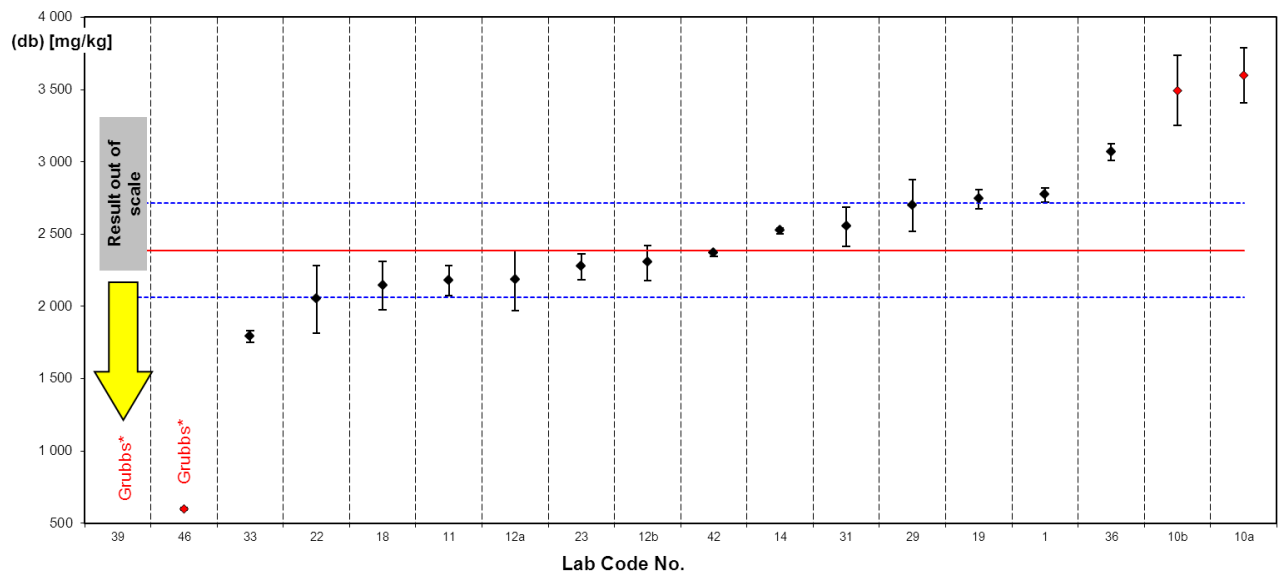
General mean = assigned value	m	267	(db) [mg/kg]
Repeatability variance	$s_r^2$	94	
Repeatability standard deviation	$s_r$	10	(db) [mg/kg]
Repeatability coefficient of variation		3.6	%
Between-laboratory variance	$s_L^2$	734	
Between-laboratory standard deviation	$s_L$	27	(db) [mg/kg]
Between-laboratory coefficient of variation		10.2	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	827	
Reproducibility standard deviation	$s_R$	29	(db) [mg/kg]
Reproducibility coefficient of variation		10.8	%
Repeatability limit	r	27	(db) [mg/kg]
		10.2	%
Reproducibility limit	R	81	(db) [mg/kg]
		30.2	%
Number of participants	n	16	

### Results for the determination of content of the major Element P according to EN 15290



General mean = assigned value	m	757	(db) [mg/kg]
Repeatability variance	$s_r^2$	727	
Repeatability standard deviation	$s_r$	27	(db) [mg/kg]
Repeatability coefficient of variation		3.6	%
Between-laboratory variance	$s_L^2$	5589	
Between-laboratory standard deviation	$s_L$	75	(db) [mg/kg]
Between-laboratory coefficient of variation		9.9	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	6315	
Reproducibility standard deviation	$s_R$	79	(db) [mg/kg]
Reproducibility coefficient of variation		10.5	%
Repeatability limit	r	75	(db) [mg/kg]
		10.0	%
Reproducibility limit	R	223	(db) [mg/kg]
		29.4	%
Number of participants	n	16	

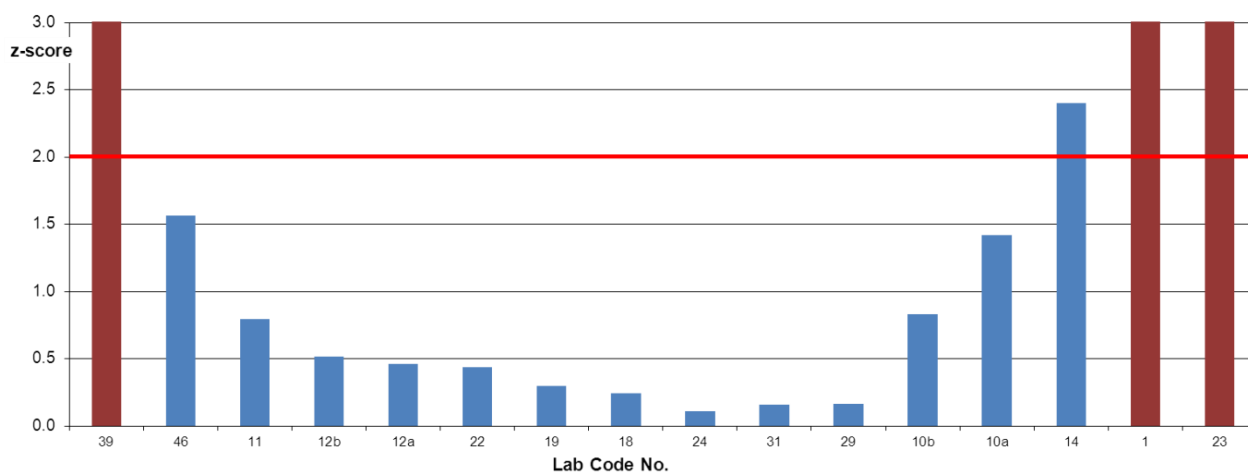
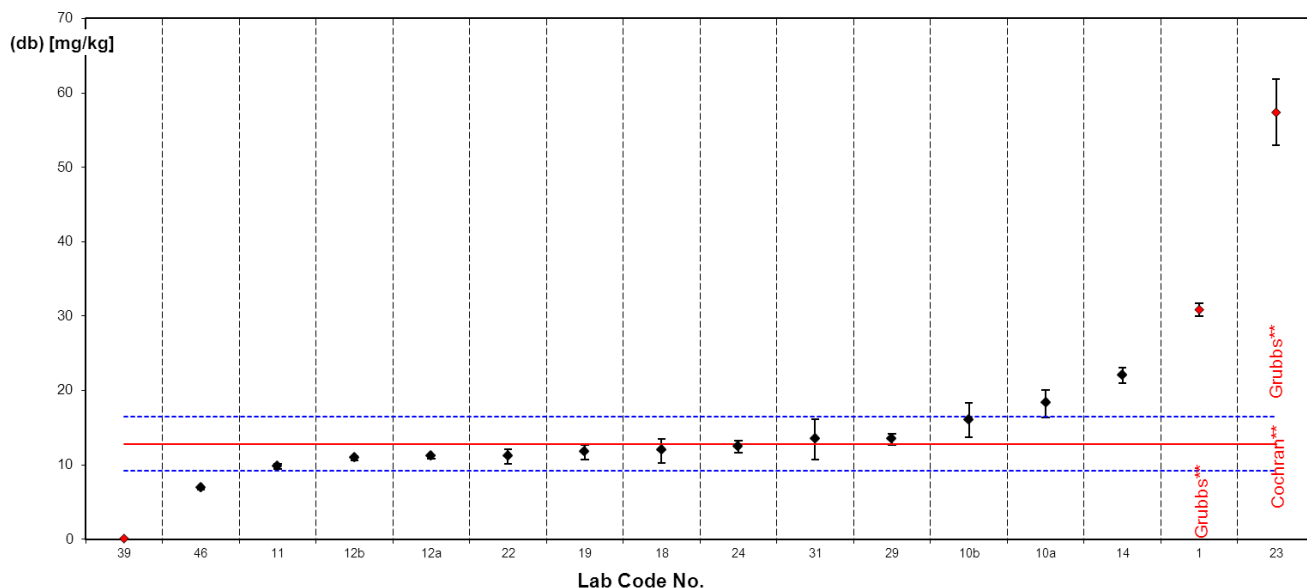
### Results for the determination of content of the major Element Si according to EN 15290



General mean = assigned value	m	2389	(db) [mg/kg]
Repeatability variance	$s_r^2$	14994	
Repeatability standard deviation	$s_r$	122	(db) [mg/kg]
Repeatability coefficient of variation		5.1	%
Between-laboratory variance	$s_L^2$	107885	
Between-laboratory standard deviation	$s_L$	328	(db) [mg/kg]
Between-laboratory coefficient of variation		13.8	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	122879	
Reproducibility standard deviation	$s_R$	351	(db) [mg/kg]
Reproducibility coefficient of variation		14.7	%
Repeatability limit	r	343 14.4	(db) [mg/kg] %
Reproducibility limit	R	982 41.1	(db) [mg/kg] %
Number of participants	n	14	

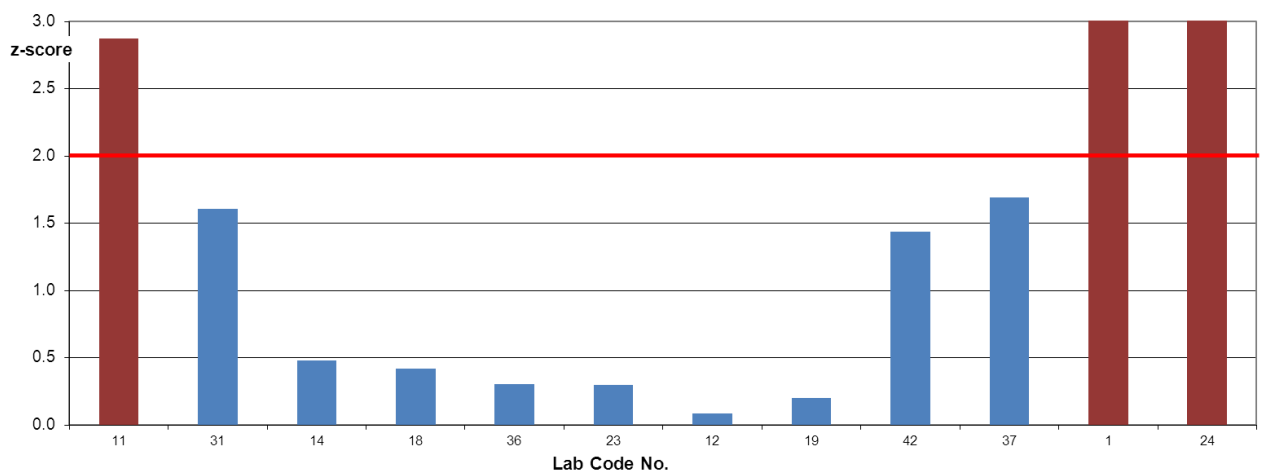
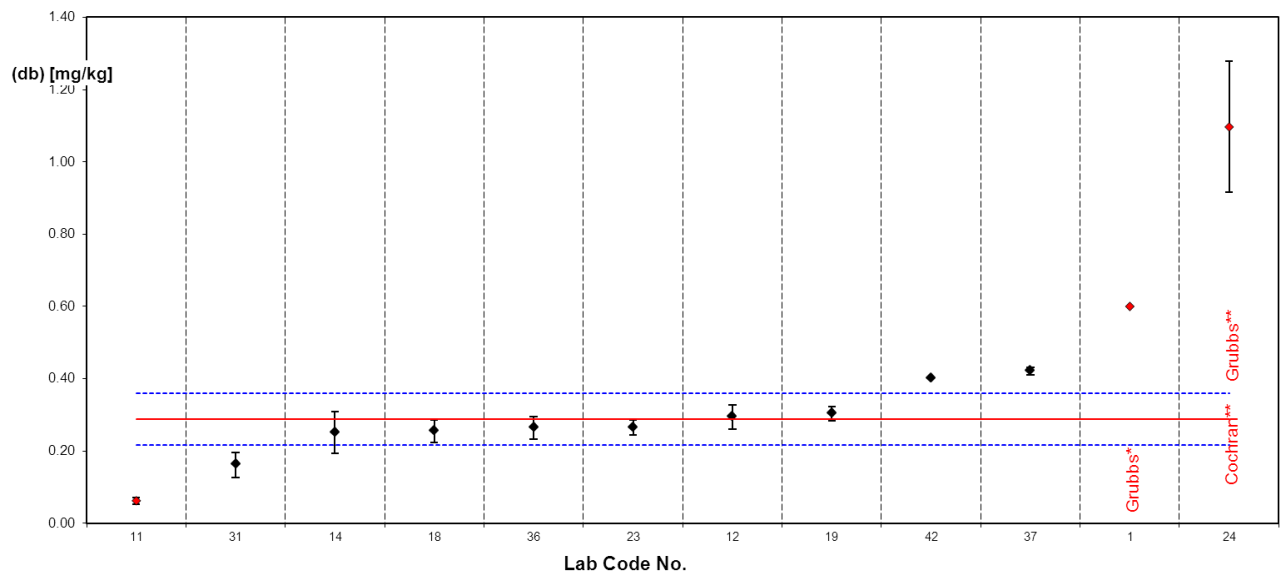


### Results for the determination of content of the major Element Ti according to EN 15290



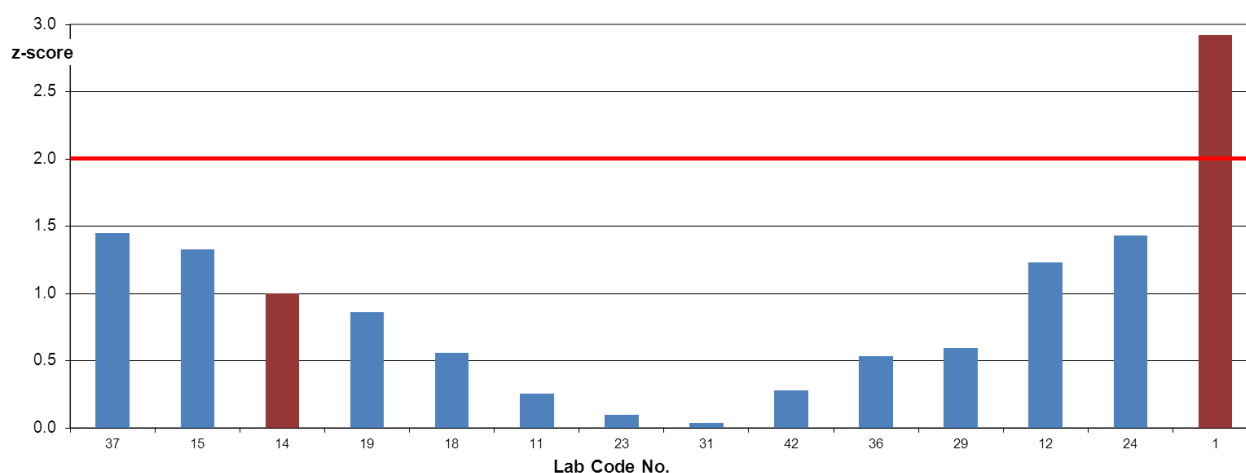
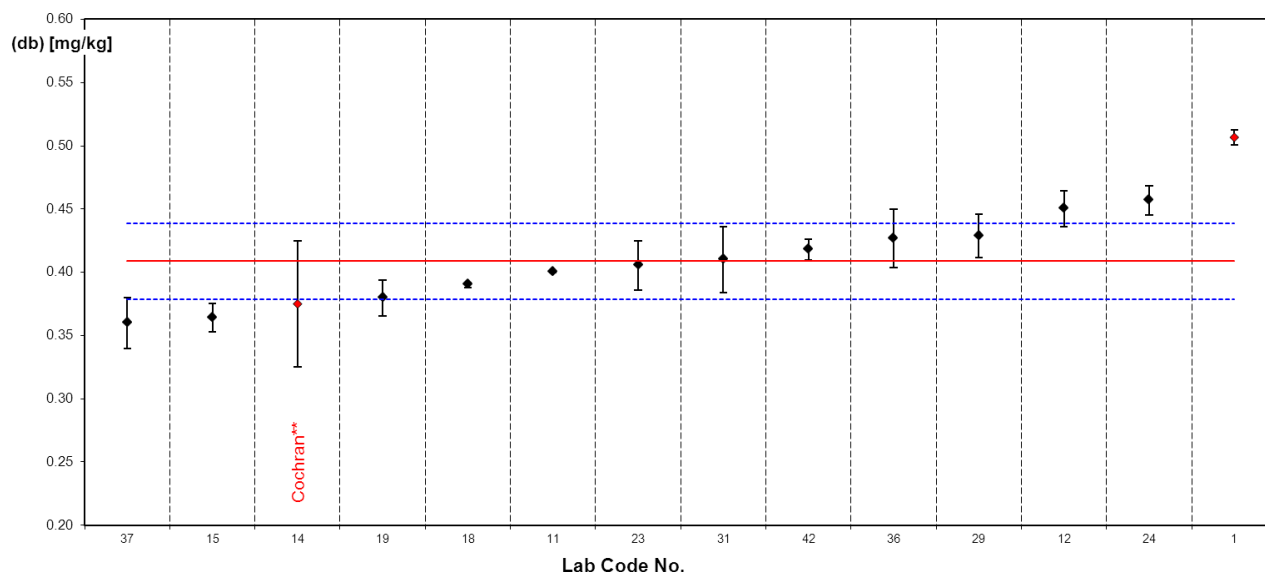
General mean = assigned value	m	12.8	(db) [mg/kg]
Repeatability variance	$s_r^2$	1.50	
Repeatability standard deviation	$s_r$	1.2	(db) [mg/kg]
Repeatability coefficient of variation		9.5	%
Between-laboratory variance	$s_L^2$	13	
Between-laboratory standard deviation	$s_L$	3.6	(db) [mg/kg]
Between-laboratory coefficient of variation		28.3	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	15	
Reproducibility standard deviation	$s_R$	3.8	(db) [mg/kg]
Reproducibility coefficient of variation		29.8	%
Repeatability limit	r	3.4	(db) [mg/kg]
		26.7	%
Reproducibility limit	R	10.7	(db) [mg/kg]
		83.5	%
Number of participants	n	13	

### Results for the determination of content of the minor Element As according to EN 15297



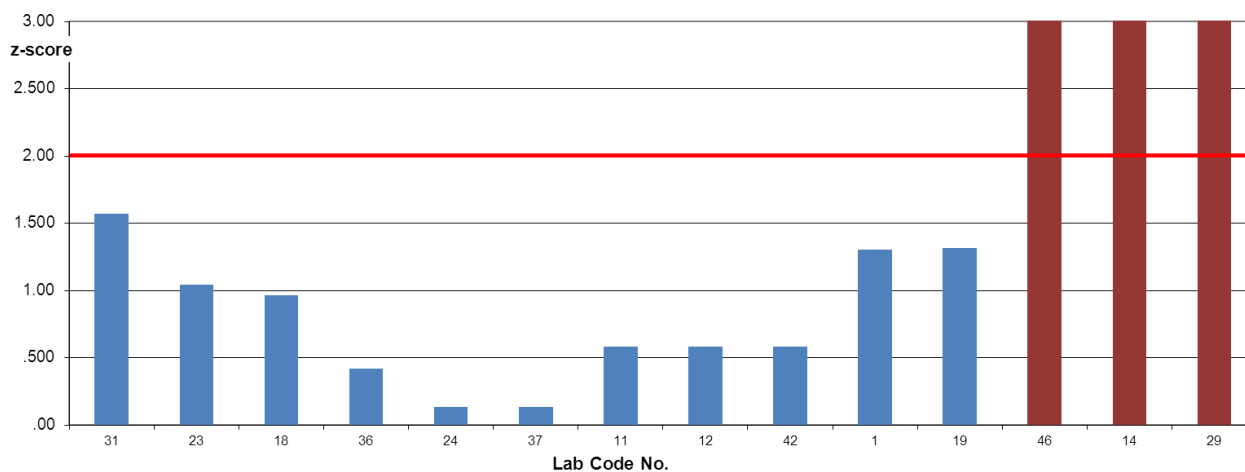
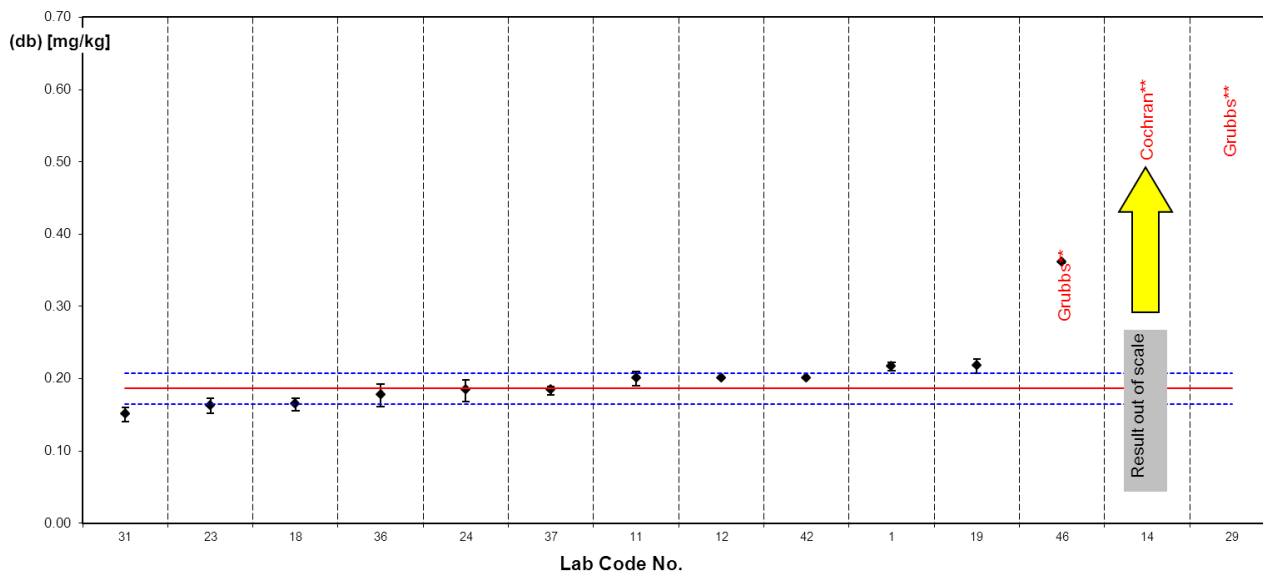
General mean = assigned value	m	0.29	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.001	
Repeatability standard deviation	$s_r$	0.03	(db) [mg/kg]
Repeatability coefficient of variation		11.1	%
Between-laboratory variance	$s_L^2$	0.005	
Between-laboratory standard deviation	$s_L$	0.07	(db) [mg/kg]
Between-laboratory coefficient of variation		24.9	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.006	
Reproducibility standard deviation	$s_R$	0.08	(db) [mg/kg]
Reproducibility coefficient of variation		27.3	%
Repeatability limit	r	0.089	(db) [mg/kg]
		31.1	%
Reproducibility limit	R	0.22	(db) [mg/kg]
		76.3	%
Number of participants	n	9	

### Results for the determination of content of the minor Element Cd according to EN 15297



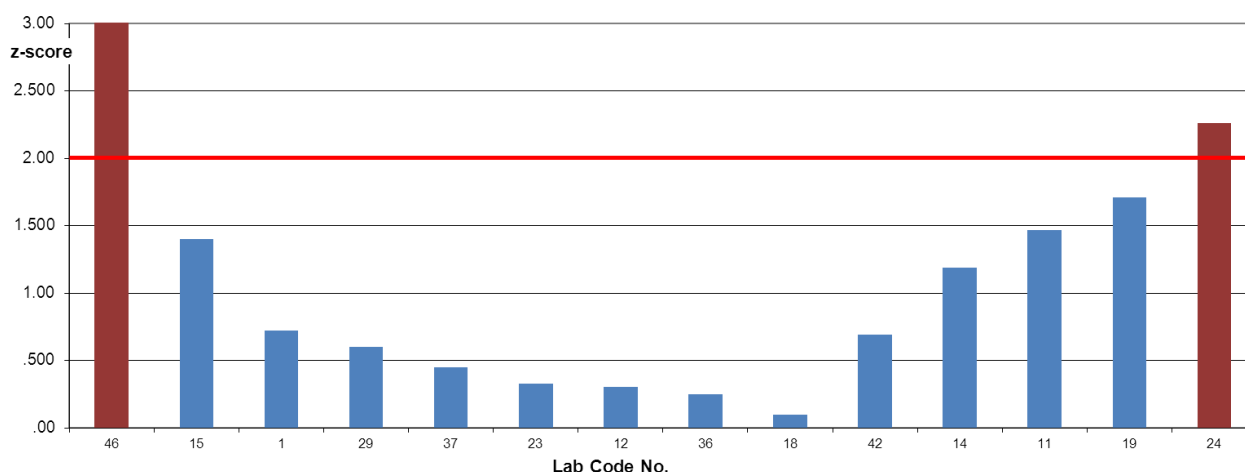
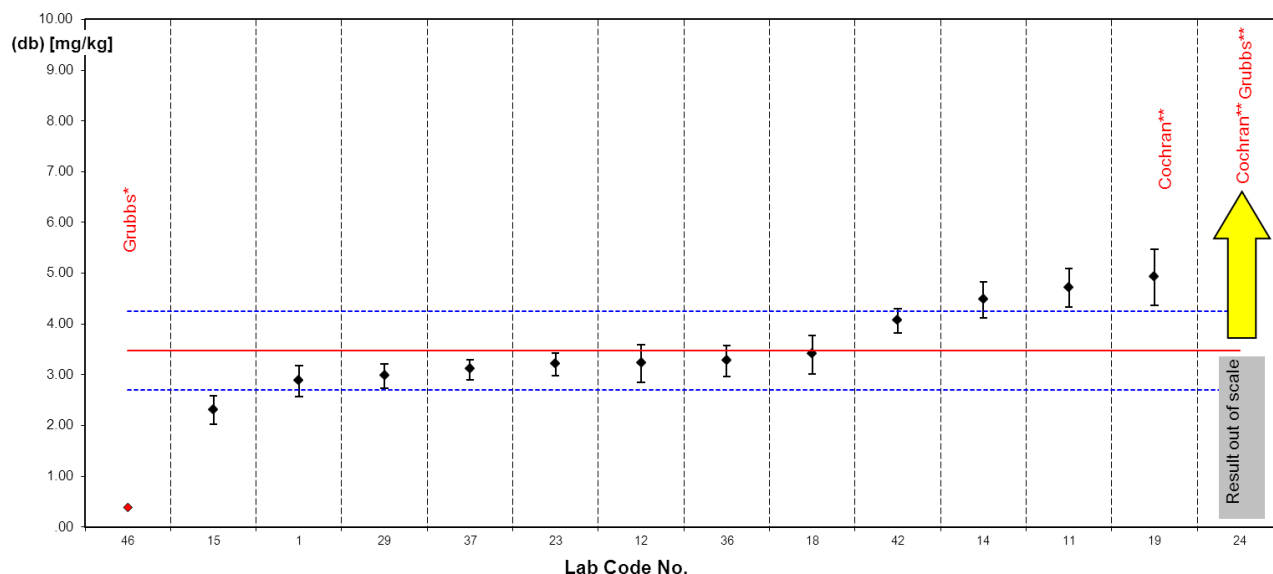
General mean = assigned value	m	0.41	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.0002	
Repeatability standard deviation	$s_r$	0.016	(db) [mg/kg]
Repeatability coefficient of variation		3.8	%
Between-laboratory variance	$s_L^2$	0.001	
Between-laboratory standard deviation	$s_L$	0.030	(db) [mg/kg]
Between-laboratory coefficient of variation		7.3	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.001	
Reproducibility standard deviation	$s_R$	0.03	(db) [mg/kg]
Reproducibility coefficient of variation		8.2	%
Repeatability limit	r	0.044	(db) [mg/kg]
		10.7	%
Reproducibility limit	R	0.094	(db) [mg/kg]
		23.0	%
Number of participants	n	12	

### Results for the determination of content of the minor Element Co according to EN 15297



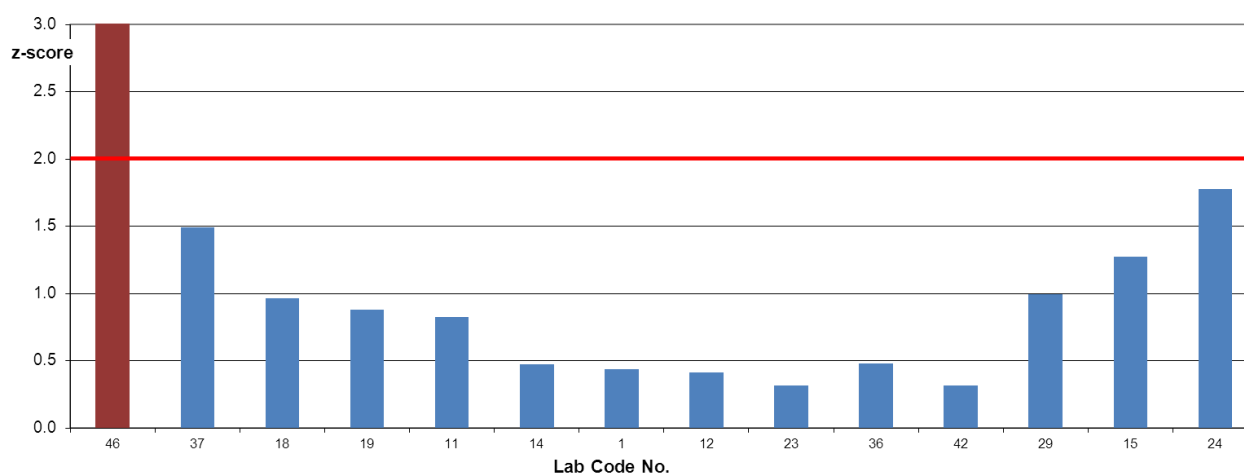
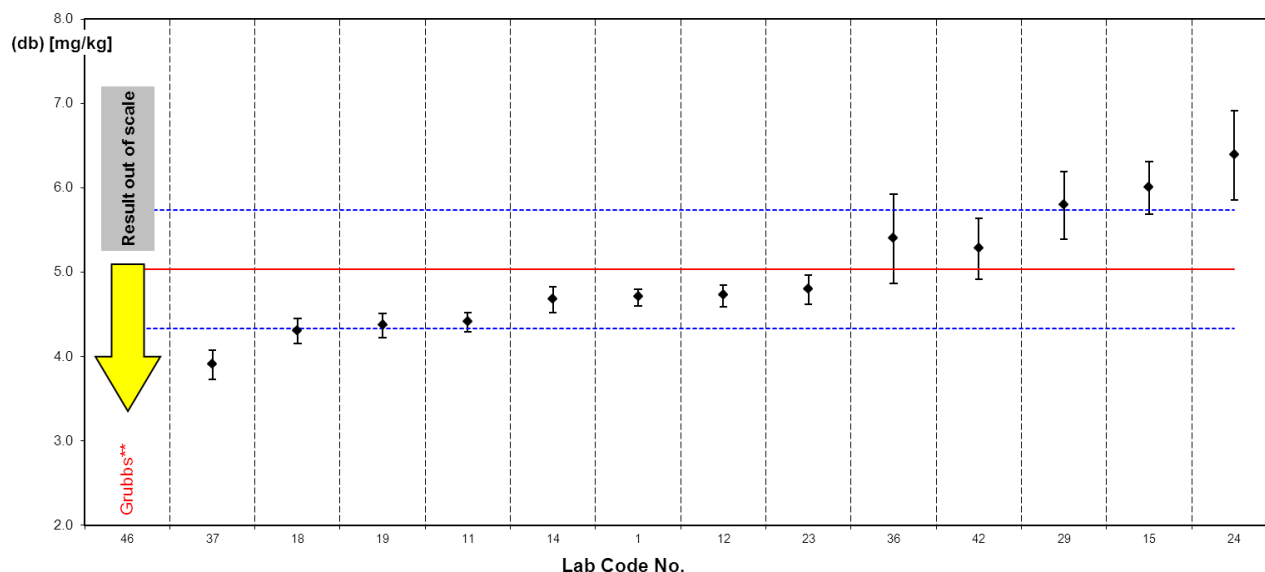
General mean = assigned value	m	0.41	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.0002	
Repeatability standard deviation	$s_r$	0.016	(db) [mg/kg]
Repeatability coefficient of variation		3.8	%
Between-laboratory variance	$s_L^2$	0.001	
Between-laboratory standard deviation	$s_L$	0.030	(db) [mg/kg]
Between-laboratory coefficient of variation		7.3	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.001	
Reproducibility standard deviation	$s_R$	0.03	(db) [mg/kg]
Reproducibility coefficient of variation		8.2	%
Repeatability limit	r	0.044 10.7	(db) [mg/kg] %
Reproducibility limit	R	0.094 23.0	(db) [mg/kg] %
Number of participants	n	12	

### Results for the determination of content of the minor Element Cr according to EN 15297



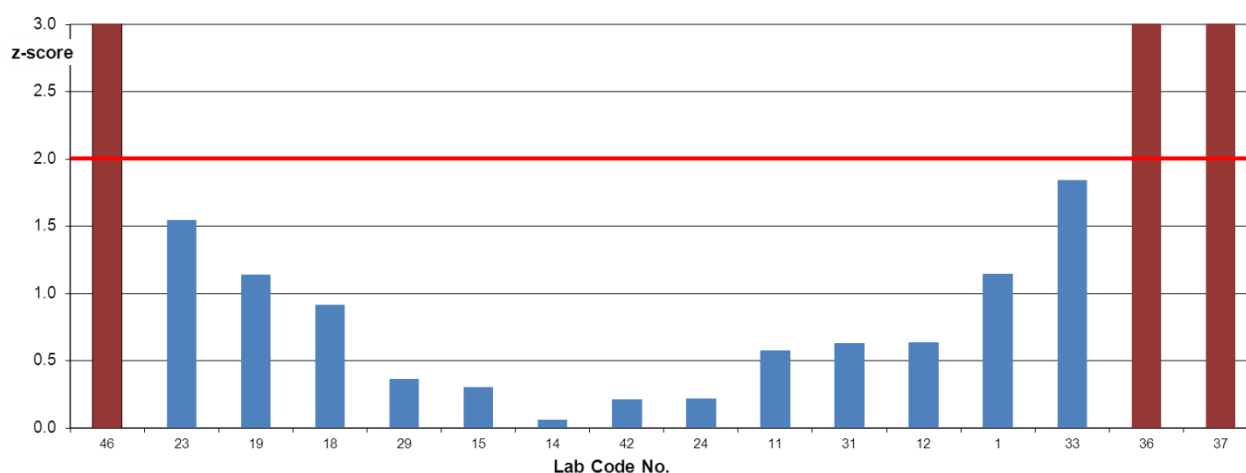
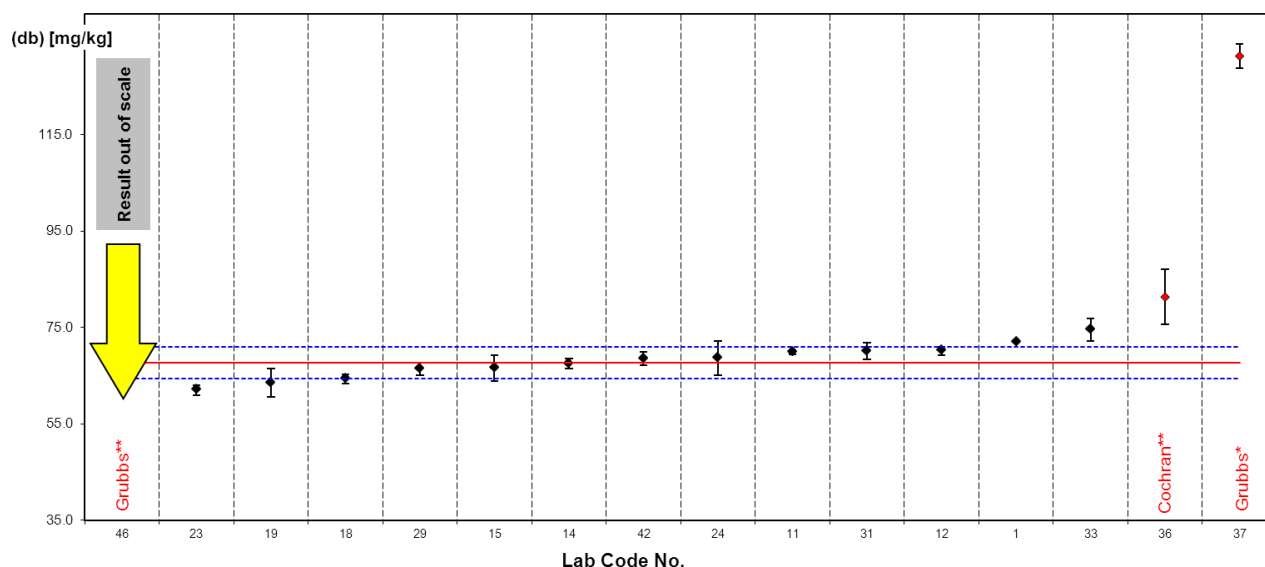
General mean = assigned value	m	3.48	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.101	
Repeatability standard deviation	$s_r$	0.32	(db) [mg/kg]
Repeatability coefficient of variation		9.1	%
Between-laboratory variance	$s_L^2$	0.61	
Between-laboratory standard deviation	$s_L$	0.78	(db) [mg/kg]
Between-laboratory coefficient of variation		22.4	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.71	
Reproducibility standard deviation	$s_R$	0.84	(db) [mg/kg]
Reproducibility coefficient of variation		24.2	%
Repeatability limit	r	0.89	(db) [mg/kg]
		25.6	%
Reproducibility limit	R	2.35	(db) [mg/kg]
		67.7	%
Number of participants	n	12	

### Results for the determination of content of the minor Element Cu according to EN 15297



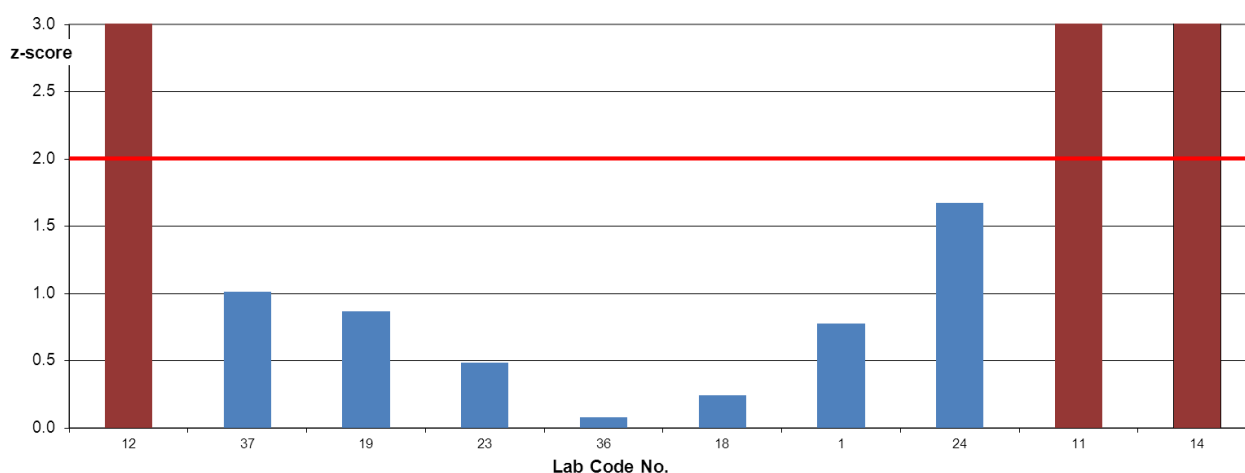
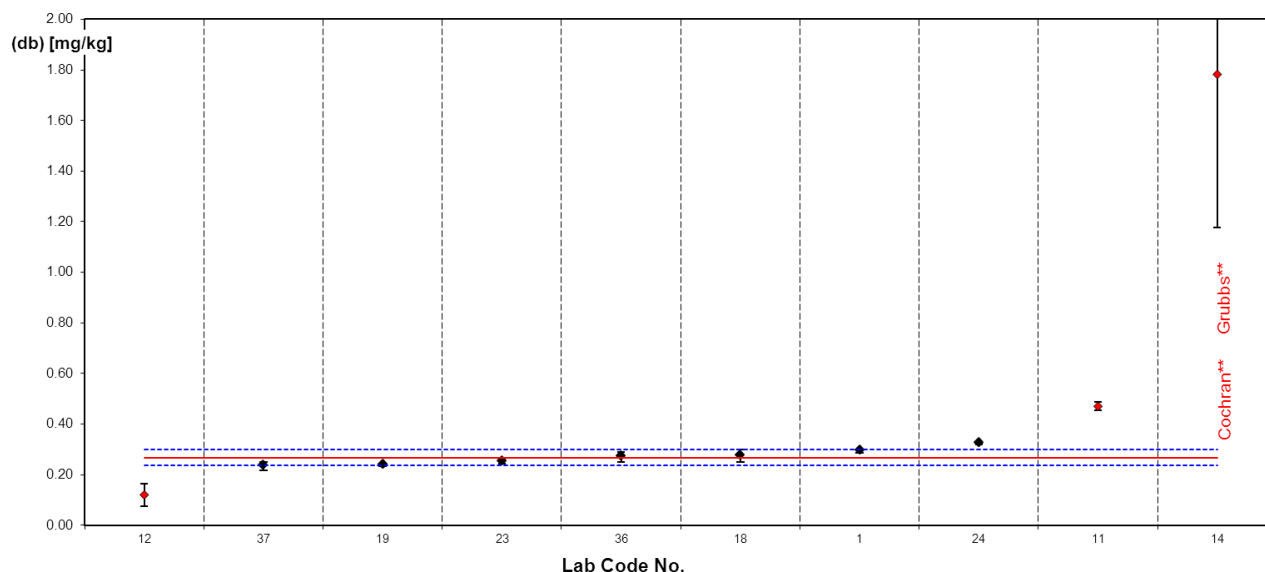
<b>General mean = assigned value</b>	<b>m</b>	<b>5.03</b>	<b>(db) [mg/kg]</b>
<b>Repeatability variance</b>	<b><math>s_r^2</math></b>	<b>0.083</b>	
<b>Repeatability standard deviation</b>	<b><math>s_r</math></b>	<b>0.29</b>	<b>(db) [mg/kg]</b>
<b>Repeatability coefficient of variation</b>		<b>5.7</b>	<b>%</b>
<b>Between-laboratory variance</b>	<b><math>s_L^2</math></b>	<b>0.49</b>	
<b>Between-laboratory standard deviation</b>	<b><math>s_L</math></b>	<b>0.70</b>	<b>(db) [mg/kg]</b>
<b>Between-laboratory coefficient of variation</b>		<b>14.0</b>	<b>%</b>
<b>Reproducibility variance <math>s_R^2</math></b>	<b><math>s_r^2 + s_L^2</math></b>	<b>0.58</b>	
<b>Reproducibility standard deviation</b>	<b><math>s_R</math></b>	<b>0.76</b>	<b>(db) [mg/kg]</b>
<b>Reproducibility coefficient of variation</b>		<b>15.1</b>	<b>%</b>
<b>Repeatability limit</b>	<b>r</b>	<b>0.81</b>	<b>(db) [mg/kg]</b>
		<b>16.0</b>	<b>%</b>
<b>Reproducibility limit</b>	<b>R</b>	<b>2.13</b>	<b>(db) [mg/kg]</b>
		<b>42.3</b>	<b>%</b>
<b>Number of participants</b>	<b>n</b>	<b>13</b>	

### Results for the determination of content of the minor Element Mn according to EN 15297



General mean = assigned value	m	67.7	(db) [mg/kg]
Repeatability variance	$s_r^2$	3.11	
Repeatability standard deviation	$s_r$	1.76	(db) [mg/kg]
Repeatability coefficient of variation		2.6	%
Between-laboratory variance	$s_L^2$	10.7	
Between-laboratory standard deviation	$s_L$	3.28	(db) [mg/kg]
Between-laboratory coefficient of variation		4.8	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	13.9	
Reproducibility standard deviation	$s_R$	3.72	(db) [mg/kg]
Reproducibility coefficient of variation		5.5	%
Repeatability limit	r	4.94	(db) [mg/kg]
		7.3	%
Reproducibility limit	R	10.42	(db) [mg/kg]
		15.4	%
Number of participants	n	13	

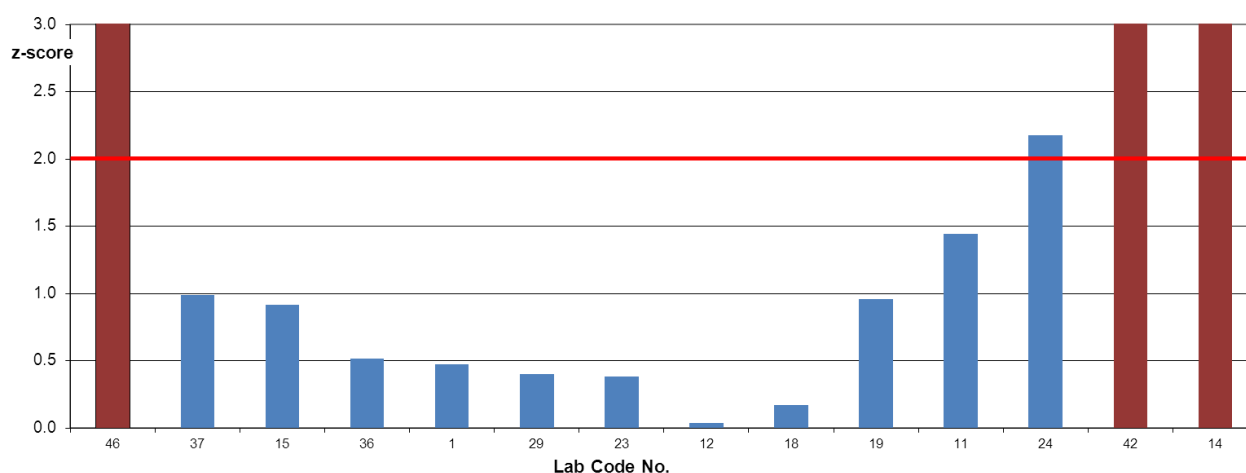
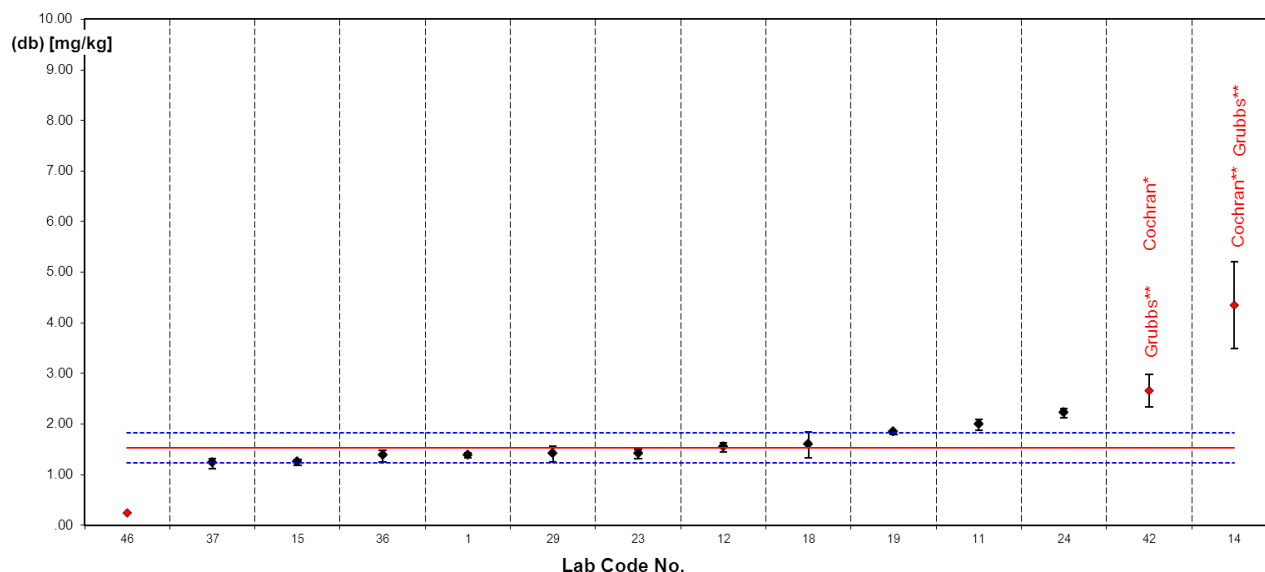
### Results for the determination of content of the minor Element Mo according to EN 15297



General mean = assigned value	m	0.27	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.0002	
Repeatability standard deviation	$s_r$	0.01	(db) [mg/kg]
Repeatability coefficient of variation		4.6	%
Between-laboratory variance	$s_L^2$	0.001	
Between-laboratory standard deviation	$s_L$	0.03	(db) [mg/kg]
Between-laboratory coefficient of variation		11.6	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.001	
Reproducibility standard deviation	$s_R$	0.03	(db) [mg/kg]
Reproducibility coefficient of variation		12.5	%
Repeatability limit	r	0.035 13.0	(db) [mg/kg] %
Reproducibility limit	R	0.094 35.0	(db) [mg/kg] %
Number of participants	n	7	

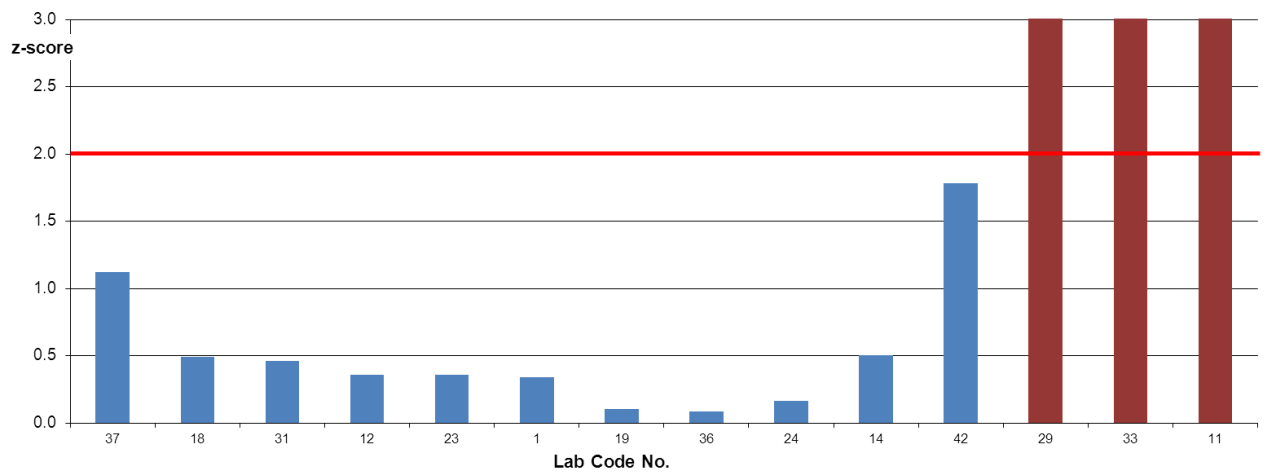
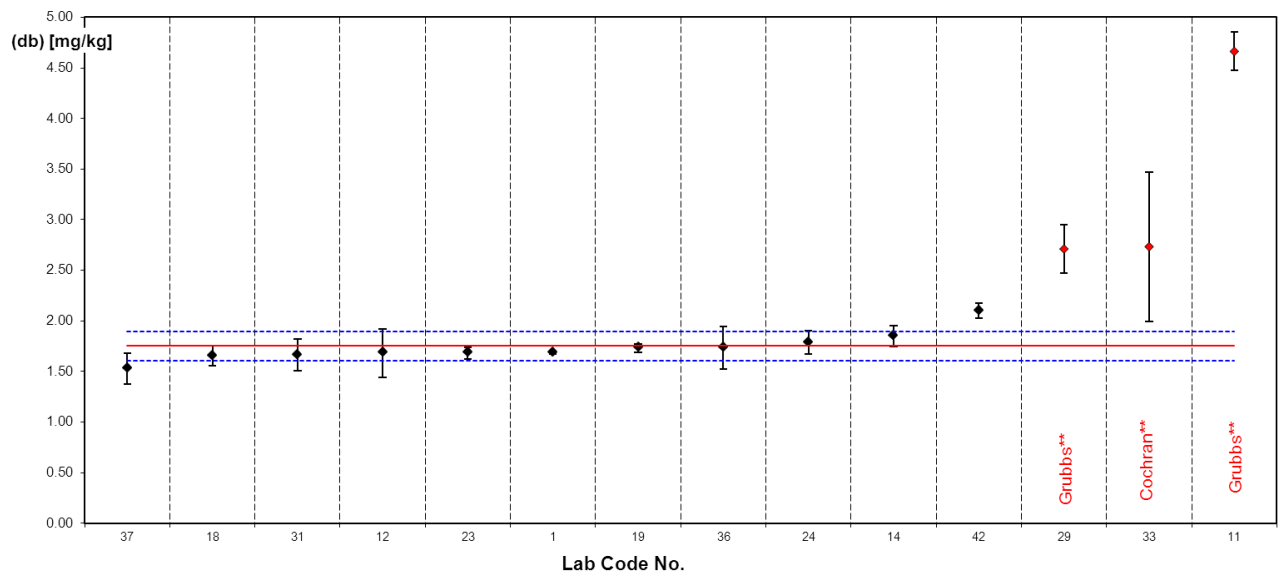


### Results for the determination of content of the minor Element Ni according to EN 15297



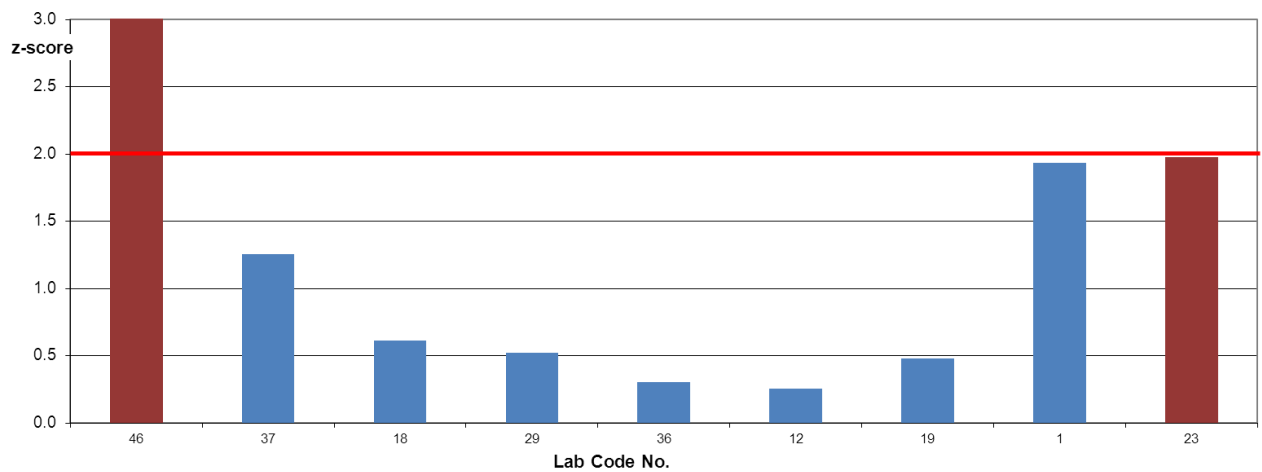
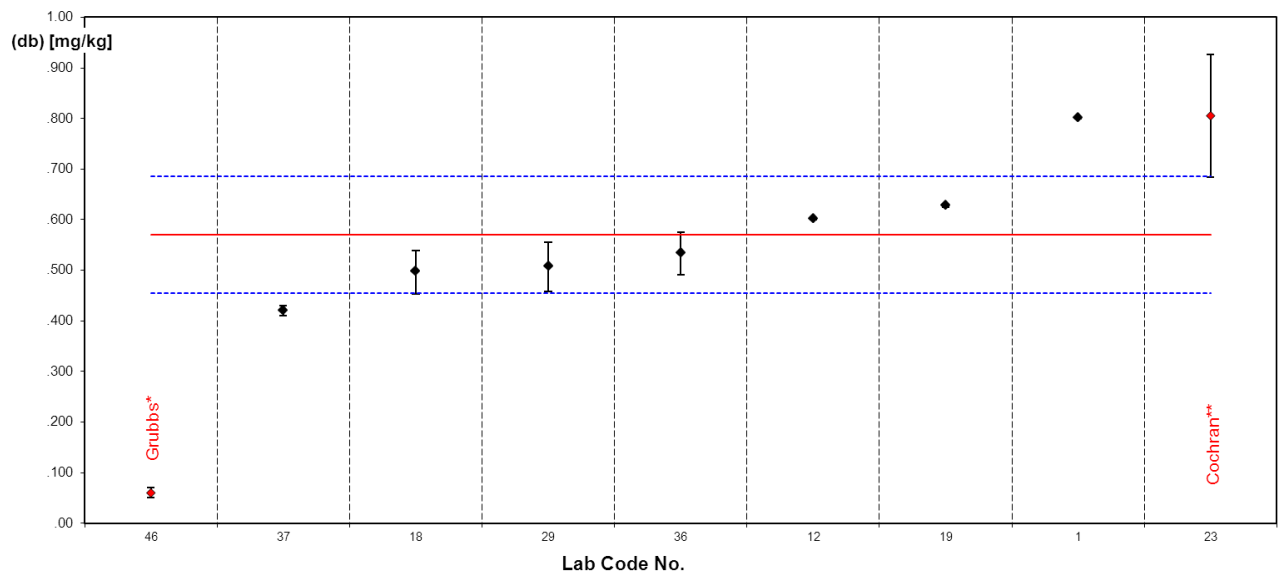
General mean = assigned value	m	1.53	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.0132	
Repeatability standard deviation	$s_r$	0.11	(db) [mg/kg]
Repeatability coefficient of variation		7.5	%
Between-laboratory variance	$s_L^2$	0.086	
Between-laboratory standard deviation	$s_L$	0.29	(db) [mg/kg]
Between-laboratory coefficient of variation		19.2	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.099	
Reproducibility standard deviation	$s_R$	0.31	(db) [mg/kg]
Reproducibility coefficient of variation		20.6	%
Repeatability limit	r	0.32	(db) [mg/kg]
		21.1	%
Reproducibility limit	R	0.88	(db) [mg/kg]
		57.7	%
Number of participants	n	11	

### Results for the determination of content of the minor Element Pb according to EN 15297



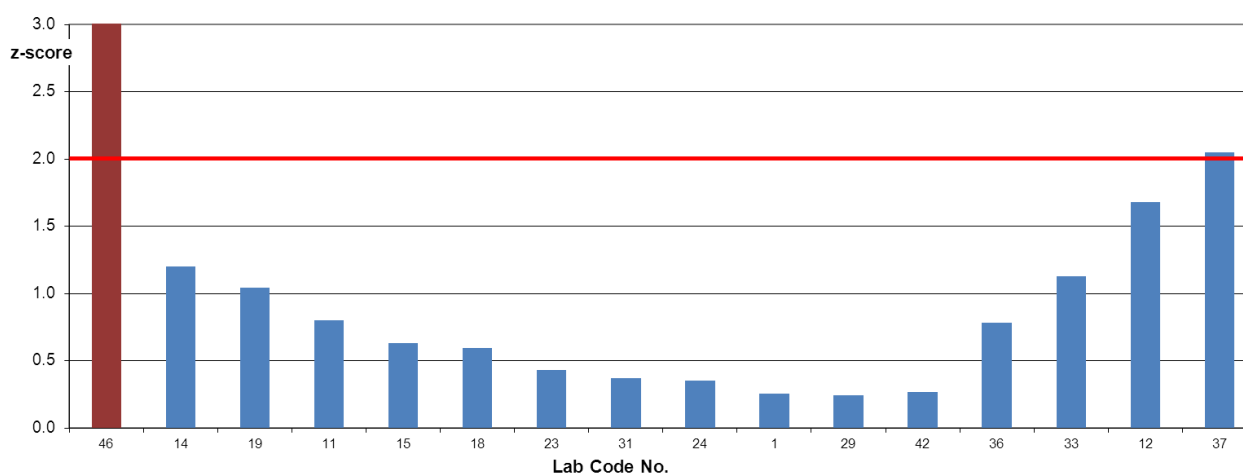
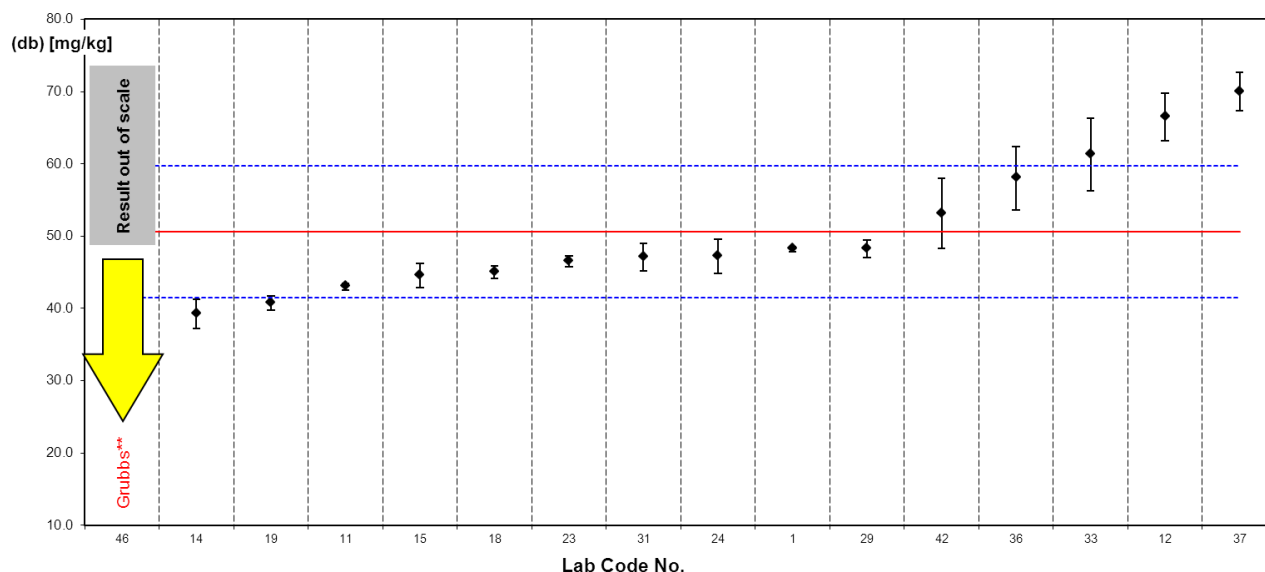
General mean = assigned value	m	1.75	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.0181	
Repeatability standard deviation	$s_r$	0.13	(db) [mg/kg]
Repeatability coefficient of variation		7.7	%
Between-laboratory variance	$s_L^2$	0.020	
Between-laboratory standard deviation	$s_L$	0.14	(db) [mg/kg]
Between-laboratory coefficient of variation		8.2	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.038	
Reproducibility standard deviation	$s_R$	0.20	(db) [mg/kg]
Reproducibility coefficient of variation		11.2	%
Repeatability limit	r	0.38	(db) [mg/kg]
		21.5	%
Reproducibility limit	R	0.55	(db) [mg/kg]
		31.4	%
Number of participants	n	11	

### Results for the determination of content of the minor Element V according to EN 15297



General mean = assigned value	m	0.57	(db) [mg/kg]
Repeatability variance	$s_r^2$	0.0009	
Repeatability standard deviation	$s_r$	0.03	(db) [mg/kg]
Repeatability coefficient of variation		5.2	%
Between-laboratory variance	$s_L^2$	0.013	
Between-laboratory standard deviation	$s_L$	0.12	(db) [mg/kg]
Between-laboratory coefficient of variation		20.3	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	0.014	
Reproducibility standard deviation	$s_R$	0.12	(db) [mg/kg]
Reproducibility coefficient of variation		20.9	%
Repeatability limit	r	0.083 14.6	(db) [mg/kg] %
Reproducibility limit	R	0.33 58.6	(db) [mg/kg] %
Number of participants	n	7	

### Results for the determination of content of the minor Element Zn according to EN 15297



General mean = assigned value	m	50.6	(db) [mg/kg]
Repeatability variance	$s_r^2$	7.16	
Repeatability standard deviation	$s_r$	2.68	(db) [mg/kg]
Repeatability coefficient of variation		5.3	%
Between-laboratory variance	$s_L^2$	82.4	
Between-laboratory standard deviation	$s_L$	9.08	(db) [mg/kg]
Between-laboratory coefficient of variation		17.9	%
Reproducibility variance $s_R^2$	$s_r^2 + s_L^2$	89.5	
Reproducibility standard deviation	$s_R$	9.46	(db) [mg/kg]
Reproducibility coefficient of variation		18.7	%
Repeatability limit	r	7.49	(db) [mg/kg]
		14.8	%
Reproducibility limit	R	26.5	(db) [mg/kg]
		52.4	%
Number of participants	n	15	

## 6 Summary and conclusions

For some of the standardised solid biofuels test methods e.g. **ash content analysis (EN 14775)**, **moisture content analysis (EN 14774-1 and 2)**, **Chlorine and Sulphur content analysis (EN 15289)**, **CHN analysis (EN 15104)** the performance data for torrefied material obtained in this round robin are comparable to the performance data for solid biofuels given in the standards (based on the results from the round robin in the BioNorm II project). These results are very pleasing, because these methods are applicable without any adoption for torrefied material. In the following figures and tables selected results for solid biofuels are compared with results for torrefied material.

**Table 3: comparison of the performance data of moisture content for solid biofuels and torrefied material**

Moisture content		torrefied Pellets (SECTOR)	Orujillo (BIONORM II) <sup>1</sup>	Woodchips (BIONORM II) <sup>1</sup>	
General mean = assigned value	m	8.00	6.32	5.34	wt.-%
<b>Repeatability limit</b>	<b>r</b>	0.15	0.19	0.40	wt.-%
		1.83	3.03	7.51	%
<b>Reproducibility limit</b>	<b>R</b>	0.64	1.33	1.99	wt.-%
		7.95	21.07	37.19	%
Number of participants	n	38	31	32	
Overall number of individual results	l	137	145	151	

<sup>1</sup>BIONORM II project no. 038644 funded by European Commission

**Table 4: comparison of the performance data of ash content for solid biofuels and torrefied material**

Ash content		torrefied Pellets (SECTOR)	Orujillo (BIONORM II) <sup>1</sup>	Woodchips (BIONORM II) <sup>1</sup>	
General mean = assigned value	m	3.12	11.13	0.59	wt.-%
<b>Repeatability limit</b>	<b>r</b>	<b>0.20</b>	<b>0.56</b>	<b>0.05</b>	<b>wt.-%</b>
		6.40	5.03	9.15	%
<b>Reproducibility limit</b>	<b>R</b>	<b>0.42</b>	<b>1.26</b>	<b>0.11</b>	<b>wt.-%</b>
		13.4	11.28	17.88	%
Number of participants	n	39	30	34	
Overall number of individual results	l	158	138	154	

<sup>1</sup>BIONORM II project no. 038644 funded by European Commission

**Table 5: comparison of the performance data of chlorine content for solid biofuels and torrefied material**

Chlorine content		torrefied Pellets (SECTOR)	Orujillo (BIONORM II) <sup>1</sup>	Woodchips (BIONORM II) <sup>1</sup>	
General mean = assigned value	m	0.022	0.20	0.01	wt.-%
<b>Repeatability limit</b>	<b>r</b>	0.004	0.02	0.002	wt.-%
		16.43	7.72	35.6	%
<b>Reproducibility limit</b>	<b>R</b>	0.010	0.04	0.01	wt.-%
		47.86	22.35	144.5	%
Number of participants	n	23	22	20	
Overall number of individual results	l	87	98	90	

<sup>1</sup>BIONORM II project no. 038644 founded by European Commission

**Table 6: comparison of the performance data of carbon content for solid biofuels and torrefied material**

Carbon content		torrefied Pellets (SECTOR)	Orujillo (BIONORM II) <sup>1</sup>	Woodchips (BIONORM II) <sup>1</sup>	
General mean = assigned value	m	53.0	48.1	50.3	wt.-%
<b>Repeatability limit</b>	<b>r</b>	0.43	0.78	0.40	wt.-%
		0.81	1.63	0.80	%
<b>Reproducibility limit</b>	<b>R</b>	1.93	1.55	1.54	wt.-%
		3.64	3.23	3.07	%
Number of participants	n	32	30	30	
Overall number of individual results	l	125	145	143	

<sup>1</sup>BIONORM II project no. 038644 founded by European Commission

**Table 7: comparison of the performance data of nitrogen content for solid biofuels and torrefied material**

Nitrogen content		torrefied Pellets (SECTOR)	Orujillo (BIONORM II) <sup>1</sup>	Woodchips (BIONORM II) <sup>1</sup>	
General mean = assigned value	m	0.45	1.39	0.12	wt.-%
<b>Repeatability limit</b>	<b>r</b>	0.06	0.12	0.03	wt.-%
		14.45	8.95	20.79	%
<b>Reproducibility limit</b>	<b>R</b>	0.19	0.32	0.10	wt.-%
		45.59	22.73	83.25	%
Number of participants	n	29	29	26	
Overall number of individual results	l	114	131	120	

<sup>1</sup>BIONORM II project no. 038644 founded by European Commission

**Table 8: comparison of the performance data of sulphur content analysis for solid biofuels and torrefied material**

Sulphur content		torrefied Pellets (SECTOR)	Orujillo (BIONORM II) <sup>1</sup>	Woodchips (BIONORM II) <sup>1</sup>	
General mean = assigned value	m	0.036	0.12	0.01	wt.-%
<b>Repeatability limit</b>	<b>r</b>	0.008	0.02	0.003	wt.-%
		21.66	15.17	34.3	%
<b>Reproducibility limit</b>	<b>R</b>	0.027	0.06	0.01	wt.-%
		75.16	48.42	94.8	%
Number of participants	n	28	28	27	
Overall number of individual results	l	108	133	121	

<sup>1</sup>BIONORM II project no. 038644 funded by European Commission

An evaluation of the Z-score graphs show nearly ideal normal distributions as should be expected for these kind of round robins for some determinations e.g. Chlorine or Carbon content. For some other determination biased results are found e.g. nitrogen and sulphur were Z-score graphs suggest to compare used methods more carefully and investigate systematic differences in methods used. However, this was not done within this round robin yet.

For **net calorific value** the repeatability limit of the EN 14918 is met for the torrefied material but not the reproducibility limit. The reproducibility limit for torrefied material is higher than for solid biofuels. This result should be checked again because the net calorific value is extremely sensitive to inhomogeneous torrefaction is not unexpected for the industrial process in development supplying the sample.

One of the methods that must be adapted or described better is the **ash melting analysis** (CEN/TS 15370-1). This analysis method is still a technical specification and no European standard, because the method is not developed and validated sufficiently. It is remarkable that the reproducibility of the flow temperature is fairly good but the very important deformation temperature seems to be difficult to measure. The authors suppose that it is not the instrument itself but details of the method and the interpretation of the observations. Similar problems found during the analysis for solid biofuels were also observed during this round robin test of torrefied material. E.g. the shrinking temperature which is often not possible to identify according to definition in the TS, the influence of sample preparation and storage of ash before analysis, the possibility of carbon dioxide absorption during the test of calcium rich ashes etc. These points should be verified and also new ore more detailed definition for critical temperatures is needed to gain comparable results.

This technical specification (CEN/TS 15370-1) is very important for the biofuel end user and should be adopted. The authors themselves have gathered experience with ash deformation

temperature in the last 2 years and found this parameter to be a very good indicator for wood pellet quality well knowing that determination requires a lot of experience. The parameters (deformation temperature and flow temperature) are very helpful in practical use of solid biomass fuels, since these points correlate with practical use.

The analysis of **minor elements** (EN 15297) is in general more difficult to evaluate. One reason is the low concentrations of single elements and the detection limits of the participating laboratory. Similar problems were observed for the minor elements determination for solid biofuels and will not be solved with adaption of the analysis method. Maybe a testing material with higher contents on minor elements would be advisable, but this material would not represent the typical natural and uncontaminated solid biomass fuels which are nearly free of heavy metals.

The elements **Mercury and Antimony** could not be evaluated because of too less results. Mercury is usually found in very low concentrations in most biomass types. Often concentration is below detection limits. In a thermally treated biomass (torrefaction temperature > 250 °C) Mercury will not be found in relevant concentrations since it can be assumed that Mercury is lost during treatment due to the low heat of vaporization.

Some parameters like mechanical durability and bulk density were not validated in BioNorm II so results presented here are the first ones to provide performance data on a broad basis.

## 7 References

- EN 14961 “Solid biofuels — Fuel specifications and classes — Part 1: General requirements”
- ISO 5725-1 “Accuracy (trueness and precision) of measurement methods and results General principles and definitions”
- ISO 5725-2 "Accuracy (trueness and precision) of measurement methods and results" - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method"
- ISO/IEC Guide 43-1:1997 “Proficiency testing by interlaboratory comparisons - Part 1: Development and operation of proficiency testing schemes”
- CEN GUIDE 13:2008 “Validation of environmental test methods”