

Final Report
Evaluation of the
interlaboratory test on the method
UN test O.1 “Test for oxidizing solids”
with sodium perborate monohydrate
2005 / 06



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BAM Federal Institute for Materials Research and Testing

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1 Introduction

The classification of solid oxidizers according to the GHS (Globally Harmonized System of Classification and Labelling of Chemicals) and according to regulations on the transport of dangerous goods (based on the UN Recommendations/Model Regulations and implemented in all carrier domains as transport by road, railway, sea, air) is performed on the basis of the results of the UN test O.1 (“Test for oxidizing solids” described in chapter 34.4.1 in the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fifth revised edition, United Nations, New York and Geneva, 2009). This test was introduced into the UN Test Manual in 1995 as a replacement for a similar test from 1986. Even though the O.1 test is much better than the previous one there are still many problems with this test. For this reason the IGUS-EOS working group (international group of experts on the explosion risks of unstable substances – working group: energetic and oxidizing substances) installed an ad-hoc working group in 2002 assigned with the task of proposing solutions for the existing problems. The adequacy of such proposals has to be proven preferably by interlaboratory comparison (interlaboratory test) before they are presented to the UN Sub Committee for adoption into the UN Test Manual. The present report is the evaluation of an interlaboratory test which was designed by the Ad-hoc working group in order to find out whether the current method of comparing combustion times of test mixtures with those of reference mixtures is suitable in principle and whether some approaches for improvement of the method can be identified.

The classification of solid oxidizers according to the UN test O.1 is based on the comparison of their combustion times in mixtures with cellulose with those of defined mixtures of potassium bromate with cellulose as reference mixtures. However, the combustion times of the reference mixtures for packing group I, II or III already vary considerably. There are several reasons for this variation, but their influence is not completely known. These questions have to be resolved in order to ensure the correct classification of solid oxidizers as a basis for their safe handling.

Originally, two aspects should be covered by the design of this interlaboratory (“Round Robin”) test (see chapter 7.1 “Test instruction” and chapter 7.2 “Laboratory data input form”):

- (1) The performance of the UN test O.1 considering additional modifications/specifications in the test procedure (*1st part / test series of the RR-Test*)
and
- (2) the effect of narrowing the particle size range of potassium bromate in the reference mixtures from 150-300 μm to 180-250 μm (*2nd part / optional test series*).

With reference to the results of a provisional data analysis and due to low participation in the optional test series the present report only describes the results of the 1st part of the interlaboratory test (using potassium bromate with a particle size of 150-300 μm).

2 Test material

2.1 Interlaboratory test sample

Sodium perborate monohydrate was chosen as test substance for the interlaboratory test. The interlaboratory test samples were homogenized and divided by BAM and distributed to the participants of the interlaboratory test.

2.1.1 Preparation of the interlaboratory test samples

Sodium perborate monohydrate (25 kg sodium perborate monohydrate, Qual. 40, content $\geq 94\%$) was provided by Degussa, Germany.

The original sample (25 kg) was divided in 16 sub-samples by aid of a spinning (rotating) riffler (see Figure 1).



Figure 1: Dividing of the 25 kg sample on a spinning (rotating) riffler at BAM
right picture: the sample flows from the hopper to a vibrating chute and travels along the chute to the receivers (8 glass containers)

The homogenising procedure was performed in accordance with the principles of the cross-riffling-procedure [3] (see Figure 2).

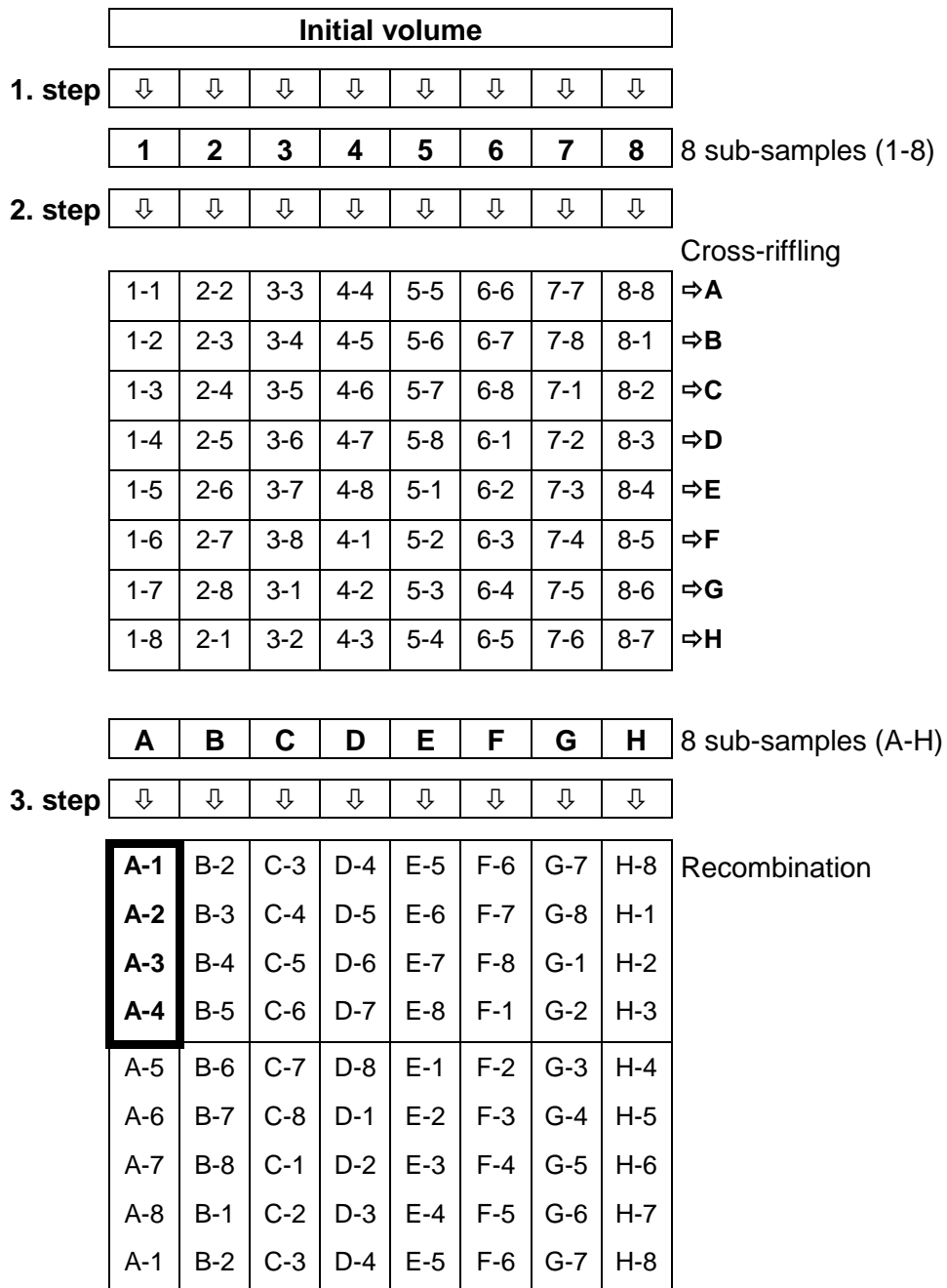


Figure 2: Division of the sample and recombination table of the cross riffling procedure

Steps 1 and 2 were executed in a standard way. In order to obtain a total of 16 samples at the 3rd step each sample was recombined by 4 sub-samples, e.g. sample 1 is a recombination of sub-sample A-1, A-2, A-3 and A-4 (bold frame in Figure 2). After each step, the divided sub-samples are repacked into small plastic bags (see Figure 3) and finally – at step 3 – the final interlaboratory test samples are repacked into transport containers for the participants of the interlaboratory test (see Figure 4).



Figure 3: Repacking of the divided sub-samples



Figure 4: 16 divided interlaboratory test samples for the participants of the interlaboratory test

2.1.2 Homogeneity and stability of interlaboratory test samples

Due to the fact that the interlaboratory test samples were homogenised in accordance with the principles of the cross-riffling-procedure ([3], chapter 2.1.1) it is assumed that the homogeneity is sufficiently high for the interlaboratory test.

The particle size distribution of the sub-samples of each of the 12 distributed interlaboratory samples (sodium perborate monohydrate) was determined (results see Figure 5). The results of the particle size distribution tests are given for information only and might be used for comparison within future tests.

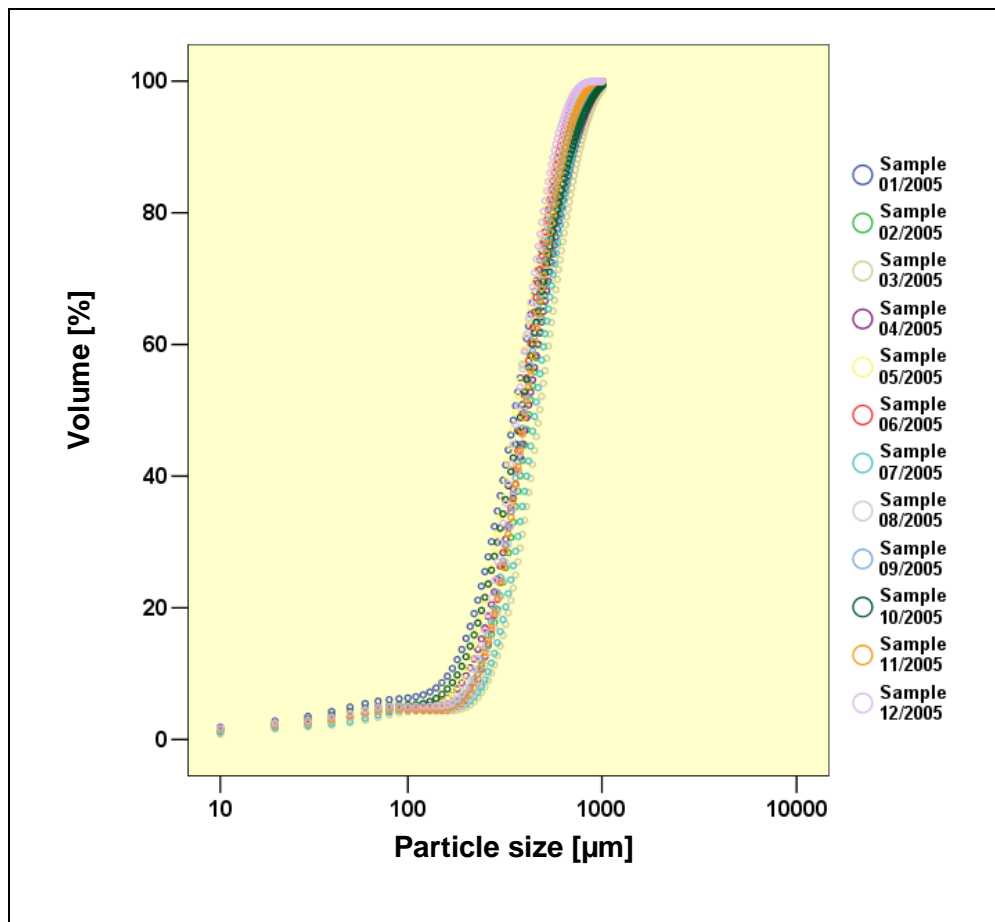


Figure 5: Particle size distribution of sodium perborate monohydrate of the laboratory test samples

Based on the experience of the manufacturer sodium perborate monohydrate is known to be sufficiently stable during the period of the interlaboratory test (January to February 2006) and no further test to control the stability was performed.

2.2 Further test substances and test mixtures relating to the test method

The other substances (potassium bromate and cellulose) which are necessary to perform the UN test O.1 were not distributed by BAM; i.e. the mixtures were prepared by the laboratories themselves using the substances they normally use.

In this interlaboratory test three different mixtures of potassium bromate with cellulose (three reference substance mixtures for the assignment to the dangerous goods packing groups PG1, PG2 and PG3) and two different mixtures of the interlaboratory test sample (sodium perborate monohydrate) with cellulose (two test sample mixtures TS41 and TS11) were used (see Table 1):

Table 1: Mixtures which are prepared by the different laboratories

Name of the mixture (short name)	Composition of the mixture
Reference substance mixture for packing group I (PG1)	potassium bromate : cellulose = 3:2
Reference substance mixture for packing group II (PG2)	potassium bromate : cellulose = 2:3
Reference substance mixture for packing group III (PG3)	potassium bromate : cellulose = 3:7
Test sample mixture (TS41)	sodium perborate monohydrate : cellulose = 4:1
Test sample mixture (TS11)	sodium perborate monohydrate : cellulose = 1:1

3 Procedure of the interlaboratory test

3.1 Organisation

The interlaboratory test samples together with a test instruction (see Appendix 7.1) were sent to the 12 participating laboratories (see Table 2) by BAM. Table 3 shows the schedule of the study.

**Table 2: List of all 12 participating laboratories (10 laboratories have performed the test)
*... Laboratories, which did not perform the test within the testing period**

Laboratory / Agency (short name)	Country
Akzo Nobel	Netherlands
BAM	Germany
Bayer	Germany
Degussa / AQura	Germany
HKGL	Hong Kong
INERIS	France
LOM	Spain
Solvay	Germany
TNO	Netherlands
Yara	Norway
HSL*	Great Britain
Siemens (Axiva)*	Germany

Table 3: Time schedule of the interlaboratory test

Round robin step	Time period
Distribution of the test sample and the test instruction	December 2005
Laboratory testing period	January – February 2006
Statistical evaluation	March – April 2006

BAM received results from 10 laboratories within the pre-set time frame. None of these 10 laboratories had to be excluded from the evaluation because of insufficient data.

3.2 Test procedures

The standardised test instruction (see Appendix 7.1 Test instruction) and the data input form (see Appendix 7.2 Laboratory data input form) were prepared in co-operation with the IGUS EOS ad-hoc oxidizer working group and quo data. The test instruction (which is more detailed than the current description of UN test O.1 according to the UN Manual of Tests and Criteria) included:

- use of a specified windshield,
- stop of electrical power of the ignition wire after 20 seconds,
- no change of the laboratory assistant within the test steps, e.g. the time measuring should be performed always by the same laboratory assistant,
- the test substance sodium perborate monohydrate as received from BAM should not be treated by any method.

All other procedures were performed as stipulated in UN test O.1, i.e. the main reaction is determined by: “flames, incandescence or glowing combustion. Intermittent reaction, such as sparking or sputtering, after the main reaction should not be taken into account.”

The participants were requested to measure the combustion times¹ of reference substance mixtures for packing groups I, II and III (PG1, PG2, PG3) and test sample mixtures TS11 and TS41 with 5 replicates in accordance with UN test O.1.

¹ The term „combustion time“ is used equivalently to „burning time“ in the sense of method UN test O.1.

4 Evaluation

4.1 Background

After an exploratory analysis (see chapter 4.3) evaluation of the data was performed using ProLab 2006, a software program for the evaluation of interlaboratory comparisons (see chapter 4.4).

The following Table 4 gives an overview of the three types of data which were analysed statistically for each of the test sample mixtures and reference substance mixtures and for all combinations of the test sample mixtures and reference substance mixtures, respectively, in the following sections.

Table 4: Overview of analysed data types

Data type	Evaluation according to	Elimination of outliers?	Background	Resulting in
<p>single combustion times (see chapter 4.4.1)</p>	<p>ISO 5725-2 (standard method)</p>	<p>yes</p>	<p>standard analysis for interlaboratory test results (generally based on single values)</p>	<p>→ total mean of single combustion times ... → reproducibility standard deviation ... → repeatability standard deviation ... → 95 % confidence band ... → tolerance limits according to ISO 5725-2 (based on outlier-free data)</p>
<p>laboratory mean combustion times (see chapter 4.4.2.1)</p>	<p>DIN 38402 A 45 (robust method)</p>	<p>no</p>	<p>robust analysis of laboratory mean combustion times because of no outlier elimination in the laboratory practise</p>	<p>→ mean of laboratory mean combustion times ... → reproducibility standard deviation ... → 95 % confidence band ... → tolerance limits according to DIN 38402 A 45 (no outliers have been eliminated)</p>
<p>ratios of laboratory mean combustion times (see chapter 4.4.2.2)</p>			<p>robust analysis of ratios of laboratory mean combustion times because of no outlier elimination in the laboratory practise and correction of systematic effects</p>	<p>→ mean of ratios of laboratory mean combustion times ... → reproducibility standard deviation ... → 95 % confidence band ... → tolerance limits according to DIN 38402 A 45 (no outliers have been eliminated)</p>

Data type: single combustion times

The standard method according to ISO 5725-2 was applied for the statistical analysis of single combustion times. This method is based on normal distribution of the test results, hence outlier tests are required. The identified outliers (outlier laboratories due to excessive variance see Table 6) were eliminated for calculating the precision parameters.

Data type: laboratory mean combustion times

There is no recommendation concerning the outlier determination / handling with outliers in UN test O.1. Therefore, in practise the laboratories do not eliminate outlying values and the “simple” arithmetic mean value of single combustion times of the respective tests will be used as result. Hence for these so-called laboratory mean combustion times the assumption of normal distribution is not valid necessarily. Furthermore, each laboratory provides only one laboratory mean combustion time of the respective reference substance mixtures and the test sample mixtures, hence no replicates of the laboratory mean combustion time are available.

For this reason, the laboratory mean combustion times were evaluated on the basis of the statistical method according to DIN 38402 A 45 (=ISO/DIS 20612). This method is a robust method and no outlier examination is required.

Data type: ratios of laboratory mean combustion times

According to UN test O.1 the laboratory mean combustion time of the test sample mixture is compared to those of the reference substance mixtures in order to decide whether a substance is classified as an oxidizing solid and if so to which category (or packing group) it is assigned. Therefore not only the combustion times but also their ratios were analysed and evaluated.

Moreover, systematic effects might be compensated when evaluating ratios of laboratory mean combustion times, because a proportional behaviour of the combustion times within a laboratory is expected. Thus, the ratios of the laboratory mean combustion times of different laboratories should be similar.

The ratios of laboratory mean combustion times for 8 combinations (see Table 5) of reference mixtures and test sample mixtures were considered in the statistical analysis. For the same reason as for the laboratory mean combustion times, the ratios of laboratory mean combustion times were evaluated on the basis of the statistical method according to DIN 38402 A 45 (=ISO/DIS 20612) and hence no outlier examination is required.

Table 5: Ratios of laboratory mean combustion times

Symbol	Description
PG2/PG1	Ratio of laboratory mean combustion times for PG1 and PG2
PG3/PG2	Ratio of laboratory mean combustion times for PG2 and PG3
TS11/PG1	Ratio of laboratory mean combustion times for TS11 and PG1
TS11/PG2	Ratio of laboratory mean combustion times for TS11 and PG2
TS11/PG3	Ratio of laboratory mean combustion times for TS11 and PG3
TS41/PG1	Ratio of laboratory mean combustion times for TS41 and PG1
TS41/PG2	Ratio of laboratory mean combustion times for TS41 and PG2
TS41/PG3	Ratio of laboratory mean combustion times for TS41 and PG3

For all three data types described above, the respective mean as well as the respective reproducibility standard deviation were calculated over all laboratories. The repeatability standard deviation was calculated only for the first data type (single combustion times) and the third data type (ratio of laboratory mean combustion times).

The reproducibility standard deviation characterizes the variability of the data (single combustion times, laboratory mean combustion times or ratios of laboratory mean combustion times) under reproducibility conditions, i.e. test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

The repeatability standard deviation describes the variability of the data under repeatability conditions, i.e. 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. For determining the repeatability standard deviation, replicates of the measurements are necessary. Thus, for the two data types *laboratory mean combustion times* and *ratios of laboratory mean combustion times*, repeatability standard deviations cannot be obtained from the data as for each laboratory and sample only one “measurement value” (= laboratory mean value) is available. However, the repeatability standard deviation of the ratios of laboratory mean combustion times were predicted by means of error propagation methods.

4.2 Data pre-processing

Before the statistical evaluation by quo data and in contrast to the UN test O.1 the submitted raw data were cleared of data that are based on combustion times, where no flames were observed, because – after consultation with the organisation panel (IGUS EOS Ad-hoc working group on the solid oxidizer test) – the flame was considered as the typical indicator for the main reaction and extinction of the flame as the end of the reaction of the mixtures. In total, 276 measurements (single combustion times) were provided by the laboratories for which 18 measurements were obtained without flames (5 from laboratory 03, 3 from laboratory 05, 1 from laboratory 07, 5 from laboratory 09 and 4 from laboratory 10). 17 out of these 18 measurements belong to the test sample mixtures and 1 belongs to the reference sample mixture PG3.

The following analyses are based on combustion time values with flames only.

4.3 Exploratory analysis of the single combustion times

In the first step – the exploratory analysis of the single combustion times – the relationship between logarithmised combustion time [s] and logarithmised concentration of the oxidizer [% by mass] in the reference substance mixtures PG1, PG2 and PG3 is diagrammed for each laboratory. In Figure 6 this is shown exemplarily for laboratory 01. For the figures of the remaining laboratories please refer to Appendix 7.3.

In each of the figures, the respective equation for the regression line is given. In addition, the logarithmised combustion times of the test sample mixtures TS11 and TS41 are indicated on the regression line.

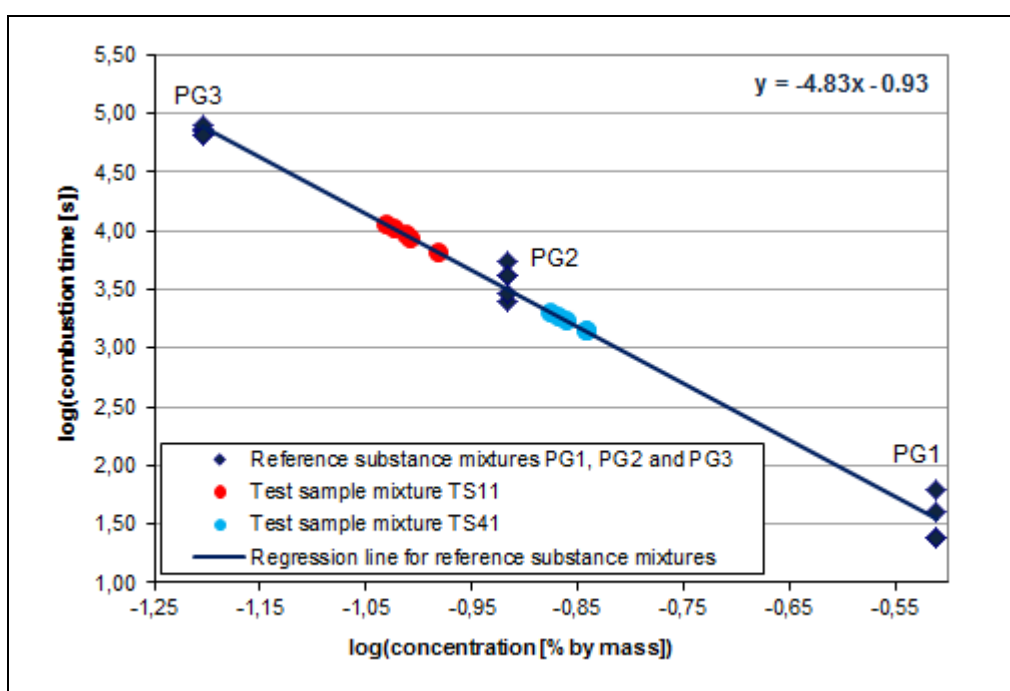


Figure 6: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 01 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

A linear dependency between the logarithmised combustion time and the logarithmised concentration of the oxidizer in the reference substance mixtures PG1, PG2, PG3 was determined for each laboratory except for laboratory 09. For this laboratory a quadratic regression curve proved to fit the data significantly better (tested by Mandel test 5 %).

It has to be noted that the slope of the linear relationship is varying considerably for the different laboratories (slope between -2.3 and -4.8).

4.4 Evaluation of UN test O.1 method

4.4.1 Standard method: Analysis of single combustion times according to ISO 5725-2

The single combustion times were analysed by the statistical method according to ISO 5725-2. The laboratory mean values of the single combustion times of each laboratory (laboratory mean combustion times) are given in Table 6.

The precision parameters, i.e. the total mean of single combustion times, the relative reproducibility standard deviations and the relative repeatability standard deviations over all laboratories, which are all based on outlier-free data, are given in Table 7.

It has to be noted that the total mean of single combustion times according to ISO 5725-2 conforms to a weighted mean of all laboratory's single values and therefore is also influenced by the number of available single values per laboratory. Only in the case that all laboratories exhibit the same number of measurements, the total mean of single combustion times is equal to the arithmetic mean of laboratory mean combustion times. Furthermore, the total mean of single combustion times according to ISO 5725-2 neither includes single outliers nor outlier laboratories. A laboratory is referred to as "outlier laboratory", where all laboratory's single combustion times are eliminated, either because the laboratory mean combustion time of this laboratory differs significantly from the laboratory mean combustion times of the other laboratories or because the single combustion times of this laboratory shows an excessive variance compared to the other laboratories.

In this interlaboratory test, all laboratories provided 5 measurements per reference substance mixture and test sample mixture (i.e. 5 replicates of each mixture) – except for laboratory 03 which provided 10 measurements in total for PG1, PG2, PG3 and TS11. As a consequence, the total mean of single combustion times for PG1, PG2, PG3 and TS11, respectively, differs from the arithmetic mean of the laboratory mean combustion times.

Table 6: Laboratory mean combustion times [s] (values in brackets: outlier laboratories due to excessive variance, which are not included into the total mean of single combustion times according to ISO 5725-2 but into the mean of laboratory mean combustion times according to DIN 38402 A 45)

Laboratory	PG1	PG2	PG3	TS11	TS41
01	4.6	35.6	127.4	52.0	24.8
02	9.6	34.4	122.1	67.7	33.1
03	10.9	43.0	119.4	50.1	42.2
04	11.2	38.2	96.4	52.2	32.0
05	13.2	61.4	144.4	75.3	38.0
06	22.6	66.8	(147.6)	57.6	36.8
07	28.6	(79.0)	139.8	(55.8)	43.6
08	11.0	45.6	124.8	51.6	42.6
09	7.0	(67.0)	(125.0)	81.0	33.5
10	11.4	33.4	90.9	61.0	29.1

Table 7: Total mean of single combustion times and relative standard deviations based on outlier-free data for single combustion times [s] for the reference mixture substances and the test sample mixtures

		PG1	PG2	PG3	TS11	TS41
Method according to ISO 5725-2 (based on outlier-free data)	Total mean of single combustion times	12.8 s	44.6 s	120.5 s	58.5 s	35.6 s
	Rel. reproducibility s.d.	55.2 %	28.5 %	16.4 %	21.6 %	20.6 %
	Rel. repeatability s.d.	12.2 %	10.0 %	7.8 %	12.7 %	10.8 %

Figure 7 shows the laboratory mean combustion times as well as the total mean of single combustion times according to ISO 5725-2 (based on outlier-free data) and the relative standard deviations according to ISO 5725-2 (based on outlier-free data) for the reference substance mixture of packing group II (PG2) of all laboratories as an example. Equivalent figures for the other reference substance mixtures of the packing groups and the test sample mixtures are shown in Appendix 7.4. In the figures, boxes symbolize the variability of the single combustion times of one laboratory. The larger the box, the higher is the variability of the single combustion times in this laboratory. The horizontal line in the middle of box indicates the laboratory mean combustion time of the laboratory, while the small triangles mark the single combustion times. The figures also include the 95 % confidence band (green band) of the total mean of single combustion times according to ISO 5725-2 (black line) as well as the tolerance limits for the laboratory mean combustion times (red lines) – also according to ISO 5725-2. These tolerance limits are derived from the assumed limits of ± 2 for the Z scores (see chapter 4.5).

In Figure 7 the results of laboratories that proved to be outlier laboratories according to the outlier tests in ISO 5725-2 are shown for additional information only (marked by red boxes). Note that these values were not used to derive the total mean of single combustion times and the standard deviations according to ISO 5725-2.

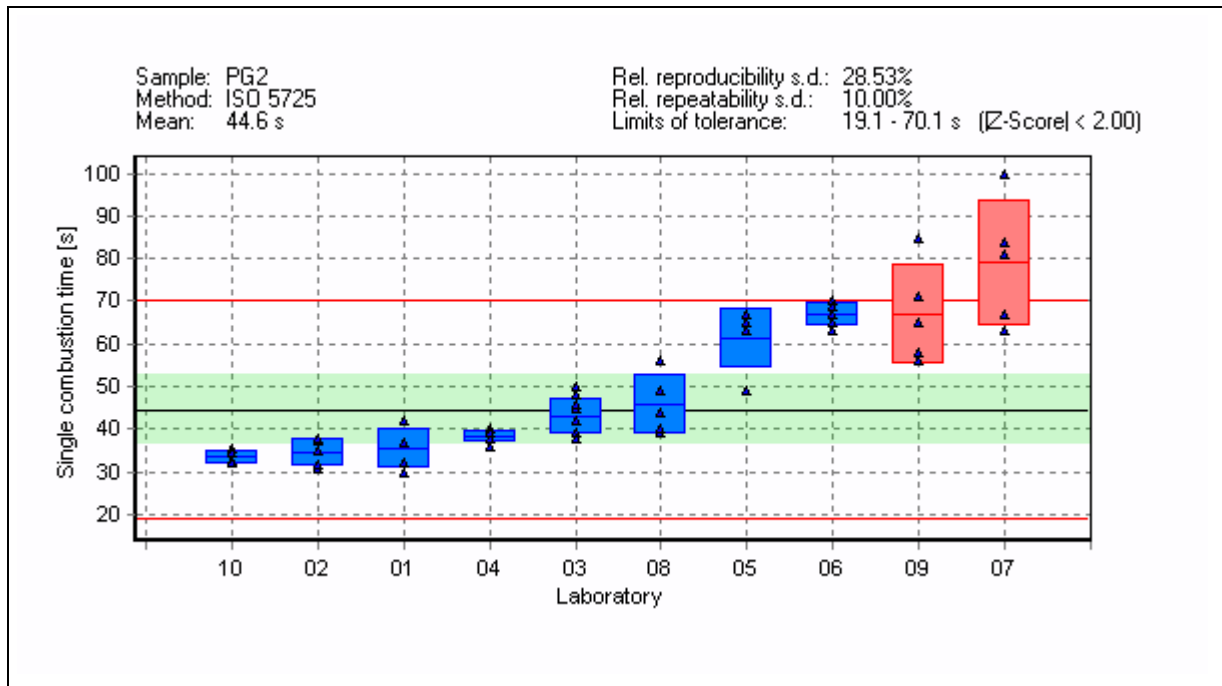


Figure 7: Analysis of single combustion times [s] – PG2

For the reference substance mixture of packing group II only the laboratory mean combustion time of laboratory 07 lies above the upper tolerance limit. Thus, for this laboratory the laboratory mean combustion time is significantly higher than the total mean of single combustion times. Furthermore, this laboratory 07 and also laboratory 09 are outlier laboratories due to a significantly higher variability of single combustion times.

For the reference substance mixture of packing group I (see Appendix 7.4) the laboratory mean combustion time of laboratory 07 lies outside the tolerance limits as well, thus again it is significantly larger than the total mean of single combustion times. However, laboratory 07 was not identified as an outlier laboratory.

For the reference substance mixture of packing group III, for none of the laboratories the laboratory mean combustion time lies outside the tolerance limits. The variability of the single combustion times of laboratories 06 and 09 is significantly higher than for the other laboratories. These two laboratories were identified as outlier laboratories and not taken into account for the statistical analysis.

For test sample mixture 1:1 (TS11), none of the laboratory mean combustion times lies outside the tolerance limits. The standard deviation of laboratory 07 significantly exceeds the standard deviation of the other laboratories and thus laboratory 07 was identified as outlier laboratory and not taken into account for the statistical analysis according to ISO 5725-2 (based on outlier-free data).

For test sample mixture 4:1 (TS41), neither a laboratory mean combustion time lies outside the tolerance limits nor an outlier laboratory was identified.

4.4.2 Robust method: Analysis of laboratory mean combustion times as well as their ratios

4.4.2.1 Analysis of laboratory mean combustion times

The laboratory mean combustion times (see Table 6) were analysed based on the statistical method according to DIN 38402 A 45 (=ISO/DIS 20612, see [4]). This robust method does not require replicates for the laboratory mean combustion times. Given the small number of laboratory mean combustion times, a further advantage is that an outlier examination – which might reduce the number of values used in the analysis – is not required.

In the following Table 8 the mean of laboratory mean combustion times and the relative reproducibility standard deviations over all laboratories are summarized.

Table 8: Mean of laboratory mean combustion times and relative standard deviations for laboratory mean combustion times [s] for the reference substance mixtures and the test sample mixtures

		PG1	PG2	PG3	TS11	TS41
Method according to DIN 38402 A 45 (no outliers have been eliminated)	Mean of laboratory mean combustion times	10.9 s	49.7 s	126.3 s	60.0 s	35.6 s
	Rel. reproducibility s.d.	39.9 %	29.0 %	9.8 %	18.4 %	25.8 %

Figure 8 shows the laboratory mean combustion times for packing group I of all laboratories. Equivalent figures for the other packing groups and the test sample mixtures are shown in Appendix 7.5.1.

In the figures, blue lines with blue diamonds symbolize the laboratory mean combustion time. The figures also include the 95 % confidence band (green band) of the mean of laboratory mean combustion times according to DIN 38402 A 45 (black line). Furthermore, the tolerance limits for the laboratory mean combustion times are shown as red lines – also according to DIN 38402 A 45. These tolerance limits are derived from the assumed limits of ± 2 for the Z scores.

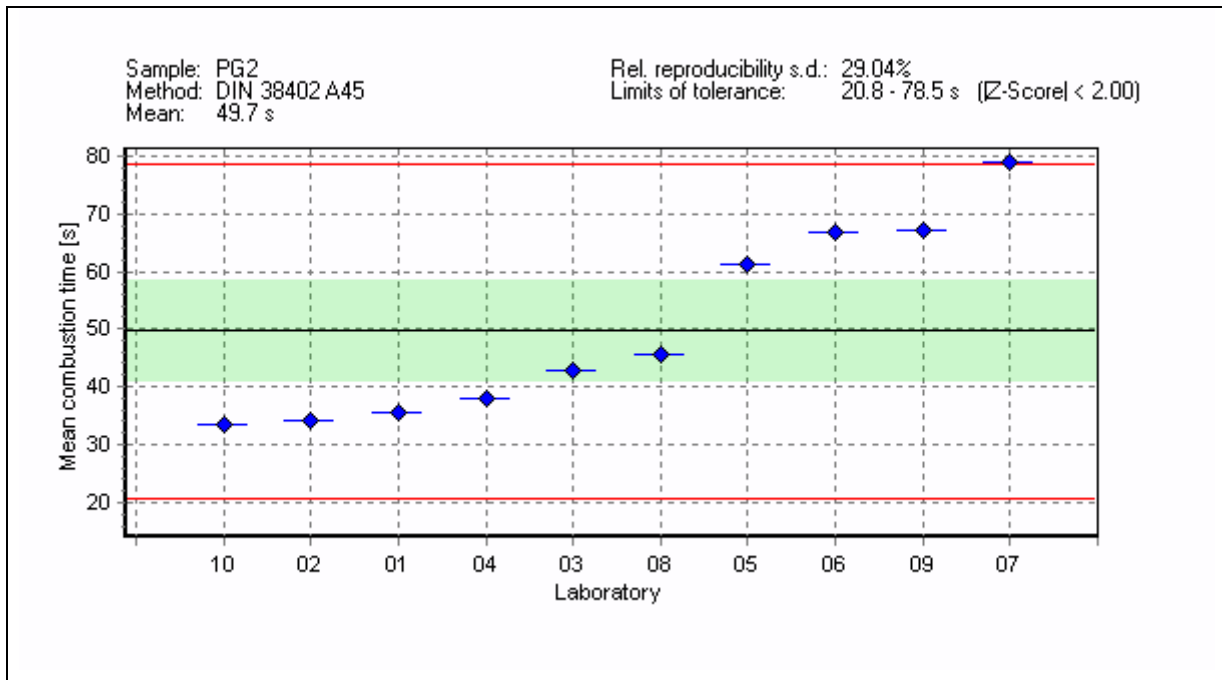


Figure 8: Analysis of laboratory mean combustion times [s] – PG2

For the reference substance mixture of packing group II, the laboratory mean combustion time of laboratory 07 lies above the upper tolerance limit, and thus it is significantly higher than the mean of laboratory mean combustion times.

For the reference substance mixture of packing group I the laboratory mean combustion times of laboratories 06 and 07 are above the upper tolerance limit.

For the reference substance mixture of packing group III, the laboratory mean combustion times of laboratories 10 und 04 are below the lower tolerance limit. In contrast to the reference substance mixtures of packing groups I and II, their laboratory mean combustion times are significantly lower than the mean of laboratory mean combustion times.

For both test sample mixtures (TS11 and TS41), no laboratory mean combustion time outside the tolerance limits is observed, which is similar to the results obtained for the single combustion times (see chapter 4.4.1).

In Figure 9, the laboratory mean combustion times for each reference substance mixture and the test sample mixtures are plotted against each other. From this it can be seen that the correlation of the laboratory mean combustion times between different samples is relatively low. The correlation amounts to only 10 % to 40 %.

This indicates that the test results are also influenced by sample-specific systematic effects.

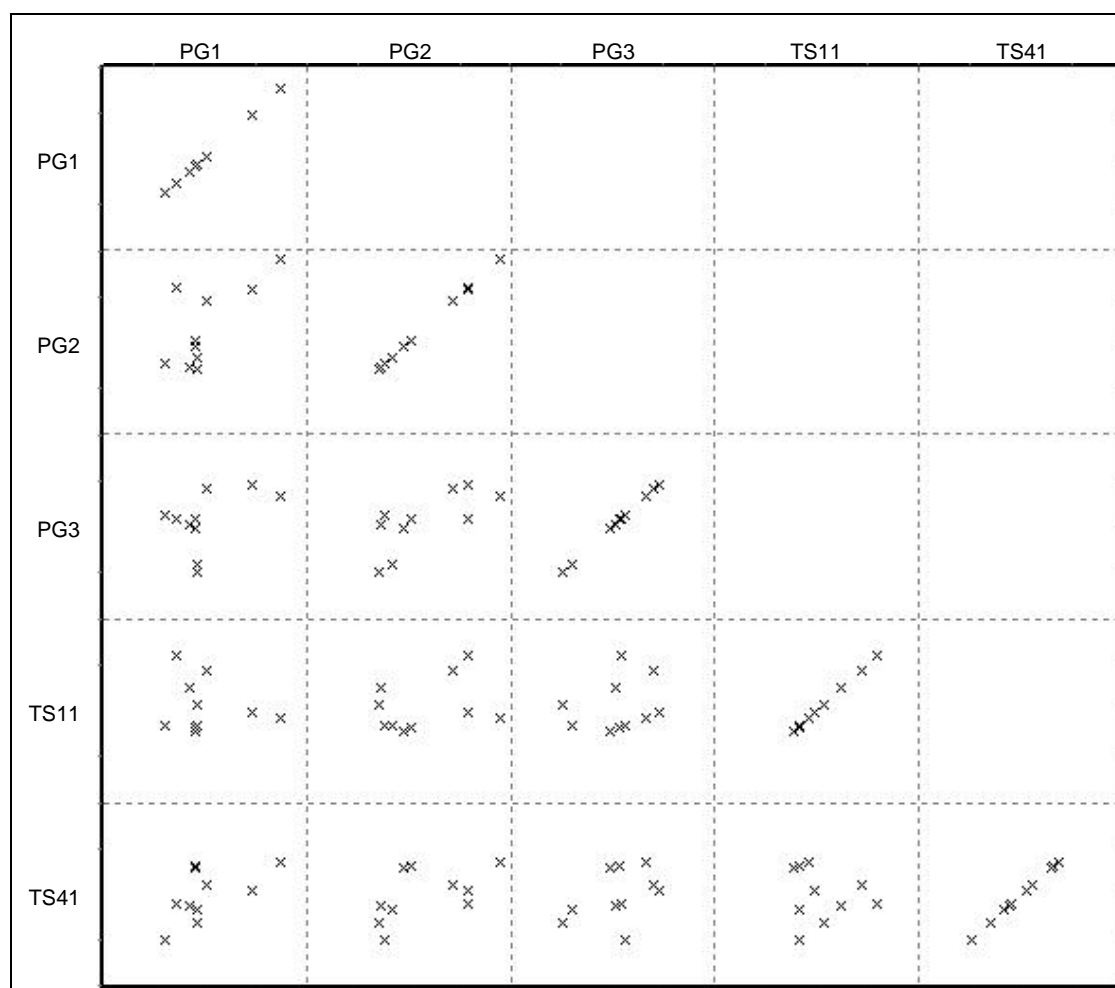


Figure 9: Youdenplot for laboratory mean combustion times [s] for each combination of reference substance mixture (packing group PG1, PG2 and PG3) and test sample mixture (TS11 and TS41) – simplified view

4.4.2.2 Analysis of ratios of laboratory mean combustion times

The ratios of the laboratory mean combustion times were analysed by the method according to DIN 38402 A 45 (= ISO/DIS 20612) (same method as applied for the laboratory mean combustion times in chapter 4.4.2.1), i.e. no outliers have been eliminated. The ratios of laboratory mean combustion times as well as the mean values of these ratios, the relative reproducibility standard deviation and the relative repeatability standard deviation of these ratios over all laboratories are given in Table 9 and Table 10.

Table 9: Ratios of laboratory mean combustion times

Laboratory	PG2/ PG1	PG3/ PG2	TS11/ PG1	TS11/ PG2	TS11/ PG3	TS41/ PG1	TS41/ PG2	TS41/ PG3
1	7.74	3.58	11.30	1.46	0.41	5.39	0.70	0.19
2	3.59	3.55	7.05	1.97	0.55	3.45	0.96	0.27
3	3.95	2.78	4.60	1.17	0.42	3.87	0.98	0.35
4	3.41	2.52	4.66	1.37	0.54	2.86	0.84	0.33
5	4.65	2.35	5.70	1.23	0.52	2.88	0.62	0.26
6	2.96	2.21	2.55	0.86	0.39	1.63	0.55	0.25
7	2.76	1.77	1.95	0.71	0.40	1.52	0.55	0.31
8	4.15	2.74	4.69	1.13	0.41	3.87	0.93	0.34
9	9.57	1.87	11.57	1.21	0.65	4.79	0.50	0.27
10	2.92	2.72	5.33	1.83	0.67	2.55	0.87	0.32

Table 10: Mean values and relative standard deviations for ratios of laboratory combustion times

		PG2/ PG1	PG3/ PG2	TS11/ PG1	TS11/ PG2	TS11/ PG3	TS41/ PG1	TS41/ PG2	TS41/ PG3
Method according to DIN 38402 A 45 (no outliers have been eliminated)	Mean of ratios of laboratory mean combustion times	3.85	2.61	5.47	1.29	0.46	3.28	0.75	0.29
	Relative reproducibility s.d.	35.3 %	28.6 %	11.1 %	33.4 %	11.1 %	61.6 %	25.9 %	16.3 %
	Relative repeatability s.d.	11.7 %	7.1 %	10.1 %	7.5 %	8.8 %	9.9 %	7.1 %	7.6 %
	Lower limit of tolerance	1.13	1.12	0.64	0.43	0.36	-0.76	0.36	0.20
	Upper limit of tol- erance	6.57	4.10	10.30	2.15	0.57	7.32	1.14	0.39

Figure 10 shows the ratios of laboratory mean combustion times of the reference substance mixture of packing group II and packing group I (PG2/PG1) for each laboratory as an example. For the other ratios refer to Appendix 7.5.2. In these figures, boxes symbolize the variability of the ratios of the respective combustion times of one laboratory, which were predicted by means of error propagation methods. The larger the box, the higher is the variability of the ratios within this laboratory. The horizontal line in the middle of the box indicates the ratio of laboratory mean combustion times. The figures also include the 95 % confidence band (green band) of the mean of ratios of laboratory mean combustion times according to DIN 38402 A 45 (no outliers have been eliminated) (black line) as well as the tolerance limits for the ratio of laboratory mean combustion times (red lines) – also according to DIN 38402 A 45 (no outliers have been eliminated).

The ratios PG2/PG1 and TS11/PG1 of laboratories 01 and 09 are above the upper tolerance limit. Thus, significantly higher ratios for these two laboratories in comparison to the mean of ratios of laboratory mean combustion times are observed.

The ratio TS11/PG3 of laboratories 09 and 10 are also above the upper tolerance limits.

The ratio TS41/PG3 of laboratory 01 lies below the lower limit of tolerance.

The remaining four ratios (PG3/PG2, TS41/PG1, TS11/PG2 and TS41/PG2) of all laboratories lie within the tolerance limits.

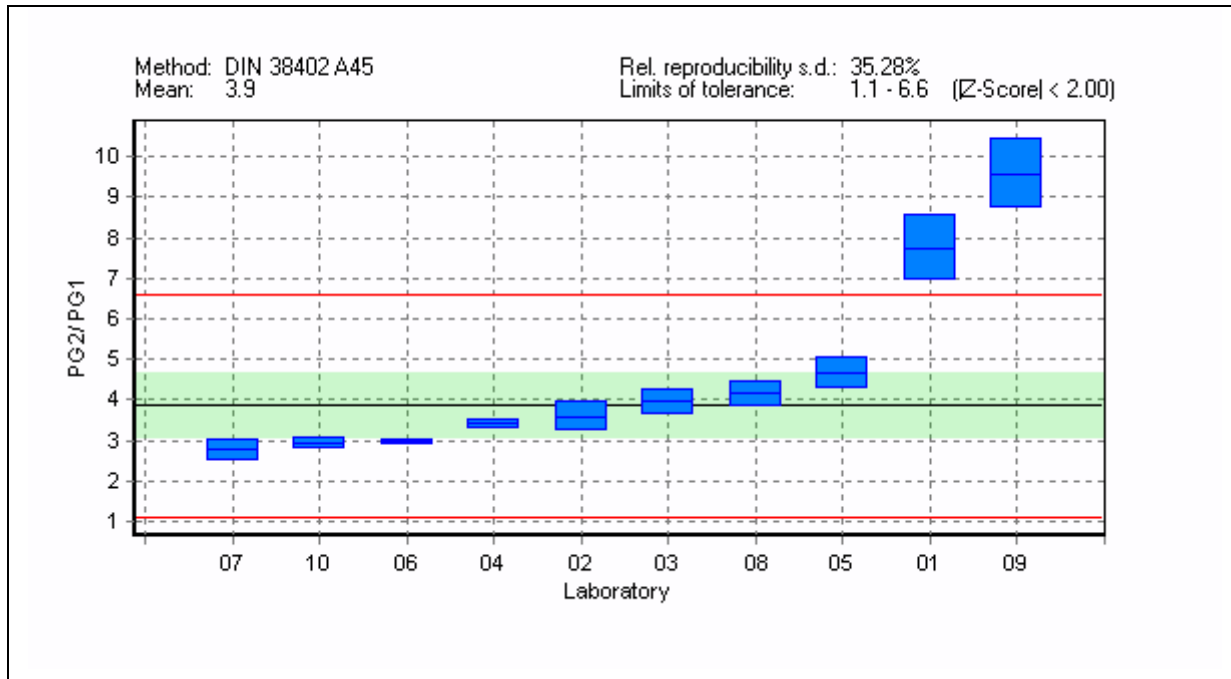


Figure 10: Analysis of ratios of laboratory mean combustion times – PG2/PG1

4.4.3 Comparison between the analysed data types

In the following Table 11 a summary of the obtained mean values, relative repeatability and reproducibility standard deviations is given for the single combustion times and laboratory mean combustion times of all reference substance mixtures relating to packing groups PG1, PG2 and PG3 and test sample mixtures TS11 and TS41 as well as for the eight ratios of laboratory mean combustion times of reference substance mixtures and test sample mixtures.

Table 11: Mean values and relative standard deviations for the three different data types

Data type	Mean value	Relative reproducibility s.d.	Relative repeatability s.d.
Single combustion times (see chapter 4.4.1) Method according to ISO 5725-2 (based on outlier-free data)			
PG1	12.8 s *	55.2 %	12.2 %
PG2	44.6 s *	28.5 %	10.0 %
PG3	120.5 s *	16.4 %	7.8 %
TS11	58.5 s *	21.6 %	12.7 %
TS41	35.6 s *	20.6 %	10.8 %
Laboratory mean combustion times (see chapter 4.4.2.1) Method according to DIN 38402 A 45 (no outliers have been eliminated)			
PG1	10.9 s **	39.9 %	n/a****
PG2	49.7 s **	29.0 %	n/a****
PG3	126.3 s **	9.8 %	n/a****
TS11	60.0 s **	18.4 %	n/a****
TS41	35.6 s **	25.8 %	n/a****
Ratios of laboratory mean combustion (see chapter 4.4.2.2) Method according to DIN 38402 A 45 (no outliers have been eliminated)			
PG2/ PG1	3.85 ***	35.3 %	11.7 %
PG3/ PG2	2.61 ***	28.6 %	7.1 %
TS11/ PG1	5.47 ***	44.1 %	10.1 %
TS11/ PG2	1.29 ***	33.4 %	7.5 %
TS11/ PG3	0.46 ***	11.1 %	8.8 %
TS41/ PG1	3.28 ***	61.6 %	9.9 %
TS41/ PG2	0.75 ***	25.9 %	7.1 %
TS41/ PG3	0.29 ***	16.3 %	7.6 %

* Total mean value of single combustion times

** Mean value of laboratory mean combustion time

*** ... Mean value of ratios of laboratory mean combustion time

**** .. n/a = not available

The variability of the relative repeatability standard deviations over all laboratories is small and varies between 7 % and 13 % only (see Table 11).

The relative reproducibility standard deviations for PG1 (single values) and TS41/PG1 (ratios) are extremely high (55 % and 62 %, resp.) compared to the other measurands. PG3 exhibits the smallest relative reproducibility standard deviation for the single combustion times, the laboratory mean combustion times and also for the two ratios of laboratory mean combustion times with TS11 and TS41.

The relative reproducibility standard deviations obtained for the ratios are partly even higher than for the single combustion times. For example, the relative reproducibility standard deviation for the laboratory mean combustion times of TS11 equals 18.4 %, for PG2 equals 29.0 %, however, for the ratio TS11/PG2 it amounts to 33.4 %.

Normally it could be expected that the ratios of laboratory mean combustion times behave more similar than the laboratory mean combustion times, and smaller reproducibility standard deviations could be expected as well. But in opposition to this it was observed that the variability of the ratios is not lower than the variability of the laboratory mean combustion times. This might be due to considerable sample-specific systematic effects. Such sample-specific systematic effects can neither be reduced by increasing the number of replicates nor be eliminated by considering the ratios instead of the combustion times itself.

4.5 Laboratory assessment: Z scores based on ratios of laboratory mean combustion times

The assessment of the laboratory's performance in determining the combustion time of the test sample mixtures and the reference substance mixtures was carried out using Z scores according to IUPAC and EURACHEM [1] [2]. In general, Z scores describe the standardised deviation of laboratory mean values from the total mean value. Under normal distribution, Z is within the limits -2 and 2 with probability 95 %.

The Z scores considered in this chapter are based on the ratios of laboratory mean combustion times because these ratios are used to decide whether a substance is classified as an oxidizing solid and if so to which category (or packing group) it is assigned (see chapter 4.1). The Z scores were calculated using the respective mean of ratios of laboratory mean combustion times (as assigned value) and the respective reproducibility standard deviation (as target standard deviation) according to DIN 38402 A 45.

The Z scores of all laboratories are presented in Figure 11. It can be seen that 7 out of 10 laboratories obtained satisfactory Z scores ($|Z| \leq 2$) for all of the eight considered ratios.

It has to be noted that the red triangles in Figure 11, which represent Z scores, for which $|Z| > 2$ hold, are never drawn below -2 or above 2 (for the lack of space), but the respective values are given directly.

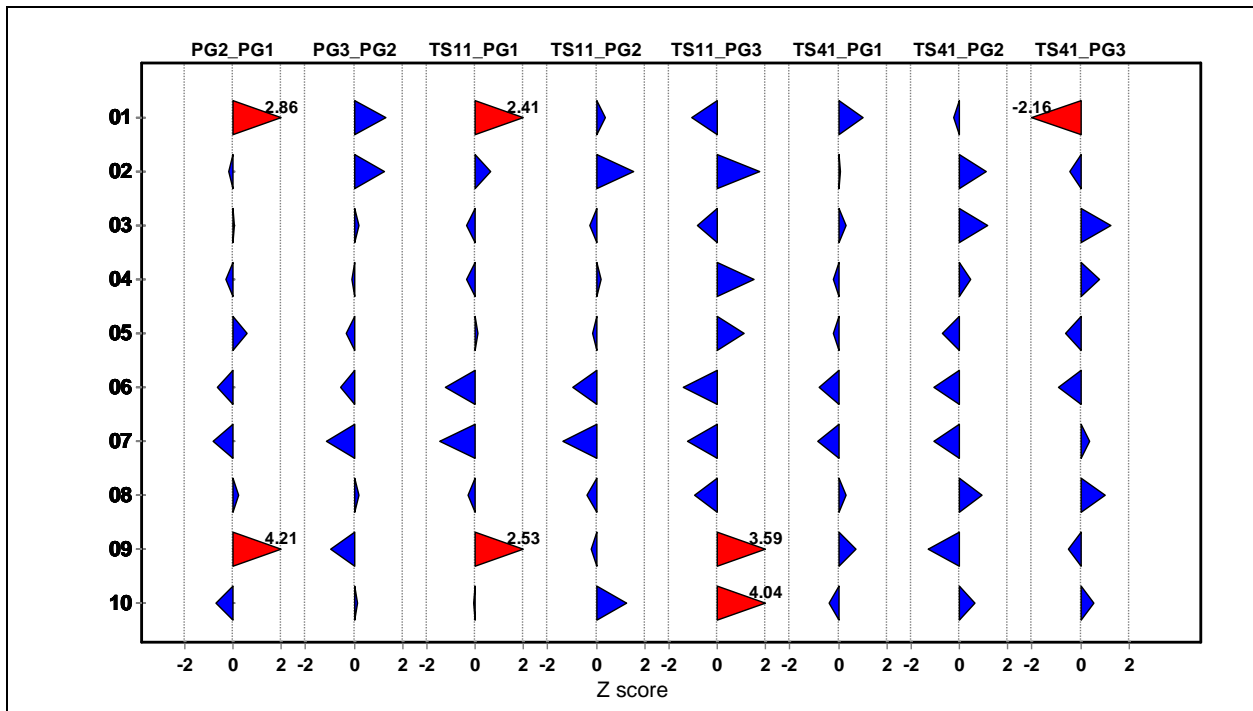


Figure 11: Z scores based on ratios of laboratory mean combustion times
 (Note: The triangles corresponding to Z scores with $|Z| > 2$ are graphically limited by -2 and 2 resp. and therefore the actual value is indicated.)

For laboratory 01 and laboratory 09 the quality criterion is not fulfilled for three ratios of laboratory mean combustion times as follows: PG2/PG1, TS11/PG1 for both laboratories and TS41/PG3 for laboratory 01 and TS11/PG3 for laboratory 09. This may be caused by their relatively large slope in the relationship between oxidizer concentration and combustion time in comparison to all other laboratories (see Appendix 7.3). For laboratory 10 the quality criterion is not fulfilled for the ratio TS11/PG3. For the remaining ratios, the quality criterion is fulfilled by all participating laboratories. Also noticeable is the fact that Z scores for laboratories 06 and 07 are almost always negative. This may be due to their small slope in the relationship between oxidizer concentration and combustion time.

The relative laboratory performance (RLP) can be calculated for each laboratory from the Z scores [7]. The RLP equals the quadratic mean of Z scores of the different test sample mixtures and reference substance mixtures of the respective laboratory. The respective values are given in Table 12.

A rough classification of the RLP values is:

RLP < 0.67: laboratory exhibits a performance above average with small measurement deviations

RLP \approx 1: laboratory exhibits an average performance

RLP > 1.5: laboratory exhibits a performance below average with large measurement deviations

Table 12: Relative laboratory performance for each laboratory based on Z scores for ratios of laboratory mean combustion times

Laboratory	RLP
01	1.438
02	0.913
03	0.575
04	0.488
05	0.463
06	0.938
07	1.038
08	0.538
09	1.750
10	0.975

Laboratories 01 and 09 exhibit a relatively high variability from sample to sample. For laboratories 03, 04, 05 and 08, the variability from sample to sample is smaller than for the other laboratories.

All in all it can be concluded that:

- There are no clear outliers regarding Z scores, i.e. no Z scores below -5 or above +5.
- There are some differences in the relative laboratory performance.

4.6 Further statistical analysis: Probability of incorrect classification

4.6.1 Probability of incorrect classification of the test samples of the interlaboratory test

The percentage of laboratories which incorrectly classified the test samples in the interlaboratory test provides only a very rough estimate of the actual probability of incorrect classification. A more reliable estimation of this probability can be obtained by using the quantitative properties of the data. In this study the probability of incorrect classification of the test samples of the interlaboratory test is derived by evaluating the ratios of laboratory mean combustion times of the test sample mixtures and the reference substance mixtures. It is assumed that the data are normally distributed.

The following calculations are based on the means of ratios of laboratory mean combustion times and the respective reproducibility standard deviations according to DIN 38402 A 45 as summarized in Table 9.

4.6.1.1 Distribution of the ratios of laboratory mean combustion times of the interlaboratory test

Figure 12, Figure 13 and Figure 14 show the distributions of the ratios of the laboratory mean combustion times of test sample mixtures and the reference substance mixtures – separately for each of the three packing groups. On the x-axis the ratios are displayed, and the left axis shows the probability density of the ratios of laboratory mean combustion times of the test sample mixtures and the respective reference substance mixtures. This probability density is neither the probability nor the frequency.

It can, however, be thought of as showing the relative frequency of values occurring at different points along the x-axis. These probability density curves are similar to the bell curve by Gauss. Thereby not the values on the left axis are of interest, but the position of the curve (Is the x-position of the maximum smaller than 1 or larger?) and the shape of the curve (Is it flat or steep, is it skewed?). As for all probability densities, the area beneath one curve equals 100 %.

In Figure 12 the curves of the probability density for the classification in PG2 demonstrate that the distribution for test sample mixture TS11 is wider than for test sample mixture TS41, i.e. for TS11 the laboratory results deviate more than for TS41. Furthermore, for TS41 the x-position of the maximum is smaller than 1 (located left of the black line), while for TS11 the x-position of the maximum is larger than 1 (located right of black line). Generally, these figures can be interpreted as follows:

A ratio of 1 corresponds to identical combustion times of the test sample mixture and the reference substance mixture of the packing group. The x-position of the maximum of a curve indicates the mean ratio of laboratory mean combustion times for the respective test sample mixture and packing group and is regarded as “true” ratio. This “true” ratio is considered to be the factor from which the “true” combustion time for the test sample mixture may be derived. For packing group II (PG2), e.g., the mean (“true”) ratio of laboratory mean combustion times for TS11/PG2 (blue) equals 1.29, while this value for TS41/PG2 (red) equals 0.75 (see also Table 10).

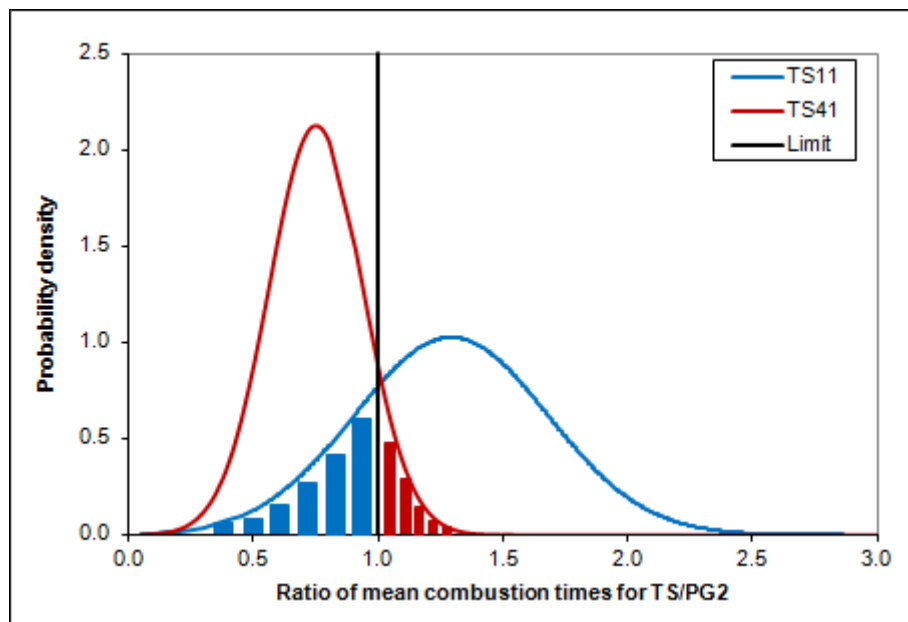


Figure 12: Probability density for the classification in PG2

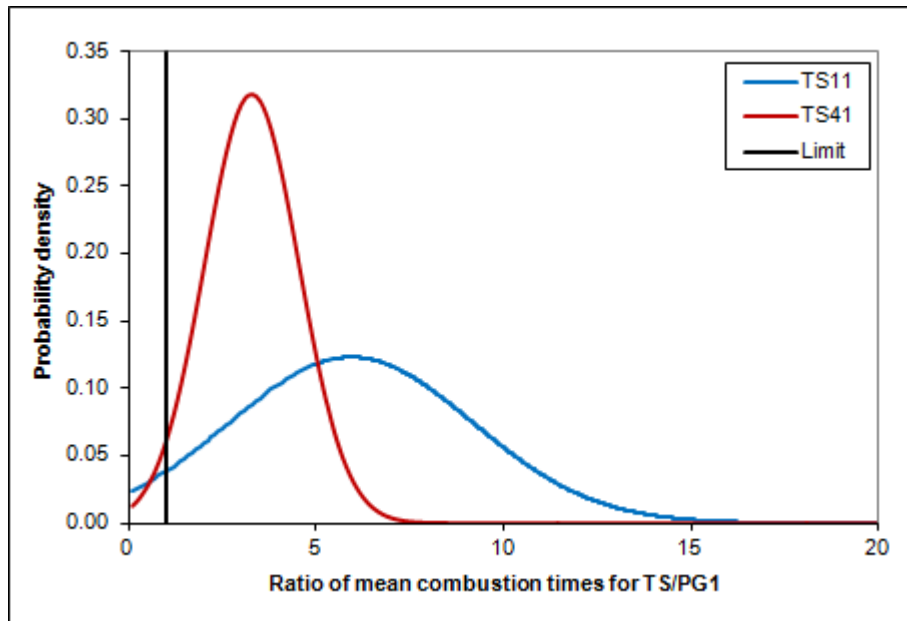


Figure 13: Probability density for the classification of PG1

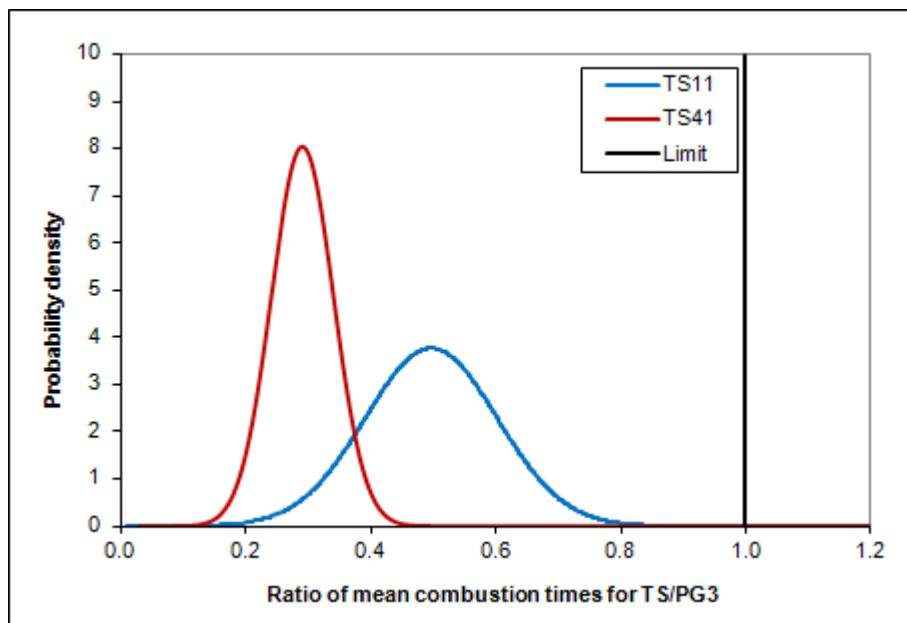


Figure 14: Probability density for the classification of PG3

4.6.1.2 False positive and false negative error of classification

False positive error of classification: In the following it is assumed that a false positive error indicates that the test sample mixture is classified by a laboratory to a lower packing group (of higher safety), although a higher packing group (of lower safety) would be correct because this is the “true” packing group. For example, a laboratory has classified the test sample mixture in packing group PG I but the “true” packing group is PG II. That is, the laboratory’s mean combustion time of the test sample mixture is shorter than the combustion time of the reference substance mixture of packing group I,

although the “true” combustion time of the test sample mixture (derived from the “true” ratio) is longer. Expressed by ratios this means that the measured ratio is smaller than the limit 1, while the “true” ratio is larger than 1. The probability for such a false positive error can be derived from the distribution figures given in Figure 12, Figure 13 and Figure 14.

As mentioned above, the “true” ratio is given by the x-position of the maximum of a probability density curve. Only if this “true” ratio is larger than 1, a false positive error may occur. Then the probability for a false positive result is indicated by the area beneath the curve for ratios smaller than 1, i.e. the area on the left side of the vertical black line.

For packing group II this holds for test sample mixture TS11 (see Figure 12), the respective area is marked with blue bars. In this example the area equals 0.23, i.e. the probability for the false positive result $TS11 < PG2$ equals 23 %, while the true value of TS11 equals $TS11 = 1.29 \times PG2$.

False negative error of classification: A false negative error, though, indicates that the test sample mixture is classified by a laboratory to a higher packing group (of lower safety), although a lower packing group (of higher safety) would be necessary. For example, a laboratory has classified the test sample mixture in packing group PG III but the true packing group is PG II. That is, the laboratory’s mean combustion time of the test sample mixture is longer than the combustion time of the reference substance mixture of packing group II, although the “true” combustion time of the test sample mixture (derived from the “true” ratio) is shorter. Expressed by ratios this means that the measured ratio is larger than 1, while the “true” ratio is smaller than 1. The probability for such a false negative error can again be derived from the distribution figures given in Figure 12, Figure 13 and Figure 14. Again, the “true” ratio is given by the x-position of the maximum of a curve. Only if this “true” ratio is smaller than 1, a false negative error may occur. Then the probability for a false negative result is indicated by the area beneath the curve for ratios larger than 1, i.e. the area on the right side of the vertical black line.

For packing group II this holds for test sample mixture TS41 (see Figure 12), the respective area is marked with red bars. In this example the area equals 0.09, i.e. the probability for the false negative result $TS41 > PG2$ equals 9 %, while the true value of TS41 equals $TS41 = 0.75 \times PG2$.

4.6.1.3 Probabilities of false positive and false negative classification

The whole proceeding in the previous section 4.6.1.2 is similar to statistical testing with a null hypothesis ($TS > PG$) and an alternative hypothesis ($TS < PG$). However, in a statistical test generally the aim is that the probability for a false positive result is kept below a certain limit (significance level), whereas the probability for the false negative error can hardly be controlled. In this case, however, the intention is to keep both probabilities as low as possible. But it cannot be ensured that they are both kept below a specific limit. Therefore, both probabilities may become 50 %.

For packing group I (PG1), the x-values of the maxima are larger than 1, thus neither for TS11 nor for TS41 a false negative error with regard to classification as packing group I is possible (see Figure 13). The probability of the false positive error $TS11 < PG1$ equals 6.4 % and for the false positive error $TS41 < PG1$ it equals 3.4 %.

Finally, for packing group III (PG3), the x-values of the maxima are smaller than 1 for both test sample mixtures, thus no false positive error is possible. Furthermore, there is no area beneath the curves for ratios larger than 1, thus the probability for a false negative error equals 0. This holds for both test sample mixtures TS11 and TS41.

4.6.2 Probability of incorrect classification for an arbitrary sample

The probability of incorrect classification can also be predicted for an arbitrary test sample mixture, i.e. not only for the test sample mixtures which were used in the interlaboratory test.

Here again the normal distribution is used as an approximation of the distribution of the combustion ratios.

The following three figures (Figure 15, Figure 16, Figure 17) show the probabilities for an incorrect classification $TS > PG$ of the test sample mixtures TS11 and TS41 with regard to each of the three packing groups. Also the probabilities for false positive and false negative errors of the classification can be taken from these figures.

For packing group I (PG1) and test sample mixture TS41, the probability for a false negative error is about 11 %, when the true value of the ratio TS41/PG2 equals 0.5 (see Figure 15). For a decreasing true value of the ratio, this probability decreases as well. The smaller the ratio, the shorter is the combustion time of the test sample mixture compared to the combustion time of the reference substance mixture of the respective packing group. However, with a decreasing combustion time the probability to choose a packing group of higher safety increases, thus the error to choose a packing group with an insufficient safety (false negative error) decreases.

The probability for a false positive error is about 22.4 % (= 100 % - 77.6 %), when the true value equals 1.5 (see Figure 15). For an increasing true value of the ratio, this probability decreases: if 2.5 is the true value for the ratio of mean combustion times of TS41 and PG2, the probability for a false positive error is only 6.4 %. The larger the ratio the longer is the combustion time of the test sample mixture compared to the combustion time of the packing group. However, with an increasing combustion time the probability to choose a packing group of lower safety increases, thus the error to choose a packing group with an overly safety (false positive error) decreases.

For equal combustion times of test sample mixture and packing group, i.e. at ratio 1, the probabilities for both the false negative and the false positive error are 50 %.

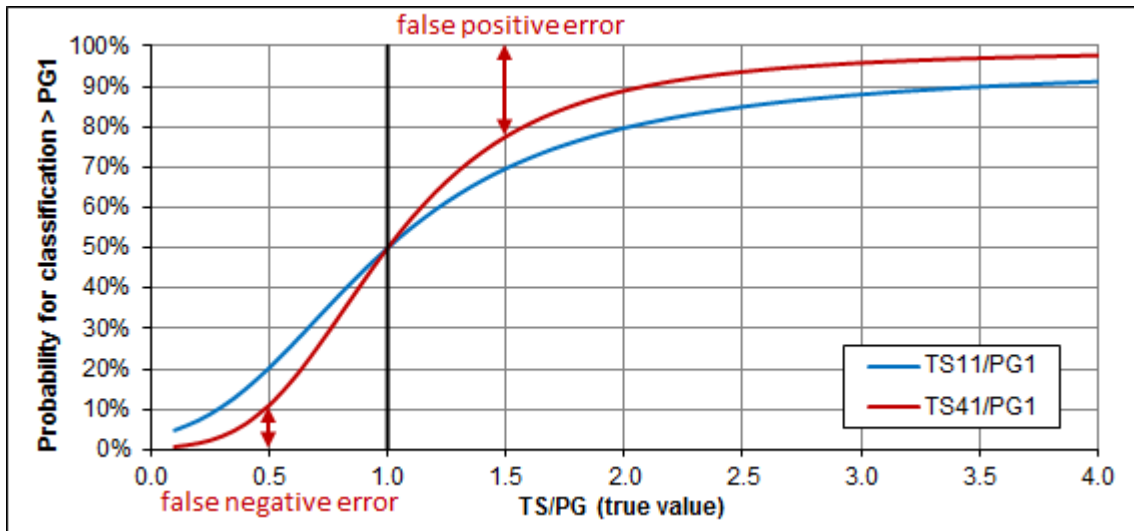


Figure 15: Probability of incorrect classification (PG1) as a function of the ratios of laboratory mean combustion times

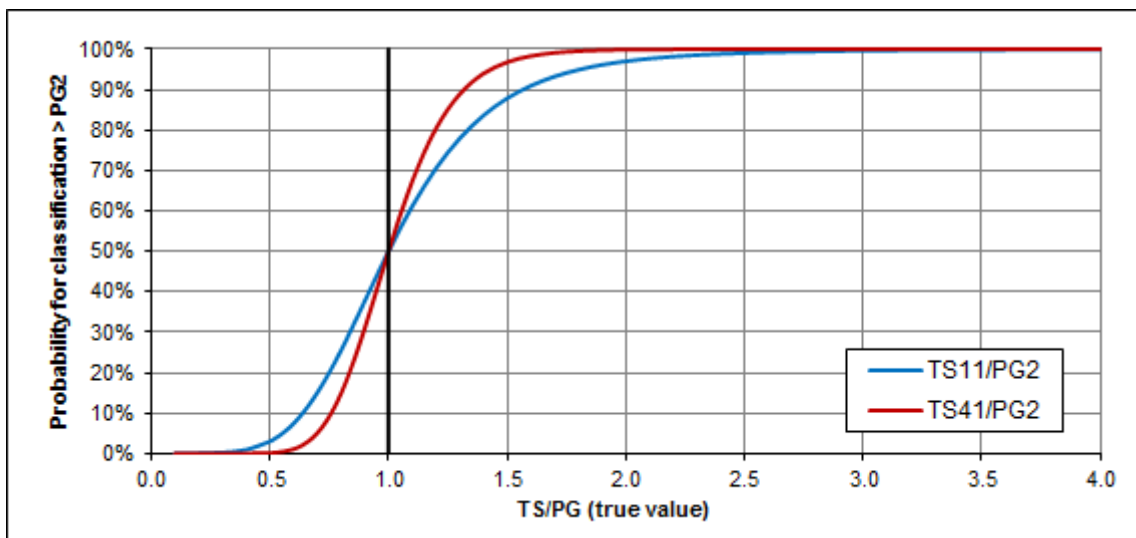


Figure 16: Probability of incorrect classification (PG2) as a function of the ratios of laboratory mean combustion times

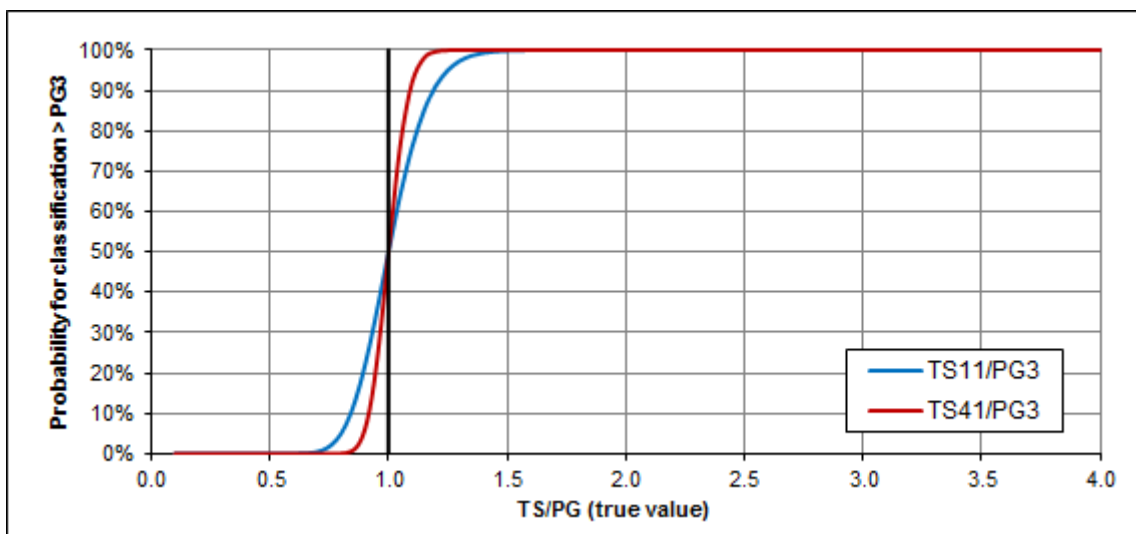


Figure 17: Probability of incorrect classification (PG3) as a function of the ratios of laboratory mean combustion times

Figure 18 shows the probability of incorrect classification for an arbitrary test sample mixture derived by extrapolating the relative standard deviation of the ratios TS41/PG1, TS41/PG2 and TS41/PG3. Due to the form of the curves, Figure 18 is also referred to as shark profile, which can be interpreted as follows:

The increasing arm of a curve of the probability of incorrect classification in a respective packing group indicates the probability of the false negative classification (false negative error) for the true combustion time of the test sample mixture, i.e. an arbitrary laboratory is classified the test sample mixture to the packing group belonging to the curve, although it should be assigned to a packing group of higher safety. Whereas, the decreasing arm of a curve of one packing group indicates the false positive classification (false positive error), i.e. the test sample is assigned to the packing group belonging to the curve, although it should be assigned to a packing group of lower safety.

In particular, this means:

Left arm of packing group I (red)	Probability that a laboratory has classified the test sample in PG II, although PG I would be necessary, i.e. it needs higher safety because the true classification is PG I → false negative classification
Right arm of packing group I (red)	Probability that a laboratory has classified the test sample in PG I, although PG II would be correct (true) , i.e. it needs lower safety because the true classification is PG II → false positive classification
Left arm of packing group II (blue)	Probability that a laboratory has classified the test sample in PG III, although PG II would be necessary, i.e. it needs higher safety because the true classification is PG II → false negative classification
Right arm of packing group II (blue)	Probability that a laboratory has classified the test sample in PG II, although PG III would be correct (true), i.e. it needs lower safety because the true classification is PG II → false positive classification
Left arm of packing group III (green)	Probability that a laboratory has not classified the test sample, although PG III would be necessary, i.e. it needs higher safety because the true classification is PG III → false negative classification
Right arm of packing group III (green)	Probability that a laboratory has classified the test sample in PG III, although no classification would be correct (true), i.e. it needs lower safety because the true classification "no" PG → false positive classification

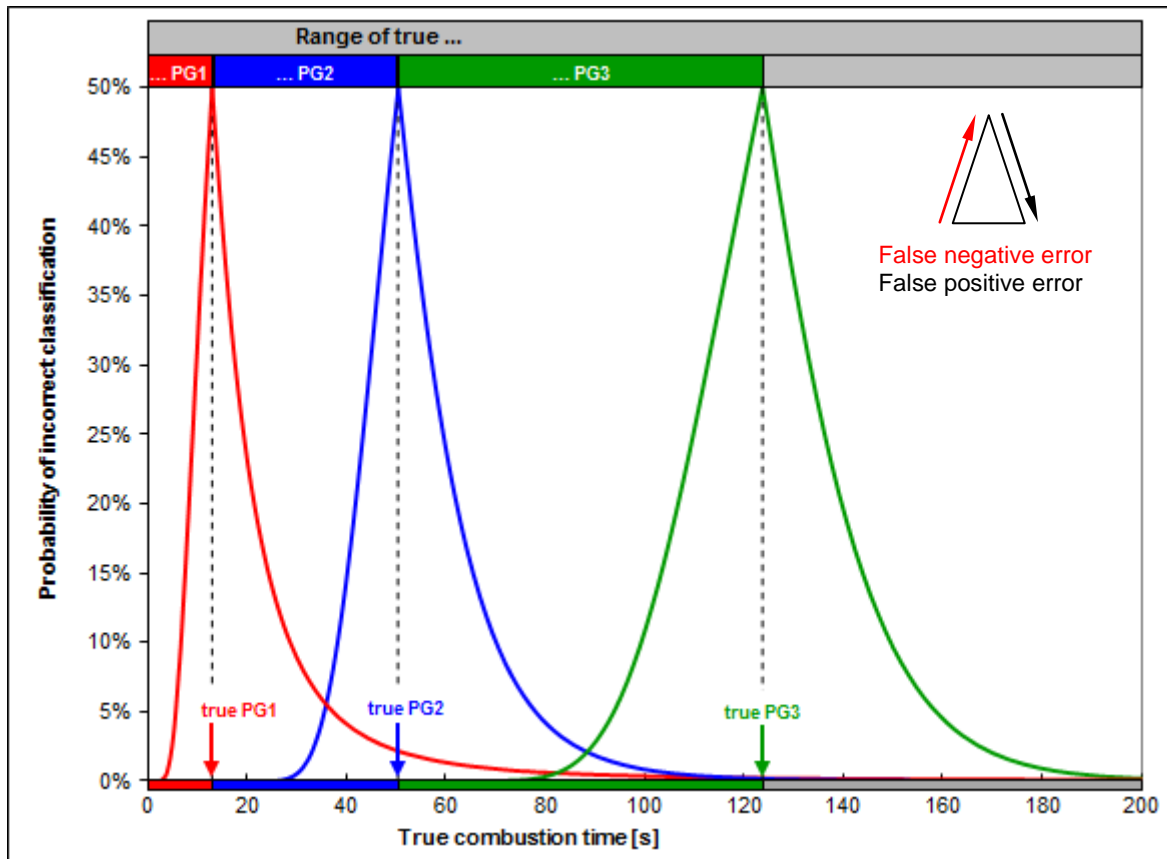


Figure 18: The shark profile – probability of incorrect classification in PG1, PG2 or PG3 as a function of the "true" combustion times of an arbitrary sample mixture (values of PG1, PG2 and PG3 see laboratory mean combustion times in Table 11)

As long as the curves do not overlap, only one kind of error can occur. Therefore crucial ranges are those where two curves overlap.

If for example the "true" combustion time of an arbitrary test sample mixture equals 40 s, the probability for a false positive classification with regard to packing group I, i.e. the probability to classify the test sample mixture to packing group I instead of the "true" packing group II, equals about 4 % (value of red curve for 40 s). At the same time, for a mean combustion time of 40 s, there is the possibility for a false negative error as well: The probability for a false negative classification, i.e. the probability to classify the test sample mixture to packing group III instead of "true" packing group II, equals about 15 % (value of blue curve for 40 s).

5 Summary and conclusions regarding the method UN test O.1

The performance of the laboratories and the UN test UN O.1 was investigated by aid of an interlaboratory test.

The variability of the relative repeatability standard deviations over all laboratories is small and varies between 7 % and 13 % only (see Table 11).

The relative reproducibility standard deviations for PG1 (single values) and TS41/PG1 (ratios) are extremely high (55 % and 62 %, resp.) compared to the other measurands. PG3 exhibits the smallest relative reproducibility standard deviation for the single combustion times, the laboratory mean combustion times and also for the two ratios of laboratory mean combustion times with TS11 and TS41.

The relative reproducibility standard deviations obtained for the ratios are partly even higher than for the single combustion times. For example, the relative reproducibility standard deviation for the laboratory mean combustion times of TS11 equals 18.4 %, for PG2 equals 29.0 %, however, for the ratio TS11/PG2 it amounts to 33.4 %.

Normally it could be expected that the ratios of laboratory mean combustion times behave more similar than the laboratory mean combustion times, and smaller reproducibility standard deviations could be expected as well. However, it was observed that the variability of the ratios is not lower than the variability of the laboratory mean combustion times. Such effects can neither be reduced by increasing the number of replicates nor be eliminated by considering the ratios instead of the combustion times itself.

The relative laboratory performance of almost all laboratories varies in the range from 0.46 to 1.75 corresponding to an average performance or a performance above average with small measurement deviations. Only one laboratory (laboratory 09) shows a RLP greater than 1.5. Furthermore it could be shown that there are no clear outliers based on Z scores, i.e. no Z scores below -5 or above +5.

The classification error (probability of incorrect classification) depends on the combustion time and the packing group, respectively. The classification with regard to packing group PG1 causes very high classification errors maybe caused by the very high reproducibility standard deviation of the combustion times for PG1.

The results show a relatively good overall performance of the participating laboratories for the classification regarding packing group PG3, whereas the probabilities for incorrect classification regarding PG2 are always above 10 % and often higher than 30 %.

The success rates based on the Z-scores for the individual laboratories are satisfying. 7 out of 10 laboratories meet all proficiency criteria for all combustion ratios.

Based on the high ratio of reproducibility and repeatability standard deviation (see Table 11) it can be concluded that there is a considerable potential of improvement of the method. Nevertheless, the precision to determine the ratio of laboratory mean combustion times has to be improved, e.g. by providing unambiguous measurement SOPs and by individual training. Interlaboratory comparisons may be useful for the stepwise improvement and harmonisation of the method.

Also the human factor is a major source of error in classification.

Considering the interlaboratory test results and after consultation with the IGUS EOS Ad-hoc working group on the solid oxidizer test the following measures / actions are recommended:

1. Training of personnel:

- A training video “Determination of the end point of main reaction” should be produced.
- Special samples should be manufactured and distributed centrally in order to be used for internal quality control.
- An appropriate proficiency test scheme should be developed in order to be used for external quality control.

2. Revision of the method UN test O.1

- The description of the UN test O.1 should be revised in a clear and unmistakable manner.
- In the UN test O.1 the use of a windshield should be recommended.
- In the UN test O.1 the replacing of the ignition wire after each trial should be recommended.
- In the UN test O.1 decrease of the particle size of the reference substance should be recommended.

3. Technical development of the method UN test O.1

- New procedures to determine the end point of reaction that do not depend on the subjective assessment of the testing personnel, e.g. by gravimetry, time-pressure apparatus or surface temperature should be investigated.
- Replacement of the reference substance potassium bromate by another substance with less toxic properties.

6 References

- [1] Thompson M., Ellison S., Wood R.: The international harmonized protocol for the proficiency testing of analytical chemistry laboratories (IUPAC Technical Report). Pure Appl Chem 2006; 78 (1):145-196.
- [2] EURACHEM Guide on selection use and interpretation of proficiency testing (PT) schemes of laboratories, edition 1.0-2000; www.eurachem.bam.de
- [3] A.M.H. van der Veen, D.A.G. Nater: Sample preparation from bulk samples – an overview; Fuel Processing Technology 36 (1993) 1-7
- [4] DIN 38402 A 45: German standard methods for the examination of water, waste water and sludge — General information (group A) — Part 45: Interlaboratory comparisons for proficiency testing of laboratories (A 45), September 2003.
- [5] Uhlig, S.: Robust estimation of variance components with high breakdown point in the 1-way random effect model. In: Kitsos, C.P. und Edler, L.; Industrial Statistics; Physica-Verlag, S. 65–73 (1997).
- [6] Müller, C. H.; Uhlig, S.: Estimation of variance components with high breakdown point and high efficiency; Biometrika; 88 (2001), No. 2, p. 353–366.
- [7] Uhlig, S., Lischer P.: Statistically-based performance characteristics in laboratory performance studies. The Analyst 123 (1998) 167-172

7 Appendix

7.1 Test instruction

Ad-hoc working group on solid oxidizer test

O.1 – Round Robin Test

2005/2006

with Sodium perborate monohydrate

Dear colleagues,

1st Test

As announced at the last OECD-IGUS-EOS meeting in Buxton (June 2005) the ad-hoc working group agreed to perform an “official” standardized round robin test (according to the principles of ISO 5725-2 or DIN 38402 A 42, A 45 and other). For this test the substance “sodium perborate monohydrate” was chosen as test substance. Therefore we ask the participating laboratories to perform the O.1 test with this substance submitted to you by BAM (Peter Lueth) according to the test procedure in the UN Test Manual (4th rev. edition, 2003, 34.4.1), **with 4:1 and 1:1 mixtures with cellulose and all three reference mixtures** (3:2, 2:3, 3:7 potassium bromate with cellulose) with the following exceptions (i.e. the already agreed changes/improvements of the test procedure):

- Do not change the laboratory assistant within the test steps, e.g. the time measuring should be performed by the same laboratory assistant.
- Form the piles by tapping the funnel slightly after filling with the powder. Cover it with the plate (bench mat, equipped with the wire loop) and invert plate and filled funnel together. Tap again slightly at the funnel before removing it.
- Prepare the 30.0 g mixtures individually (do not take them from a batch). The combustion test should be started within at most 10 minutes after start of mixing. The mixing process should be mechanical as thoroughly as possible without excessive stress. Keep the time for weighing in the substances after taking them from the desiccator and before closing the mixing vessel as short as possible.
- The electrical power of ignition wire is switched off after 20 seconds application time.
- Use a wind shield (it is very important that all laboratories use a wind shield of this geometry): diameter 30 cm (complete cylindrical wall), staying on the table level of the fume cupboard with only small holes for the wires, height above the level of the bench mat plate: 20 cm:

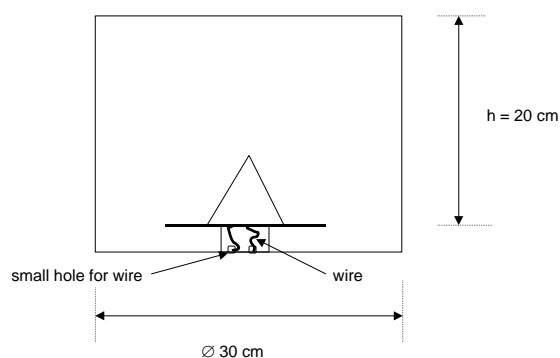


Fig.: windshield

All the other procedures as prescribed in the UN test manual should be applied as usual. Please use cellulose and potassium bromate from your own supplier and treat them according to paragraph 34.4.1 of the UN Test Manual.

For statistical purposes it is necessary to perform the tests in the following sequence (order):

- | | |
|---|-----------|
| 1. Test reference mixture PG III (3:7): | Trial 1-3 |
| 2. Test reference mixture PG II (2:3): | Trial 1-3 |
| 3. Test reference mixture PG I (3:2): | Trial 1-3 |
| 4. Test sample 4:1: | Trial 1-3 |
| 5. Test sample 1:1: | Trial 1-3 |
| 6. Test reference mixture PG III (3:7): | Trial 4-5 |
| 7. Test reference mixture PG II (2:3): | Trial 4-5 |
| 8. Test reference mixture PG I (3:2): | Trial 4-5 |
| 9. Test sample 4:1: | Trial 4-5 |
| 10. Test sample 1:1: | Trial 4-5 |

2nd Test (additional, optional)

We additionally ask you to perform a second modified test series with “sodium perborate monohydrate”.

In this additional series the **potassium bromate** should be ground and sieved to particles in the **range 180 µm to 250 µm** before drying.

Important: The test substance sodium perborate monohydrate and cellulose should be used in the same way as in the 1st test. Only potassium bromate should be treated by grinding and sieving, and only in this additional series! The additional test should be performed with the exceptions as mentioned above as well as in the statistically required sequence of tests.

Remark: Please remember that the test substance sodium perborate monohydrate as received from BAM should not be treated by any method.

We also ask you to perform a particle size analysis of the potassium bromate used in both test series for the reference mixtures (i.e. after the final sieving process) by any method which is available for you

and to forward the results together with the other test results to Peter. In case that you do not dispose of such method you can fill the two samples in the prepared bottles (you receive together with the test substance) and send them back to Peter. Then he will perform the particle size analysis at BAM laboratories.

The following 12 laboratories did confirm to participate in this new round robin test:

- INERIS, France
- TNO, Netherlands
- Yara, Norway
- Solvay, Germany
- BAM, Germany
- Akzo, Netherlands
- AQura (Degussa) Germany
- Siemens (Axiva), Germany
- HSL, UK
- Bayer Industry Services, Germany
- Laboratorio Oficial J.M. Madariaga, Spain
- Hong Kong Government Laboratory HKSA, China

Together with the test substance sodium perborate monohydrate (ca. 1 kg) you receive from BAM a prepared data file for the acquisition of your measurement data.

We ask you **to perform the tests by middle of February 2006** and to send back the data files by February 24th 2006 to Peter Lueth (peter.lueth@bam.de).

If you still have any questions, please do not hesitate to contact us.

We thank you for participating in this round robin test and wish you a successful performance. We are looking forward to discussing the results with you at our next working group meeting (planned at Degussa, Frankfurt in March 2006, exact date not yet fixed). The results of this test should be presented at the next OECD-IGUS-EOS meeting in Washington D.C. (5th – 7th April 2006).

Peter Lueth and Werner Wildner

December 2005

7.2 Laboratory data input form

OECD IGUS EOS ad hoc Working Group on the Solid Oxidizer Test (UN Test O.1)
 (Round robin tests 2005-2006 with Sodium perborate monohydrate)

Laboratory-No:

Test series 1: testsubstance, cellulose and potassium bromate treated according to paragraph 34.4.1 of the UN Test Manual

Drying parameters
Potassium bromate:

Supplier:
 Batch No.:
 Drying temperature [°C]:
 Drying time [h]:
 Residual moisture [%]:
 Remarks:

Cellulose:

Supplier:
 Batch No.:
 Drying temperature [°C]:
 Drying time [h]:
 Residual moisture [%]:
 Remarks:

Results

PG III (PB:Cell. = 3:7):

!!!! Please note the special order to perform the trials!!!!

Order no:	1	2	3	16	17
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

↓

PG II (PB:Cell. = 2:3):

Order no:	4	5	6	18	19
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

↓

PG I (PB:Cell. = 3:2):

Order no:	7	8	9	20	21
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

↓

Test Sodium perborate monohydrate 4:1 mixture with cellulose

Order no:	10	11	12	22	23
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

↓

Test Sodium perborate monohydrate 1:1 mixture with cellulose

Order no:	13	14	15	24	25
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

Test series 2 (additional): testsubstance and cellulose like in the 1th test, only potassium bromate >180 - < 250 µm,

Drying parameters
Potassium bromate:

Supplier:
 Batch No.:
 Drying temperature [°C]:
 Drying time [h]:
 Residual moisture [%]:
 Remarks:

Cellulose:

Supplier:
 Batch No.:
 Drying temperature [°C]:
 Drying time [h]:
 Residual moisture [%]:
 Remarks:

Results

PG III (PB:Cell. = 3:7):

!!!! Please note the special order to perform the trials!!!!

Order no:	1	2	3	16	17
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

PG II (PB:Cell. = 2:3):

Order no:	4	5	6	18	19
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

PG I (PB:Cell. = 3:2):

Order no:	7	8	9	20	21
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

Test Sodium perborate monohydrate 4:1 mixture with cellulose

Order no:	10	11	12	22	23
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

Test Sodium perborate monohydrate 1:1 mixture with cellulose

Order no:	13	14	15	24	25
Date:	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006	xx.xx.2006
Time:[hh:mm]	xx:xx	xx:xx	xx:xx	xx:xx	xx:xx
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Combustion times [s] (1 decimals, e.g. 1,5):					
Mixing time [min] (1 decimals, e.g. 1,5):					
Time: start mixing until start combustion [min] (1 decimals, e.g. 1,5):					
Remarks:					

7.3 Exploratory analysis of single combustion times

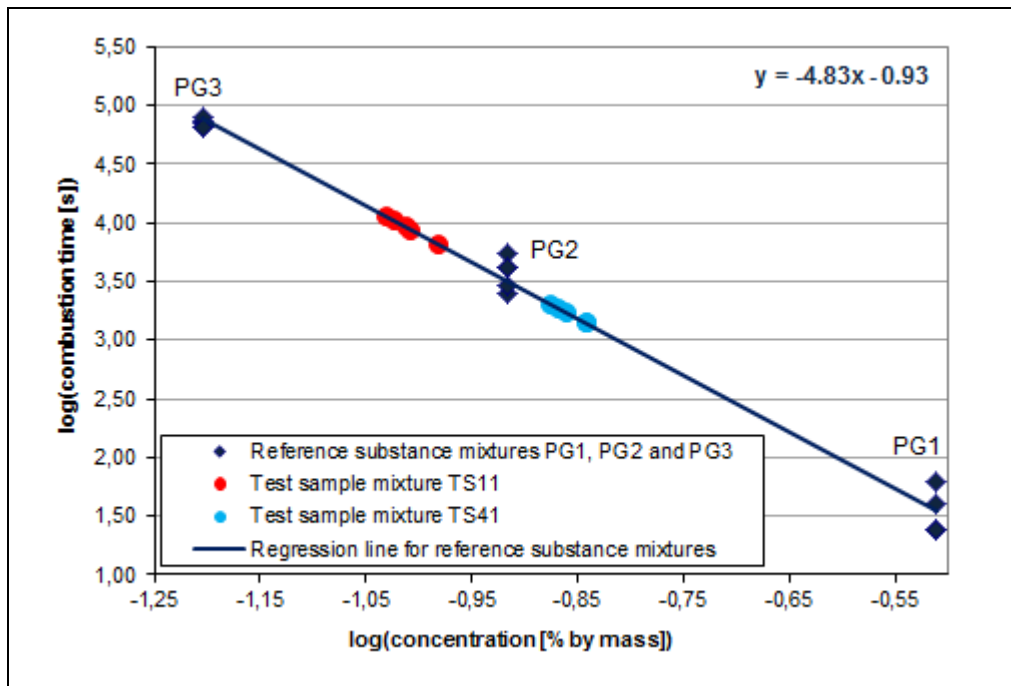


Figure 19: Relationship between the logarithmised combustion time [s] and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 01 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

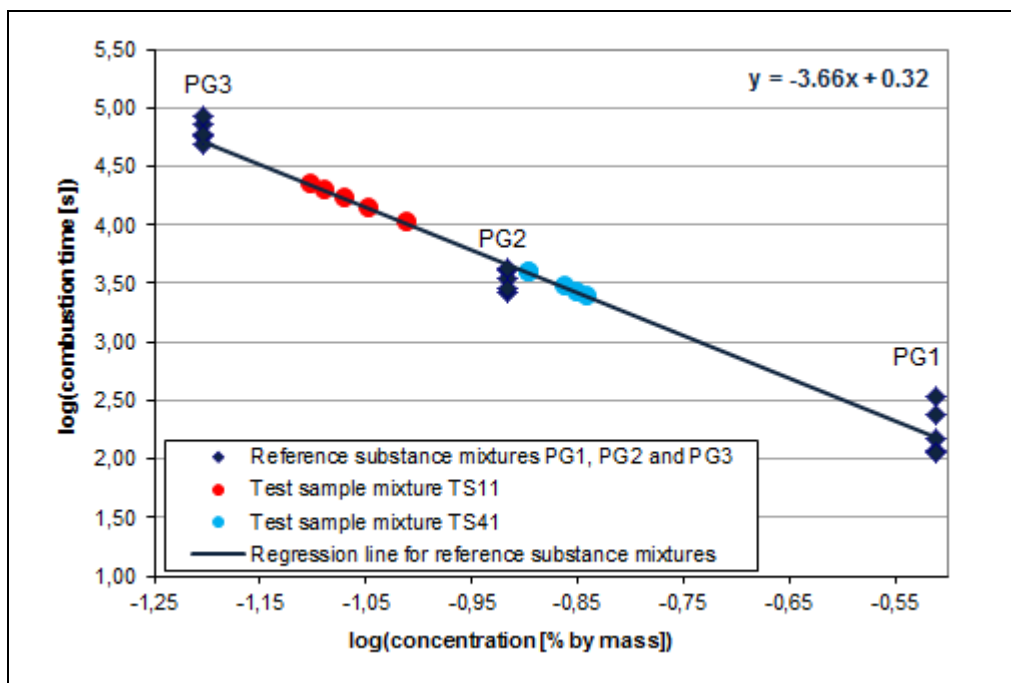


Figure 20: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 02 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

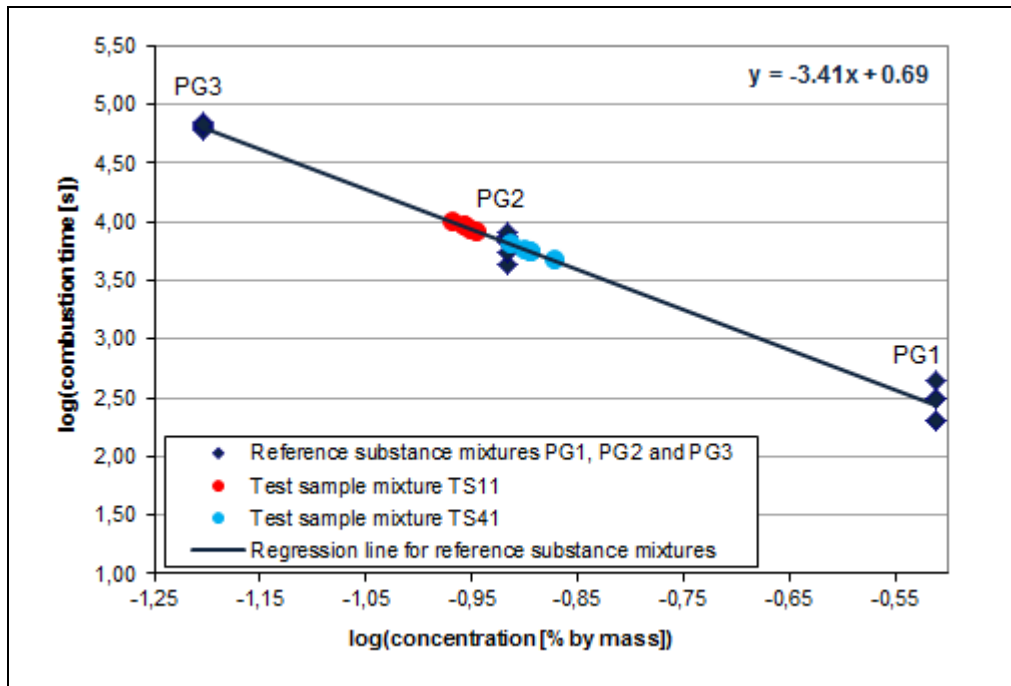


Figure 21: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 03 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

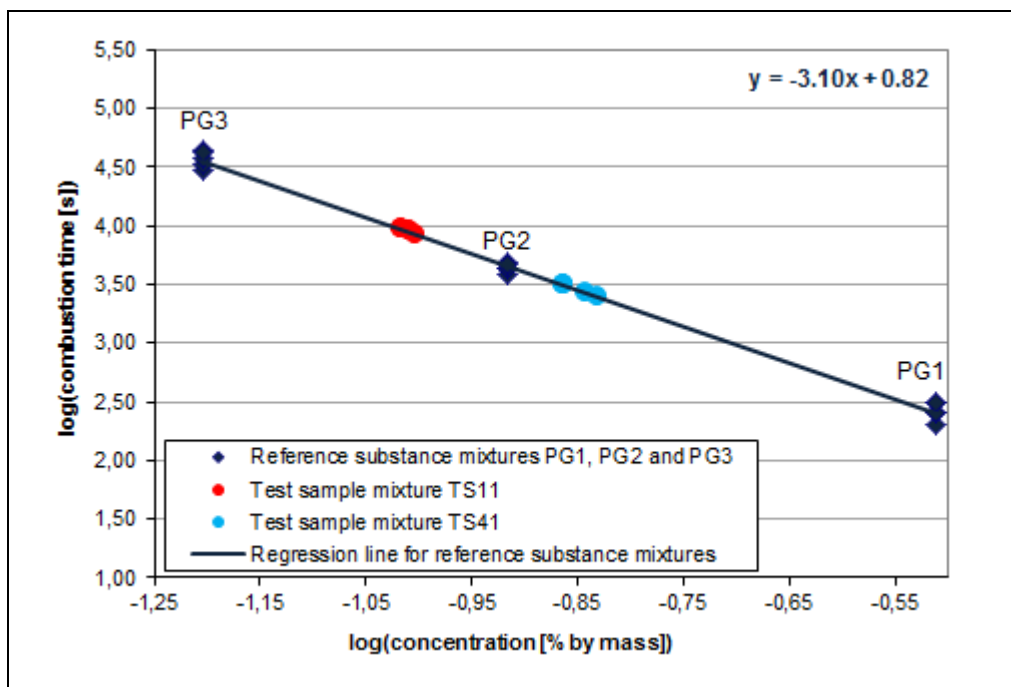


Figure 22: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 04 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

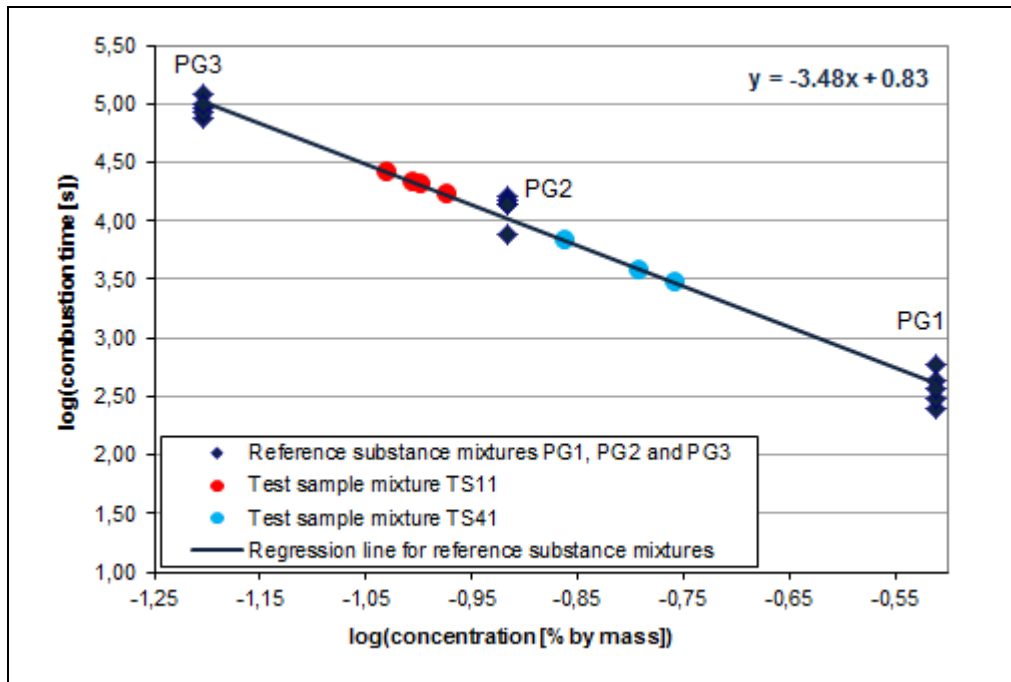


Figure 23: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 05 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

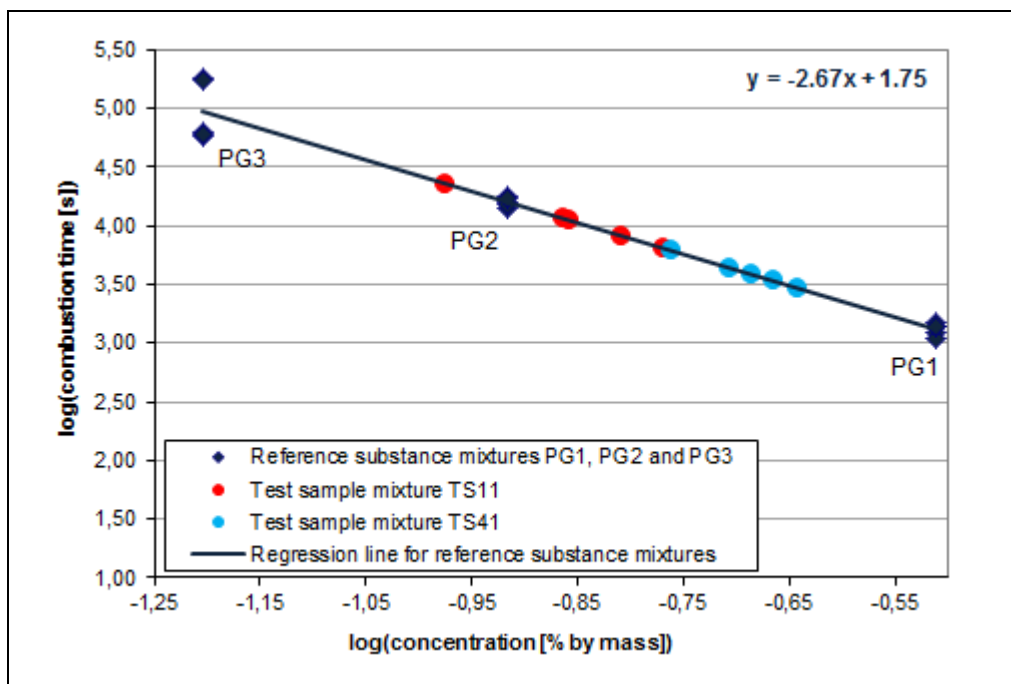


Figure 24: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 06 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

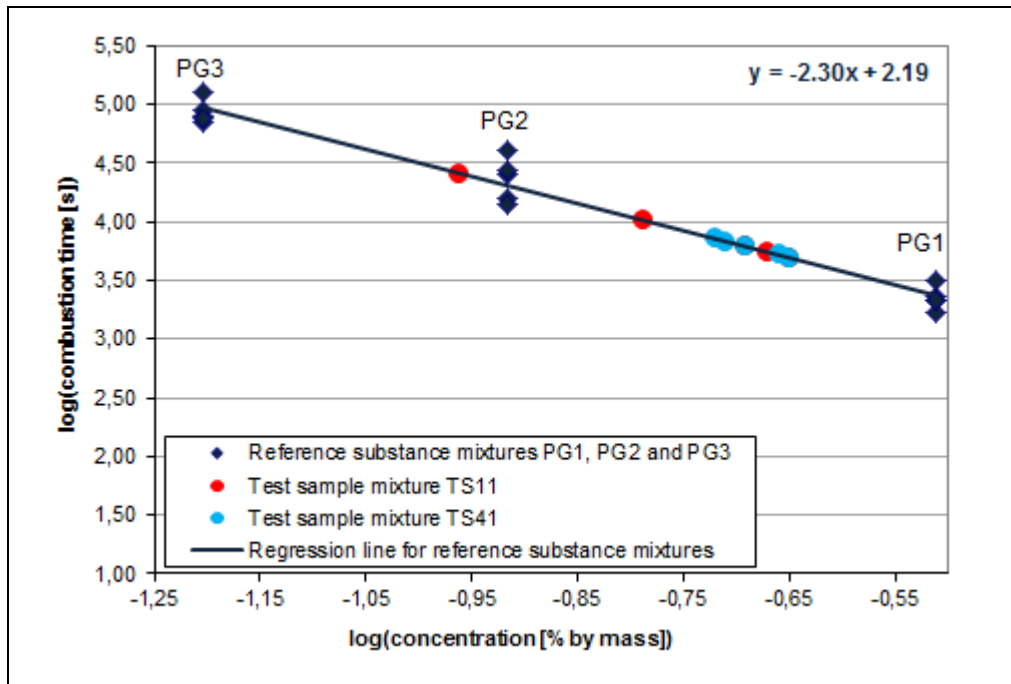


Figure 25: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 07 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

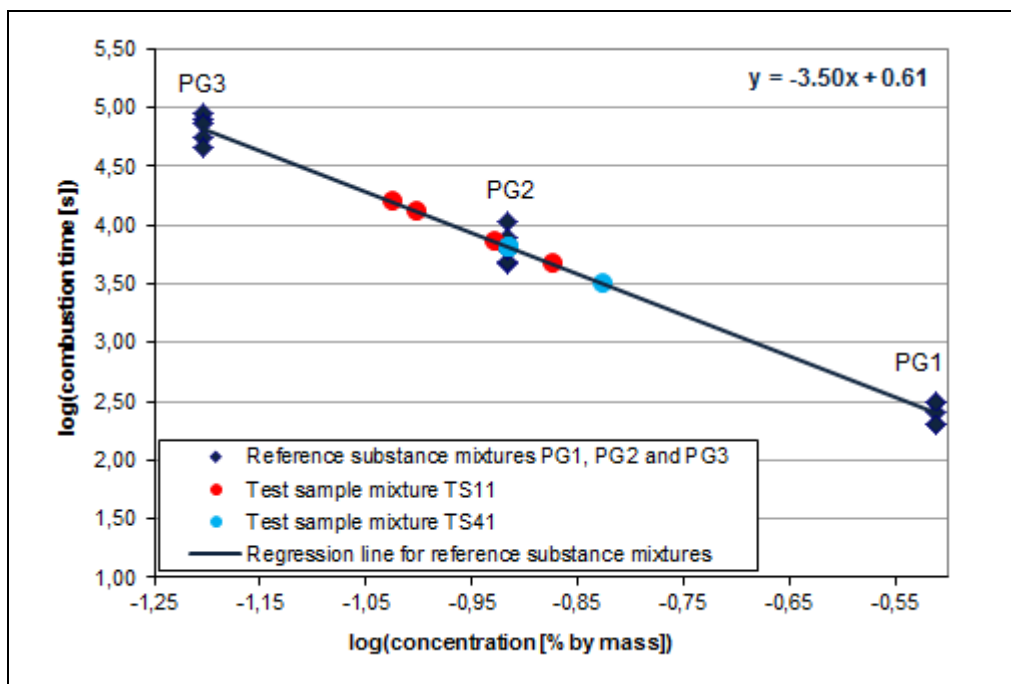


Figure 26: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 08 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

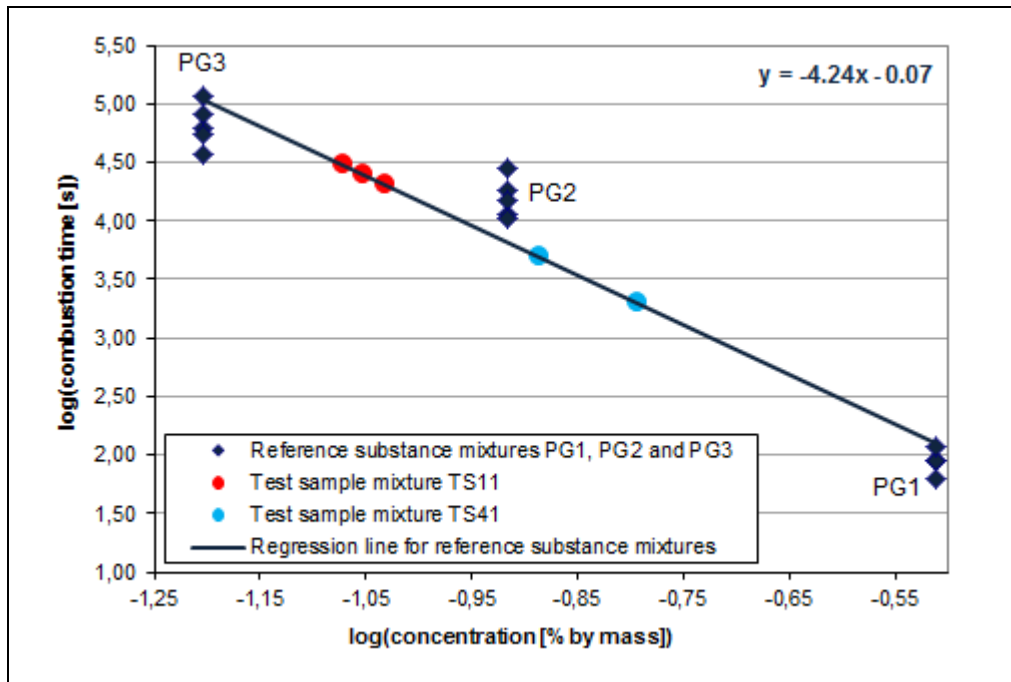


Figure 27: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 09 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

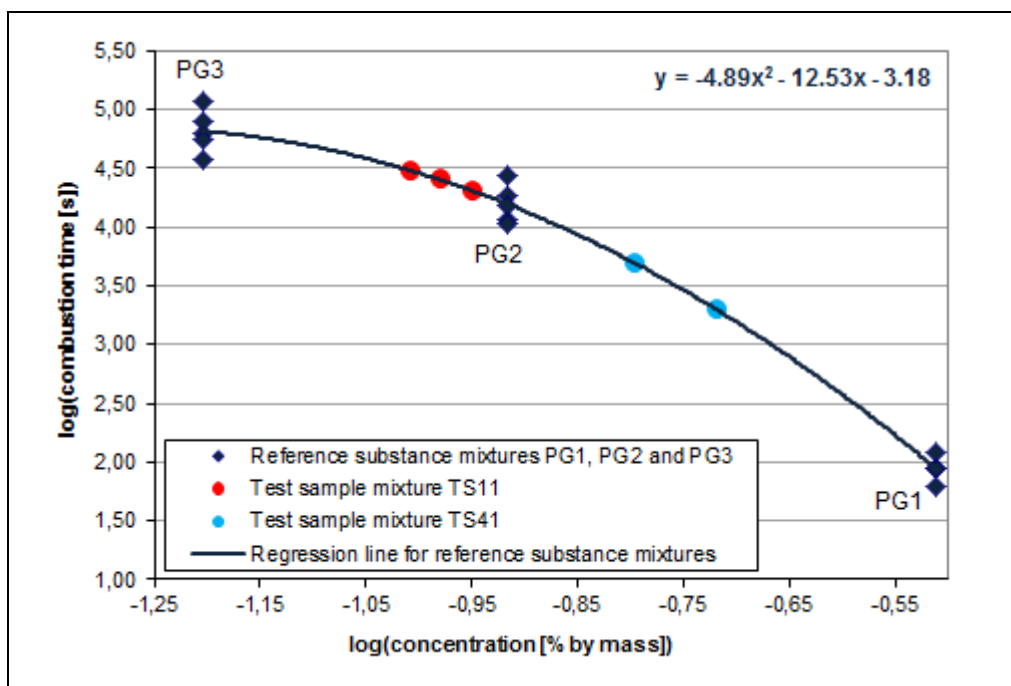


Figure 28: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 09 – *nonlinear relationship* (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

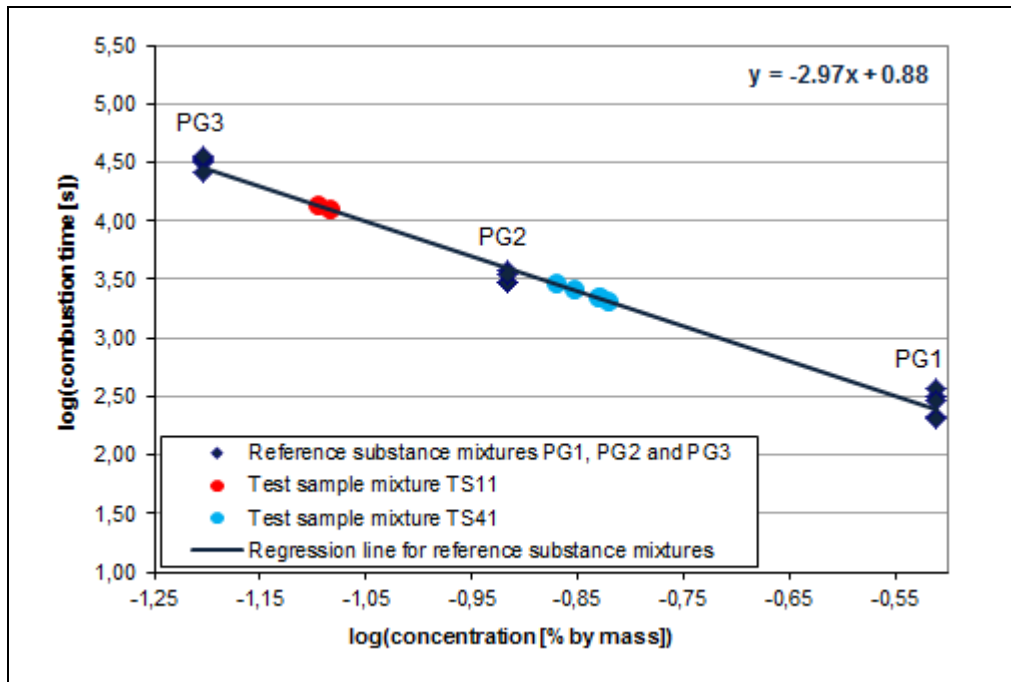


Figure 29: Relationship between the logarithmised combustion time and the logarithmised concentration of reference substance mixtures PG1, PG2 and PG3 for laboratory 10 (The red and light blue points of test sample mixtures TS11 and TS14 are only for information.)

7.4 Standard method: Analysis of single combustion times according to ISO 5725-2

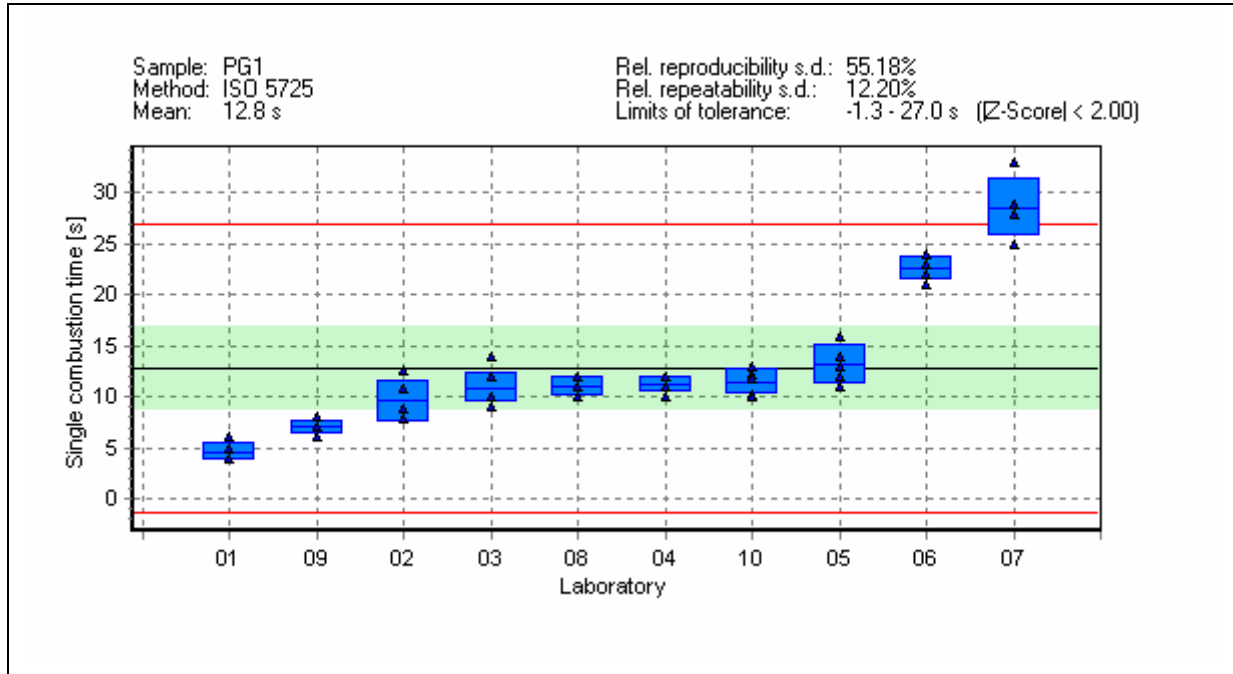


Figure 30: Analysis of single combustion times [s] – PG1

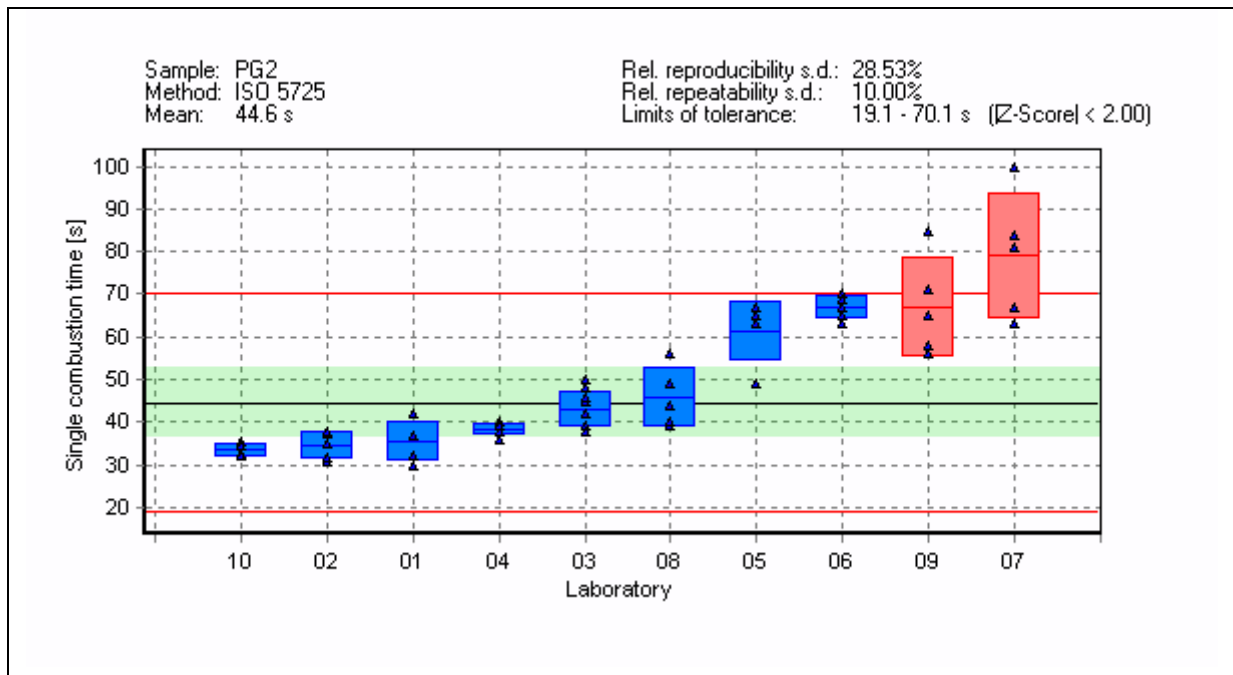


Figure 31: Analysis of single combustion times [s] – PG2

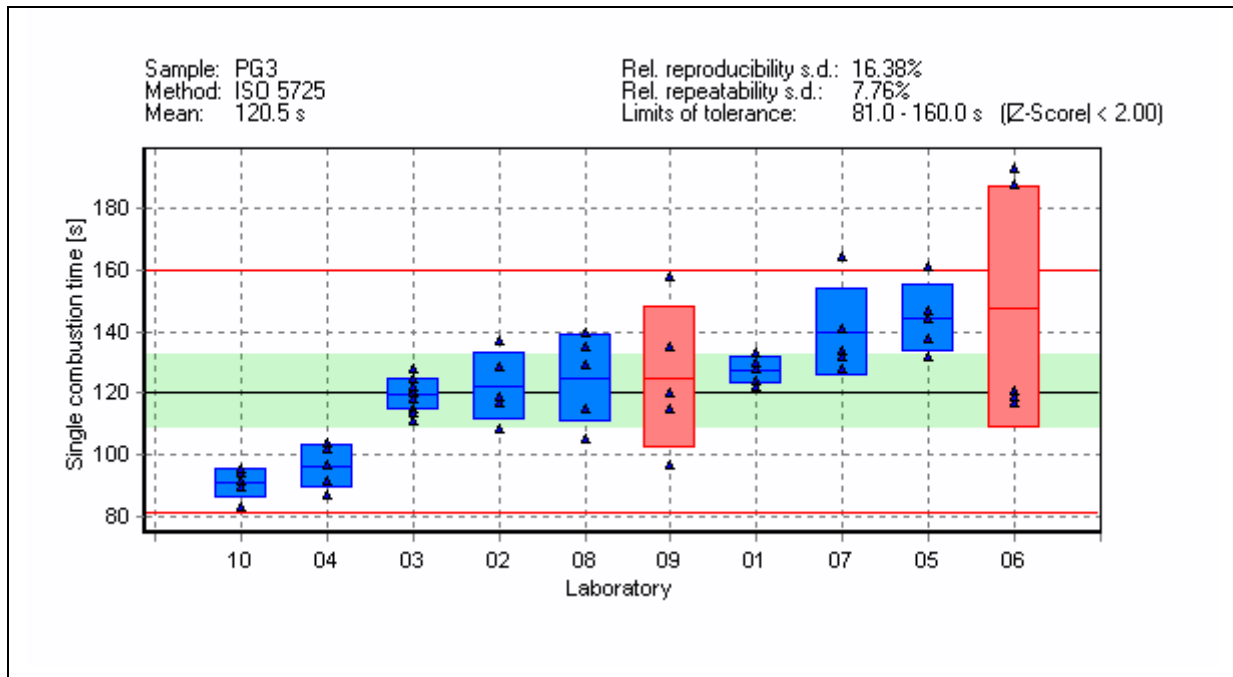


Figure 32: Analysis of single combustion times [s] – PG3

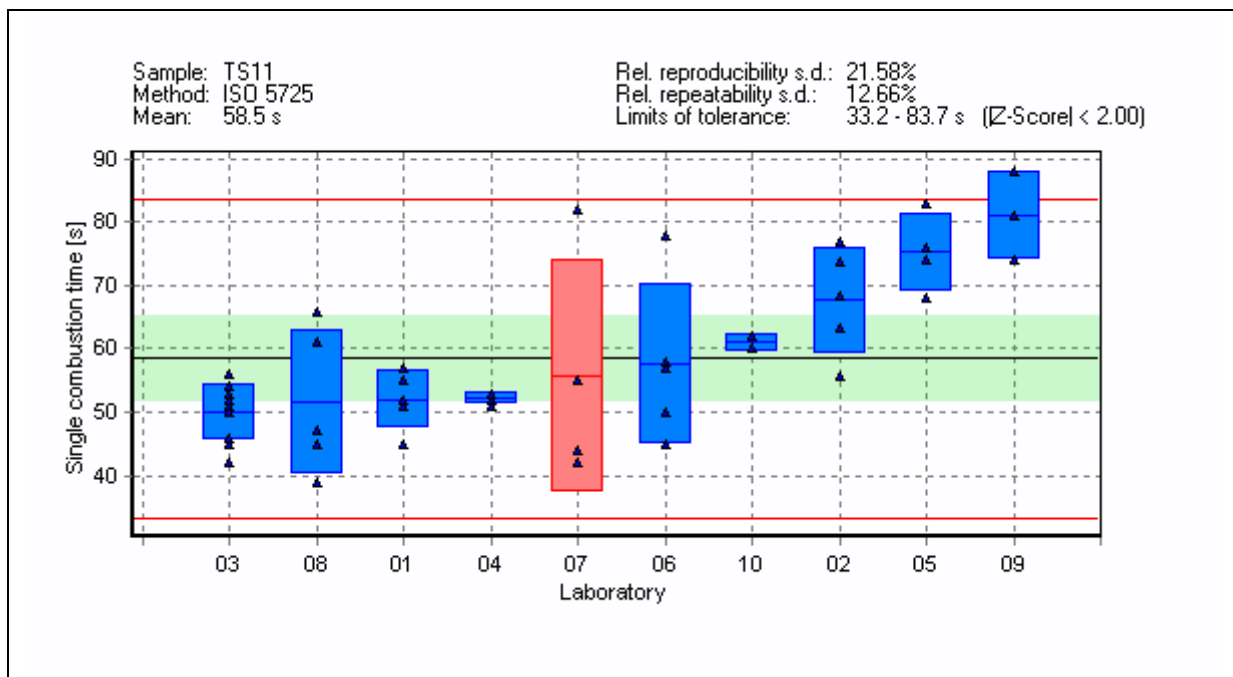


Figure 33: Analysis of single combustion times [s] – TS11

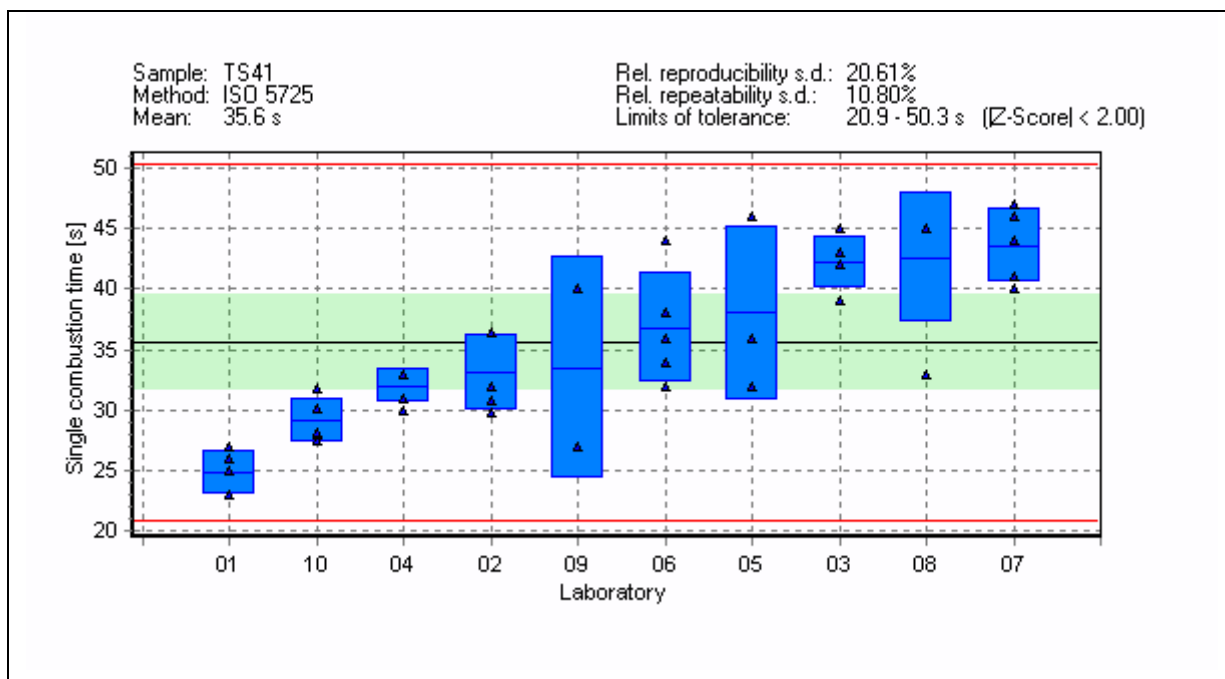


Figure 34: Analysis of single combustion times [s] – TS41

7.5 Robust method: Analysis of laboratory mean combustion times as well as their ratios

7.5.1 Analysis of laboratory mean combustion times according to DIN 38402 A 45 (no outliers have been eliminated)

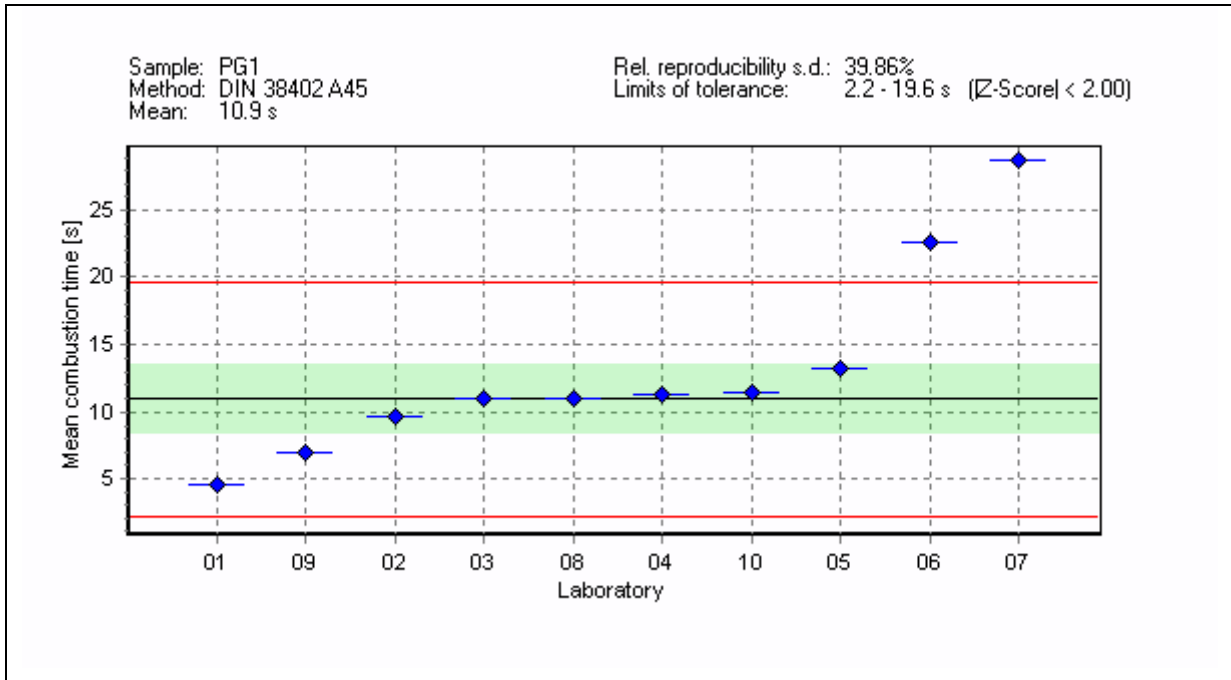


Figure 35: Analysis of laboratory mean combustion times [s] – PG1

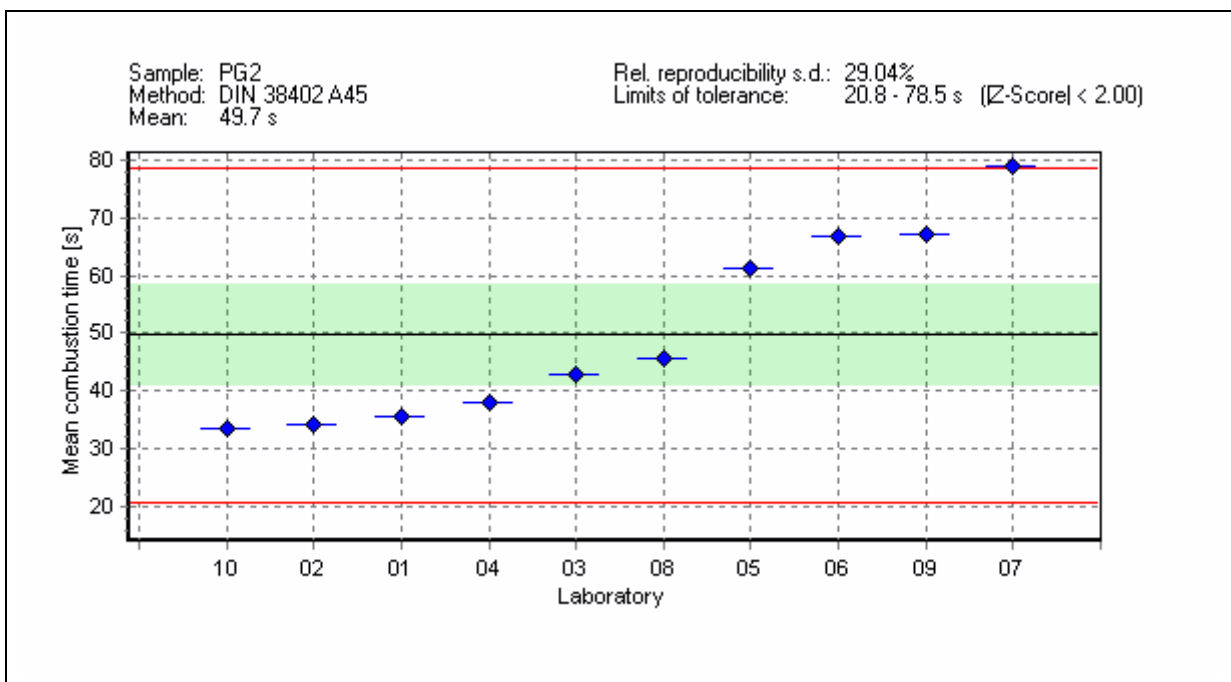


Figure 36: Analysis of laboratory mean combustion times [s] – PG2

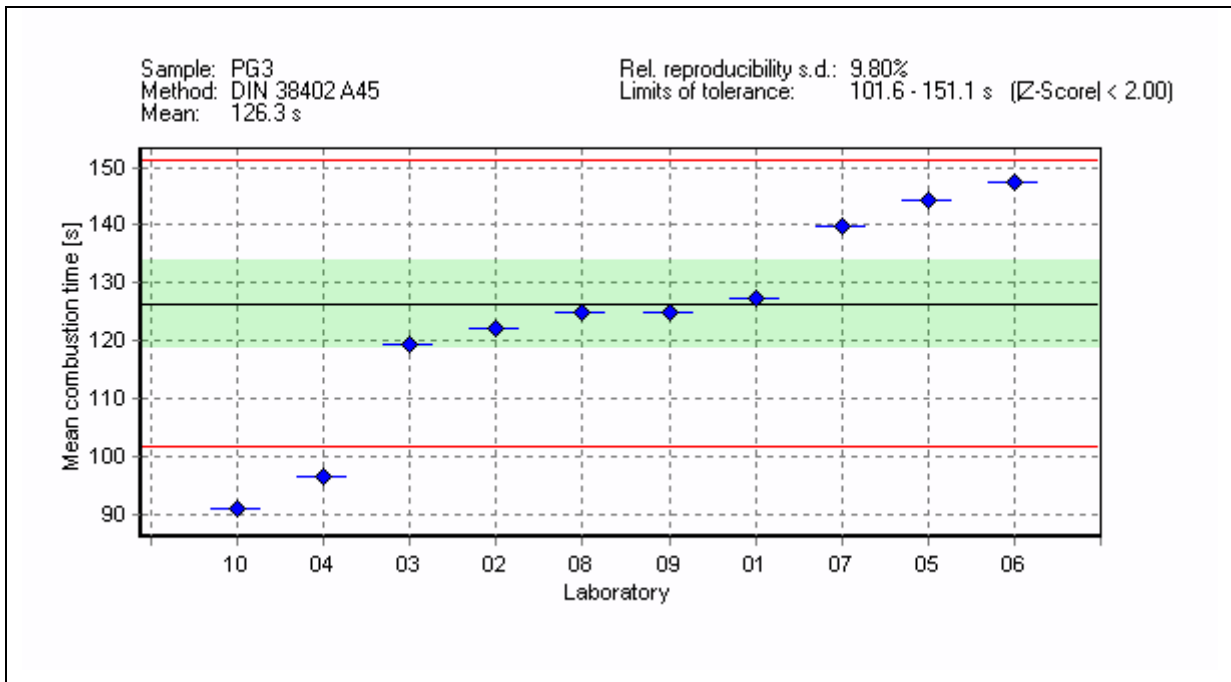


Figure 37: Analysis of laboratory mean combustion times [s] – PG3

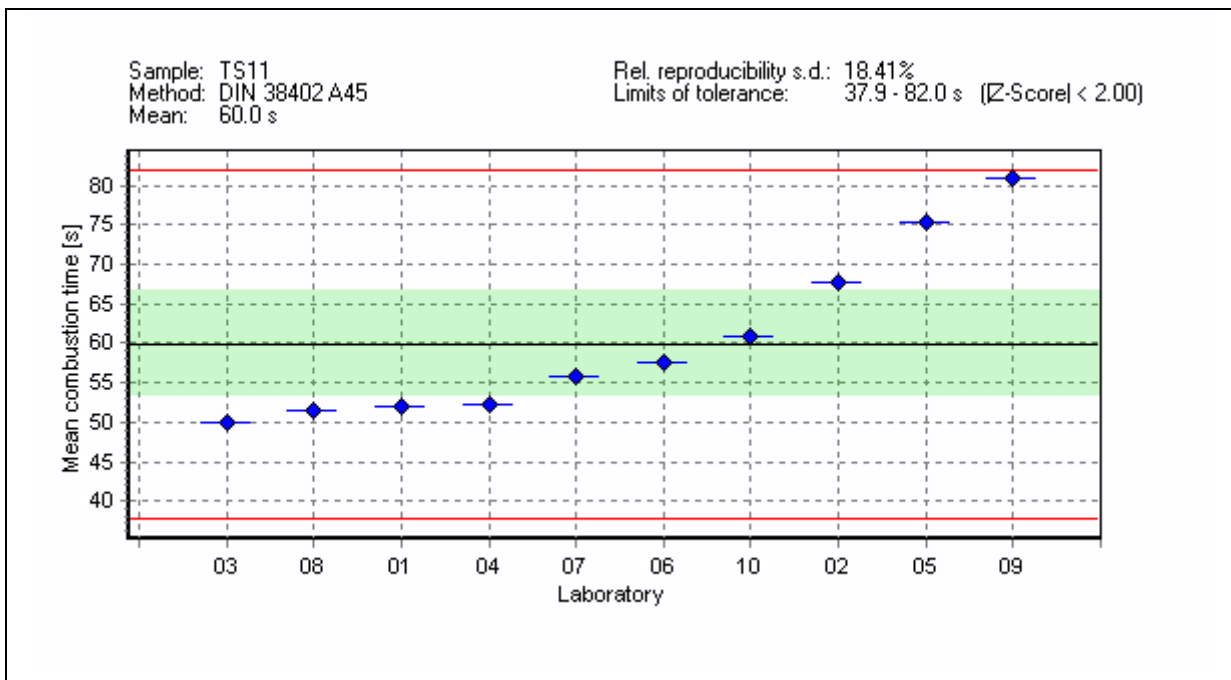


Figure 38: Analysis of laboratory mean combustion times [s] – TS11

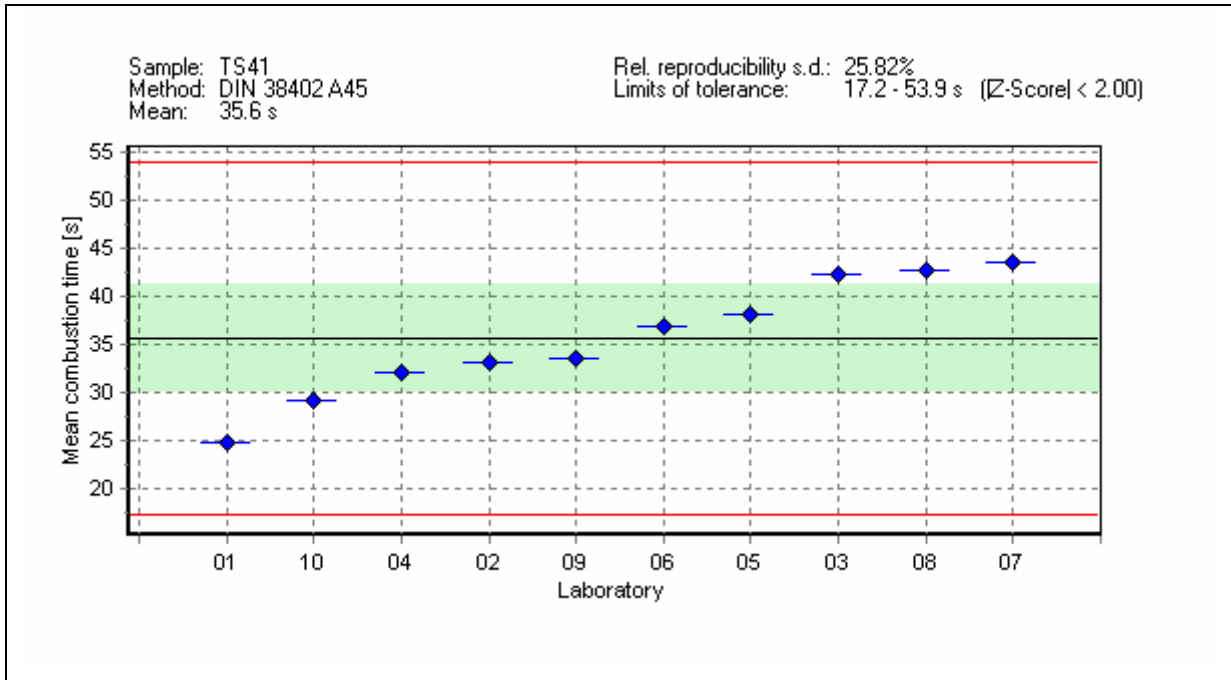


Figure 39: Analysis of laboratory mean combustion times [s] – TS41

7.5.2 Analysis of ratios of laboratory mean combustion times according to DIN 38402 A 45 (no outliers have been eliminated)

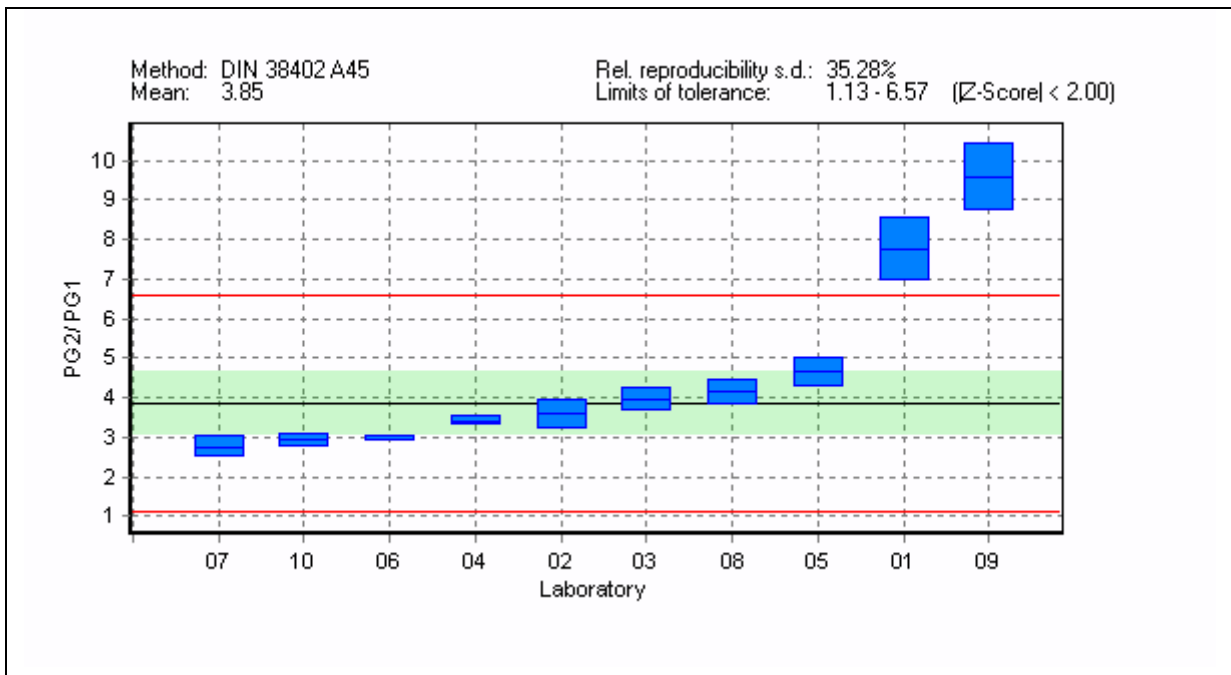


Figure 40: Analysis of ratios of laboratory mean combustion times – PG2/PG1

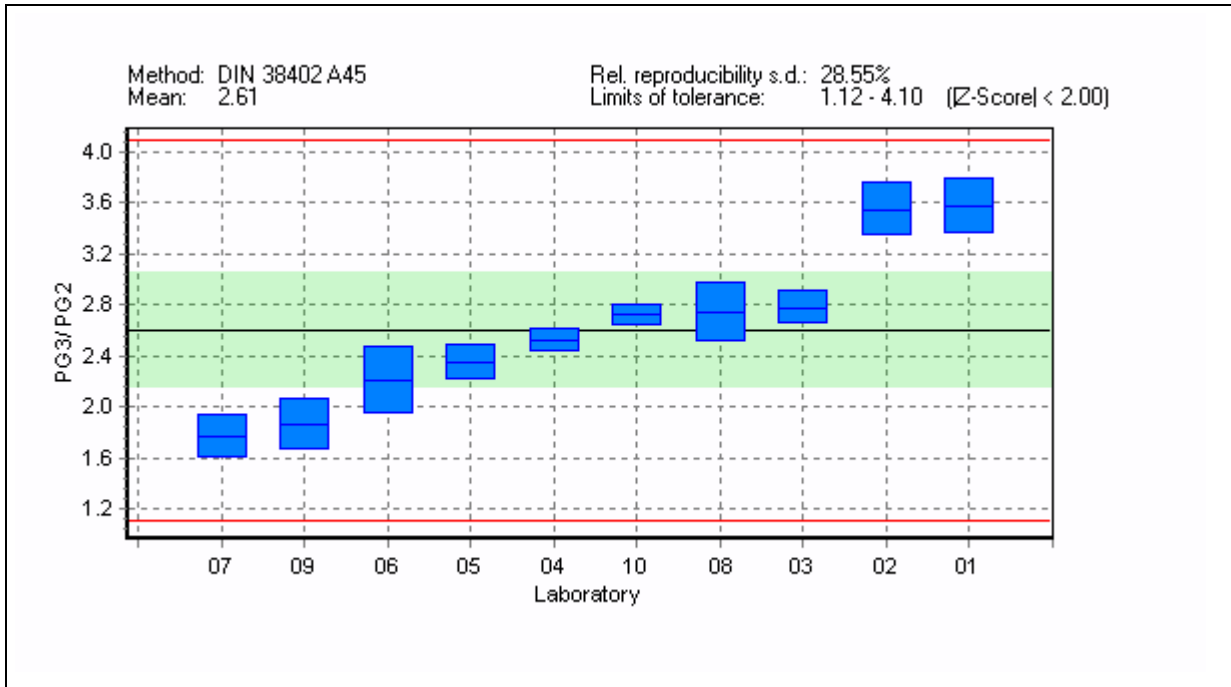


Figure 41: Analysis of ratios of laboratory mean combustion times – PG3/PG2

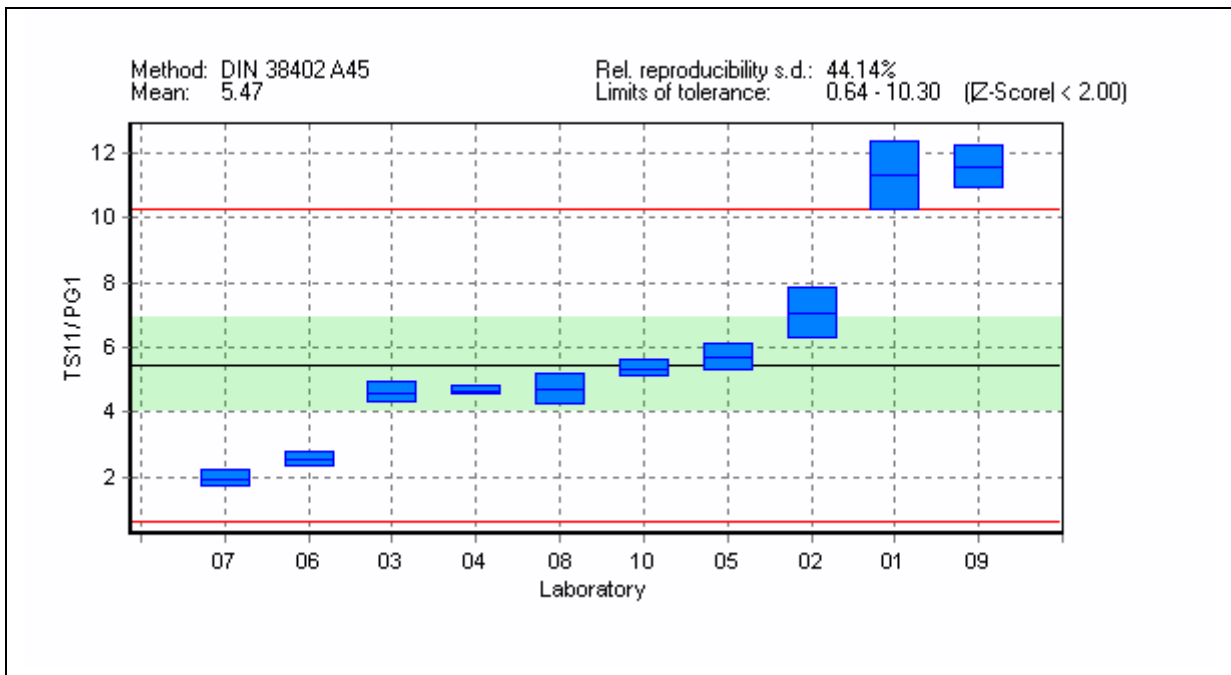


Figure 42: Analysis of ratios of laboratory mean combustion times – TS11/PG1

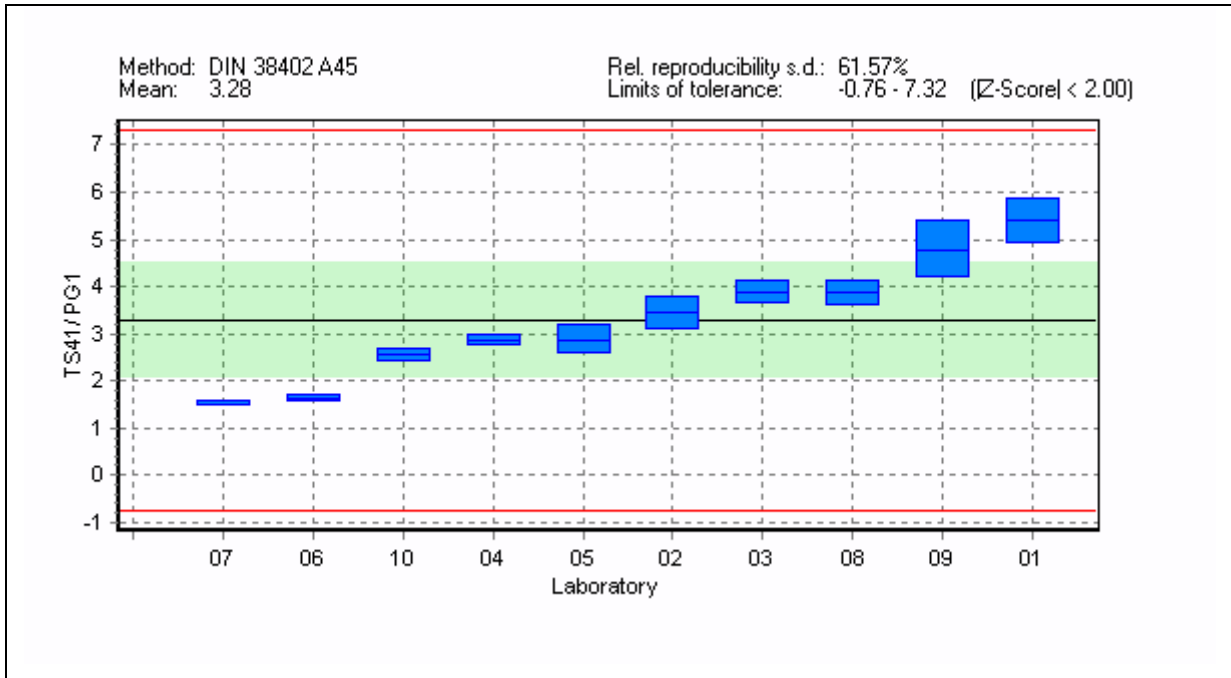


Figure 43: Analysis of ratios of laboratory mean combustion times – TS41/PG1

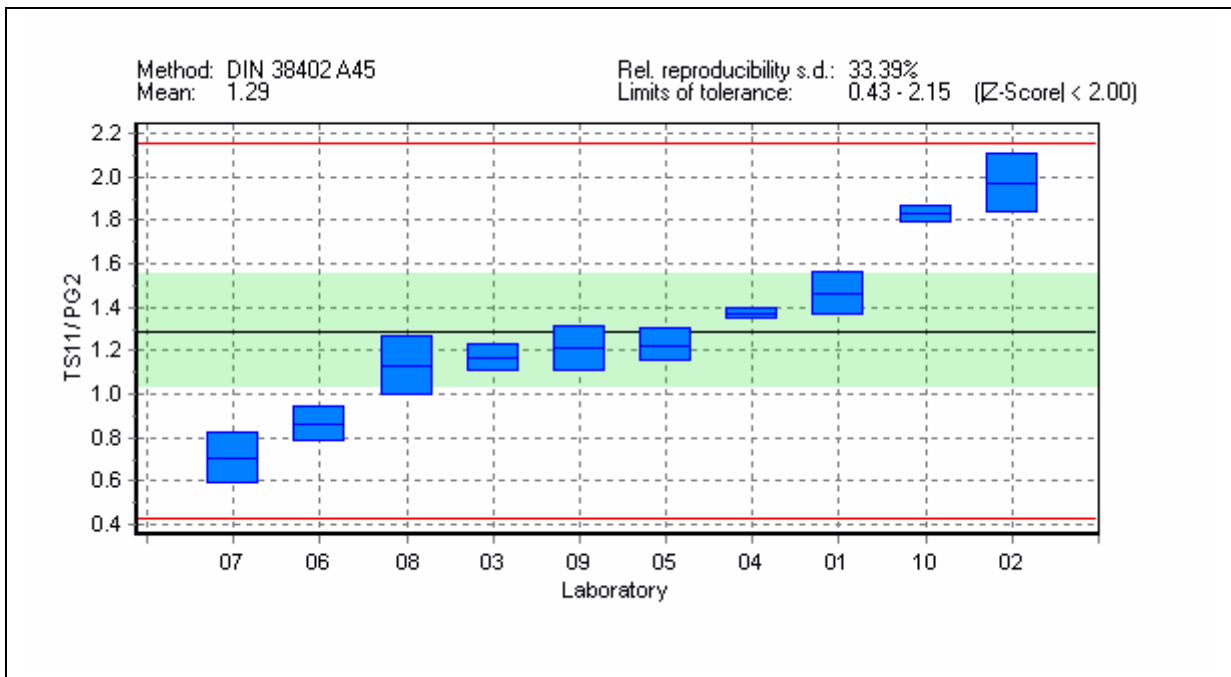


Figure 44: Analysis of ratios of laboratory mean combustion times – TS11/PG2

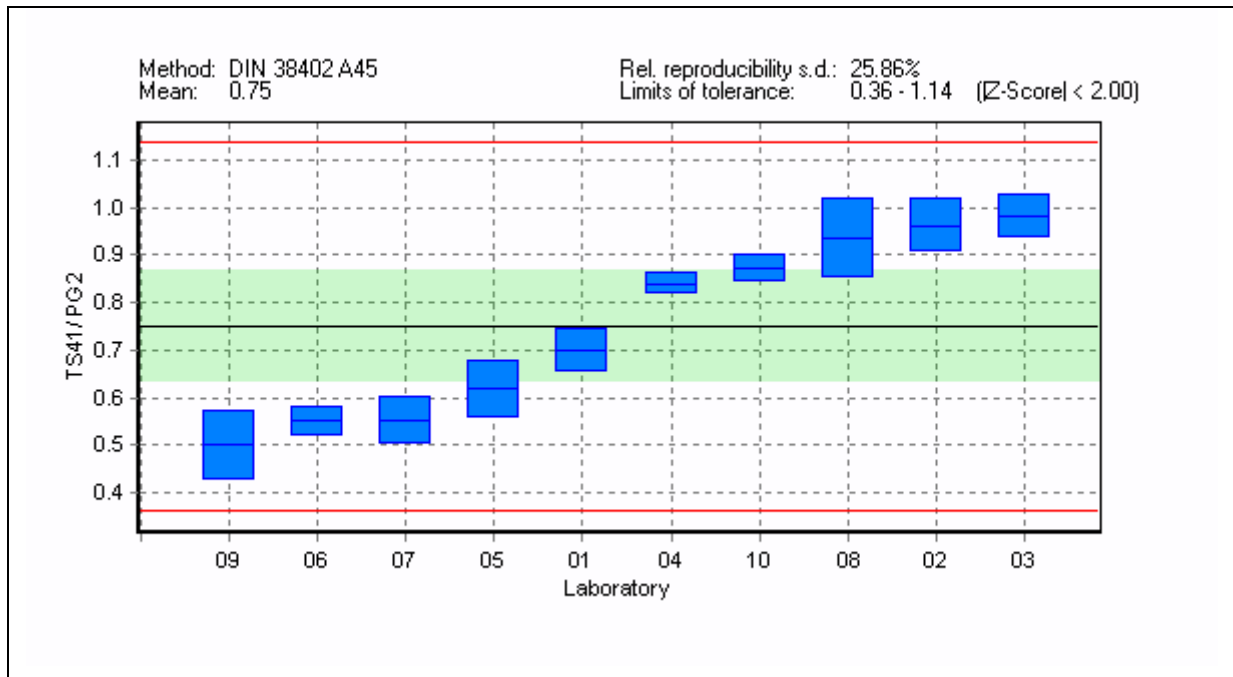


Figure 45: Analysis of ratios of laboratory mean combustion times – TS41/PG2

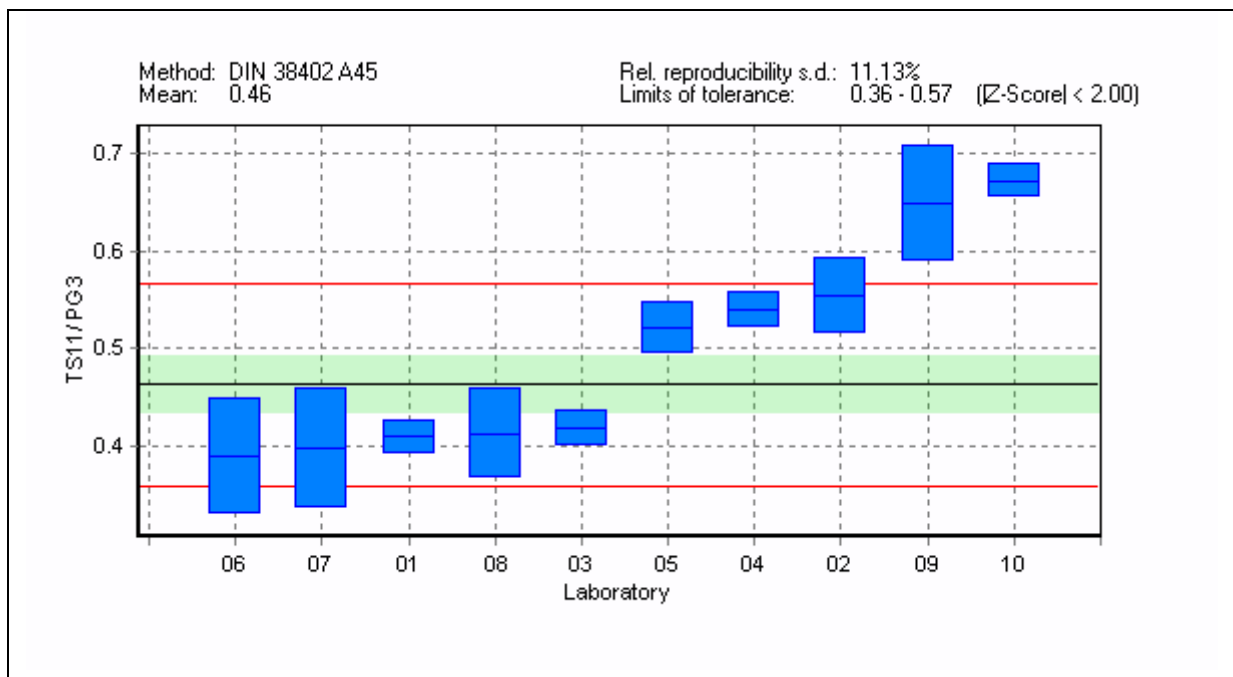


Figure 46: Analysis of ratios of laboratory mean combustion times – TS11/PG3

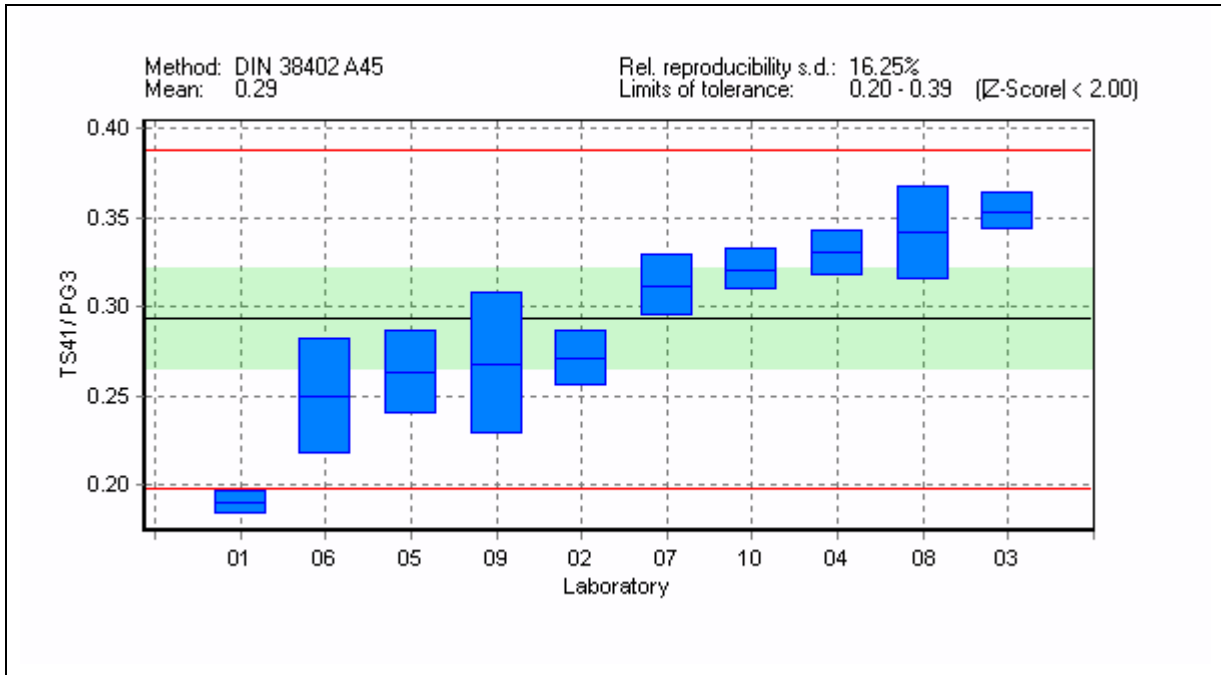


Figure 47: Analysis of ratios of laboratory mean combustion times – TS41/PG3