

**Evaluation of the
3rd Round Robin on
Solid Oxidizer Test (UN O.1)
with Calcium peroxide,
Sodium nitrate,
Sodium perborate monohydrate**

Final Report, 2009-2011



Impressum

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Herausgeber:
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ISBN 978-3-9813853-7-3

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1 Introduction

The classification of solid oxidizers according to the regulations on the transport of dangerous goods (based on the UN Recommendations/Model Regulations and accepted by all international organisations for the transport of dangerous goods as ADR, IMO, IATA) and in future also according to the GHS (Globally Harmonized System of Classification and Labelling of Chemicals) is performed on the basis of the results of the UN test O.1 (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, see [1]). This test was introduced into the UN Manual of Tests and Criteria in 1995 as a replacement for a similar test from 1986. Even if the UN O.1 test as described in the current 5th revised edition of UN Manual of Tests and Criteria gives some improvements compared to the old test, which had had many deficiencies, there are still some problems left with this test in terms of e.g. repeatability or reproducibility of test results, how to handle compacted or multilayer formulations like tablets, toxicity and partly significantly varying particle size distribution within defined fractions of 150 µm to 300 µm of the reference oxidizer potassium bromate (KBrO₃). For this reason the IGUS EOS working group installed an ad-hoc working group in 2002 assigned with the task to propose solutions for the existing problems. The appropriateness of such proposed solutions has to be proved by the method of interlaboratory (round robin) tests before they are presented for the adoption to the UN Committee of Experts on the TDG and on the GHS with a proposal of a completely revised test procedure.

This study is a follow-up investigation on requested expedient revision of the current UN O.1 test method based on previous interlaboratory test findings as ultimately performed in 2005/2006 by the ad-hoc working group. Besides required training of personnel or editorial revision of the current test description, round robin studies conclude the concomitant need for objective classification parameters to define an undoubted end of combustion by any innovative technical procedure like e.g. time-pressure apparatus or surface temperature monitoring devices and recommends the replacement of the toxic reference oxidizer potassium bromate by any harmless and preferable eco-friendly alternative in a more general manner [2].

The present report assesses the results of the 3rd UN O.1 round robin test, which was designed by the ad-hoc working group in order to find out:

- if any modification of UN O.1 test by gravimetric modification as introduced here for the first time is recommendable compared to the current test method and
- if any related possible classification criterion is more appropriate to identify real intrinsic oxidizing potential of solid oxidizers compared to individually determined burning time $t_{O,1}$ and
- if the proposed reference oxidizer calcium peroxide is capable to substitute potassium bromate in every respect.

Oxidizing solids are defined as substances which are, while in themselves not necessarily combustible, they may cause or contribute to the combustion of other material. The scope of the test method is to measure the potential for a solid substance to increase the burning rate (consumption rate) or burning intensity of a combustible substance when both are thoroughly mixed as introduced in chapter 34.4 of the Manual of Tests and Criteria. The test involves igniting and subsequently individual measurement of the burning time of a granular oxidizer mixed in two ratios with dried cellulose powder (4:1 or 1:1) and comparing the fastest mean burning time with related reference oxidizer mixtures, which are correlated to oxidizing potentials, classified by packing group I to III for strong, medium or weak oxidizers. Among others, one point of criticism is here that in the current test method, although officially defined as purpose of the test, no available amount of combustible material is considered to assess the related consumption rate of combustible material or intensity – neither in reference, nor in sample mixtures of solid with combustible cellulose as expressed by the current classification criterion ‘fastest mean burning time’ derived from usually 4:1 mixtures. Furthermore, the 3rd UN O.1 round robin is designed by the ad-hoc working group in order to find out if the modified gravimetric approach enables any advantages in terms of e.g. final classification of solid oxidizers or improvement of test performance itself, especially in consideration of the determination of a clear end point of combustion in an objective manner and therefore improvement of discriminatory power.

Here, calcium peroxide (CaO_2) in a content of 75% [m/m] is introduced for the first time as a possible reference oxidizer to substitute the toxic potassium bromate (KBrO_3) as currently recommended by UN and as used in the previous round robin test (2005/2006) [2]. Beforehand it is ensured by AQura GmbH, BAM and Solvay Chemicals GmbH in interlaboratory studies for basic adjustment that those combustion times of CaO_2 reference mixtures in their proposed and tested ratios, in order to describe oxidizing potentials as expressed by related packing group I to III, equals currently established burning times of KBrO_3 reference mixtures in comparison.

The combustion parameters of the reference mixtures of packing group I, II or III are partly varying in a wide range while using KBrO_3 . There are several reasons for this variation but its influence is not clear at all points, although it is shown by previous studies of the ad-hoc working group, that even slight deviations of mean within defined fraction of particle sizes of 150 μm to 300 μm may impact the combustion time of reference mixture significantly. Because of the necessity of a safe classification of solid oxidizers it is mandatory to solve the question of the variation of combustion time, which is basically individually determined by evaluation of burning behaviour of sample or reference mixtures.

It was planned to clarify the following two questions primarily:

1. Can potassium bromate be substituted by calcium peroxide as reference oxidizer in further tests?
2. Which of the following five proposed classification criteria, explained in detail in chapter 3.2, provide the best classification of solid oxidizers according to the regulations on the transport of dangerous goods, given the definition of solid oxidizers and intended scope of test method:
 - individual combustion time – $t_{O,1}$ as established
 - main combustion time – t_{20-80}
 - mass loss rate within 20 % to 80 % of total mass loss – MLR_{20-80}
 - mass loss rate by linear regression within 20 % to 80 % of total mass loss – R^2MLR_{20-80}
 - consumption rate of 60 % of balanced combustible material – BR_{20-80}

According to collected past experiences of experts for the determination of oxidizing properties of solids according to European Test Method A.17 – horizontal burn rate test (for details refer to: Council Regulation (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)) – the optimal mixture of solids with cellulose usually ranges within a ratio of 50 % to 80 %, mainly 60 % to 70 % by weight of solid oxidizer in its mixture with combustible material, which is indicated by the fastest burning speed in cm/second in comparison of all tested ratios in 10 % [m/m] increments. Although UN O.1 test methods recommend sample mixtures containing 50 % or 80 % by mass of test solid only, an additional ratio of 66 % [m/m] (ratio 2:1) is carried out on a voluntary basis to ensure that established ratios capture peak oxidizing potential of solid test sample sufficiently in comparison.

2 Test material

For this round robin test, three different mixtures of

- calcium peroxide as reference mixture of dangerous goods packing groups PG I, II and III
- sodium perborate monohydrate and
- sodium nitrate

were used:

Packing group I (SA PG I)	calcium peroxide: cellulose = 3:1
Packing group II (SA PG II)	calcium peroxide: cellulose = 1:1
Packing group III (SA PG III)	calcium peroxide: cellulose = 1:2
Test sample SB 41	sodium perborate monohydrate: cellulose = 4:1
Test sample SB 21	sodium perborate monohydrate: cellulose = 2:1
Test sample SB 11	sodium perborate monohydrate: cellulose = 1:1
Test sample SC 41	sodium nitrate: cellulose = 4:1
Test sample SC 21	sodium nitrate: cellulose = 2:1
Test sample SC 11	sodium nitrate: cellulose = 1:1

The test substances calcium peroxide and sodium perborate monohydrate were produced by Solvay Chemicals GmbH. The test substance sodium nitrate was supplied by Fisher Scientific and the combustible material cellulose CF11 by Whatman.

All test substances were centrally prepared, homogenized and distributed by Solvay Chemicals GmbH to ensure that all participating laboratories received an equal test basis.

2.1 Delivered raw materials

All participating laboratories were provided with:

- 500 g of reference oxidizer CaO_2 as produced by Solvay Chemicals GmbH on 09th of January 2009 (Batch No: 736-90109 4). The reference oxidizer requires no kind of sample preparation or pre-treatment for test purposes.
- 1000 g of test sample sodium perborate monohydrate as produced by Solvay Chemicals GmbH on 15th of January 2009 (Batch No: 220/90115 0).
- 500 g sodium nitrate per analysis as distributed by Fisher Scientific (Batch No: 0889790)
- 500 g CF11 Cellulose (Batch-No: 8311119) from Whatman as commercially distributed. Each laboratory was responsible for pre-treatment of combustible material according to the test method. Further combustible material could be ordered on demand.

2.1.1 Reference oxidizer calcium peroxide

The reference oxidizer is produced in pilot plant scale of one ton at Solvay Chemicals site in Bad Hönningen, Germany on 9th January 2009. The reference batch is exactly adjusted to 75% CaO₂ [m/m] excluding any contaminations of e.g. inorganic halogenides or water generating compounds during combustion like calcium hydroxide which both impact the burning behaviour partly significantly according to previously performed internal studies. The particle size distribution is determined by a Coulter LS 230 laser device, utilizing a static light scattering principle. The respective results shown in Table 1 and Table 2 are based on the Fraunhofer- and Mie-Theorie for calculation of particle size distributions in idealized spheres.

The particle size distribution is determined and confirmed for each packed volume as follows:

Table 1: Statistical values of the particle size distribution

Mean value	12.59 μm	10 th percentile	0.485 μm
Median (50 th percentile)	5.87 μm	90 th percentile	33.37 μm

Table 2: Particle size vs. packed volume

Particle size [μm]	≥ 0.1	≥ 0.5	≥ 1	≥ 2	≥ 10
Packed volume [%]	98.9	89.5	85.1	77.5	36.6

2.1.2 Preparation of test samples sodium perborate monohydrate and sodium nitrate

Each batch of 25 kg of test sample sodium perborate monohydrate and reference calcium peroxide or 10 kg of sodium nitrate, respectively, was homogenized in once by Rhönrad mixer ELTE650 (Engelsmann AG) for one hour at about 30 turns per minute beforehand (see Figure 1). Subsequently, each solid was divided into 14 sub-samples by the aid of a spinning (rotating) riffler as similarly used in the round robin test 2005/2006. The divided sub-samples were repacked into 500 cm³ or 1 dm³ plastic transport containers, which were properly labelled according to 3rd round robin test instructions beforehand. Based on the wide experience of the manufacturer with these test oxidizers, packed solids have been characterised to be sufficiently stable during transport, storage or time frame of round robin test performance, hence no further test to control stability before dispatch or after delivery is indicated.



Figure 1: Rhönrad Mixer ELTE650

Being ahead of following chapters, Table 3 lists the means of the individual combustion times $t_{0,1}$ over all laboratories involved and as generated during 2nd or 3rd round robin for sodium perborate monohydrate in its 50 % (TS 11 and SB 11) or 80 % [m/m] (TS 41 and SB 41) mixture with cellulose. The data outline an adequate suitability of performed sample preparation efforts beforehand and similar quality of distributed test sample sodium perborate monohydrate in comparison to 2nd round robin test – especially by taking into account that the delivered test sample is provided by different manufacturers in the 2nd and 3rd round robin test (2nd RRT: Evonik Industries AG former Degussa GmbH; 3rd RRT: Solvay Chemicals GmbH).

Table 3: Means of combustion time $t_{0,1}$ – comparison of the 2nd and 3rd round robin test for sodium perborate monohydrate (single values)

Round Robin Test	Test Code	Mean $t_{0,1}$ [s]	Rel. repeatability s. d. [%]
2 nd (2005/2006)	TS 11	58	12.7
	TS 41	36	10.8
3 rd (2008)	SB 11	56	11.7
	SB 41	30	8.6

3 Interlaboratory study

3.1 Organisation

The test samples were distributed to the participating laboratories of the study by Solvay. Results had to be sent to Solvay, where a first check on the entirety and validity of data is performed in agreement and coordination with quo data GmbH and laboratories involved, if needed. Table 4 shows the time schedule of the study.

Table 4: Time schedule of the 3rd UN O.1 Round Robin test

Round Robin step	Time period
Distribution of the test sample and the test instruction	2009/02/10
Laboratory testing period	2009/04/24
First statistical basic evaluation	2009/06/09

The test samples, attached by a test instruction (see Appendix 10.1), the test equipment besides balance and digital data acquisition unit, the data acquisition software as well as the calculation templates were sent to 14 laboratories (see Table 5). Altogether, data sets of 12 out of 14 laboratories had been received within the pre-set time frame and are considered in this study. None of these 12 laboratories had to be excluded from evaluation because of any insufficient data set.

Table 5: List of all 14 participating laboratories (12 laboratories have performed the test)

Laboratory / Agency (short name)	Country
Akzo Nobel	Netherlands
AQura	Germany
Arch Chemicals	USA
BAM	Germany
BASF	Germany
Currenta	Germany
FMLR	USA
INERIS	France
Siemens	Germany
Solvay	Germany
Syngenta	UK
Yara	Norway
TNO*	Netherlands
HSL*	Great Britain

*) Laboratories, which have not performed the test during the testing period

The special, high standardized test instructions (see Appendix 10.1 Test instructions) focus on detailed explanation of innovated gravimetric test modification in written and audio/video form. The data input form (see Appendix 10.2 Laboratory data input form) follows basically previous test instruction of the 2nd UN O.1 round robin test as performed in 2005/2006 to ensure high comparability of data sets.

3.2 Analytical procedures and classification criteria

Each laboratory received sodium nitrate as supposed to be a medium oxidizer of packing group II (UN1498, PG III) in consideration of its oxidizing properties, chemical nature and related experiences of the majority of safety experts and sodium perborate monohydrate as a reference for weak oxidizing potential and as used as such in previous round robin tests (UN3377, PGIII). Both oxidizers are officially listed as weak oxidizers of packing group III. All test performances based on 2:1 ratios of test solids are not mandatory, but these additional tests may provide further important data on reliability and suitability of the proposed UN O.1 test modification as explained in Chapter 1 in the major understanding of experts of the ad-hoc working group. Furthermore, the determination of combustion time $t_{0,1}$ by individual time-take of reference oxidizer piles representing strong oxidizers (PG I – ratio 3:1) should be performed on a voluntary basis as well.

The following five combustion parameters for classification purposes should be derived for statistical analysing:

Table 6: Classification parameters for statistical analysis

Parameter	Description
$t_{0,1}$ [s]	Individually determined combustion time by visual assessment of main combustion of conical pile
t_{20-80} [s]	main combustion time as derived from 20% to 80% of monitored total mass loss
MLR ₂₀₋₈₀ [g/s]	mass loss rate within 20 % to 80 % of total mass loss - $\Delta m_{20-80} / t_{20-80}$ (slope of two-points straight line)
R ² MLR ₂₀₋₈₀ [g/s]	mass loss rate by linear regression within 20 % to 80 % of total mass loss
BR ₂₀₋₈₀ [g/s]	consumption rate of 60 % of balanced combustible material in mixture

In this context, the *individual combustion time* $t_{0,1}$ is defined as the individually recorded burning time by an analyst from when the power of ignition source is switched on to when the main reaction ends (e.g. flames, incandescence or glowing combustion). Intermittent reaction such as sparking or sputtering, after the main reaction ended should not be taken into account. The UN text provides no further details on ‘main reaction’ to be determined.

The *main combustion time* t_{20-80} defines the duration of time within 20 % to 80 % of total mass loss of burning trial as continuously monitored by balance. This criterion is supposed to be more objective compared to $t_{0,1}$.

The *mass loss rate* MLR_{20-80} describes the slope of the line within 20 % to 80 % of total mass loss of burning trial as monitored by balance while plotting data mass as a function of the time (= linear regression with the two data points at 20 % and 80 %).

The *mass loss rate by linear regression* $R^2 MLR_{20-80}$ equals the slope of the line within 20 % and 80 % of total mass loss of burning trial as monitored by balance while plotting mass as a function of time (= linear regression with all data points within 20 % to 80 % of total mass loss).

Last but not least, the *consumption rate* BR_{20-80} , which equals the burning rate or burning intensity of balanced combustible materials in consideration of given UN definition of oxidizing substances, is defined as the quotient of 60 % of the real balanced / total available amount of combustible material in conical pile and the main combustion time t_{20-80} . In previous gravimetric and calorimetric heat-flux studies of the ad-hoc working group it could be shown that the relative consumption of combustible material in ideal mixtures or in mixtures with a surplus of solid oxidizer correlates proportional to total mass loss of burning trial within an acceptable manner. The burning rate is therefore calculated by the following equation: $BR_{20-80} = 0.6 \times m_{cellulose} / t_{20-80}$ [g/s]. Exemplarily for SA PGIII, 12 g cellulose will be consumed within the main combustion time t_{20-80} : ratio 2:1, 30g in total → $0.6 \times 20g = 12g$ consumed cellulose within 20% to 80% of total mass loss. For any sample mixture with a ratio 4:1, the consumed cellulose within the main combustion time t_{20-80} is equal to 3.6 g (→ $0.6 \times 6g = 3.6g$).

The participants were requested to measure the combustion parameters of

- packing groups SA PG I (optional and only $t_{0.1}$), SA PG II and SA PG III;
- sodium perborate monohydrate test samples SB 11, SB 21 (optional), SB 41;
- sodium nitrate samples SC 11, SC 21 (optional), SC 41.

While in the 2nd UN O.1 round robin test, the order of test performance varied between the laboratories, in the current round robin test the tests had to be performed in the following fixed order for statistical purposes:

Test Series A

Test Sequence 1 (code: SA PG III) : Test reference mixture CaO_2 - PG III (1:2) Trial 1-5 (6-7)

Test Sequence 2 (code: SA PG II) : Test reference mixture CaO_2 - PG II (1:1) Trial 1-5 (6-7)

Test Series B

Test Sequence 3 (code SB 41) : Test sample $NaBO_3 \cdot xH_2O$ (4:1) Trial 1-5 (6-7)

Test Sequence 4 (code SB 11) : Test sample $NaBO_3 \cdot xH_2O$ (1:1) Trial 1-5 (6-7)

Test Series C

Test Sequence 5 (code SC 41) : Test sample $NaNO_3$ (4:1) Trial 1-5 (6-7)

Test Sequence 6 (code SC 11) : Test sample $NaNO_3$ (1:1) Trial 1-5 (6-7)

Additional, but optional tests from Test Series A to C

Test Sequence 7 (code SA PG I) : Test reference mixture CaO_2 - PG I (3:1) Trial 1-3 (4-5)

Test Sequence 8 (code SB 21) : Test sample $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ (2:1) Trial 1-5 (6-7)

Test Sequence 9 (code SC 21) : Test sample NaNO_3 (2:1) Trial 1-5 (6-7)

In addition to the measurement values, all laboratories submitted information on the dry time of cellulose [h], moisture of cellulose [%], relative humidity [%] and temperature in the laboratory [°C].

The following pie charts show the percentages for these four environmental parameters for the three test reference mixtures and the six test samples. Here, several levels (e.g. of temperature) have been summarized into groups (pooled) to get a better survey of the ranges.

It has to be noted that the given percentages are rounded values so that the sum in the pie charts is not necessarily 100 %.

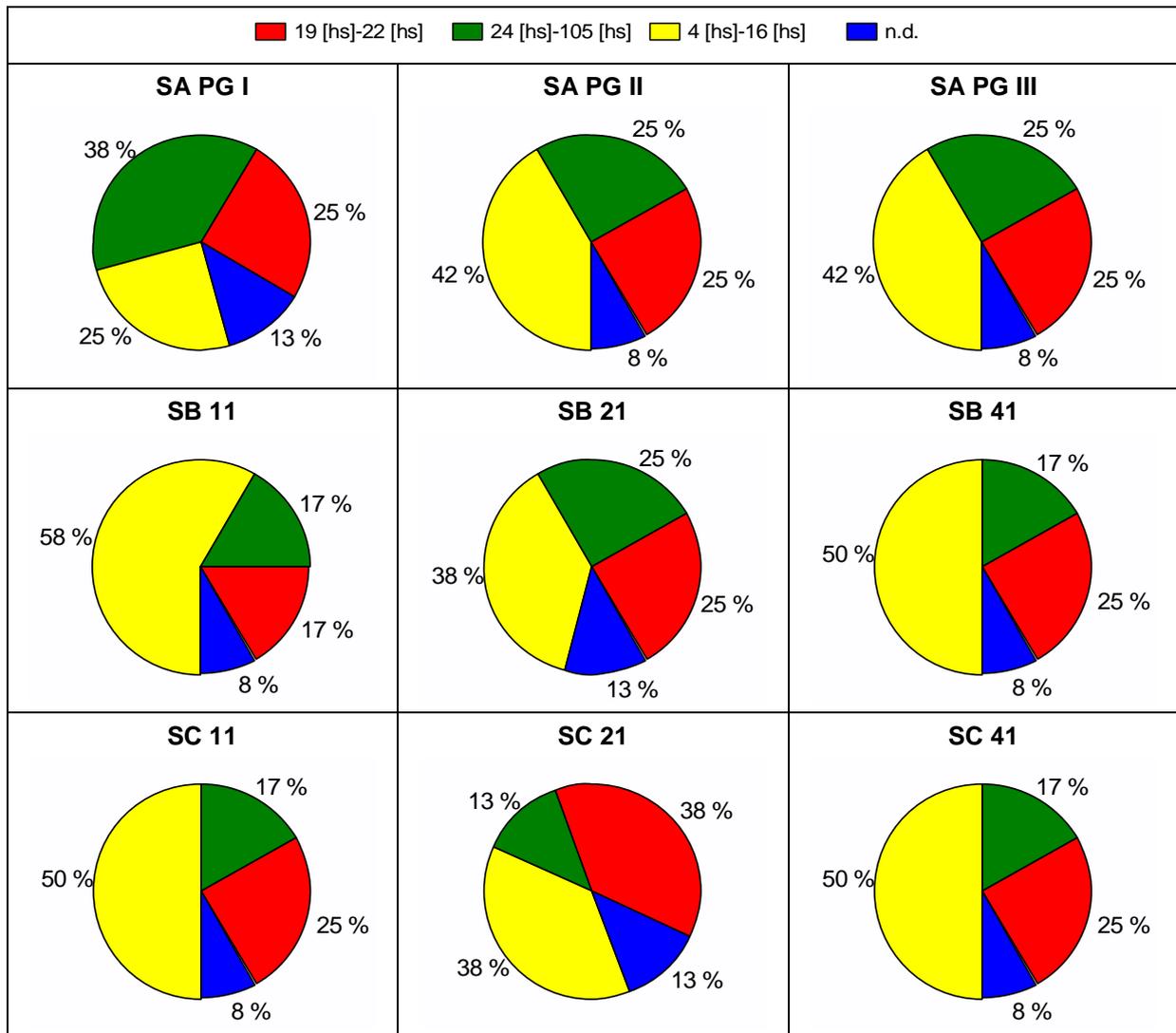


Figure 2: Percentages for dry time of cellulose (pooled)

Here, it can be stated that neither no clear standard ambient lab conditions, nor drying procedure or minimum moisture content left in cellulose can be identified.

Approximately 50 % of all laboratories dry cellulose only 4 to 16 hours instead of up to 19 to 24 hours (see Figure 2).

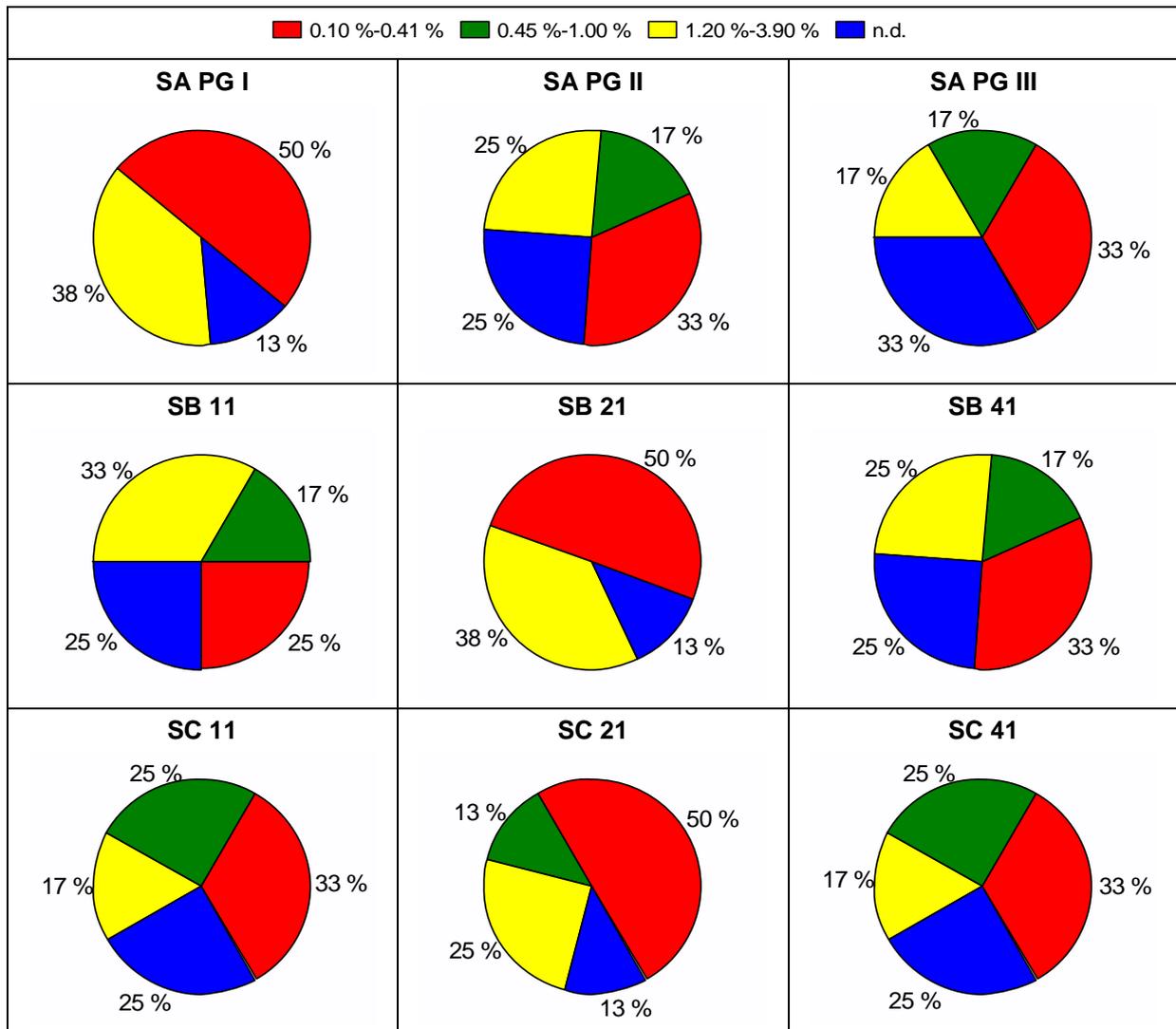


Figure 3: Percentages for moisture cellulose (pooled)

In consequence, the determined moisture content left in cellulose after drying procedure varies between less than 0.41 % as required by official test method UN O.1 (<0.5%) up to even 3.9 % as a maximum.

It can neither be quantified how this fact may impact further burning trials nor related statistical evaluation in every respect, nor reasons of responsible analysts to miss given UN recommendations can be addressed (see Figure 3).

The same statement remains valid for the assessment of ambient conditions during test performance and possible impacts on test results in comparison as shown in Figure 4 and Figure 5.

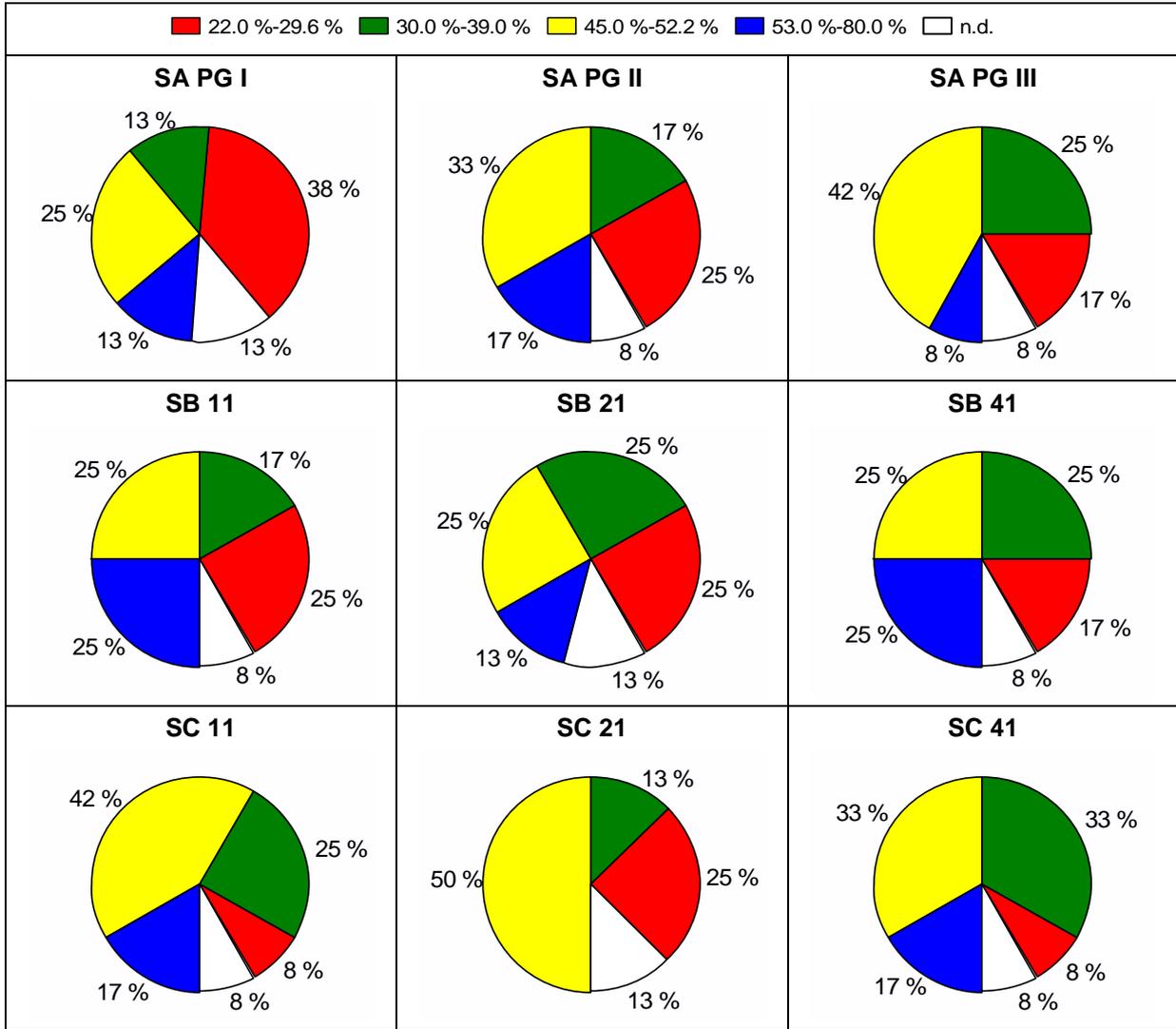


Figure 4: Percentages for relative humidity in labs during RR test performance (pooled)

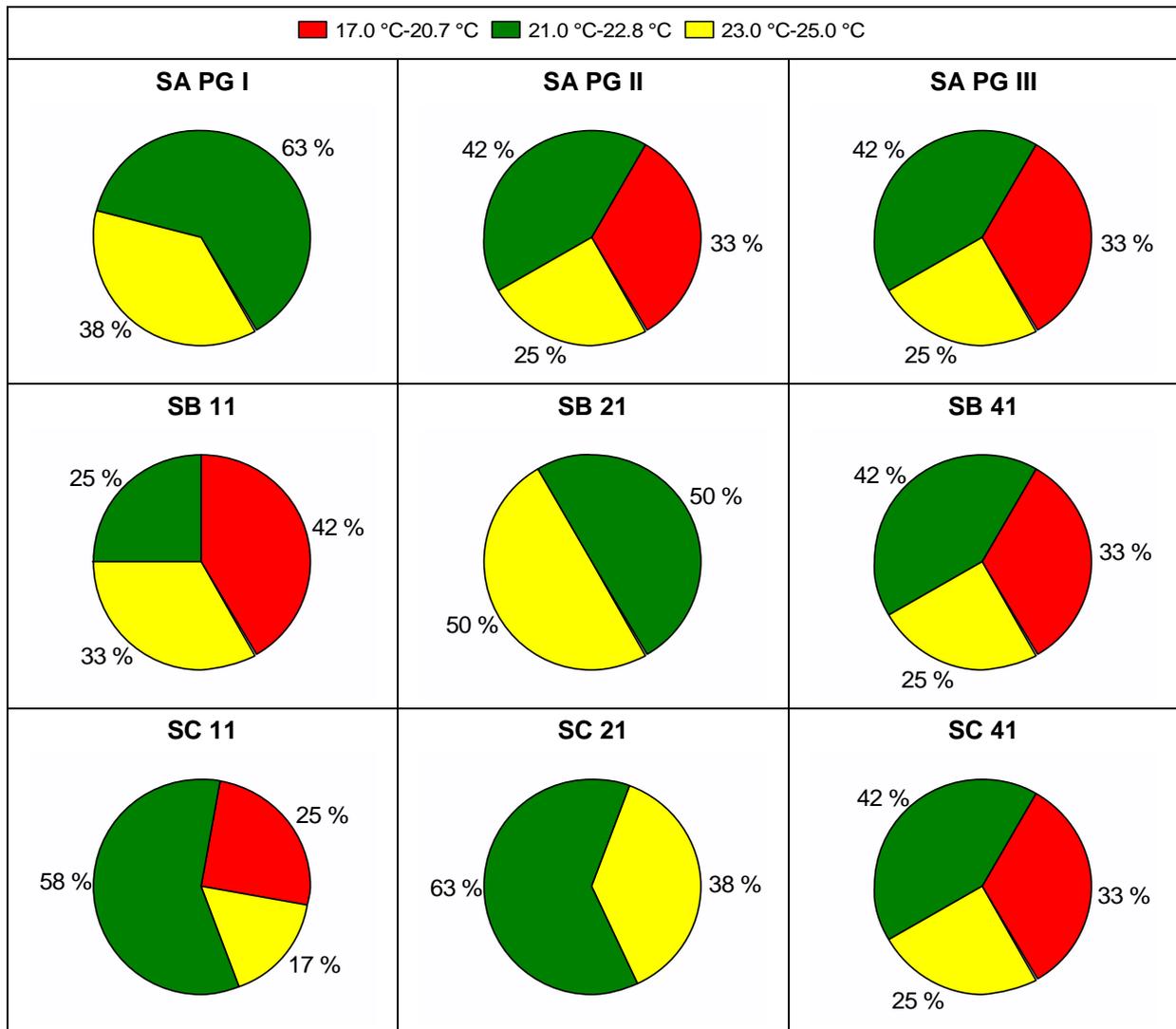


Figure 5: Percentages for ambient temperature in labs during RR test performance (pooled)

3.3 Data pre-processing

Before starting the statistical evaluation by the quo data GmbH, the submitted raw data had been checked for plausibility by Solvay Chemicals GmbH in coordination with quo data GmbH and participating laboratories in case of any uncertainty. The following Table 7 gives an overview of problems that occurred during the tests. Furthermore, it gives the total number of trials carried out as well as the number of considered valid trials for this study.

Table 7: Results of plausibility check by Solvay

Laboratory	break of wire	out of spec.	inconsistent profile	total trials	valid trials	filtered trials
01	3	2	3	33	28	5
02	5	0	0	46	46	0
03	9	0	0	47	47	0
04	4	5	1	50	43	7
05	3	0	7	46	40	6
06	0	1	0	33	33	0
08	0	0	0	44	44	0
09	0	2	3	49	44	5
10	4	3	1	35	31	4
11	8	0	0	32	32	0
13	4	2	0	45	43	2
14	1	0	1	47	45	2
				460	429	31

For laboratories 02, 03, 06, 08 and 11 none of the trials proved was invalid. All preselected or ‘filtered’ trials are identified by the responsible laboratory itself beforehand and had been immediately repeated to complete the required data set without further request.

Of the 460 trials carried out in total, only 31 trials (6.7 %) did not pass the plausibility check. This low percentage underlines as well the robustness of the modified test method in terms of practicability, because the introduced test design by the ad-hoc working group is performed and tested in each participating laboratory for the first time – besides Solvay Chemicals GmbH, BAM and AQura GmbH. The plausibility check focuses on any early opening of wire before 2/3 of the individually determined combustion time $t_{0.1}$ (“break of wire”), any “phi-factor” out of given specification of +/- 15 % in comparison of “MLR₂₀₋₈₀” to mean of mass loss slopes within 20 % to 80% of total mass loss in 10 % increments (“out of spec.”) or any obvious inconstant mass loss profiles (“inconsistent profile”) as exemplarily shown in Figure 6. The phi-factor is a temporarily proposed quality criterion by the ad-hoc working group for the quick evaluation of test performance of burning trial to assess accuracy of monitored mass loss profile. In the major understanding of safety experts at the ad-hoc working group, it seems to be improvable that no related test performance criterion is given in current UN recommendations compared to e.g. test method A.17 as described in European Directive 67/548/EEC. Further details are given in attached test instructions to this study (see Appendix 10.1).

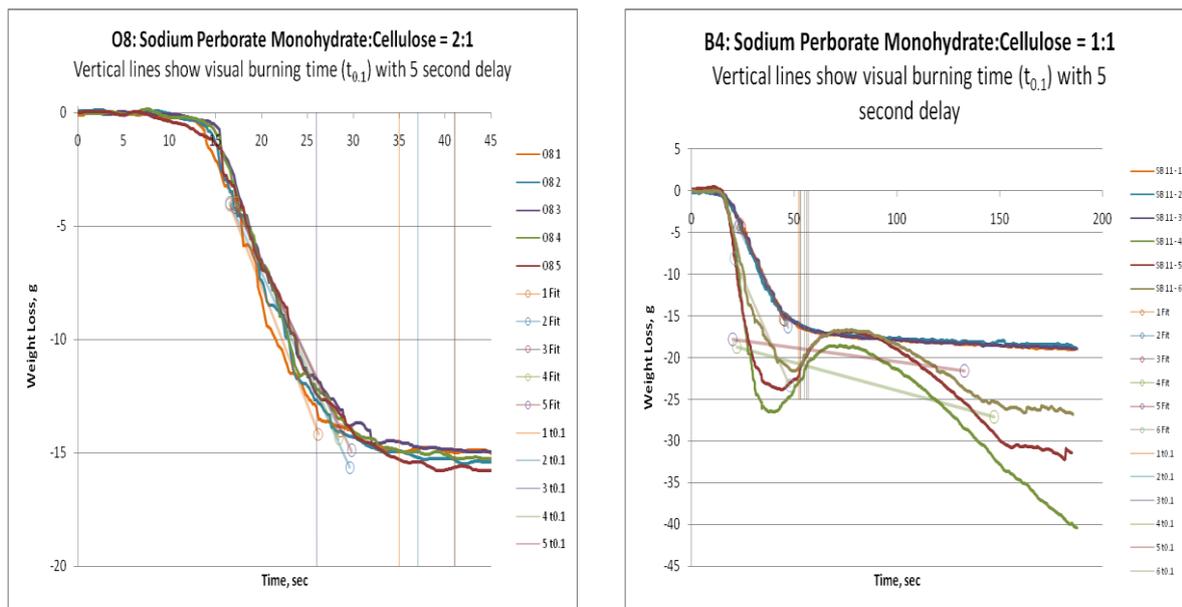


Figure 6: Examples for mass loss profiles in regard to plausibility check

Table 8 lists all serial numbers of not considered burning trials per test sequence according to test scheme of round robin. Each sequence comprises at least five burning trials in repetition, but any test sequence should not exceed more than seven trials in total in case of any implausibility of test performance according to instructions to keep the RR demands for all participating laboratories in an acceptable time frame.

Table 8: Serial number of burning test trial eliminated from raw data during plausibility check

Laboratory	SA PG I	SA PG II	SA PG III	SB 11	SB 21	SB 41	SC 11	SC 21	SC 41	Sum of eliminated trials
01		5	1	4		2			4	5
04			3, 5				4, 6		2, 3	6
05			2		1, 2, 3, 4, 5					6
09				4, 5, 6				4, 5	3, 5	7
10		3					2, 3, 5			4
13						5		5		2
14									4	1

It is shown that the proposed reference oxidizer CaO_2 causes only 6 failures in total compared to 14 failed burning trials in total for coded SC sequences with sodium nitrate, which is basically caused due to known physical and chemical properties of the tested oxidizer itself like e.g. melting during test performance and subsequent possibility of salt bridges (short circuit of power loop) or generally known

sensitivity of ignition wires to nitrate anions or related oxidation reactions ('break of wire').

Finally, Table 9 gives a summarization of the type of ignition wire in charge and monitored opening of wire during test performances depending on the laboratory. Within this round robin frame, no clear recommendation on most suitable ignition wire can be given, although AluChrom alloys may indicate an improved durability compared to NiCr or even AlSiChrom alloy in comparison.

Further studies in detail have to be carried out to minimize the risk of any early openings and related impacts on burning behaviour of conical pile to identify most suitable ignition wire for testing solid oxidizers according to UN O.1. Therefore any recommendations of most appropriate ignition wires should be postponed to future studies on test methods.

Table 9: Comparison of openings, laboratories and type of ignition wire

Laboratory	Type of wire	Number of total trials	Break of wire	%
02	AlSiChrom	46	5	10,9
03	AlSiChrom	47	9	19,1
05	AluChrom	46	3	6,5
06	AluChrom	33	0	0,0
13	AluChrom	45	4	8,9
14	AluChrom	47	1	2,1
01	NiCr	33	3	9,1
04	NiCr	50	4	8,0
08	NiCr	44	0	0,0
09	NiCr	49	0	0,0
10	NiCr	35	4	11,4
11	NiCr	32	8	25,0

In consideration of total breaks of wires (b.o.w.) and number of labs utilizing related type of wire, following hierarchy by factorization ($f_{\text{wire}} = \sum \text{b.o.w.} / \sum \text{labs}$) may be derived from existing data pool at the current state of affairs:

$$\text{AluChrom (factor ~2)} < \text{NiCr (factor ~3)} < \text{AlSiChrom (factor ~7)}$$

4 Assessment of modified test method UN O.1 and classification criteria

4.1 Background

The assessment of the data was performed using the software package ProLab Plus 2008/2009, which is widely employed for the evaluation of method interlaboratory tests and laboratory proficiency tests. All trials considered as valid in the plausibility check served as the data basis.

Two different types of measurands were considered:

1. single values (pre-processed raw data) of the five parameters in all nine test references and samples and
2. ratios of laboratory mean values for 21 combinations (see Table 10) of test references and test samples – again for all five parameters.

It has to be noted that for the optional test reference mixture SA PG I, only values for the individual combustion time $t_{O,1}$ [s] are available. This pays respect to the fact that strong oxidizer or related reference mixtures of PG I already show unambiguous and such vigorous burning behaviour that no additional technical efforts are indicated for the determination of strong oxidizing potentials according to experiences and major understanding of all safety experts involved. In the major understanding of the ad-hoc working group, the challenge of test method UN O.1 is basically to decide on 'NOT 5.1' or, if any substance meets classification criterion for an oxidizing solid of Division 5.1, to distinguish between weak and medium oxidizing properties of substance in a doubtless manner.

For the optional test reference mixture SA PG I and the optional samples SB 21 and SC 21, 4 out of 12 laboratories did not submit any data. This applies to laboratories 01, 06, 10 and 11.

Table 10: Test reference and sample combinations considered for measurand “ratio of laboratory mean values”

Symbol	Description
SA PG II/ SA PG I	Ratio of mean values for SA PG II and SA PG I
SA PG III/ SA PG I	Ratio of mean values for SA PG III and SA PG I
SA PG III/ SA PG II	Ratio of mean values for SA PG III and SA PG II
SB 11/ SA PG I	Ratio of mean values for SB 11 and SA PG I
SB 11/ SA PG II	Ratio of mean values for SB 11 and SA PG II
SB 11/ SA PG III	Ratio of mean values for SB 11 and SA PG III
SB 21/ SA PG I	Ratio of mean values for SB 21 and SA PG I
SB 21/ SA PG II	Ratio of mean values for SB 21 and SA PG II
SB 21/ SA PG III	Ratio of mean values for SB 21 and SA PG III
SB 41/ SA PG I	Ratio of mean values for SB 41 and SA PG I
SB 41/ SA PG II	Ratio of mean values for SB 41 and SA PG II
SB 41/ SA PG III	Ratio of mean values for SB 41 and SA PG III
SC 11/ SA PG I	Ratio of mean values for SC 11 and SA PG I
SC 11/ SA PG II	Ratio of mean values for SC 11 and SA PG II
SC 11/ SA PG III	Ratio of mean values for SC 11 and SA PG III
SC 21/ SA PG I	Ratio of mean values for SC 21 and SA PG I
SC 21/ SA PG II	Ratio of mean values for SC 21 and SA PG II
SC 21/ SA PG III	Ratio of mean values for SC 21 and SA PG III
SC 41/ SA PG I	Ratio of mean values for SC 41 and SA PG I
SC 41/ SA PG II	Ratio of mean values for SC 41 and SA PG II
SC 41/ SA PG III	Ratio of mean values for SC 41 and SA PG III

For the single values, the statistical method ISO 5725-2 (see [7]) is applied. This method requires replicates and is based on normal distribution, hence outlier tests are included. Within the outlier tests it is looking for differing single and mean values as well as for single values with excessive variance within laboratories. Here, significantly deviating values at a level of 5 % will be denoted as “stragglers”, and significantly deviating values at a level of 1 % will be denoted as “outliers”. Only “outliers” will be excluded from the data set for the further statistical analysis. The results of the outlier tests are summarized in the Appendix, separately for each parameter.

For the ratios of the mean values, the statistical method DIN 38402 A 45 (=ISO/DIS 20612, see [8]) is applied. This method does not require replicates and since it is a robust method, no outlier examination is required either.

Both statistical methods provide the total mean value and the reproducibility standard deviation. The reproducibility standard deviation characterizes the variability of the measurands (single values or ratios of mean values) between different laboratories. For the single values also the repeatability

standard deviation is obtained, whereas for the ratios no repeatability standard deviation is available since there are no replicates. The repeatability standard deviation describes the variability within a laboratory and under constant conditions.

In the following five sections, for each of the five classification parameters at first a summary of the obtained total mean value, relative repeatability and reproducibility standard deviation for all test reference mixtures, test samples and all ratios is given. The next subsection summarizes the results of the statistical analysis of the single values of reference mixtures and test samples including a table with the laboratory mean values and a figure which shows the laboratory mean values and standard deviations exemplarily for the test reference mixture of packing group II (SA PG II). For the remaining reference mixtures and samples please refer to the Appendix.

In these figures the laboratory values are displayed in form of a box. The larger the box the larger is the laboratory standard deviation. The boxes are coloured according to the temperature (T-Lab) just for simplified charting reasons, however, the original temperatures have been pooled into classes and should not be misread as any identified correlation of analysed standard deviation and ambient temperature conditions of participating laboratory. Boxes of outlier laboratories that have been excluded from the analysis are marked by diagonal lines. Within each box, the laboratory mean is marked by a horizontal line, while the single values are shown as little triangles. The total mean value with the 95 % confidence band is shown as a horizontal line with a green band. The tolerance limits are shown as red lines. These are derived from the limits ± 2 for the Z scores (see also section 5.1), laboratory mean values are accepted if they do not differ from the total mean value more than two times the reproducibility standard deviation. The absolute values of the repeatability standard deviation (Sr) and the reproducibility standard deviation (SR) are shown as grey bars.

Finally, in the last subsection a summary of the results of the statistical analysis of the ratios is given. Again, this includes a table with the laboratory mean values and a figure which shows the ratios of the laboratory mean values exemplarily for the ratio of test reference mixtures of packing group III and packing group II (SA PG III / SA PG II). For the figures of the remaining ratios refer to the Appendix. In this figure the ratio of each laboratory are shown as bars. The total mean is displayed as a horizontal line over the whole range. Laboratory bars pointing down stand for laboratory mean values smaller than the total mean, while bars pointing up stand for laboratory mean values larger than the total mean. Furthermore, the absolute reproducibility standard deviation (SR) is shown as a grey bar and the tolerance limits are displayed as red lines.

If the relative reproducibility standard deviation is not greater than 30 %, the applied test method can be generally regarded as validated in terms of the related classification criterion.

4.2 Individual combustion time $t_{0.1}$ by visual assessment of main combustion of conical pile

4.2.1 Summary

From Table 11 it can be seen that for the single values the relative repeatability standard deviation is almost constant (8 % - 13 %). The highest relative reproducibility standard deviation is obtained for the test sample SC 41 (27.83 %), while the lowest value is obtained for the optional test sample SC 21 (9.99 %). However, the latter is based on the single values of five laboratories only and should therefore be interpreted with caution. The relative reproducibility standard deviations for the remaining test reference mixtures and samples lie within 13 % and 22 %.

The relative reproducibility standard deviations of the ratios of the laboratory mean values of the individual combustion time $t_{0.1}$ lie within 7.47 % for the optional test sample SC 21 / SA PG III and 33.66 % for the test sample SC 41 / SA PG I.

Table 11: Mean values and relative standard deviations for single values and ratios for individual combustion time $t_{0.1}$

	Sample / Ratio	Number of laboratories after outlier elimination	Mean	Relative reproducibility s.d.	Relative repeatability s.d.
Single values	SA PG I	8	9.75 s	17.83 %	10.61 %
	SA PG II	11	51.07 s	16.65 %	9.03 %
	SA PG III	12	119.63 s	15.51 %	10.02 %
	SB 11	12	55.73 s	17.27 %	11.65 %
	SB 21	7	33.31 s	13.24 %	12.30 %
	SB 41	12	30.36 s	14.57 %	8.60 %
	SC 11	12	36.39 s	21.68 %	13.13 %
	SC 21	5	19.07 s	9.99 %	7.95 %
	SC 41	12	26.58 s	27.83 %	11.72 %
Ratios of mean values	SA PG II / SA PG I	8	5.49	26.12 %	
	SA PG III / SA PG I	8	13.08	33.18 %	
	SA PG III / SA PG II	12	2.28	18.95 %	
	SB 11 / SA PG I	8	5.48	22.58 %	
	SB 11 / SA PG II	12	1.07	20.35 %	
	SB 11 / SA PG III	12	0.46	16.75 %	
	SB 21 / SA PG I	7	3.48	7.72 %	
	SB 21 / SA PG II	7	0.64	31.68 %	
	SB 21 / SA PG III	7	0.27	23.37 %	
	SB 41 / SA PG I	8	3.17	9.02 %	
	SB 41 / SA PG II	12	0.59	26.34 %	
	SB 41 / SA PG III	12	0.26	21.70 %	
	SC 11 / SA PG I	8	3.59	14.13 %	
	SC 11 / SA PG II	12	0.70	26.34 %	
	SC 11 / SA PG III	12	0.30	21.39 %	
	SC 21 / SA PG I	8	2.02	14.15 %	
	SC 21 / SA PG II	8	0.39	24.46 %	
	SC 21 / SA PG III	8	0.18	7.47 %	
	SC 41 / SA PG I	8	2.65	33.66 %	
SC 41 / SA PG II	12	0.51	28.98 %		
SC 41 / SA PG III	12	0.23	30.45 %		

Being ahead of Chapter 8, the following

Table 12 compares the individual combustion time $t_{0.1}$ for both round robin tests as performed in 2005/2006 and 2009. The results clearly point out that:

1. in consideration of test samples SB 11 and SB 41 (oxidizer: sodium perborate monohydrate in its 1:1 or 4:1 ratio), comparability of data sets and test conditions in terms of mean combustion times and relative repeatability of the 2nd and 3rd round robin test is given,
2. significant improvement of relative reproducibility of the test method by substitution of KBrO_3 by CaO_2 is proofed, at least for strong and medium oxidizing potentials and
3. both reference oxidizers or better related adjusted packing group mixtures of potassium bromate or calcium peroxide respectively represent similar oxidizing potentials expressed by individually determined mean combustion time $t_{0.1}$ of conical piles as tested and determined in previous works by the ad-hoc working group.

Table 12: Comparison of the results of individual combustion time (single values) of the UN O.1 round robin test in 2005/2006 (2nd) and in 2009 (3rd)

Test sample	Round Robin Test	Oxidizer	Number of labs after outlier elimination	Mean [s]	Relative reproducibility s.d. [%]	Relative repeatability s.d. [%]
SA PG I	2 nd	KBrO_3	10	12.82	55.18	12.02
	3 rd	CaO_2	8	9.75	17.83	10.61
SA PG II	2 nd	KBrO_3	10	44.60	28.54	10.00
	3 rd	CaO_2	11	51.07	16.65	9.03
SA PG III	2 nd	KBrO_3	10	120.50	16.38	7.76
	3 rd	CaO_2	12	119.63	15.51	10.02
SB 11	2 nd	KBrO_3	10	58.46	21.58	12.66
	3 rd	CaO_2	12	55.73	17.27	11.65
SB 41	2 nd	KBrO_3	10	35.60	20.61	10.80
	3 rd	CaO_2	12	30.36	14.57	8.60

4.2.2 Analysis of single values

For the single values regarding the individual combustion time $t_{0,1}$, the laboratory mean values as well as the total mean values, the relative reproducibility standard deviation and the relative repeatability standard deviation over all laboratories are given in Table 13. Outlier laboratories are marked in red, and “straggler” laboratories, which were not excluded from data set for statistical analyses, are marked in yellow.

Table 13: Analysis of single values of individual combustion time $t_{0,1}$ [s]
(red: outlier laboratories (not used in the statistical analysis); yellow: “straggler” laboratories (used in the statistical analysis))

Laboratory	SA PG I	SA PG II	SA PG III	SB 11	SB 21	SB 41	SC 11	SC 21	SC 41
01		60.60	116.60	56.75		33.20	36.00		24.25
02	9.00	52.00	128.67	43.60	31.00	26.60	30.40	17.60	26.20
03	9.67	49.33	125.40	60.00	36.67	33.00	40.67	18.00	23.40
04	10.05	66.20	141.75	67.96	36.17	34.75	44.20	19.40	35.00
05	8.00	52.17	133.50	48.67		24.33	28.40	18.40	12.60
06		52.76	113.23	62.84		33.08	33.36		25.75
08	13.33 ^M	78.60 ^V	119.40	49.20	32.60	27.43	32.20	25.00 ^V	30.80
09	9.00	43.50	147.60 ^V	48.67	31.00	30.33	33.80	30.25 ^V	20.00
10		53.60	113.60	55.57		27.00	48.00		25.00
11		44.80	101.50	66.67		36.33	47.60		36.40
13	10.00	39.60	100.40	50.60	33.20	30.00	33.00	21.20 ^V	24.40
14	9.33	48.80	104.20	54.33	32.20 ^V	29.40	31.20	19.80	35.60
Mean	9.75	51.07	119.63	55.73	33.31	30.36	36.39	19.07	26.58
Rel. reproducibility s.d.	17.83 %	16.65 %	15.51 %	17.27 %	13.24 %	14.57 %	21.68 %	9.99%	27.83 %
Rel. repeatability s.d.	10.61 %	9.03 %	10.02 %	11.65 %	12.30 %	8.60 %	13.13 %	7.95 %	11.72 %

M: outlier/straggler due to differing mean value;

V: outlier/straggler due to excessive variance

In Figure 7, laboratory mean values and standard deviations are shown exemplarily for packing group II (SA PG II). For the remaining test reference mixtures and samples refer to the Appendix 10.3.2.

For packing group I (SA PG I) only the mean value of laboratory 08, which had been identified as straggler but not as outlier, lies outside of the tolerance limits. For packing group II (SA PG II) this again applies to laboratory 08 which had been identified as an outlier laboratory. For the test sample SC 21 the mean values of laboratories 08 and 09 lie outside the tolerance limits. Both laboratories have been identified as outliers. For the remaining test reference mixtures and test samples, none of

the laboratory mean values lie outside the tolerance limits. However, some of the single values lie outside the tolerance limits; e.g. for laboratory 09 for SA PG III two of the five combustion times, where an excessive variance of the single values to the significance level of 5% (= straggler) can be observed. However, these single values of laboratory 09 will be used in the analysis.



Figure 7: Laboratory results for individual combustion time $t_{0.1}$ – SA PG II

4.2.3 Analysis of ratios

The following Table 14 shows the ratios of the laboratory mean values of the individual combustion time $t_{0.1}$ for each laboratory as well as the total mean values and the relative reproducibility standard deviation over all laboratories.

Table 14: Ratios of mean laboratory values, total mean value and relative reproducibility standard deviation of individual combustion time $t_{0.1}$

Laboratory	SA PG II / SA PG I	SA PG III / SA PG I	SA PG III / SA PG II	SB 11 / SA PG I	SB 11 / SA PG II	SB 11 / SA PG III	SB 21 / SA PG I	SB 21 / SA PG II	SB 21 / SA PG III	SB 41 / SA PG I	SB 41 / SA PG II	SB 41 / SA PG III	SC 11 / SA PG I	SC 11 / SA PG II	SC 11 / SA PG III	SC 21 / SA PG I	SC 21 / SA PG II	SC 21 / SA PG III	SC 41 / SA PG I	SC 41 / SA PG II	SC 41 / SA PG III
01			1.92		0.94	0.49					0.55	0.29		0.59	0.31					0.40	0.21
02	5.78	14.30	2.47	4.84	0.84	0.34	3.44	0.60	0.24	2.96	0.51	0.21	3.38	0.59	0.24	1.96	0.34	0.14	2.91	0.50	0.20
03	5.10	12.97	2.54	6.21	1.22	0.48	3.79	0.74	0.29	3.41	0.67	0.26	4.21	0.82	0.32	1.86	0.37	0.14	2.42	0.47	0.19
04	6.59	14.10	2.14	6.76	1.03	0.48	3.60	0.55	0.26	3.46	0.53	0.25	4.40	0.67	0.31	1.93	0.29	0.14	3.48	0.53	0.25
05	6.52	16.69	2.56	6.08	0.93	0.37				3.04	0.47	0.18	3.55	0.54	0.21	2.30	0.35	0.14	1.58	0.24	0.09
06			2.15		1.19	0.56					0.63	0.29		0.63	0.30					0.49	0.23
08	5.90	8.96	1.52	3.69	0.63	0.41	2.45	0.42	0.27	2.06	0.35	0.23	2.42	0.41	0.27	1.88	0.32	0.21	2.31	0.39	0.26
09	4.83	16.40	3.39	5.41	1.12	0.33	3.44	0.71	0.21	3.37	0.70	0.21	3.76	0.78	0.23	3.36	0.70	0.21	2.22	0.46	0.14
10			2.12		1.04	0.49					0.50	0.24		0.90	0.42					0.47	0.22
11			2.27		1.49	0.66					0.81	0.36		1.06	0.47					0.81	0.36
13	3.96	10.04	2.54	5.06	1.28	0.50	3.32	0.84	0.33	3.00	0.76	0.30	3.30	0.83	0.33	2.12	0.54	0.21	2.44	0.62	0.24
14	5.23	11.17	2.14	5.82	1.11	0.52	3.45	0.66	0.31	3.15	0.60	0.28	3.34	0.64	0.30	2.12	0.41	0.19	3.81	0.73	0.34
Mean	5.49	13.08	2.28	5.48	1.07	0.46	3.48	0.64	0.27	3.17	0.59	0.26	3.59	0.70	0.30	2.02	0.39	0.18	2.65	0.51	0.23
Rel. reproducibility s.d. [%]	26.12	33.18	18.95	22.58	20.35	16.75	7.72	31.68	23.37	9.02	26.34	21.70	14.13	26.34	21.39	14.15	24.46	7.47	33.66	28.98	30.45

In Figure 8, the ratios of the laboratory mean values of the individual combustion time $t_{0.1}$ are shown exemplarily for the ratio of packing group III and packing group II (SA PG III / SA PG II). For the remaining ratios refer to the Appendix 10.3.3.

For the ratio SA PG III / SA PG II only the ratio of the mean values of laboratory 09 lies outside of the tolerance limits. For 11 of all 21 possible ratios, the ratio of the mean values of one laboratory in each case lies outside the tolerance limits and for one ratio (SC 21 / SA PG III) the values of 5 laboratories are not within the tolerance limits.

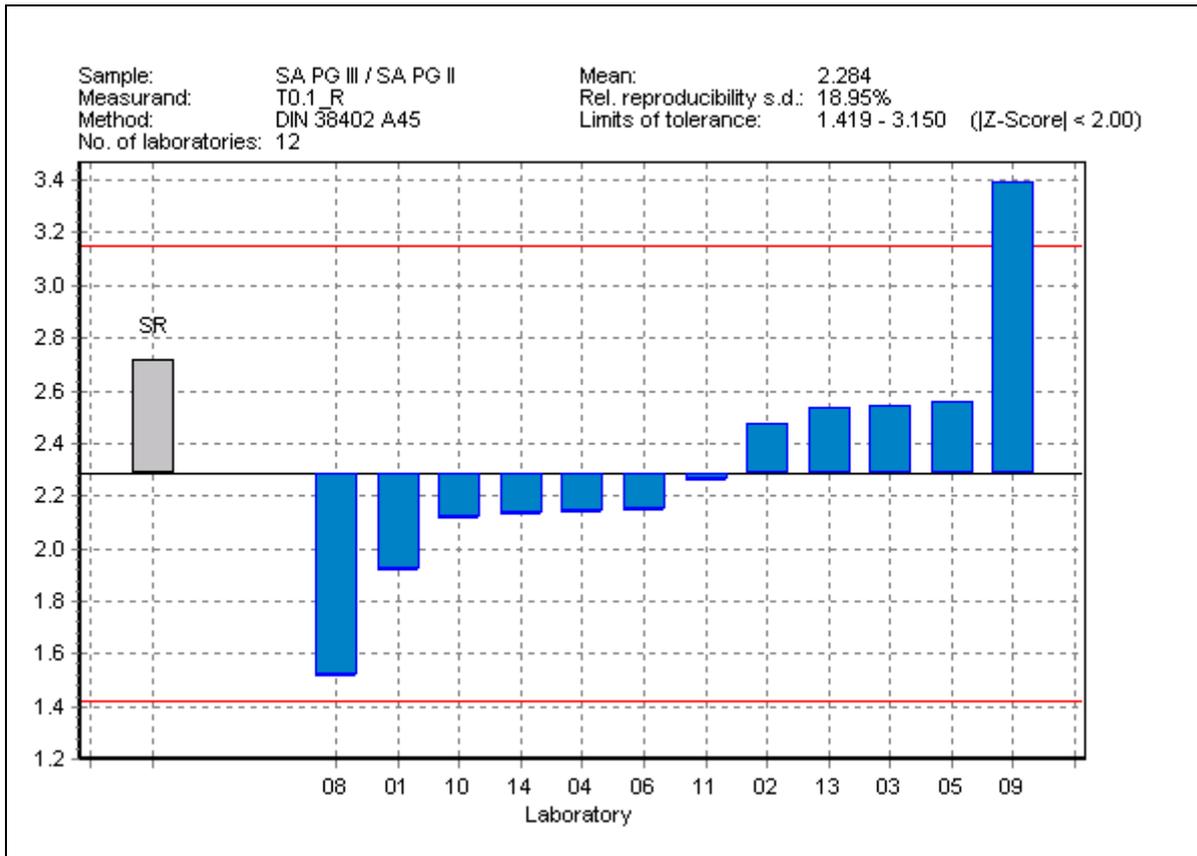


Figure 8: Laboratory results for individual combustion time $t_{0.1}$ – SA PG III / SA PG II

4.3 Main combustion time t_{20-80} as derived from 20% to 80% of monitored total mass loss

4.3.1 Summary

For the single values of all test samples the relative repeatability standard deviation lies between 11 % and 21 %. The lowest relative reproducibility standard deviation (17.47 %) is obtained for the optional test sample SB 21, while the highest value (36.21%) is obtained for test sample SC 41. The relative reproducibility standard deviations for the remaining test reference mixtures and samples do not vary noticeably and lie between 17 % and 23 %. These values are comparable to the individual combustion time $t_{0.1}$ criterion and the current test performance of UN O.1, respectively. This is at least remarkable because the majority of participating laboratories perform the modified test method or introduced gravimetric approach for the first time, which partly requires differing handling sequences and chronology. Therefore no experienced background of lab assistance has to be assumed to some respect.

For the ratios, the highest relative reproducibility standard deviations can be observed for SC 21 / SA PG II (44.93 %), whereas the values for the remaining ratios lie within 16 % and 37 %. The ratio SA PG III / SA PG II exhibits the smallest relative reproducibility standard deviation of 16.24 %.

Table 15: Mean values and relative standard deviations for single values and ratios for main combustion time t_{20-80}

	Sample / Ratio	Number of laboratories after outlier elimination	Mean	Relative reproducibility s.d.	Relative repeatability s.d.
Single values	SA PG II	12	16.46 s	21.18 %	14.75 %
	SA PG III	11	46.26 s	20.06 %	12.59 %
	SB 11	12	23.22 s	18.14 %	12.69 %
	SB 21	7	10.13 s	17.47 %	10.95 %
	SB 41	11	9.61 s	17.87 %	13.22 %
	SC 11	10	9.69 s	22.66 %	17.00 %
	SC 21	7	6.09 s	18.15 %	13.03 %
	SC 41	11	10.00 s	36.21 %	20.76 %
Ratios of mean values	SA PG III / SA PG II	12	2.68	16.24 %	
	SB 11 / SA PG II	12	1.44	21.29 %	
	SB 11 / SA PG III	12	0.51	20.06 %	
	SB 21 / SA PG II	7	0.68	36.09 %	
	SB 21 / SA PG III	7	0.22	23.60 %	
	SB 41 / SA PG II	12	0.60	28.46 %	
	SB 41 / SA PG III	12	0.21	24.41 %	
	SC 11 / SA PG II	12	0.64	30.74 %	
	SC 11 / SA PG III	12	0.23	28.06 %	
	SC 21 / SA PG II	8	0.42	44.93 %	
	SC 21 / SA PG III	8	0.14	36.52 %	
	SC 41 / SA PG II	12	0.64	37.22 %	
SC 41 / SA PG III	12	0.23	35.87 %		

4.3.2 Analysis of single values

For the single values, the mean value of the main combustion time t_{20-80} of each laboratory as well as the total mean value, the relative reproducibility standard deviation and the relative repeatability standard deviation over all laboratories are given in Table 16. Outlier laboratories are marked in red, and “straggler” laboratories, which were not excluded from data set for statistical analyses, are marked in yellow.

Table 16: Analysis of single values of main combustion time t_{20-80} [s]
(red: outlier laboratories (not used in the statistical analysis); yellow: “straggler” laboratories (used in the statistical analysis))

Laboratory	SA PG II	SA PG III	SB 11	SB 21	SB 41	SC 11	SC 21	SC 41
01	19.20	44.56	22.75		8.08	9.20		8.85
02	19.40	53.53	19.32	9.34	8.04	11.00	4.92	10.36
03	17.33	50.60	25.83	11.67	8.80	11.33	6.20	7.60
04	16.60	46.25	26.80	8.04	12.00	12.00 ^V	9.60 ^V	21.00 ^V
05	19.67	43.50 ^V	20.50		9.67	7.60	6.40	7.00
06	18.28	43.27	29.28		9.80	11.20		8.40
08	16.00	43.60	20.60	11.20	8.57	8.20	7.29	13.20
09	13.83	65.00 ^M	22.20	11.56	11.17	9.36	6.05	7.33
10	17.56	44.20	24.86		9.20	13.50 ^V		10.00
11	13.60	40.17	25.33		11.17	12.20		11.40
13	10.76	39.40	18.72	10.68	9.72	8.80	6.12	7.64
14	15.00	38.66	21.27	8.82	8.92	7.90	5.14	17.22 ^M
Mean	16.46	46.26	23.22	10.13	9.61	9.69	6.09	10.00
Rel. reproducibility s.d.	21.18 %	20.06 %	18.14 %	17.47 %	17.87 %	22.66 %	18.15 %	36.21 %
Rel. repeatability s.d.	14.75 %	12.59 %	12.69 %	10.95 %	13.22 %	17.00 %	13.03 %	20.76 %

M: outlier/straggler due to differing mean value;

V: outlier/straggler due to excessive variance

In Figure 9, laboratory mean values and standard deviations are shown exemplarily for packing group III (SA PG III). For the remaining test reference mixtures and samples please refer to the Appendix 10.4.2.

For packing group III (SA PG III) only the mean value of laboratory 09, which has been identified as straggling value, lies marginally outside the tolerance limit. The mean value of laboratory 04 lies outside the tolerance limit for the test samples SC 21 and SC 41. This laboratory values have been identified as outlier values for both test samples due to excessive variance.

In many cases at least one of the single values lies outside the tolerance limits.



Figure 9: Laboratory results for main combustion time t_{20-80} – SA PG III

4.3.3 Analysis of ratios

The following Table 17 summarizes the ratios of the laboratory mean values of the main combustion time t_{20-80} as well as the total mean values and the relative reproducibility standard deviation over all laboratories.

Table 17: Ratios of mean laboratory values, total mean value and relative reproducibility standard deviation of main combustion time t_{20-80}

Laboratory	SA PG III / SA PG II	SB 11 / SA PG II	SB 11 / SA PG III	SB 21 / SA PG II	SB 21 / SA PG III	SB 41 / SA PG II	SB 41 / SA PG III	SC 11 / SA PG II	SC 11 / SA PG III	SC 21 / SA PG II	SC 21 / SA PG III	SC 41 / SA PG II	SC 41 / SA PG III
01	2.32	1.19	0.51			0.42	0.18	0.48	0.21			0.46	0.20
02	2.76	1.00	0.36	0.48	0.18	0.41	0.15	0.57	0.21	0.25	0.09	0.53	0.19
03	2.92	1.49	0.51	0.67	0.23	0.51	0.17	0.65	0.22	0.36	0.12	0.44	0.15
04	2.79	1.61	0.58	0.48	0.17	0.72	0.25	0.72	0.26	0.58	0.21	1.27	0.45
05	2.21	1.04	0.47			0.49	0.22	0.39	0.18	0.33	0.15	0.36	0.16
06	2.37	1.60	0.68			0.54	0.23	0.61	0.26			0.46	0.19
08	2.73	1.29	0.47	0.70	0.26	0.54	0.20	0.51	0.19	0.46	0.17	0.83	0.30
09	4.70	1.61	0.34	0.84	0.18	0.81	0.17	0.68	0.14	0.44	0.09	0.53	0.11
10	2.52	1.42	0.56			0.52	0.21	0.77	0.31			0.57	0.23
11	2.95	1.86	0.63			0.82	0.28	0.90	0.30			0.84	0.28
13	3.66	1.74	0.48	0.99	0.27	0.90	0.25	0.82	0.22	0.56	0.16	0.71	0.19
14	2.58	1.42	0.55	0.59	0.23	0.60	0.23	0.53	0.20	0.34	0.13	1.15	0.45
Mean	2.68	1.44	0.51	0.68	0.22	0.60	0.21	0.64	0.23	0.42	0.14	0.64	0.23
Relative reproducibility s.d. [%]	16.24	21.29	20.06	36.09	23.60	28.46	24.41	30.74	28.06	44.93	36.52	37.22	35.87

In Figure 10, for each laboratory the ratio of the mean values of the main combustion time t_{20-80} is shown exemplarily for the ratio of packing group III and packing group II (SA PG III / SA PG II). For the remaining ratios please refer to the Appendix 10.4.3.

For SA PG III / SA PG II, the ratios of laboratories 09 and 13 lie above the tolerance limits. For the two combinations of SC 41 with packing groups II and III (SA PG II and SA PG III), the ratios of laboratories 04 and 14 exceed the upper limit.

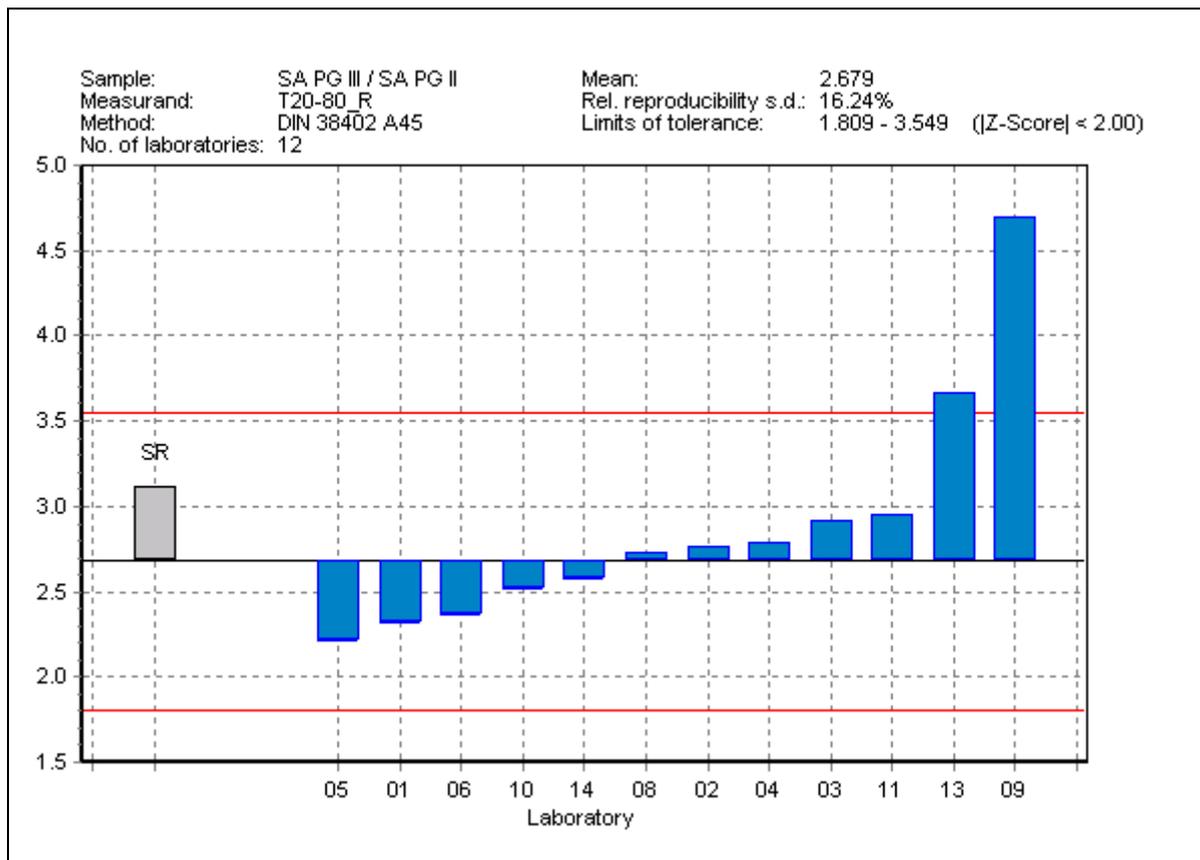


Figure 10: Laboratory results for main combustion time t_{20-80} – SA PG III / SA PG II

4.4 Mass loss rate within 20 % and 80 % of total mass loss – MLR₂₀₋₈₀

4.4.1 Summary

From Table 18 it can be seen that for the single values the relative repeatability standard deviations lie between 9 % and 22 % and the relative reproducibility standard deviations between 12 % and 40 %. The lowest values for both standard deviations can be observed for the optional test sample SB 21, although only 6 laboratories has provided related data sets, while the highest values are obtained by test sample SC 41 again. For the remaining test reference mixtures and test samples the relative reproducibility standard deviation lies between 15 % and 27 %.

For the ratios, the highest relative reproducibility standard deviations of about 50 % can be observed for SC 41 / SA PG II and SC 41 / SA PG III, whereas the values for the remaining ratios lie between 19 % and 44 %. This may partly pay respect to the particular physical and chemical properties of sodium nitrate as explained on page 16.

Table 18: Mean values and relative standard deviations for single values and ratios for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀

	Sample / Ratio	Number of laboratories after outlier elimination	Mean	Relative reproducibility s.d.	Relative repeatability s.d.
Single values	SA PG II	12	0.84 g/s	27.02 %	15.59 %
	SA PG III	12	0.24 g/s	20.66 %	14.71 %
	SB 11	12	0.46 g/s	15.57 %	11.60 %
	SB 21	6	0.87 g/s	12.10 %	9.27 %
	SB 41	11	0.89 g/s	15.06 %	9.53 %
	SC 11	11	1.43 g/s	21.79 %	17.20 %
	SC 21	8	1.67 g/s	22.28 %	17.17 %
	SC 41	12	0.68 g/s	39.79 %	21.61 %
Ratios of mean values	SA PG III / SA PG II	12	0.29	20.05 %	
	SB 11 / SA PG II	12	0.56	19.09 %	
	SB 11 / SA PG III	12	2.01	22.00 %	
	SB 21 / SA PG II	7	1.14	43.88 %	
	SB 21 / SA PG III	7	4.06	32.31 %	
	SB 41 / SA PG II	12	1.10	36.88 %	
	SB 41 / SA PG III	12	3.79	26.30 %	
	SC 11 / SA PG II	12	1.76	25.54 %	
	SC 11 / SA PG III	12	6.32	29.10 %	
	SC 21 / SA PG II	8	2.10	39.79 %	
	SC 21 / SA PG III	8	7.83	26.90 %	
	SC 41 / SA PG II	12	0.83	51.23 %	
SC 41 / SA PG III	12	2.97	52.60 %		

4.4.2 Analysis of single values

The mean values of the mass loss rate within 20 % and 80 % of total mass loss MLR_{20-80} of each laboratory as well as the total mean values, the relative reproducibility standard deviation and the relative repeatability standard deviation over all laboratories are given in Table 19. Outlier laboratories are marked in red, and “straggler” laboratories, which were not excluded from data set for statistical analyses, are marked in yellow.

Table 19: Analysis of single values of mass loss rate within 20 % and 80 % of total mass loss MLR_{20-80} [g/s] (red: outlier laboratories (not used in the statistical analysis); yellow: “straggler” laboratories (used in the statistical analysis))

Laboratory	SA PG II	SA PG III	SB 11	SB 21	SB 41	SC 11	SC 21	SC 41
01	0.73	0.27	0.49		1.05	1.51		0.79
02	0.67	0.20	0.50	0.93	0.99	1.24	2.07	0.57
03	0.67	0.19	0.38	0.78	0.88	1.15	1.52	0.80
04	0.91	0.23	0.46	2.01 ^V	0.63	1.97 ^V	1.39 ^V	0.28
05	0.57	0.18	0.50		0.99	1.75	1.69	0.98
06	0.77	0.25	0.36		0.74 ^V	1.34		0.79
08	0.90	0.24	0.48	0.77	0.94	1.66	1.33	0.45
09	0.98	0.20	0.51	0.89	0.86	1.51	1.94	1.08
10	0.76	0.25	0.43		0.90	1.06		0.65
11	1.02	0.30	0.49		0.81	1.27		0.58
13	1.28	0.28	0.54	0.87	0.85	1.55	1.77	0.86
14	0.87	0.25	0.45	0.95	0.86	1.61	1.82	0.31
Mean	0.84	0.24	0.46	0.87	0.89	1.43	1.67	0.68
Rel. reproducibility s.d.	27.02 %	20.66 %	15.57 %	12.10 %	15.06 %	21.79 %	22.28 %	39.79 %
Rel. repeatability s.d.	15.59 %	14.71 %	11.60 %	9.27 %	9.53 %	17.20 %	17.17 %	21.61 %

M: outlier/straggler due to differing mean value;
V: outlier/straggler due to excessive variance

In Figure 11, laboratory mean values and standard deviations are shown exemplarily for packing group II (SA PG II). For the remaining test reference mixtures and samples please refer to the Appendix 10.5.2.

Only for the optional test sample SB 21 the mean value of laboratory 04, which had been identified as an outlier laboratory, lies outside the tolerance limit. For the remaining test reference mixtures and test samples, none of the laboratory mean values lies outside the tolerance limits. However, in several cases at least one of the single values exceeds the tolerance limits.

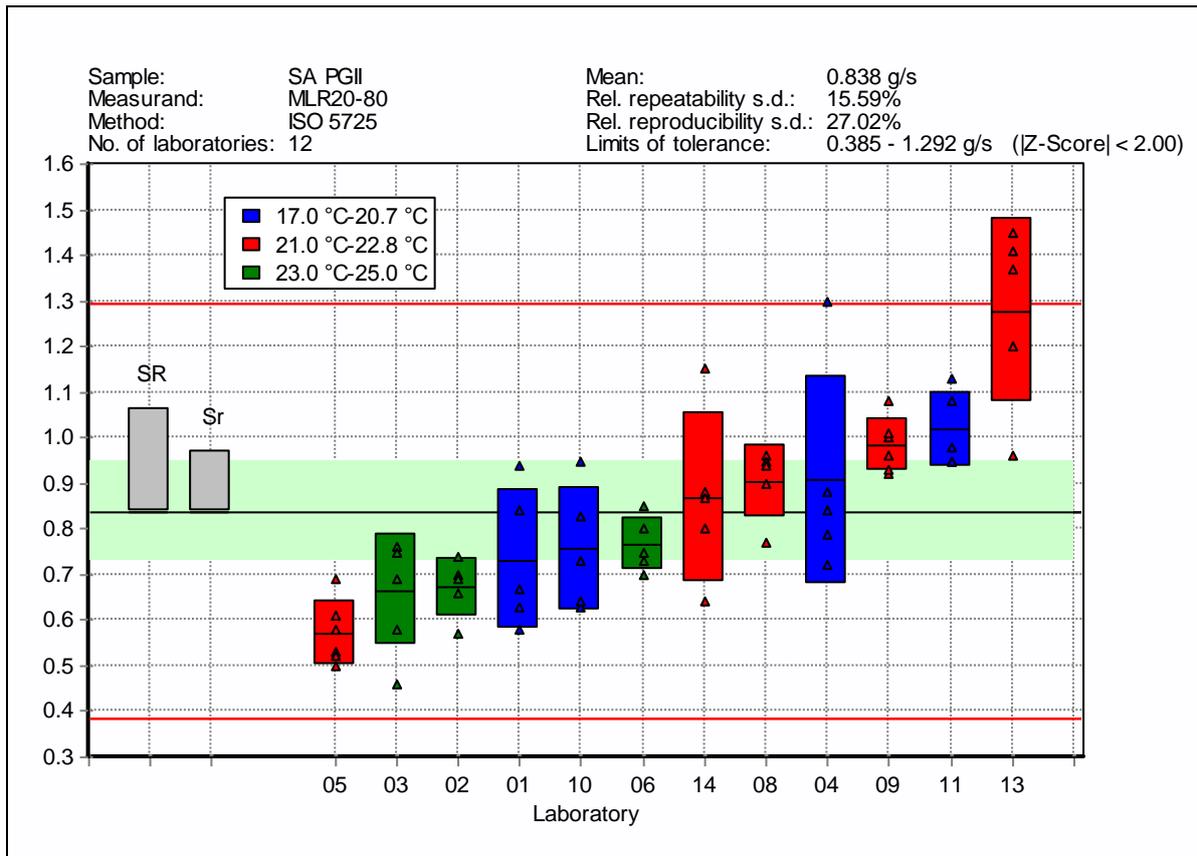


Figure 11: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SA PG II

4.4.3 Analysis of ratios

The ratios of the mean values of the mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ of each laboratory as well as the total mean value and the relative reproducibility standard deviation over all laboratories are given in the following Table 20.

Table 20: Ratios of mean laboratory values, total mean value and relative reproducibility standard deviation of mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀

Laboratory	SA PG III / SA PG II	SB 11 / SA PG II	SB 11 / SA PG III	SB 21 / SA PG II	SB 21 / SA PG III	SB 41 / SA PG II	SB 41 / SA PG III	SC 11 / SA PG II	SC 11 / SA PG III	SC 21 / SA PG II	SC 21 / SA PG III	SC 41 / SA PG II	SC 41 / SA PG III
01	0.37	0.67	1.80			1.43	3.82	2.06	5.50			1.08	2.88
02	0.29	0.74	2.54	1.39	4.74	1.48	5.04	1.85	6.32	3.08	10.51	0.84	2.87
03	0.29	0.58	2.00	1.18	4.08	1.32	4.58	1.73	5.99	2.29	7.92	1.20	4.17
04	0.25	0.51	2.04	2.22	8.94	0.70	2.80	2.18	8.76	1.53	6.18	0.31	1.23
05	0.32	0.87	2.75			1.74	5.46	3.05	9.59	2.95	9.26	1.72	5.41
06	0.32	0.47	1.46			0.96	2.99	1.74	5.41			1.03	3.18
08	0.26	0.53	2.03	0.85	3.26	1.04	4.00	1.83	7.02	1.47	5.64	0.49	1.89
09	0.21	0.52	2.53	0.91	4.43	0.88	4.27	1.54	7.48	1.98	9.61	1.10	5.35
10	0.33	0.57	1.70			1.19	3.58	1.40	4.19			0.87	2.60
11	0.29	0.48	1.63			0.79	2.71	1.24	4.25			0.57	1.94
13	0.22	0.43	1.94	0.68	3.10	0.66	3.02	1.21	5.53	1.38	6.31	0.67	3.07
14	0.29	0.51	1.75	1.09	3.73	0.99	3.37	1.86	6.34	2.10	7.18	0.36	1.22
Mean	0.29	0.56	2.01	1.14	4.06	1.10	3.79	1.76	6.32	2.10	7.83	0.83	2.97
Rel. reproducibility s.d. [%]	20.05	19.09	22.00	43.88	32.31	36.88	26.30	25.54	29.10	39.79	26.90	51.23	52.60

In Figure 12, the ratios of the laboratory mean values of the mass loss rate within 20 % and 80 % of total mass loss MLR_{20-80} are shown exemplarily for the ratio of packing group III and packing group II (SA PG III / SA PG II). For the remaining ratios refer to the Appendix 10.5.3.

For laboratory 05 an exceeding of the tolerance limits can be observed for three ratios: SB 11, SC 11 and SC 41 with SA PG II.

For SB 21 / SA PG II and SB21 / SA PG III, the ratio of laboratory 04 lies above the tolerance limits.

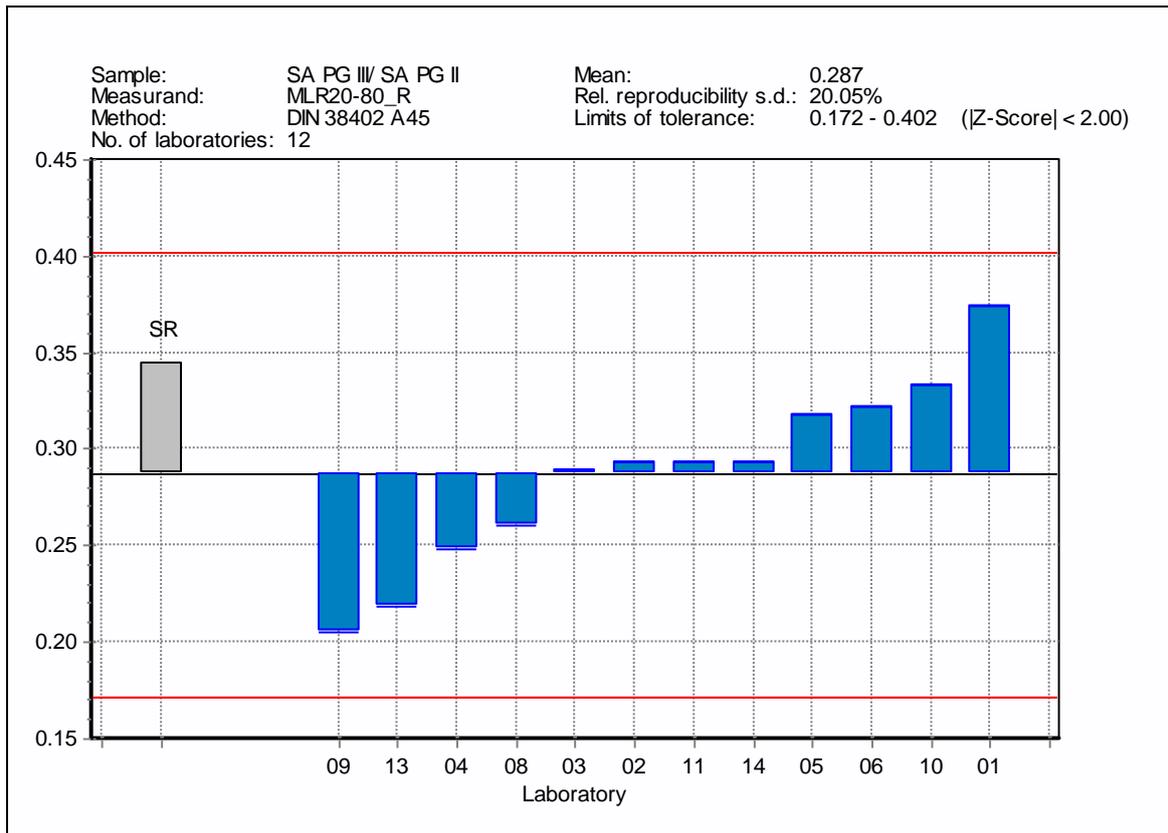


Figure 12: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR_{20-80} – SA PG III / SA PG II

4.5 Mass loss rate by linear regression within 20 % to 80 % of total mass loss

$$R^2 \text{MLR}_{20-80}$$

4.5.1 Summary

As can be seen in Table 21 for the single values the relative repeatability standard deviation lies between 8 % and 22 %. The relative reproducibility standard deviations range between 15 % and 42 %. Again, the highest values for both standard deviations are obtained for test sample SC 41.

For the ratios a broad distribution of the relative reproducibility standard deviation can be observed. For the ratio SC 41 / SA PG II the highest value (58.34 %) can be observed, whereas the lowest value equals 13.27 % for SA PG III / SA PG II.

Table 21: Mean values and relative standard deviations for single values and ratios for mass loss rate by linear regression within 20 % to 80 % of total mass loss $R^2 \text{MLR}_{20-80}$

	Sample / Ratio	Number of laboratories after outlier elimination	Mean	Relative reproducibility s.d.	Relative repeatability s.d.
Single values	SA PG II	12	0.86 g/s	27.29 %	15.81 %
	SA PG III	12	0.24 g/s	21.86 %	14.60 %
	SB 11	12	0.48 g/s	15.92 %	12.30 %
	SB 21	7	0.85 g/s	22.55 %	8.44 %
	SB 41	12	0.92 g/s	15.41 %	9.21 %
	SC 11	11	1.47 g/s	23.84 %	18.90 %
	SC 21	7	1.76 g/s	21.31 %	12.75 %
	SC 41	12	0.68 g/s	41.76 %	22.32 %
Ratios of mean values	SA PG III / SA PG II	12	0.28	13.27 %	
	SB 11 / SA PG II	12	0.57	21.05 %	
	SB 11 / SA PG III	12	2.06	25.79 %	
	SB 21 / SA PG II	7	0.96	45.72 %	
	SB 21 / SA PG III	7	3.75	38.39 %	
	SB 41 / SA PG II	12	1.11	35.63 %	
	SB 41 / SA PG III	12	3.84	21.95 %	
	SC 11 / SA PG II	12	1.75	22.48 %	
	SC 11 / SA PG III	12	6.26	24.59 %	
	SC 21 / SA PG II	8	2.19	26.59 %	
	SC 21 / SA PG III	8	8.46	25.17 %	
	SC 41 / SA PG II	12	0.83	58.34 %	
SC 41 / SA PG III	12	2.88	49.04 %		

4.5.2 Analysis of single values

Table 22 shows the mean values of the mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ of each laboratory as well as the total mean values, the relative reproducibility standard deviation and the relative repeatability standard deviation over all laboratories. Outlier laboratories are marked in red, and “straggler” laboratories, which were not excluded from data set for statistical analyses, are marked in yellow.

Table 22: Analysis of single values of mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ [g/s] (red: outlier laboratories (not used in the statistical analysis); yellow: “straggler” laboratories (used in the statistical analysis))

Laboratory	SA PG II	SA PG III	SB 11	SB 21	SB 41	SC 11	SC 21	SC 41
01	0.74	0.29	0.52		1.04	1.57		0.82
02	0.70	0.20	0.52	0.95	1.02	1.26	2.14	0.55
03	0.68	0.19	0.42	0.80	0.89	1.14	1.61	0.79
04	0.96	0.21	0.49	0.49	0.62 ^M	2.12 ^V	2.07 ^V	0.30
05	0.59	0.18	0.53		1.04	1.79	1.68	0.99
06	0.79	0.25	0.37		0.88	1.40		0.81
08	0.91	0.25	0.51	0.79	0.93	1.70	1.33	0.45
09	1.00	0.21	0.55	1.07	1.05	1.67	2.23	1.21
10	0.78	0.27	0.44		0.91	1.05		0.64
11	1.05	0.31	0.48		0.83	1.29		0.58
13	1.32	0.28	0.54	0.87	0.86	1.61	1.77	0.84
14	0.90	0.26	0.45	0.99	0.88	1.65	1.85	0.30
Mean	0.86	0.24	0.48	0.85	0.92	1.47	1.76	0.68
Rel. reproducibility s.d.	27.29 %	21.86 %	15.92 %	22.55 %	15.41 %	23.84 %	21.31 %	41.76 %
Rel. repeatability s.d.	15.81 %	14.60 %	12.30 %	8.44 %	9.21 %	18.90 %	12.75 %	22.32 %

M: outlier/straggler due to differing mean value;

V: outlier/straggler due to excessive variance

In Figure 13 laboratory mean values and standard deviations are shown exemplarily for packing group II (SA PG II). For the remaining test reference mixtures and samples please refer to the Appendix 10.6.2.

Only for the test sample SB 41 the mean value of laboratory 04 lies outside of the tolerance limits. This value has been identified as straggler but was not excluded from data set. For the remaining test reference mixtures and test samples, none of the laboratory mean values lies outside the tolerance limits. However, in several cases single values exceed the tolerance limits.

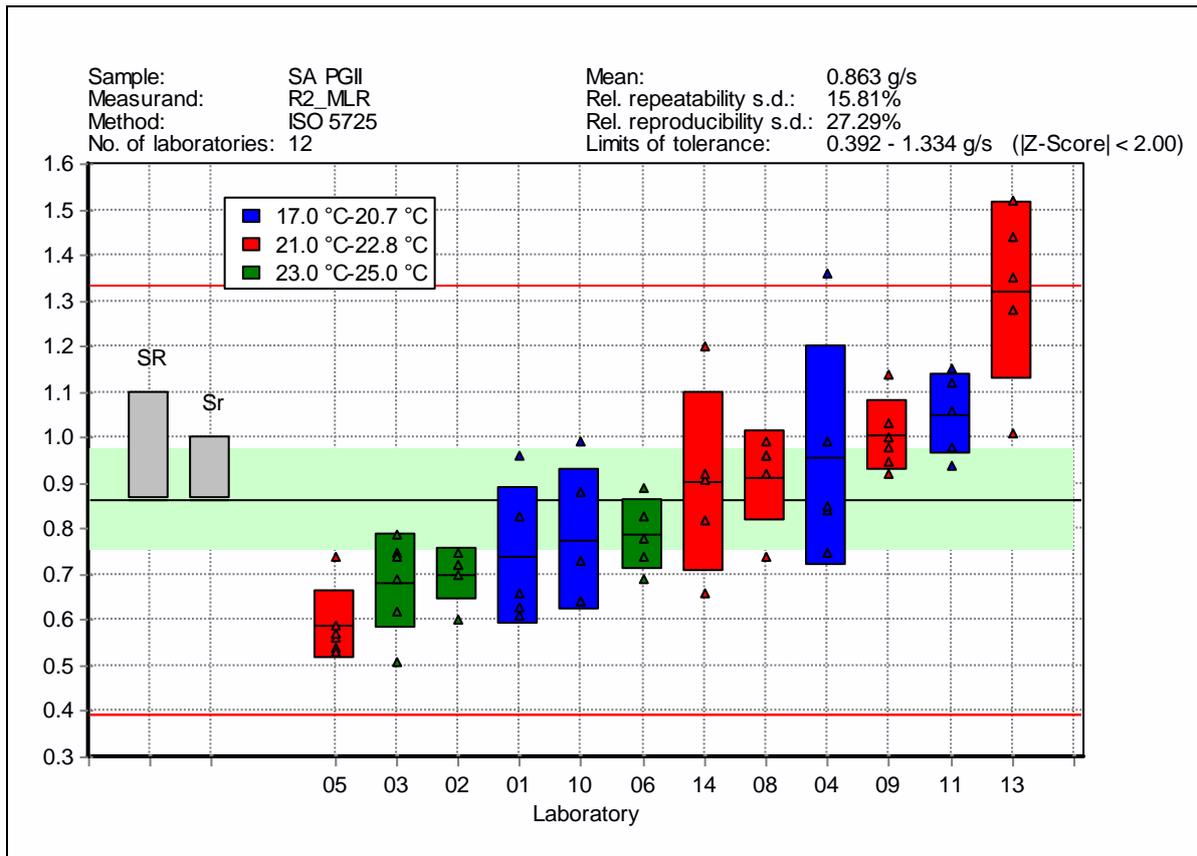


Figure 13: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss $R^2 MLR_{20-80}$ – SA PG II

4.5.3 Analysis of ratios

In the following Table 23, for each laboratory the ratio of the mean values of the mass loss rate by linear regression within 20 % to 80 % of total mass loss $R^2 MLR_{20-80}$ as well as the total mean values and the relative reproducibility standard deviation over all laboratories are given.

Table 23: Ratios of mean laboratory values, total mean value and relative reproducibility standard deviation of mean values of mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀

Laboratory	SA PG III / SA PG II	SB 11 / SA PG II	SB 11 / SA PG III	SB 21 / SA PG II	SB 21 / SA PG III	SB 41 / SA PG II	SB 41 / SA PG III	SC 11 / SA PG II	SC 11 / SA PG III	SC 21 / SA PG II	SC 21 / SA PG III	SC 41 / SA PG II	SC 41 / SA PG III
01	0.39	0.70	1.80			1.41	3.60	2.13	5.46			1.11	2.84
02	0.29	0.75	2.58	1.36	4.70	1.46	5.06	1.80	6.22	3.06	10.57	0.79	2.72
03	0.28	0.61	2.16	1.17	4.12	1.30	4.59	1.67	5.86	2.36	8.32	1.15	4.06
04	0.21	0.51	2.38	0.52	2.41	0.64	3.01	2.21	10.33	2.16	10.11	0.31	1.45
05	0.30	0.91	3.04			1.76	5.91	3.04	10.21	2.85	9.58	1.68	5.65
06	0.31	0.47	1.50			1.13	3.58	1.78	5.66			1.02	3.26
08	0.27	0.56	2.07	0.86	3.19	1.02	3.75	1.86	6.86	1.45	5.35	0.49	1.80
09	0.21	0.55	2.58	1.07	4.99	1.04	4.89	1.67	7.80	2.22	10.41	1.21	5.65
10	0.35	0.56	1.63			1.18	3.41	1.35	3.91			0.83	2.40
11	0.30	0.46	1.54			0.79	2.67	1.23	4.15			0.55	1.87
13	0.21	0.41	1.93	0.66	3.07	0.66	3.06	1.22	5.70	1.34	6.27	0.64	2.99
14	0.29	0.50	1.73	1.10	3.80	0.98	3.39	1.83	6.35	2.05	7.11	0.34	1.16
Mean	0.28	0.57	2.06	0.96	3.75	1.11	3.84	1.75	6.26	2.19	8.46	0.83	2.88
Rel. reproducibility s.d. [%]	13.27	21.05	25.79	45.72	38.39	35.63	21.95	22.48	24.59	26.59	25.17	58.34	49.04

In Figure 14, the ratios of the mean values of the mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2MLR_{20-80} are shown for each laboratory exemplarily for the ratio of packing group III and packing group II (SA PG III / SA PG II). For the remaining ratios please refer to the Appendix 10.6.3.

For the two packing groups (SA PG III / SA PG II) the ratio of laboratory 01 lies outside the tolerance limit. Laboratory 04 exhibits one ratio outside the limits: SC 11 / SA PG III. For laboratory 05, in total four ratios can be observed that do not lie within the tolerance limits, these applies to SB 11 and SC 11 for packing group II (SA PG II) and to SB 41 and SC 11 for packing group III (SA PG III).

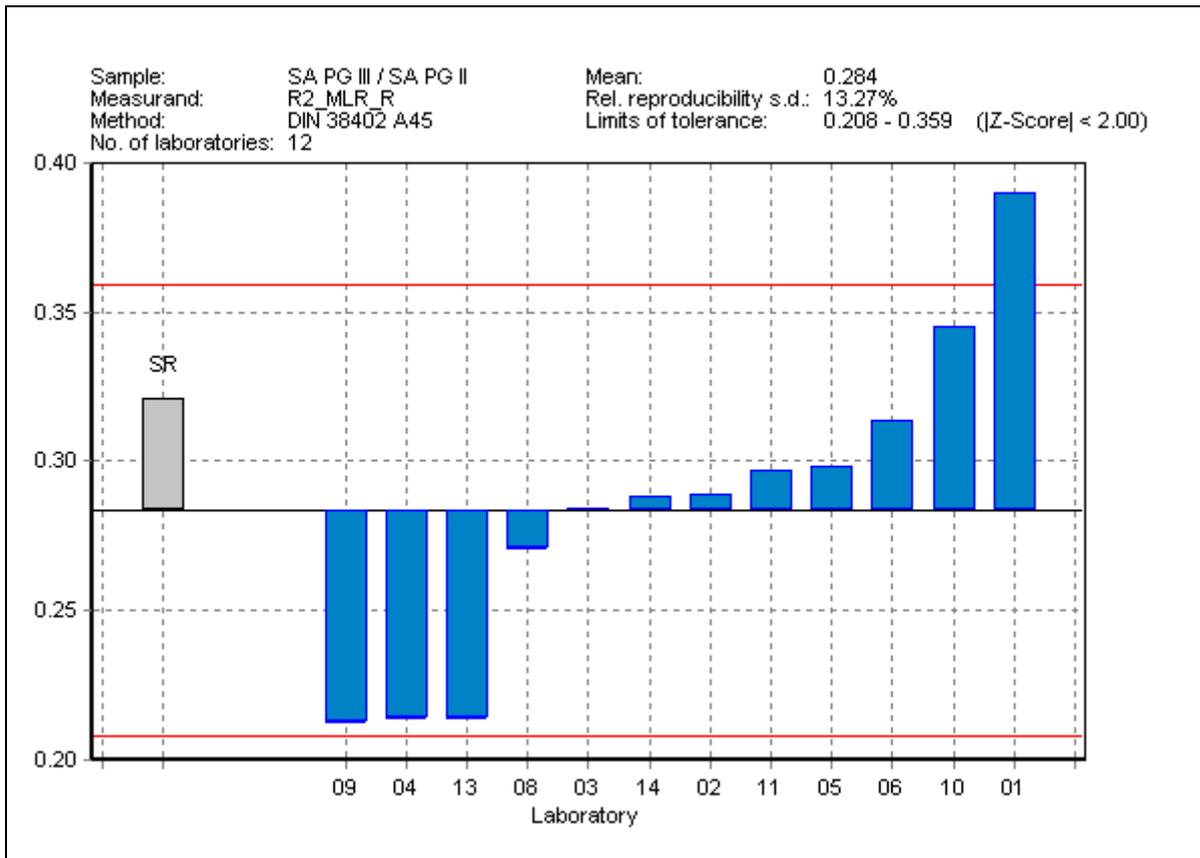


Figure 14: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2MLR_{20-80} – SA PG III / SA PG II

4.6 Consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ in mixture

4.6.1 Summary

From Table 24 it can be seen that for the single values the relative repeatability standard deviations lie between 10 % and 21 % and the relative reproducibility standard deviations between 15 % and 34 %. The lowest values for both standard deviations can be observed for the optional test sample SB 21, while the highest values are obtained by test sample SC 41 again. For the remaining test reference mixtures and test samples the relative reproducibility standard deviation lies between 15 % and 24 %.

For the ratios, the highest relative reproducibility standard deviation can be observed for SC 41 / SA PG II (49.83 %), whereas the values for the remaining ratios lie between 20 % and 40 %.

Table 24: Mean values and relative standard deviations for single values and ratios for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀

	Sample / Ratio	Number of laboratories after outlier elimination	Mean	Relative reproducibility s.d.	Relative repeatability s.d.
Single values	SA PG II	11	0.57 g/s	23.99 %	13.96 %
	SA PG III	11	0.27 g/s	17.65 %	11.78 %
	SB 11	12	0.40 g/s	17.06 %	11.99 %
	SB 21	6	0.59 g/s	14.53 %	10.30 %
	SB 41	11	0.39 g/s	15.92 %	12.76 %
	SC 11	12	0.95 g/s	23.93 %	19.62 %
	SC 21	7	1.02 g/s	17.84 %	12.93 %
	SC 41	12	0.39 g/s	33.71 %	20.64 %
Ratios of mean values	SA PG III / SA PG II	12	0.48	23.44 %	
	SB 11 / SA PG II	12	0.71	23.18 %	
	SB 11 / SA PG III	12	1.49	23.38 %	
	SB 21 / SA PG II	7	0.98	31.42 %	
	SB 21 / SA PG III	7	2.31	20.17 %	
	SB 41 / SA PG II	12	0.74	28.43 %	
	SB 41 / SA PG III	12	1.53	28.20 %	
	SC 11 / SA PG II	12	1.66	27.16 %	
	SC 11 / SA PG III	12	3.45	19.60 %	
	SC 21 / SA PG II	8	1.90	38.30 %	
	SC 21 / SA PG III	8	4.25	29.52 %	
	SC 41 / SA PG II	12	0.70	49.83 %	
SC 41 / SA PG III	12	1.43	39.96 %		

4.6.2 Analysis of single values

The mean values of the consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ of each laboratory as well as the total mean values, the relative reproducibility standard deviation and the relative repeatability standard deviation over all laboratories are given in Table 25. Outlier laboratories are marked in red, and “straggler” laboratories, which were not excluded from data set for statistical analyses, are marked in yellow.

Table 25: Analysis of single values of consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ [g/s] (red: outlier laboratories (not used in the statistical analysis); yellow: “straggler” laboratories (used in the statistical analysis))

Laboratory	SA PG II	SA PG III	SB 11	SB 21	SB 41	SC 11	SC 21	SC 41
01	0.48	0.27	0.41		0.45	0.99		0.43
02	0.47	0.23	0.47	0.65	0.45	0.86	1.25	0.36
03	0.53	0.24	0.37	0.53	0.42 ^V	0.83	0.98	0.50
04	0.66 ^V	0.27	0.35	0.64 ^V	0.66 ^M	0.88	1.61 ^V	0.20
05	0.46	0.32 ^V	0.45		0.38	1.17	0.97	0.54
06	0.49	0.29	0.31		0.38	0.84		0.45
08	0.57	0.28	0.44	0.54	0.42	1.14	0.85	0.28
09	0.65	0.18	0.41	0.53	0.33	0.97	1.02	0.50
10	0.52	0.27	0.37		0.41	0.72		0.37
11	0.68	0.30	0.36		0.33	0.75		0.32
13	0.85	0.31	0.49	0.57	0.37	1.03	0.98	0.47
14	0.62	0.32	0.42	0.68	0.40	1.16	1.17	0.21
Mean	0.57	0.27	0.40	0.59	0.39	0.95	1.02	0.39
Rel. reproducibility s.d.	23.99 %	17.65 %	17.06 %	14.53 %	15.92 %	23.93 %	17.84 %	33.71 %
Rel. repeatability s.d.	13.96 %	11.78 %	11.99 %	10.30 %	12.76 %	19.62 %	12.93 %	20.64 %

M: outlier/straggler due to differing mean value;

V: outlier/straggler due to excessive variance

In Figure 15 laboratory mean values and standard deviations are shown exemplarily for packing group II (SA PG II). For the remaining test reference mixtures and samples please refer to the Appendix 10.7.2.

For packing group II (SA PG II) the mean value of laboratory 13 lies outside of the tolerance limits, but has neither been identified as outlier nor as straggler. Furthermore, the mean values of laboratory 04 exceed the tolerance limits for two test samples: SB 41 and SC 21. For these two samples, the values of laboratory 04 have been identified as outlier values.

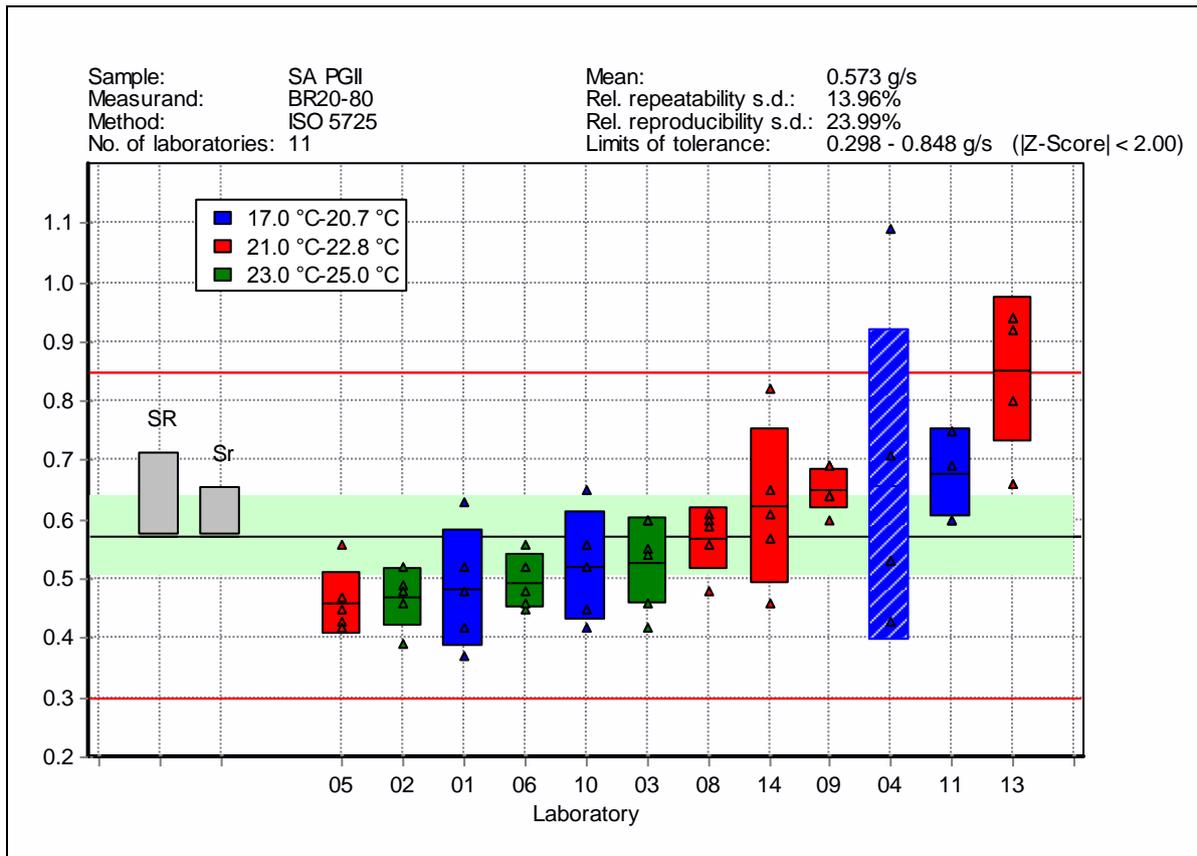


Figure 15: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SA PG II

4.6.3 Analysis of ratios

The following Table 26 summarizes the ratios of the mean values of the consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ for each laboratory and the total mean and relative reproducibility standard deviation over all laboratories.

Table 26: Ratios of mean laboratory values, total mean value and relative reproducibility standard deviation of mean values of consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀

Laboratory	SA PG III / SA PG II	SB 11 / SA PG II	SB 11 / SA PG III	SB 21 / SA PG II	SB 21 / SA PG III	SB 41 / SA PG II	SB 41 / SA PG III	SC 11 / SA PG II	SC 11 / SA PG III	SC 21 / SA PG II	SC 21 / SA PG III	SC 41 / SA PG II	SC 41 / SA PG III
01	0.56	0.85	1.52			0.94	1.67	2.05	3.64			0.89	1.59
02	0.50	1.00	2.01	1.38	2.79	0.96	1.93	1.84	3.72	2.66	5.37	0.76	1.53
03	0.46	0.70	1.52	1.01	2.20	0.80	1.74	1.58	3.44	1.86	4.05	0.95	2.07
04	0.41	0.53	1.29	0.97	2.37	1.01	2.48	1.34	3.30	2.45	6.02	0.31	0.76
05	0.69	0.97	1.40			0.83	1.20	2.56	3.69	2.11	3.04	1.17	1.69
06	0.58	0.64	1.09			0.77	1.32	1.70	2.93			0.91	1.56
08	0.49	0.78	1.59	0.95	1.95	0.75	1.52	2.01	4.11	1.50	3.07	0.50	1.01
09	0.28	0.63	2.21	0.81	2.87	0.51	1.78	1.49	5.26	1.56	5.52	0.77	2.73
10	0.52	0.70	1.35			0.78	1.49	1.38	2.64			0.71	1.36
11	0.45	0.53	1.18			0.48	1.08	1.10	2.48			0.47	1.06
13	0.36	0.57	1.59	0.67	1.86	0.44	1.22	1.21	3.37	1.15	3.21	0.56	1.55
14	0.51	0.68	1.34	1.10	2.16	0.65	1.28	1.87	3.67	1.88	3.70	0.34	0.67
Mean	0.48	0.71	1.49	0.98	2.31	0.74	1.53	1.66	3.45	1.90	4.25	0.70	1.43
Rel. reproducibility s.d. [%]	23.44	23.18	23.38	31.42	20.17	28.43	28.20	27.16	19.60	38.30	29.52	49.83	39.96

In Figure 16, the ratios of the laboratory mean values of the consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ are shown exemplarily for packing group III and packing group II (SA PG III / SA PG II). For the remaining ratios refer to the Appendix 10.7.3.

For SB 41 / SA PG III the ratio of laboratory 04 lies outside of the tolerance limits. The same effect can be observed for laboratory 05 for the SC 11 / SA PG II. Furthermore, the ratios for SB 11 / SA PG III, SC 11 / SA PG III and SC 41 / SA PG III of laboratory 09 exceed the limits.

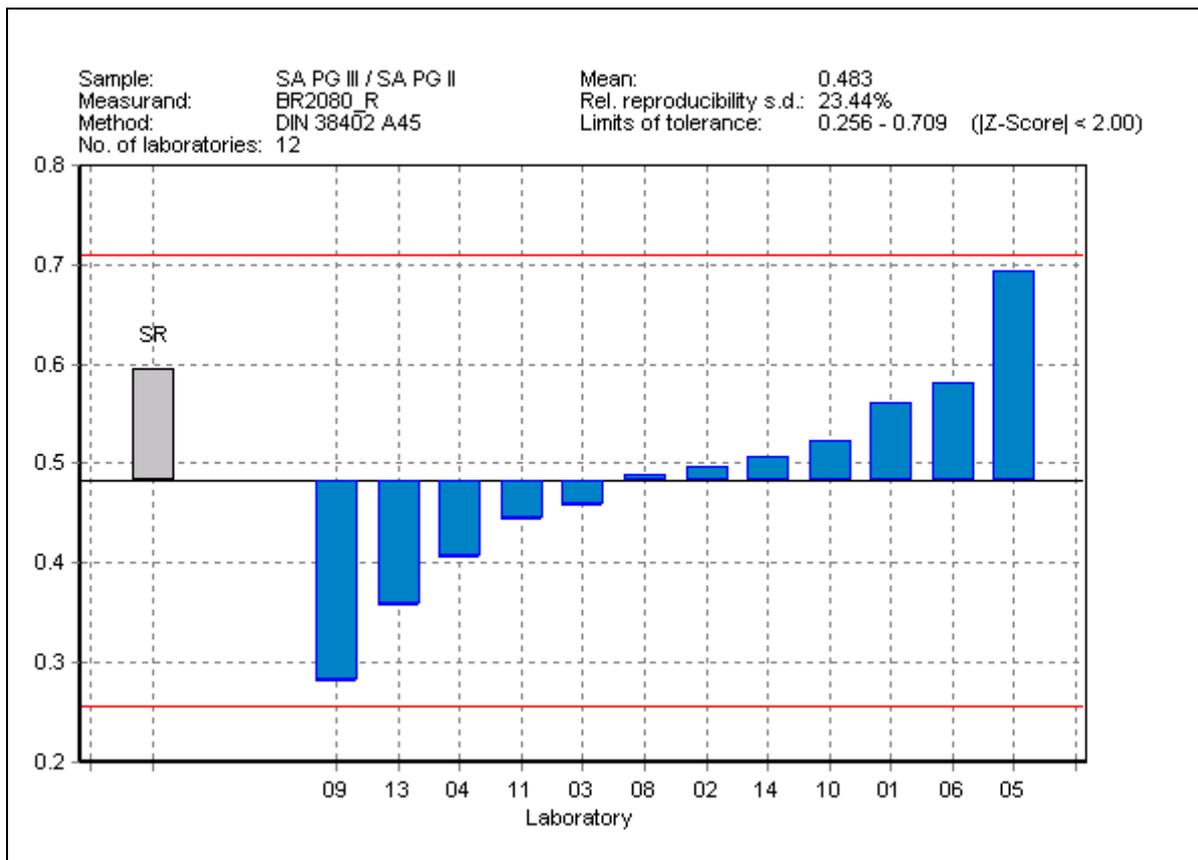


Figure 16: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SA PG III/SA PG II

5 Laboratory assessment: Z scores and combination scores based on ratios of mean values

5.1 Z scores

An evaluation of the laboratory's performance with regard to the five parameters is carried out using Z scores according to IUPAC and EURACHEM (see [4] and [5]). Z scores describe the standardised deviation of the laboratory mean value from the total mean:

$$Z = \frac{\text{laboratory mean value} - \text{total mean value}}{\text{reproducibility standard deviation}}$$

Given normal distribution, Z is within the limits -2 and 2 with a probability of 95 % and therefore if $|Z| > 2$ (or $|Z| > 3$) holds, the quality criterion is not fulfilled. The Z scores considered here are based on the ratios of the mean values and are calculated using reproducibility standard deviations and mean values as described in the last sections.

5.1.1 Individual combustion times $t_{0,1}$

For the ratios of the mean individual combustion time $t_{0,1}$, the Z scores of all laboratories are presented in Figure 17. It can be seen that only 4 out of 12 laboratories obtained satisfactory Z scores ($|Z| < 2$) for all of the analysed ratios. However, it has to be noted that 3 of these 8 laboratories (01, 06 and 10) did only analyse the obligatory samples and the measurands of sample SB 21 of laboratory 05 were not taken into account because of implausible data. Therefore fewer ratios could be determined than for laboratories 02, 03, 04 and 14, which analysed all obligatory and optional samples. In the following Table 27, the laboratories with the respective ratios are summarized for which the quality criterion is not fulfilled. This negative assessment can be stated with a statistical certainty of more than 95 %.

Table 27: Summary of laboratories with the respective ratios for which the quality criterion is not fulfilled for ratios of mean individual combustion time $t_{0,1}$

Lab code	Ratios			
02	SC 21/SA PG III			
03	SC 21/SA PG III			
04	SC 21/SA PG III			
05	SC 21/SA PG III			
08	SB 11/SA PG II	SB 21/SA PG I	SB 41/SA PG I	SC 11/SA PG I
09	SA PG III/SA PG II	SC 21/SA PG I	SC 21/SA PG II	
11	SB 11/SA PG III	SC 11/SA PG III	SC 41/SA PG II	
13	SC 21/SA PG III			

Also noticeable is the fact that Z scores for laboratory 08 are almost negative, whereas for laboratory 11 all Z scores are positive.

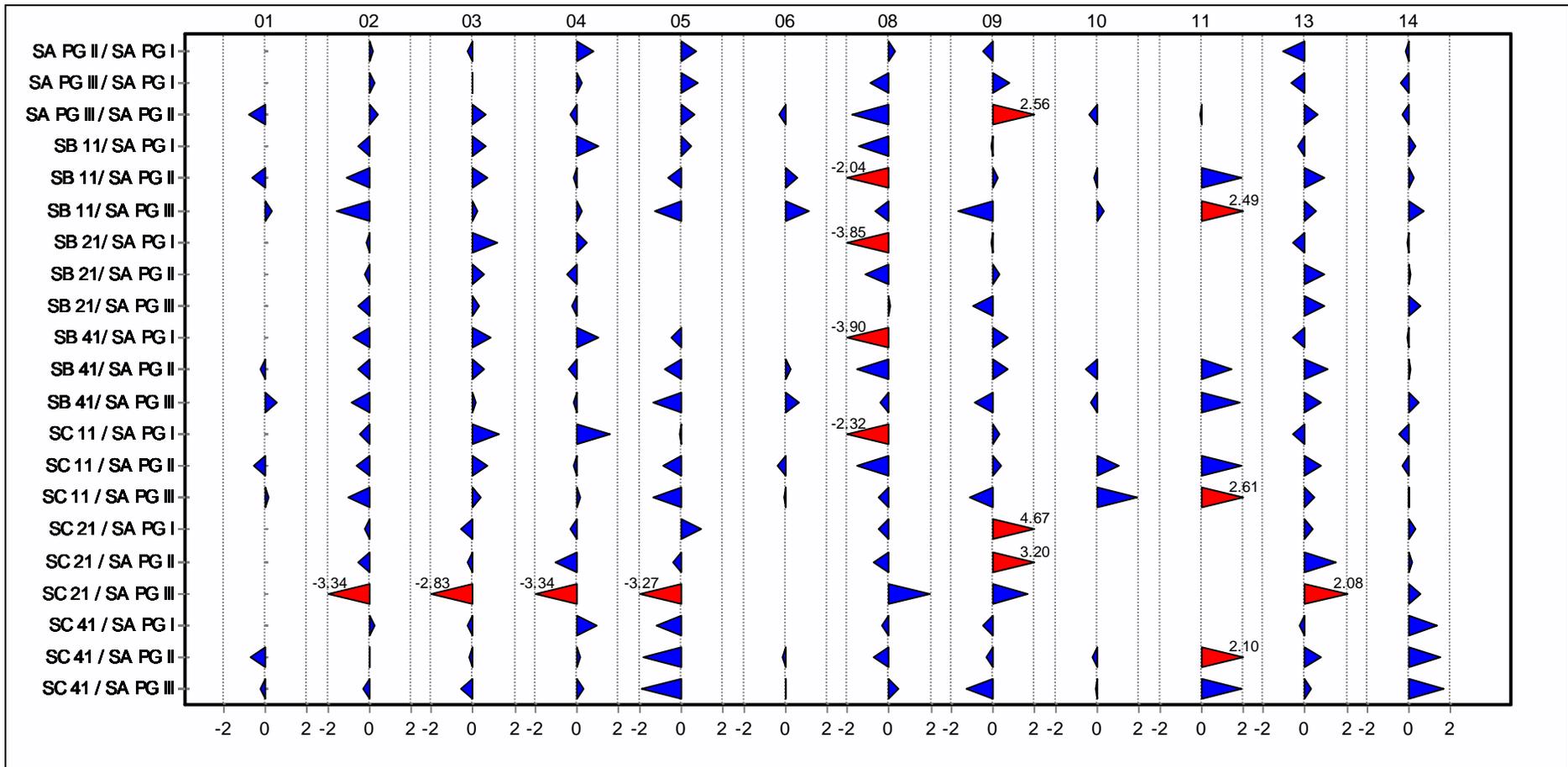


Figure 17: Z scores based on ratios of mean values of individual combustion times $t_{0,1}$

5.1.2 Main combustion time t_{20-80}

For the ratios of the main combustion time t_{20-80} , the Z scores of all laboratories are presented in Figure 18. In total, 8 out of 12 laboratories obtained satisfactory Z scores ($|Z| < 2$) for all of the analysed ratios. Again, 3 of these 8 laboratories (02, 03 and 08) did only analyse the obligatory samples and the measurement values of sample SB 21 of laboratory 05 were not taken into account because of implausible data. Therefore fewer ratios could be determined than for the other laboratories.

In comparison to the individual combustion time $t_{O,1}$, modified gravimetric approach improves significantly laboratories performance to meet quality criterion by at least factor 2. This tendency remains valid for all gravimetric based criteria in principal.

In the following Table 28, the laboratories with the respective ratios are summarized for which the quality criterion is not fulfilled. This negative assessment can be stated with a statistical certainty of more than 95 %.

Table 28: Summary of laboratories with the respective ratios for which the quality criterion is not fulfilled for ratios of mean main combustion times t_{20-80}

Lab code	Ratios	
04	SC 41/SA PG II	SC 41/SA PG III
09	SA PG III/SA PG II	
13	SA PG III/SA PG II	
14	SC 41/SA PG II	SC 41/SA PG III

Also noticeable is the fact that Z scores for laboratories 01, 02 and 05 are almost always negative, whereas for laboratory 11 all Z scores are positive.

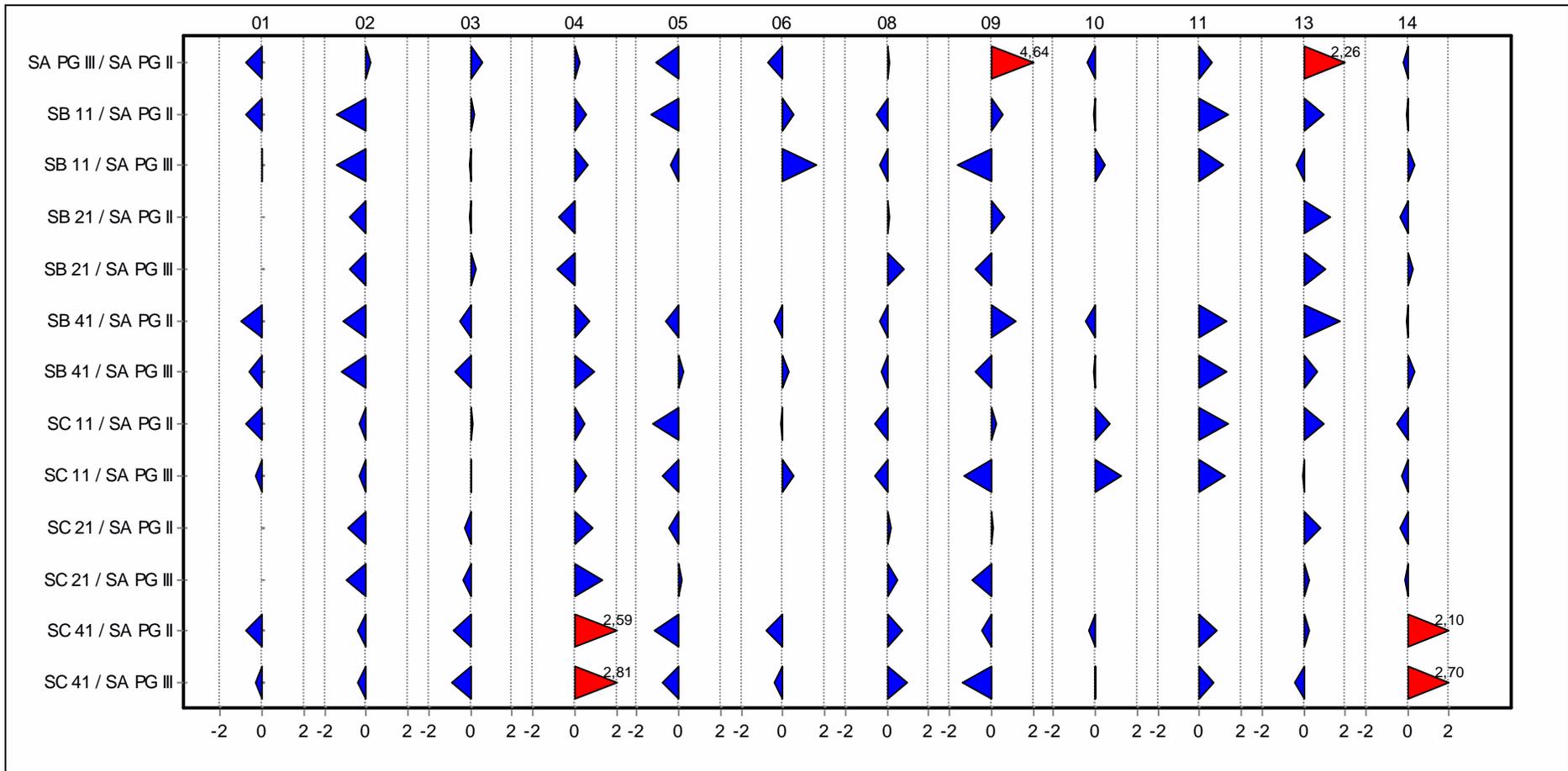


Figure 18: Z scores based on ratios of mean values of main combustion times t_{20-80}

5.1.3 Mass loss rates within 20 % and 80 % of total mass loss (slope of straight line)

For the ratios of the mean mass loss rates within 20 % and 80 % of total mass loss MLR_{20-80} , the Z scores of all laboratories are presented in Figure 19. It can be seen that 10 out of 12 laboratories obtained satisfactory Z scores ($|Z| < 2$) for all of the analysed ratios. For laboratory 05 no measurement values of sample SB 21 were taken into account because of implausible data. Therefore for this laboratory fewer ratios could be determined than for the other laboratories.

In the following Table 29, the laboratories with the respective ratios are summarized for which the quality criterion is not fulfilled. This negative assessment can be stated with a statistical certainty of more than 95 %.

Table 29: Summary of laboratories with the respective ratios for which the quality criterion is not fulfilled for ratios of mean mass loss rates within 20 % and 80 % of total mass loss MLR_{20-80}

Lab code	Ratios		
04	SB 21/SA PG II	SB 21/SA PG III	
05	SB 11/SA PG II	SC 11/SA PG II	SC 41/SA PG II

Also noticeable is the fact that Z scores for laboratories 08, 11 and 13 are almost always negative, whereas for laboratories 02 and 05 almost all Z scores are positive.

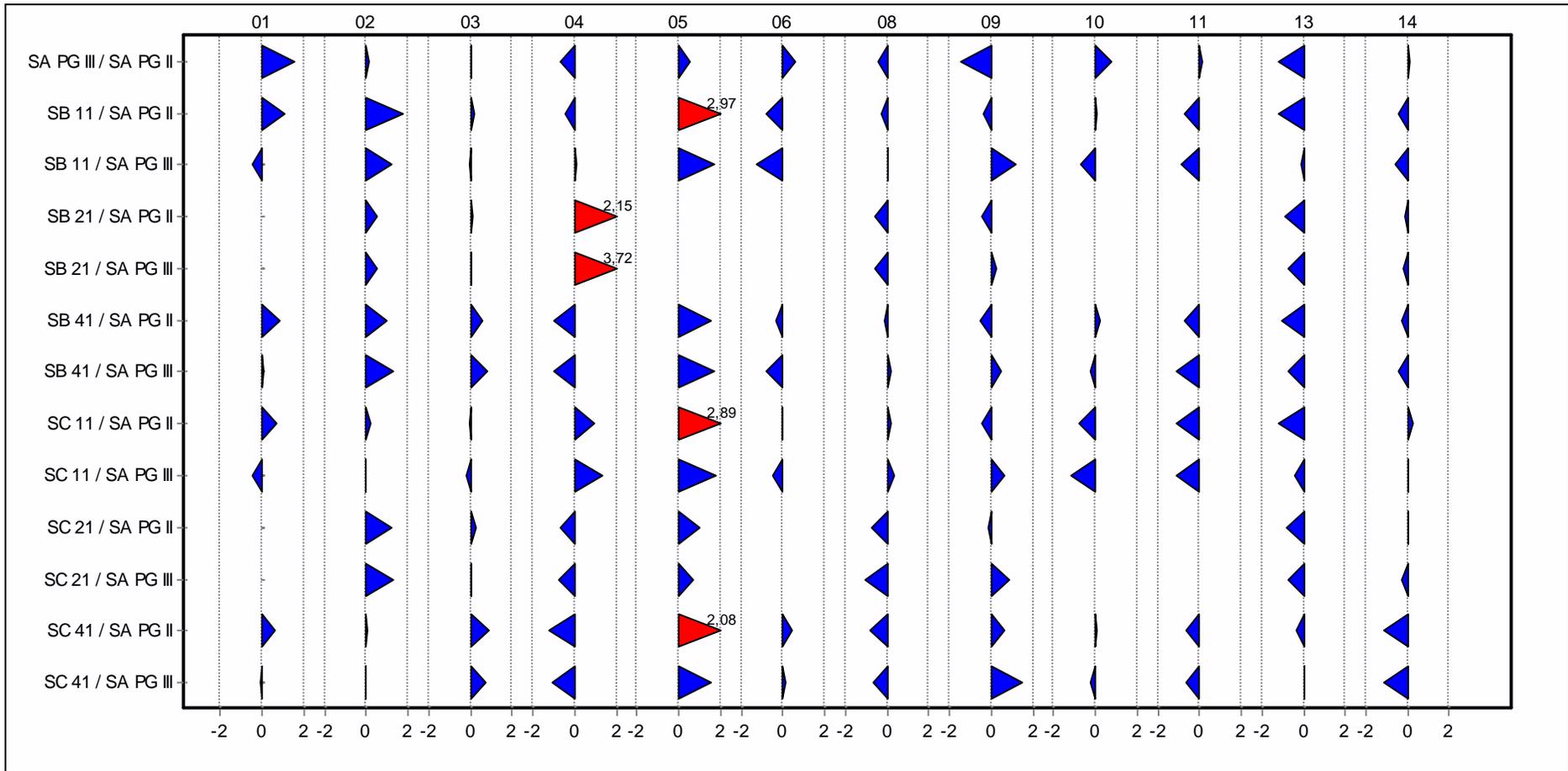


Figure 19: Z scores based on ratios of mean values of mass loss rates within 20 % and 80 % of total mass loss MLR_{20-80}

5.1.4 Mass loss rates by linear regression within 20 % to 80 % of total mass loss

For the ratios of the mean mass loss rates by linear regression within 20 % to 80 % of total mass loss $R^2 \text{MLR}_{20-80}$, the Z scores of all laboratories are presented in Figure 20. For 9 out of 12 laboratories satisfactory Z scores ($|Z| < 2$) were obtained for all of the analysed ratios. Again, it should be noted that 3 of these 9 laboratories (06, 10 and 11) did only analyse the obligatory samples and the measurement values of sample SB 21 of laboratory 05 were not taken into account because of implausible data. Therefore fewer ratios could be determined than for the other laboratories.

In the following Table 30, the laboratories with the respective ratios are summarized for which the quality criterion is not fulfilled. This negative assessment can be stated with a statistical certainty of more than 95 %.

Table 30: Summary of laboratories with the respective ratios for which the quality criterion is not fulfilled for ratios of mean mass loss rates by linear regression within 20 % to 80 % of total mass loss $R^2 \text{MLR}_{20-80}$

Lab code	Ratios			
01	SA PGIII/SA PGII			
04	SC 11/SA PGIII			
05	SB 11/SA PG II	SB 41/SA PG III	SC 11/SA PG II	SC 11/SA PG III

The Z scores of laboratory 05 are all positive and noticeably large compared to the Z scores of the other laboratories.

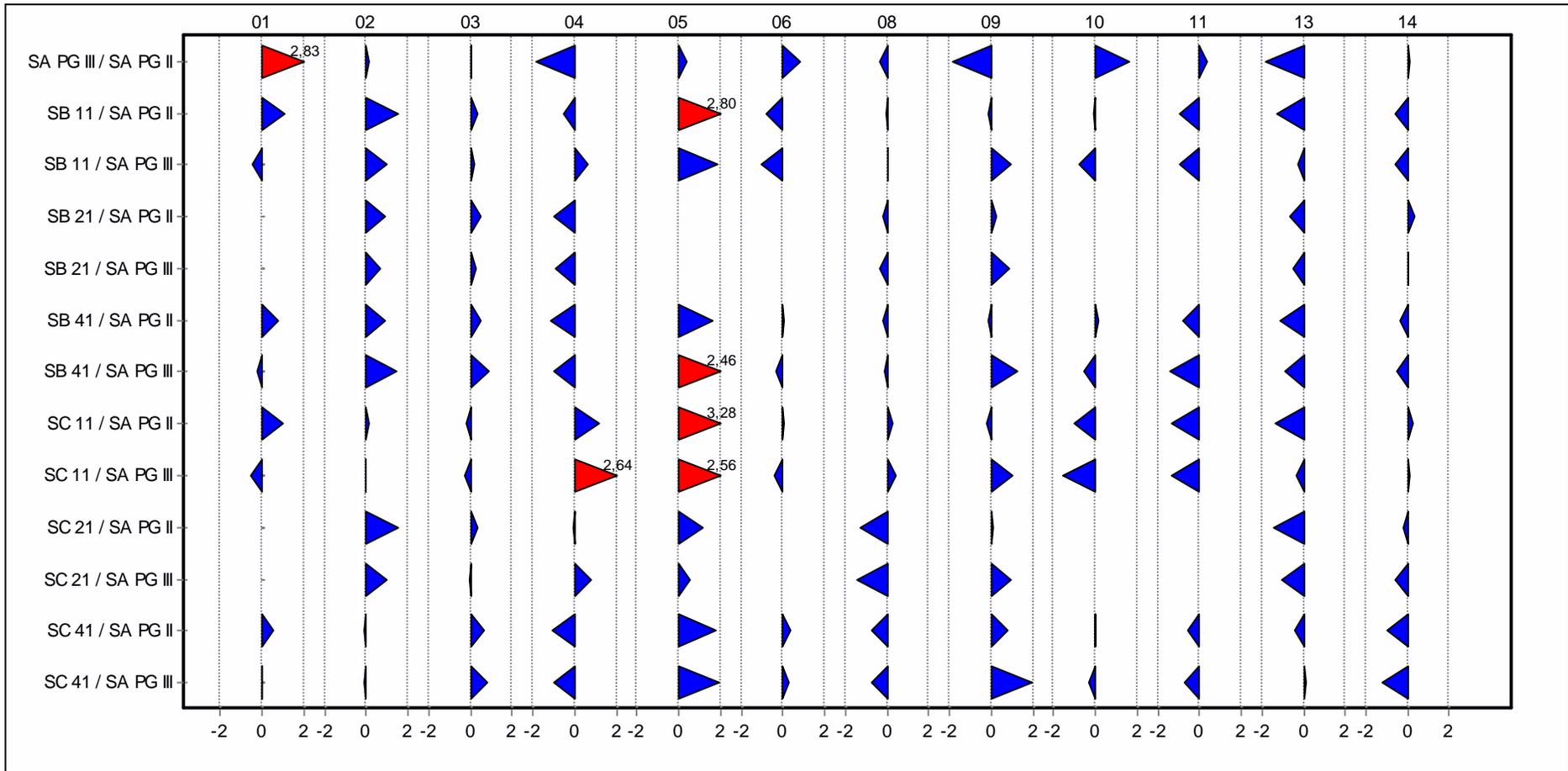


Figure 20: Z scores based on ratios of mean values of mass loss rates by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀

5.1.5 Consumption rates of 60 % of balanced combustible material BR₂₀₋₈₀

For the ratios of the mean consumption rates of 60 % of balanced combustible material BR₂₀₋₈₀, the Z scores of all laboratories are presented in Figure 21. Satisfactory Z scores ($|Z| < 2$) for all analysed ratios were obtained by 9 out of 12 laboratories. It should be kept in mind that 4 of these 9 laboratories (01, 06, 10 and 11) did only analyse the obligatory samples and the measurement values of sample SB 21 of laboratory 05 were not taken into account. Therefore fewer ratios have been determined than for the other laboratories.

In the following Table 31, the laboratories with the respective ratios are summarized for which the quality criterion is not fulfilled. This negative assessment can be stated with a statistical certainty of more than 95 %.

Table 31: Summary of laboratories with the respective ratios for which the quality criterion is not fulfilled for ratios of mean consumption rates of 60 % of balanced combustible material BR₂₀₋₈₀

Lab code	Ratios		
04	SB 41/SA PG III		
05	SC 11/SA PG II		
09	SB 11/SA PG III	SC 11/SA PG III	SC 41/SA PG III

Furthermore, laboratories 11 and 13 exhibit almost negative Z scores, while for laboratories 01 and 02 almost only positive Z scores can be observed.

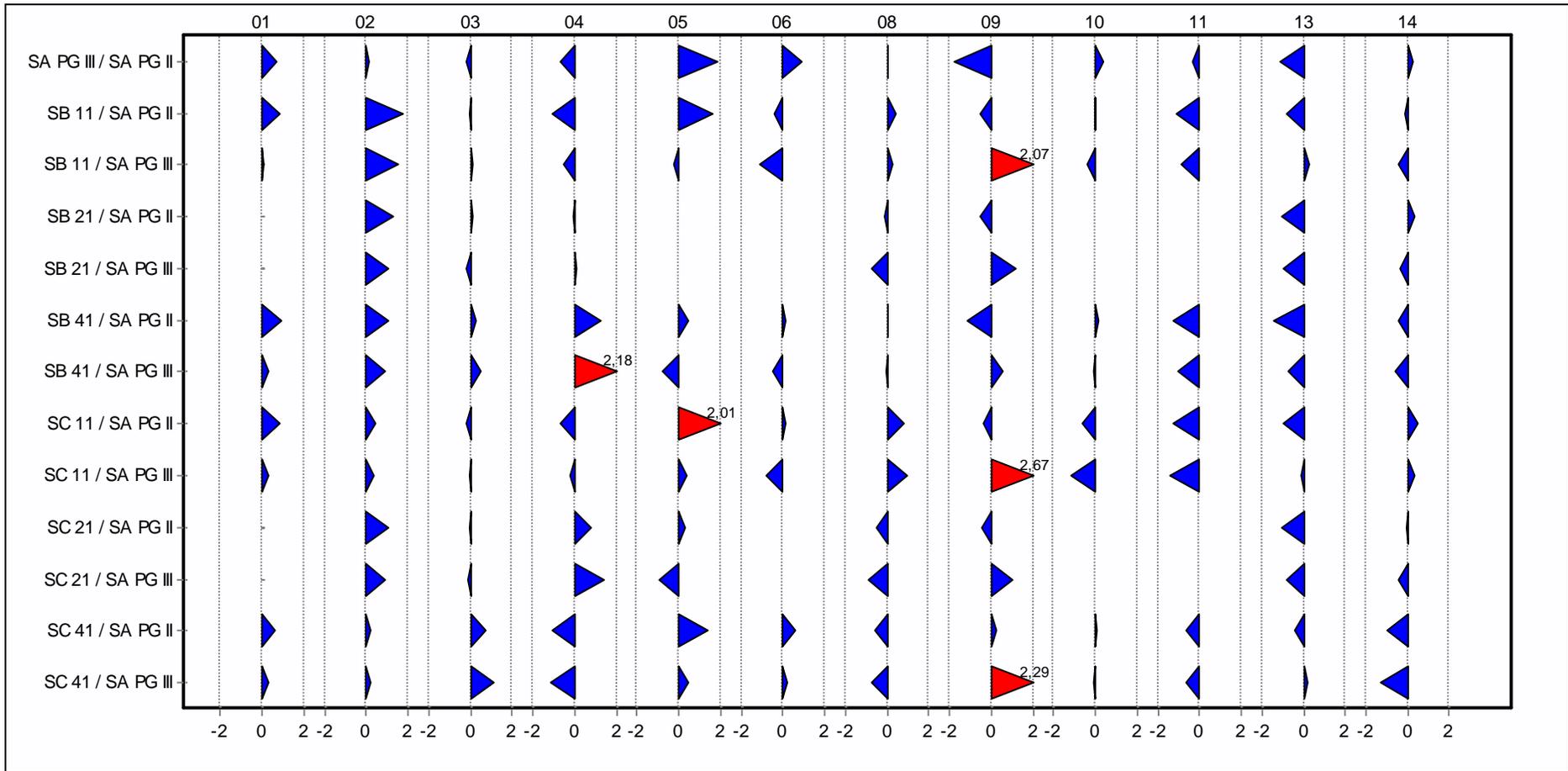


Figure 21: Z scores based on ratios of mean values of consumption rates of 60 % of balanced combustible material BR₂₀₋₈₀

5.2 Combination scores

From the Z scores the combination scores of the systematic deviations (rescaled sum of Z scores – RSZ) and the relative laboratory performance (RLP) can be obtained. The RSZ is based on a standardized sum of all Z scores. The standardization of the sum ensures that the RSZ may be interpreted as a single Z score, however, now not a single assessment of one ratio but a ratio comprehensive assessment is carried out. As long as the RSZ is within the tolerance range of -2 to +2, the respective laboratory does not exhibit any significant systematic deviations for the ratio comprehensive consideration.

The combination score of the relative laboratory performance – which equals the quadratic mean length of Z over all samples – ideally lies around 1. In this case, the deviation of the measurement values of the respective laboratory exhibit is about average. If the RLP is around 0.5, the performance of the laboratory is above average since the deviation of the values of this laboratory is only about 50 % of a laboratory with an average performance. In the following for each of the five parameters, a figure with the combination scores is shown. The green square displays the tolerance limits (between -2 and +2 for RSZ and below 1.5 for RLP).

For the ratios of mean individual combustion time $t_{0,1}$ (see Figure 22), the RSZ values of laboratories 02, 05 and 08 lie below the tolerance limits, therefore it can be assumed that these laboratories show significantly smaller combustion time ratios when averaged over all available ratios. On the contrary, laboratory 11 exhibits an RSZ value clearly larger than the upper tolerance limit. Therefore, the deviation of the values of this laboratory – averaging over all available ratios – is clearly larger than the reproducibility standard deviation.

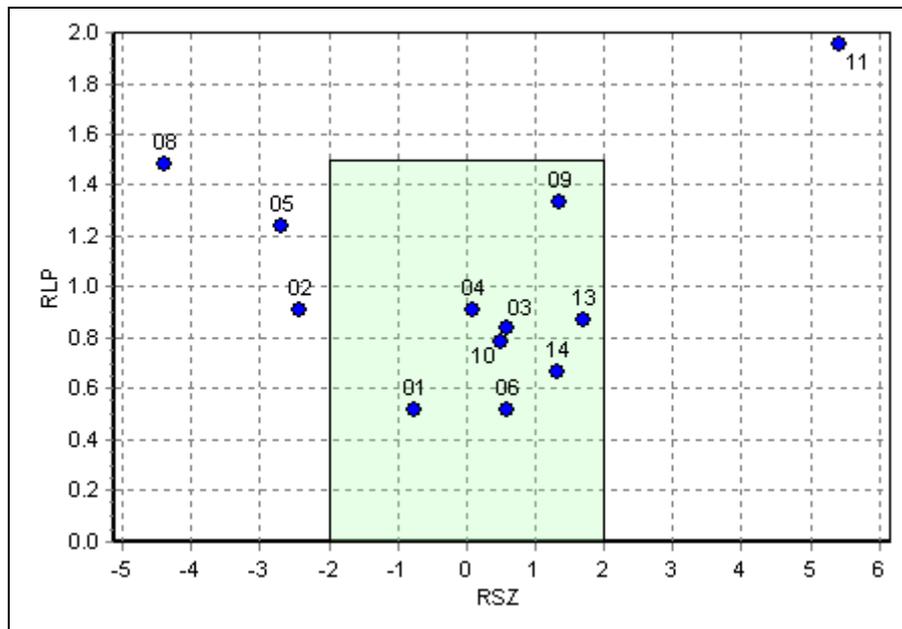


Figure 22: Combination scores for ratios of mean individual combustion time $t_{0,1}$

When considering the ratios of mean main combustion times t_{20-80} (see Figure 23), the RSZ values of laboratories 02 and 05 are still smaller than the lower limit (but also still close to the lower limit), while the RSZ of laboratory 08 now lies within the limits. The RSZ value for laboratory 08 now lies within the limits. The RSZ value for laboratory 11 is still larger than the upper tolerance limit, although the value becomes smaller now. Additionally, the RSZ values of laboratories 04 and 13 are now larger than the upper limit, for the ratios of the mean individual combustion times the respective value had been within the tolerance limits.

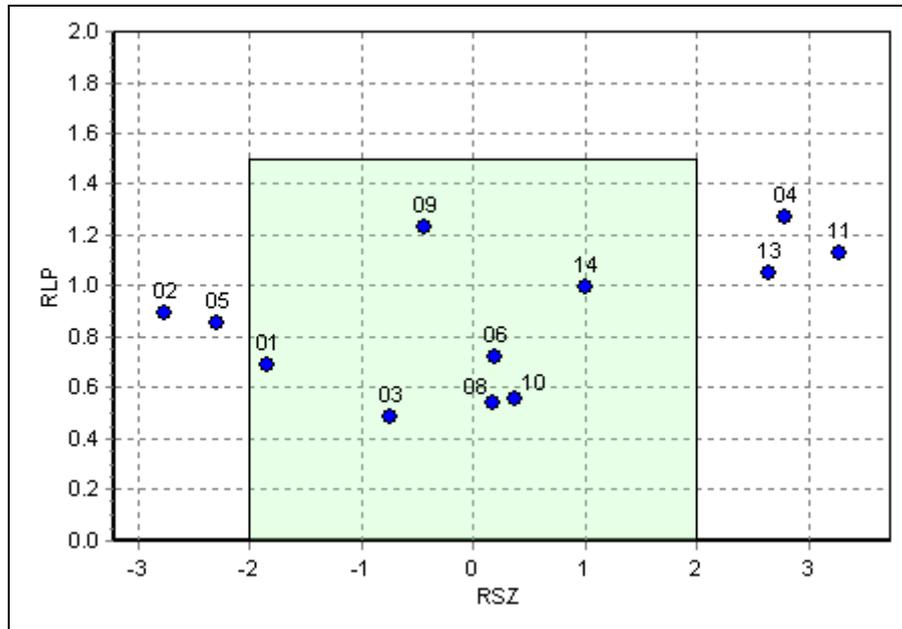


Figure 23: Combination scores for ratios of mean main combustion time t_{20-80}

The behaviour of the combustion time and the mass loss rates are reciprocally proportional, therefore the RSZ values for ratios of mean mass loss rates within 20 % and 80 % of total mass loss MLR_{20-80} (see Figure 24) are now contrarily significant.

Now the RSZ values of laboratories 11 and 13 lie below the tolerance limits, whereas the RSZ values of laboratories 02 and 05 lie above the upper limit. While the value of laboratory 04 is close to the upper limit, the value of laboratory 05 is clearly larger than the upper limit. Therefore it can be assumed that – averaging over all ratios – the first two laboratories show significantly smaller ratios of the mean mass loss rate, while the other two laboratories show significantly larger ratios of the mean mass rate. Furthermore, now the RLP value of laboratory 05 is larger than 1.5.

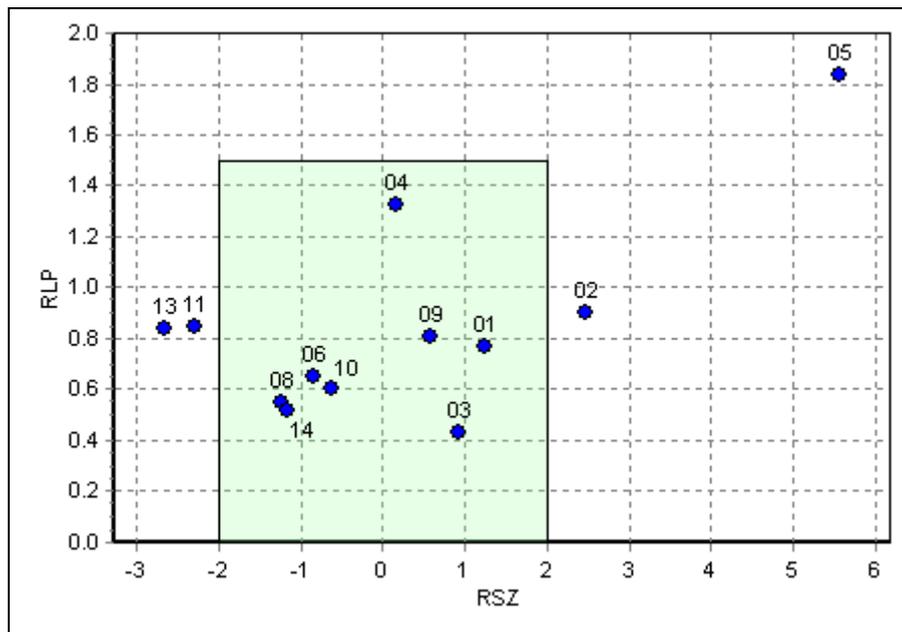


Figure 24: Combination scores for ratios of mean mass loss rates within 20 % and 80 % of total mass loss MLR_{20-80}

For the ratios of mass loss rates by linear regression within 20 % to 80 % of total mass loss R^2MLR_{20-80} (see Figure 25), almost the same results can be observed as for mass loss rates within 20 % and 80 % of total mass loss without linear regression.

Again, the RSZ values of laboratories 11 and 13 lie below the lower tolerance limit, while the RSZ values of laboratories 02 and 05 lie above the upper tolerance limit. Furthermore, the RLP value of laboratory 05 is clearly higher than 1.5.

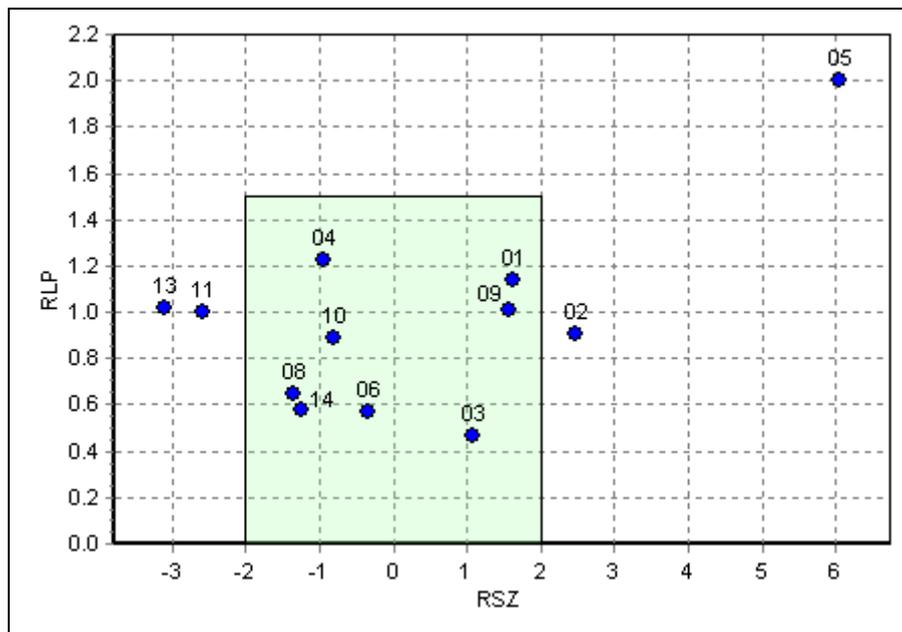


Figure 25: Combination scores for ratios of mean mass loss rates by linear regression within 20 % to 80 % of total mass loss R^2MLR_{20-80}

For the ratios of mean consumption rates of 60 % of balanced combustible material BR₂₀₋₈₀ (see Figure 26), again the RSZ values of laboratories 11 and 13 lie below the tolerance limits, whereas the RSZ value of laboratory 02 lies above the upper limit.

Therefore it can be assumed that – averaging over all ratios – the first two laboratories show significantly smaller ratios, while laboratory 02 shows significantly larger ratios. Now, neither the RSZ value nor the RLP value of laboratory 05 lies outside the tolerance limits.

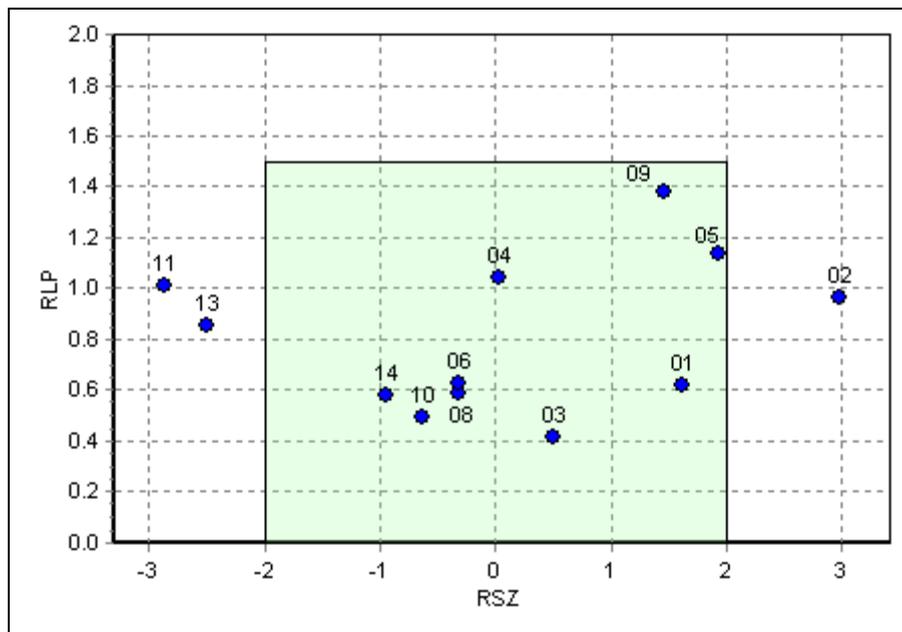


Figure 26: Combination scores for ratios of mean consumption rates of 60 % of balanced combustible material BR₂₀₋₈₀

Finally, Table 32 summarizes the combination scores for ratios for all five classification parameters expressed by '+' as 'within tolerance limits' or '-' for 'out of tolerance limits', where the green boxes mark the tolerance limits. In average, 8 of 12 laboratories are within the tolerance limits for both, time-based and mass-based criteria. Only two laboratories do not pass tolerance limits in any combination: laboratory 02 and laboratory 11. Any recommendation on practicability of test method or preferable criterion of combined parameters expressed by the combination scores cannot be derived from this approach.

Table 32: Summary of combination scores for ratios (,+ = laboratory s values lie within the tolerance limits; ,- = laboratory s values lie out of the tolerance limits)

Laboratory	t _{0,1}	t ₂₀₋₈₀	MLR ₂₀₋₈₀	R ² MLR ₂₀₋₈₀	BR ₂₀₋₈₀	Sum
01	+	+	+	+	+	5/5
02	-	-	-	-	-	0/5
03	+	+	+	+	+	5/5
04	+	-	+	+	+	4/5
05	-	-	-	-	+	4/5
06	+	+	+	+	+	5/5
08	-	+	+	+	+	4/5
09	+	+	+	+	+	5/5
10	+	+	+	+	+	5/5
11	-	-	-	-	-	0/5
13	+	-	-	-	-	1/5
14	+	+	+	+	+	5/5
Sum	8/12	7/12	8/12	8/12	9/12	

6 Further statistical analyses: probability of wrong classification

In further statistical analysis, the probability of wrong classification of the test samples is derived. These analyses are based on the ratios between the test samples and the packing groups. It is assumed that the data are normally distributed with the variance calculated from the relative reproducibility standard deviation and the mean values as summarized in section 4.

In the following sections, for each considered combustion parameter three kinds of figures are displayed:

1. *Distribution (histogram) for the classification of the respective packing group* (PG I, PG II or PG III);
2. *Probability of wrong classification* for different combustion times (parameters $t_{0,1}$ and t_{20-80}) and for different rates (parameters MLR_{20-80} , $R^2 MLR_{20-80}$ and BR_{20-80});
3. *Shark Profile*.

In the first kind of figure (*Distribution (histogram) for the classification of the respective packing group*), the distributions of the ratios between the test samples and the packing groups based on the results of the participating laboratories are shown – separately for each test sample and each packing group.

For the second kind of figure, the probability of wrong classification for an arbitrary sample can be calculated by extrapolating the relative standard deviation of the ratios. Here again the normal distribution is used as an approximation of the distribution of the respective ratios. Therefore it is assumed that the relative standard deviation of the arbitrary sample is a linear function of the relative standard deviation of the ratios.

The *shark profiles* show the probability of wrong classification for an arbitrary sample derived by extrapolating the relative standard deviation of the respective ratios only.

Since the *time-based combustion parameters* $t_{0,1}$ and t_{20-80} and the *mass-based combustion parameters* MLR_{20-80} , BR_{20-80} and $R^2 MLR_{20-80}$ behave reciprocally proportional, the interpretation of the figures is reverse as well. Therefore, for the two time-based combustion parameters an exemplary explanation is given for the individual combustion times $t_{0,1}$ (see section 6.1), and for the three mass-based combustion parameters an exemplary explanation is given for the mass loss rate within 20% and 80% of total mass loss MLR_{20-80} (see section 6.3).

6.1 Individual combustion time $t_{0.1}$

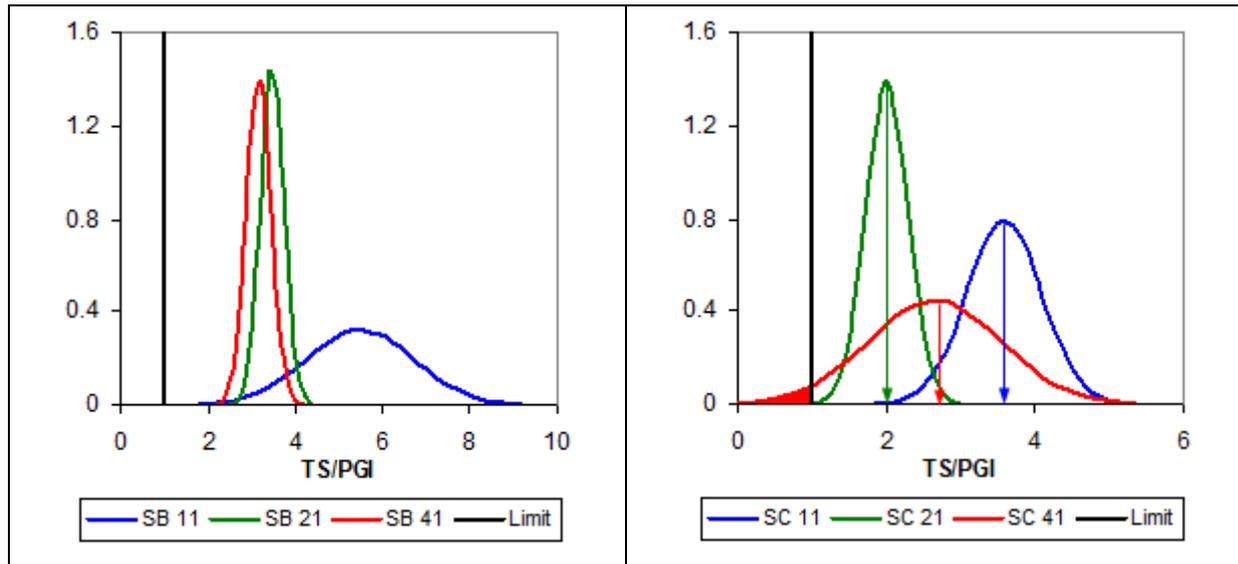


Figure 27: Distribution (histogram) for the classification of PG I regarding $t_{0.1}$
left: sodium perborate monohydrate; right: sodium nitrate

This kind of figures for *time-based combustion parameters* can be interpreted as follows:

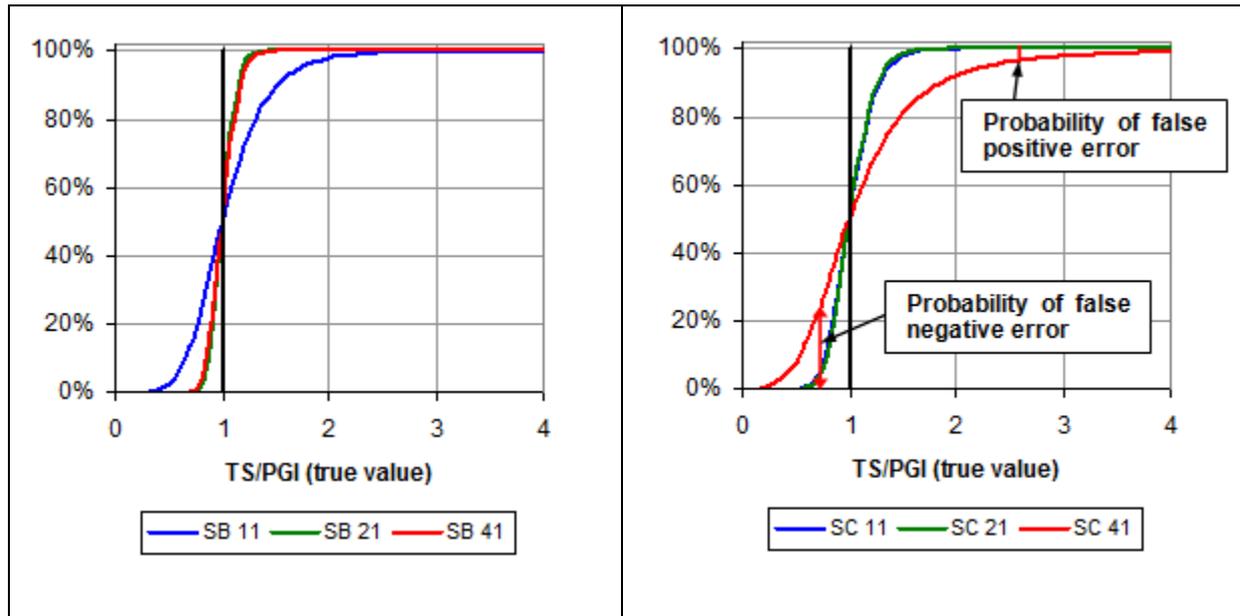
A ratio of 1 corresponds to identical individual combustion times of the test sample (TS) and the packing group. The maxima of the curves indicate the empirical mean ratio (value on x-axis) for the respective test sample and packing group. These empirical mean ratios are considered to be the factor from which the “true” combustion time for a test sample may be derived. For packing group I (PG I) and sodium nitrate (Figure 27, right), e.g., the empirical mean ratio for SC 11 / PG I (blue) equals 3.59, while the empirical mean value for SC 21 / PG I (green) equals 2.02 and the mean value for SC 41 / PG I (red) equals 2.65. (see also Table 11 on page 34).

In the following it is assumed that a *false positive error* indicates that an arbitrary test sample is assigned to a packing group of higher safety, although less safety would have been enough, e.g. a test sample actually belonging to packing group II is assigned to packing group I. That is, the measured combustion time of the test sample is shorter than the combustion time of the packing group, although the “true” combustion time of the test sample actually is longer. Expressed by ratios this means that the measured ratio is smaller than 1, while the true ratio is larger than 1. The probability for such a false positive error can be derived from the distribution figures (see Figure 27). The true ratio is the maximum of a curve. Only if this true ratio is larger than 1, a false positive error may occur. Then the probability 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 I and sodium nitrate (Figure 27, right) this holds only for test sample SC 41 (red), the respective area is filled in red. In this example the area equals 0.05, i.e. the probability for the false positive result $t_{0.1}(\text{SC 41}) < t_{0.1}(\text{PG I})$ equals 3 %, although the true value of SC 41 equals $\text{SC 41} = 2.65 \times \text{PG I}$. The probability for false positive results for the other ratios considered equals 0 % because there are no ratios smaller than 1 and therefore there is no area beneath the curve.

A *false negative error*, though, indicates that an arbitrary test sample is assigned to a packing group of lower safety, although a higher safety would be necessary, e.g. a test sample actually belonging to packing group II is assigned to packing group III¹. That is, the measured combustion time of the test sample is longer than the combustion time of the packing group, although the “true” combustion time of the test sample actually 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 (see Figure 27). The true ratio is the maximum of a curve. Only if this true ratio is smaller than 1, a false negative error may occur. Then the probability 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. As can be seen from Figure 27 for packing group I, for all three test samples the probability of a false negative error ($t_{0.1}(\text{SC 41}) > t_{0.1}(\text{PG I})$) equals zero since for none of the three samples the true ratio is smaller than 1 (no maximum of distribution curves on the left side of the vertical black line).

The whole proceeding is similar to statistical testing with a null hypothesis ($\text{TS} > \text{PG}$) and an alternative hypothesis ($\text{TS} < \text{PG}$). However, in a statistical test it is aimed for 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 that specific case, of course, it is aimed for keeping both probabilities as low as possible; however, none of them is kept below a specific limit. Therefore, both probabilities may become 50 %. Furthermore, the null hypothesis in statistical testing is defined that way that a wrongly rejection of the null hypothesis (which probability is kept below a limit) causes the more momentous problems. This is always the false positive error, however, in the current ring trial this false positive error (choosing a packing group with a too high safety) does appear less dangerous than the false negative error (choosing a packing group with a too low safety).

¹ This is conservatively spoken the most meaningful error in terms of safe transport of dangerous goods.



**Figure 28: Probability of wrong classification (PG I) for different combustion times $t_{0,1}$
left: sodium perborate monohydrate; right: sodium nitrate**

This kind of figures for *time-based combustion parameters* can be interpreted as follows:

Figure 28 shows the probabilities for a wrong classification in PG I for the test samples sodium perborate monohydrate (left) and sodium nitrate (right) with regard to packing group I (SA PG I), corrected for the laboratory effect.

Also the probabilities for false positive and false negative errors can be read off these figures. For packing group I and test sample SC 41, the probability for a false negative error is about 26 % when the true value of the ratio SC 41 / PG I equals 0.75. For a decreasing true value, this probability decreases as well. The probability for a false positive error is about 3 % (=100 %-97 %) when the true value equals 2.65. For an increasing true value of the ratio, this probability decreases: if 4 is the true value for the ratio of the combustion times of SC 41 and PG I, the probability for a false negative error is less than 1 %.

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

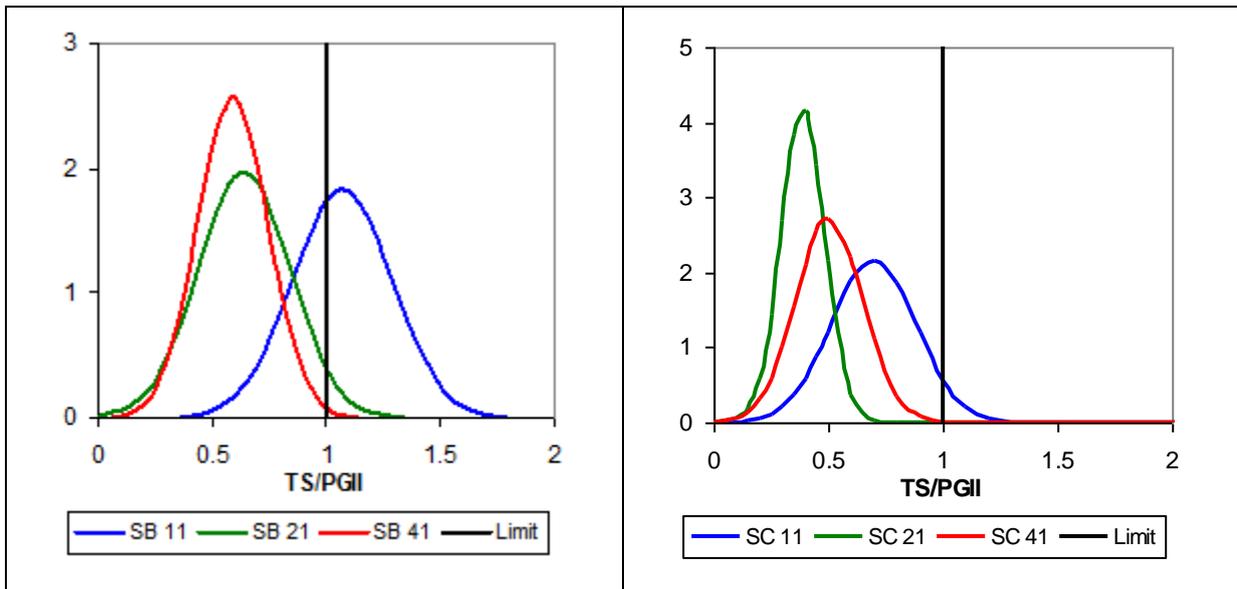


Figure 29: Distribution (histogram) for the classification of PG II (TS – test sample) regarding $t_{0.1}$
 left: sodium perborate monohydrate; right: sodium nitrate

Table 33: Probability for the false positive/negative error for the classification of PG II depending on the test sample regarding $t_{0.1}$

Test sample (TS)	Kind of error	Probability
SB 11	false positive	37 %
SB 21	false negative	4 %
SB 41	false negative	0 %
SC 11	false negative	5 %
SC 21	false negative	0 %
SC 41	false negative	0 %

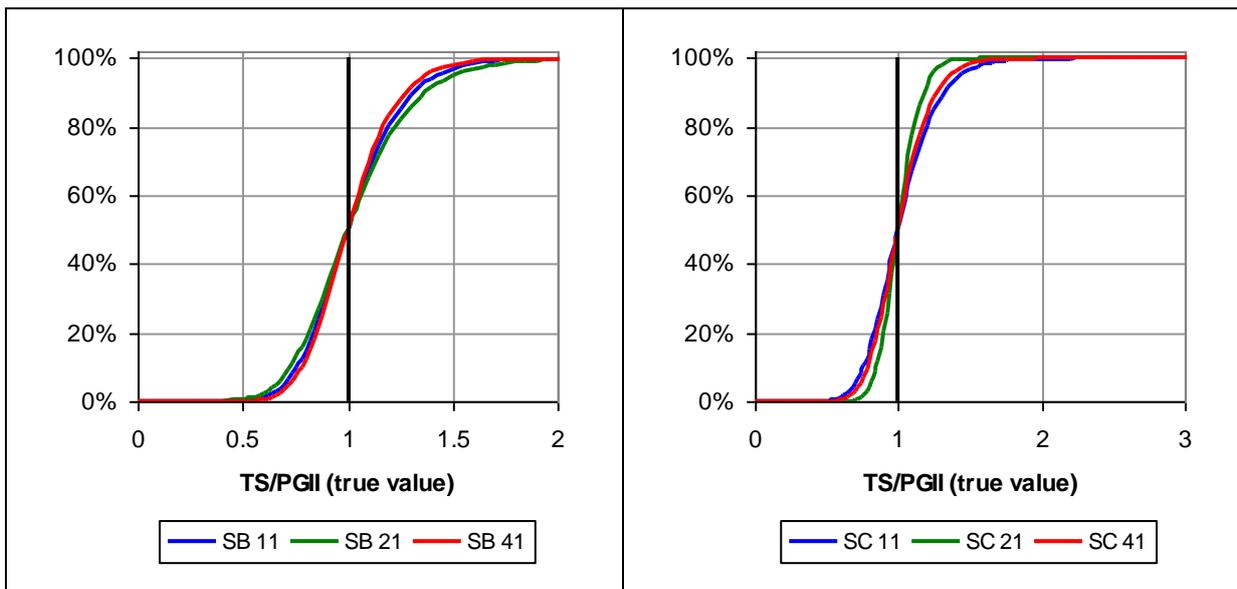


Figure 30: Probability of wrong classification (PG II) for different combustion times $t_{0.1}$ (TS – test sample)
 left: sodium perborate monohydrate; right: sodium nitrate

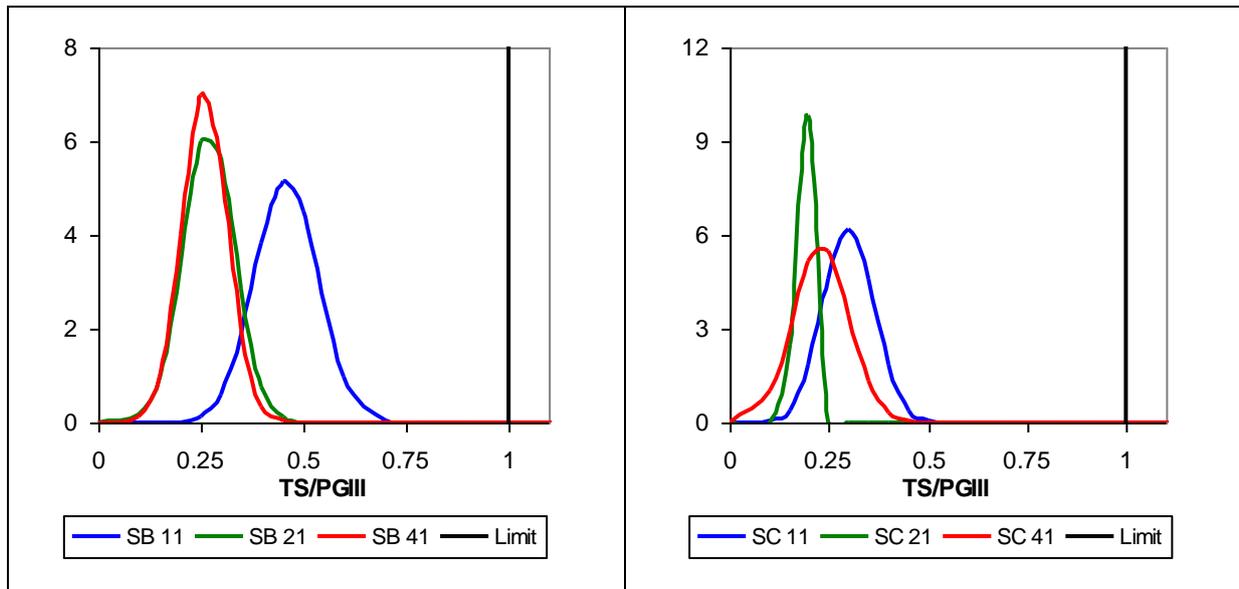


Figure 31: Distribution (histogram) for the classification of PG III regarding $t_{0.1}$
 left: sodium perborate monohydrate; right: sodium nitrate

Table 34: Probability for the false positive/negative error for the classification of PG III depending on the test sample regarding $t_{0.1}$

Test sample (TS)	Kind of error	Probability
SB 11	false negative	0 %
SB 21	false negative	0 %
SB 41	false negative	0 %
SC 11	false negative	0 %
SC 21	false negative	0 %
SC 41	false negative	0 %

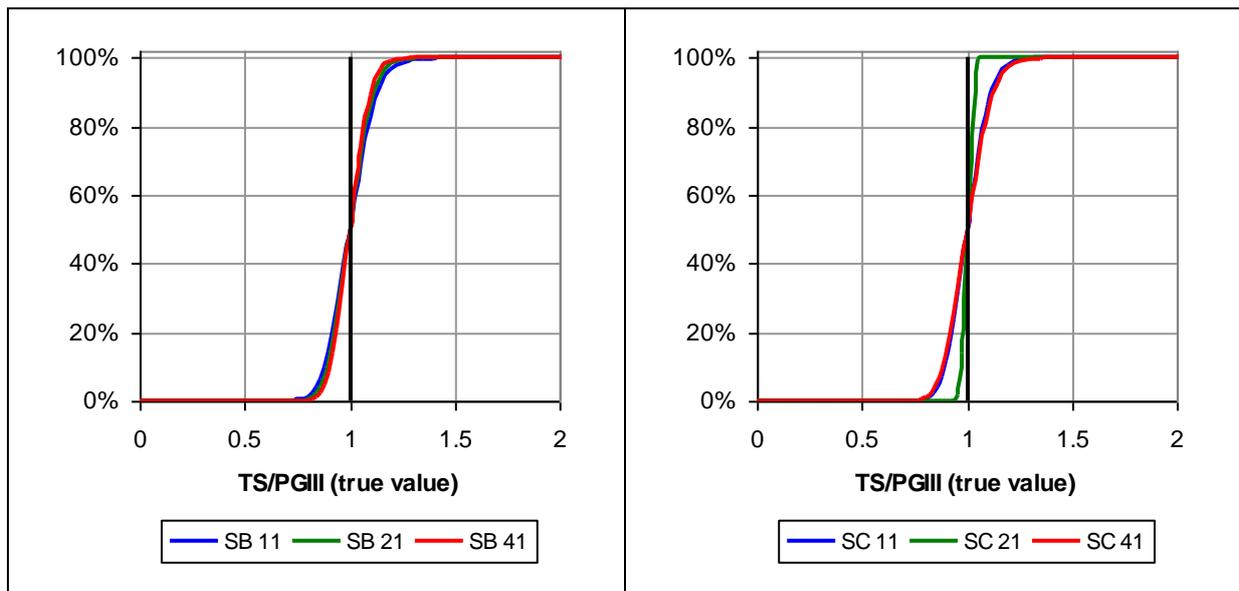


Figure 32: Probability of wrong classification (PG III) for different combustion times $t_{0.1}$
 left: sodium perborate monohydrate; right: sodium nitrate

The following shark profiles (Figure 33 and Figure 34) show the probability of wrong classification for an arbitrary sample of sodium perborate monohydrate or sodium nitrate. Here, the probability is presented as a function of the true individual combustion time $t_{0,1}$.

For *time-based combustion parameters*, the shark profile is derived by folding down the part of the probability curve, which lies on the *right* side of the limit 1. Therefore the probabilities for a false negative error are now located on the left side of the maximum of the respective packing group curve (this part equals the above shown probability distributions), while the probabilities for a false positive error are located on the right side of the maximum of the respective curve.

The shark profiles for time-based combustion parameters can be interpreted as follows (exemplarily for sodium perborate monohydrate, see Figure 33):

The increasing arm of a curve of one packing group indicates the false negative classification, 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 higher safety. Whereas, the decreasing arm of a curve of one packing group indicates the false positive classification, 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:

increasing arm of packing group I (blue)	test sample is assigned to packing group I, although it needs higher safety
decreasing arm of packing group I (blue)	test sample is assigned to packing group I, although packing group II would be sufficient
increasing arm of packing group II (red)	test sample is assigned to packing group II, although packing group I would be necessary
decreasing arm of packing group II (red)	test sample is assigned to packing group II, although packing group III would be sufficient
increasing arm of packing group III (black)	test sample is assigned to packing group III, although packing group II would be necessary
decreasing arm of packing group III (black)	test sample is assigned to packing group II, although less safety is necessary

As long as the curves do not overlap, only one kind of error can occur. Therefore the crucial ranges are the ones where two curves overlap, as in Figure 33 between about 50 s and 170 s. If for example the mean individual combustion time of an arbitrary sample equals 65 s, the probability for a false positive classification with regard to packing group II (red curve), i.e. the probability to classify the test sample to packing group II instead of the “true” packing group III, equals 24 %. At the same time, for a mean individual combustion time of 65 s, there is the possibility for a false negative error as well: the probability for a false negative classification of packing group III (black curve), i.e. assigning the test sample to packing group III instead of packing group II, equals 2%.

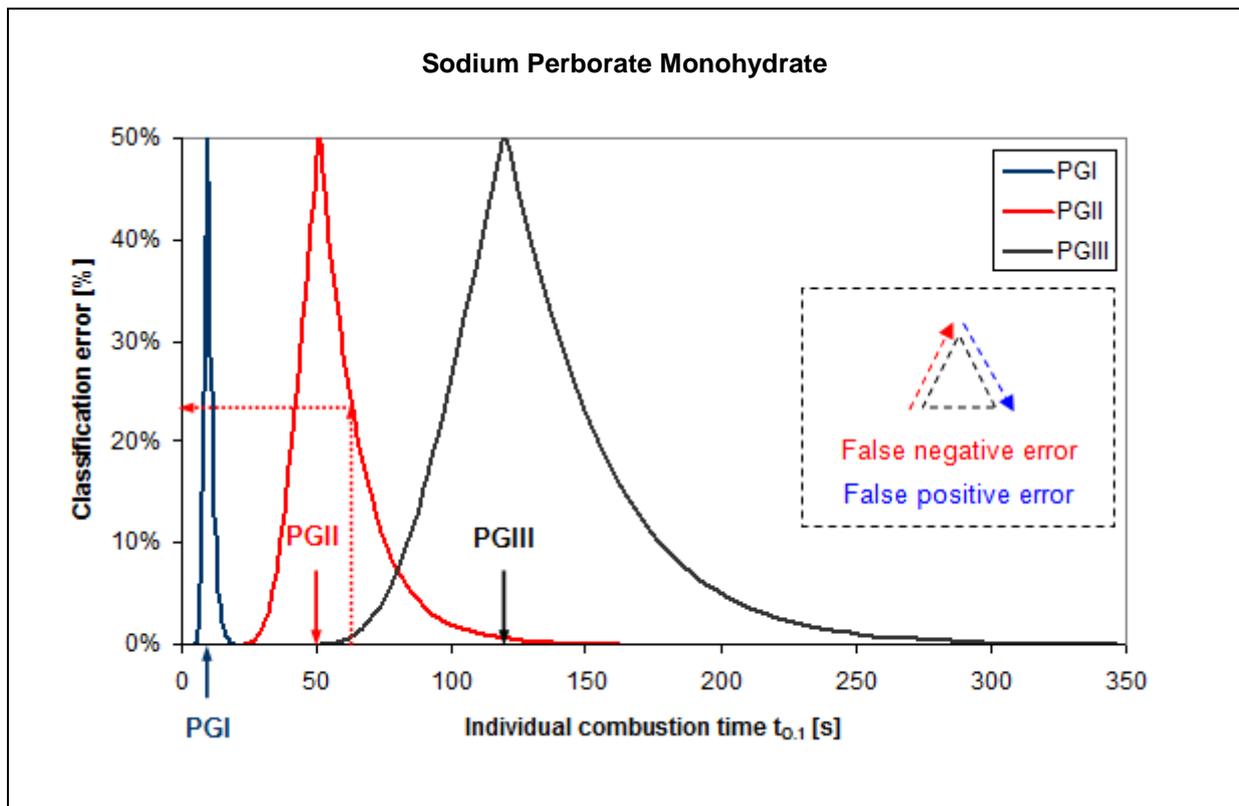


Figure 33: Shark profile for sodium perborate monohydrate and the parameter $t_{0.1}$ – probability of wrong classification in PG I, PG II or PG III

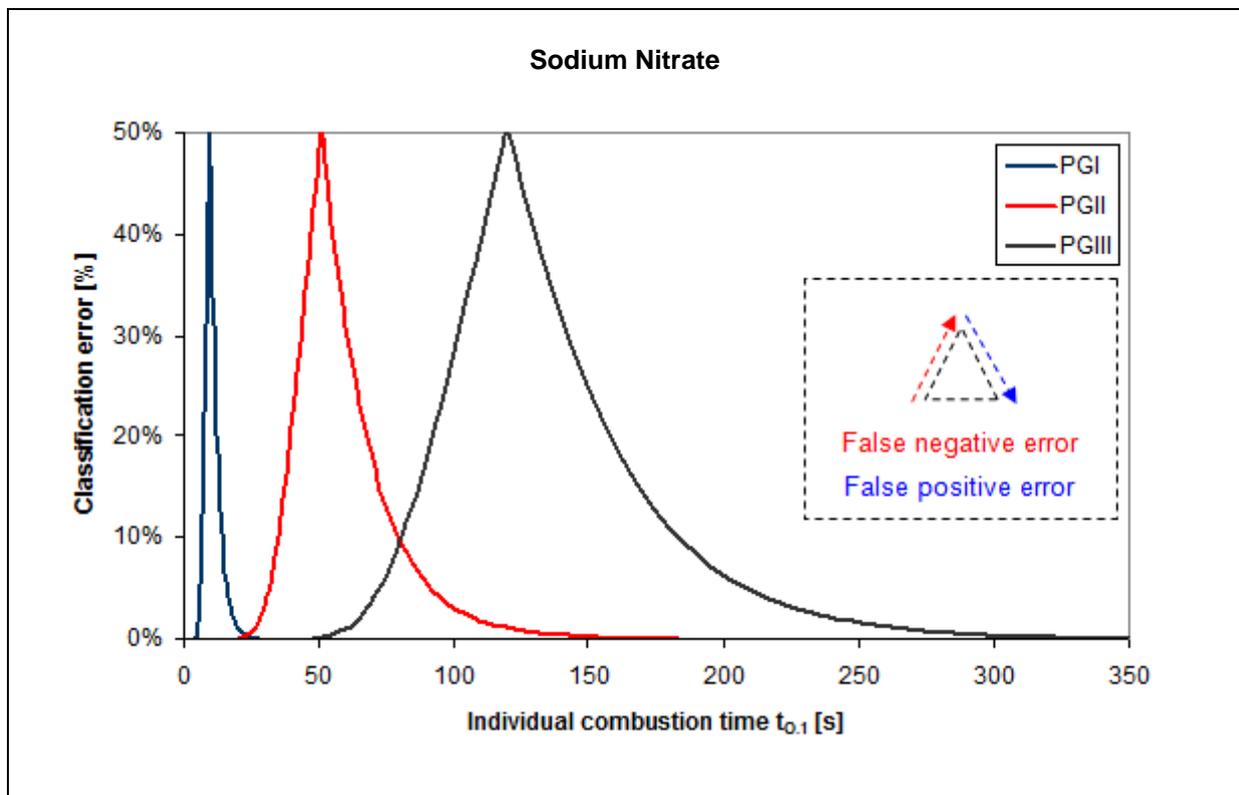


Figure 34: Shark profile for sodium nitrate and the parameter $t_{0.1}$ – probability of wrong classification in PG I, PG II or PG III

6.2 Main combustion time t_{20-80}

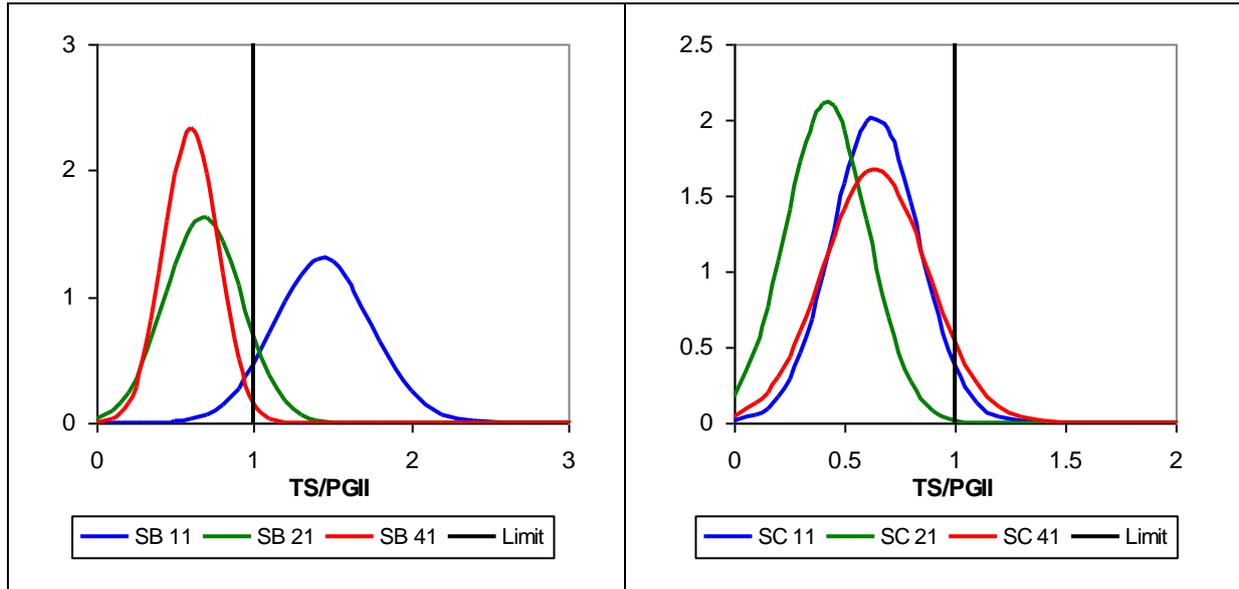


Figure 35: Distribution (histogram) for the classification of PG II regarding t_{20-80}
left: sodium perborate monohydrate; right: sodium nitrate

Table 35: Probability for the false positive/negative error for the classification of PG II depending on the test sample regarding t_{20-80}

Test sample (TS)	Kind of error	Probability
SB 11	false positive	8 %
SB 21	false negative	10 %
SB 41	false negative	1 %
SC 11	false negative	3 %
SC 21	false negative	0 %
SC 41	false negative	7 %

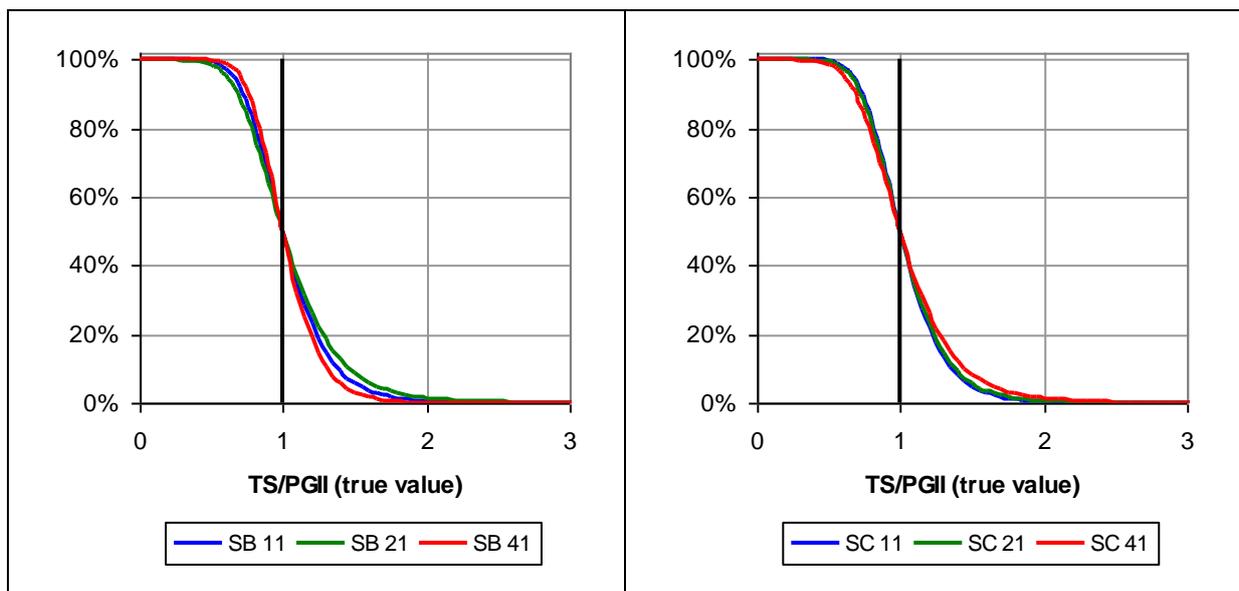


Figure 36: Probability of wrong classification (PG II) for different combustion times t_{20-80}
left: sodium perborate monohydrate; right: sodium nitrate

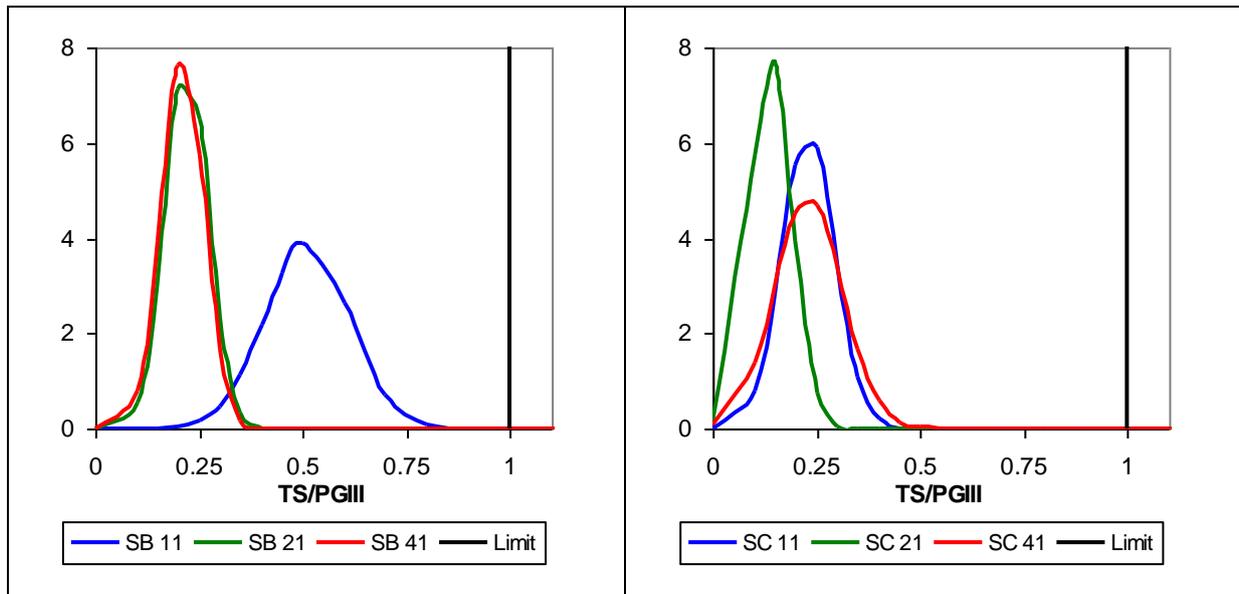


Figure 37: Distribution (histogram) for the classification of PG III regarding t_{20-80}
 left: sodium perborate monohydrate; right: sodium nitrate

Table 36: Probability for the false positive/negative error for the classification of PG III depending on the test sample regarding t_{20-80}

Test sample (TS)	Kind of error	Probability
SB 11	false negative	0 %
SB 21	false negative	0 %
SB 41	false negative	0 %
SC 11	false negative	0 %
SC 21	false negative	0 %
SC 41	false negative	0 %

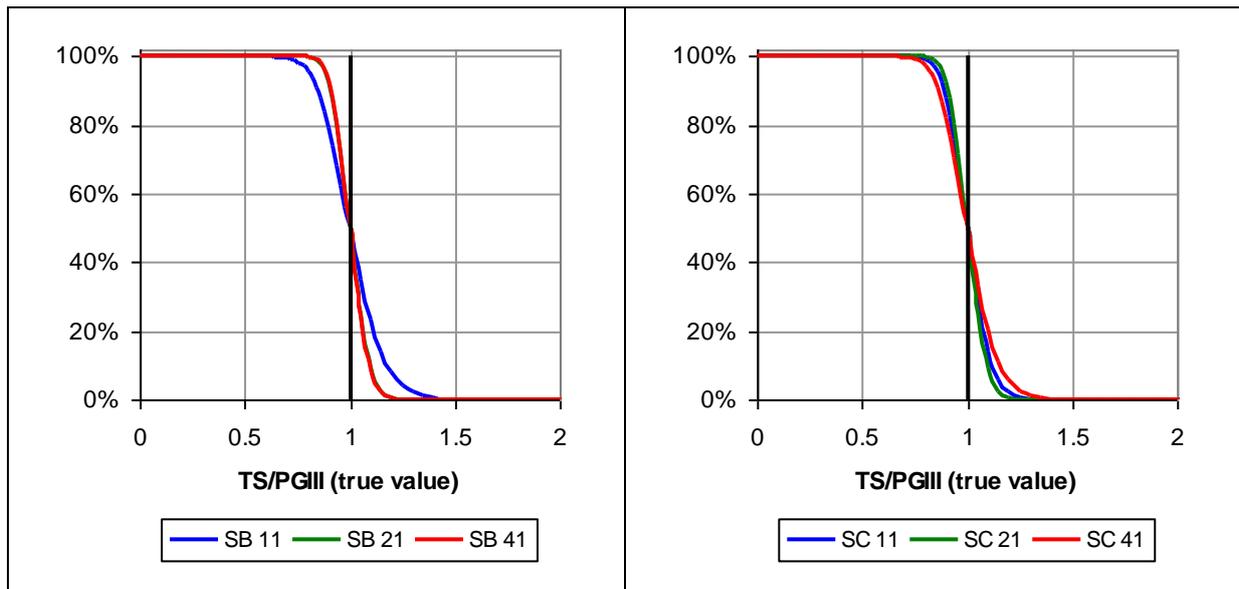


Figure 38: Probability of wrong classification (PG III) for different combustion times t_{20-80}
 left: sodium perborate monohydrate; right: sodium nitrate

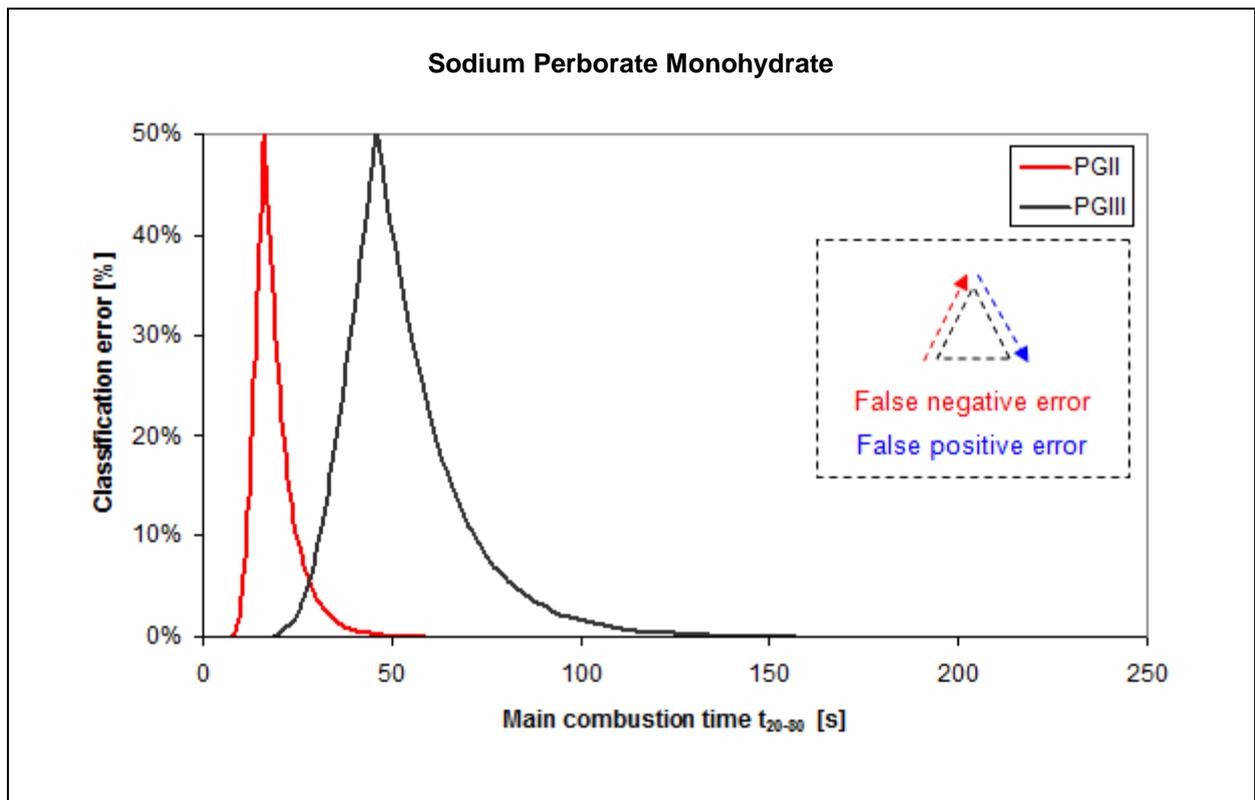


Figure 39: Shark profile for sodium perborate monohydrate and the parameter t_{20-80} – probability of wrong classification in PG II or PG III

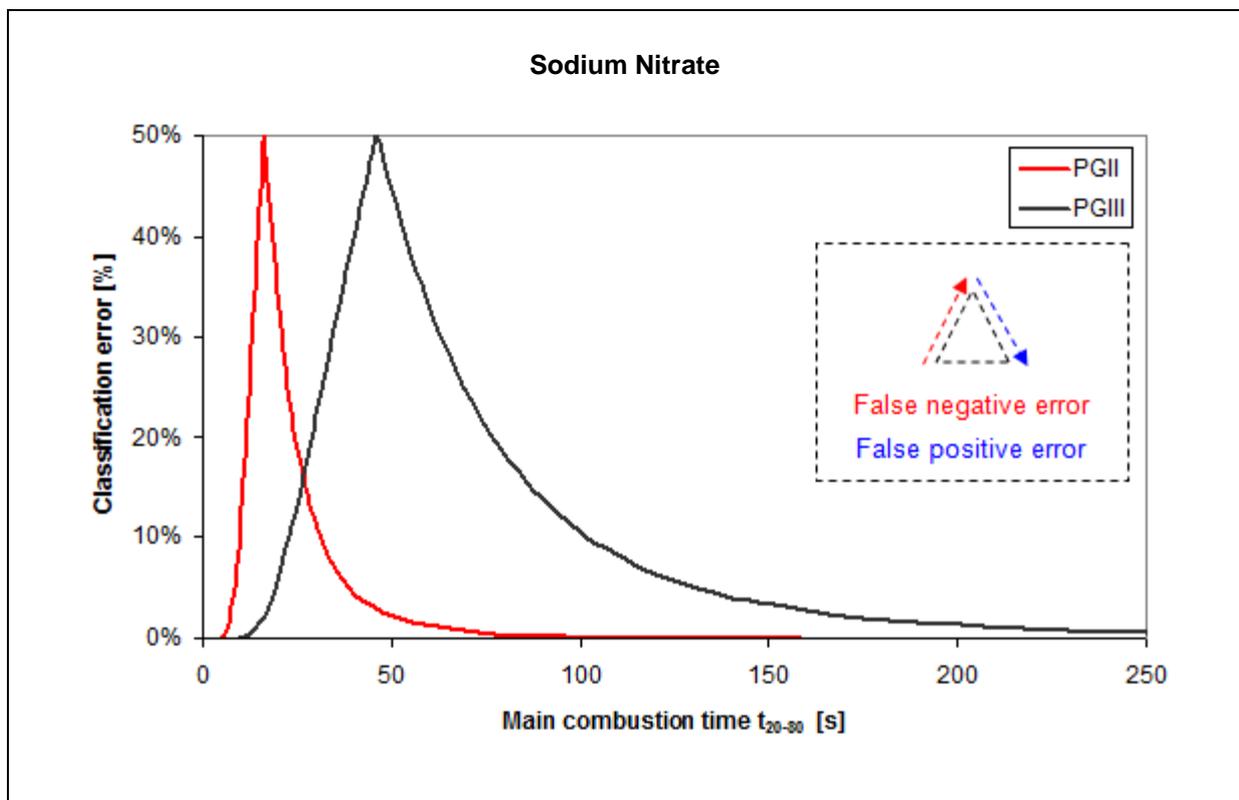


Figure 40: Shark profile for sodium nitrate and the parameter t_{20-80} – probability of wrong classification in PG II or PG III

6.3 Mass loss rate within 20 % and 80 % of total mass loss

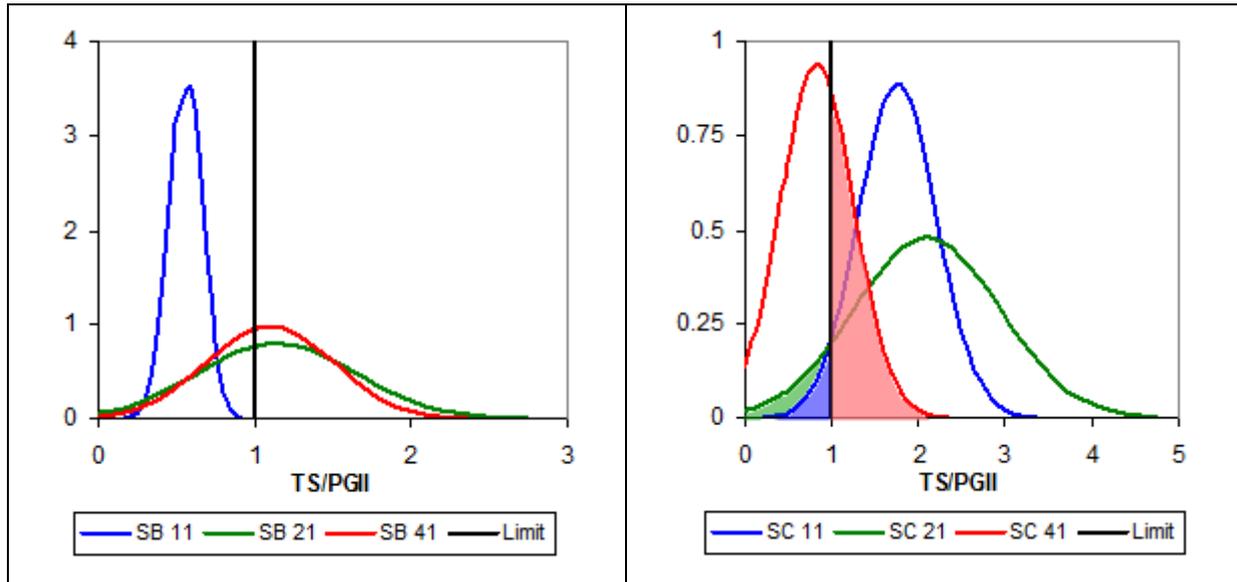


Figure 41: Distribution (histogram) for the classification of PG II regarding MLR_{20-80}
left: sodium perborate monohydrate; right: sodium nitrate

This kind of figures for *mass-based combustion parameters* can be interpreted as follows:

Similarly to time-based combustion parameters, a ratio of 1 corresponds to identical mass loss rates of the test sample (TS) and the packing group, which would describe the most critical borderline situation for classification purposes. The maxima of the curves indicate the empirical mean ratio (value on x-axis) for the respective test sample and packing group. These empirical mean ratios are considered to be the factor from which the “true” mass loss rate for a test sample may be derived. For packing group II (SA PG II) and sodium nitrate (Figure 41, right), e.g., the empirical mean ratio for SC 11 / PG II (blue) equals 1.76, while the empirical mean value for SC 21 / PG II (green) equals 2.07 and the mean value for SC 41 / PG II (red) equals 0.83. (see also Table 20 on page 49).

In the following it is assumed that a *false positive error* indicates that an arbitrary test sample is assigned to a packing group of higher safety, although less safety would have been enough, e.g. a test sample actually belonging to packing group II is assigned to packing group I. That is, the measured mass loss rate of the test sample is higher than the mass loss rate of the packing group, although the “true” mass loss rate of the test sample actually is lower. 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 positive error can be derived from the distribution figures (see Figure 41). The true ratio is the maximum of a curve. Only if this true ratio is smaller than 1, a false positive error may occur. Then the probability 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 and sodium nitrate (Figure 41, right) this holds only for test sample SC 41 (red), the respective area is filled in red. In this example the area equals 0.34, i.e. the probability for the false positive result $MLR_{20-80}(SC\ 41) > MLR_{20-80}(PG\ II)$ equals 34 %, although the true value of SC 41 equals $SC\ 41 = 0.83 \times PG\ II$. The probability for false positive results for the other ratios considered equals 0 because there are no ratios smaller than 1 and therefore there is no area beneath the curve.

A *false negative error*, though, indicates that an arbitrary test sample is assigned to a packing group of lower safety, although a higher safety would be necessary, e.g. a test sample actually belonging to packing group II is assigned to packing group III. That is, the measured mass loss rate of the test sample is smaller than the mass loss rate of the packing group, although the “true” mass loss rate of the test sample actually is higher. Expressed by ratios this means that the measured ratio is smaller than 1, while the true ratio is larger than 1. The probability for such a false negative error can again be derived from the distribution figures (see Figure 41). The true ratio is the maximum of a curve. Only if this true ratio is greater than 1, a false negative error may occur. Then the probability 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 and sodium nitrate (Figure 41, right) this holds only for test samples SC 11 (blue) and SC 21 (green), the respective areas are filled in blue and green. In this example the area corresponding to

- SC 11 equals 0.05, i.e. the probability for the false positive result
 $MLR_{20-80}(SC\ 11) < MLR_{20-80}(PG\ II)$ equals 5 %, although the true value of SC 11 equals $SC\ 11 = 1.76 \times PG\ II$;
- SC 21 equals 0.09, i.e. the probability for the false positive result
 $MLR_{20-80}(SC\ 21) < MLR_{20-80}(PG\ II)$ equals 9 %, although the true value of SC 21 equals $SC\ 21 = 2.07 \times PG\ II$.

An overview of these probabilities is given in Table 37, where also the kinds of errors with the respective probability for sodium perborate monohydrate are given.

Table 37: Probability for the false positive/negative error for the classification of PG II depending on the test sample regarding MLR_{20-80}

Test sample (TS)	Kind of error	Probability
SB 11	false positive	0 %
SB 21	false negative	39 %
SB 41	false negative	40 %
SC 11	false negative	5 %
SC 21	false negative	9 %
SC 41	false positive	34 %

Referring to practice, it has to be kept in mind that basically the closest ratio to 1 as for sodium nitrate is described here by calculated ratio SC41/PGII of 0.83. This ratio describes the most critical probability for any wrong classification due to related borderline situation. But paying respect to principle of test method only to take into account the average of fasted combustion times or consumption rates as derived in consideration of all tested ratio for classification purposes, the leading false negative error is exemplarily 5% for sodium nitrate in consideration of related ratio SC11. All other ratios or related derived probabilities for wrong classification are only interesting from a statistical point of view, but not for final classification at all.

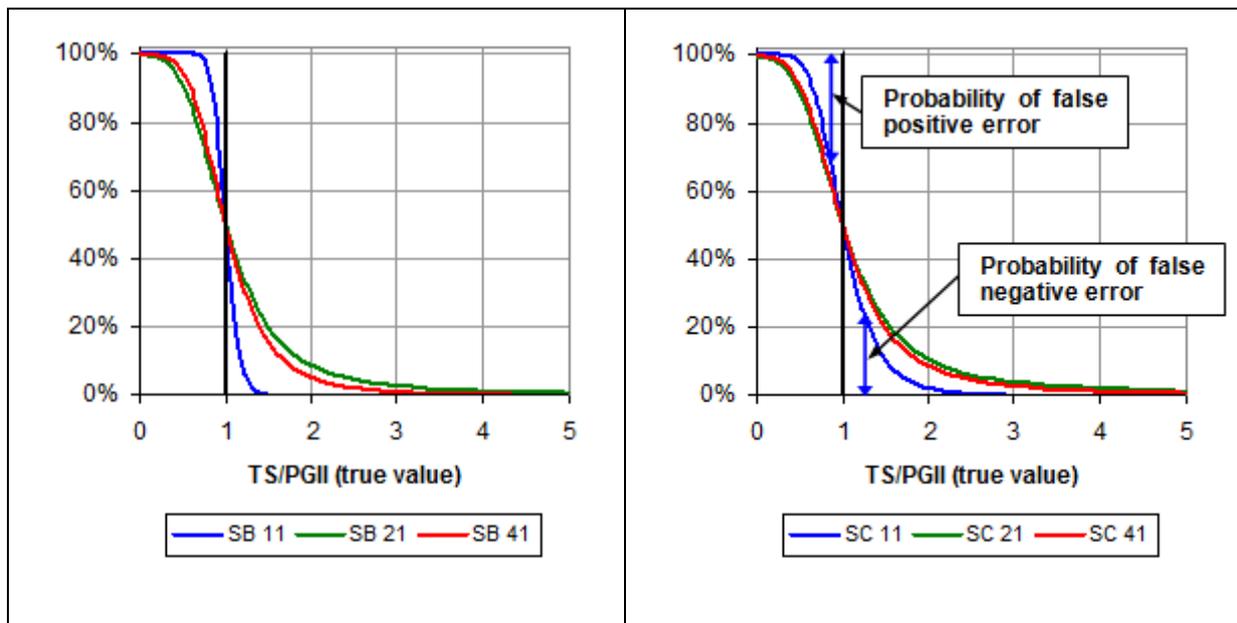


Figure 42: Probability of wrong classification (PG II) for different mass loss rates MLR_{20-80}
left: sodium perborate monohydrate; right: sodium nitrate

This kind of figures for *mass-based combustion parameters* can be interpreted as follows:

Figure 42 shows the probabilities for a wrong classification in PG II for the test samples sodium perborate monohydrate (left) and sodium nitrate (right) with regard to packing group II (SA PG II), corrected for the laboratory effect.

Also the probabilities for false positive and false negative errors can be read off of these figures. For packing group II and test sample SC 11, the probability for a false negative error is about 24 % when the true value of the ratio SC 41 / PG II equals 1.25. For an increasing true value, this probability decreases. The probability for a false positive error is about 34% (=100 % - 66 %) when the true value equals 0.83. For a decreasing true value of the ratio, this probability decreases as well. For equal mass loss rates of test sample and packing group, i.e. at ratio 1, the probabilities for both the false negative and the false positive error are 50 %.

It has to be noted that for mass-based combustion parameters false positive errors occur if the considered ratio is less than 1 and false positive errors occur if the considered ratio is greater than 1. For time-based combustion parameters it is the other way around as it is demonstrated in e.g. Figure 28.

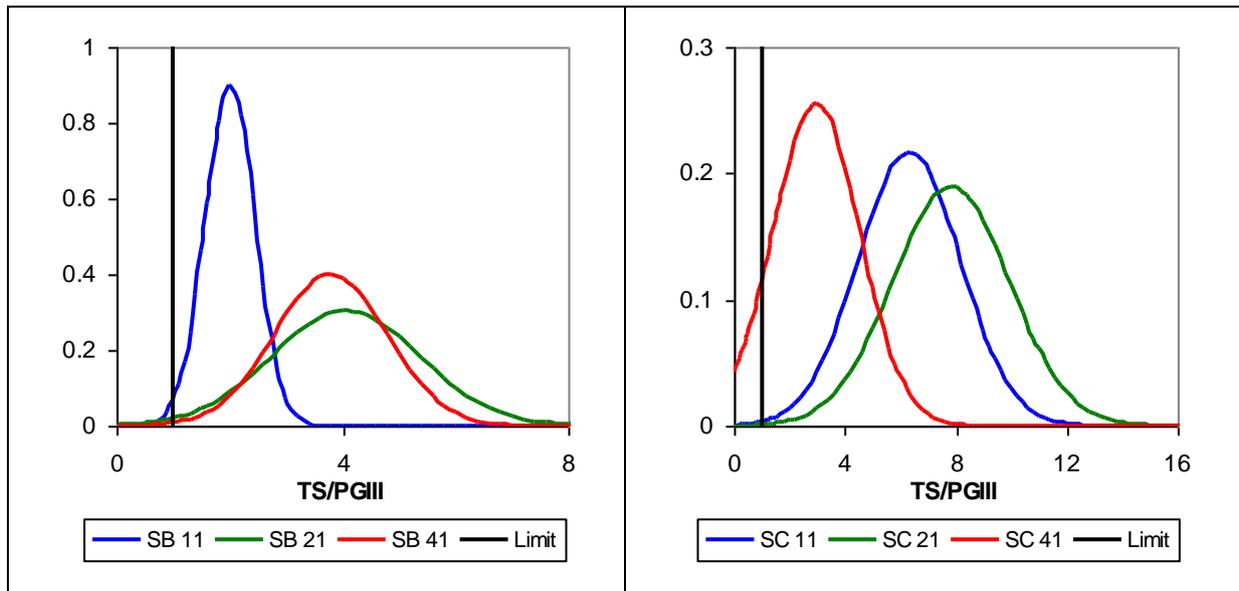


Figure 43: Distribution (histogram) for the classification of PG III regarding MLR₂₀₋₈₀
 left: sodium perborate monohydrate; right: sodium nitrate

Table 38: Probability for the false positive/negative error for the classification of PG III depending on the test sample regarding MLR₂₀₋₈₀

Test sample (TS)	Kind of error	Probability
SB 11	false negative	1 %
SB 21	false negative	1 %
SB 41	false negative	0 %
SC 11	false negative	0 %
SC 21	false negative	0 %
SC 41	false negative	10 %

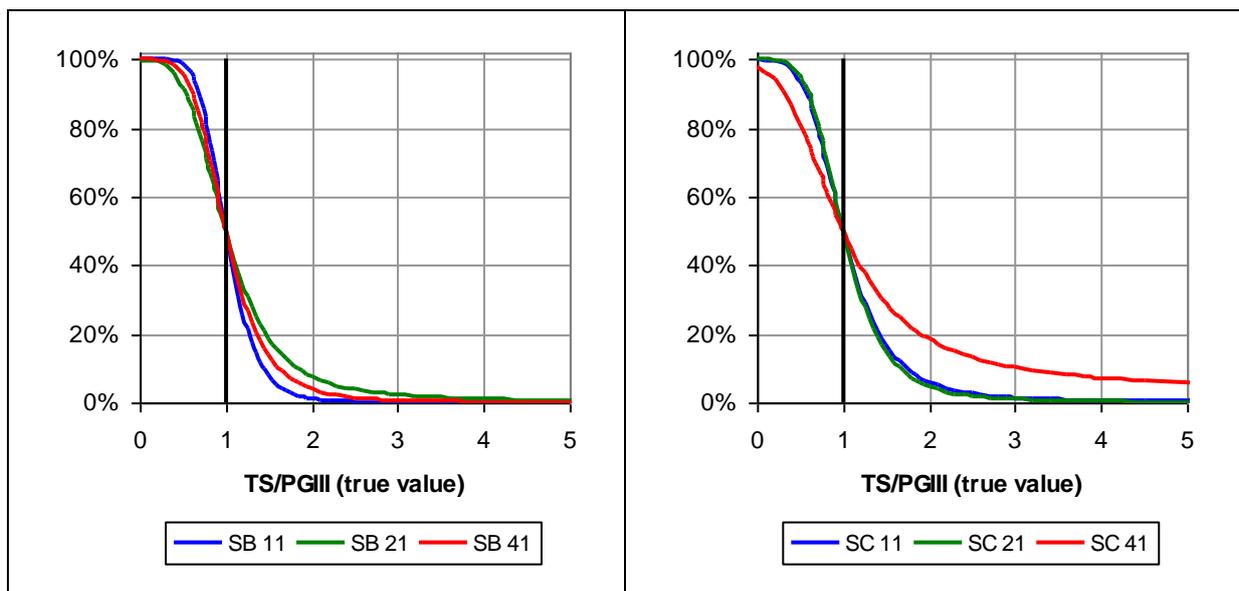


Figure 44: Probability of wrong classification (PG III) for different mass loss rates MLR₂₀₋₈₀
 left: sodium perborate monohydrate; right: sodium nitrate

The following shark profiles (Figure 45 and Figure 46) show the probability of wrong classification for an arbitrary sample of sodium perborate monohydrate or sodium nitrate. Here, the probability is presented as a function of the true mass loss rate MLR_{20-80} .

For *mass-based combustion parameters*, the shark profile is derived by folding down the part of the probability curve, which lies on the *left* side of the limit 1. Therefore the probabilities for a false negative error are now located on the right side of the maximum of the respective packing group curve (this part equals the above shown probability distributions), while the probabilities for a false positive error are located on the left side of the maximum of the respective curve.

The shark profiles for mass-based combustion parameters can be interpreted as follows (exemplarily for sodium perborate monohydrate, see Figure 45):

The increasing arm of a curve of one packing group indicates the false positive classification, 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. Whereas, the decreasing arm of a curve of one packing group indicates the false negative classification, 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 higher safety. In particular, this means:

increasing arm of packing group III (black)	test sample is assigned to packing group III, although less safety would be sufficient
decreasing arm of packing group III (black)	test sample is assigned to packing group III, although packing group II would be necessary
increasing arm of packing group II (red)	test sample is assigned to packing group II, although packing group III would be sufficient
decreasing arm of packing group II (red)	test sample is assigned to packing group II, although higher safety is necessary

Only one kind of error can occur, as long as the curves do not overlap. Therefore the crucial ranges are the ones where two curves overlap, as in Figure 45 between about 0.24 g/s and 0.84 g/s. If for example the mean mass loss rate of an arbitrary sample equals 0.5 g/s, the probability for a false positive classification with regard to packing group II (red curve), i.e. the probability to classify the test sample to packing group II instead of the “true” packing group III, equals 7 %. At the same time, for a mean mass loss rate of 0.5 g/s, there is the possibility for a false negative error as well: the probability for a false negative classification of packing group III (black curve), i.e. assigning the test sample to packing group III instead of packing group II, equals 1 %.

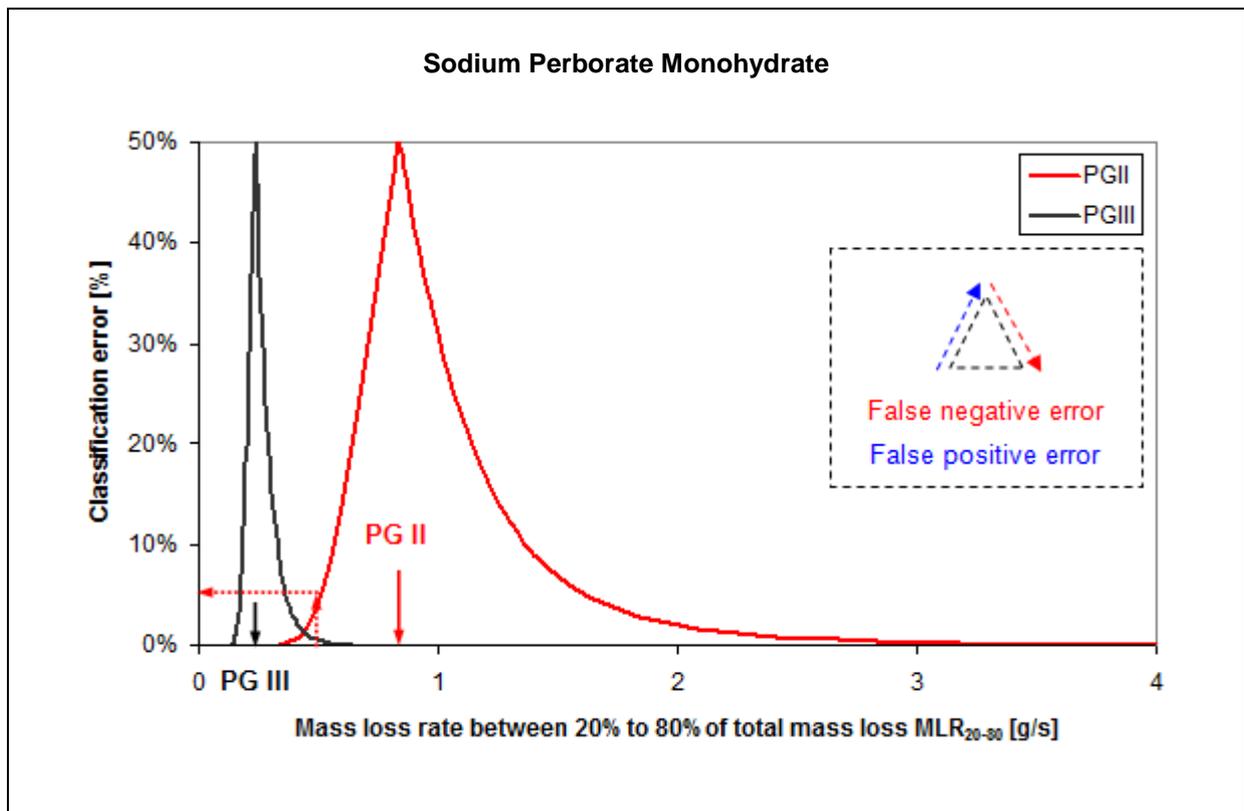


Figure 45: Shark profile for sodium perborate monohydrate and the parameter MLR_{20-80} – probability of wrong classification in PG II or PG III

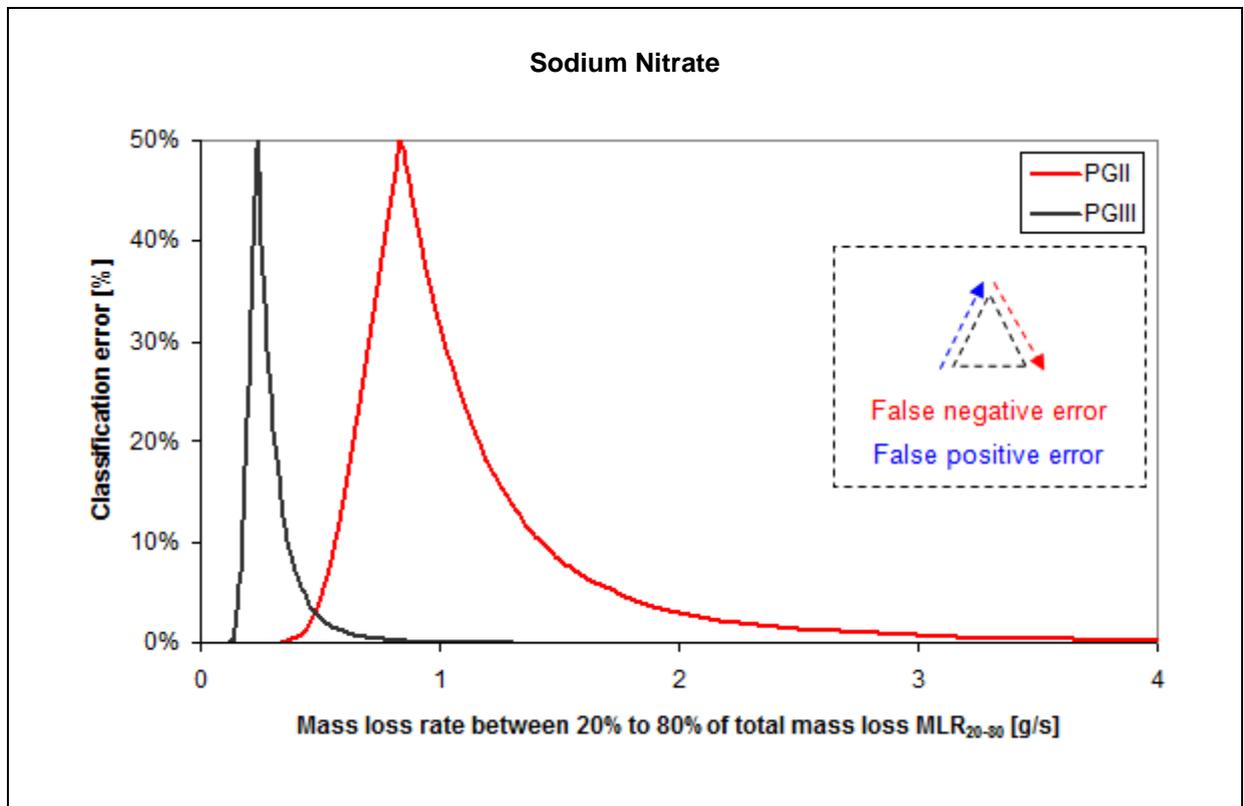


Figure 46: Shark profile for sodium nitrate and the parameter MLR_{20-80} – probability of wrong classification in PG II or PG III

6.4 Mass loss rate by linear regression within 20 % to 80 % of total mass loss

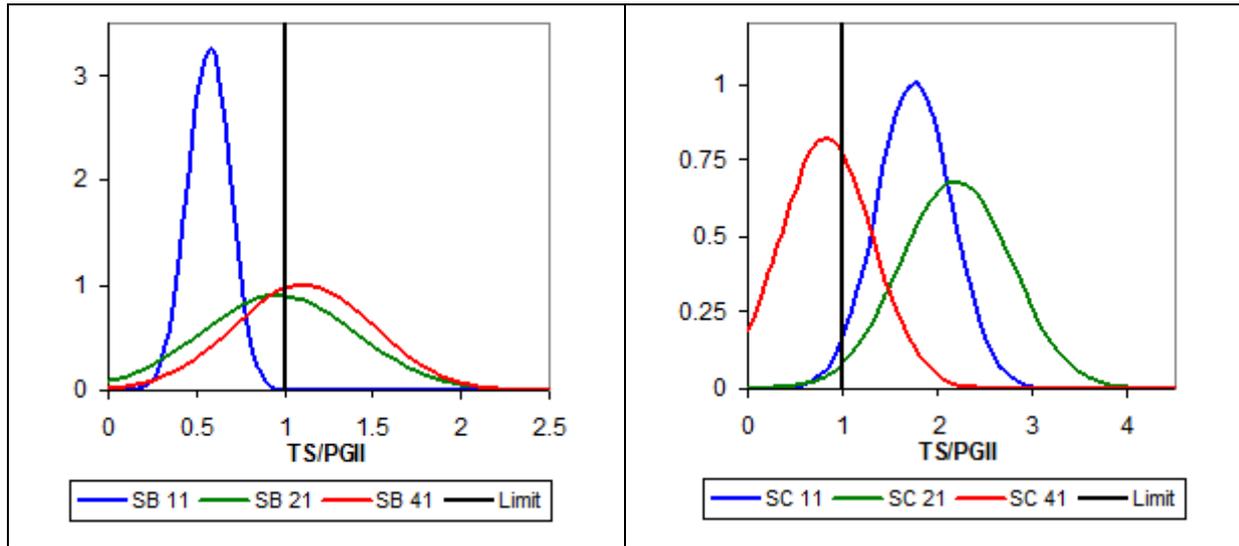


Figure 47: Distribution (histogram) for the classification of PG II regarding R^2MLR_{20-80}
 left: sodium perborate monohydrate; right: sodium nitrate

Table 39: Probability for the false positive/negative error for the classification of PG II depending on the test sample regarding R^2MLR_{20-80}

Test sample (TS)	Kind of error	Probability
SB 11	false positive	0 %
SB 21	false positive	46 %
SB 41	false negative	39 %
SC 11	false negative	3 %
SC 21	false negative	2 %
SC 41	false positive	36 %

Again the most important ratios for classification purposes and related probabilities for wrong classification are derived here from SB 11 or SC 11 (false negative error only 3 % in worst case).

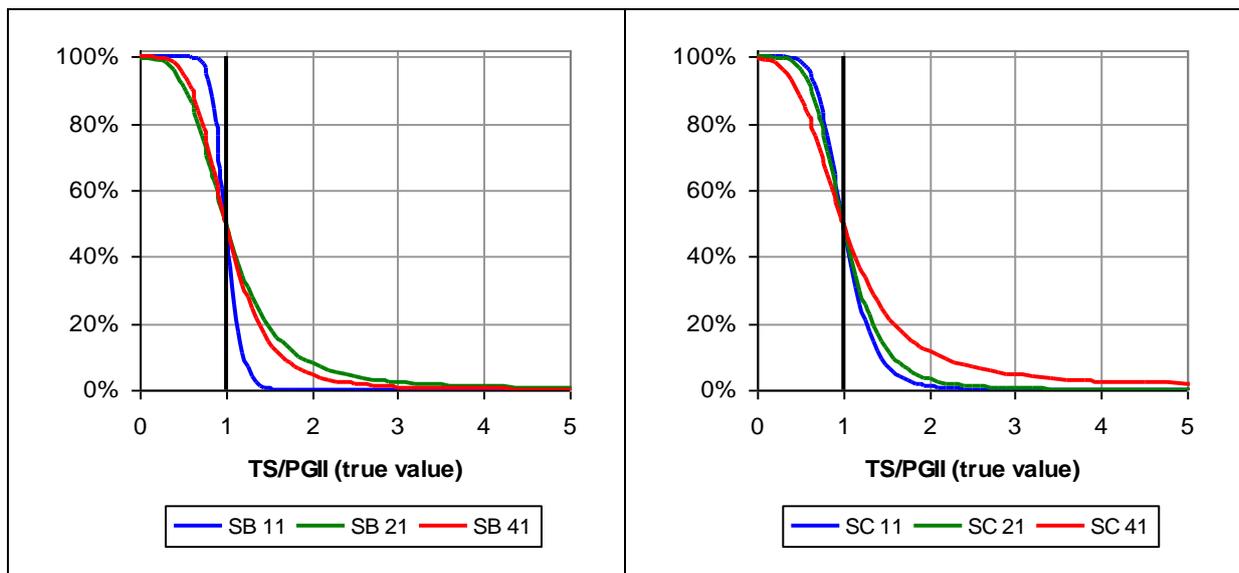


Figure 48: Probability of wrong classification (PG II) for different mass loss rates R^2MLR_{20-80}
 left: sodium perborate monohydrate; right: sodium nitrate

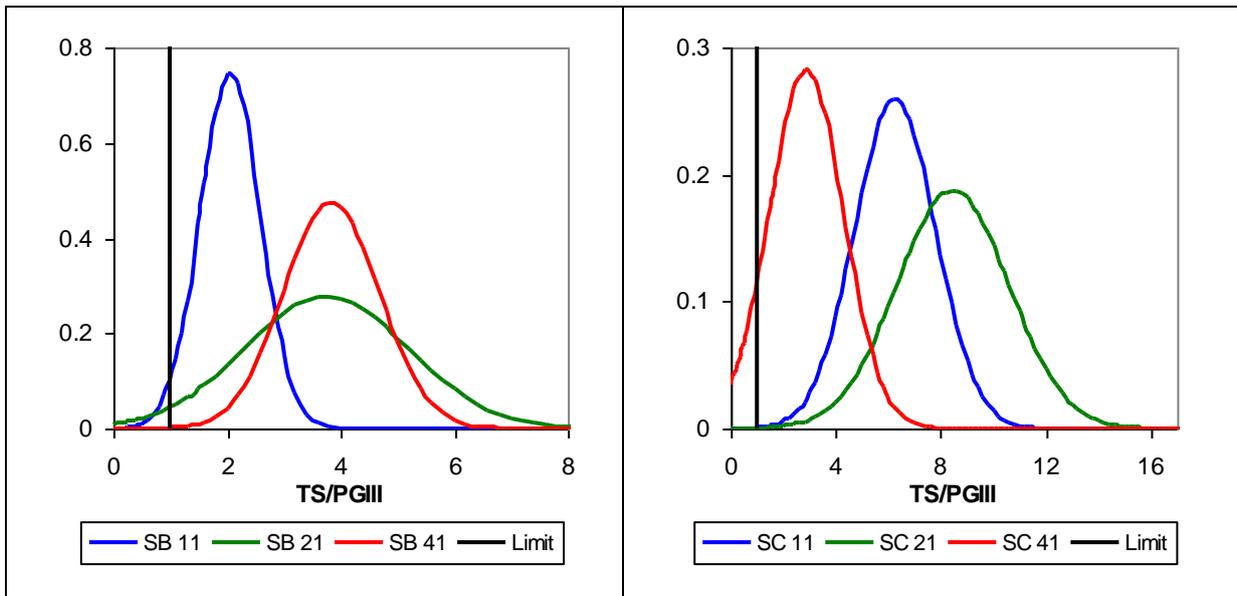


Figure 49: Distribution (histogram) for the classification of PG III regarding R^2MLR_{20-80}
 left: sodium perborate monohydrate; right: sodium nitrate

Table 40: Probability for the false positive/negative error for the classification of PG III depending on the test sample regarding R^2MLR_{20-80}

Test sample (TS)	Kind of error	Probability
SB 11	false negative	2 %
SB 21	false negative	3 %
SB 41	false negative	0 %
SC 11	false negative	0 %
SC 21	false negative	0 %
SC 41	false negative	9 %

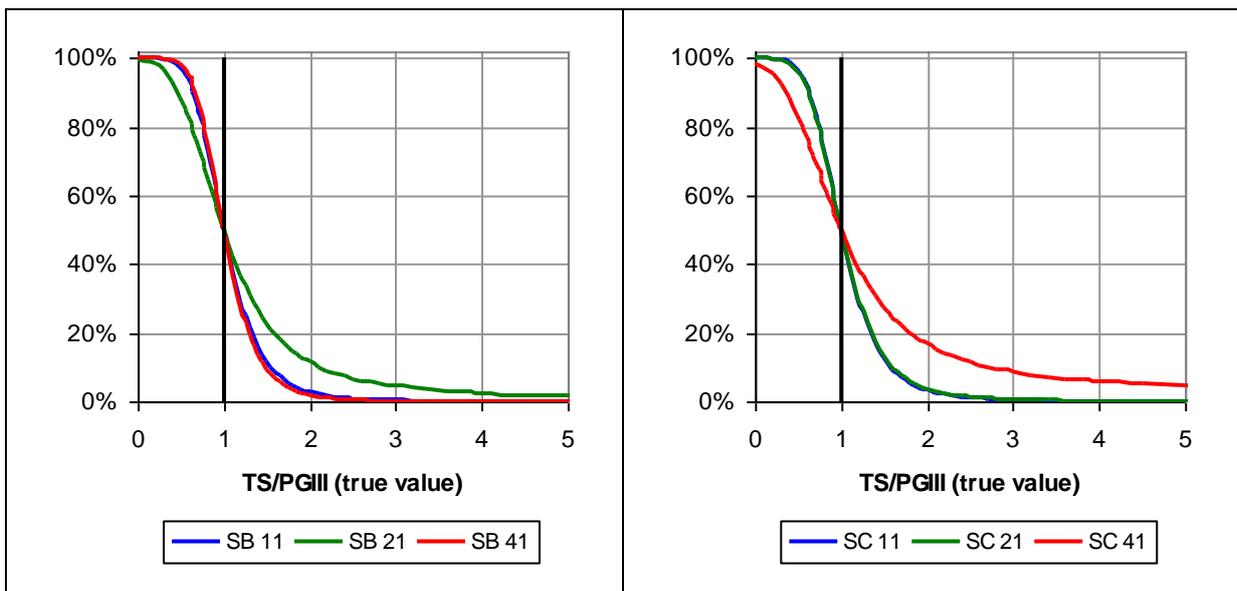


Figure 50: Probability of wrong classification (PG III) for different mass loss rates R^2MLR_{20-80}
 left: sodium perborate monohydrate; right: sodium nitrate

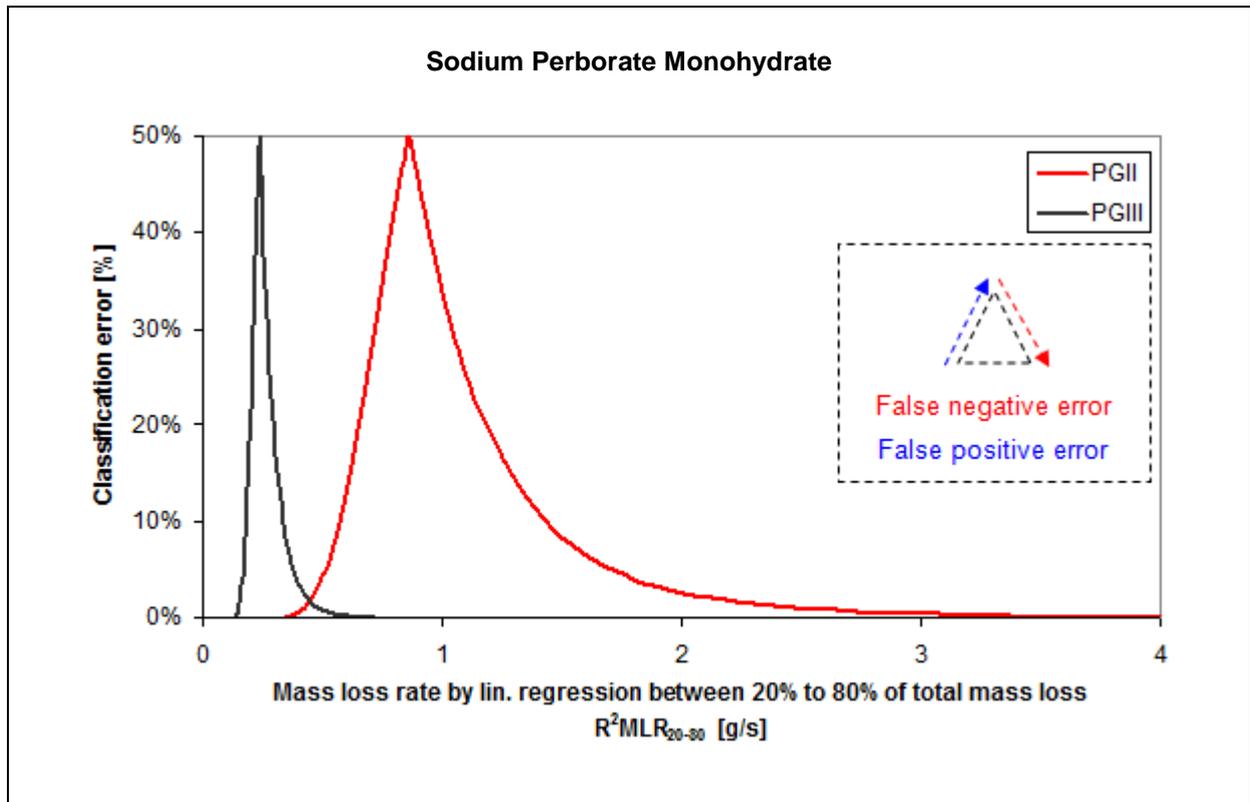


Figure 51: Shark profile for sodium perborate monohydrate and the parameter R^2MLR_{20-80} – probability of wrong classification in PG II or PG III

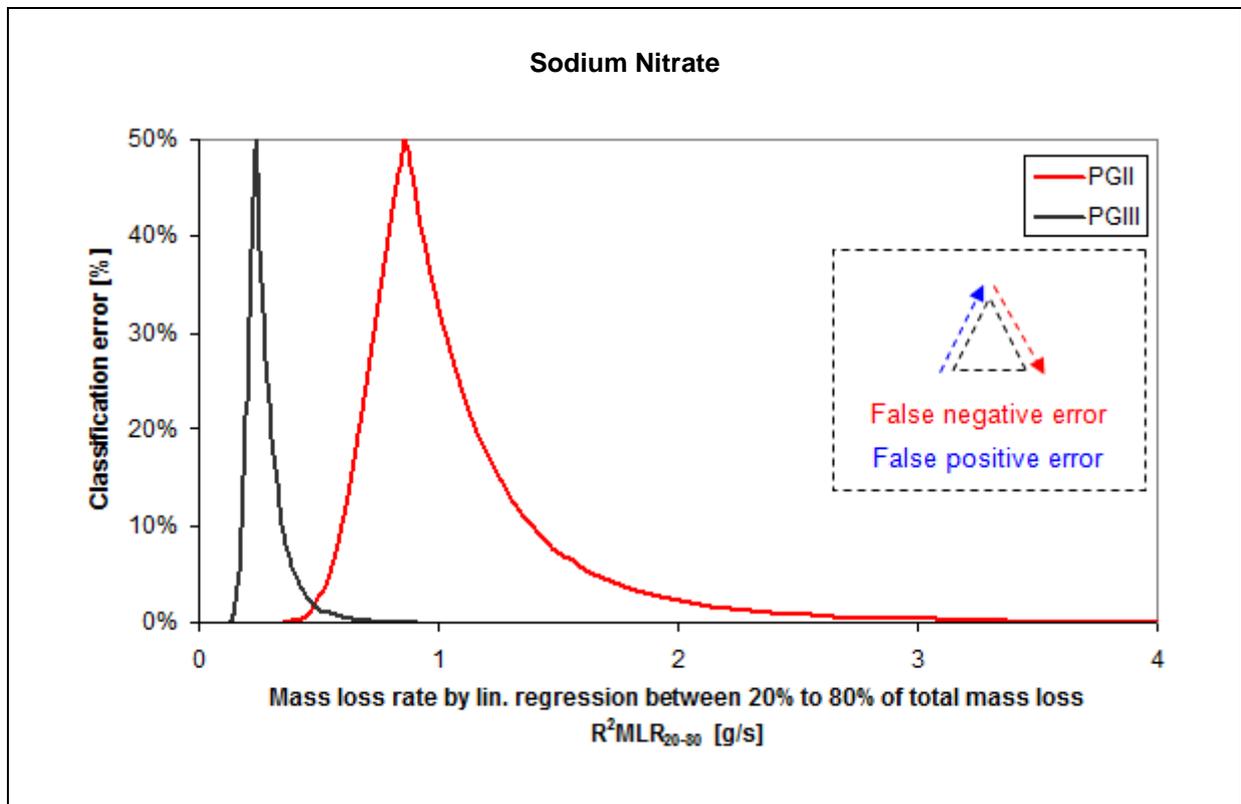


Figure 52: Shark profile for sodium nitrate and the parameter R^2MLR_{20-80} – probability of wrong classification in PG II or PG III

6.5 Consumption rate of 60 % of balanced combustible material

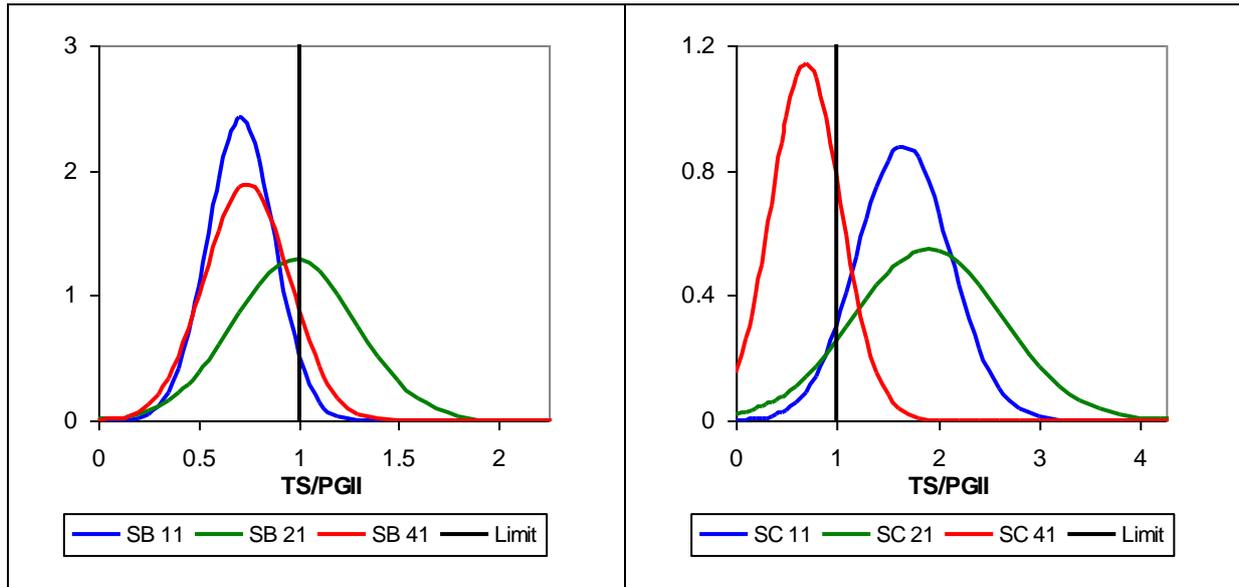


Figure 53: Distribution (histogram) for the classification of PG II regarding BR₂₀₋₈₀
 left: sodium perborate monohydrate; right: sodium nitrate

Table 41: Probability for the false positive/negative error for the classification of PG II depending on the test sample regarding BR₂₀₋₈₀

Test sample (TS)	Kind of error	Probability
SB 11	false positive	4 %
SB 21	false positive	47 %
SB 41	false positive	11 %
SC 11	false negative	7 %
SC 21	false negative	11 %
SC 41	false positive	19 %

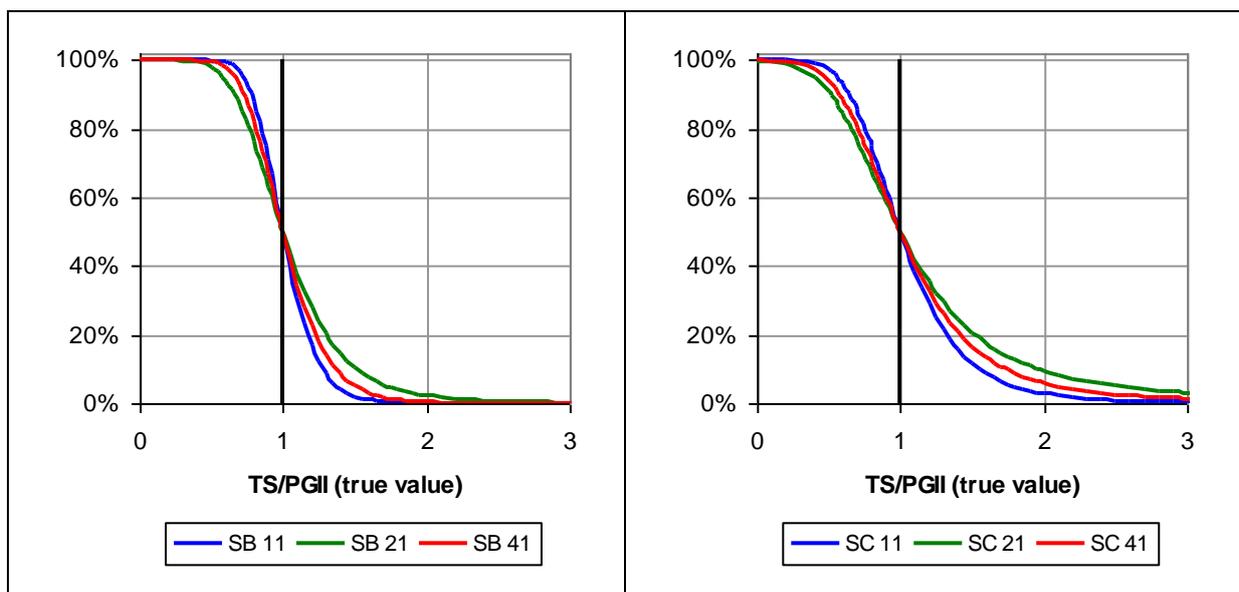


Figure 54: Probability of wrong classification (PG II) for different consumption rates BR₂₀₋₈₀
 left: sodium perborate monohydrate; right: sodium nitrate

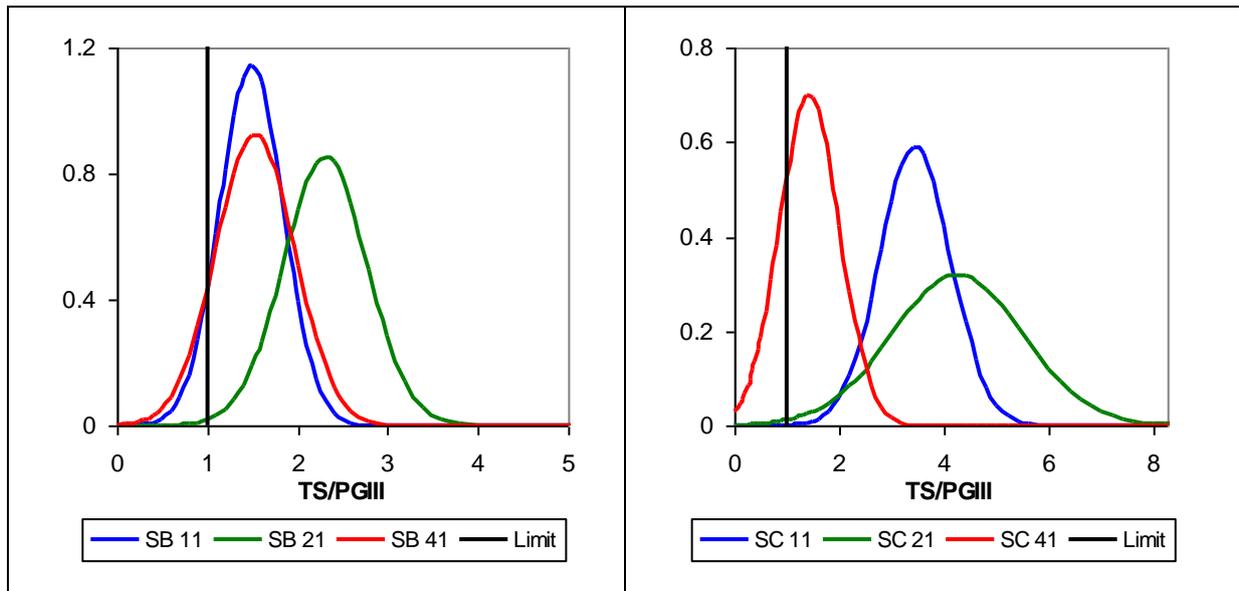


Figure 55: Distribution (histogram) for the classification of PG III regarding BR₂₀₋₈₀
 left: sodium perborate monohydrate; right: sodium nitrate

Table 42: Probability for the false positive/negative error for the classification of PG III depending on the test sample regarding BR₂₀₋₈₀

Test sample (TS)	Kind of error	Probability
SB 11	false negative	8 %
SB 21	false negative	0 %
SB 41	false negative	11 %
SC 11	false negative	0 %
SC 21	false negative	0 %
SC 41	false negative	23 %

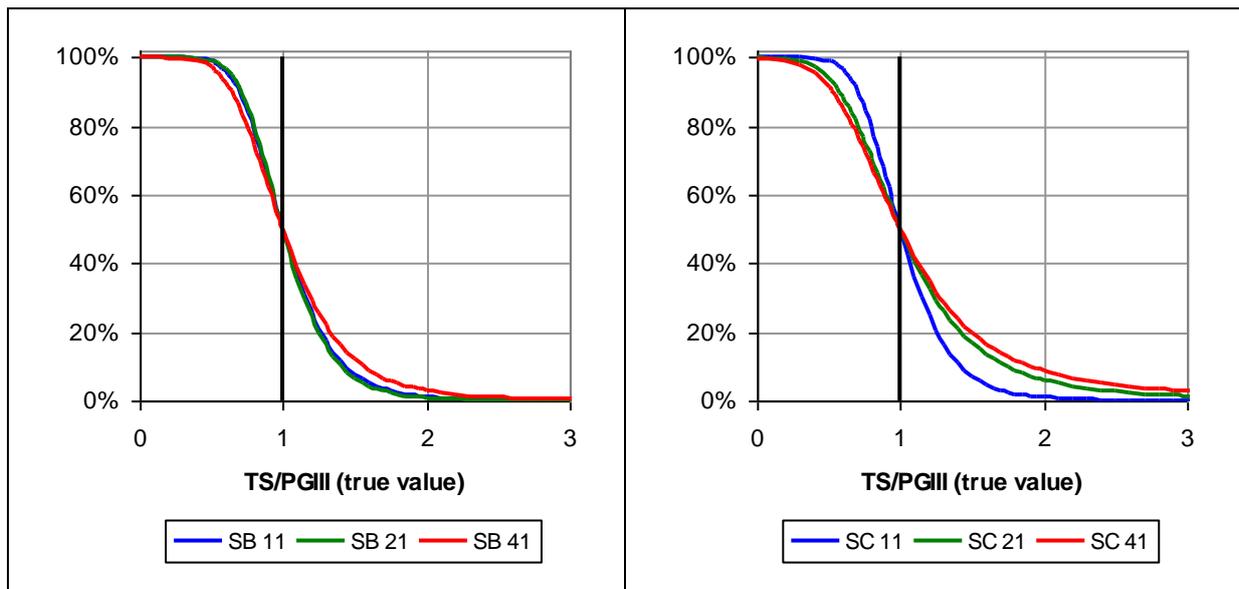


Figure 56: Probability of wrong classification (PG III) for different consumption rates BR₂₀₋₈₀
 left: sodium perborate monohydrate; right: sodium nitrate

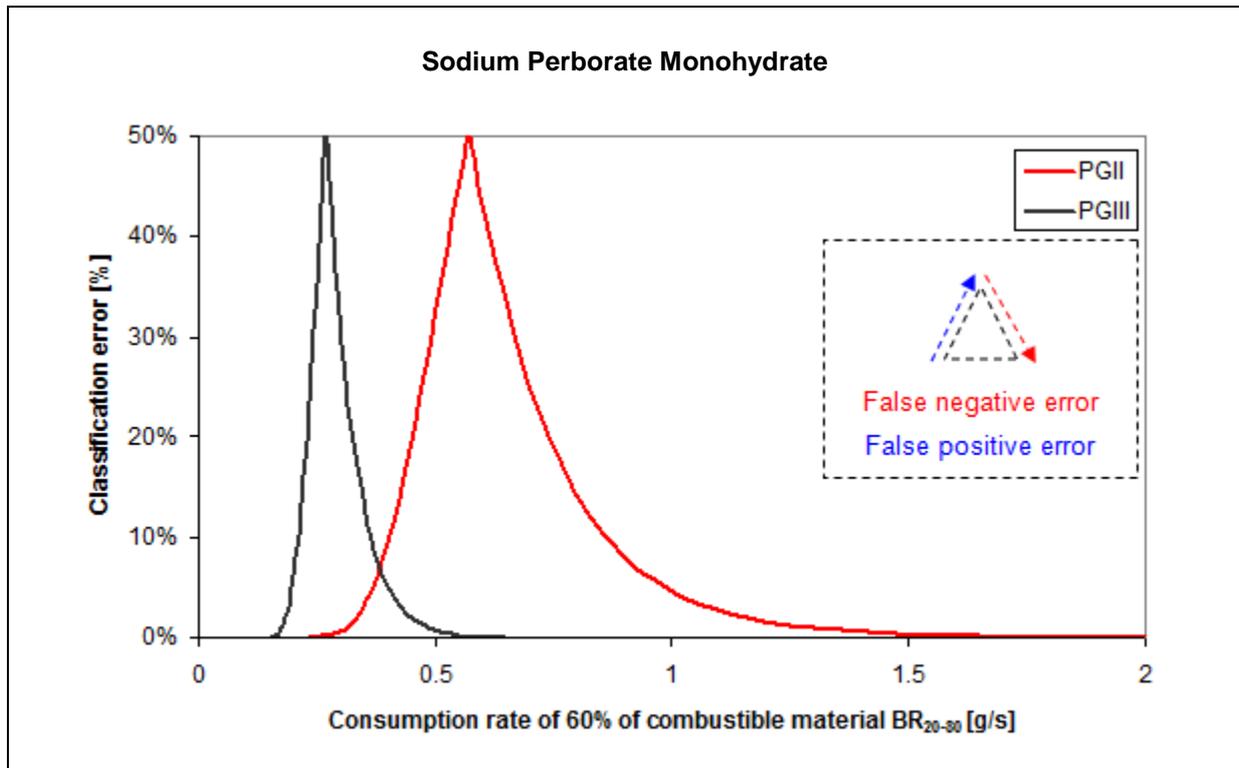


Figure 57: Shark profile for sodium perborate monohydrate and the parameter BR_{20-80} – probability of wrong classification in PG II or PG III

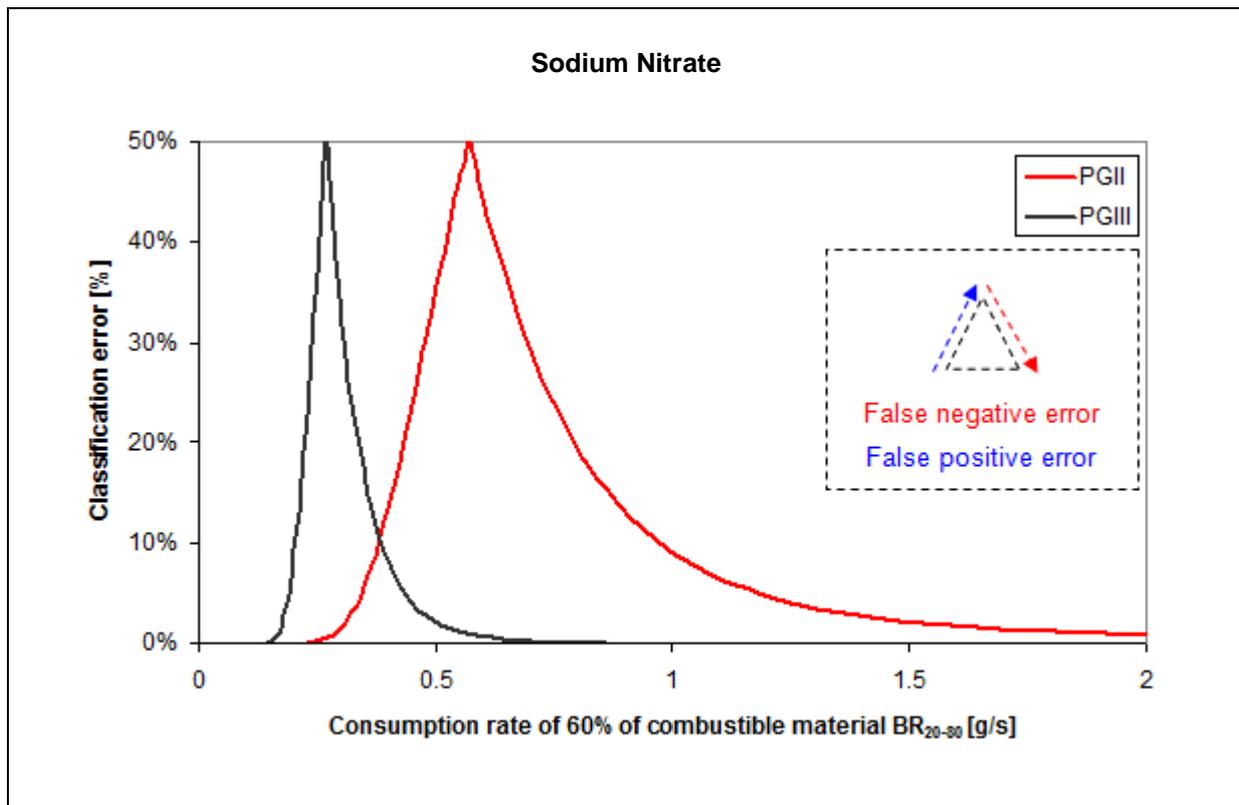


Figure 58: Shark profile for sodium nitrate and the parameter BR_{20-80} – probability of wrong classification in PG II or PG III

7 Discussion of the statistical methodology

The proceeding applied in these analyses is based on the assumption of normal distribution and equal competence of the laboratories. These assumptions may be violated especially when there are many different laboratories with very different analytical performance. Therefore – among other things – it is useful to individualise the model of classification. Then for each participating laboratory a laboratory-specific measurement uncertainty could be determined. The assessment of the laboratories would not only result from the Z scores, but directly with the probability with which a wrong classification occurs – for a given (mean) combustion parameter. The laboratory-specific classification uncertainty as well as the measurement uncertainty would become thereby a central part of the certificates for the laboratories.

For this intention, the use of robust statistical methods for the validation and measurement uncertainty is indispensable. Appropriate statistical techniques will be developed in the next years.

The proceeding applied uses also mathematical assumptions on the stochastic behaviour of the measured combustion times, e.g. it is assumed that there is a monotonic relationship between combustion time and relative standard deviation. These assumptions could be examined and adapted when more results of interlaboratory tests become available.

8 Conclusions and discussion

8.1 Conclusions regarding reproducibility and repeatability as well as laboratory performance

The analysis of the single values showed that for all parameters the lowest relative repeatability standard deviation could be obtained for the optional test sample SB 21 – except for the individual combustion time $t_{0,1}$. Here the respective relative repeatability standard deviation is the smallest for the optional test sample SC 21. For the relative reproducibility standard deviation the results are not as clear as for the relative repeatability standard deviation, now, the smallest values are obtained for the three test samples SB 21, SB 41 and SC 21 – depending on the parameter considered. It is noticeable that the smallest values of the precision measures have not been obtained for the test reference mixtures but for the test samples. Thereby it should be noted that SB 21 and SC 21 were optional samples, which have been analysed by only 8 of the 12 laboratories and furthermore, the values of laboratory 05 for sample SC 21 had to be excluded prior the analyses due to implausibility.

The highest values of the relative repeatability standard deviation and the relative reproducibility standard deviation for all five parameters can be observed for the test sample SC 41 – except for the relative repeatability standard deviation of the individual combustion times, where this applies to test sample SC 11.

Regarding the ratios of the laboratory mean values the smallest values for the relative reproducibility standard deviation is obtained for the ratio of the two packing groups III and II for the three parameters t_{20-80} , MLR_{20-80} and $R^2 MLR_{20-80}$. The highest values can be observed for the three ratios including SC 41 (SC 41 / SA PG I, SC 41 / SA PG II and SC 41 / SA PG III) and for SC 21 / SA PG II and SC 21 / SA PG III.

It can be concluded that the variability of the ratios is not clearly below the variability of mean combustion times 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 time themselves.

As for the single measurement values, regarding the performance of the laboratories it can be stated that laboratory 04 proved to be an outlier laboratory very often – mainly for the test samples. Laboratories 02 and 11, however, never exhibited a significantly higher variability or significantly deviating mean values.

Regarding the Z scores for the ratios of the laboratory mean values, especially laboratories 04, 05 and 09 failed the quality criterion clearly more often than the remaining laboratories. The rates (number of significant Z scores divided by all available Z scores of the respective laboratory) are given in the following Table 43.

Table 43: Rates of significant Z scores

Laboratory	Rate of significant Z scores
1	2.22%
2	1.37%
3	1.37%
4	9.59%
5	14.52%
6	0.00%
8	5.48%
9	9.59%
10	0.00%
11	6.67%
13	2.74%
14	2.74%

However, it has to be noted that all laboratories accomplished to obtain a rate of more than 80 % which is a common limit and especially laboratories 06 and 10 never exhibited any significant Z score.

Assessing only reproducibility, repeatability or laboratory performances as discussed, no significant improvement of the current test method by introduced gravimetric approach compared to simple time-take (individual combustion time $t_{0.1}$) can be outlined here. Nevertheless, this statistical fact may underline as well the robustness and practicability of the proposed test modification in consideration of the fact of almost unacquainted users involved in this round robin test.

8.2 Conclusion regarding the reference oxidizer CaO_2

In the last round robin test in 2005/2006, as reference oxidizer potassium bromate was used, whereas in the current round robin test 2009 calcium peroxide was used. In order to compare these two oxidizers, the individual combustion time $t_{0.1}$ is considered because only for this parameter measurement values are available for all three packing groups.

In the round robin test in 2005/2006 only the test substance sodium perborate monohydrate with mixtures 1:1 and 4:1 were considered, and 10 laboratories had performed the test (in 2009: 12 laboratories). The following Table 44 summarizes the mean values as well as the relative reproducibility standard deviations of the ratios of the mean individual combustion times and also of the three packing groups of the two round robin tests. Regarding the mean values, only small differences can be observed between the results of the two round robin tests. Furthermore Table 44 outlines as well that the adjusted intrinsic oxidizing potential of calcium peroxide in mixture with cellulose in proposed ratios for packing group III to I describes previous potentials adequately.

For the four ratios SB 11 / PG II, SB 41 / PG I, SB 41 / PG II, SB 41 / PG III and the packing groups PG I and PG II, the mean values obtained in the current round robin test are smaller than the mean value of the 2nd round robin test, whereas for the ratio SB 11 / PG I and the packing group PG II the respective mean values are greater the mean value of the 2nd round robin test. However, only for the ratio SB 41 / PG II the difference is statistically significant (significance level 5 %). The mean value for the ratio SB 11 / PG III is identical in both round robin tests.

As for the relative reproducibility standard deviation, noticeable differences between the results of the two round robin tests can be seen. For four ratios, the relative reproducibility standard deviation of the 3rd round robin test in 2009 is higher than for the 2nd round robin test. However, only for ratio SB 11 / PG I this difference is statistically significant at a significance level of 5%. For the two ratios SB 11 / PG II and SB 41 / PG I a decrease of the relative standard deviations from the 2nd round robin test to the 3rd can be observed. However, the difference is only for SB 41 / PG I statistically significant (significance level 5 %). For this ratio, the decrease from 61.57% to 9.02% is very striking. For all three packing groups, the relative reproducibility standard deviation of the 3rd round robin test in 2009 is smaller than for the 2nd round robin test. For packing group PG I, the decrease from 55.18% to 17.83% is even statistically significant (significance level 5 %).

In summary, the relative reproducibility standard deviation for the results of the 3rd round robin test in 2009 is less than 30 % in all cases, so that the applied method can be regarded as validated.

Table 44: Comparison of the results of individual combustion time ratios of the UN O.1 round robin test in 2005/2006 and in 2009

	Mean		Relative reproducibility s.d.	
	potassium bromate (2005/2006)	calcium peroxide (2009)	potassium bromate (2005/2006)	calcium peroxide (2009)
SB 11 / PG I	5.47	5.48	11.14%	22.58%
SB 11 / PG II	1.29	1.07	33.39%	20.35%
SB 11 / PG III	0.46	0.46	11.13%	16.75%
SB 41 / PG I	3.28	3.17	61.57%	9.02%
SB 41 / PG II	0.75	0.59	25.86%	26.34%
SB 41 / PG III	0.29	0.26	16.26%	21.70%
PG I	12.82 s	9.75 s	55.18%	17.83%
PG II	44.60 s	51.07 s	28.54%	16.65%
PG III	120.50 s	119.63 s	16.38%	15.51%

The extreme decreasing of the relative reproducibility standard deviation of the ratio SB 41 / PG I positively affects the shark profiles as can be seen in Figure 59 (shark profile of 2005/2006) and Figure 60 (shark profile of 2009) regarding the overlapping of the curves for PG I and PG II. As explained in Section 6.1, the range of the combustion times, where the curves overlap, are the critical ranges. For these ranges two kinds of error may occur, a false positive and a false negative classification with regard to two different packing groups. For the 3rd round robin test in 2009, the curves of PG I and PG II do

not overlap, therefore solid oxidizers with an individual combustion time up to approximately 55 s may be classified wrongly into one packing group only – up to 25 s only into packing group I and between 25 s and 55 s only into packing group II. Especially, for a mean individual combustion time of 25 s, no error at all has to be expected. However, in the 2nd round robin test in 2005/2006, an overlapping of the curves can be observed, therefore for the range of 55 s and 175 s there is the possibility of two kinds of wrong classification. Furthermore, for no individual combustion time the probability for any error equals 0, not even for the ideal combustion time between two packing groups – the point of intersection of the respective curves.

If the curves of two packing groups lie closely together and the curves overlap in a certain range of combustion time and if the probability at the point of intersection is not 0 or at least close to 0, then the discriminatory power of the method is too low. In the 3rd round robin test in 2009, for packing groups I and II the probability at the point of intersection equals 0 %, i.e. the discriminatory power between packing group I and II is ideal. Whereas in the 2nd round robin test in 2005/2006 the probability equals 8 % and therefore the discriminatory power is clearly worse. For packing groups II and III, the probability for wrong classification at the point of intersection equals 3.2 % for the 2nd round robin test and is slightly higher (4.8 %) for the 3rd round robin test.

Closing this issue it can be stated as well that in consideration of the sharpness of figured shark profiles for PG III in comparison of both round robin studies, the possibility of wrong classification or error of false positives (classification of tested solid as a dangerous good of Subdivision 5.1, PGIII, although sample should be excluded from classification – NOT 5.1) has slightly been increased, but remains below 5 % at 200 s and gets swiftly close to zero at 300 s.

It has to be noted that for the shark profile of 2009 only the test samples SB 11 and SB 41 are taken into account. Hence, this shark profile differs from the shark profile in Figure 33, where also the test sample SB 21 has been taken into account.

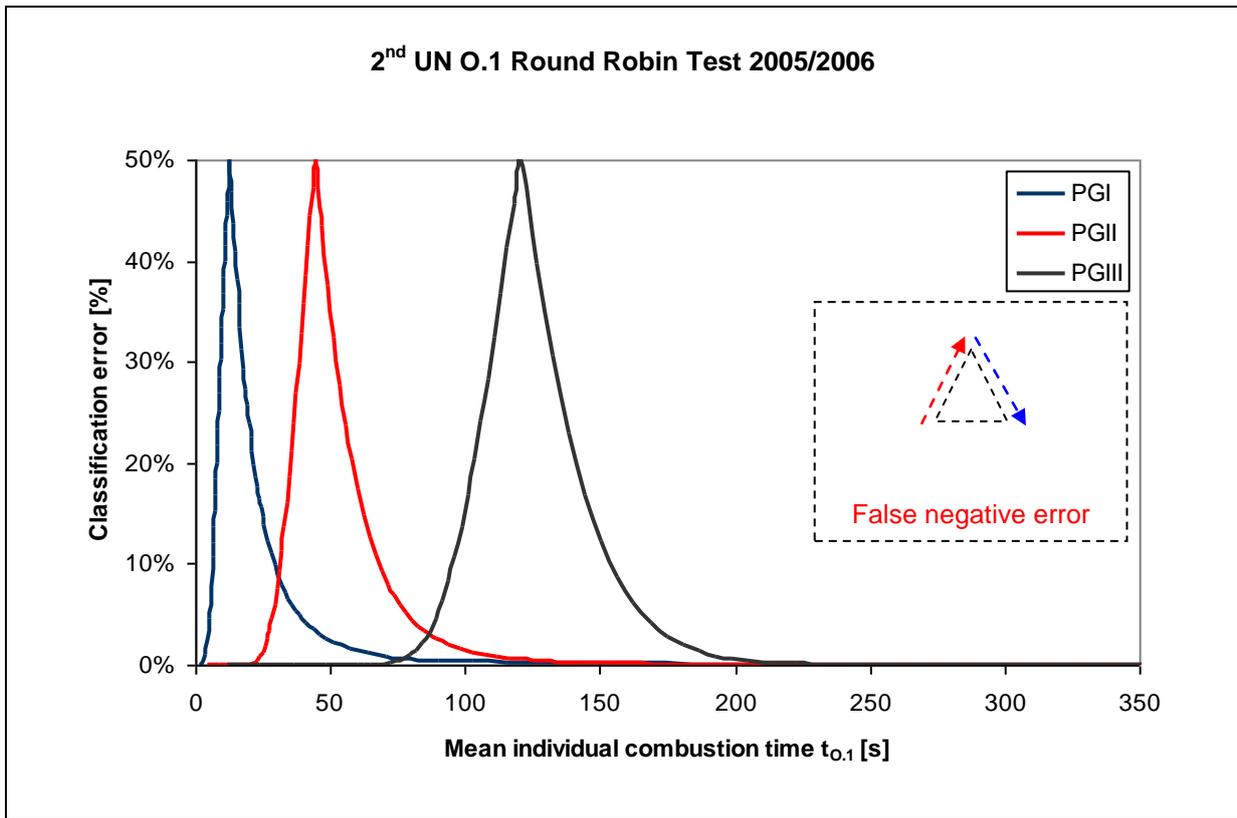


Figure 59: Shark profile for the individual combustion time $t_{0,1}$ and the test samples SB 11 and SB 41 in 2005/2006 – probability of wrong classification in PG I, PG II and PG III

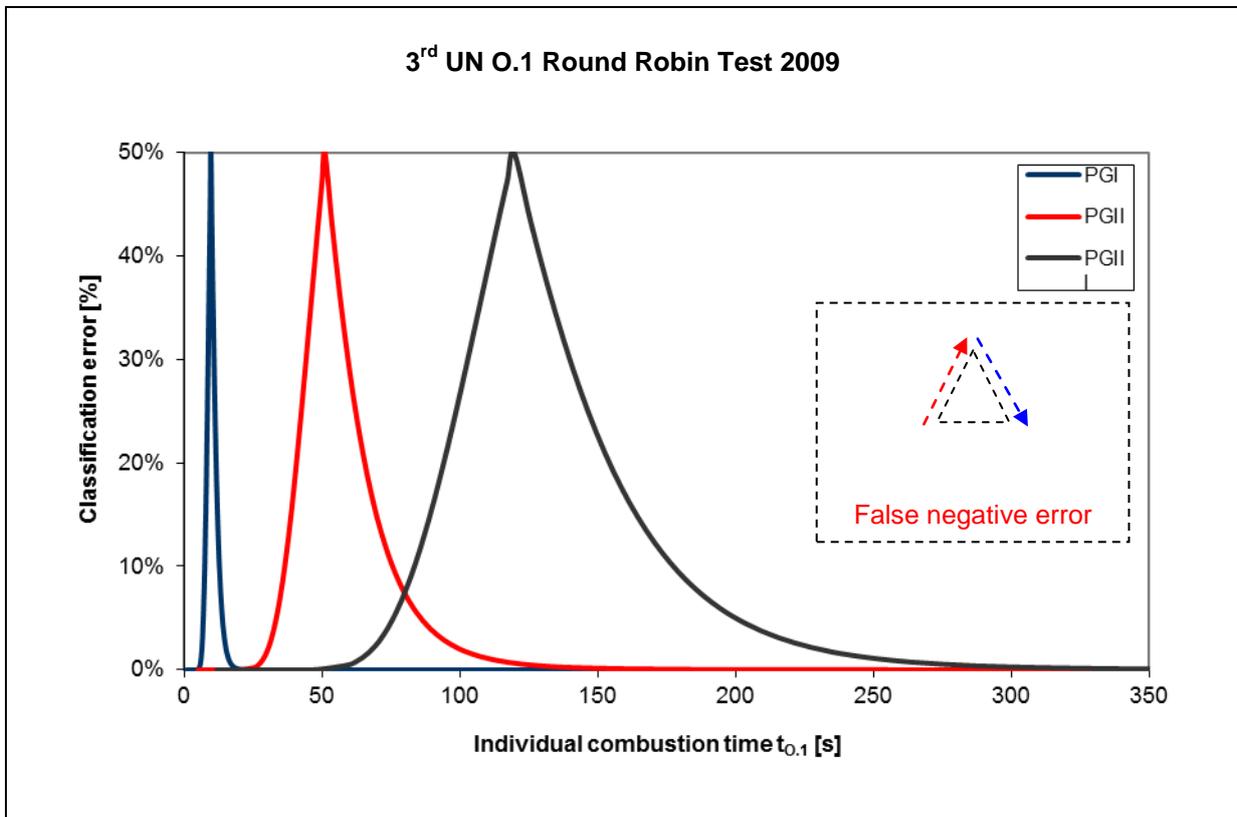


Figure 60: Shark profile for the individual combustion time $t_{0,1}$ and the test samples SB 11 and SB 41 in 2009 – probability of wrong classification in PG I, PG II and PG III

As can be seen in Table 44, the mean individual combustion times of the three packing groups are for both oxidizers, potassium bromate and calcium peroxide, nearly the same, but the relative reproducibility standard deviation is for all three packing groups smaller for calcium peroxide than for potassium bromate. Furthermore, with calcium peroxide as reference oxidizer an overall better discriminatory power compared to potassium bromate can be obtained.

- ❖ Therefore, it is highly recommendable to use calcium peroxide instead of potassium bromate as reference oxidizer for classification purposes of solid oxidizers according to the regulations on the transport of dangerous goods (UN O.1). It seems mandatory for any future test performances to ensure comparable qualities of calcium peroxide batches as tested and proofed by the ad-hoc working group.

8.3 Conclusions regarding the classification parameters

Besides others, a crucial goal of this round robin test was to find a combustion parameter, which provides:

1. a possibly better classification of solid oxidizers according to the regulations on the transport of dangerous goods than the individual combustion time $t_{0,1}$ and
2. perfect correspondence to the given definition of solid oxidizers by the United Nations and related TDG/GHS regulations.

The individual combustion time $t_{0,1}$ can be considered as a subjective parameter because each operator has another assessment for himself what the starting and end time of the combustion procedure is. Unambiguous instructions to describe 'end-point' of main combustion cannot be given by any detailed test method in consideration of the huge application field of pure or formulated oxidizing solids in chemistry, agriculture, detergents or household articles. This fact may become even more important due to the fact that any classification of oxidizing solids do not require any external expertise or permission by e.g. national authorities, compared to dangerous goods like explosives, organic peroxides or self-reactive substances to be transported.

Therefore, in the current round robin test, the following objective parameters have been considered:

- main combustion time t_{20-80}
- mass loss rate within 20% to 80% of total mass loss MLR_{20-80}
- mass loss rate by linear regression within 20 % to 80 % of total mass loss $R^2 MLR_{20-80}$.
- consumption rate of 60% of balanced combustible material BR_{20-80} .

The mass loss rates MLR_{20-80} and $R^2 MLR_{20-80}$ involve 60% of the whole consumed mass of tested solid and combustibles, whereas the consumption rate BR_{20-80} involves only the consumption of the balanced combustible material, in line with given UN definition. It can be assumed here to some respect that both proposed mass loss rate criteria (MLR) may be at least partly impacted by e.g. thermally unstable, crystal – water containing or deflagrative substances in blends, although those ingre-

dients may not have any oxidizing or further hazardous properties at all. Therefore no assessment on objectivity of such proposed criteria can be given here just from a statistical point of view and should be postponed to the expertise of safety experts and honoured authorities involved.

It was expected that the main combustion time t_{20-80} provides better results than the individual combustion time $t_{0,1}$ because for t_{20-80} only the main combustion time is being considered and the errors occurring in the initial phase and the final phase. Against these expectations, the results for the individual combustion time proved to be rather more accurate regarding the relative reproducibility standard deviations – for all ratios considered (see Figure 61).

As far as results actually pay respect due to e.g. training effects as well cannot be answered here sufficiently for the moment. This has to be postponed to further round robin testing by repeating tests ensuring trained lab assistants on introduced modified test method UN O.1 (gravimetric approach).

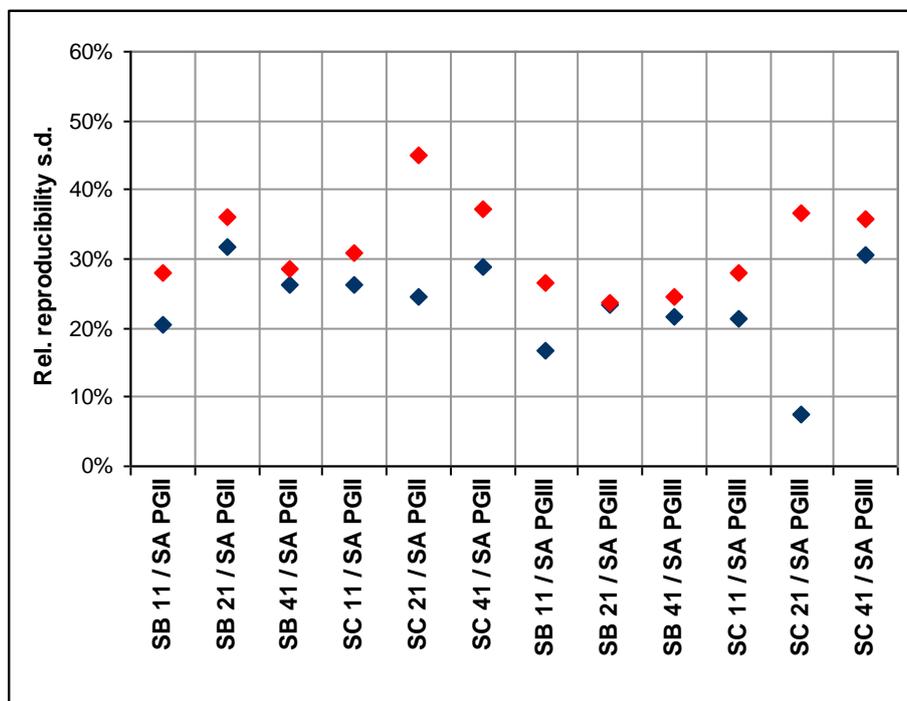


Figure 61: Comparison of the relative reproducibility standard deviations of the ratios of the individual combustion times $t_{0,1}$ (blue) and the main combustion times t_{20-80} (red)

When considering the average of the relative reproducibility standard deviations over all ratios, the value for the mean individual combustion time $t_{0,1}$ is also the lowest compared to the values of the other four combustion parameters. It has to be noted that for this comparison only the packing groups II and III can be taken into account, because for packing group I only measurements for the individual combustion time are available but not for the other four parameters as explained in chapter 4.1 *Background*. Nevertheless all determined relative reproducibility standard deviations as calculated for time-based or mass-based parameters are within common standard tolerance limits.

However, in order to find a suitable combustion parameter, not the relative reproducibility standard deviation is crucial but the shark profiles because the respective reproducibility standard deviations may be adjusted by changing the applied measuring method.

As explained before, the more curves in the shark profiles overlap the higher is the error of wrong classification. The amount of overlapping can be characterized by the probability at the point of intersection of two curves, where the probabilities for both kinds of error are in balance. Of course, if there is no overlapping, this probability equals zero.

In Table 45 for each of the five combustion parameters the respective probabilities for wrong classification at the point of intersection between packing groups II and III are listed separately for the test samples sodium perborate monohydrate and sodium nitrate. It has to be kept in mind that a comparison of the combustion parameters is possible only for packing groups II and III because for packing group I only the parameter $t_{0,1}$ had been determined.

Table 45: Lowest probability of wrong classification depending on the combustion parameter and on the test sample for packing groups II and III (reference oxidizer: calcium peroxide)

Combustion parameter	Lowest probability for wrong classification	
	Sodium perborate monohydrate	Sodium nitrate
$t_{0,1}$	7.4 %	9.6 %
t_{20-80}	5.5 %	16.0 %
MLR_{20-80}	1.3 %	3.0 %
$R^2 MLR_{20-80}$	1.7 %	1.8 %
BR_{20-80}	7.0 %	10.4 %

It can clearly be seen that at least for both tested solids, the proposed combustion parameters regarding the mass loss rate exhibit the lowest probabilities for wrong classification: For sodium perborate monohydrate with the mass loss rate within 20 % to 80 % of total mass loss (MLR_{20-80}) the lowest probability for wrong classification can be achieved; for sodium nitrate the lowest probability for wrong classification can be achieved by the parameter mass loss rate by linear regression within 20% to 80% of total mass loss ($R^2 MLR_{20-80}$).

Comparing the individual combustion time $t_{0,1}$ and mass-based parameters, especially MLR_{20-80} , the latter exhibits a better discriminatory power as it can be seen in Table 45 by means of the lowest probability for wrong classification – although the mean relative reproducibility standard deviation is higher.

Finally, it can be concluded here, that the mass loss-based parameters yield improved results regarding the discriminatory power and the probabilities of wrong classification compared to only time-based parameters, regardless to addressed limitations for such parameters as mentioned before (see top of previous page). Anyway, the burning rate criterion BR_{20-80} is from a statistical point of view at least as powerful as currently the established combustion time criterion $t_{0,1}$ in terms of reproducibility, repeatability or discriminatory power.

As a second overall conclusion it can be stated here clearly:

- ❖ In regard to improved discriminatory power of the modified test method, the implementation of gravimetric approach as developed and introduced by the ad-hoc working group and IGUS EOS is highly recommendable according to introduced round robin findings.

8.4 Conclusions regarding final classification based on different criteria

The following tables (Table 46, Table 47, Table 48 and Table 49) give a comparison of all related final classifications of tested solids sodium perborate monohydrate and sodium nitrate derived from time-based parameters (see Table 13 for $t_{0.1}$ and Table 16 for t_{20-80}). The final classifications for both tested solids as derived from mass-loss based parameters MLR_{20-80} and BR_{20-80} can be found in Table 19 and Table 22, respectively. For classification purposes, the fastest mean from all tested sample mixtures is taken into account compared to related packing group references for weak and medium oxidizers as described in UN test method. It has to be noted that laboratories with outlying values will be only regarded for final classification in a restricted way.

Table 46: Final classification by the time-based parameter $t_{0.1}$

Laboratory	$t_{0.1}$ [s]				assigned class for SB 41 and SC 41
	SA PG III	SA PG II	SB 41	SC 41	
01	117	61	33	24	5.1, PGII
02	129	52	27	26	5.1, PGII
03	125	49	33	23	5.1, PGII
04	142	66	35	35	5.1, PGII
05	134	52	24	13	5.1, PGII
06	113	53	33	26	5.1, PGII
08	119	-*	27	31	-**
09	-*	44	30	20	5.1, PGII
10	114	54	27	25	5.1, PGII
11	102	45	36	36	5.1, PGII
13	100	40	30	24	5.1, PGII
14	104	49	29	36	5.1, PGII

*) All single values of this laboratory have been identified as outliers (see also Table 13).

**) No proper classification due to outliers possible.

Table 47: Final classification by the time-based parameter t_{20-80}

Laboratory	t_{20-80} [s]				assigned class for	
	SA PG III	SA PG II	SB 41	SC 41	SB 41	SC 41
01	45	19	8	9	5.1, PGII	5.1, PGII
02	54	19	8	10	5.1, PGII	5.1, PGII
03	51	17	9	8	5.1, PGII	5.1, PGII
04	46	17	12	-*	5.1, PGII	-**
05	-*	20	10	7	5.1, PGII	5.1, PGII
06	43	18	10	8	5.1, PGII	5.1, PGII
08	44	16	9	13	5.1, PGII	5.1, PGII
09	65	14	11	7	5.1, PGII	5.1, PGII
10	44	18	9	10	5.1, PGII	5.1, PGII
11	40	14	11	11	5.1, PGII	5.1, PGII
13	39	11	10	8	5.1, PGII	5.1, PGII
14	39	15	9	17	5.1, PGII	5.1, PGIII

*) All single values of this laboratory have been identified as outliers (see also Table 16).

**) No proper classification due to outliers possible.

In consequence, all laboratories would clearly classify sodium perborate monohydrate (12/12) and sodium nitrate (10/11) as medium oxidizers by time-based parameters. Both solids officially are classified as weak oxidizers by UN list.

According to these findings, time-based data would not differ in terms of determined intrinsic oxidizing potential of both oxidizers in comparison. No assessment – neither on validity nor on reliability – can be derived here just from a statistical point of view. Any evaluation of classification results must be postponed to experienced safety experts at IGUS EOS.

Table 48: Final classification by the mass-based parameter MLR₂₀₋₈₀

Laboratory	MLR ₂₀₋₈₀ [g/s]				assigned class for	
	SA PG III	SA PG II	SB 41	SC 11	SB 41	SC 11
01	0.27	0.73	1.05	1.51	5.1, PGII	5.1, PGII
02	0.20	0.67	0.99	1.24	5.1, PGII	5.1, PGII
03	0.19	0.67	0.88	1.15	5.1, PGII	5.1, PGII
04	0.23	0.91	0.63	-*	5.1, PGIII	-**
05	0.18	0.57	0.99	1.75	5.1, PGII	5.1, PGII
06	0.25	0.77	-*	1.34	-**	5.1, PGII
08	0.24	0.90	0.94	1.66	5.1, PGII	5.1, PGII
09	0.20	0.98	0.86	1.51	5.1, PGIII	5.1, PGII
10	0.25	0.76	0.90	1.06	5.1, PGII	5.1, PGII
11	0.30	1.02	0.81	1.27	5.1, PGIII	5.1, PGII
13	0.28	1.28	0.85	1.55	5.1, PGIII	5.1, PGII
14	0.25	0.87	0.86	1.61	5.1, PGIII	5.1, PGII

*) All single values of this laboratory have been identified as outliers (see also Table 19).

**) No proper classification due to outliers possible.

Considering mass-loss based criterion MLR₂₀₋₈₀, no clear classification can be recommended for sodium perborate monohydrate by participating laboratories involved, because about 50% of labs (6 of 11) conclude sodium perborate as a weak oxidizer, about 50% as a medium one in practice. Sodium nitrate would be clearly identified as a medium oxidizer by MLR₂₀₋₈₀ (11/11).

Table 49: Final classification by consumption rate parameter BR₂₀₋₈₀ of balanced combustible

Laboratory	BR ₂₀₋₈₀ [g/s]				assigned class for	
	SA PG III	SA PG II	SB 11/41	SC 11	SB 11/41	SC 11
01	0.27	0.48	0.45	0.99	5.1, PGIII	5.1, PGII
02	0.23	0.47	0.47	0.86	5.1, PGIII	5.1, PGII
03	0.24	0.53	0.42	0.83	5.1, PGIII	5.1, PGII
04	0.27	_*	_*	0.88	_**	_**
05	_*	0.46	0.45	1.17	5.1, PGIII	5.1, PGII
06	0.29	0.49	0.38	0.84	5.1, PGIII	5.1, PGII
08	0.28	0.57	0.44	1.14	5.1, PGIII	5.1, PGII
09	0.18	0.65	0.41	0.97	5.1, PGIII	5.1, PGII
10	0.27	0.52	0.41	0.72	5.1, PGIII	5.1, PGII
11	0.30	0.68	0.36	0.75	5.1, PGIII	5.1, PGII
13	0.31	0.85	0.49	1.03	5.1, PGIII	5.1, PGII
14	0.32	0.62	0.42	1.16	5.1, PGIII	5.1, PGII

*) All single values of this laboratory have been identified as outliers (see also Table 22).

**) No proper classification due to outliers possible.

The consumption or burning rate criterion BR₂₀₋₈₀ would unarguably identify sodium perborate monohydrate as a weak oxidizer of Division 5.1, only two laboratories (02 and 04) are borderlined to a medium classification. Sodium nitrate is clearly identified as a medium oxidizer of subdivision 5.1, PGII (11 of 11).

The following Table 50 summarizes the recommended final classifications of all 12 participating laboratories in regard to related criterion.

Table 50: Summary of recommended final classifications of all 12 participating laboratories in regard to related criterion.

		t _{0,1}	t ₂₀₋₈₀	MLR ₂₀₋₈₀	BR ₂₀₋₈₀
UN3377	PG II	11	12	6	0
	PG III	0	0	5	11
	No classification due to outliers	1	0	1	1
UN1498	PG II	11	10	11	11
	PG III	0	1	0	0
	No classification due to outliers	1	1	1	1

Again, any assessment, neither on validity nor on reliability can be derived here just from a statistical point of view. This must be postponed to experienced safety experts at IGUS EOS.

8.5 Conclusions regarding additional test ratio according to A.17 of European Directive 67/548/CEE

Taking into account that all additional test mixtures in additionally proposed ratio of 2:1 (solid oxidizer to combustible substance) are only performed on a voluntary basis, 8 out of 12 laboratories provided quo data GmbH with related data sets and from these data sets, several as addressed in the text had to be exempted for this study in addition due to e.g. exceeding tolerance limits or implausibility as explained in chapter 3 and 4. In consequence the current available data pool is supposed to be statistical insufficient to derive any clear recommendation on implementation of additional sample ratio to be tested within this range of investigation and data sets.

All final classifications of tested oxidizer as introduced in section 8.4 are based on current established ratios (1:1; 4:1); in consideration of limited data pool and range of tested oxidizers, this issue should be postponed to future round robins to be examined more in detail.

9 References

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- [8] 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.

10 Appendix

10.1 Test instruction

Ad-hoc working group on solid oxidizer test

3rd UN O.1 - Round Robin Test 2009

with Calcium Peroxide, Sodium Nitrate, Sodium perborate monohydrate

Dear colleagues,

as announced at the last OECD-IGUS-EOS meeting in Berlin (November 2008), the ad-hoc working group agreed to perform a further “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, “calcium peroxide” (CaO₂) as the proposed reference oxidizer to substitute “potassium bromate” (KBrO₃) and “sodium perborate monohydrate” (PBS-1) as tested in previous round robin test (2005/2006) were chosen for comparison reasons by the committee of experts. The latter is found to be a medium oxidizer by individual time-take time to_{0.1} according to latest 2nd Round Robin, although PBS-1 is well-known as a weak oxidizer in detergent industry and classified as such by UN officially (UN3377). We hope that modified UNO.1 test approach may be helpful to decide on its real intrinsic oxidizing properties in comparison.

Furthermore you receive on a voluntary basis “sodium nitrate” (NaNO₃) as supposed to be a medium oxidizer of Packing Group II (PG II) in consideration of its oxidizing properties, although listed officially as a weak oxidizer of Packing Group III (PG III – UN1498). We hope that proposed test approach is also able to identify the assumed intrinsic oxidizer hazards in comparison. In addition we are optimistic to gain some more experiences in terms of nitrate anions and related possible early break of ignition wire. All test performances of the latter are not mandatory, but these additional tests would provide us with further important data on reliability and suitability of proposed UN O.1 test modification (gravimetric approach). Furthermore any 2/3 - mixture of test substances with cellulose (ratio 2:1) or the determination of combustion time t_{0.1} by individual time-take of reference oxidizer piles representing strong oxidizers (PG I - ratio 3:1), should be performed on a voluntary basis as well. All these additional tests as agreed are extremely welcome and helpful for us. Further comments on these issues are given in the text.

Therefore we ask the participating laboratories to perform the modified UN O.1 test with these substances submitted to you by Solvay according to the test procedure as described in the UN Test Manual (4th rev. edition, 2003, 34.4.1) principally and in consideration of related video documentation of introduced gravimetric UN O.1 test approach or general instructions as given in the text respectively.

1.) General Instructions

Read following instructions carefully and if any item remains unclear, please contact us immediately again (phone: +49-263573 -246 or -242):

- Do not change the laboratory assistant within the test steps, e.g. the individual time t_{0.1} measuring should be performed by the same laboratory assistant.

- Do not interrupt a test series e.g. for a longer break or over night. Finish each test series completely and as soon as possible.
- 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. See attached movie documentation in addition.
- 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, but should last at least one minute. Keep the time for weighing in the substances after taking them from the desiccator and before closing the mixing vessel as short as possible.
- All drying procedures as prescribed in the UN test manual are only necessary for cellulose CF11 from WHATMAN as usual. Neither the reference, nor the test substances do need any further thermal or physical treatment like e.g. grounding. Please use only cellulose and test substances as delivered.
- Ensure identical lab, extractor or balance conditions, especially in terms of the location of low conductive protection or conical pile plates on balance surface within all test series in comparison while using delivered UN O.1 template as proposed. Refer to video documentation on delivered CD-ROM first.
- Before starting Round Robin, please gain your own experiences first by using test substances or especially cellulose from your own lab stock until you feel familiar with proposed test modification or its handling. We feel free to provide you with further 500g of PBS-1 (1kg in total) for training purposes.
- Any differing impacts of used test equipment on balance during data acquisition like e.g. stretching of connection wires or any varying mechanical contact or friction must be excluded. The introduced test design or e.g. proposed connections of heating wires with power amplifier by ceramic clips or quick connectors as shown in the video documentation are not mandatory, but should be considered as a basically recommended guideline as developed in a workshop by Solvay.
- Please discuss any variation with us before performing any test series (<mailto:Joerg.Clemens@Solvay.com> or <mailto:Juergen.Rabe@Solvay.com>)
- Always use flexible windshields, at least the front shield as delivered.
- Ignition wire should not open within at least 2/3 of the individually determined burning time $t_{0,1}$ in total by stop-watch. If wire opens earlier, repeat test, but not more than seven times in repetition per test sequence. Please take a note on it. According to our experiences, a change of wire after each test sequence is sufficient (at least for CaO_2 or PBS-1 sequences). For test series C (NaNO_3), it is recommendable to change wire after each combustion trial. If any discolouring or residues on wire is observable, please change immediately.
- Set tare of balance to zero before starting any mass loss data acquisition. Data acquisition and switch-on of power amplifier for ignition must not be synchronized.

- Each monitored mass loss profile should be directly assessed at least by the so-called ‘ Φ – factor’. The Φ – factor is similar to the statistical R-squared value (R^2) in principle. According to previous findings at Solvay or AQura GmbH, a specified range of $0.85 \leq \Phi \text{ – factor} \leq 1.15$ is supposed to identify a suitable mass loss profile in an acceptable manner. The Φ – factor will be calculated automatically by the delivered data evaluation draft “Draft Template UNO.1 f=5s.xls”. Any additional calculation of R^2 by linear regression of monitored data pool from 20 % to 80 % of total mass loss by your own is welcome, but not mandatory. For further information, please refer to previous presentations as given by Solvay in 2007 (TNO - Delft) or 2008 (BAM - Berlin). At least five burning trials per test sequence should be within defined Φ – specification. Do not perform more than seven burning trials per sequence at the most.
- At least after each test sequence, check the surface temperature of balance; if needed, remove all plates and cool down balance until recommended acceptance temperature.
- Special precautionary care must be taken for test series A, optional test sequence 7 (see chapter 3). As we know perfectly from toxic potassium bromate, PG I reference piles react vigorously accompanied with throw-out of residues and huge cloud of vapour. CaO_2 reacts similar, although throw-out consists mainly of harmless decomposed CaO fine powder dust. Therefore we like to ask you only to perform three instead of five valid trials in repetition as previously required in 2nd RRT from 2005/2006. You may have to clean thoroughly your balance or extractor afterwards.
- The use of provided visual basic BalanceVB – V3.0 software or data evaluation excel draft “Draft Template UNO.1 f=5s.xls” is not mandatory, but recommendable. Any other suitable software for mass loss data acquisition or data evaluation is welcome. Any improvements or further expert proposals due to collected experiences in regard to current test equipment or test design as proposed by Solvay are extremely welcome.
- Please provide us with all monitored mass loss raw data, information on test trial and related results as required. Therefore copy / paste data from your favourite software/data evaluation or from delivered protected “Draft Template UNO.1 f=5s.xls” (Password: BAM) simply into main data archive “2009 3rd UNO.1-Round-Robin-Results Data Input.xls”

2.) General Comments on Voluntary Test Series

According to collected past experiences of experts for the determination of oxidizing properties of solids according to European Test Method A.17 (67/548/CEE), the optimal mixture of solids with cellulose usually ranges within a ratio of 50 % to 80 %, mainly 60 % to 70 % by weight of solid oxidizer in its mixture with combustible material, which is indicated by the fastest burning speed in cm/second in comparison of all tested ratios in 10 % [m/m] increments.

Therefore the committee of experts recommends performing an additional test mixture (ratio 2:1) to proof the suitability of established 1:1 or 4:1 test mixtures in general or to be able to decide in case of borderline situation respectively. This additional test mixture (2:1) is recommended as well, but not mandatory. Furthermore it is consensus on IGUS-EOS level as confirmed by previous Round Robin findings, that determination of burning time $t_{0.1}$ by stop-watch is sufficiently reproducible, reliable and valid to identify intrinsic hazard potentials of strong oxidizers of PG I for sure.

Hence and in consideration of established test method UN O.1, any further gravimetric approach or additional technical devices are not a priori indicated or necessary. Therefore related reference test series for PG I (ratio 3:1) may not be performed mandatory within this already exhaustive range of experiments, but should be performed by each participating lab voluntarily if possible.

3.) Range of Experiments and Scheme of Test Series

Any mentioned ratio in this text describes the ratio of solid to cellulose in a conical pile of each 30g in total. The range of experiments comprises three test series A to C in total. Each test series considers two mandatory and one voluntary test sequence of five burning trials each (besides PG I reference trials as pointed out in chapter 1), so at least 10 to 21 burning trials as a maximum per test series. The delivered amount of reference or test substances is calculated for 7 trials per sequence as a safety margin in case of e.g. extreme freak values or any unexpected failures like early break of ignition wire. If any unlikely shortage of cellulose in a worst case scenario may occur (seven trials required in all mandatory and optional test sequences), please contact immediately us again. We will send you directly further combustible material of equal batch. Mentioned series in italics and brackets indicate a voluntary test series. To our experiences, each test sequence may last 1 hour approximately for a trained user (+/-). We like to ask all executives to consider and enable sufficient time for your lab staff for test performances and exercise purposes beforehand as well.

For statistical purposes it is necessary to perform the tests in the following sequence (order) according to 2nd UN O.1 Round Robin test:

Test Series A

Test Sequence 1: Test reference mixture CaO₂ - PG III (1:2) Trial 1-5 (6-7)

Test Sequence 2: Test reference mixture CaO₂ - PG II (1:1) Trial 1-5 (6-7)

Test Series B

Test Sequence 3: Test sample NaBO₃xH₂O (4:1) Trial 1-5 (6-7)

Test Sequence 4: Test sample NaBO₃xH₂O (1:1) Trial 1-5 (6-7)

Test Series C

Test Sequence 5: Test sample NaNO₃ (4:1) Trial 1-5 (6-7)

Test Sequence 6: Test sample NaNO₃ (1:1) Trial 1-5 (6-7)

Optional Test Series A to C

Test Sequence 7: *Test reference mixture CaO₂ - PG I (3:1) Trial 1-3 (4-5)*

Test Sequence 8: *Test sample NaBO₃xH₂O (2:1) Trial 1-5 (6-7)*

Test Sequence 9: *Test sample NaNO₃ (2:1) Trial 1-5 (6-7)*

Remark: Please remember that the test substance calcium peroxide, sodium perborate monohydrate or sodium nitrate as received from Solvay should not be treated by any method.

4.) Delivered Items

You receive following items as listed below – please check in time the completeness of announced items after delivery. If something of evidence is missing, please contact directly Solvay again:

1. Raw Materials (all):

500g calcium peroxide (reference oxidizer) - Solvay

1kg sodium perborate monohydrate, Batch No: 220/901150 (test substance) - Solvay

500g sodium nitrate, Batch No: 0889 790 (test substance) – Fisher Scientific

500g CF11 Cellulose, Batch-No: 8311119 (combustible material) – Whatman

2. Technical Equipment (not BAM, FMLR; modification already adopted and in use):

- a) 1x UN O.1 base plate b) 5x rubber dampers, c) 2x fixing pins for defined location
incl. assembly tools of protection plate on balance



- d) 5x wind shield pins e) 5x different assembly tools f) 3x flexible wind shields
for wire /quick connectors (front/both sides)



- g) 2x low conductive h) 45x ceramic sheets for i) Test Equipment mod. UNO.1
protection plates burning trials (not reusable) (excl. balance)



3. CD-ROM containing actual video documentation on modified test equipment and previous movie as shown for the first time in Delft (May 2007), ZIP-Folder containing VB balance software, EXCEL draft as a first proposal for quick data assessment

“Draft Template UNO.1 f=5s.xls” and main data sheet “2009 - UNO.1-Round-Robin-Results Data Input.xls”. Please copy both files in folder C:\BalanceVB after following instructions as given in chapter 6.

5.) Balance Requirements, RS232 Interface

The weight of each delivered protection plate is about ~500g and in consideration of common O.1 plates plus conical pile, the total mass will be less than 1.5kg if using both plates for thermal safety reasons in total - hence a balance mass scale of +2.5kg (full scale mass) will be sufficient, but not mandatory. Solvay has collected good experiences with the attached XS4002S Delta Range from Mettler-Toledo exemplarily.

http://de.mt.com/mt/products/produkte-anwendungen_waegenlabor_praezisionswaagen_praezisionswaagen-excellence-level_excellence-xspaezisionswaagen_xs-s/XS4002SDR_0x000010084034c96e40015f25.jsp

The SICS - balance must be equipped with a RS232 interface and connectable with a standard PC by USB or serial interface. Depending of type of balance, the recommended set up as listed below may differ in details, hence only general recommendations can be given here and must be checked on the job. Any internal calibration procedure or quality criterion to be fulfilled before data transfer should be cancelled or optimized in terms of ‘as fast as possible’. Solvay recommends following RS232 interface definition (HOST):

- 1) Baud rate: 9600 - 2) Bit/Parity: 8/No - 3) Stop Bits: One - 4) Handshake: Xon / Xoff
- 5) End of Line: IBM/DOS - 6) Continuous Mode: ON

→ Definition of Continuous Mode: Output Format: MT-SICS; Updates/sec: 5 (sufficiently high data transfer frequency for weak and medium oxidizers) Ensure that your PC interface (e.g. COM1) is defined similarly. If you prefer USB, install first required driver of your RS232/USB adaptor.

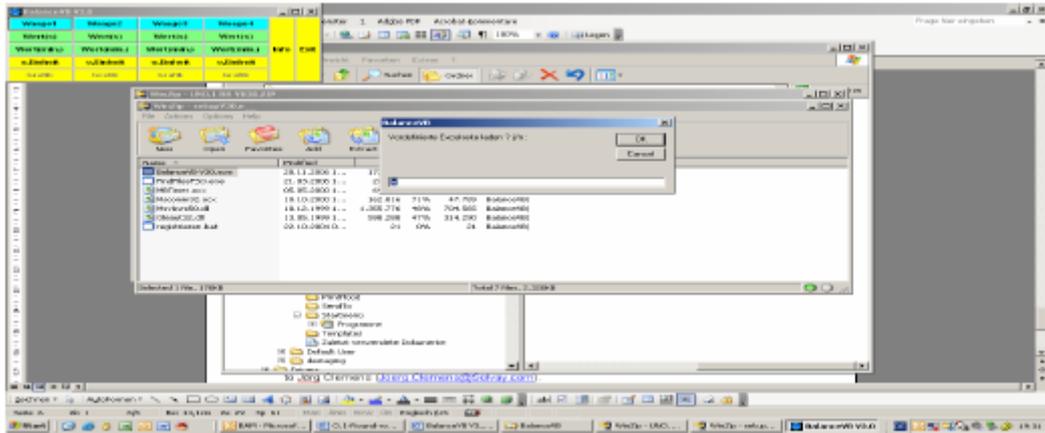
6.) Short Introduction of BalanceVB-V30

The provided BalanceVB-V30.exe software has been developed by Horst Marquardt (HGM Soft) in cooperation with BAM in 2003 for multi balance interface communication and digital data acquisition on EXCEL platform. Any internal or external distribution or commercial sale is strictly forbidden. Neither the software engineer, nor Solvay can give any guarantee in regard to possible damage to soft- or hardware or any related windows failures. No further revisions or updates will be available.

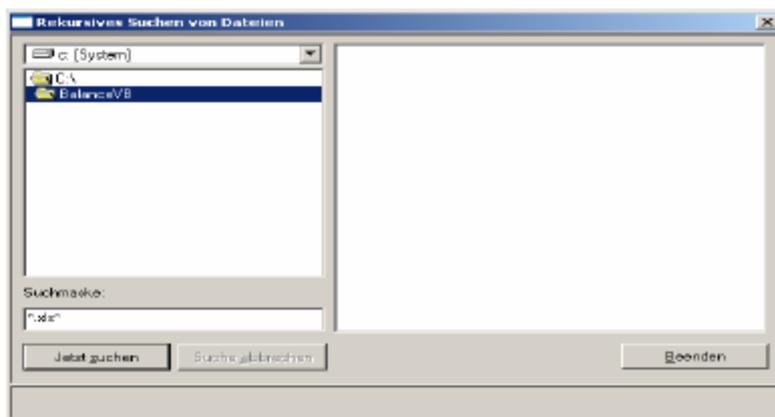
BalanceVB-V30 is only available in German, but any other suitable software is recommendable as pointed out before. The program requires basically XP or W2K (operating system) and EXCEL2000 or higher. While unzipping CD-ROM data folder “setupVB3.ZIP”, double click on “setupV30.e__”, which may have to be renamed as “setupV30.exe”. Usually all files will be automatically (or have to be manually) stored in ‘C:\BalanceVB’ on your computer. We have installed and tested this program at Solvay, AQura or BAM for several times without any significant errors. It may be possible that the actual version of your ActiveX driver “MSCOMM32.OCX” of your working system has to be updated via internet. Furthermore a manual registration by clicking on “registrieren.bat” could be required as well.

This general information may vary or differ in detail in consideration of your local IT circumstances. Solvay will try to give you any required support within limitation.

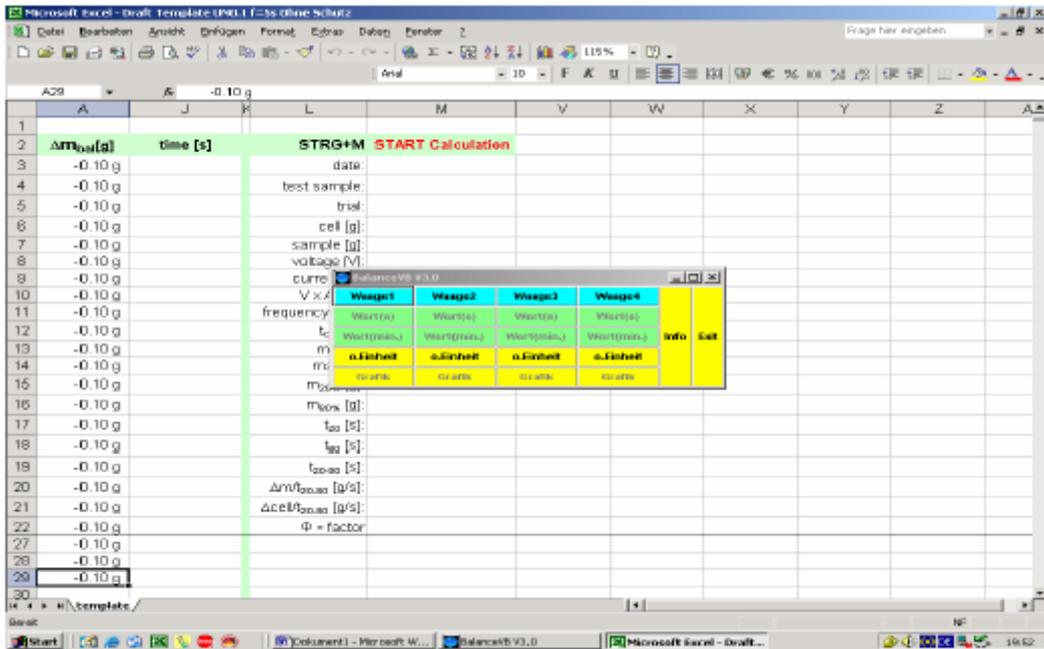
After installation, you will be asked “Load defined EXCEL sheet? yes/no” (German: “Vordefinierte Excelseite laden? j/n”) – enter “j” for “yes” in related command line.



Following window will open, click on button “search now” [Jetzt suchen] in C:\BalanceVB and open “Draft Template UNO.1 f=5s.xls”.



VB – program directly opens EXCEL and selected draft template, while starting data acquisition immediately. The balance data are usually transferred in text format.



To stop data acquisition after burning trial, click on „Exit“ in related ‚BalanceVB V3.0‘ window. You have to confirm the exit command by ‚ja‘ again.



First fill in all relevant information like date, test sample, trial, mass of balanced cellulose or solid, selected frequency of balance, etc. in the EXCEL draft and start macro afterwards by pressing [Strg] + [M] simultaneously. Please copy all raw or required result data like t_{0.1} or t₂₀₋₈₀ in main data sheet “2009 - UNO.1-Round-Robin-Results Data Input.xls” (CD-ROM).

Please notice: depending on your selected frequency, the time-scale will be automatically inserted or added by macro. Do not copy related time-scale column in main data archive as well – the known frequency will be sufficient for any recalculating or reassessment of data by Solvay.

7.) Participating Laboratories

The following 14 laboratories confirm to participate in this new round robin test (grey: Laboratories, which have not performed the test during the testing period):

Name	Company, Organization Address
Peter Schuurman	Akzo Nobel Technology & Engineering P.O. Box 10 7400 AA Deventer (NL)
Klaus Budde	AQura GmbH Building 1077/PO.No.14 Paul-Baumann-Str.1 45772 Marl (D)
Mike L. Norsworthy	Arch Chemicals 1200 Lower River Road Charleston, TN 31312 (USA)
Dr. Heike Michael-Schulz	BAM - Division II.2 Unter den Eichen 87 12205 Berlin (D)
Dr. Markus Goedde	BASF SE GCT/S - L511 67056 Ludwigshafen (Germany)
Dr. Dieter Heitkamp	Currenta GmbH & Co. OHG Cur-Sic-VA-VSC Geb.407 51368 Leverkusen (D)
Dr. Elizabeth C. Buc	Fire And Material Research Lab LLC P.O. Box 303 Eastpointe, MI 48021-0303 (USA)
Douglas Carson	INERIS B.P. 2 - Parc Technologique Alata 60550 Verneuil-en-Halatte (F)
Dr. Jörg Horn	Siemens AG IA AS PA EC C Prozesssicherheit Industriepark Höchst, C487 65926 Frankfurt a.M. (D)
Jörg Clemens	Solvay Chemicals GmbH Am Güterbahnhof 5355 Bad Honningen (Germany)
Heather J. Gibbon	Syngenta Process Hazards Leeds Road Huddersfield, HD2 1FF (UK)
Törbjorn Legard	Yara Technology Centre, B. 92 Hydroveien 67 3908 Porsgrunn (NO)
Wim A. Mak	TNO Defence, Security & Safety Energetic Materials Department P.O. Box 45 2280 AA Rijswijk (NL)
Aubrey Thyer	Health & Safety Laboratory Harpor Hill Buxton, Derbyshire, SK17 9JN (GB)

We ask you **to perform the tests by end of week 14** and to send back the data files a.s.a.p. to Jörg Clemens (<mailto:Joerg.Clemens@Solvay.com>).

If you still have any questions or comments, please do not hesitate to contact us again. 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 in St. Petersburg in June 2009, where we hope to present all results (10th – 12th June 2009).

With the hope that our intensive work of the last two years on proposed modification of established UN O.1 test will have a successful end finally, we remain with our warmest regards Dr. Jürgen Rabe (chairman of the group) and Jörg Clemens (coordinator)

Bad Hönningen in February 2009

Good luck!

10.2 Laboratory data input form

OECD IGUS EDS ad hoc Working Group on the Solid Oxidizer Test (UN Test O.1)
 (Round robin tests 2009 with Calcium Peroxide, Sodium Perborate Monohydrate, Sodium Nitrate)

Laboratory-Num: balance: supplier:
 type of ignition wire e.g. ALUCHROM: batch-Num: supplier:

Test serie A:
 Drying parameters
 Cellulose:

Supplier: WHATMAN
 Batch No.: 331119
 Drying temperature [°C]: 105°C
 Drying time [h]:
 Residual moisture [%]:
 Remarks:

Results

PG III (CaO₂:Cell. = 1:2):

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

Order no:	SAPGIII-1	SAPGIII-2	SAPGIII-3	SAPGIII-4	SAPGIII-5	SAPGIII-6	SAPGIII-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning timer t _{0.1} [s] (as decimal, e.g. 100):							
main burning timer t ₂₅₋₉₉ [s] (as decimal, e.g. 50):							
mass 20 to 30% of total mass burnt Δm ₂₅₋₉₉ [g/s] (2 decimal, e.g. 0.55):							
of 50% of combustible material Δcoll ₂₅₋₉₉ [g/s] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.88):							
R* (2 decimal, e.g. 0.88; optional):							
Remarks:							

PG II (CaO₂:Cell. = 1:1):

Order no:	SAPGII-1	SAPGII-2	SAPGII-3	SAPGII-4	SAPGII-5	SAPGII-6	SAPGII-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning timer t _{0.1} [s] (as decimal, e.g. 100):							
main burning timer t ₂₅₋₉₉ [s] (as decimal, e.g. 50):							
mass 20 to 30% of total mass burnt Δm ₂₅₋₉₉ [g/s] (2 decimal, e.g. 0.55):							
of 50% of combustible material Δcoll ₂₅₋₉₉ [g/s] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.88):							
R* (2 decimal, e.g. 0.88; optional):							
Remarks:							

CONTINUE WITH TEST SERIE B FIRST

OPTIONAL: PG I (CaO₂:Cell. = 3:1):

Order no:	SAPGI-1	SAPGI-2	SAPGI-3	SAPGI-4	SAPGI-5
Date:	xx.xx.2009	xx.xx.2009	xx.xx.2009	xx.xx.2009	xx.xx.2009
Time:[hh:mm]	xxxx	xxxx	xxxx	xxxx	xxxx
Ambient temperature [°C]:					
Ambient relative air humidity [%]:					
Remarks:					
Mixing time [min]:					
Time: start mixing until start combustion [min]:					
individual burning timer t _{0.1} [s] (as decimal, e.g. 100):					
Remarks:					

CONTINUE WITH OPTIONAL TEST SEQUENCE OF SERIE B

Figure 62: Data input form for test series A

Test serie B:
 Drying parameters
 Cellulose:

Supplier:	WHATMAN
Batch No.:	0311119
Drying temperature [°C]:	
Drying time [h]:	
Residual moisture [%]:	
Remarks:	

Results

Test Sodium perborate monohydrate 4:1 mixture with cellulose

Order no.:	SB 41-1	SB 41-2	SB 41-3	SB 41-4	SB 41-5	SB 41-6	SB 41-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning time $t_{0.1}$ [s] (an decimal, e.g. 100):							
main burning time $t_{25.00}$ [s] (an decimal, e.g. 50):							
mean 20 to 30% of total mass loss Δm_{20-30} [qtr] (2 decimal, e.g. 0.55):							
of 60% of combustible material Δc_{60} [qtr] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.88):							
R' (2 decimal, e.g. 0.88; optional):							
Remarks:							

Test Sodium perborate monohydrate 1:1 mixture with cellulose

Order no.:	SB 11-1	SB 11-2	SB 11-3	SB 11-4	SB 11-5	SB 11-6	SB 11-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning time $t_{0.1}$ [s] (an decimal, e.g. 100):							
main burning time $t_{25.00}$ [s] (an decimal, e.g. 50):							
mean 20 to 30% of total mass loss Δm_{20-30} [qtr] (2 decimal, e.g. 0.55):							
of 60% of combustible material Δc_{60} [qtr] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.88):							
R' (2 decimal, e.g. 0.88; optional):							
Remarks:							

CONTINUE WITH TEST SERIE C FIRST

OPTIONAL: Sodium perborate monohydrate 2:1 mixture with cellulose

Order no.:	SB 21-1	SB 21-2	SB 21-3	SB 21-4	SB 21-5	SB 21-6	SB 21-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning time $t_{0.1}$ [s] (an decimal, e.g. 100):							
main burning time $t_{25.00}$ [s] (an decimal, e.g. 50):							
mean 20 to 30% of total mass loss Δm_{20-30} [qtr] (2 decimal, e.g. 0.55):							
of 60% of combustible material Δc_{60} [qtr] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.88):							
R' (2 decimal, e.g. 0.88; optional):							
Remarks:							

CONTINUE WITH OPTIONAL TEST SEQUENCE OF SERIE C

Figure 63: Data input form for test series B

Test serie C:
 Drying parameters
 Cellulose:

Supplier:	WHATMAN
Batch No.:	8311119
Drying temperature [°C]:	
Drying time [h]:	
Residual moisture [%]:	
Remarks:	

Results

Test Sodium Nitrate 4:1 mixture with cellulose

Order no.:	SC41-1	SC41-2	SC41-3	SC41-4	SC41-5	SC41-6	SC41-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning timer $t_{0.1}$ [s] (as decimal, e.g. 100):							
main burning timer $t_{25.11}$ [s] (as decimal, e.g. 50):							
mass 20 to 30% of total mass $mass_{\Delta cell} t_{25.11}$ [qtz] (2 decimal, e.g. 0.55):							
of 60% of combustible material $\Delta cell t_{25.11}$ [qtz] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.33):							
E^* (2 decimal, e.g. 0.88; optional):							
Remarks:							

Test Sodium Nitrate 1:1 mixture with cellulose

Order no.:	SC11-1	SC11-2	SC11-3	SC11-4	SC11-5	SC11-6	SC11-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning timer $t_{0.1}$ [s] (as decimal, e.g. 100):							
main burning timer $t_{25.11}$ [s] (as decimal, e.g. 50):							
mass 20 to 30% of total mass $mass_{\Delta cell} t_{25.11}$ [qtz] (2 decimal, e.g. 0.55):							
of 60% of combustible material $\Delta cell t_{25.11}$ [qtz] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.33):							
E^* (2 decimal, e.g. 0.88; optional):							
Remarks:							

CONTINUE WITH OPTIONAL TEST SEQUENCE OF SERIE A FIRST

OPTIONAL: Sodium Nitrate 2:1 mixture with cellulose

Order no.:	SC21-1	SC21-2	SC21-3	SC21-4	SC21-5	SC21-6	SC21-7
Date:	xx.xx.2009						
Time:[hh:mm]	xxxx						
Ambient temperature [°C]:							
Ambient relative air humidity [%]:							
Remarks:							
Mixing time [min]:							
Time: start mixing until start combustion [min]:							
individual burning timer $t_{0.1}$ [s] (as decimal, e.g. 100):							
main burning timer $t_{25.11}$ [s] (as decimal, e.g. 50):							
mass 20 to 30% of total mass $mass_{\Delta cell} t_{25.11}$ [qtz] (2 decimal, e.g. 0.55):							
of 60% of combustible material $\Delta cell t_{25.11}$ [qtz] (2 decimal, e.g. 0.55):							
Φ - factor (2 decimal, e.g. 0.33):							
E^* (2 decimal, e.g. 0.88; optional):							
Remarks:							

FINISH

Figure 64: Data input form for test series C

It has to be noted that according to the test instruction all test performances of test series C were optional, not only sodium nitrate 2:1 mixture with cellulose (see appendix 10.1, page 114).

10.3 Individual combustion time

10.3.1 Outliers and stragglers

Table 51: Outliers and straggler for individual combustion time $t_{0.1}$ [s]

Sample	Lab code	Outlier test	Outlier/Straggler
SA PG I	08	Grubbs	straggler
SA PG II	08	Cochran	outlier
SA PG III	09	Cochran	straggler
SB 21	14	Cochran	straggler
SC 21	08	Cochran	outlier
SC 21	09	Cochran	outlier
SC 21	13	Cochran	straggler

10.3.2 Analysis of single values

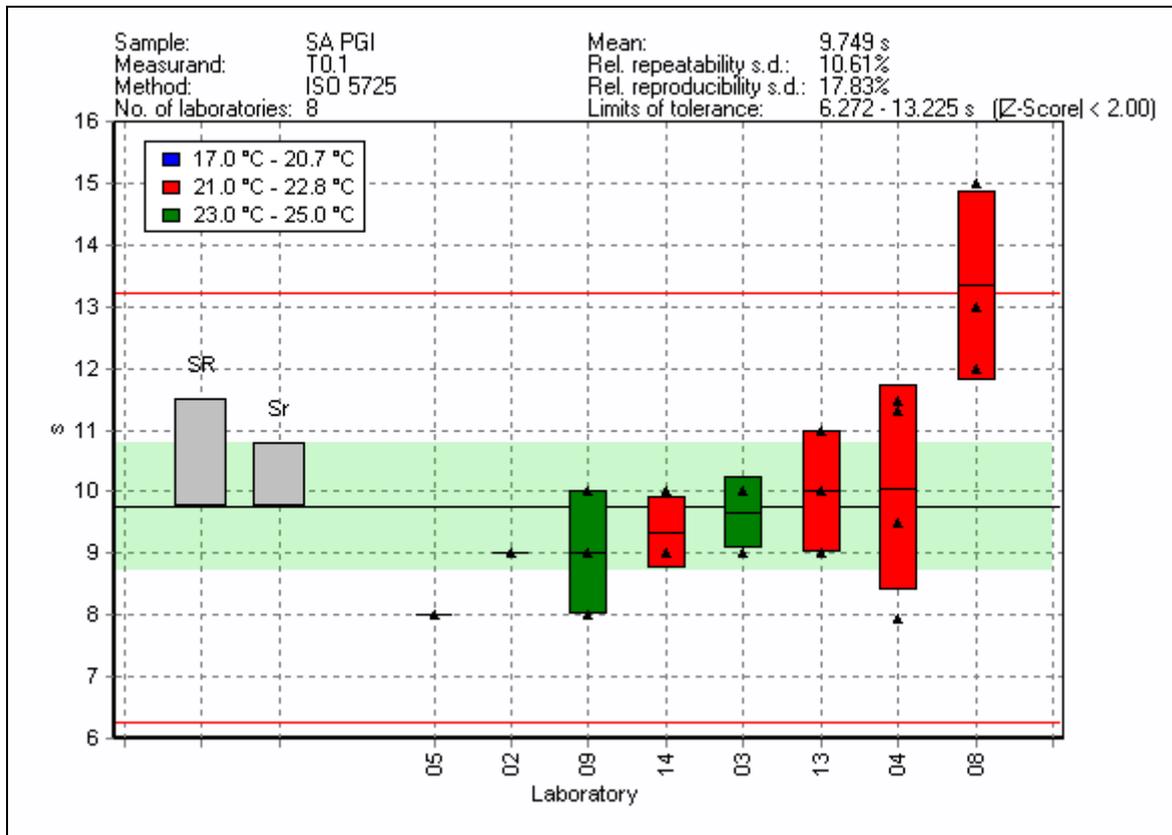


Figure 65: Laboratory results for individual combustion time $t_{0.1}$ – SA PG I

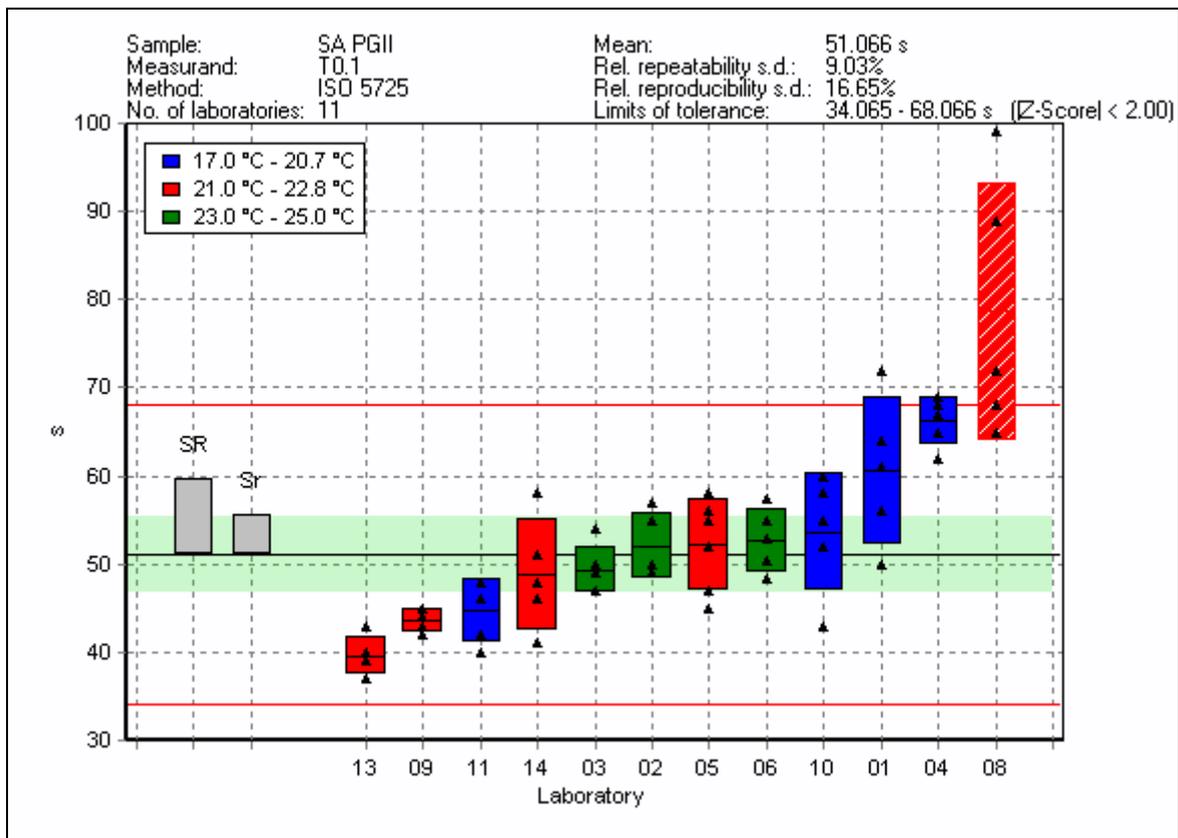


Figure 66: Laboratory results for individual combustion time $t_{0.1}$ – SA PG II

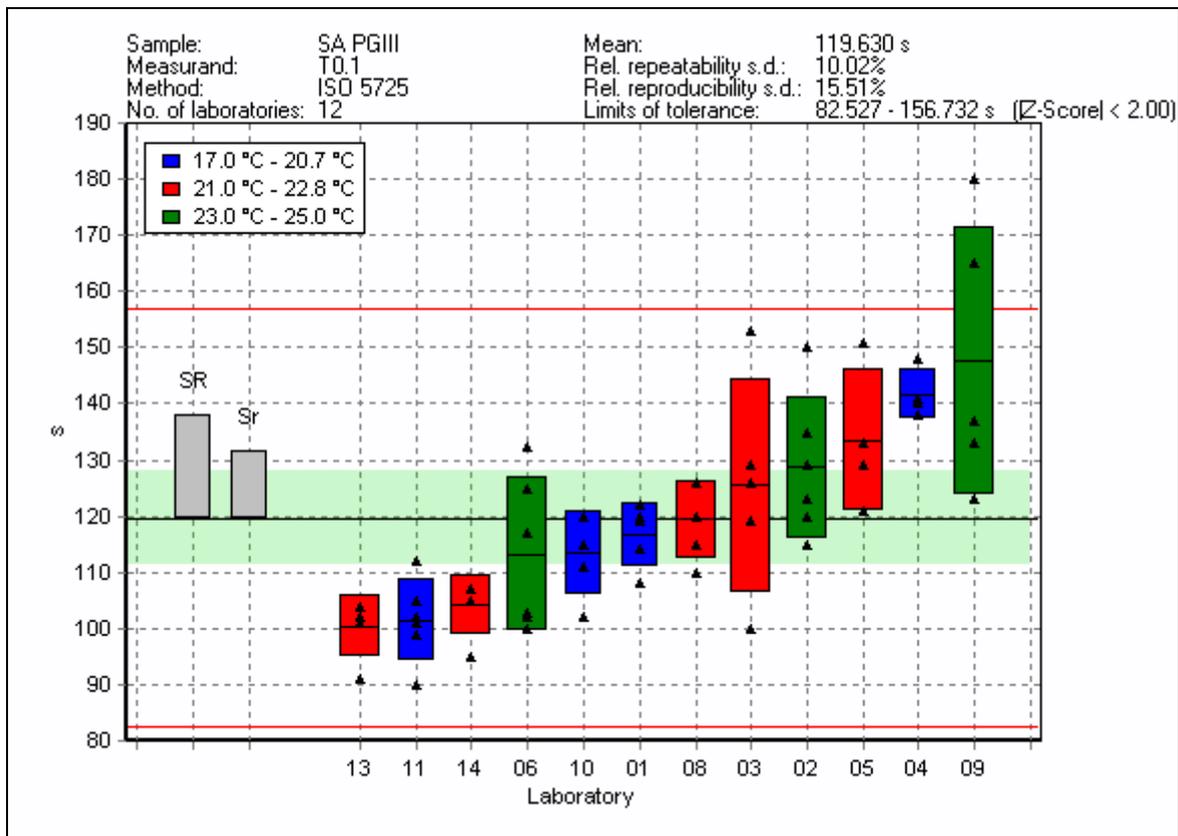


Figure 67: Laboratory results for individual combustion time $t_{0.1}$ – SA PG III

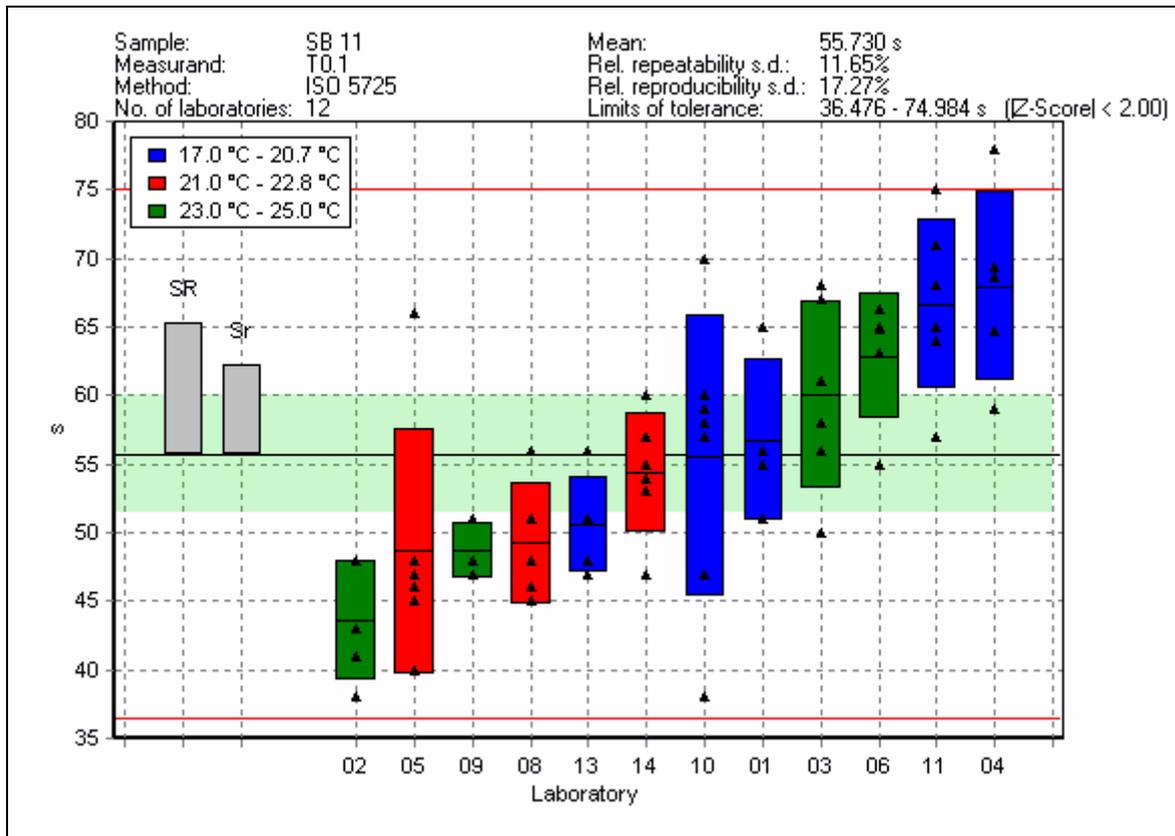


Figure 68: Laboratory results for individual combustion time $t_{0.1}$ – SB 11

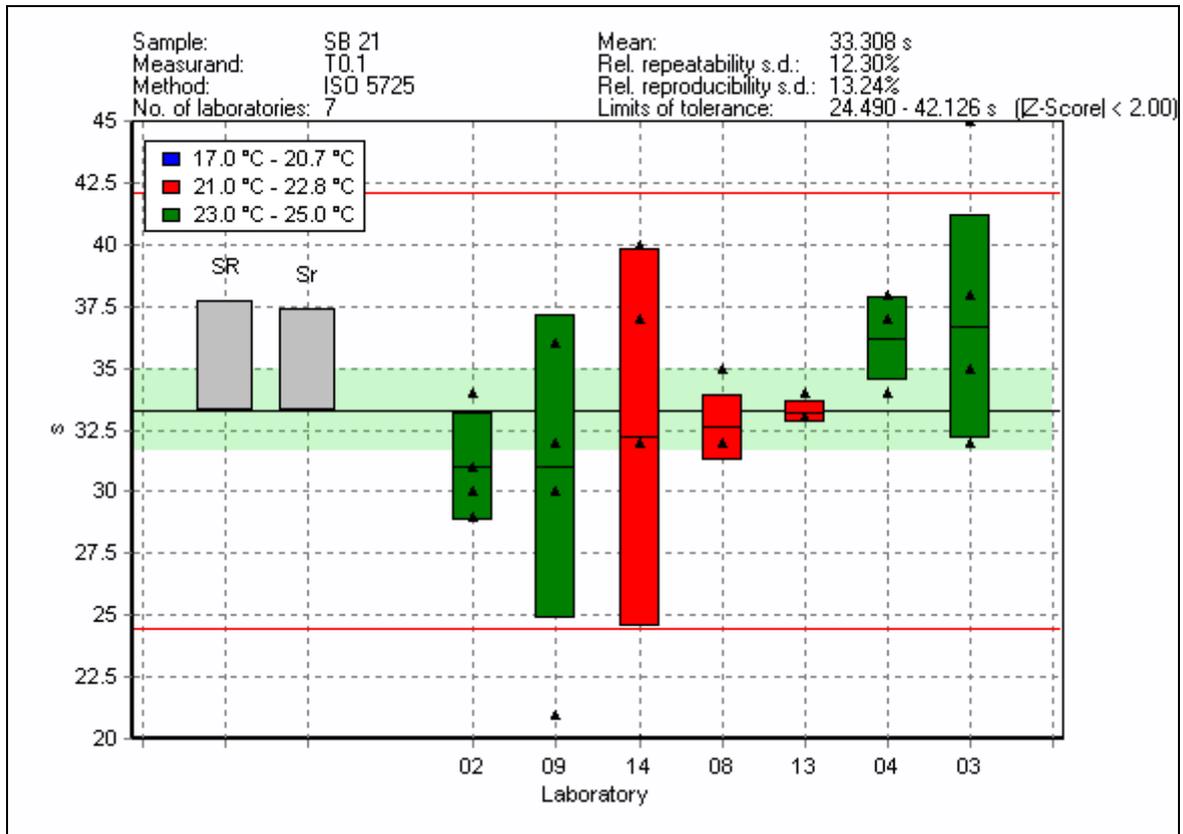


Figure 69: Laboratory results for individual combustion time $t_{0.1}$ – SB 21

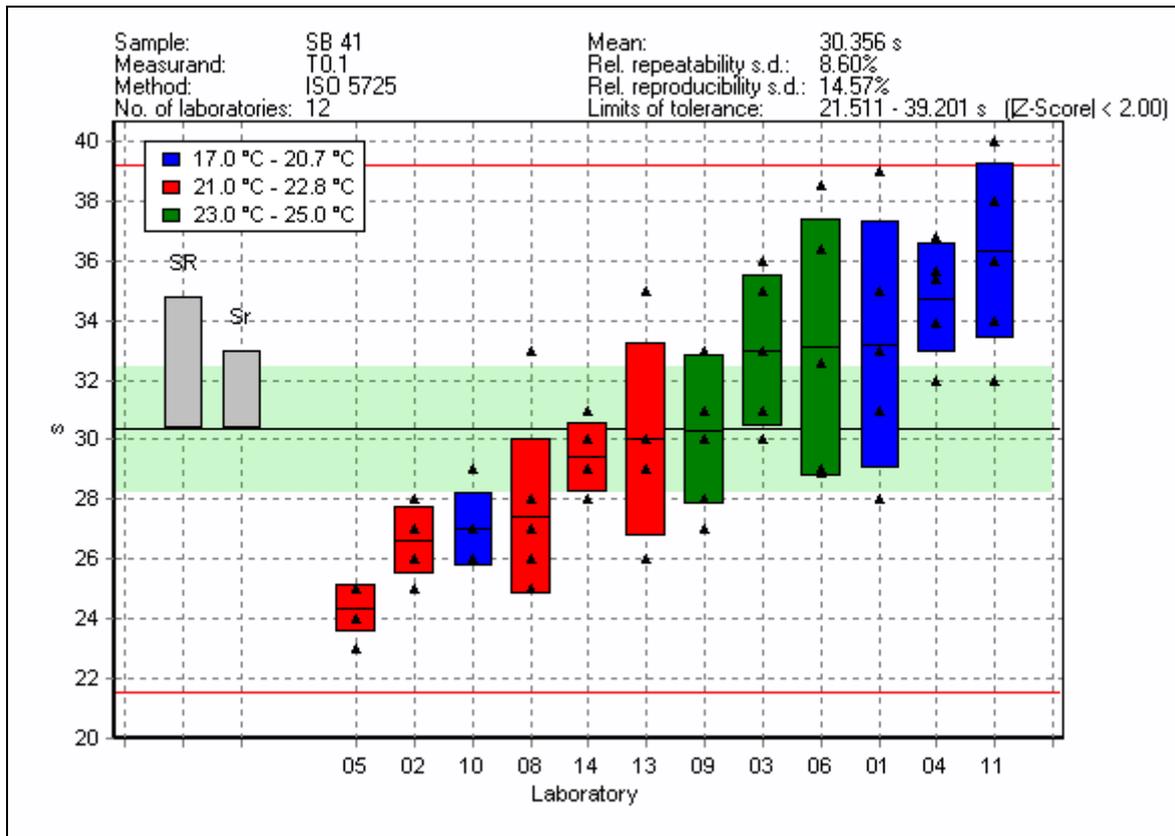


Figure 70: Laboratory results for individual combustion time $t_{0.1}$ – SB 41

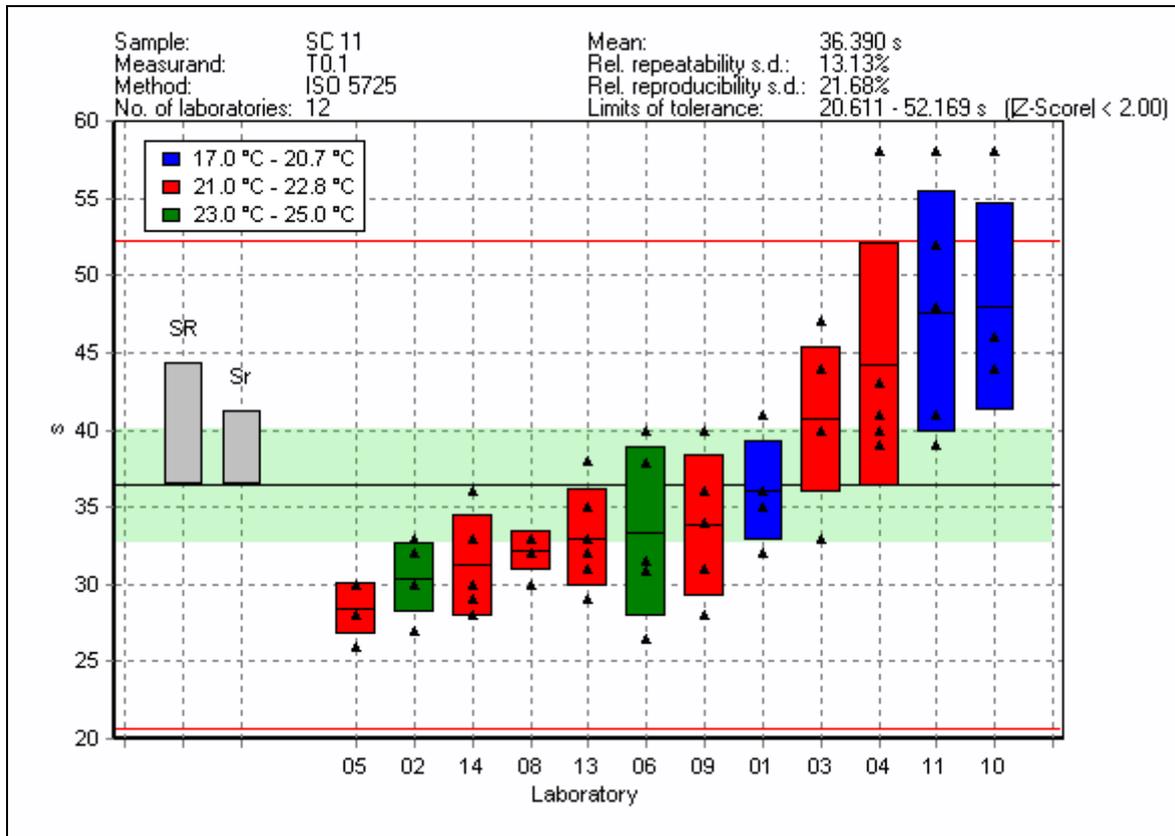


Figure 71: Laboratory results for individual combustion time $t_{0.1}$ – SC 11

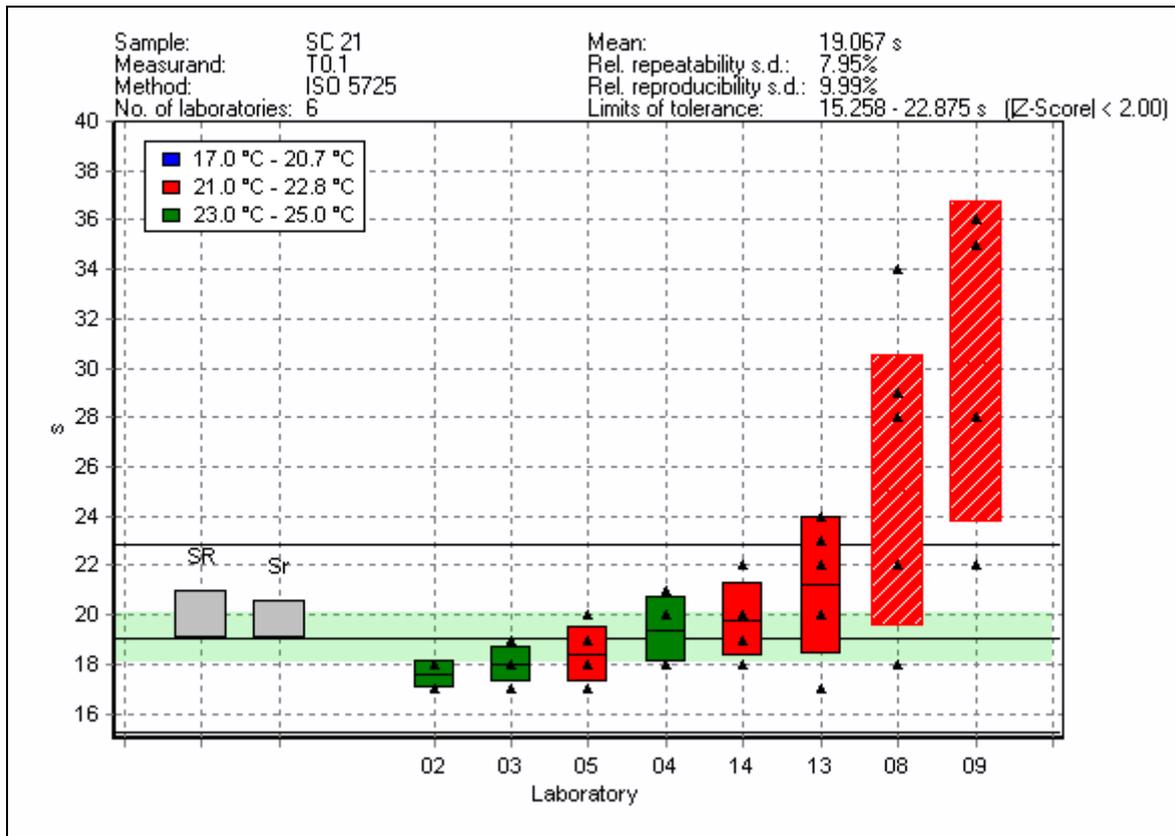


Figure 72: Laboratory results for individual combustion time $t_{0.1}$ – SC 21

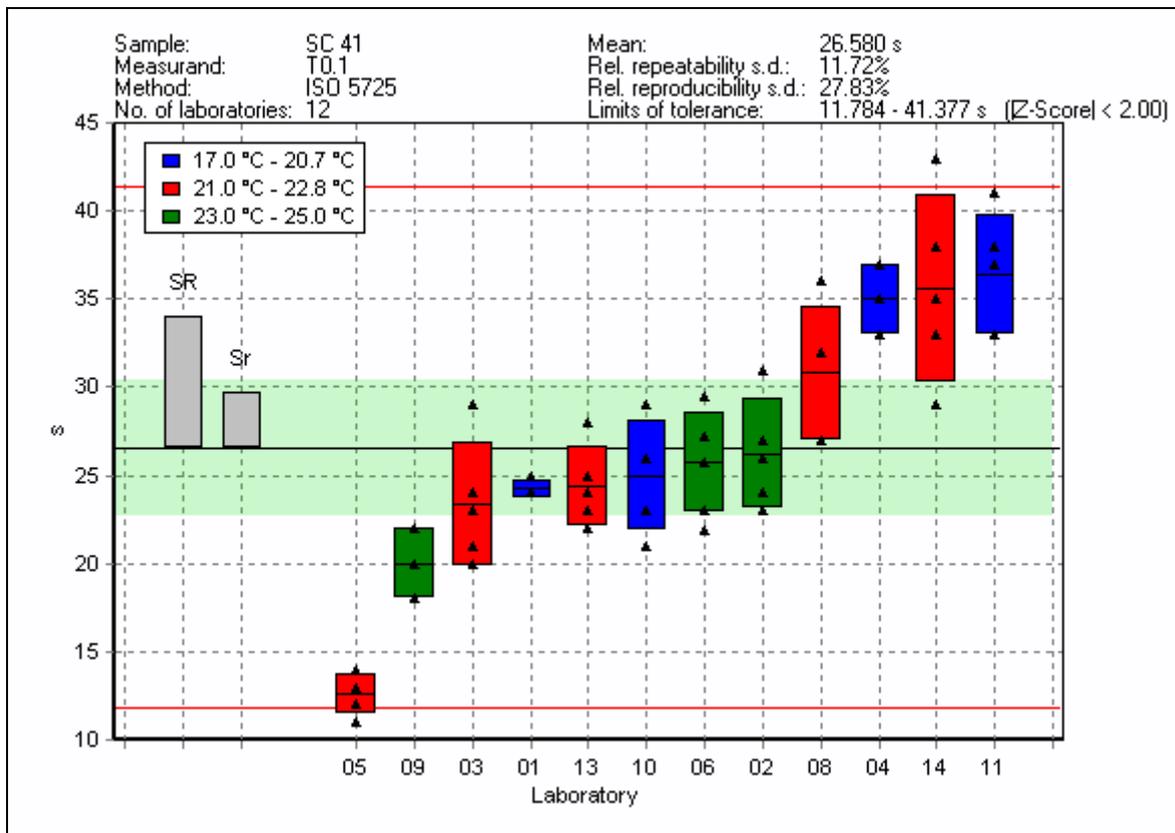


Figure 73: Laboratory results for individual combustion time $t_{0.1}$ – SC 41

10.3.3 Analysis of ratios

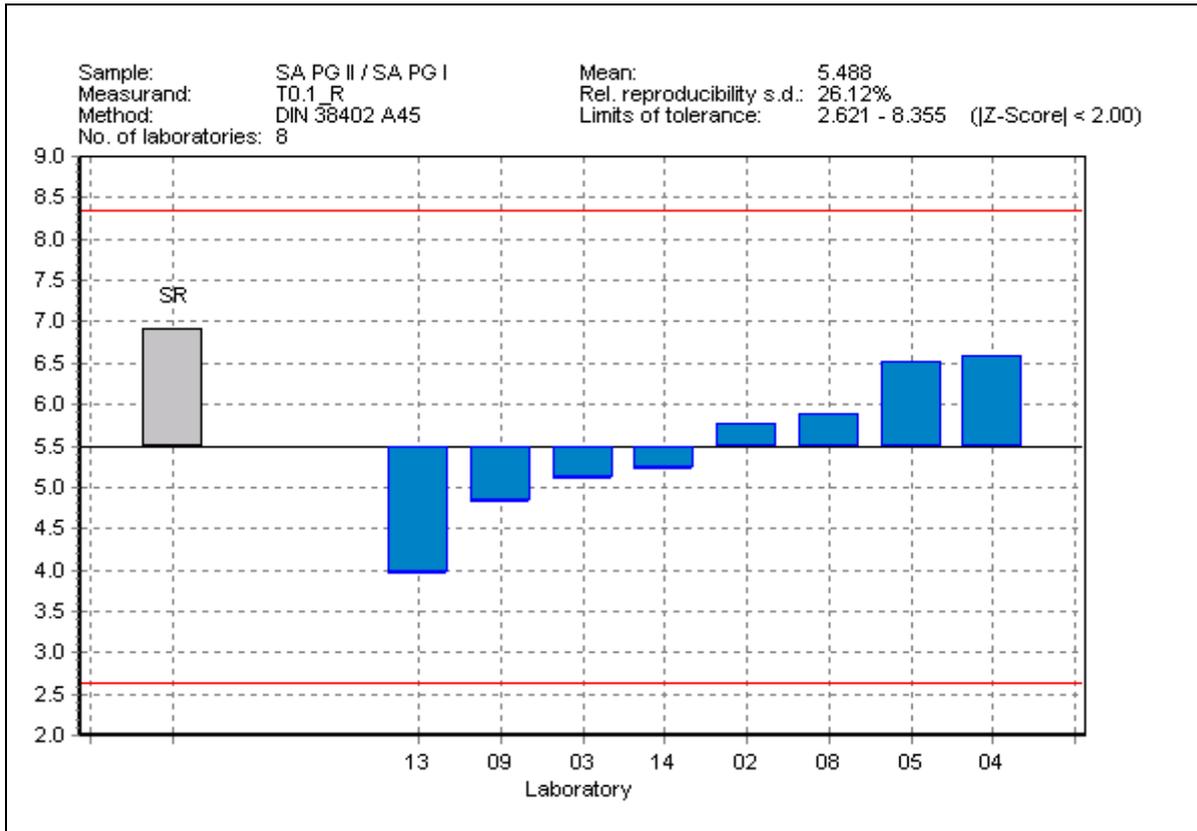


Figure 74: Laboratory results for individual combustion time $t_{0.1}$ – ratio SA PG II/SA PG I

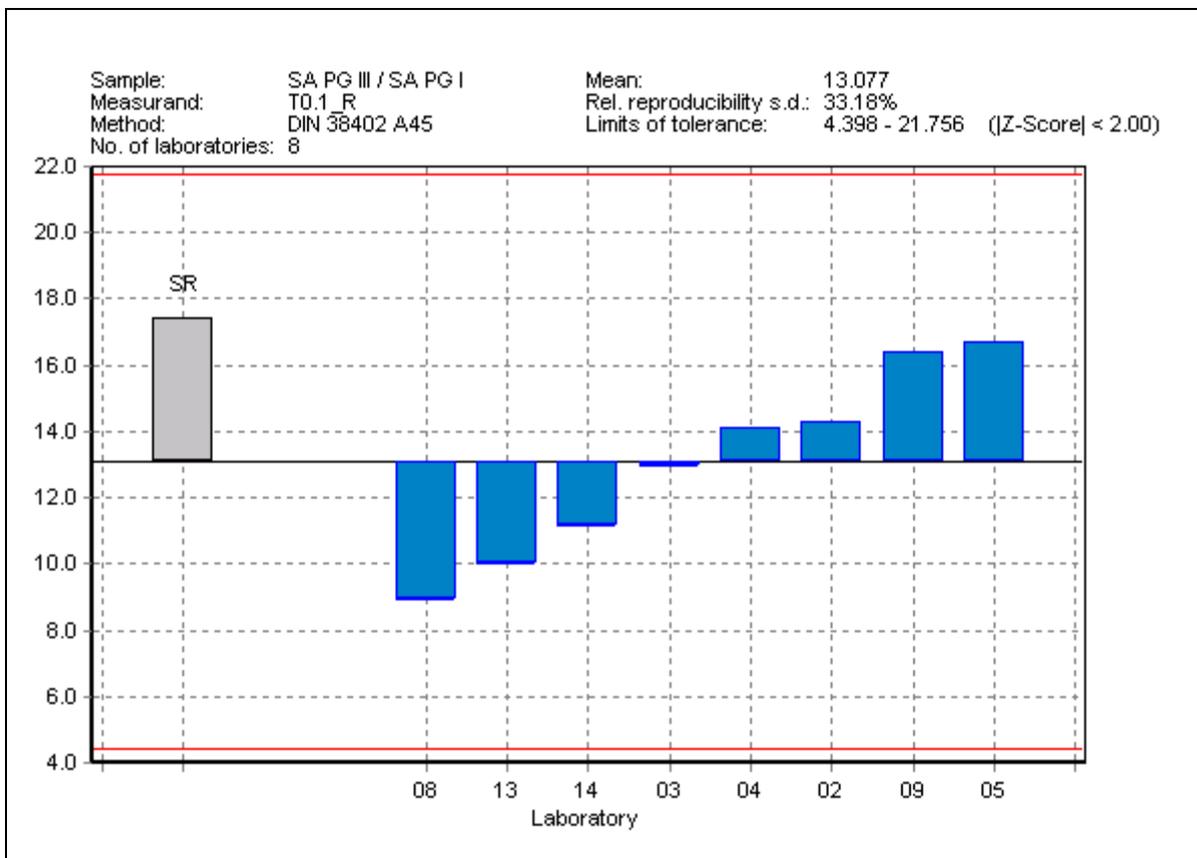


Figure 75: Laboratory results for individual combustion time $t_{0.1}$ – ratio SA PG III/SA PG I

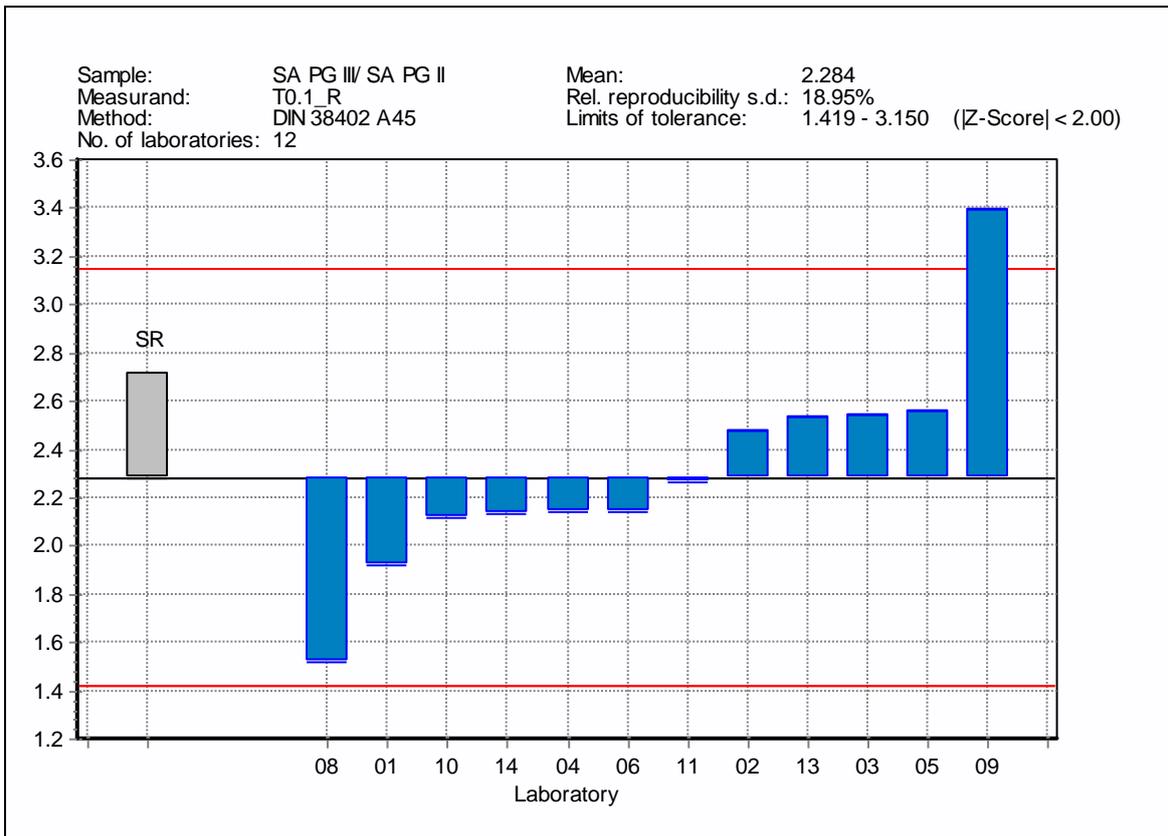


Figure 76: Laboratory results for individual combustion time $t_{0.1}$ – ratio SA PG III / SA PG II

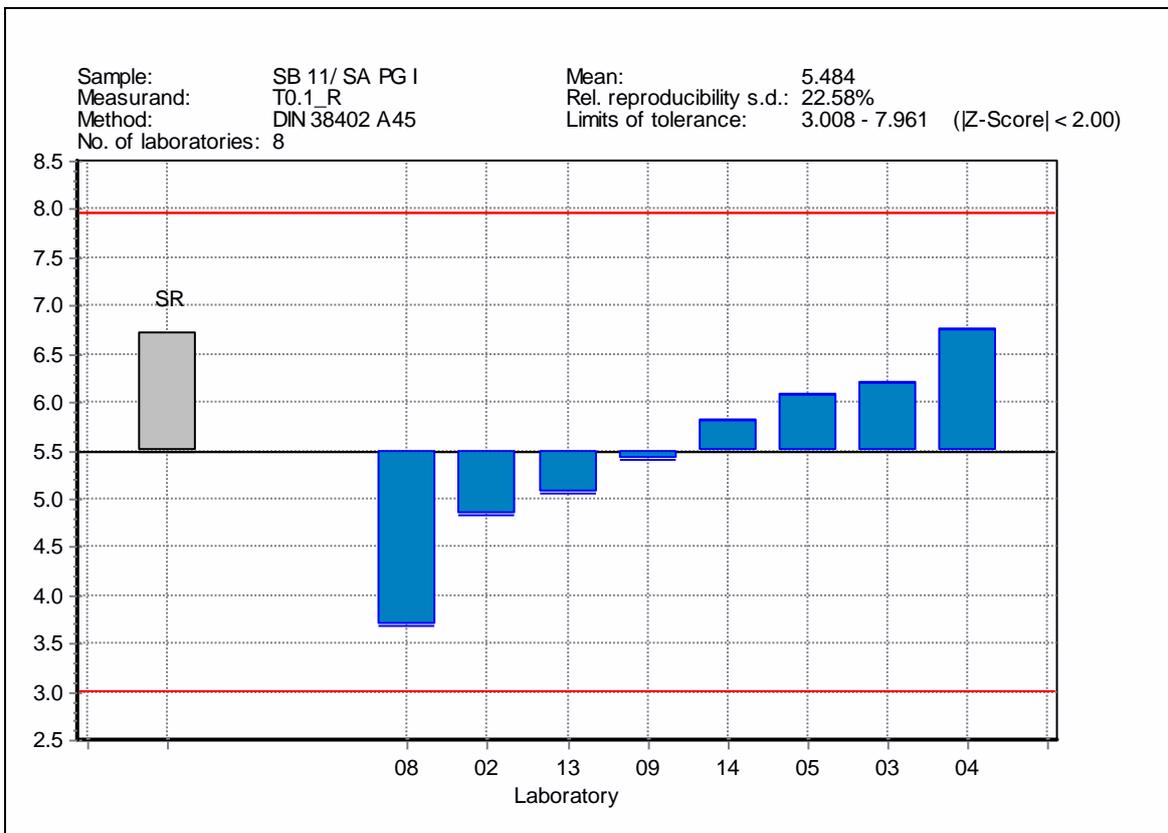


Figure 77: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 11 / SA PG I

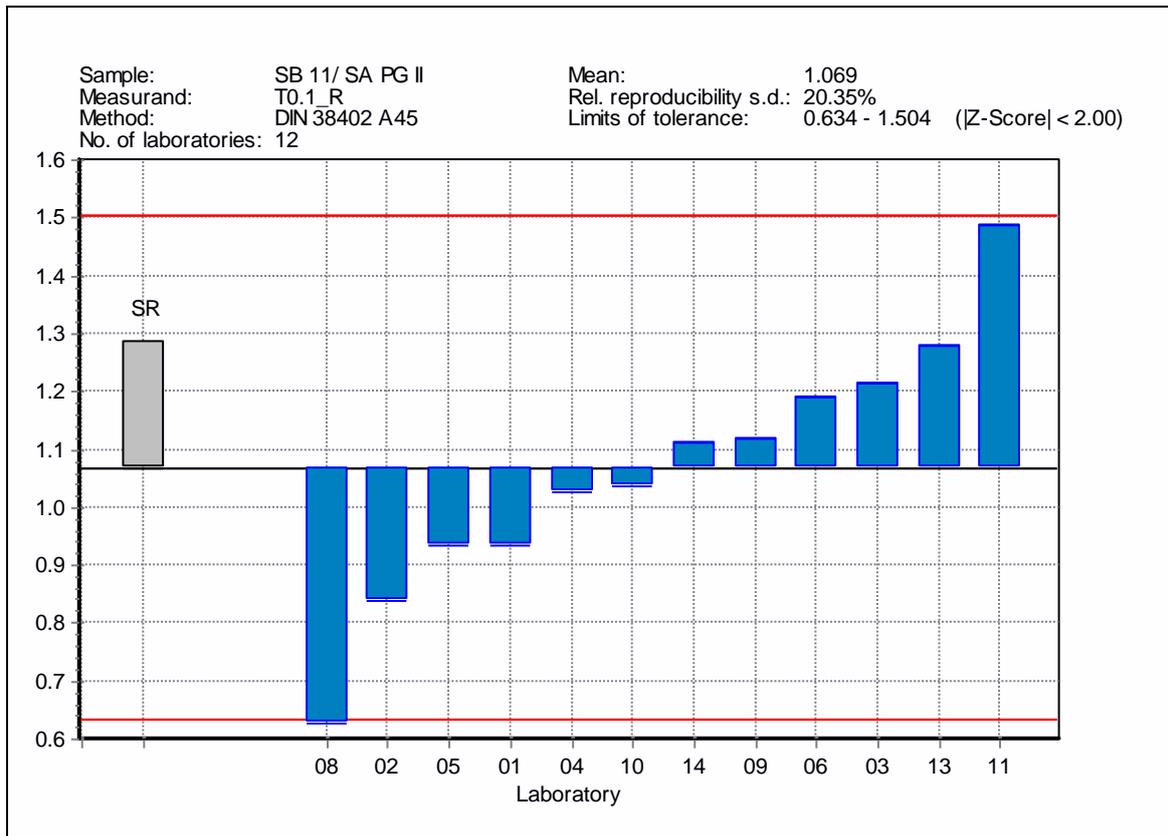


Figure 78: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 11 /SA PG II

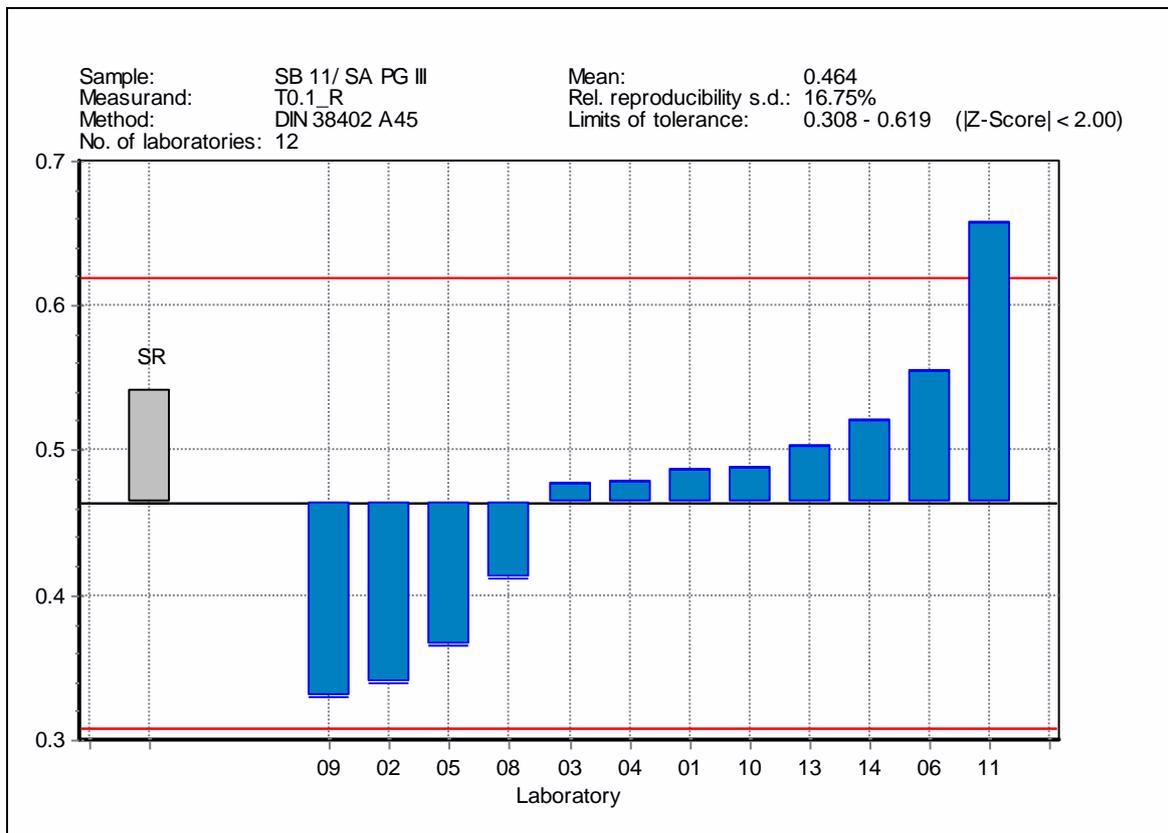


Figure 79: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 11 /SA PG III

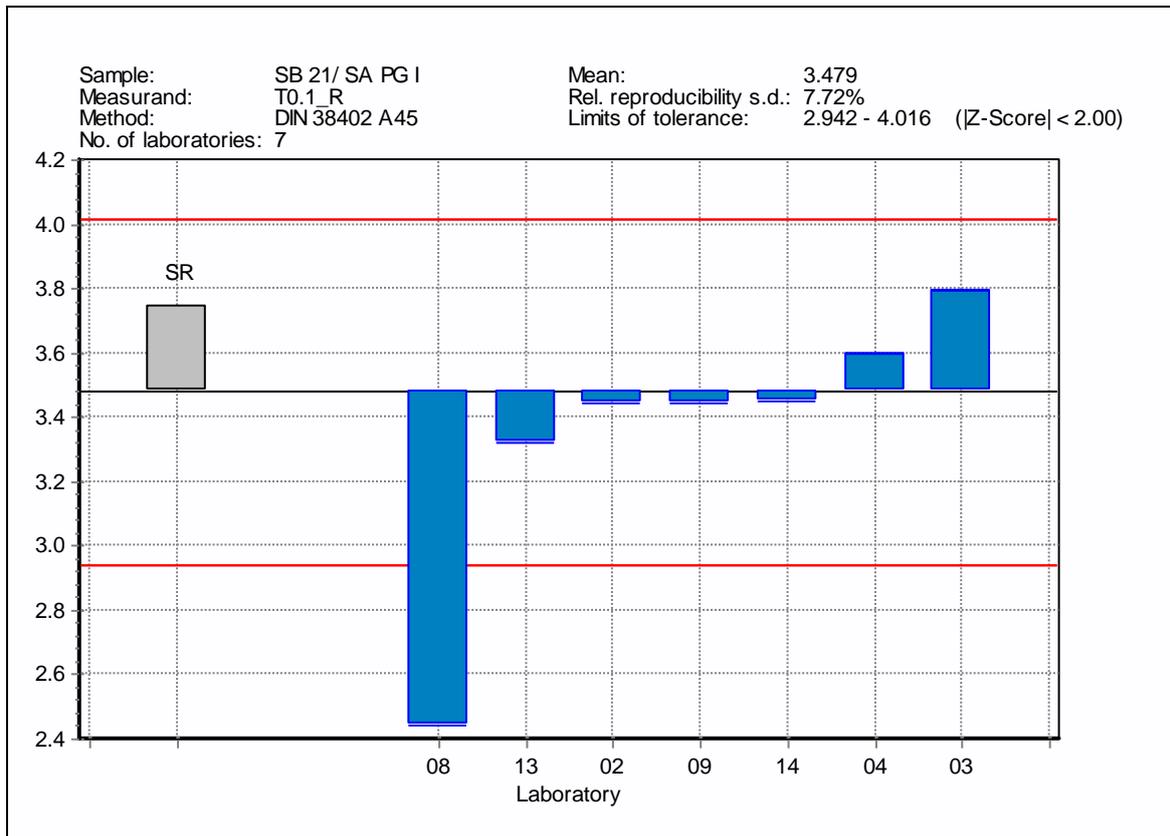


Figure 80: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 21 /SA PG I

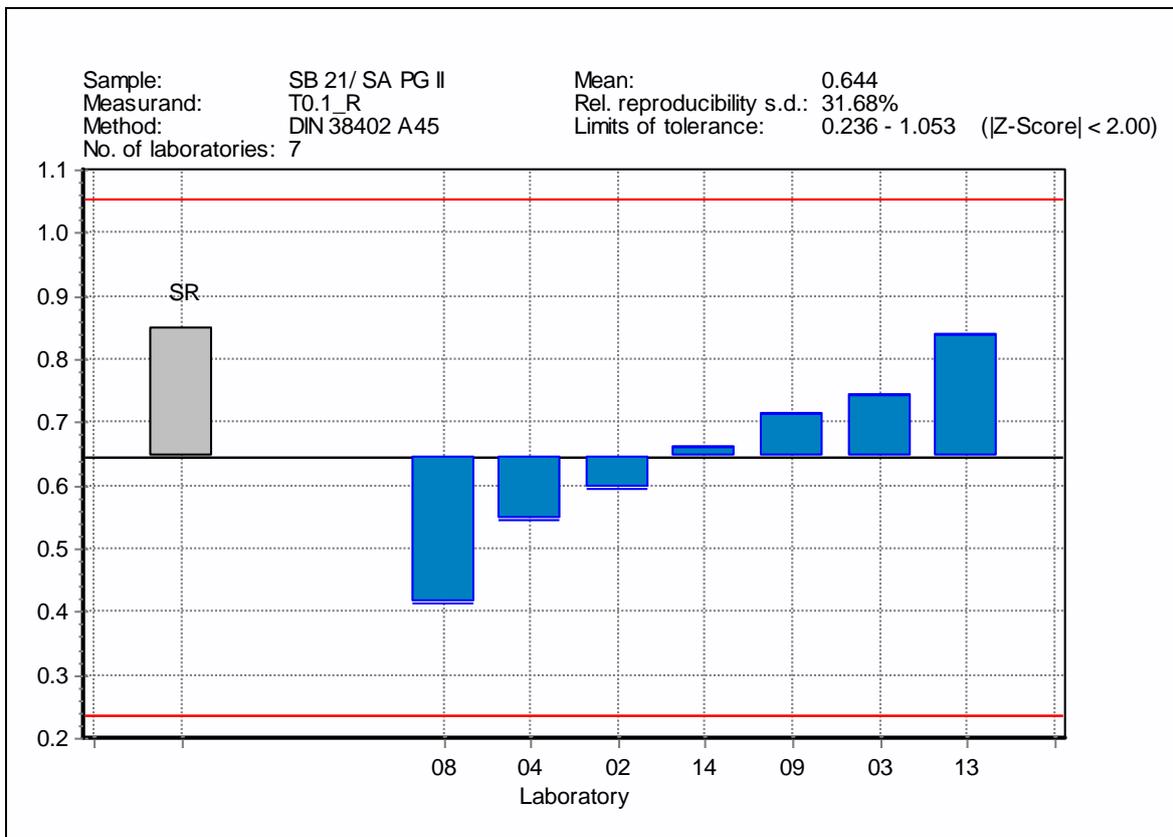


Figure 81: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 21 /SA PG II

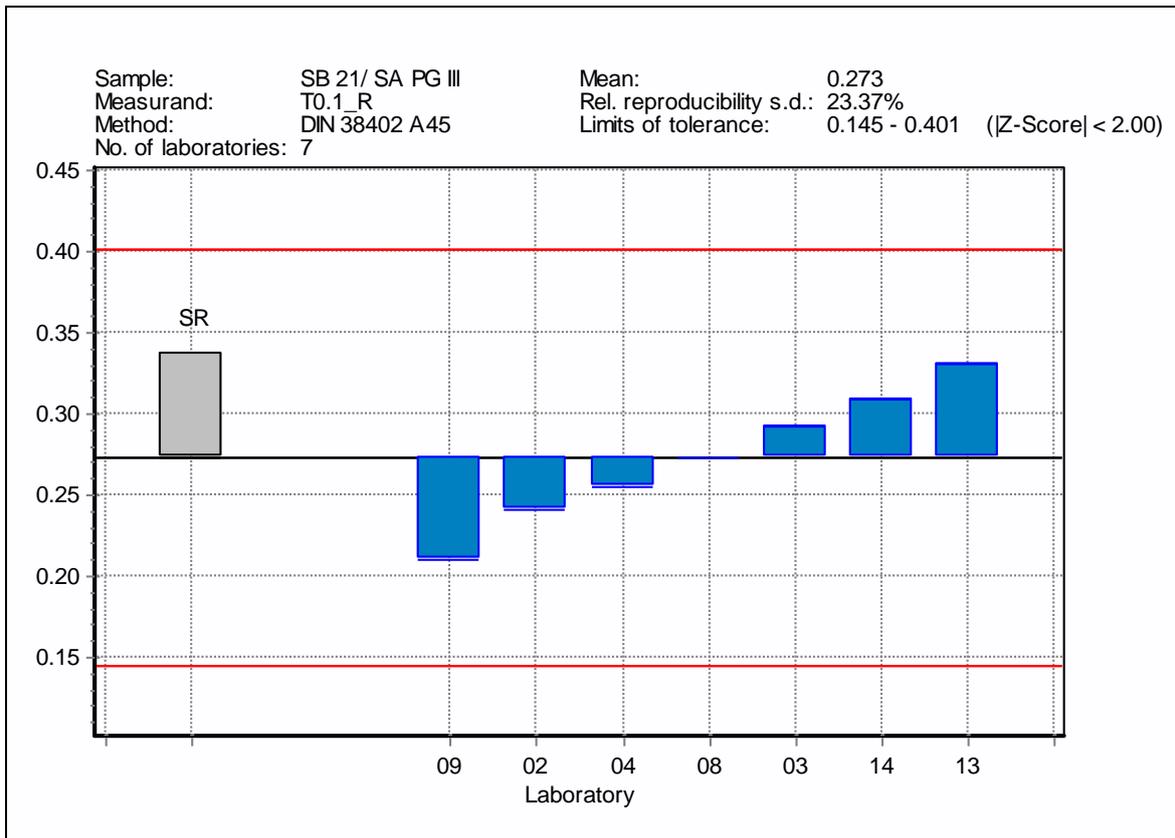


Figure 82: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 21 /SA PG III

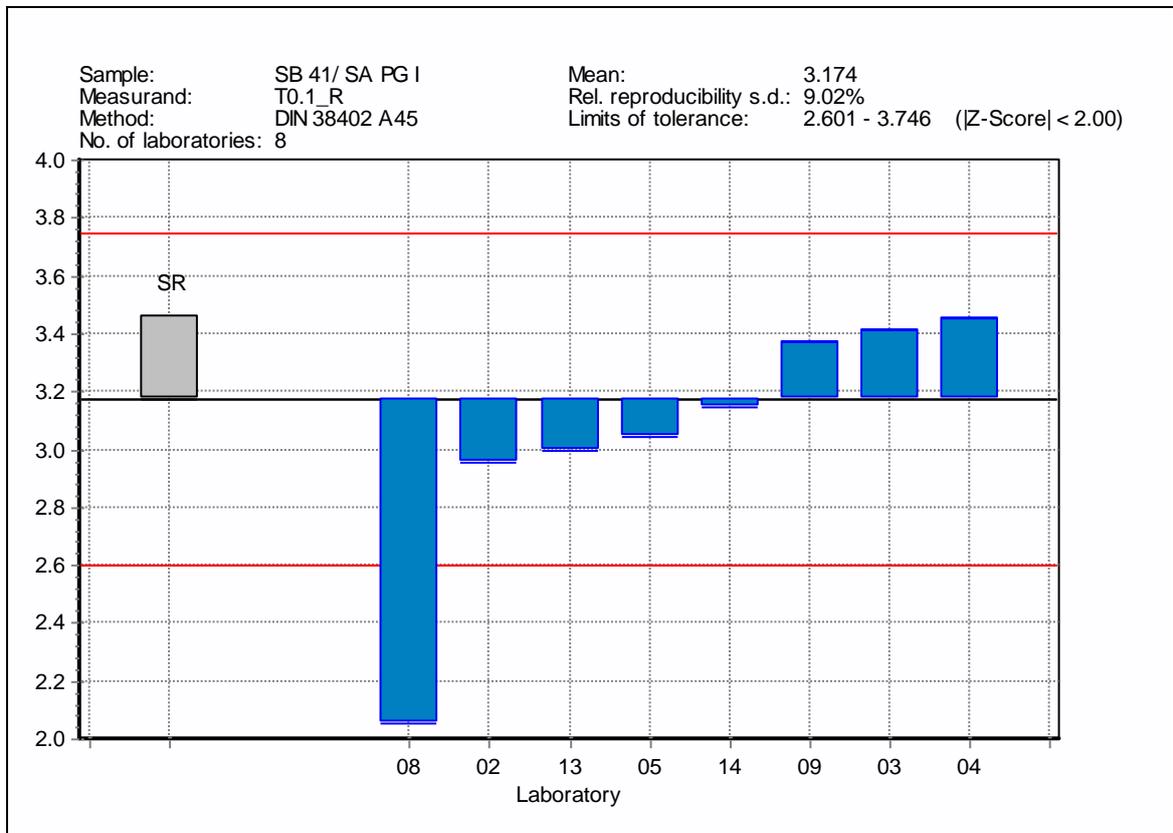


Figure 83: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 41 /SA PG I

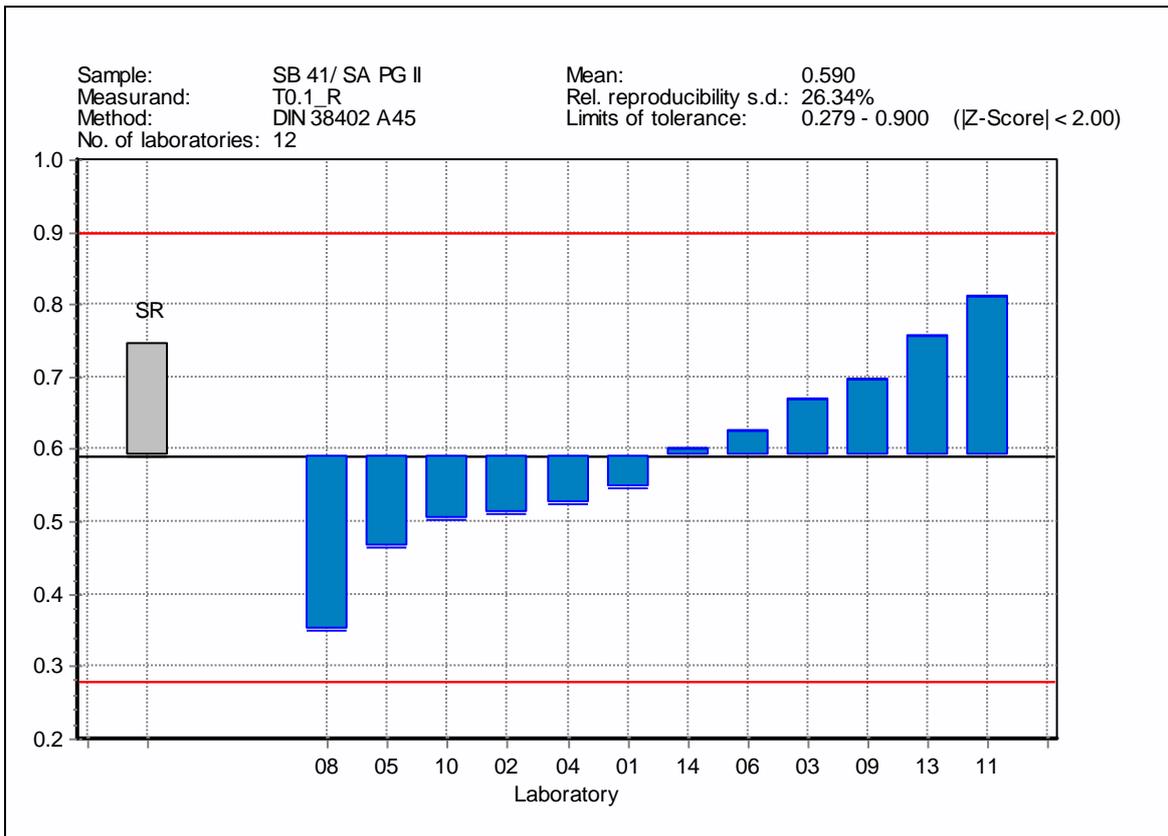


Figure 84: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 41 /SA PG II

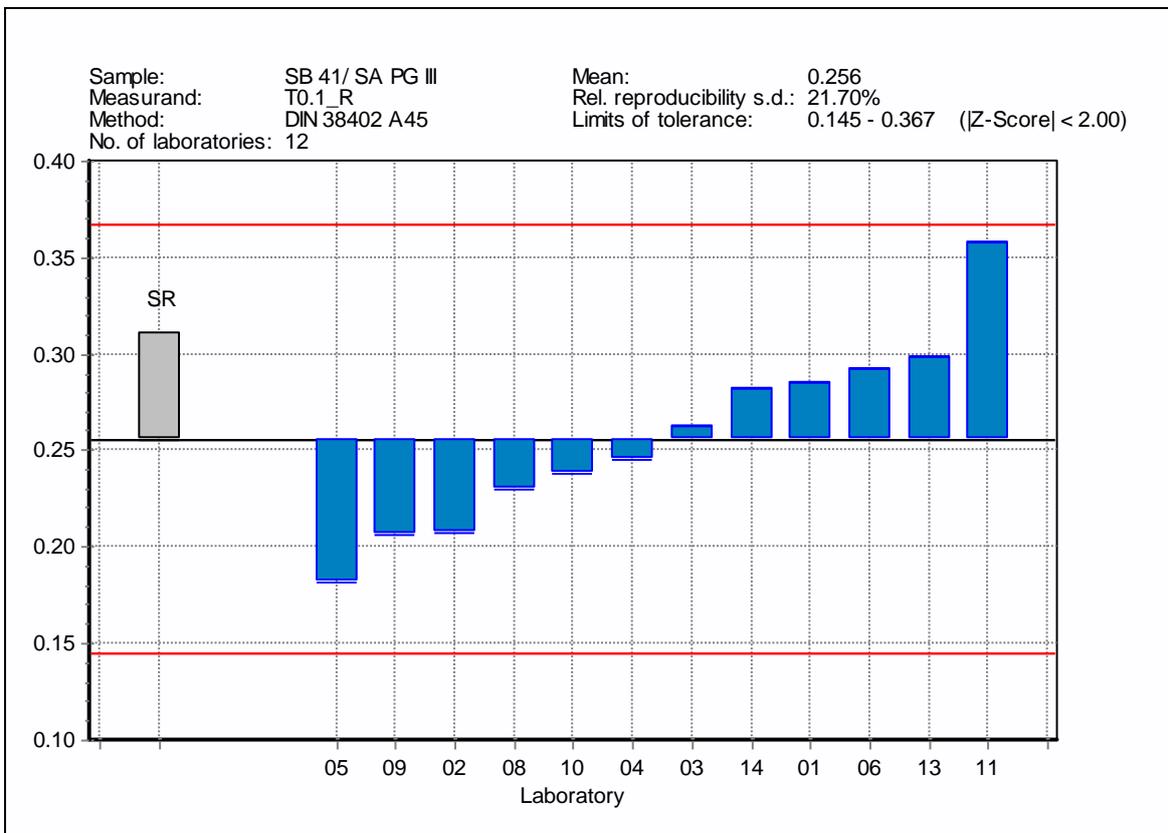


Figure 85: Laboratory results for individual combustion time $t_{0.1}$ – ratio SB 41 /SA PG III

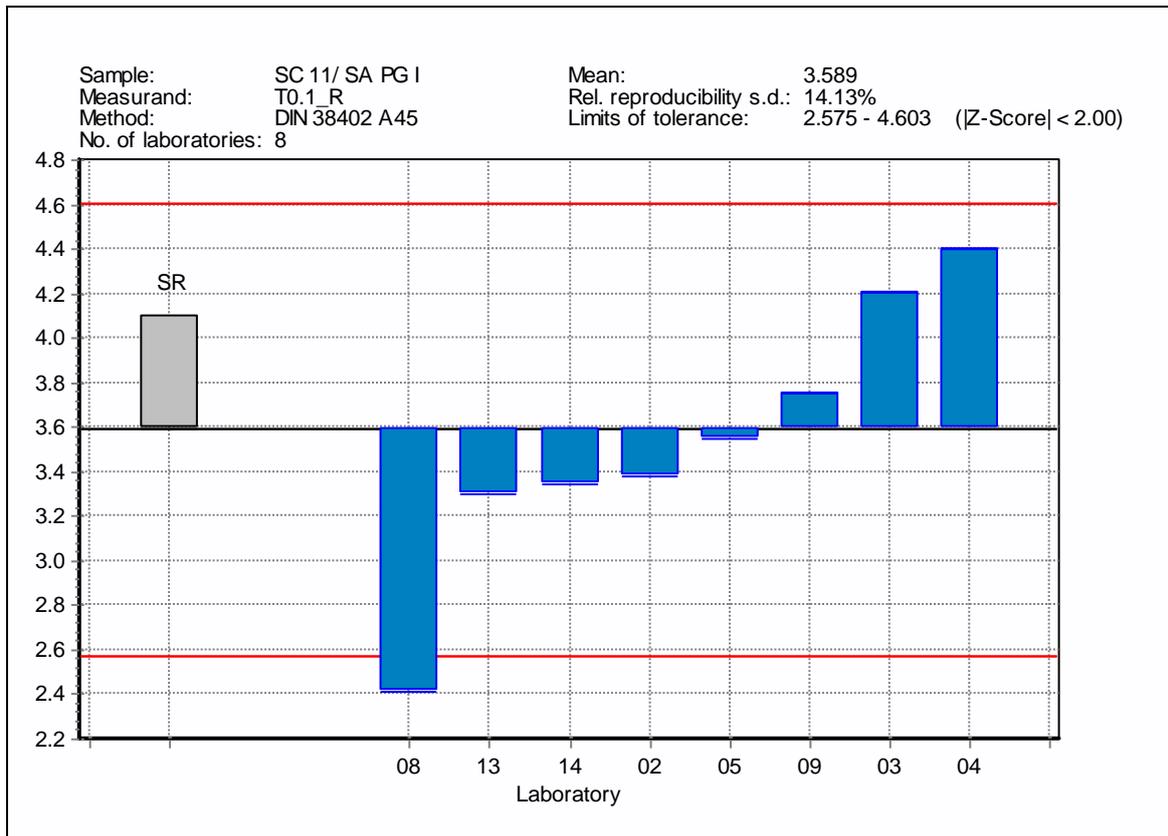


Figure 86: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 11 /SA PG I

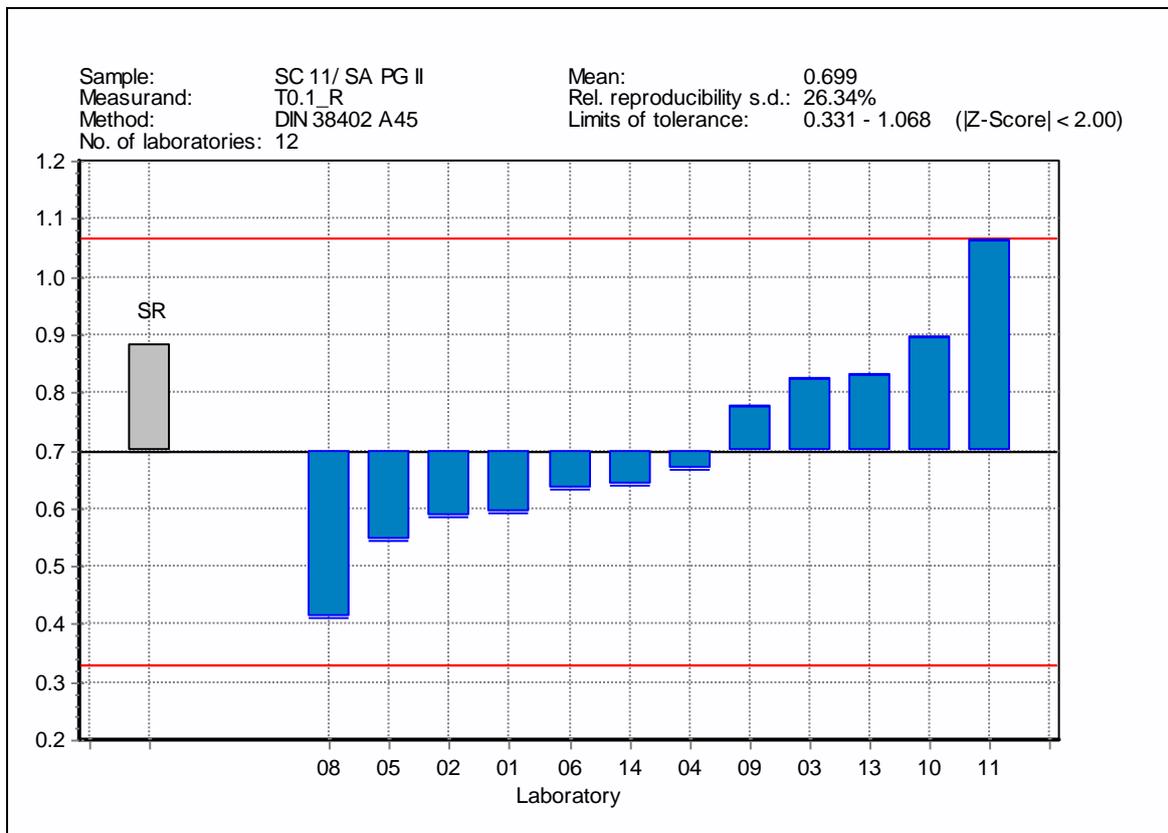


Figure 87: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 11 /SA PG II

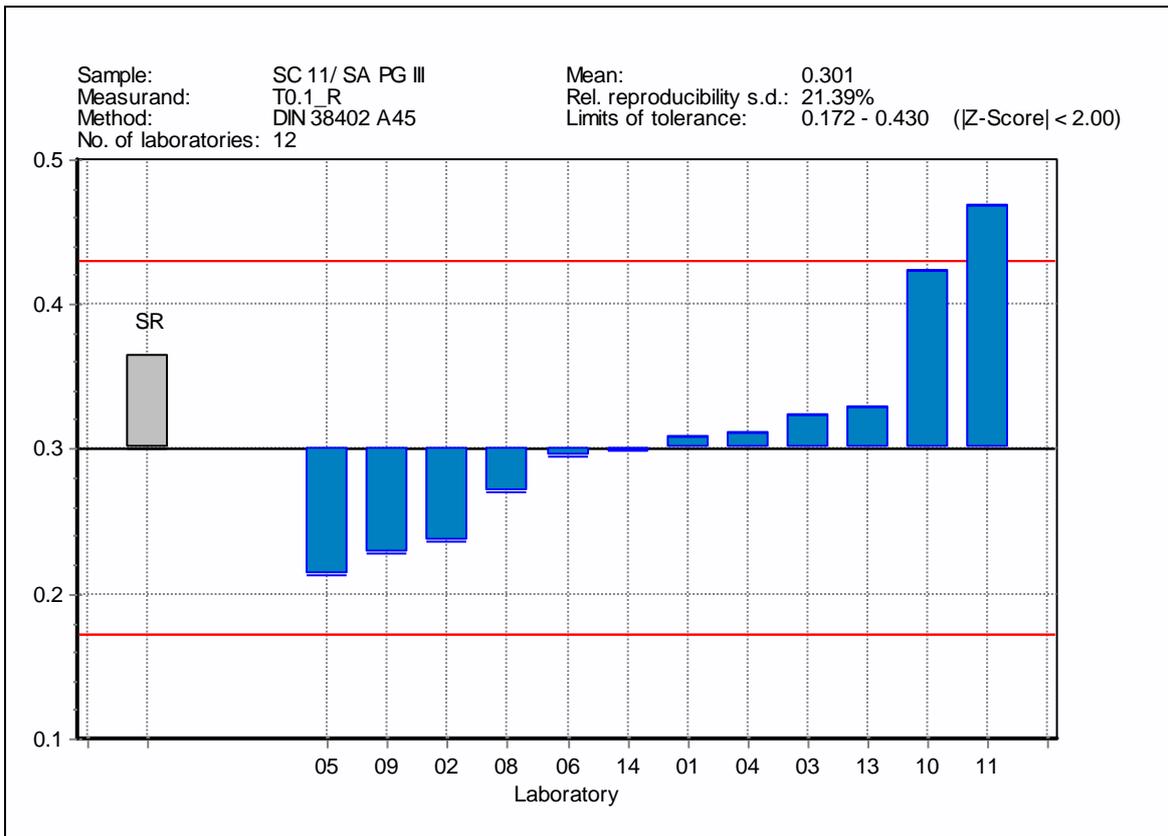


Figure 88: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 11 /SA PG III

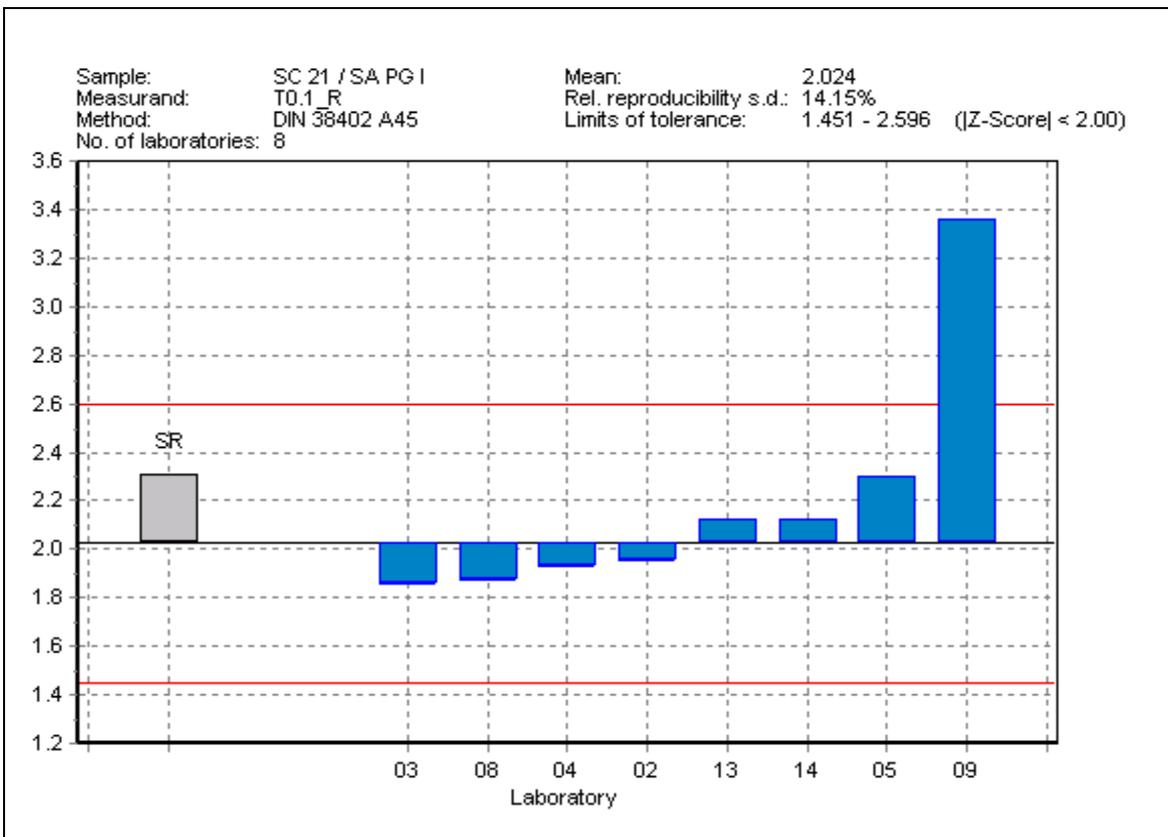


Figure 89: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 21 /SA PG I

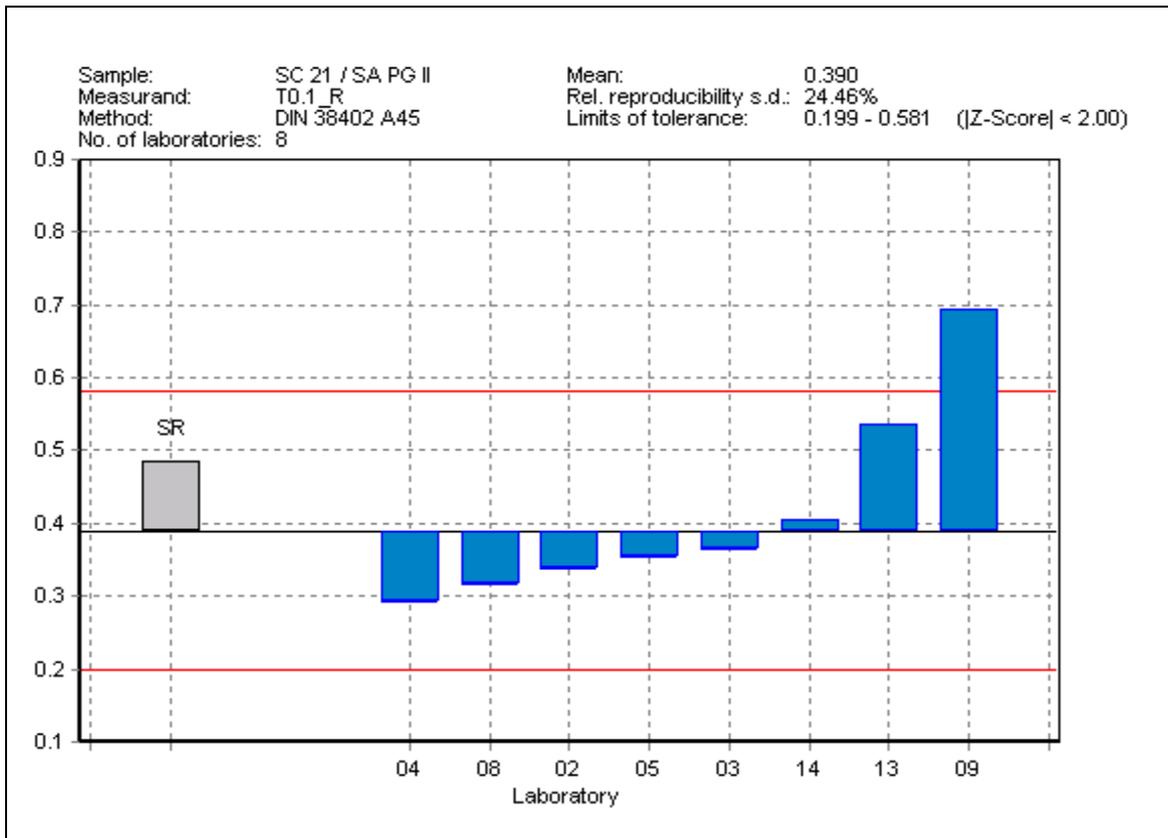


Figure 90: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 21 / SA PG II

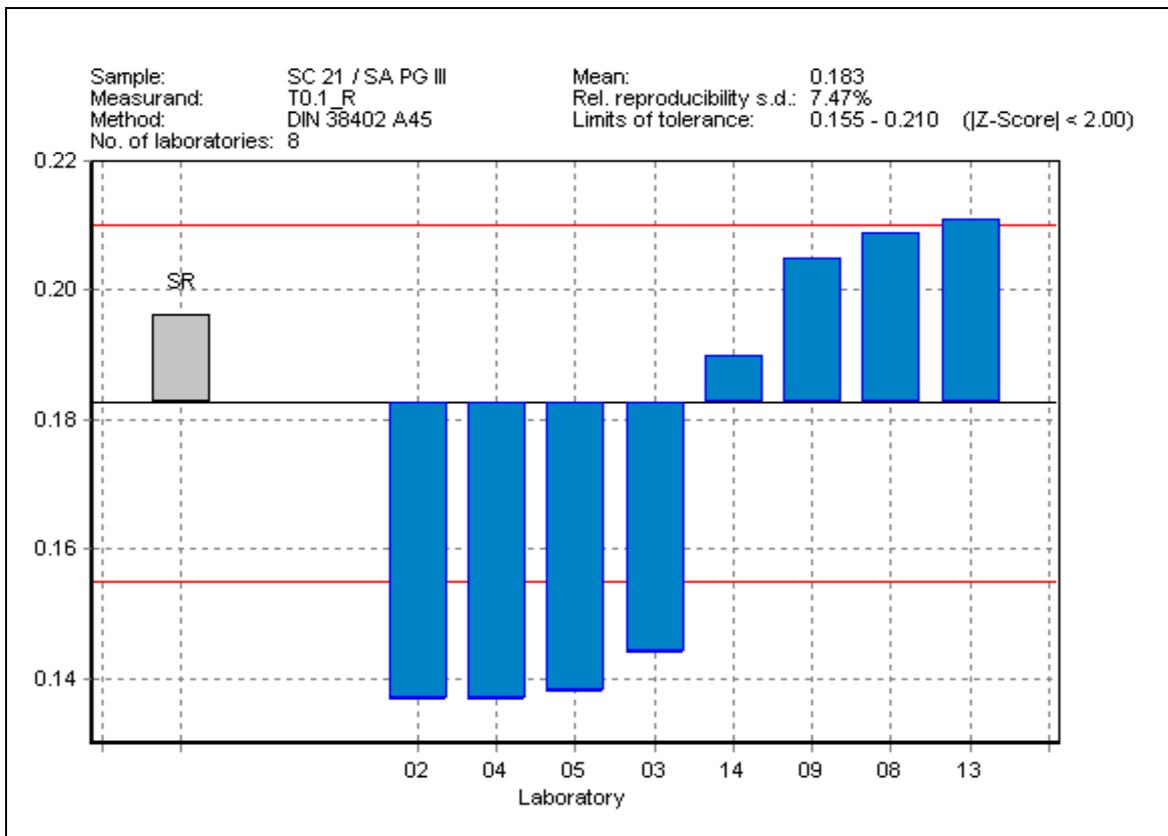


Figure 91: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 21 / SA PG III

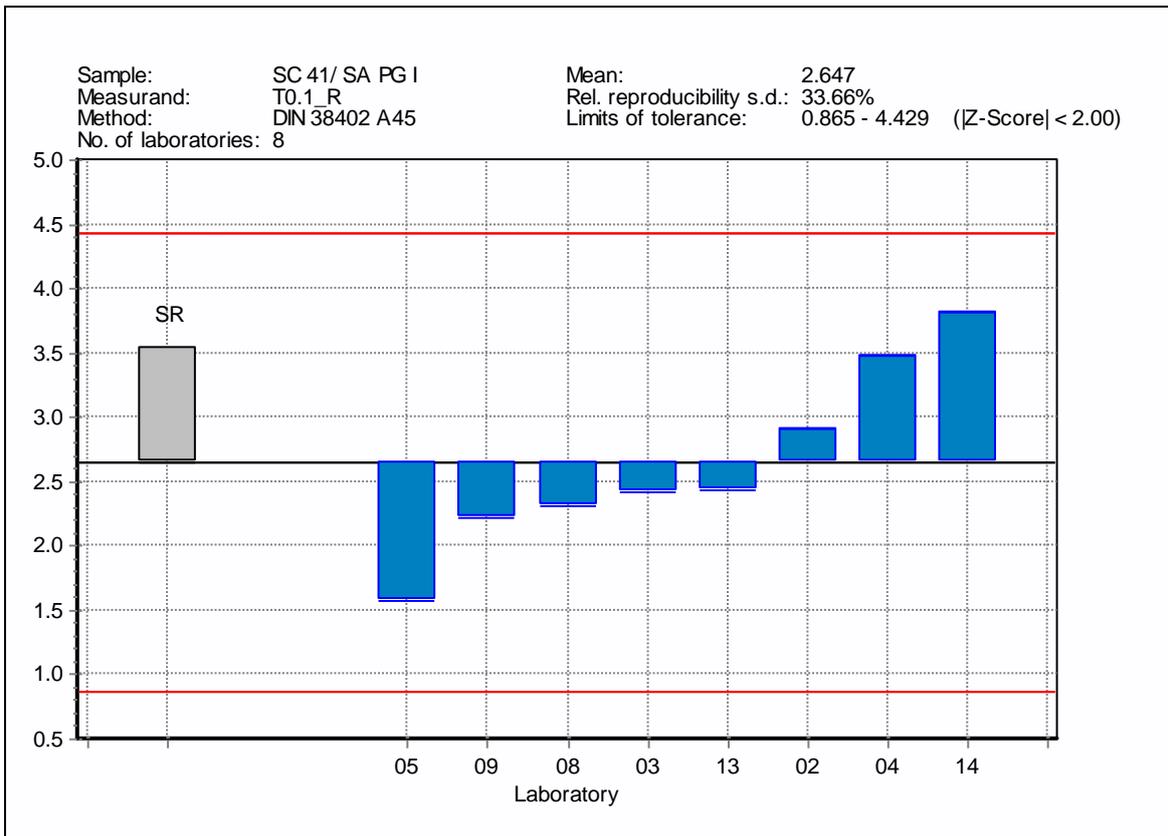


Figure 92: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 41 /SA PG I

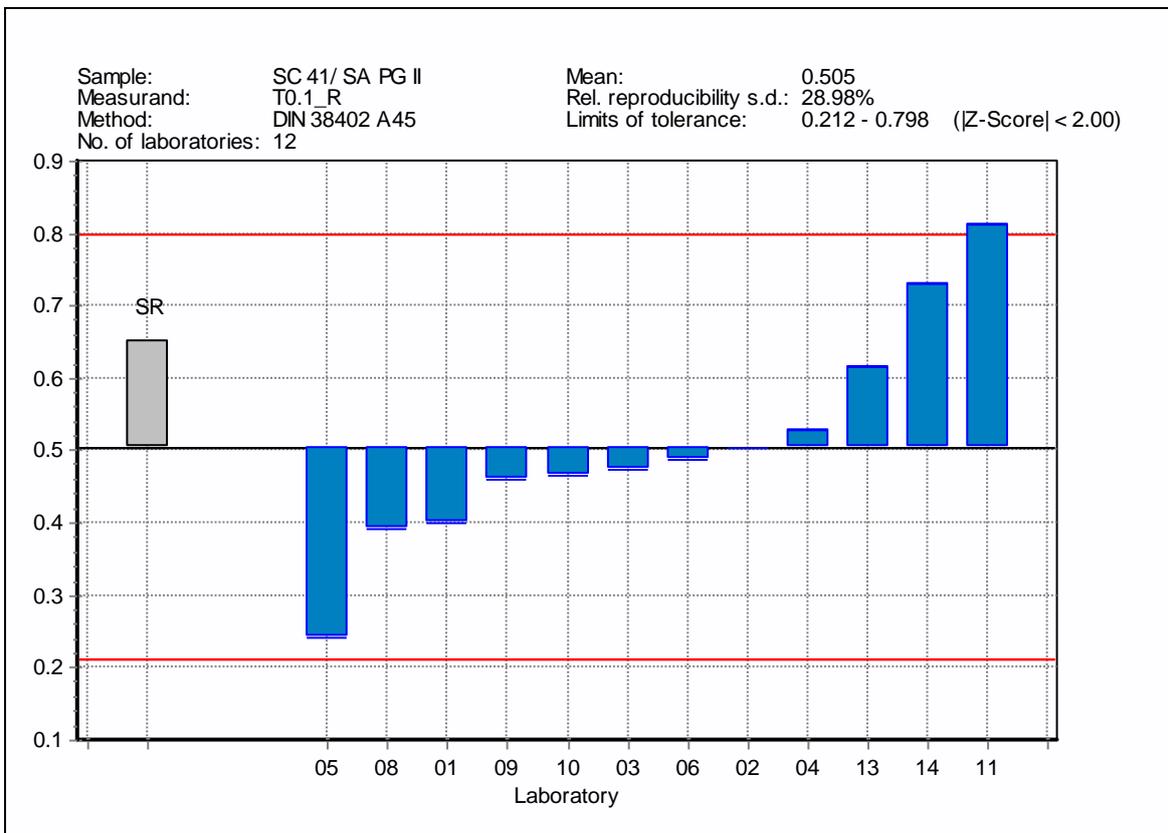


Figure 93: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 41 /SA PG II

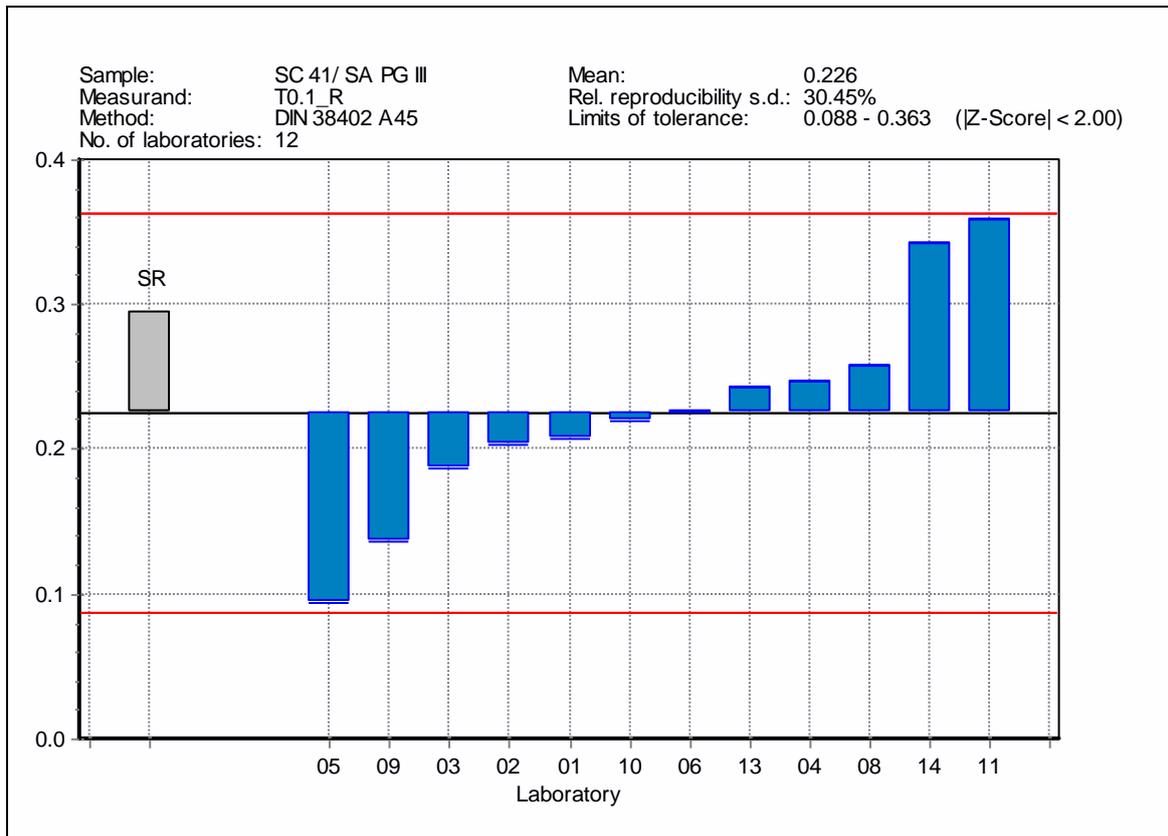


Figure 94: Laboratory results for individual combustion time $t_{0.1}$ – ratio SC 41 /SA PG III

10.4 Main combustion time

10.4.1 Outliers and stragglers

Table 52: Outliers and straggler for main combustion time t_{20-80} [s]

Sample	Lab code	Outlier test	Outlier/Straggler
SA PG III	05	Cochran	outlier
SA PG III	09	Grubbs	straggler
SC 11	10	Cochran	outlier
SC 11	04	Cochran	outlier
SC 21	04	Cochran	outlier
SC 41	14	Grubbs	straggler
SC 41	04	Cochran	outlier

10.4.2 Analysis of single values

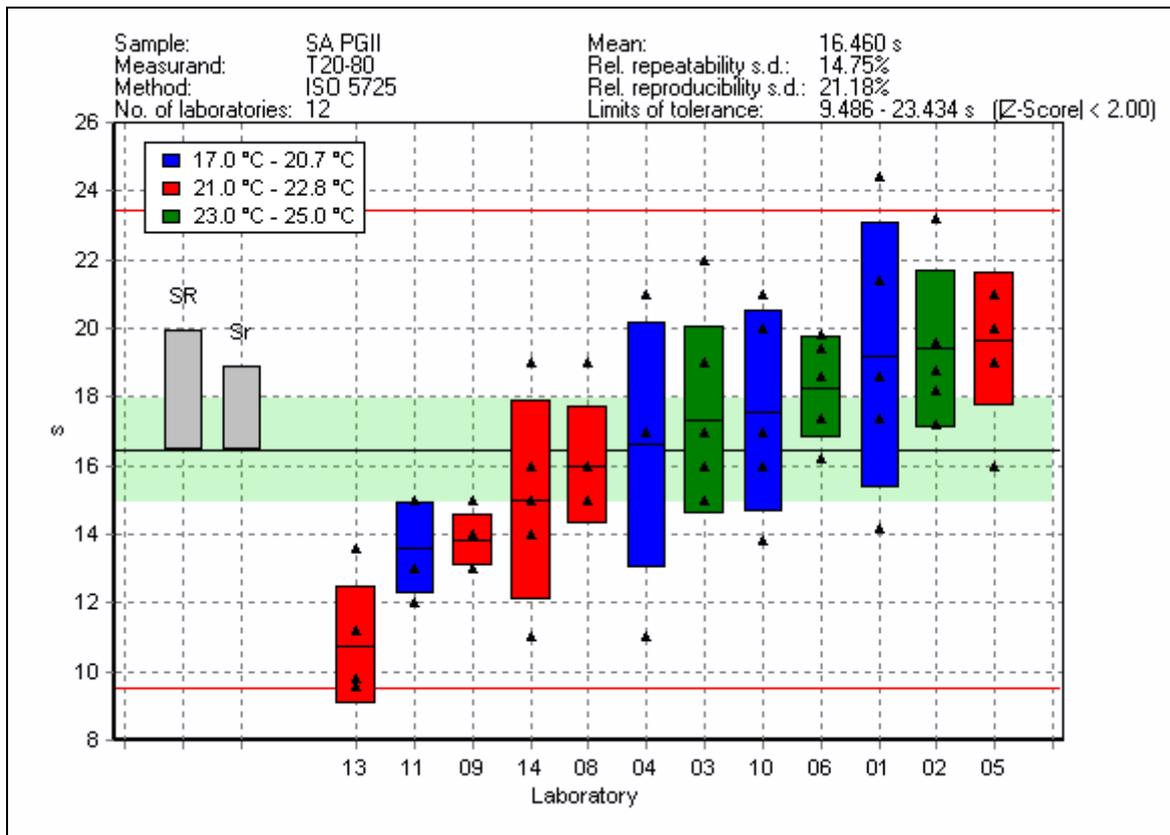


Figure 95: Laboratory results for main combustion time t_{20-80} [s] – SA PG II



Figure 96: Laboratory results for main combustion time t_{20-80} [s] – SA PG III

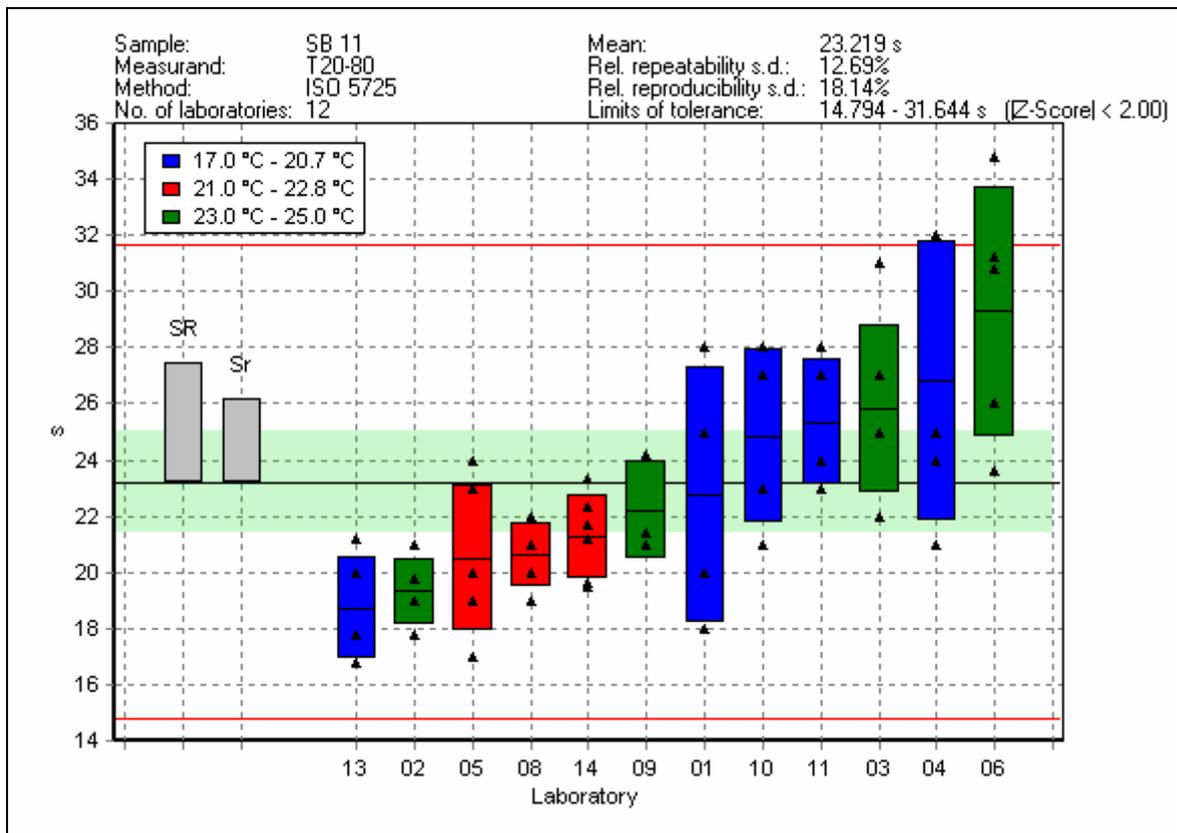


Figure 97: Laboratory results for main combustion time t_{20-80} [s] – SB 11

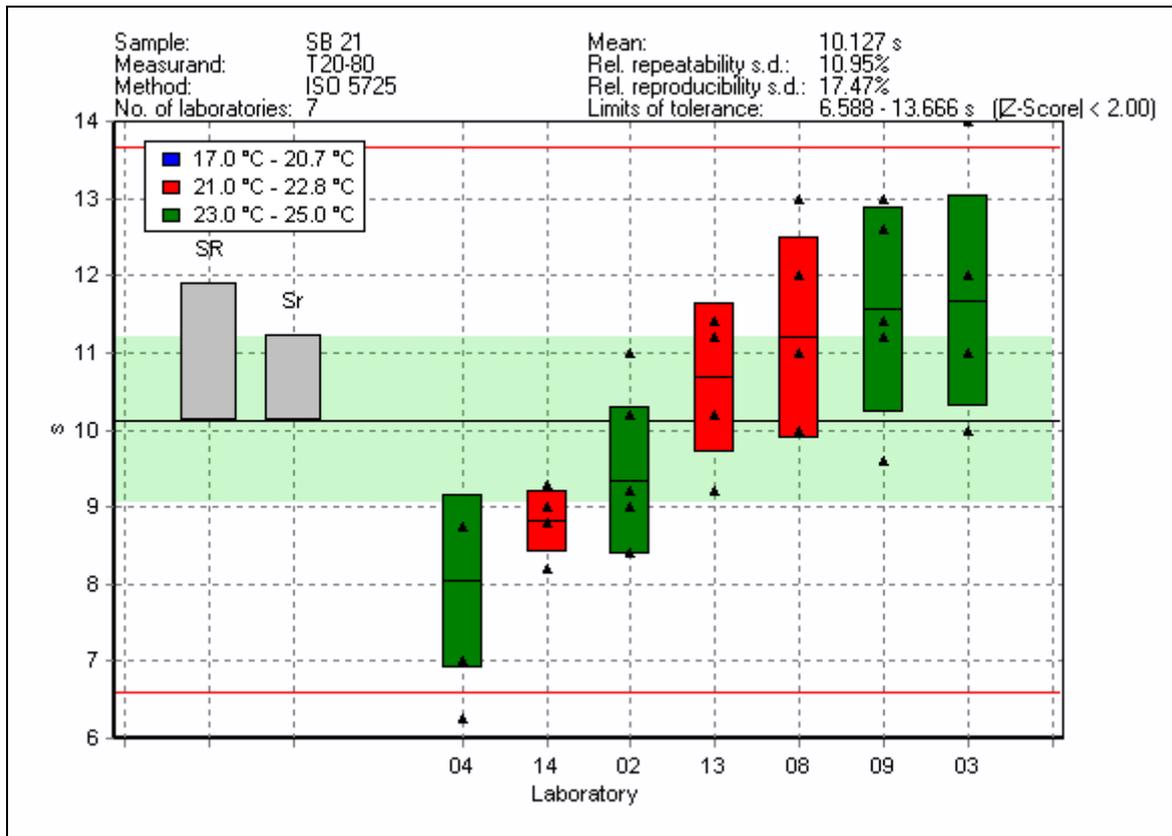


Figure 98: Laboratory results for main combustion time t_{20-80} [s] – SB 21

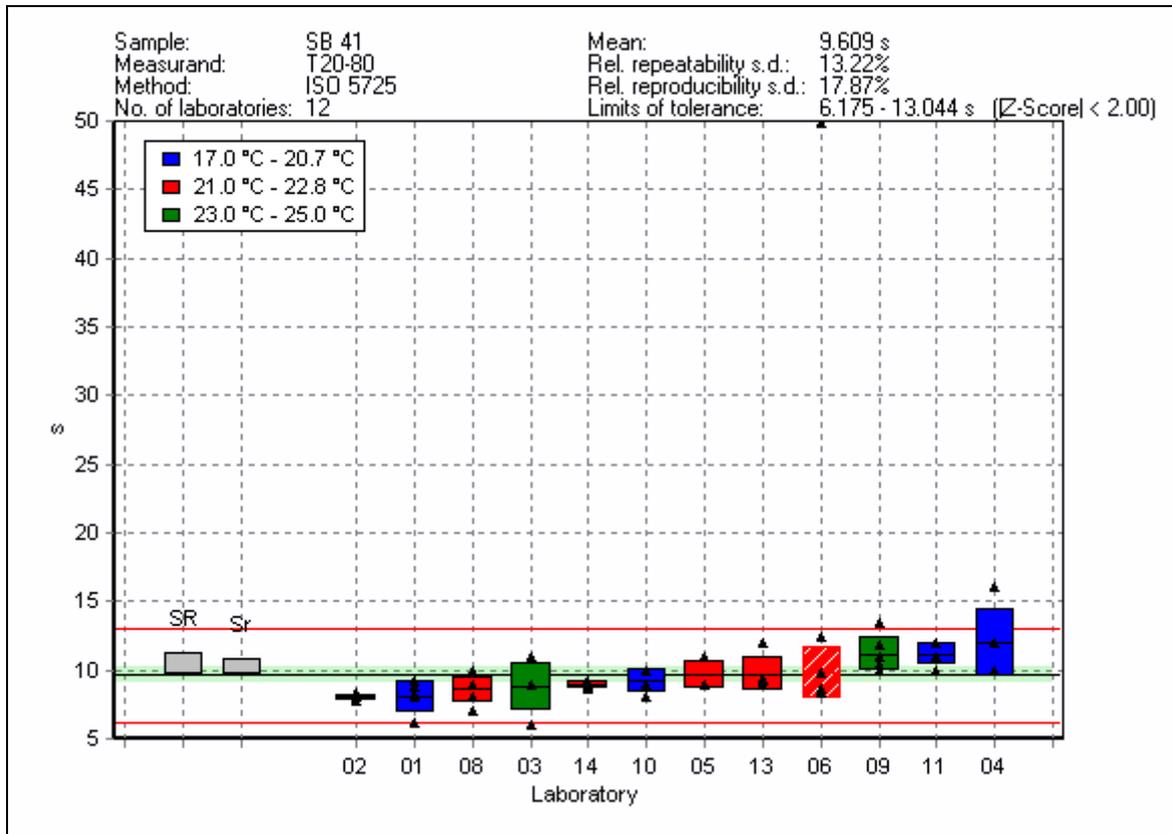


Figure 99: Laboratory results for main combustion time t_{20-80} [s] – SB 41

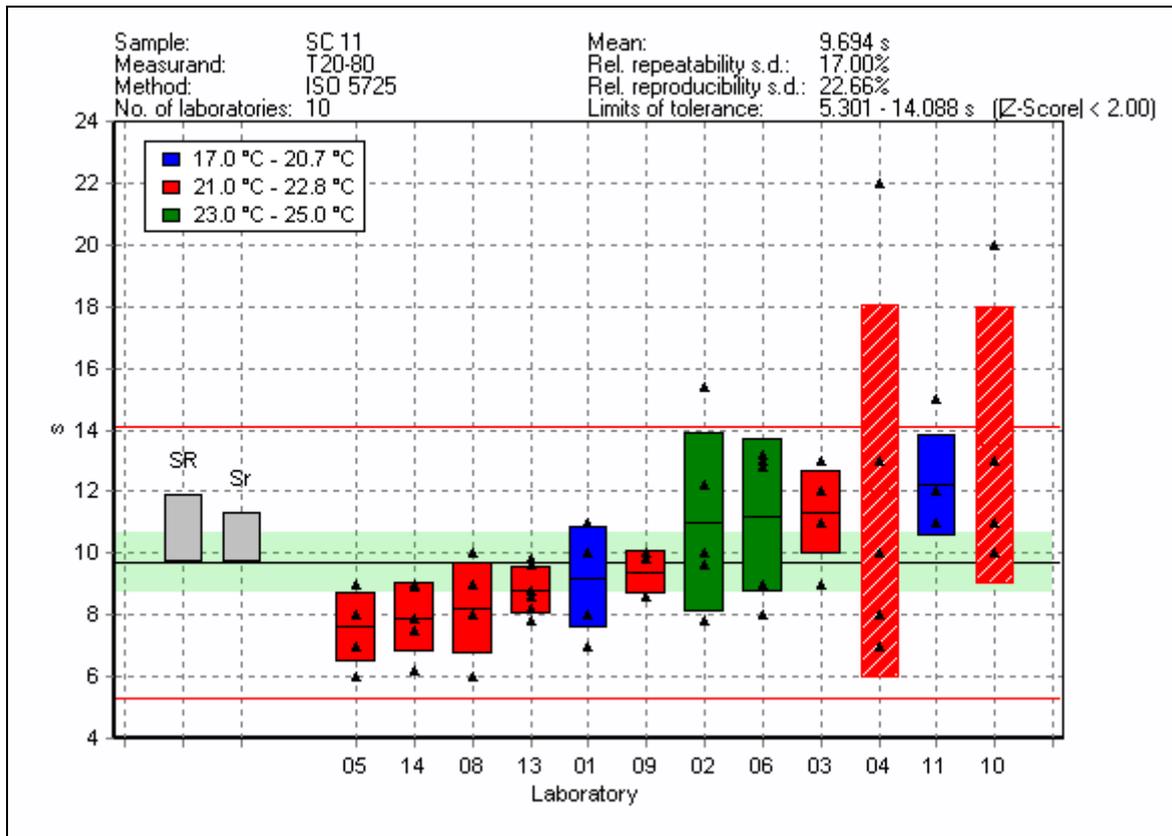


Figure 100: Laboratory results for main combustion time t_{20-80} [s] – SC 11

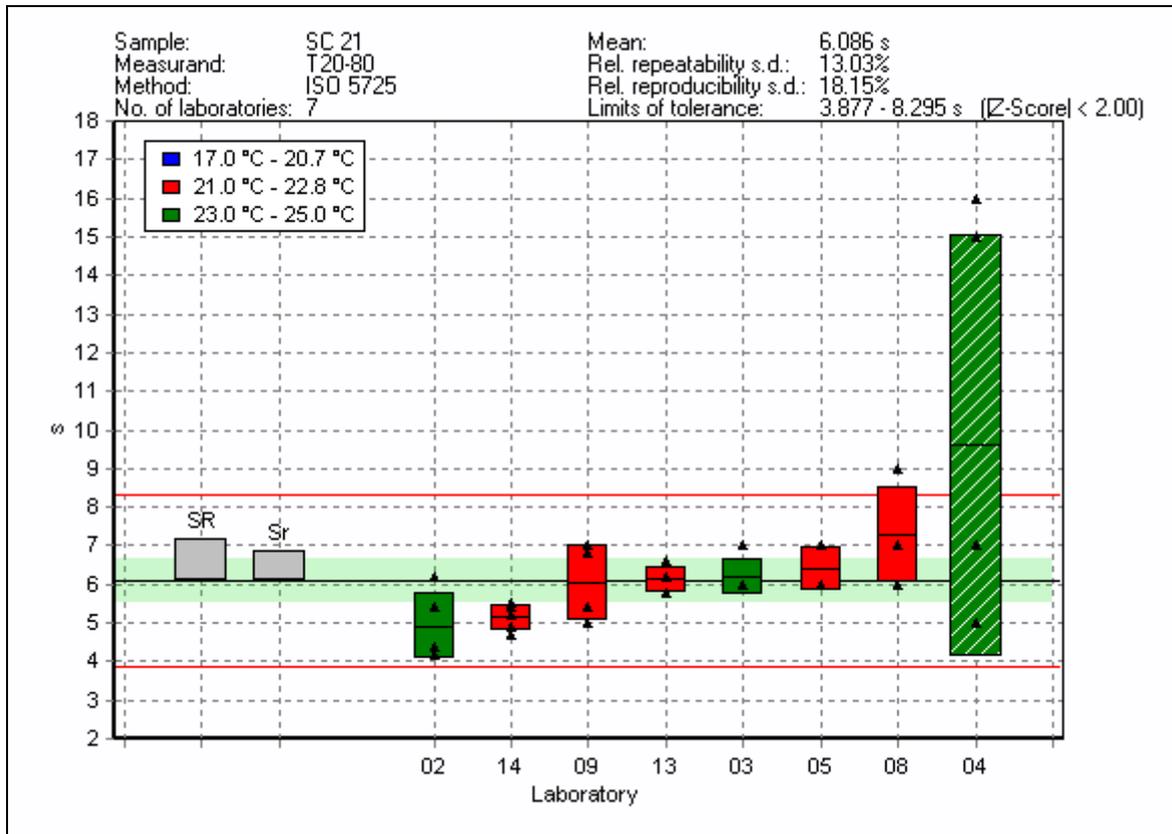


Figure 101: Laboratory results for main combustion time t_{20-80} [s] – SC 21



10.4.3 Analysis of ratios

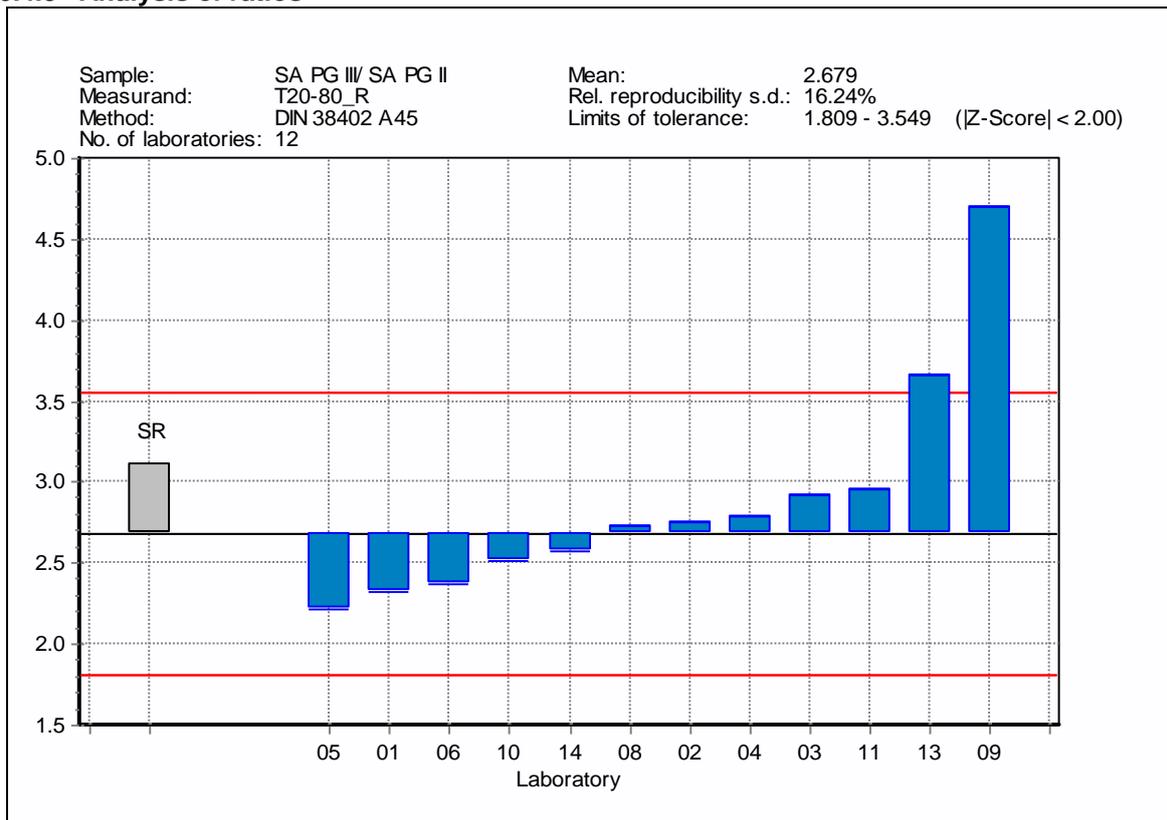


Figure 103: Laboratory results for main combustion time t_{20-80} – ratio SA PG III / SA PG II

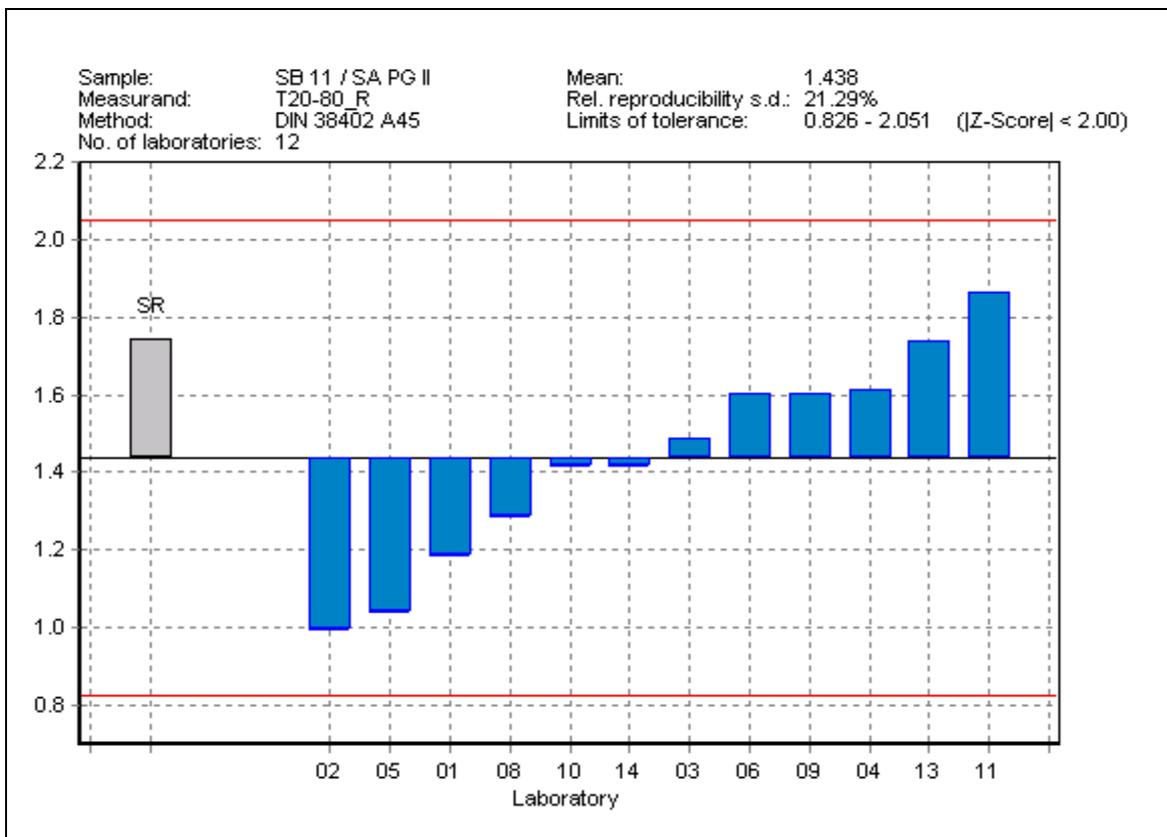


Figure 104: Laboratory results for main combustion time t_{20-80} – ratio SB 11 / SA PG II

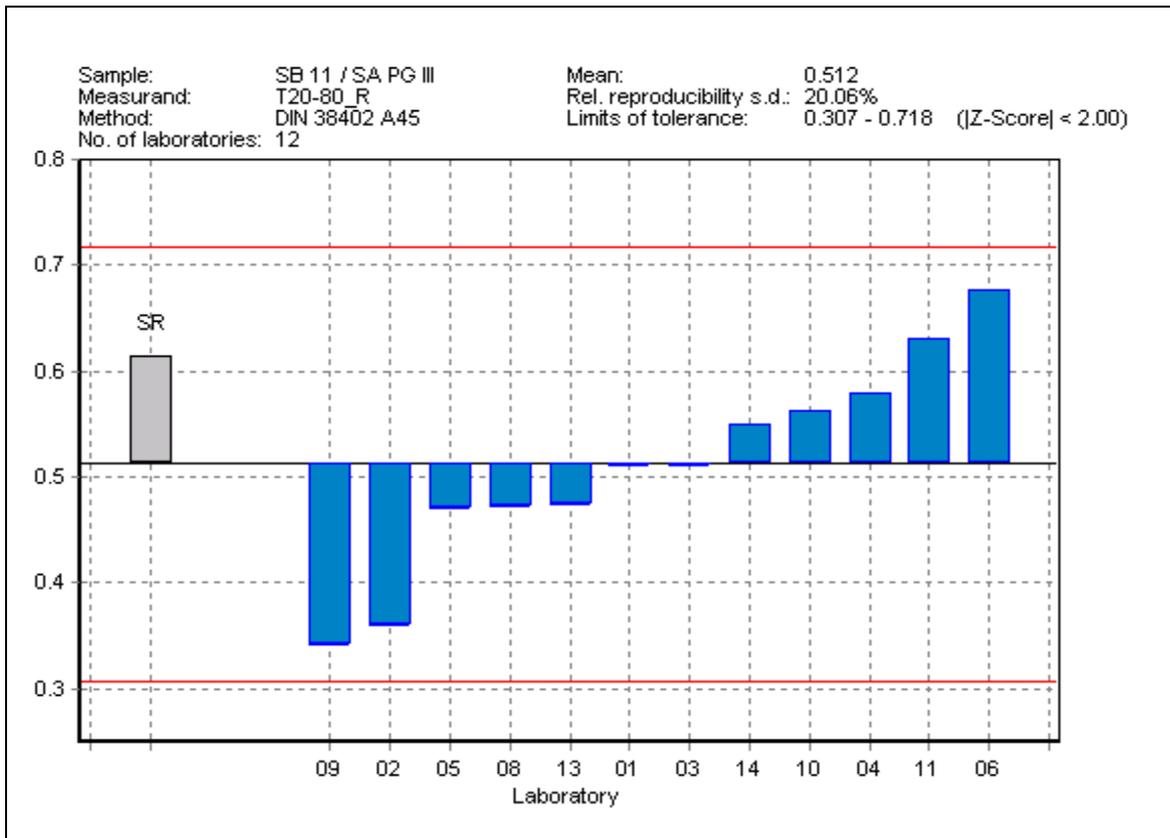


Figure 105: Laboratory results for main combustion time t_{20-80} – ratio SB 11 / SA PG III

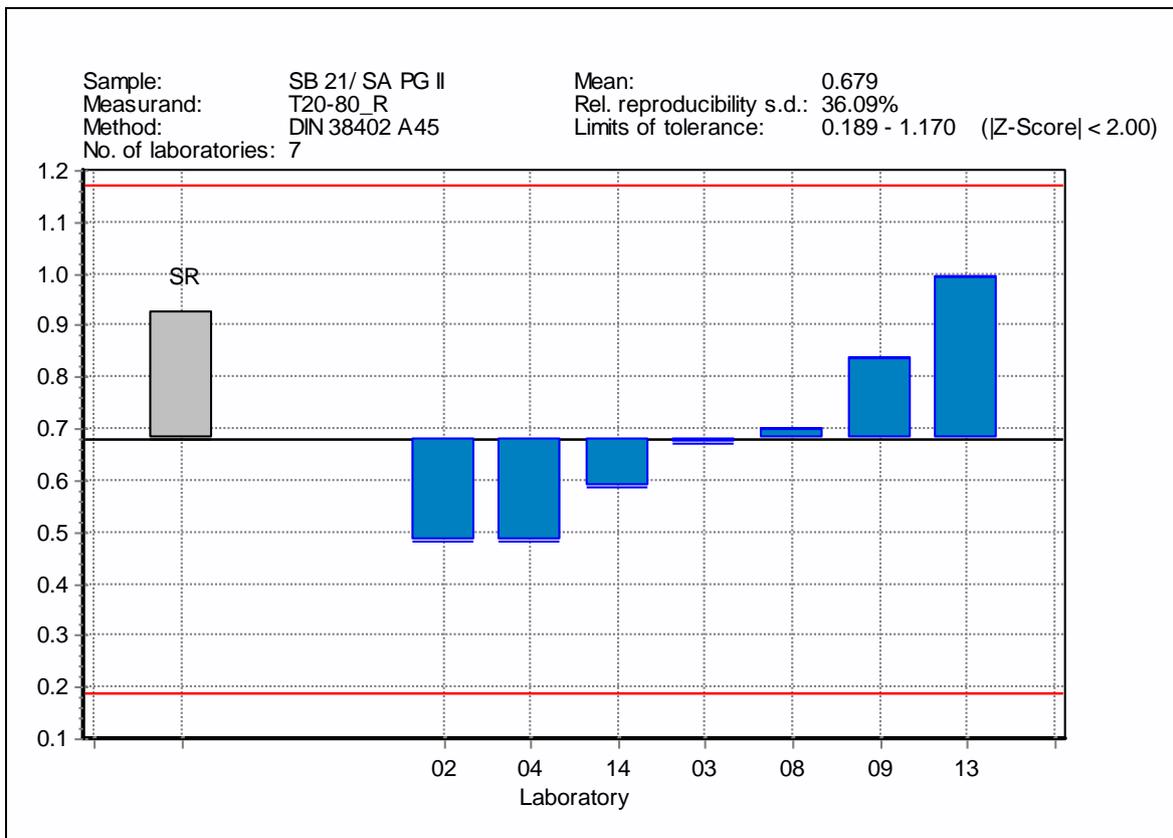


Figure 106: Laboratory results for main combustion time t_{20-80} – ratio SB 21 / SA PG II

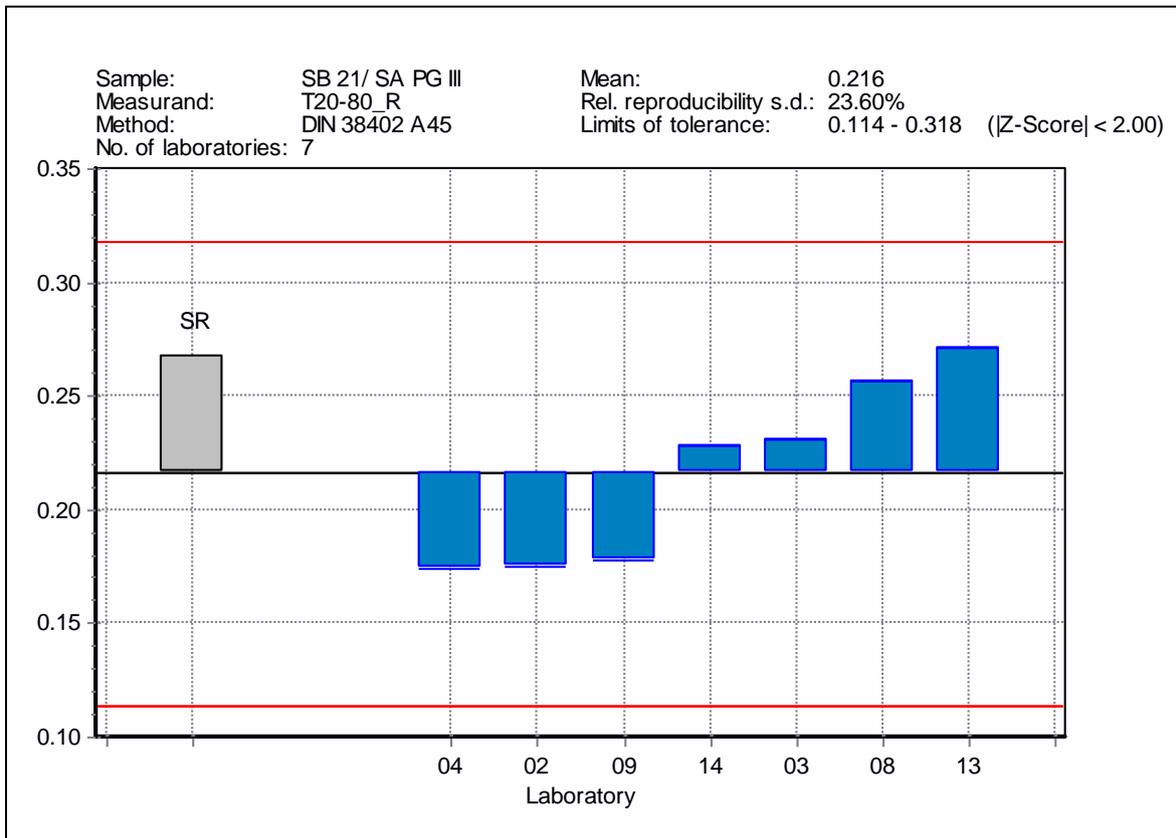


Figure 107: Laboratory results for main combustion time t_{20-80} – ratio SB 21 /SA PG III

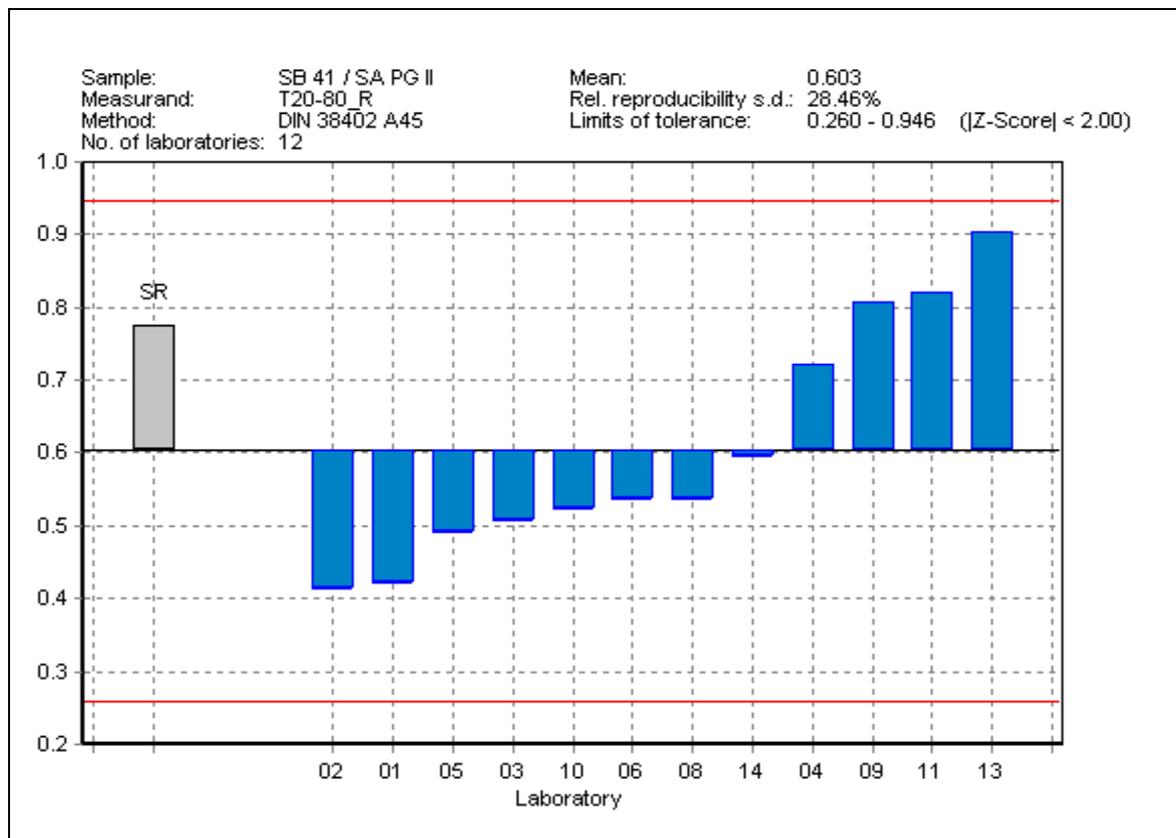


Figure 108: Laboratory results for main combustion time t_{20-80} – ratio SB 41 /SA PG II

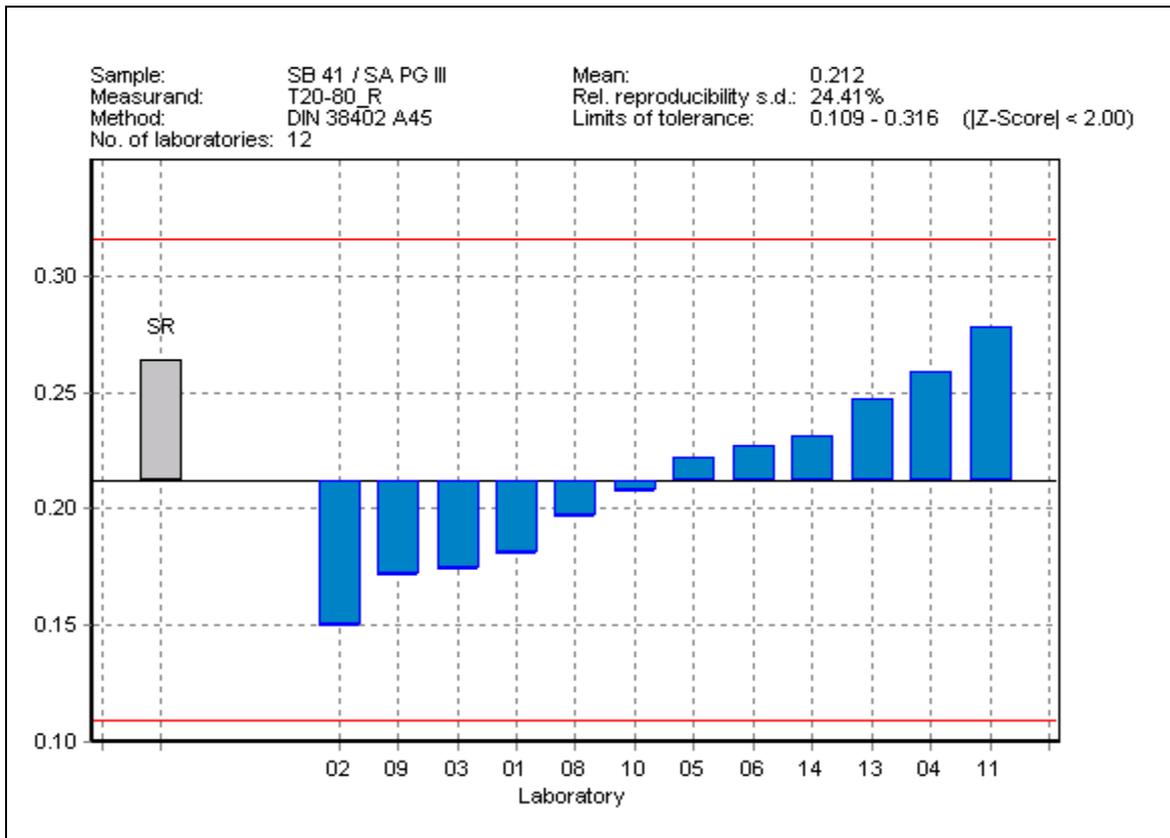


Figure 109: Laboratory results for main combustion time t_{20-80} – ratio SB 41 / SA PG III

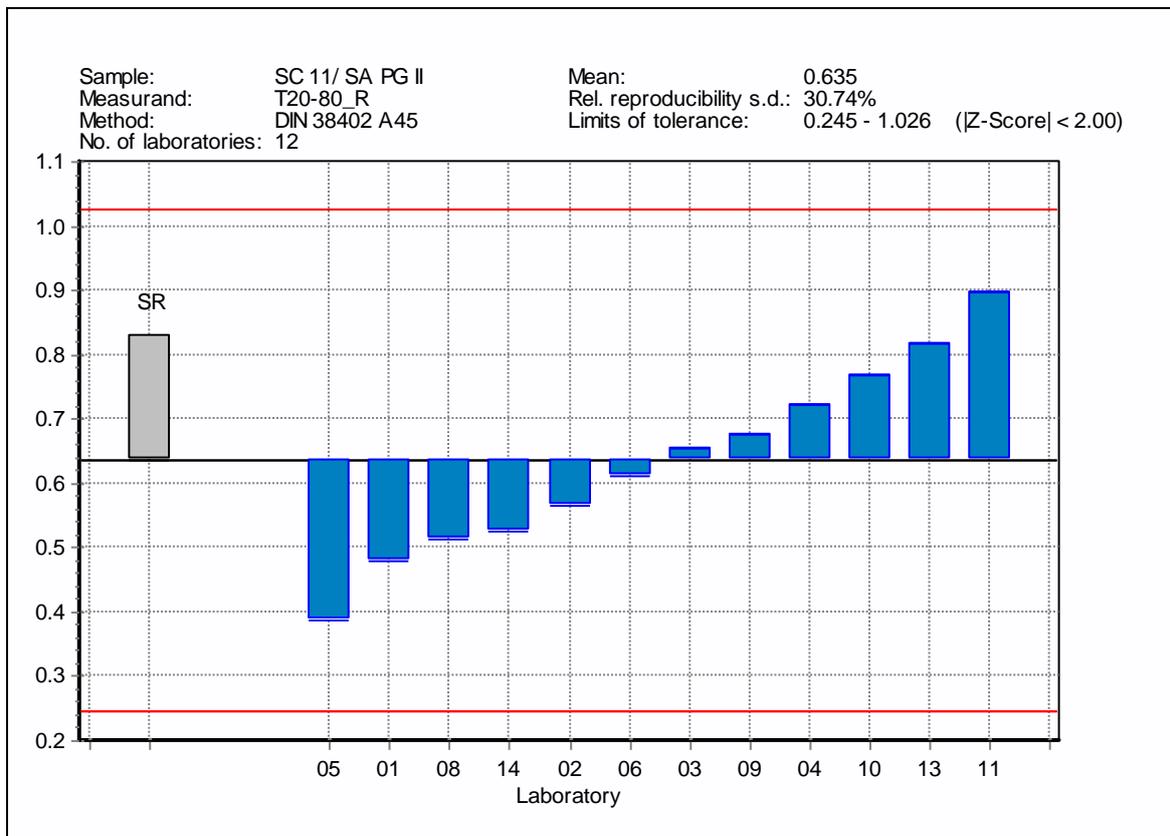


Figure 110: Laboratory results for main combustion time t_{20-80} – ratio SC 11 / SA PG II

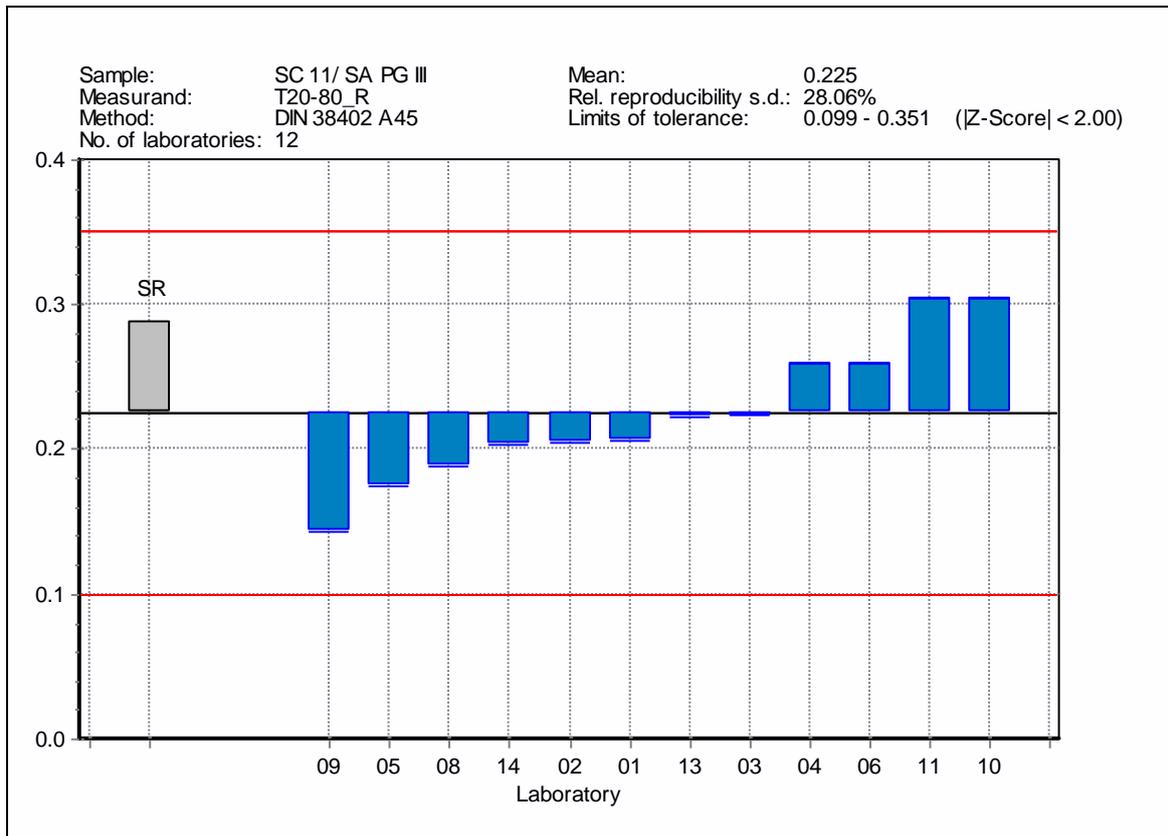


Figure 111: Laboratory results for main combustion time t_{20-80} – ratio SC 11 / SA PG III

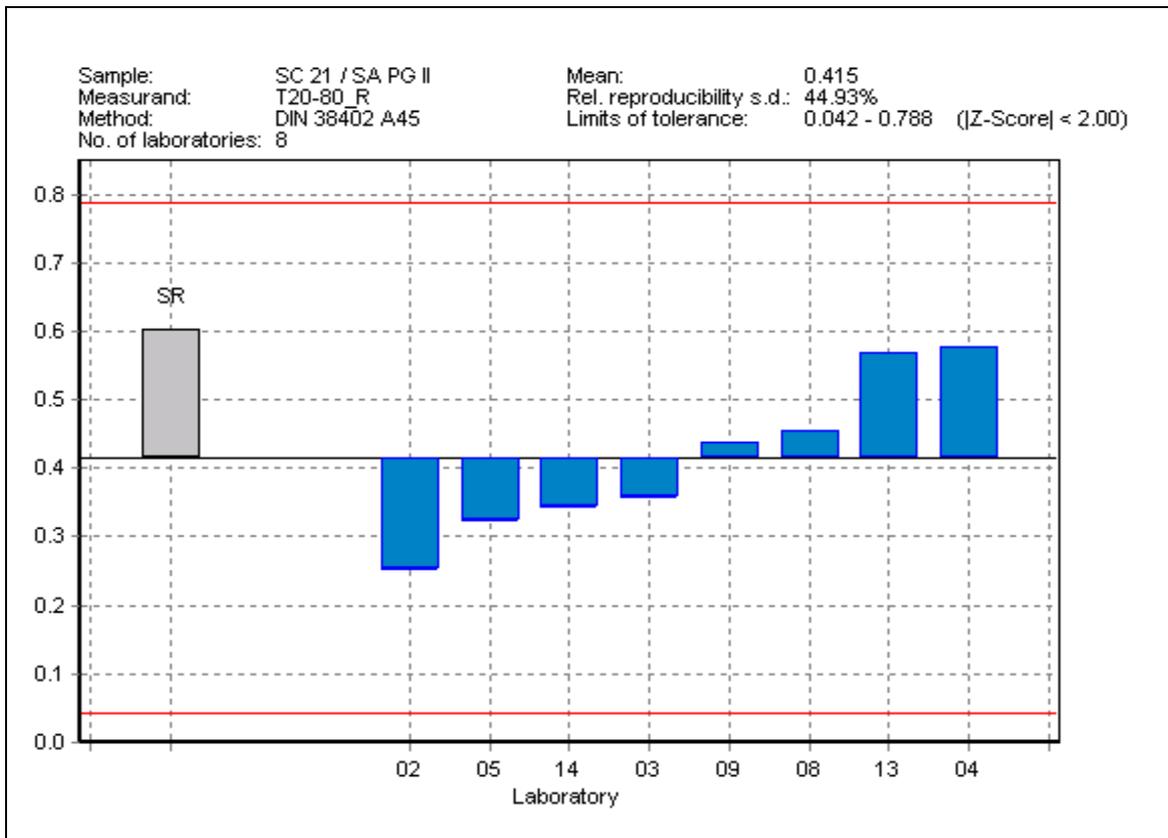


Figure 112: Laboratory results for main combustion time t_{20-80} – ratio SC 21 / SA PG II

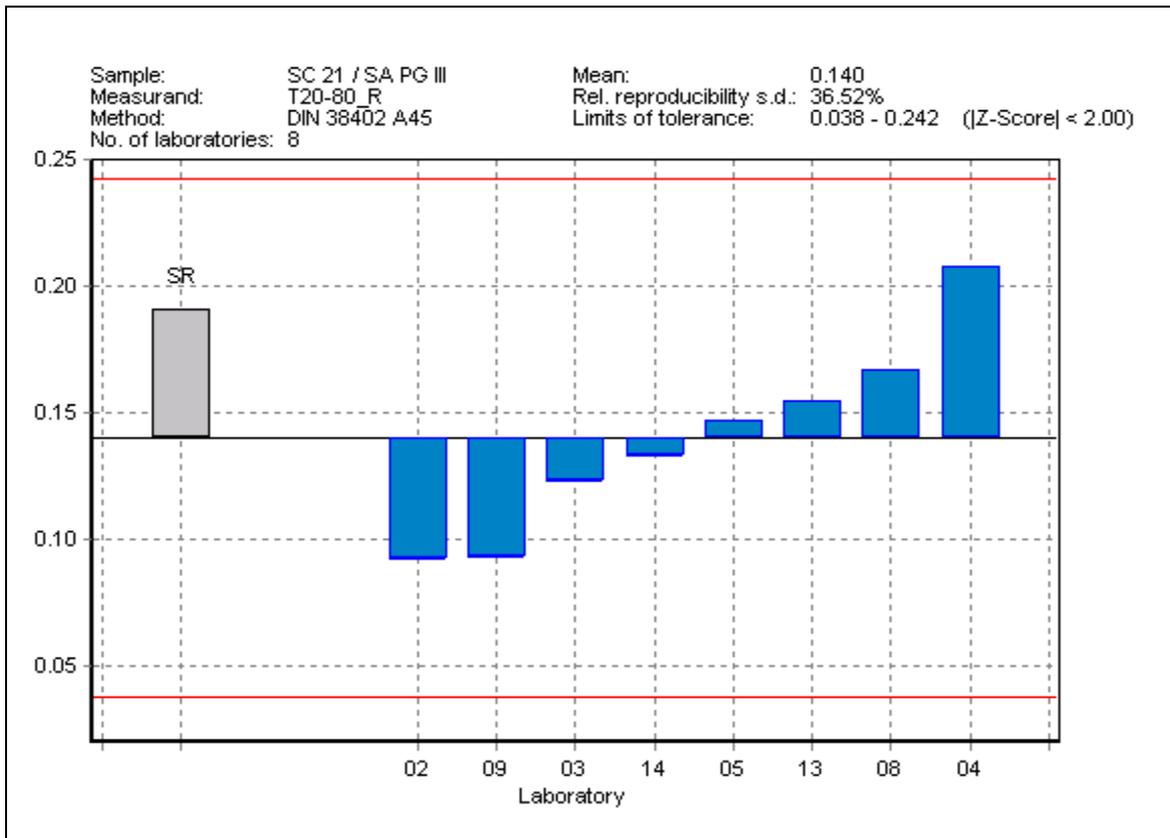


Figure 113: Laboratory results for main combustion time t_{20-80} – ratio SC 21 / SA PG III

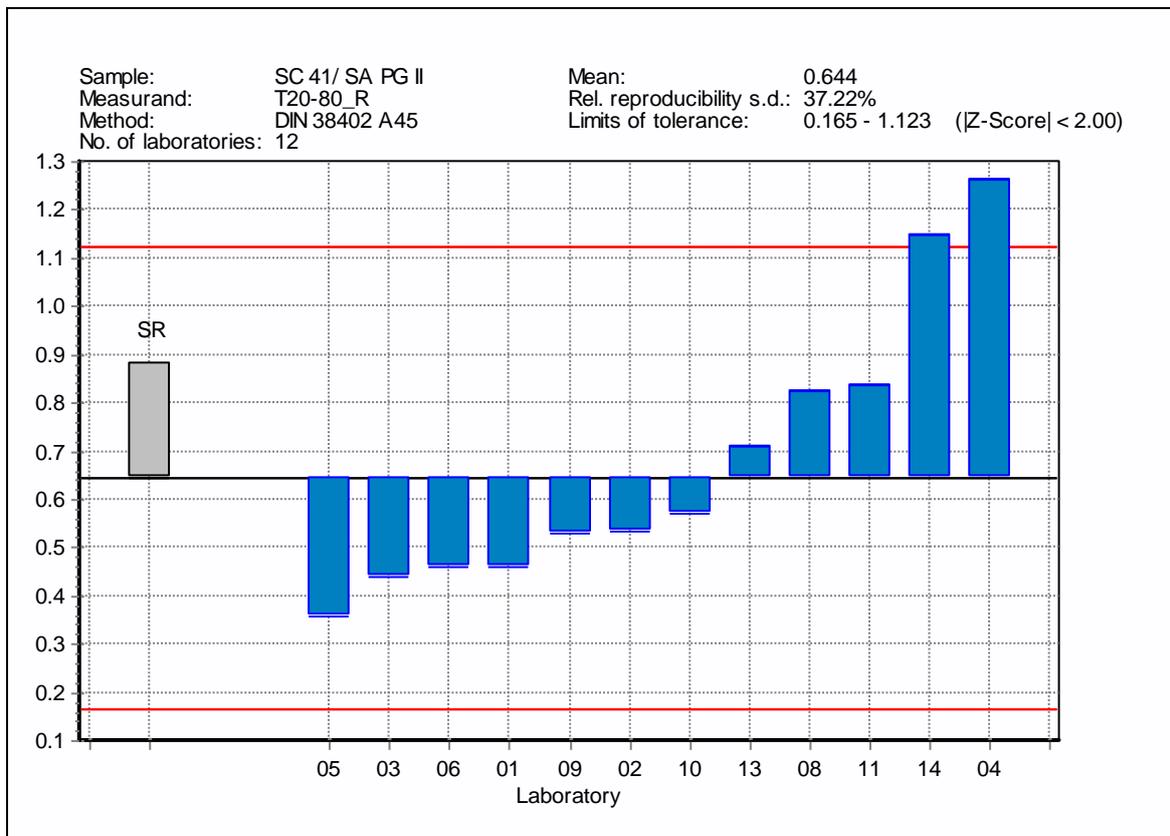


Figure 114: Laboratory results for main combustion time t_{20-80} – ratio SC 41 / SA PG II

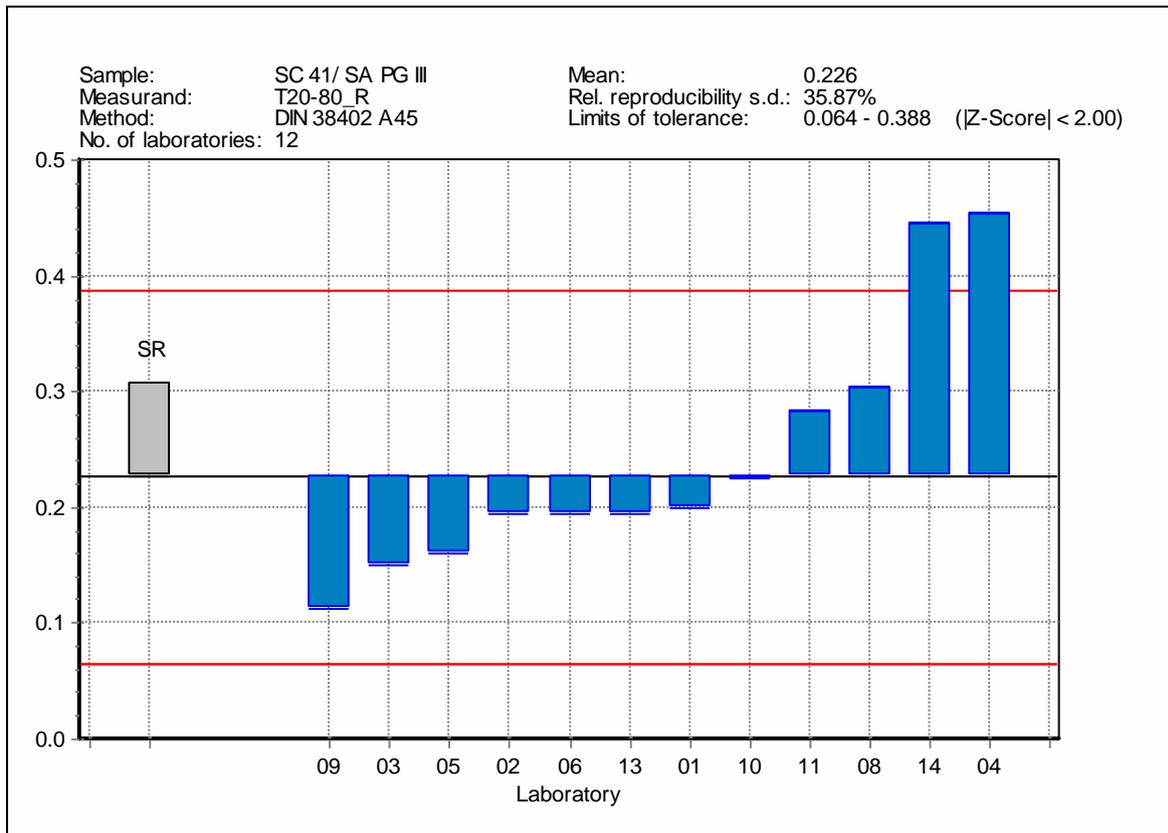


Figure 115: Laboratory results for main combustion time t_{20-80} – ratio SC 41 /SA PG III

10.5 Mass loss rate between 20 % and 80 % of total mass loss

10.5.1 Outliers and stragglers

Table 53: Outliers and straggler for Mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ [g/s]

Sample	Lab code	Outlier test	Outlier/Straggler
SB 21	04	Cochran	outlier
SB 41	06	Cochran	outlier
SC 11	04	Cochran	outlier
SC 21	04	Cochran	straggler

10.5.2 Analysis of single values

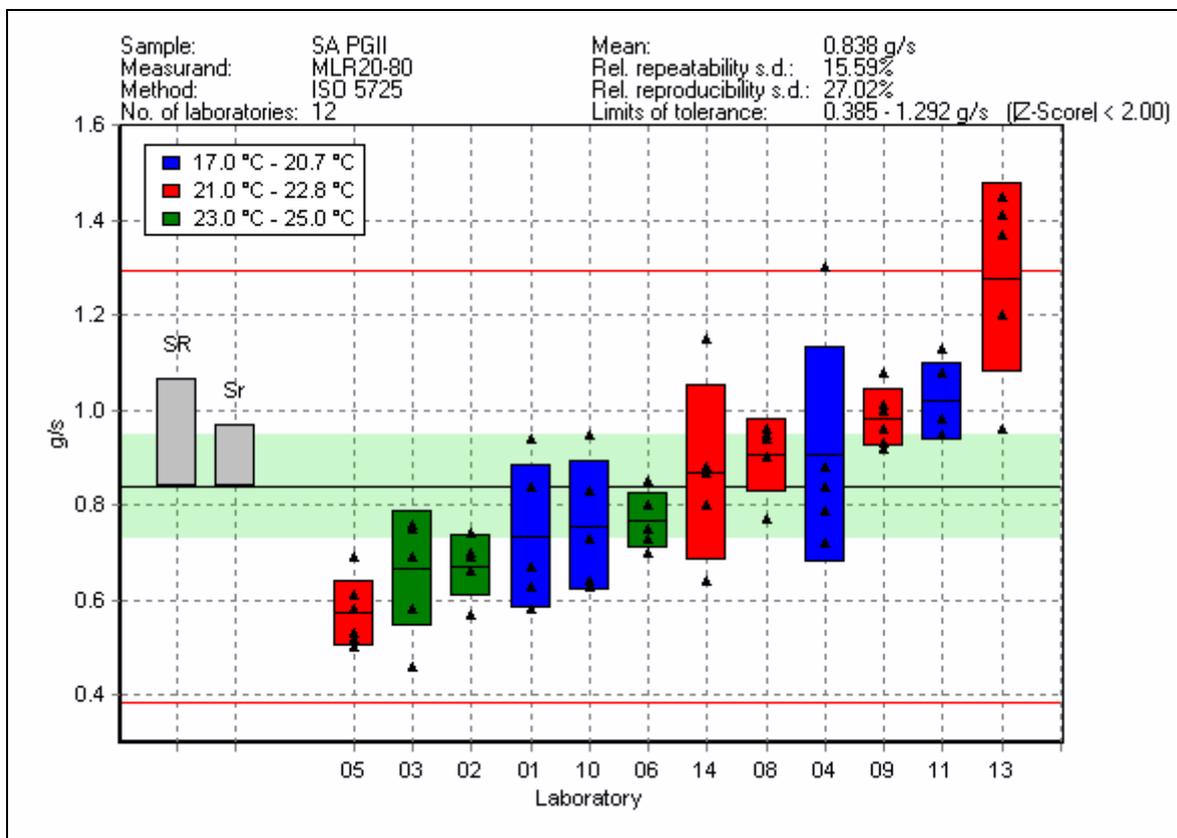


Figure 116: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SA PG II

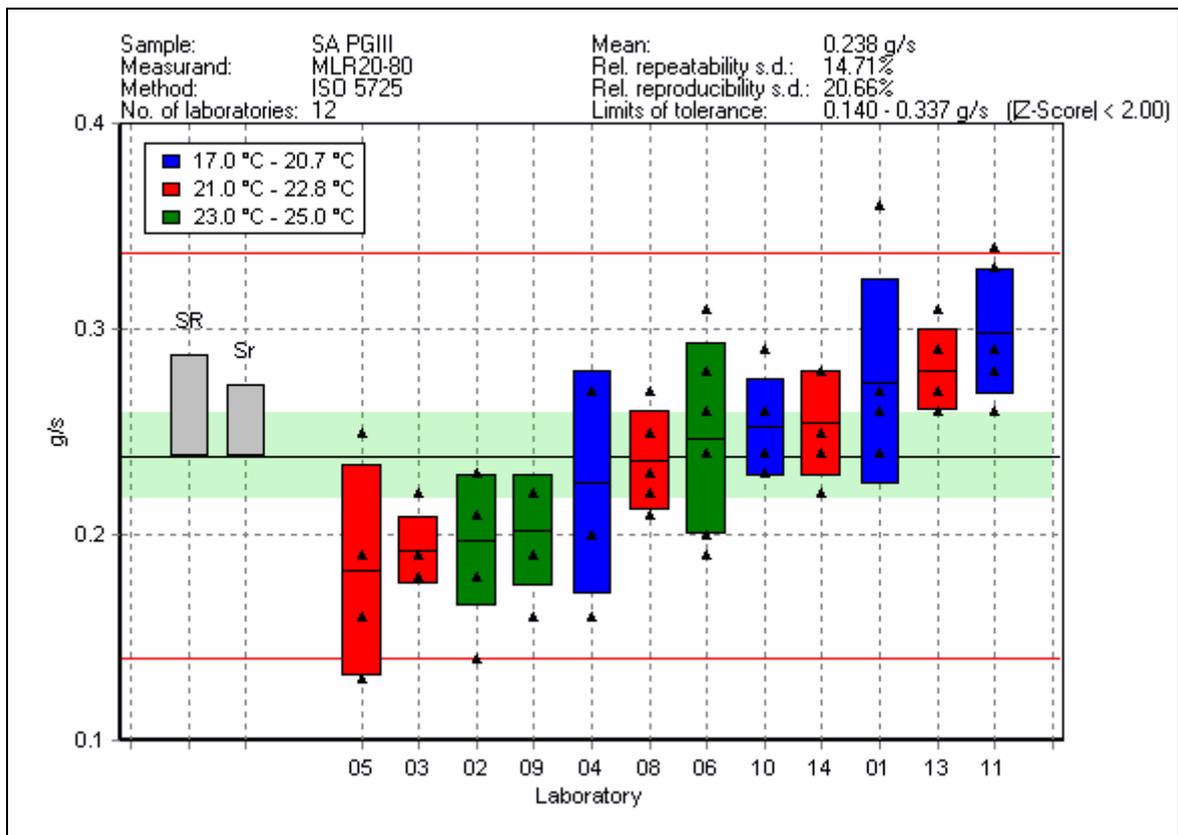


Figure 117: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SA PG III

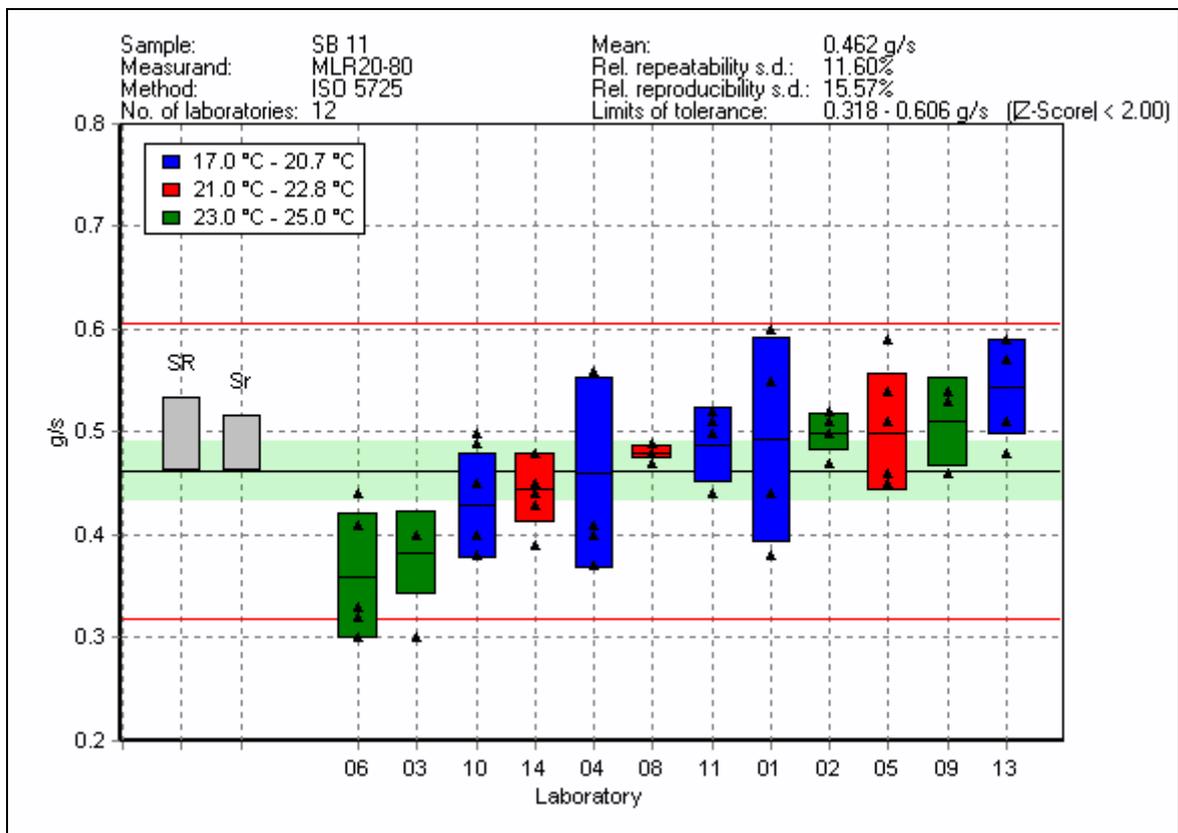


Figure 118: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SB 11

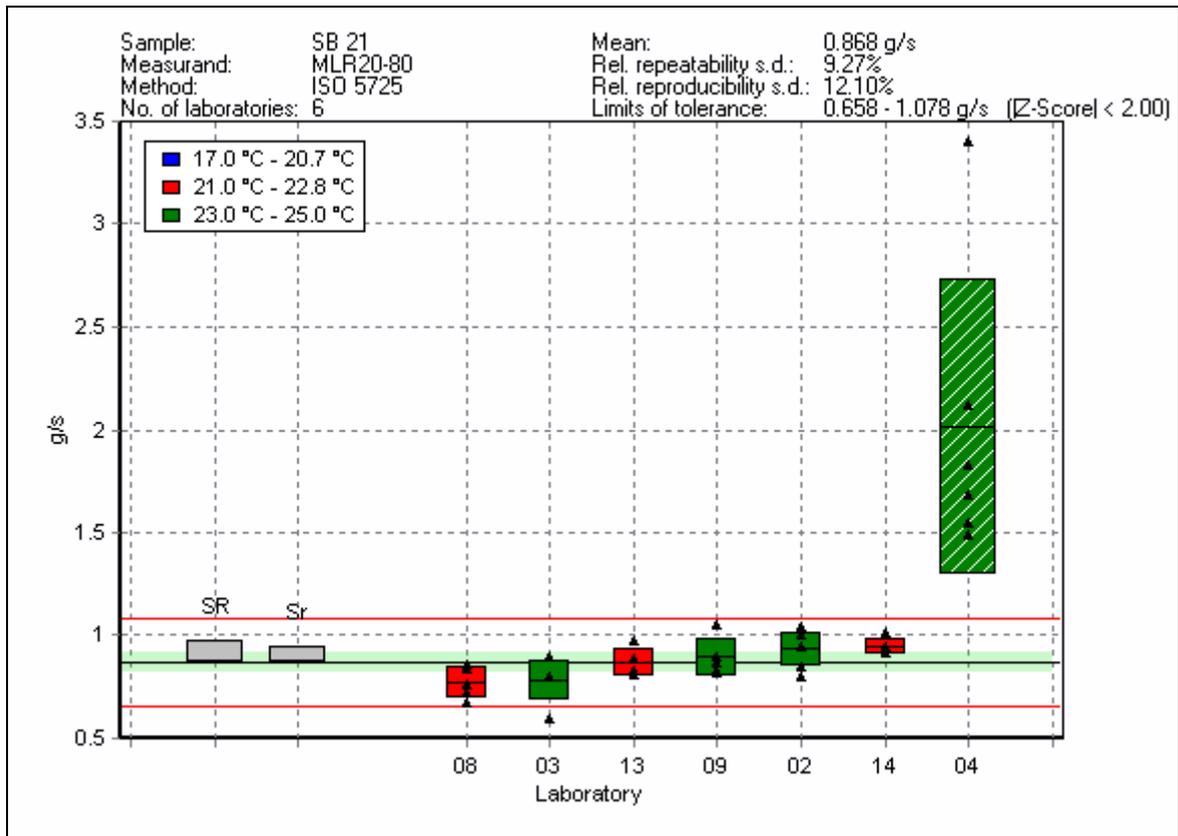


Figure 119: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SB 21

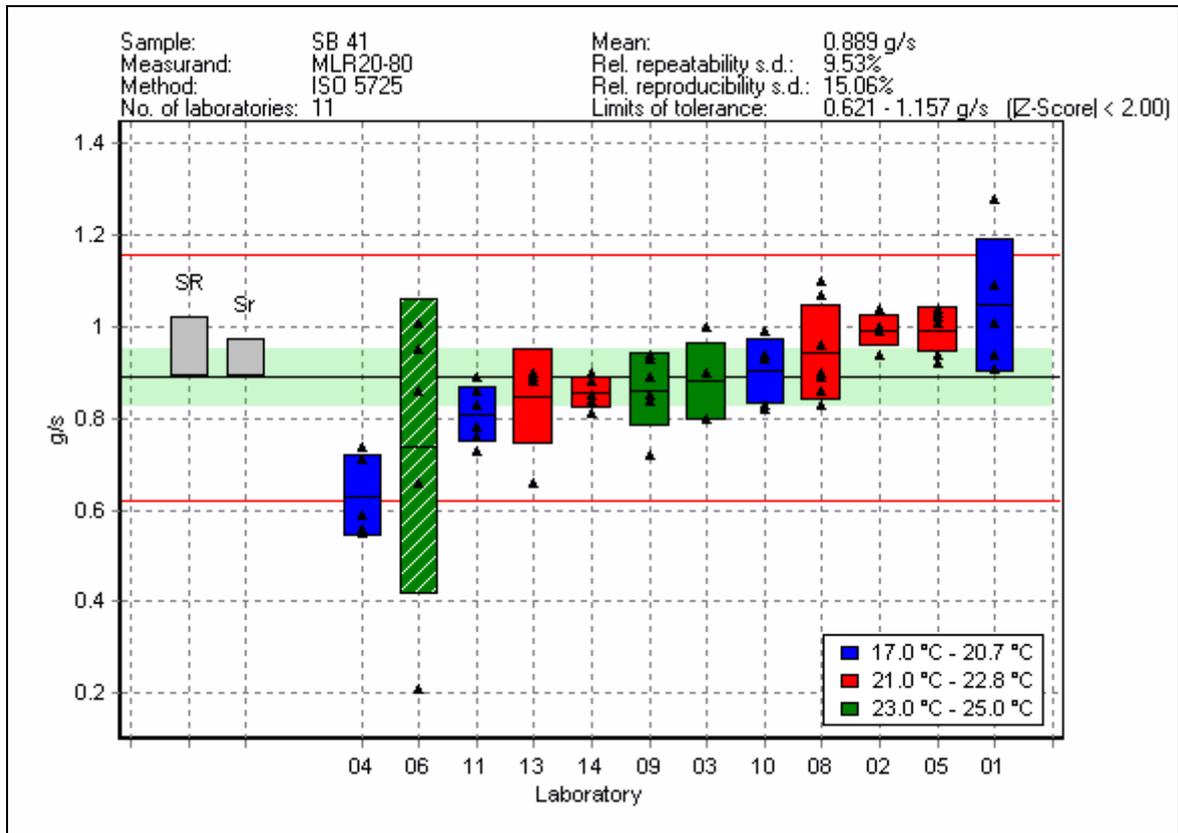


Figure 120: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SB 41

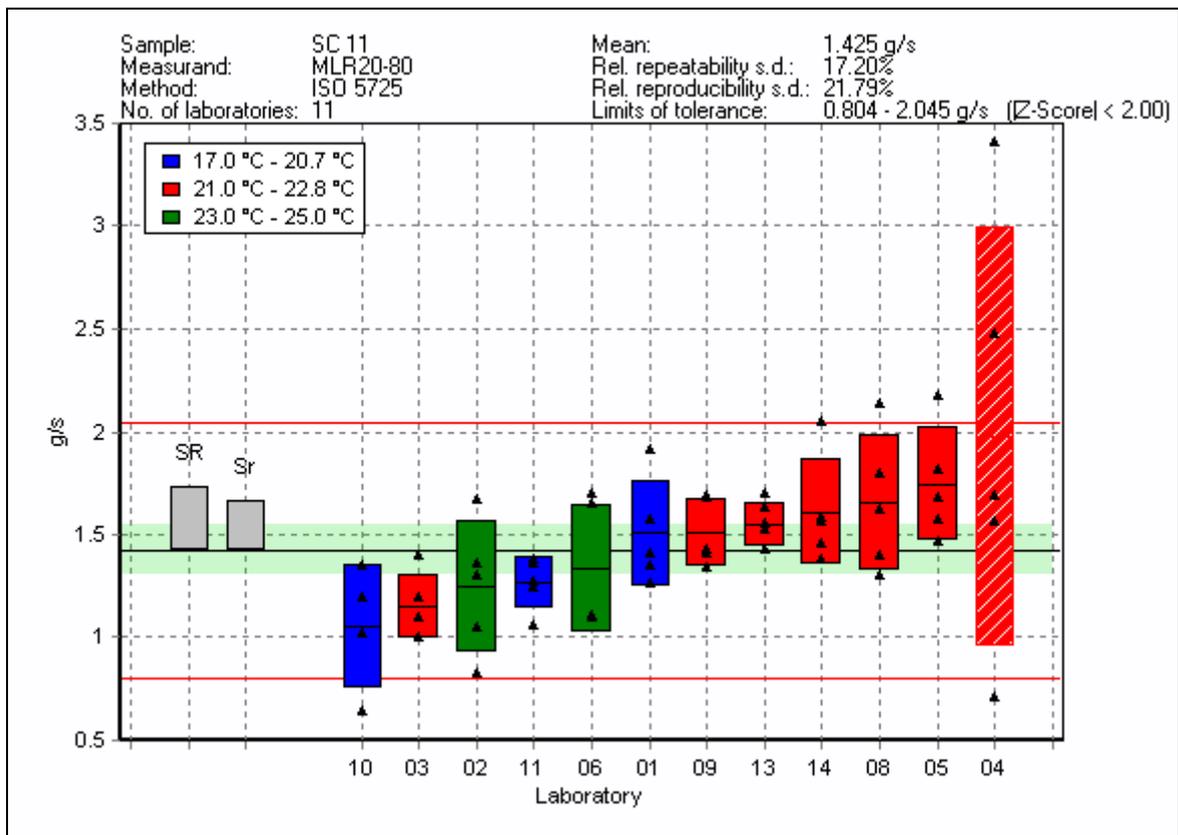


Figure 121: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SC 11

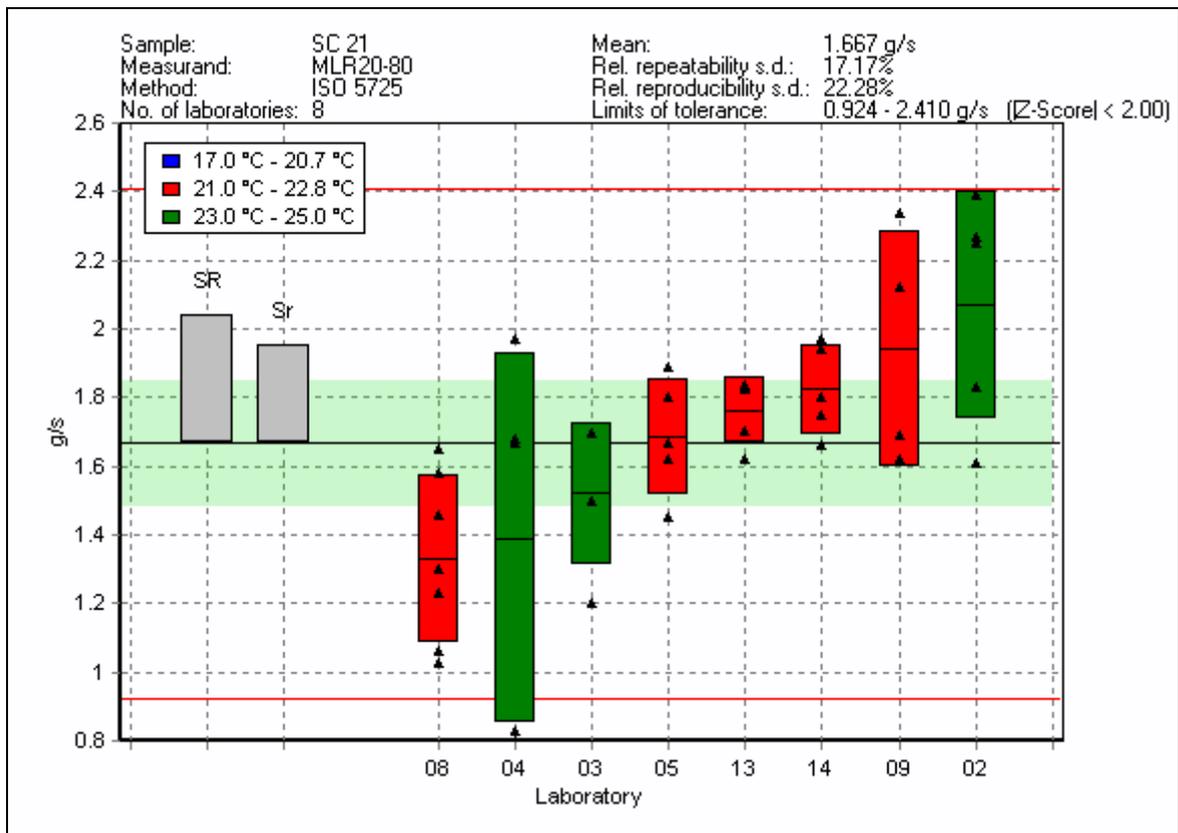


Figure 122: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SC 21

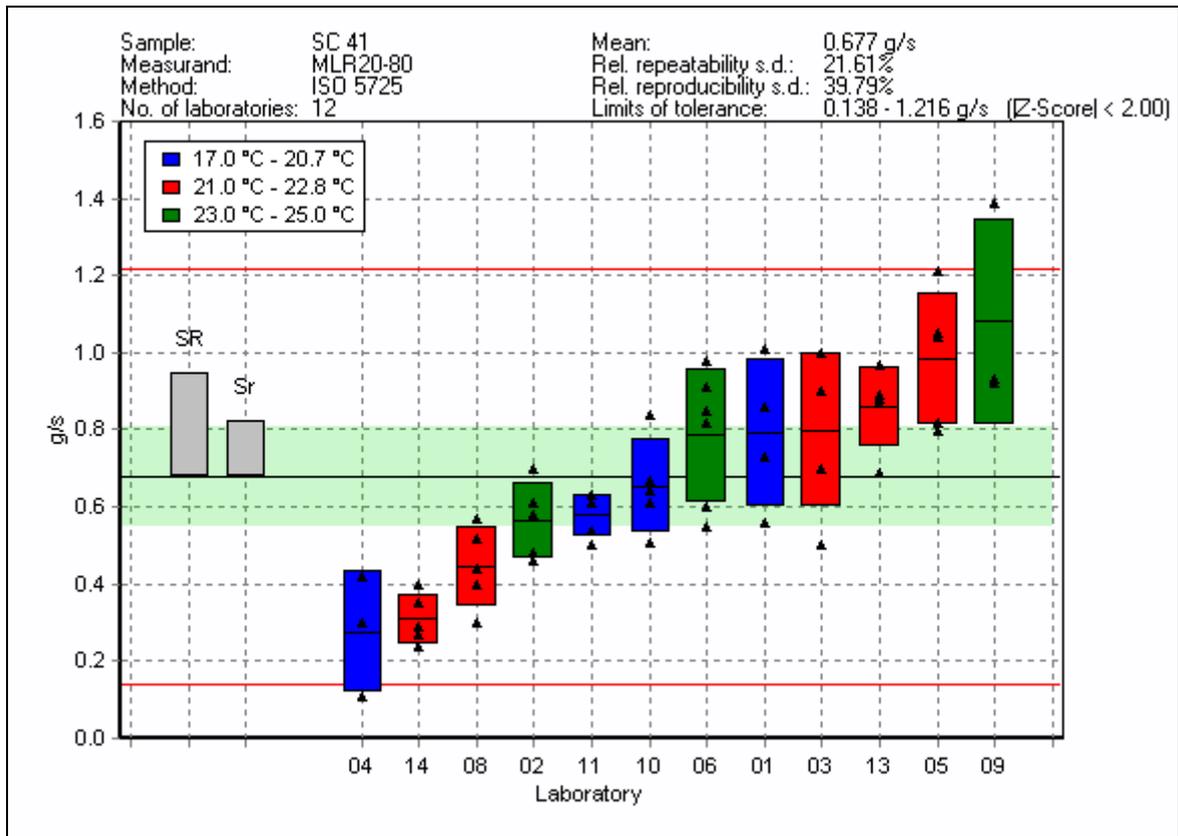


Figure 123: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – SC 41

10.5.3 Analysis of ratios

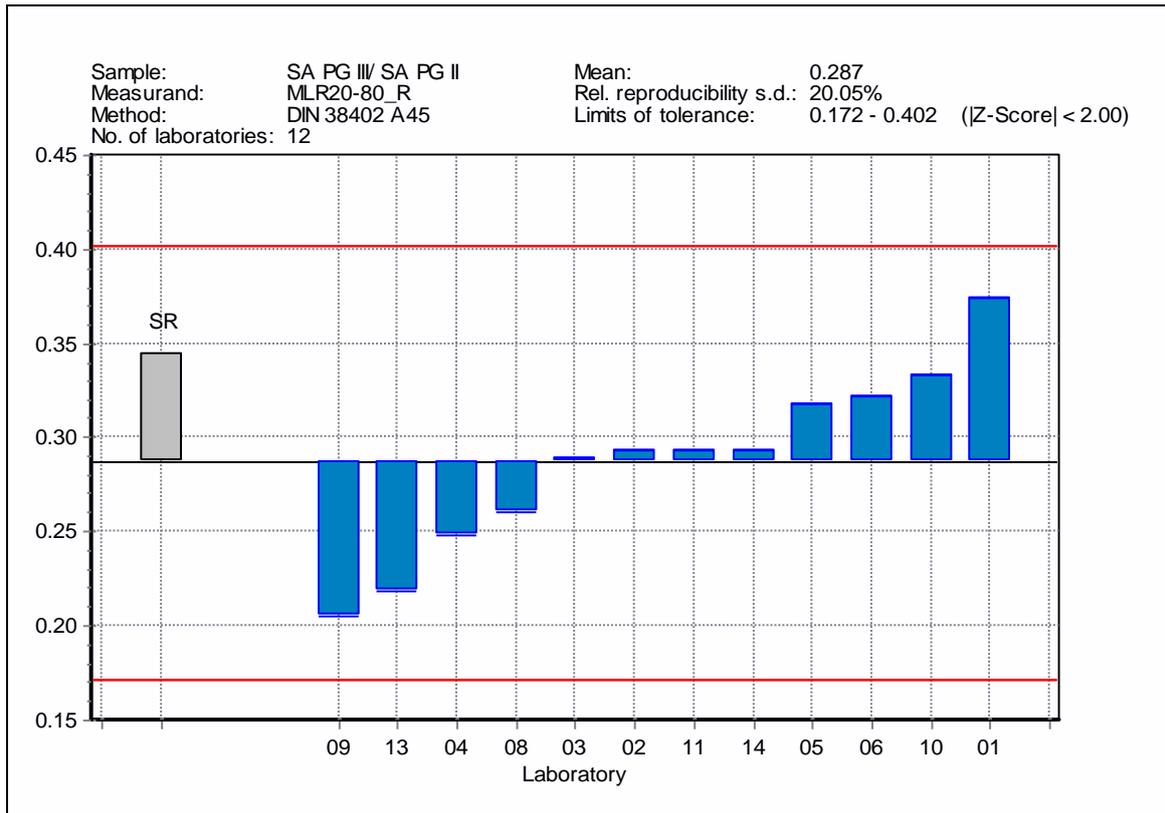


Figure 124: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SA PG III / SA PG II

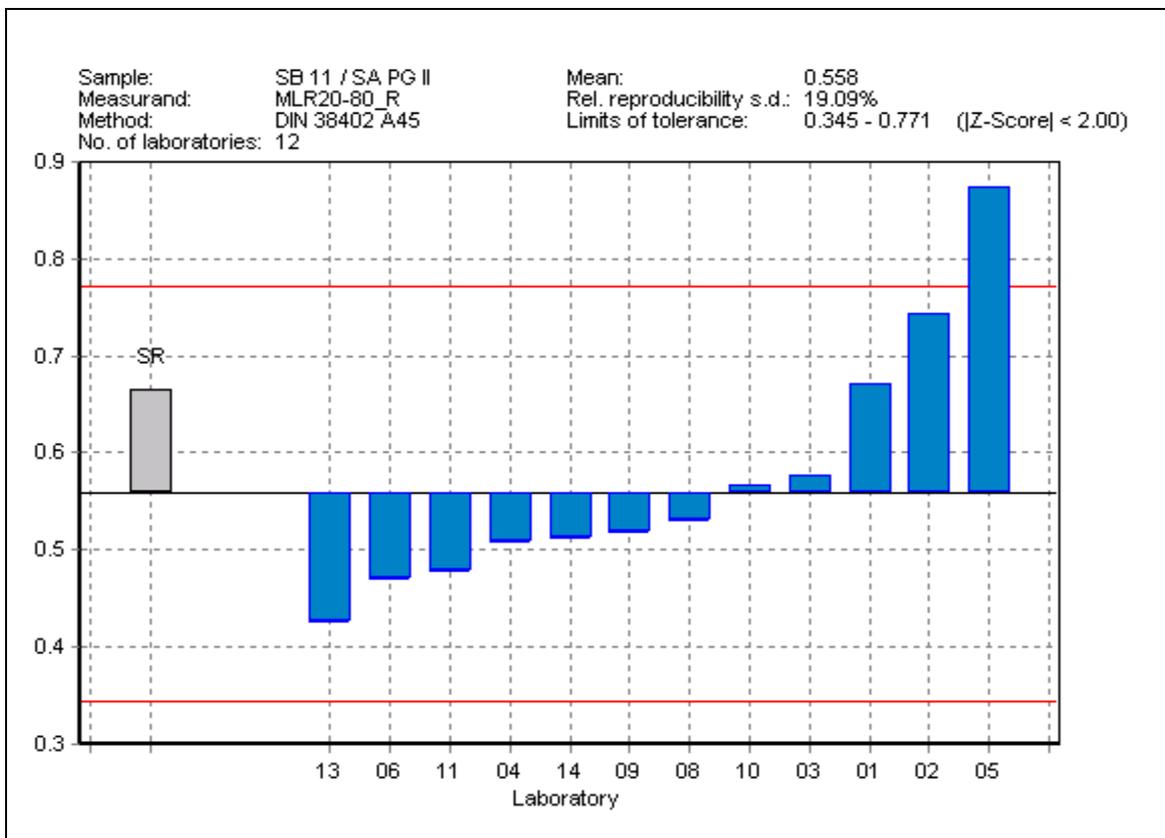


Figure 125: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SB 11 / SA PG II

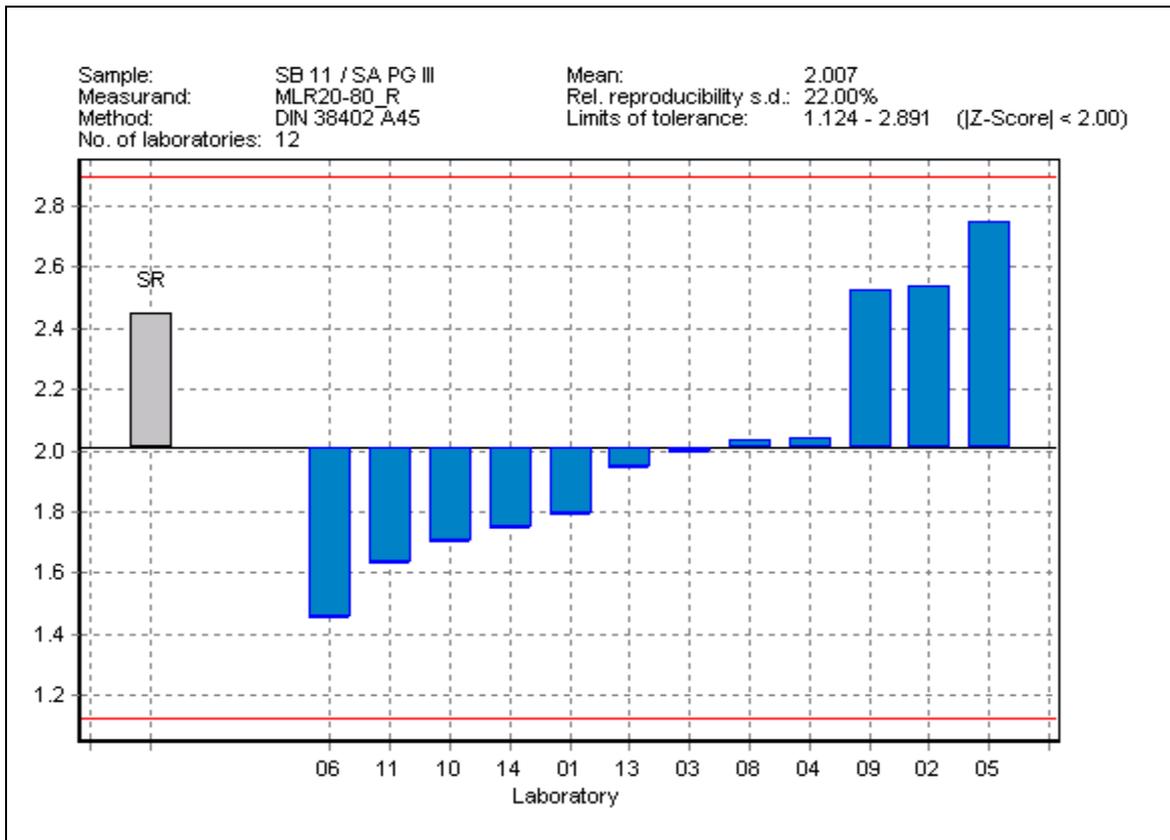


Figure 126: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SB 11 /SA PG III

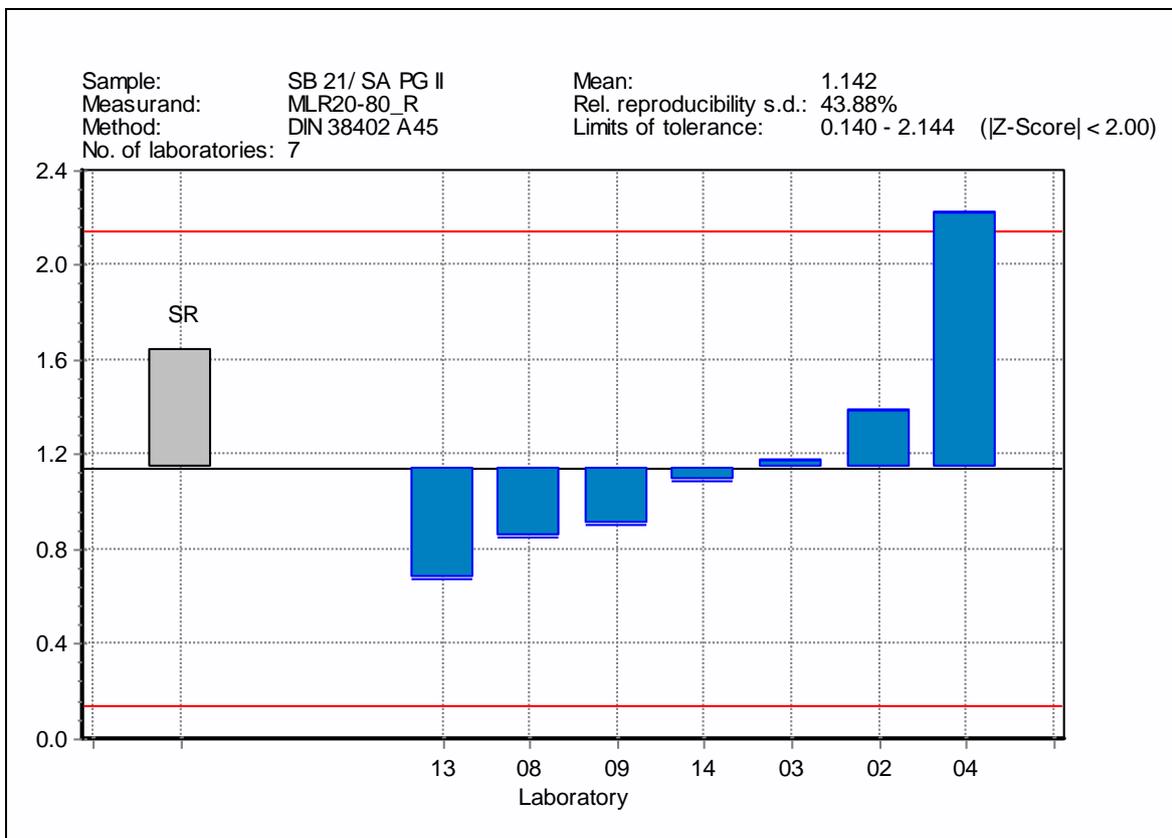


Figure 127: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SB 21 /SA PG II

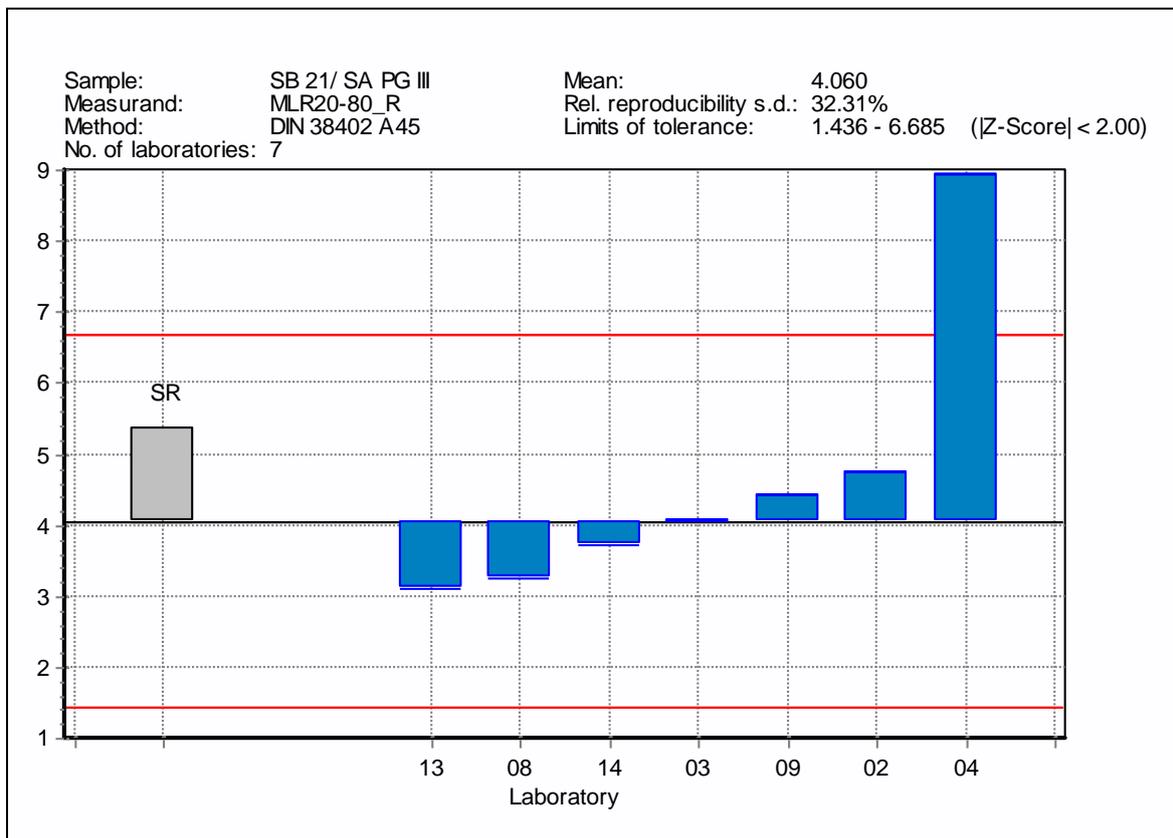


Figure 128: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SB 21 /SA PG III

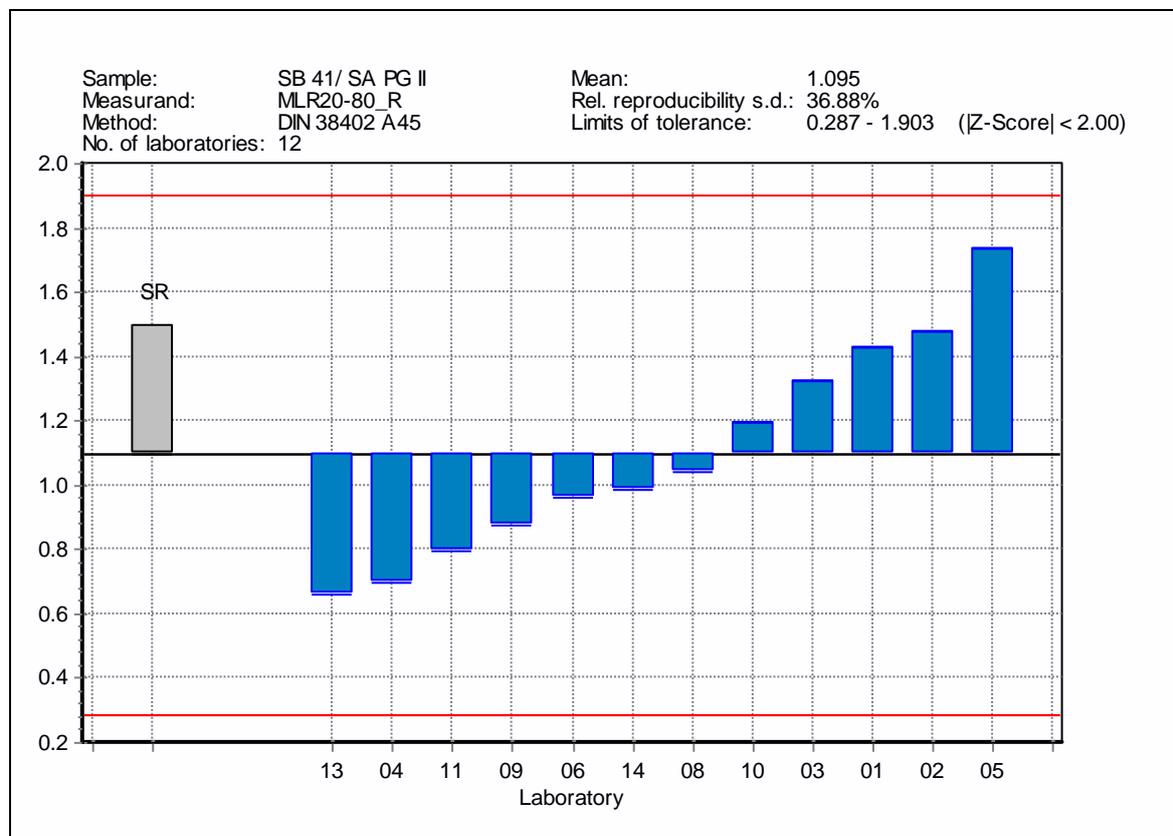


Figure 129: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SB 41 /SA PG II

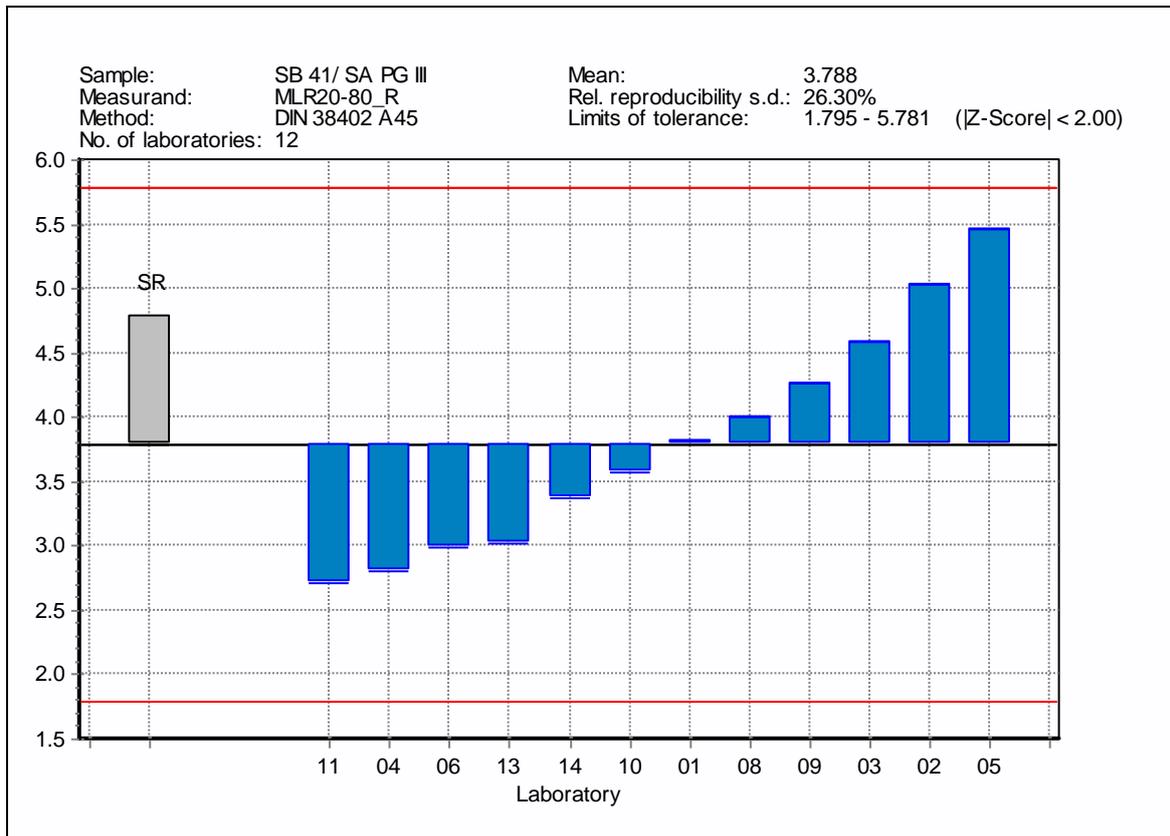


Figure 130: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SB 41 /SA PG III

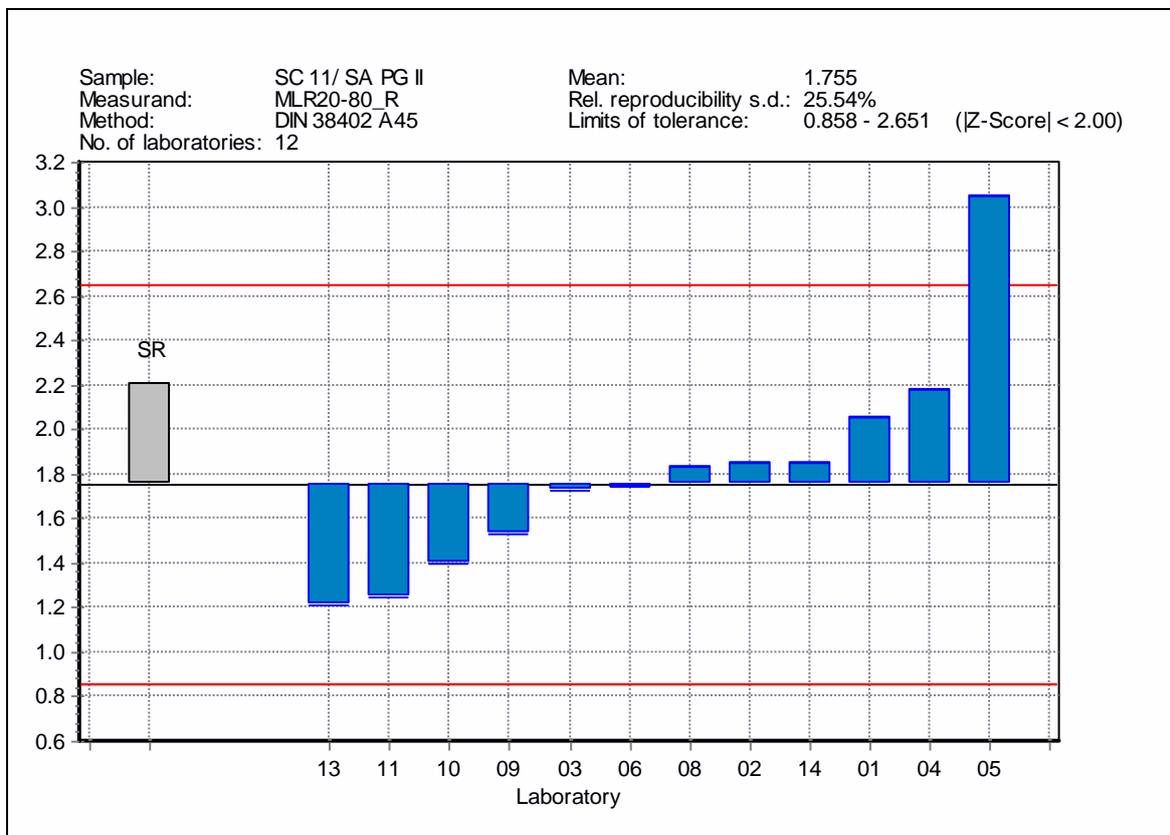


Figure 131: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SC 11 /SA PG II

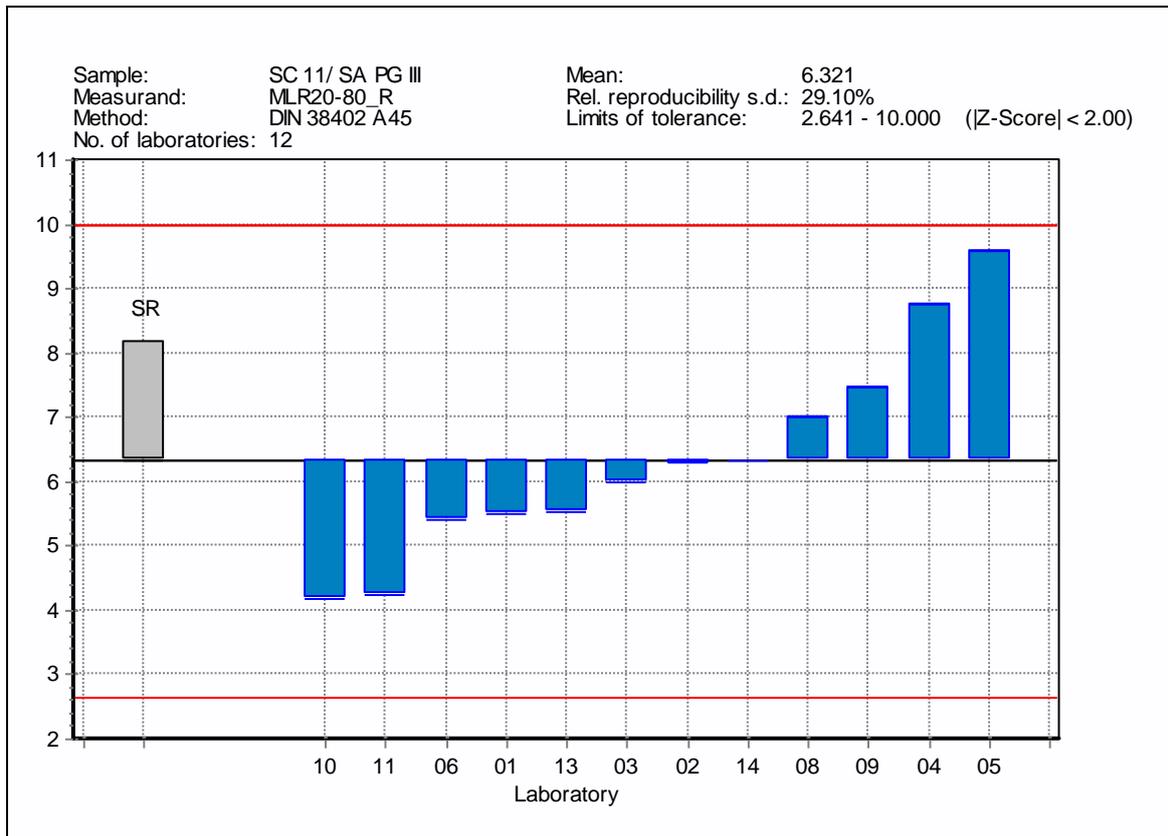


Figure 132: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SC 11 /SA PG III

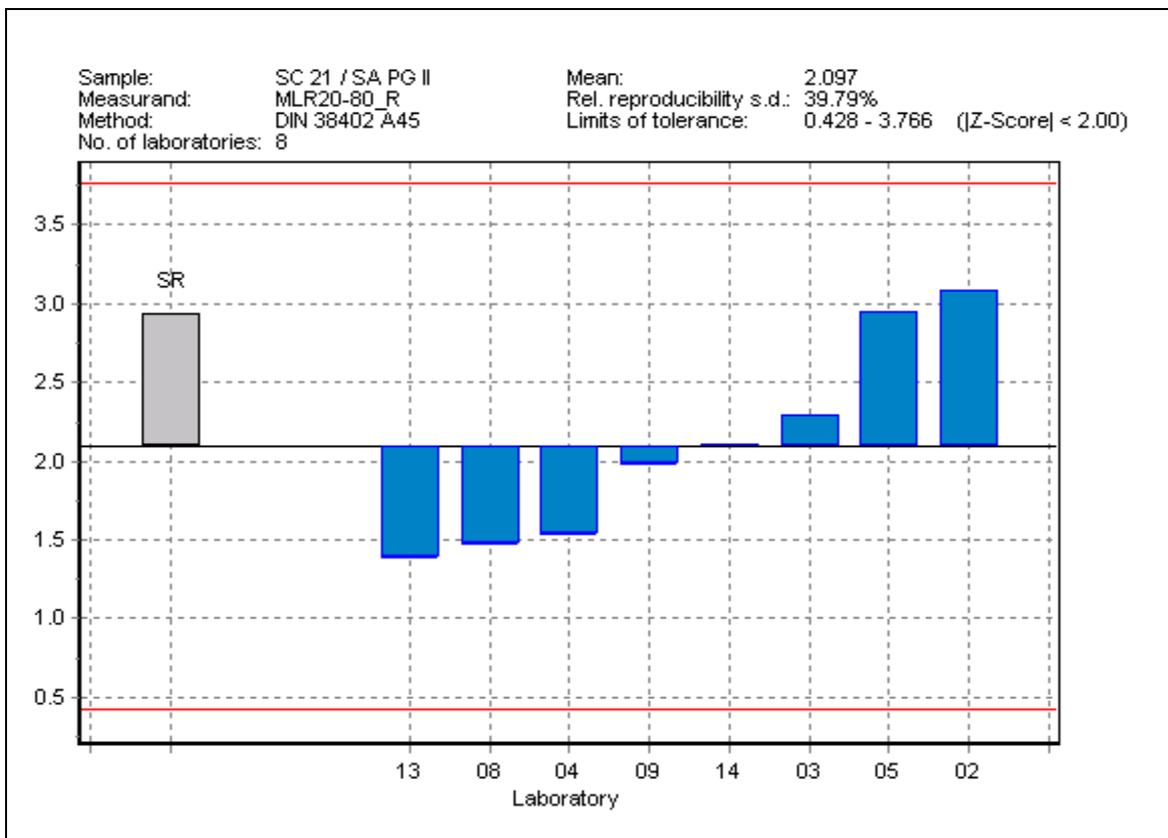


Figure 133: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SC 21 /SA PG II

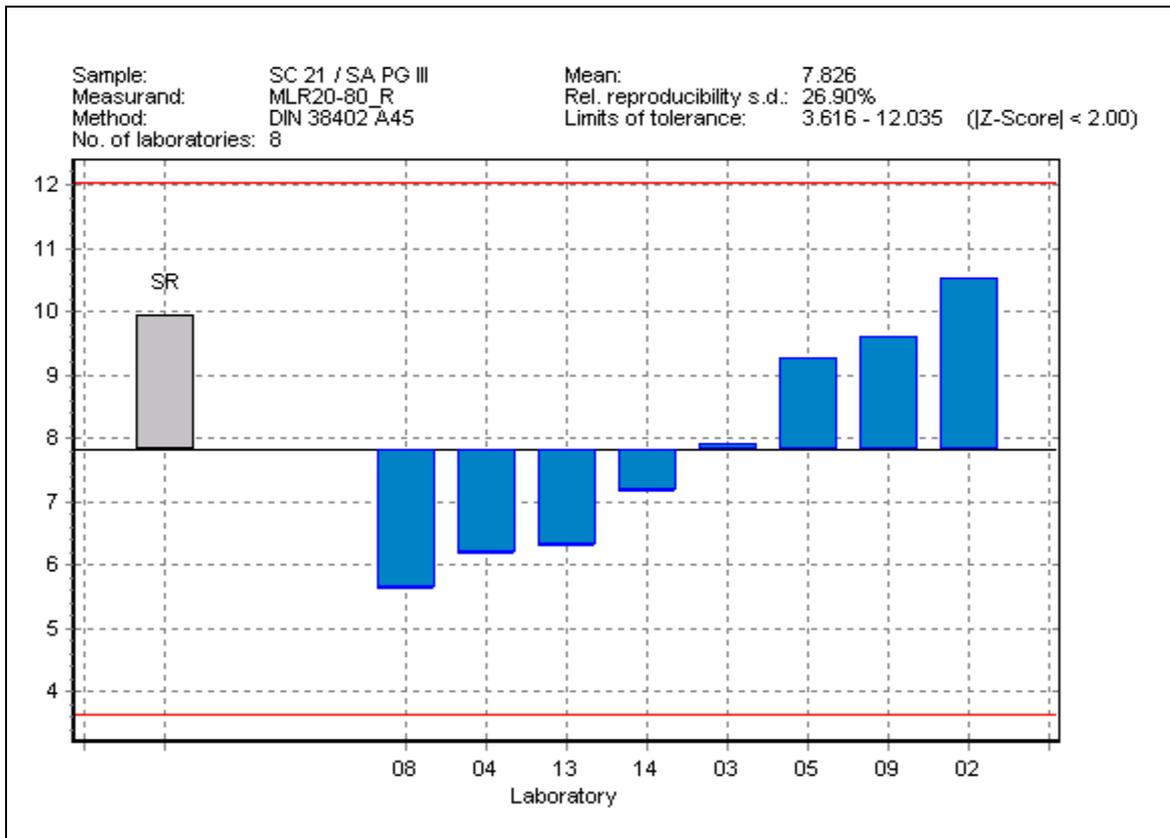


Figure 134: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SC 21 /SA PG III

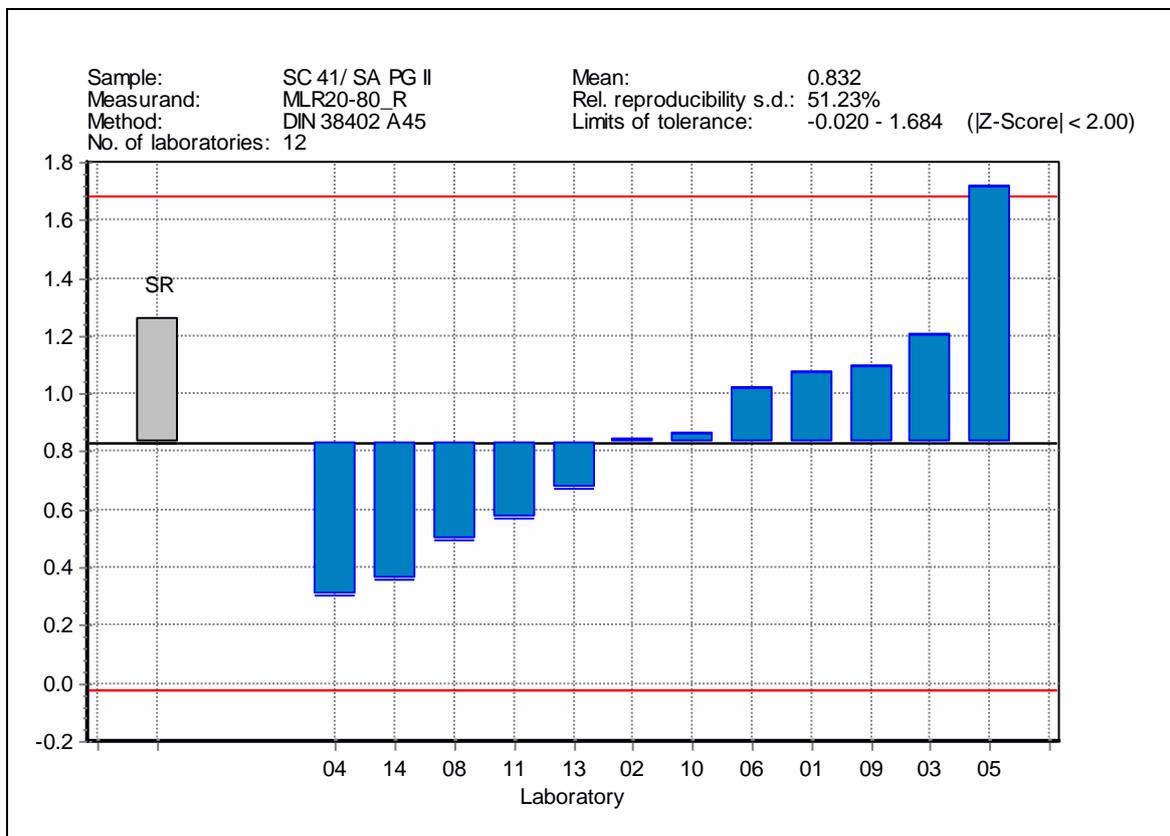


Figure 135: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SC 41 /SA PG II

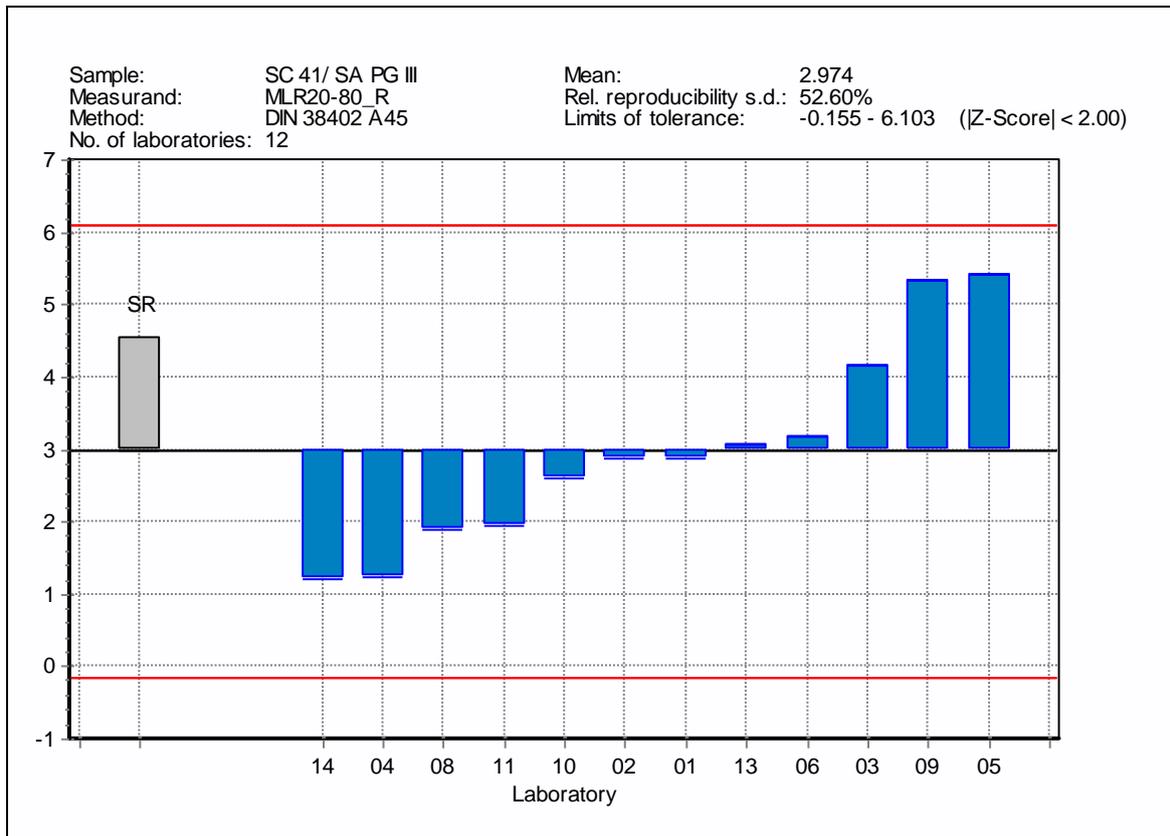


Figure 136: Laboratory results for mass loss rate within 20 % and 80 % of total mass loss MLR₂₀₋₈₀ – ratio SC 41 /SA PG III

10.6 Mass loss rate by linear regression within 20 % to 80 % of total mass loss

10.6.1 Outliers and stragglers

Table 54: Outliers and straggler for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ [g/s]

Sample	Lab code	Outlier test	Outlier/Straggler
SB 41	04	Grubbs	straggler
SC 11	04	Cochran	outlier
SC 21	04	Cochran	outlier

10.6.2 Analysis of single values

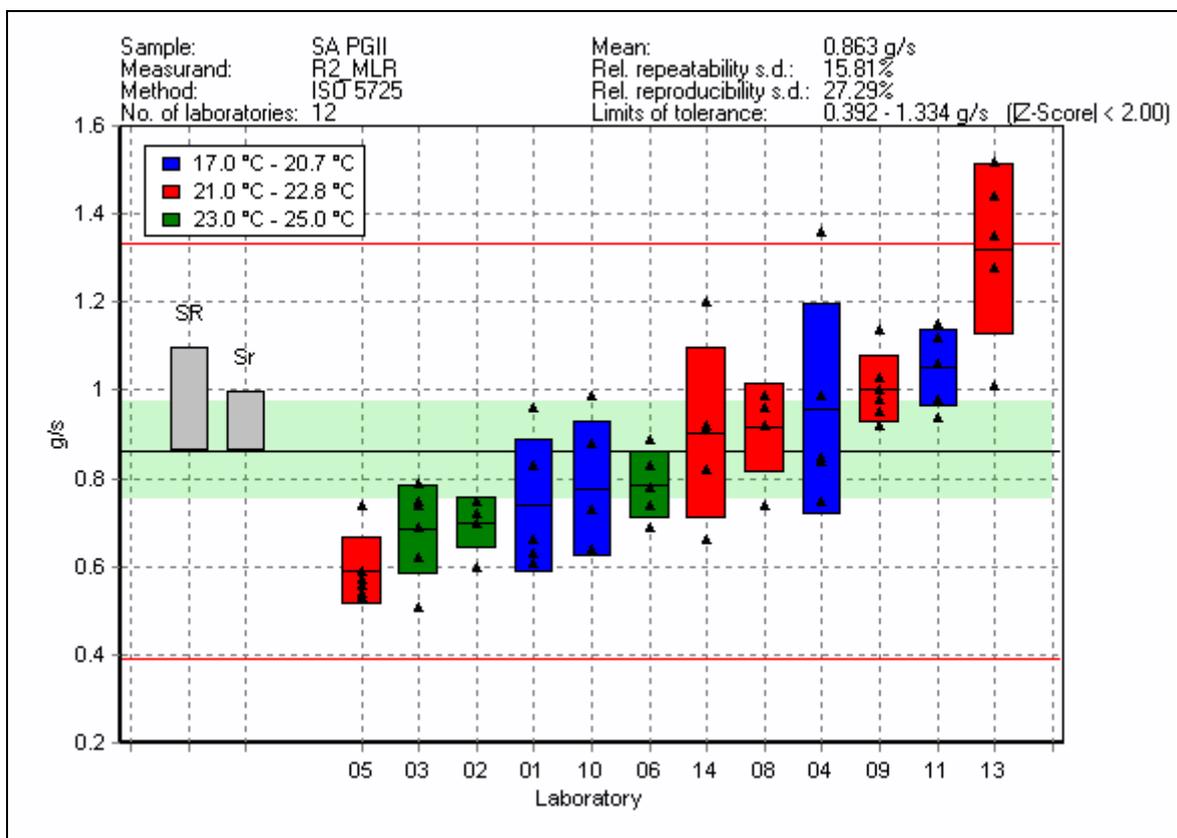


Figure 137: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – SA PG II

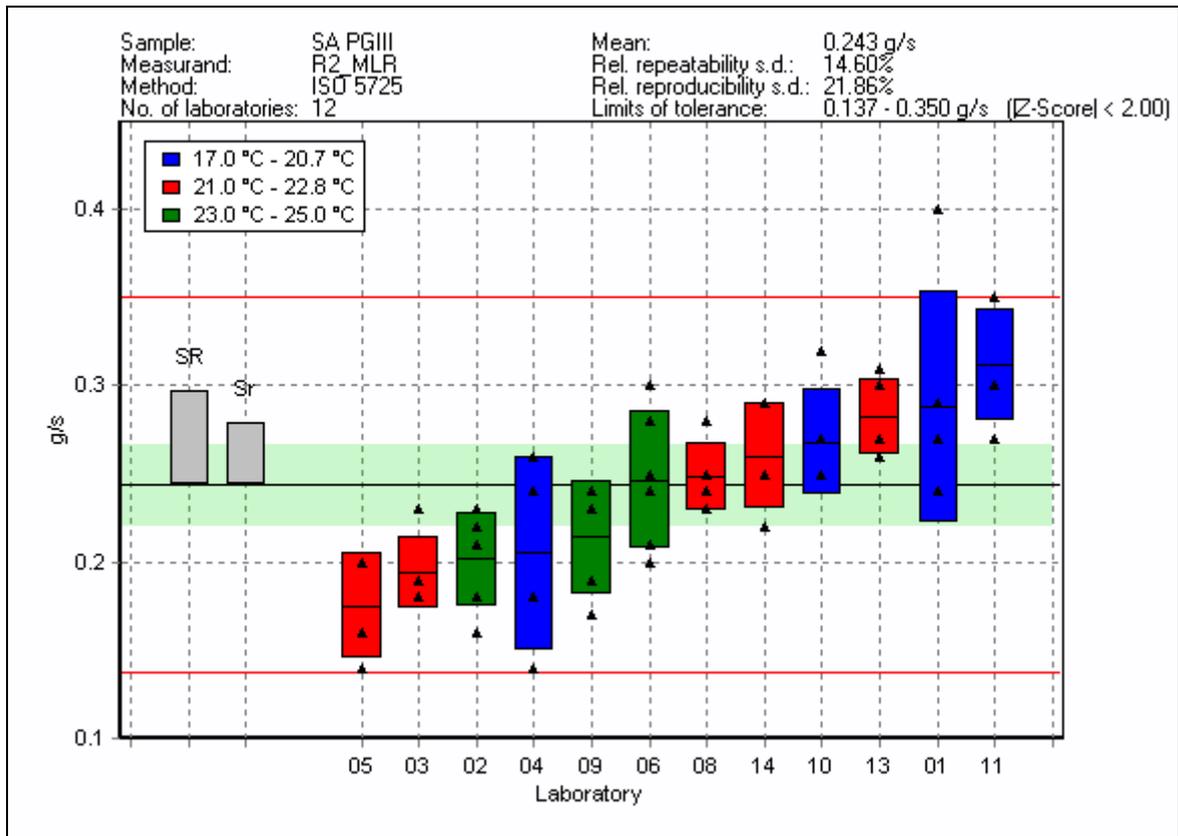


Figure 138: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – SA PG III

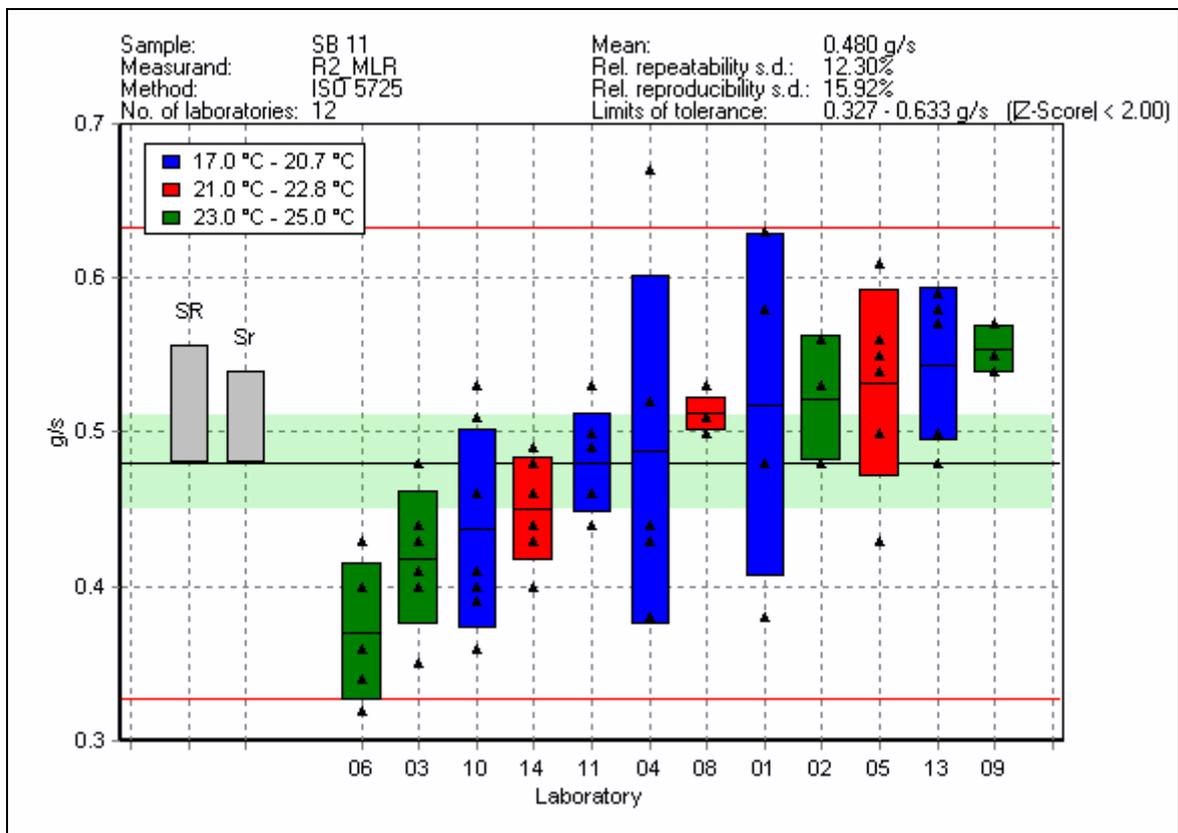


Figure 139: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – SB 11

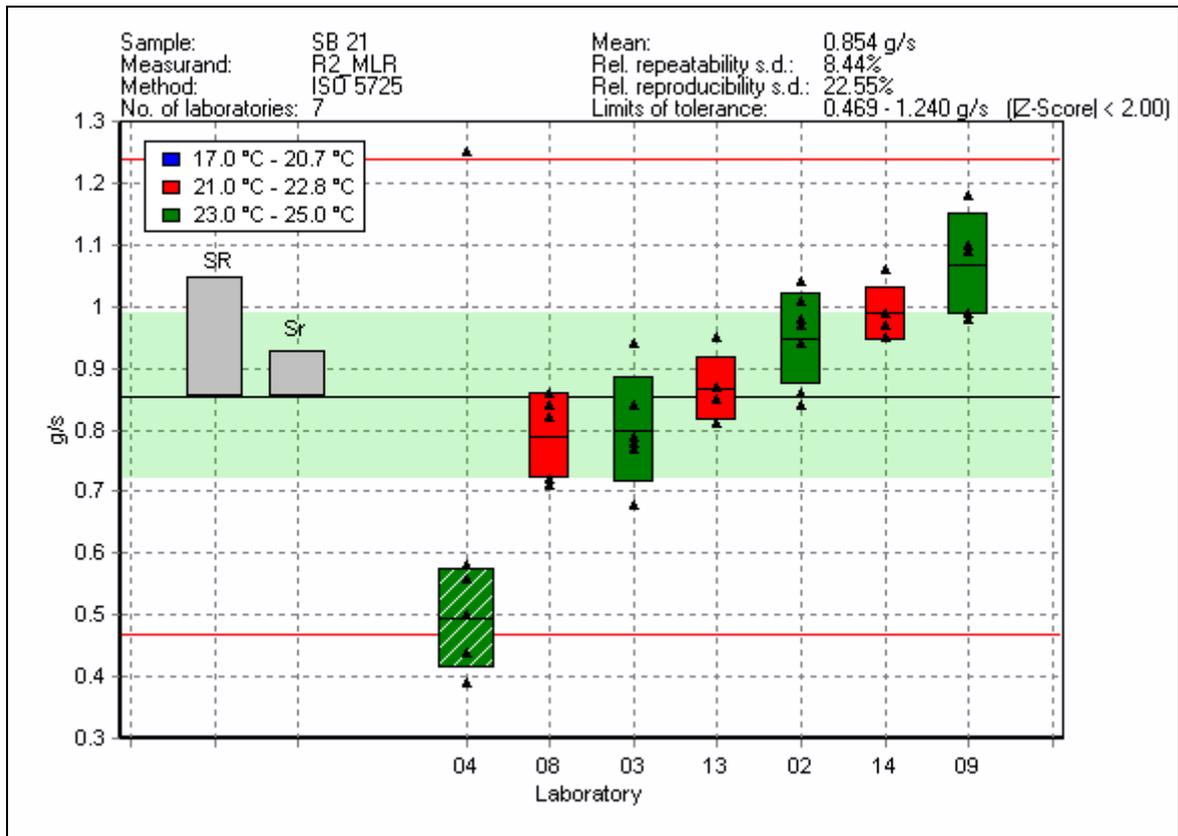


Figure 140: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – SB 21

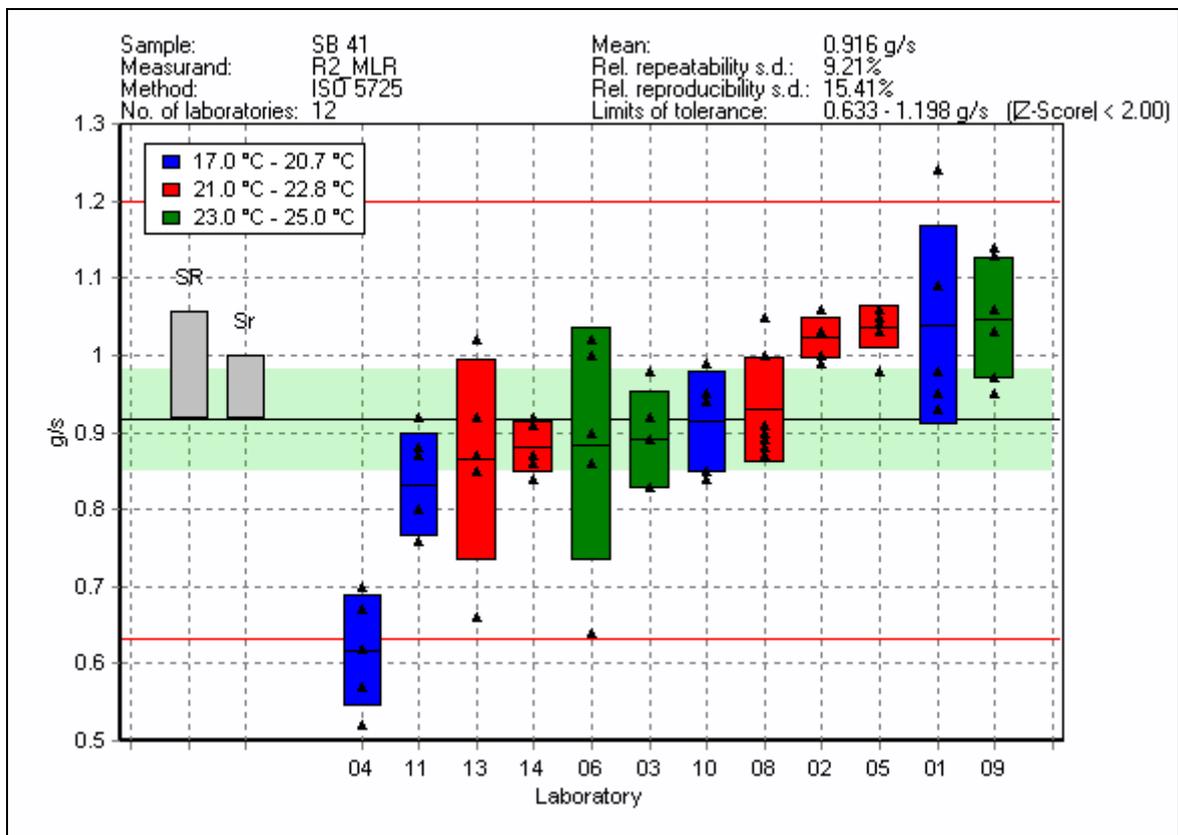


Figure 141: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – SB 41

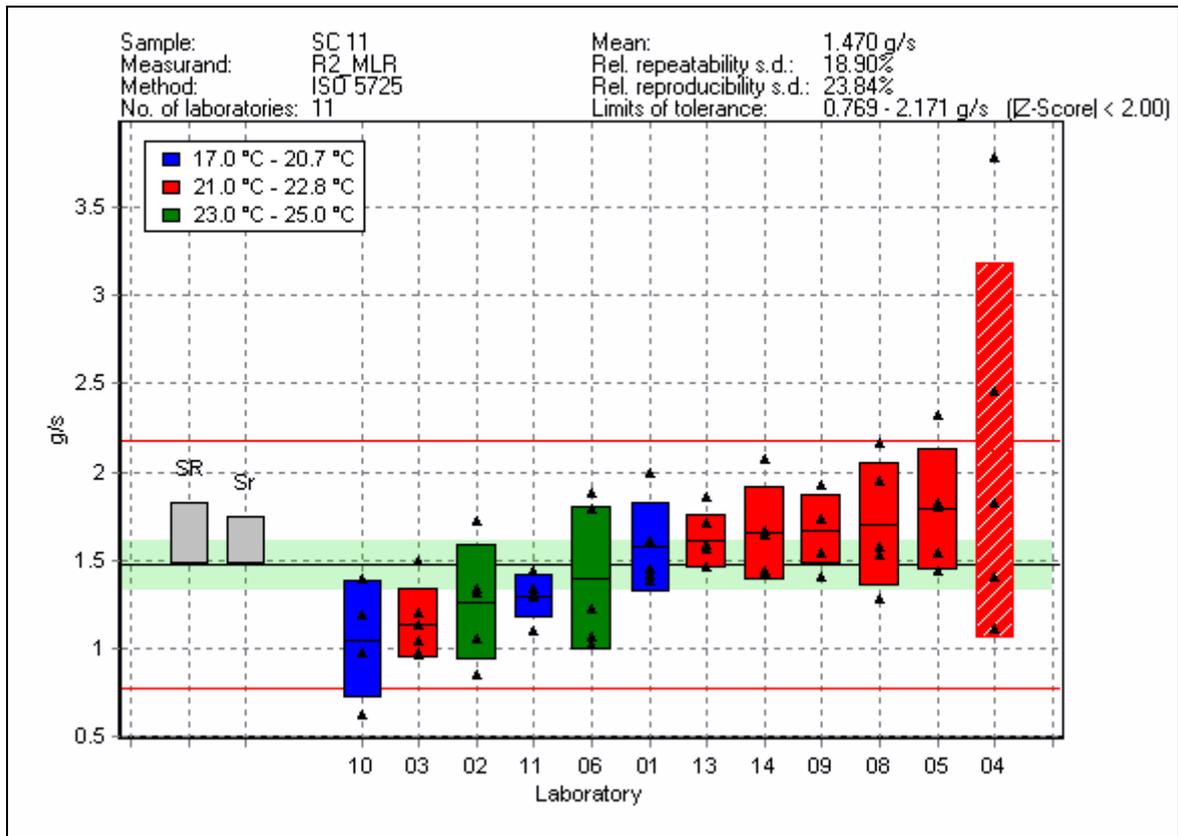


Figure 142: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R² MLR₂₀₋₈₀ – SC 11

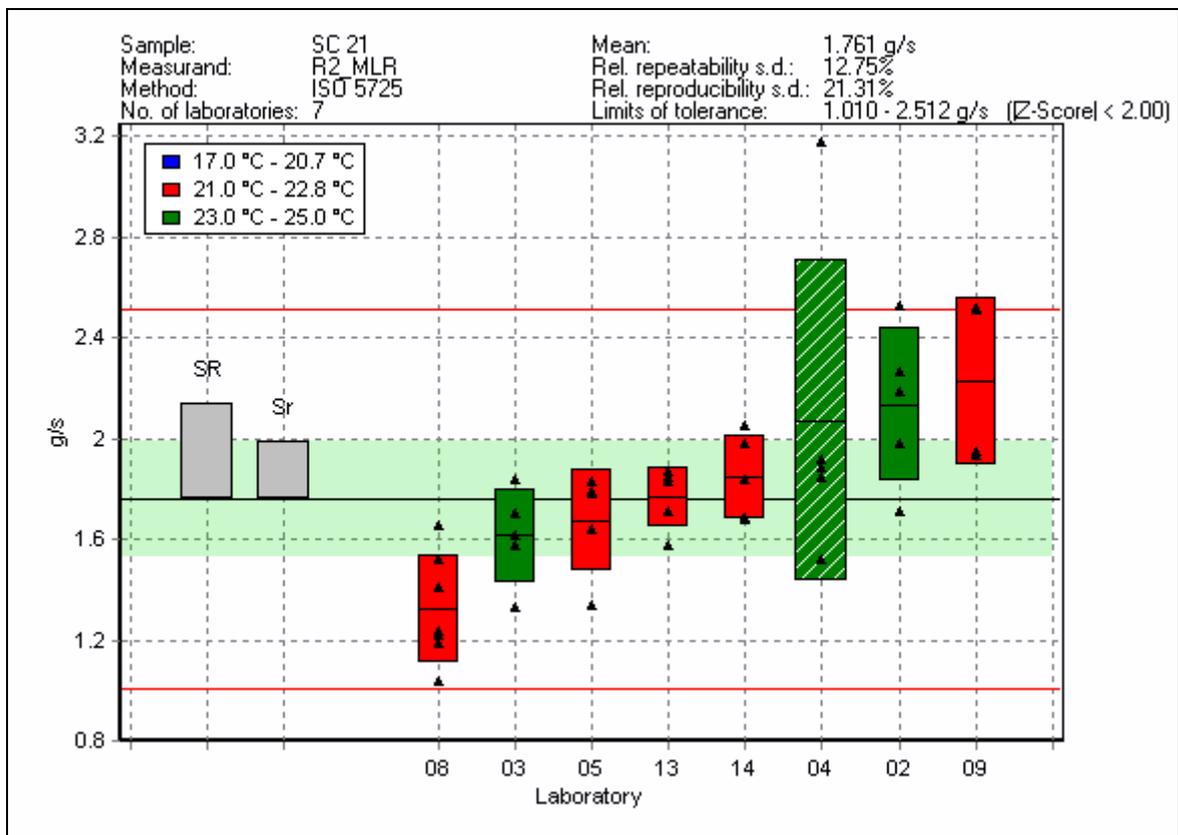
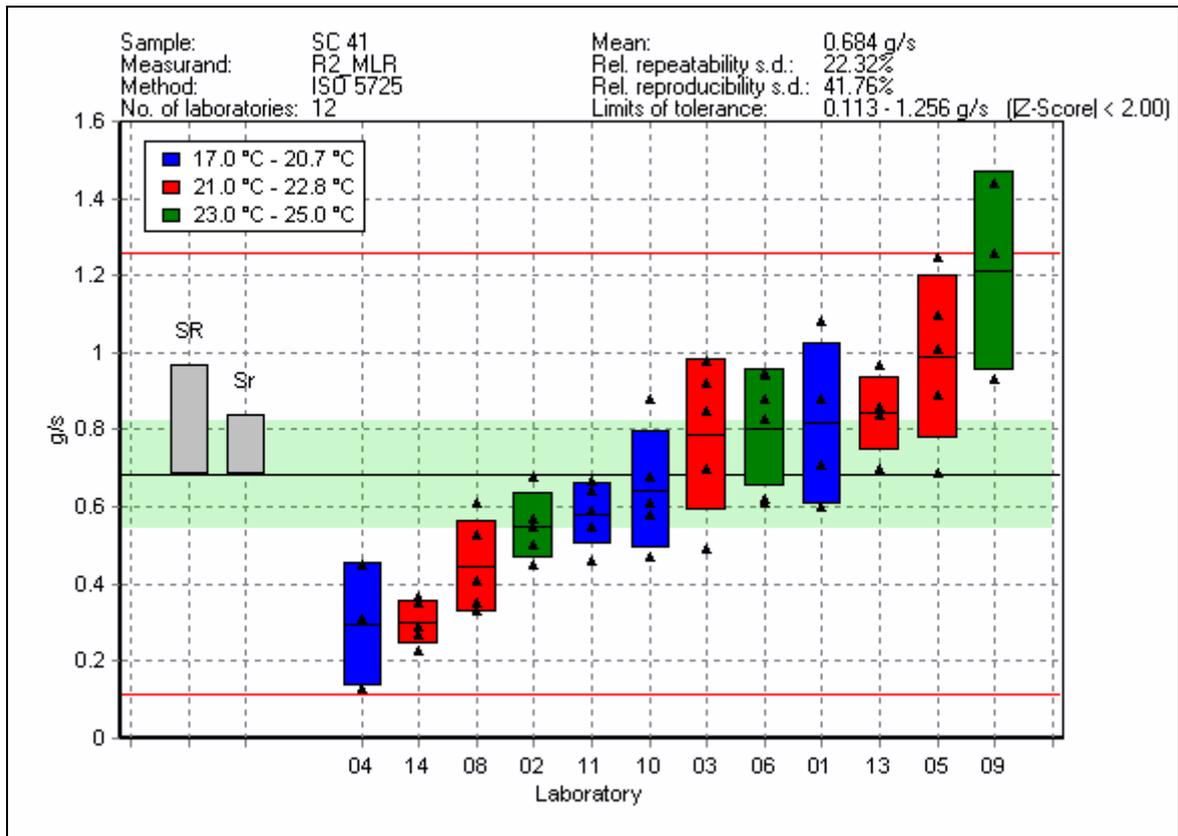


Figure 143: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R² MLR₂₀₋₈₀ – SC 21



10.6.3 Analysis of ratios

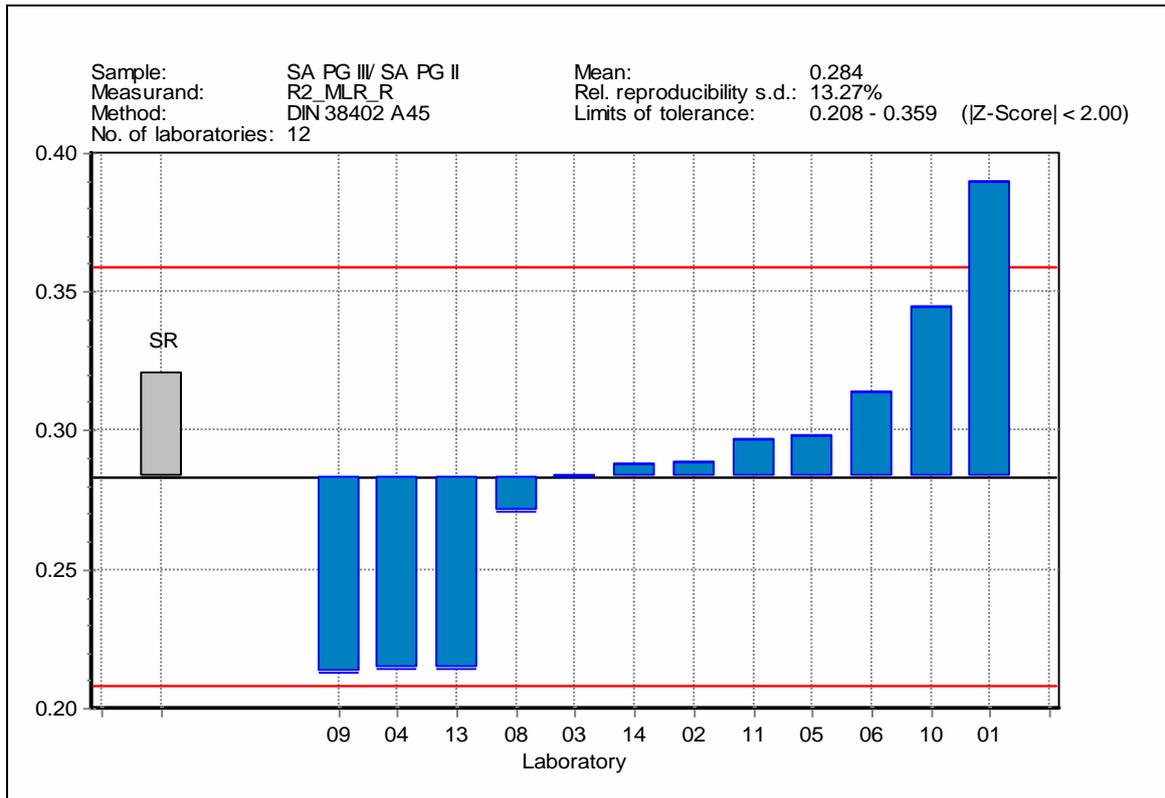


Figure 145: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SA PG III / SA PG II

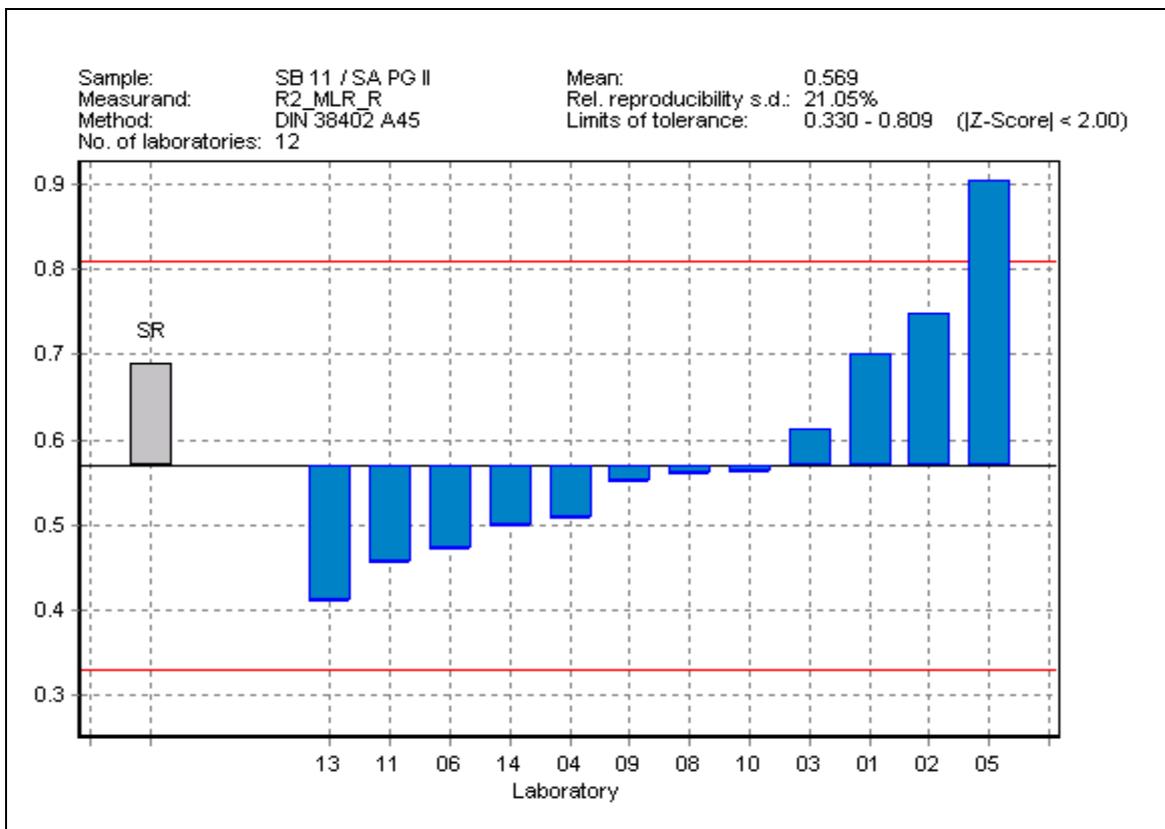


Figure 146: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SB 11 / SA PG II

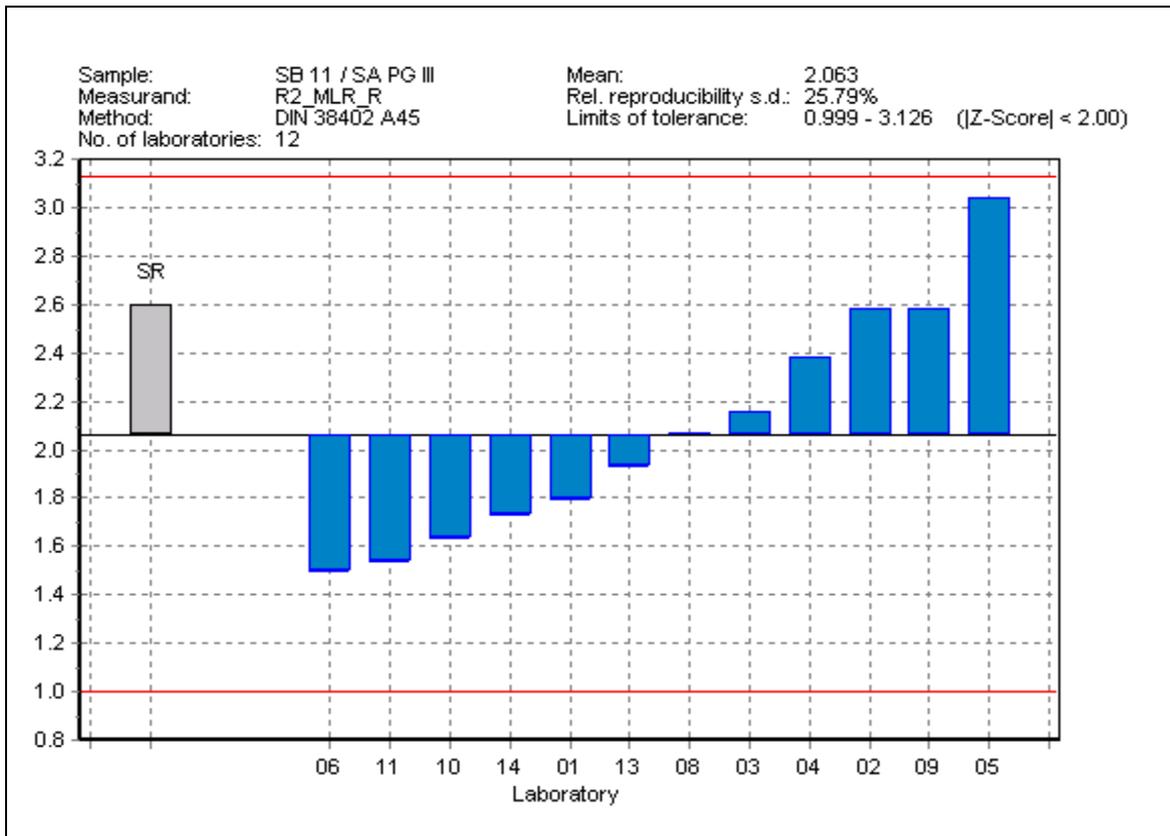


Figure 147: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SB 11 /SA PG III

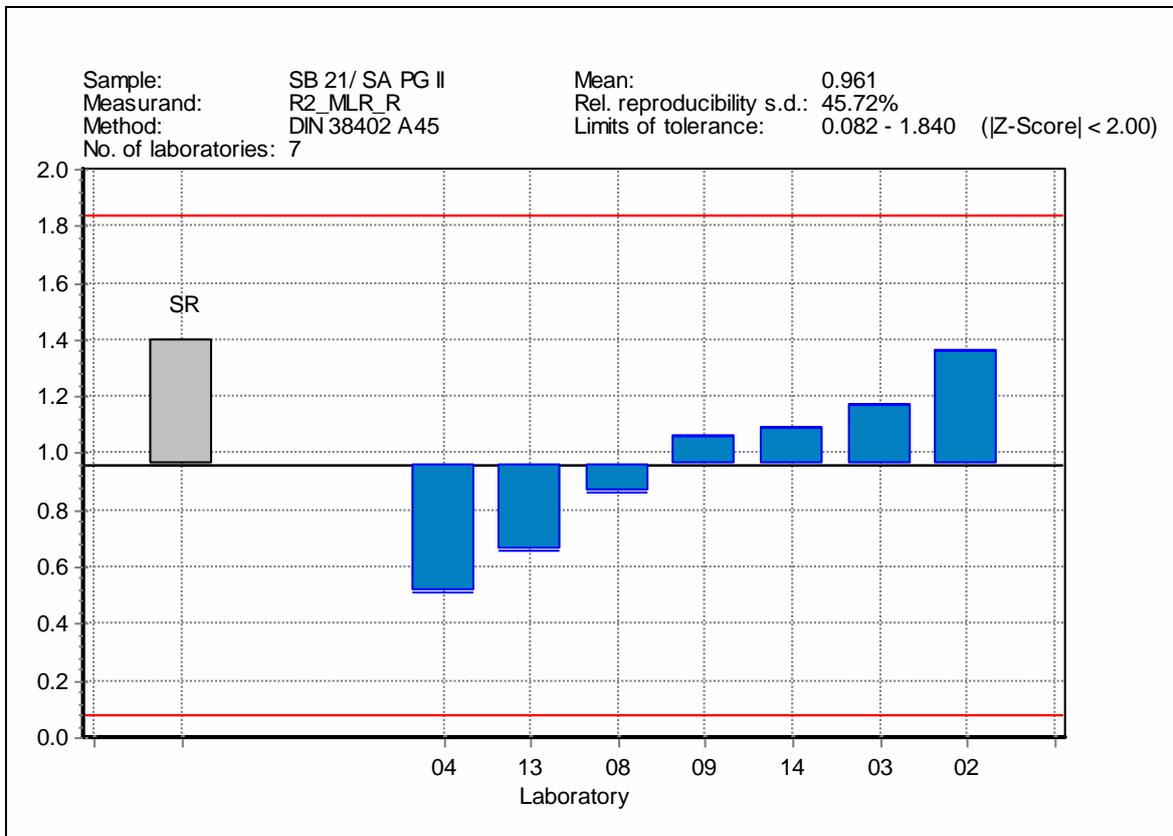


Figure 148: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SB 21 /SA PG II

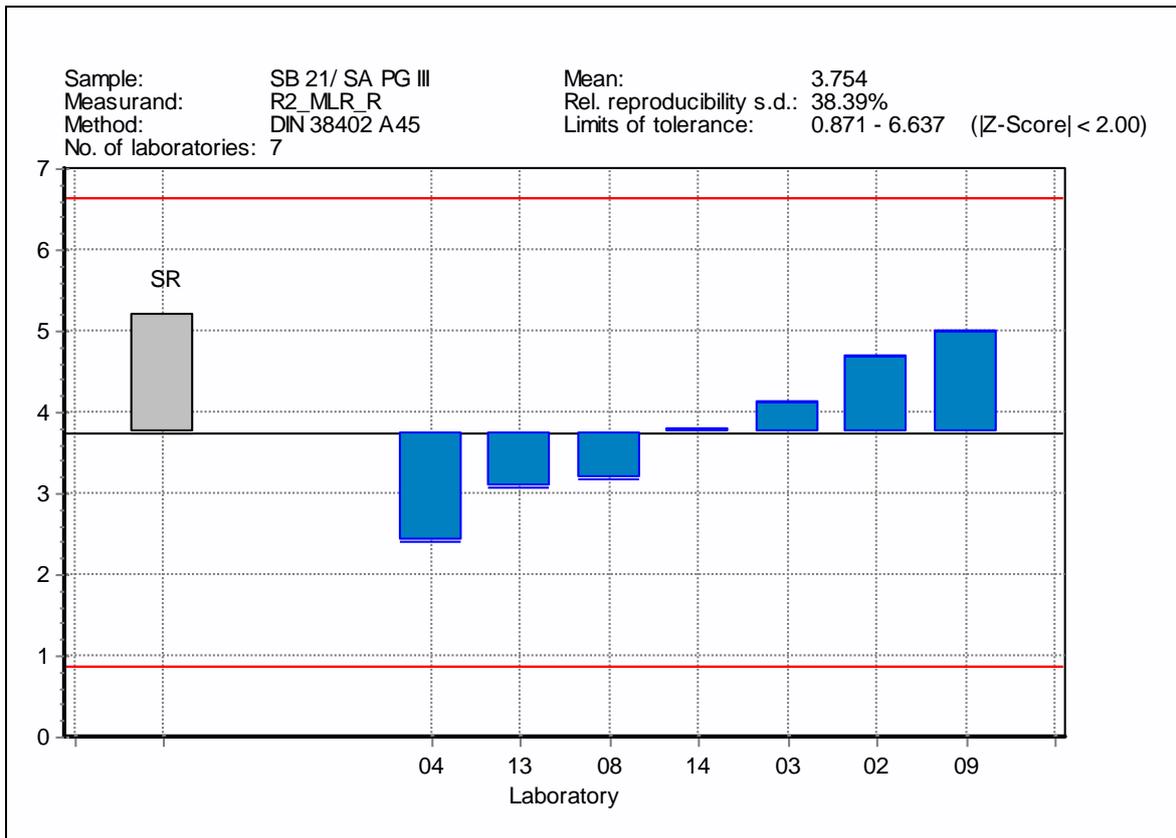


Figure 149: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – SB 21 /SA PG III

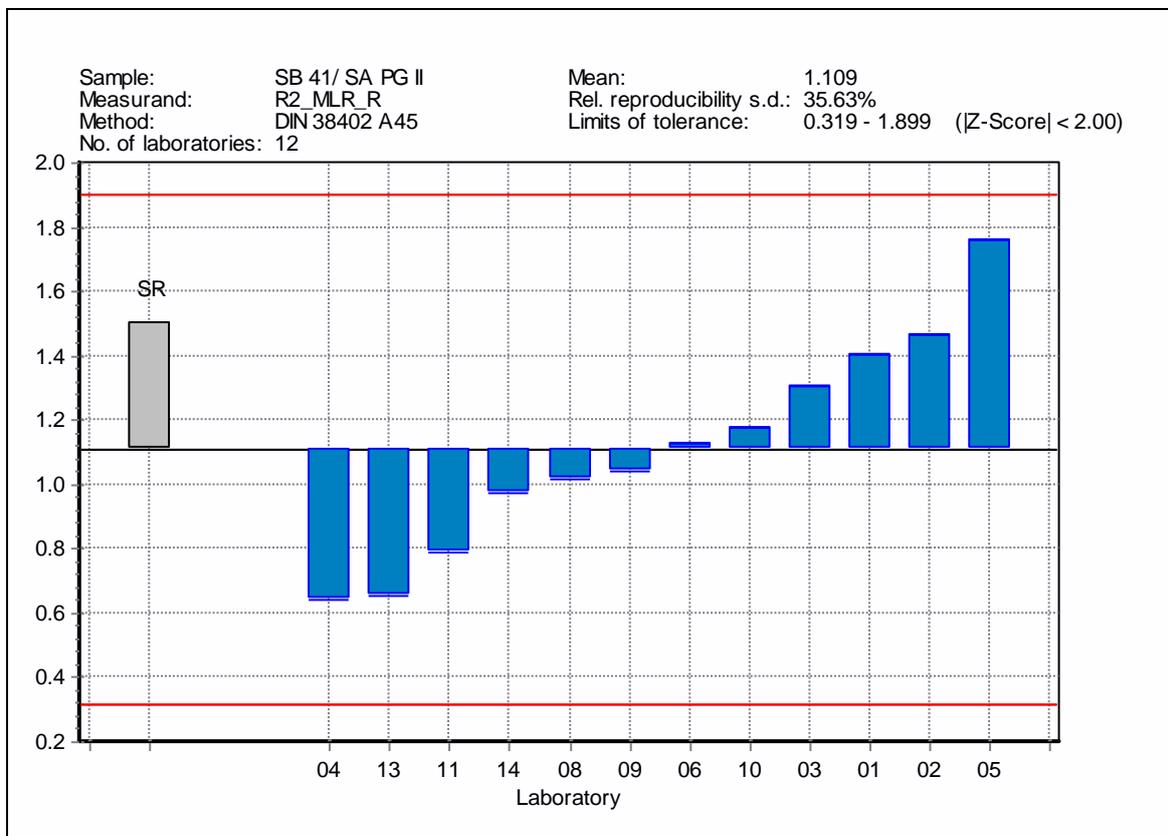


Figure 150: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SB 41 /SA PG II

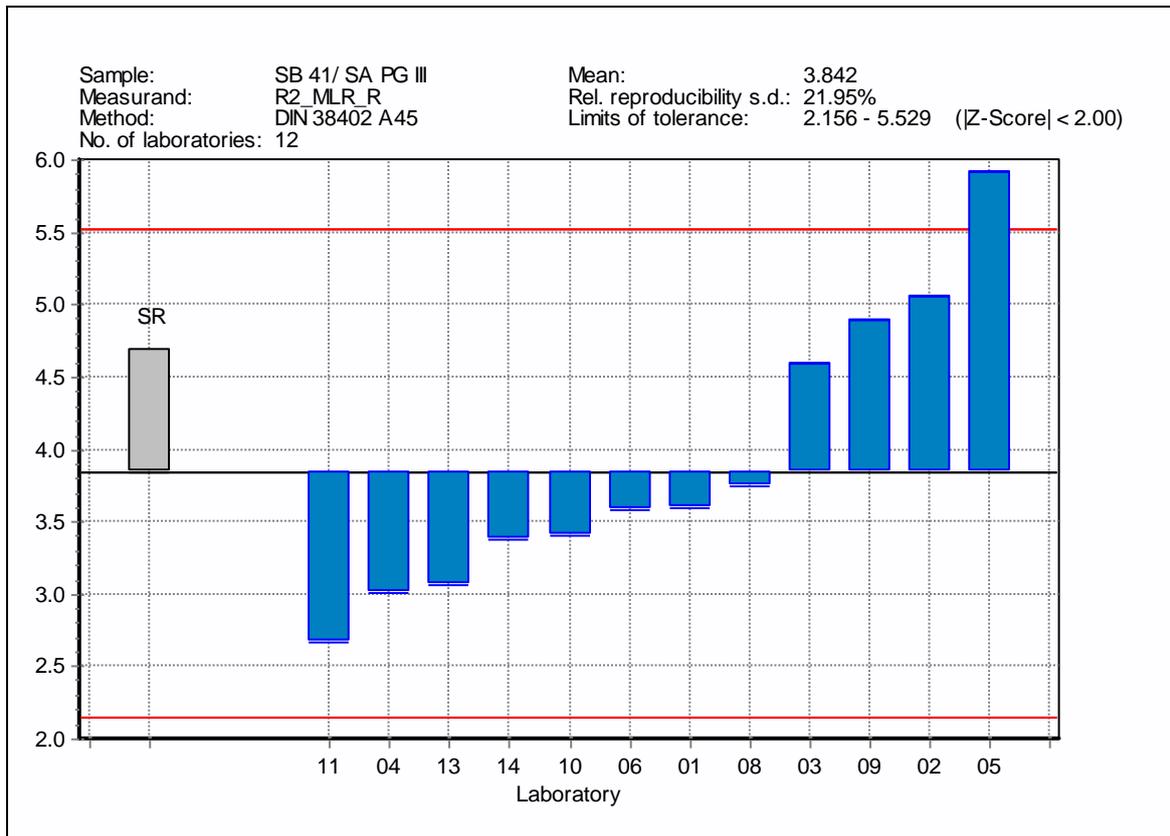


Figure 151: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SB 41 /SA PG III

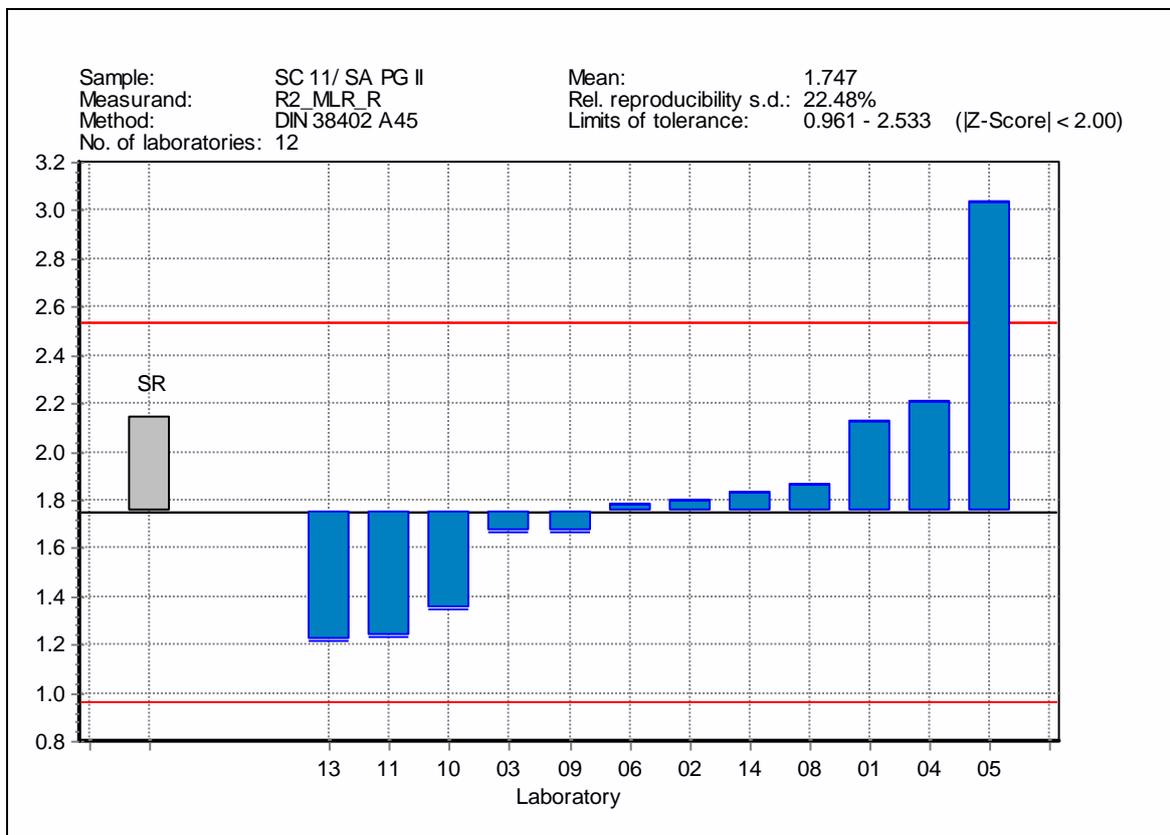


Figure 152: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SC 11 /SA PG II

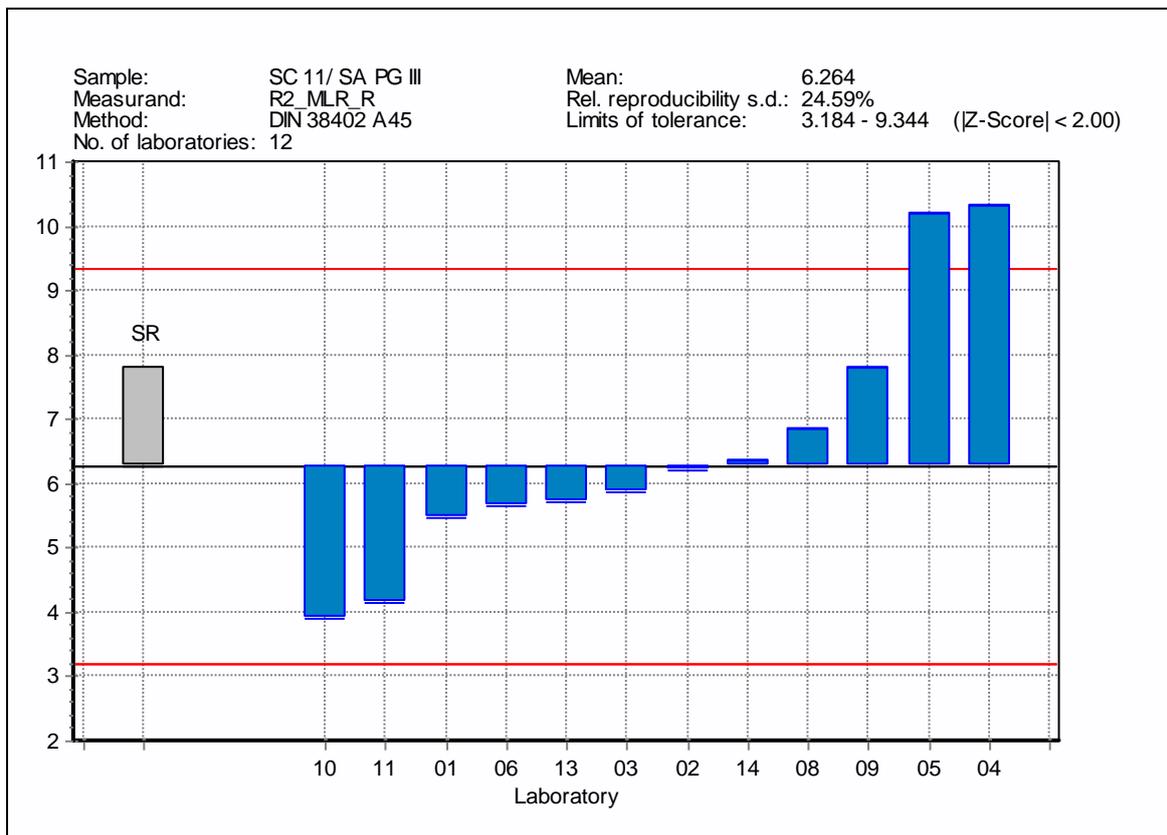


Figure 153: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SC 11 /SA PG III

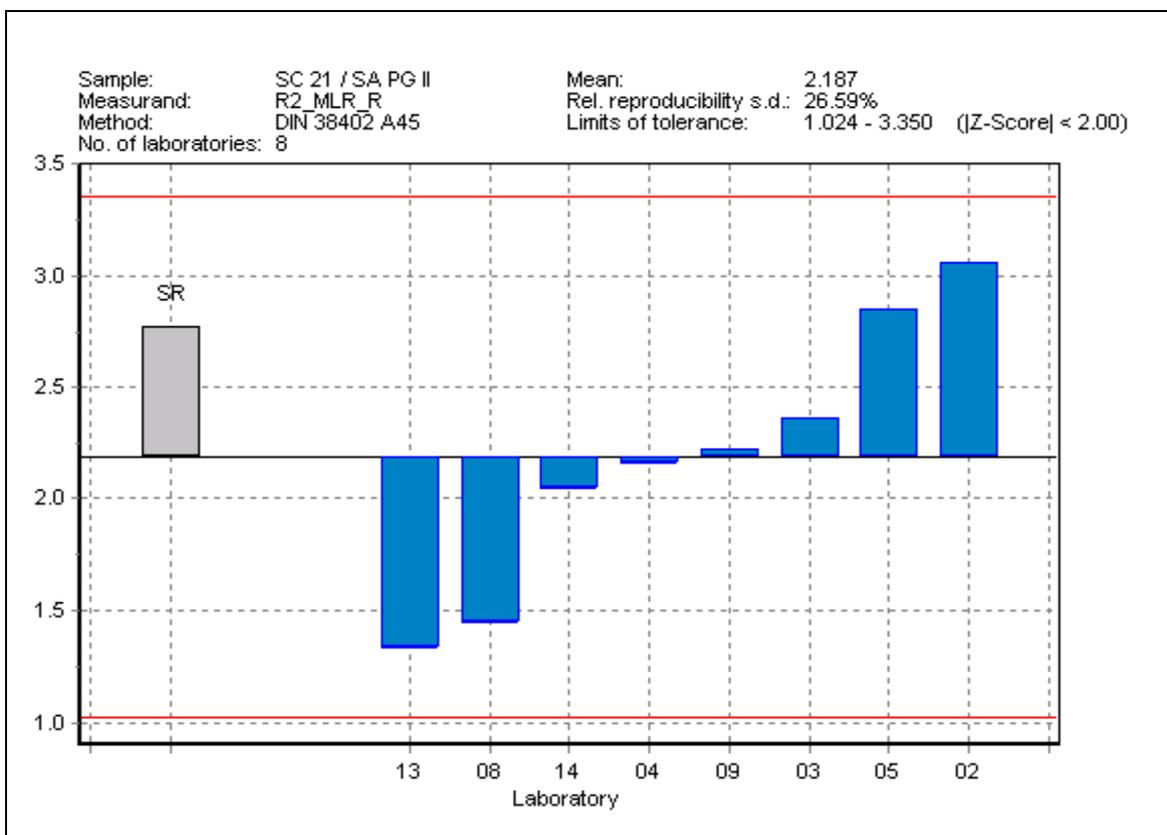


Figure 154: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SC 21 /SA PG II

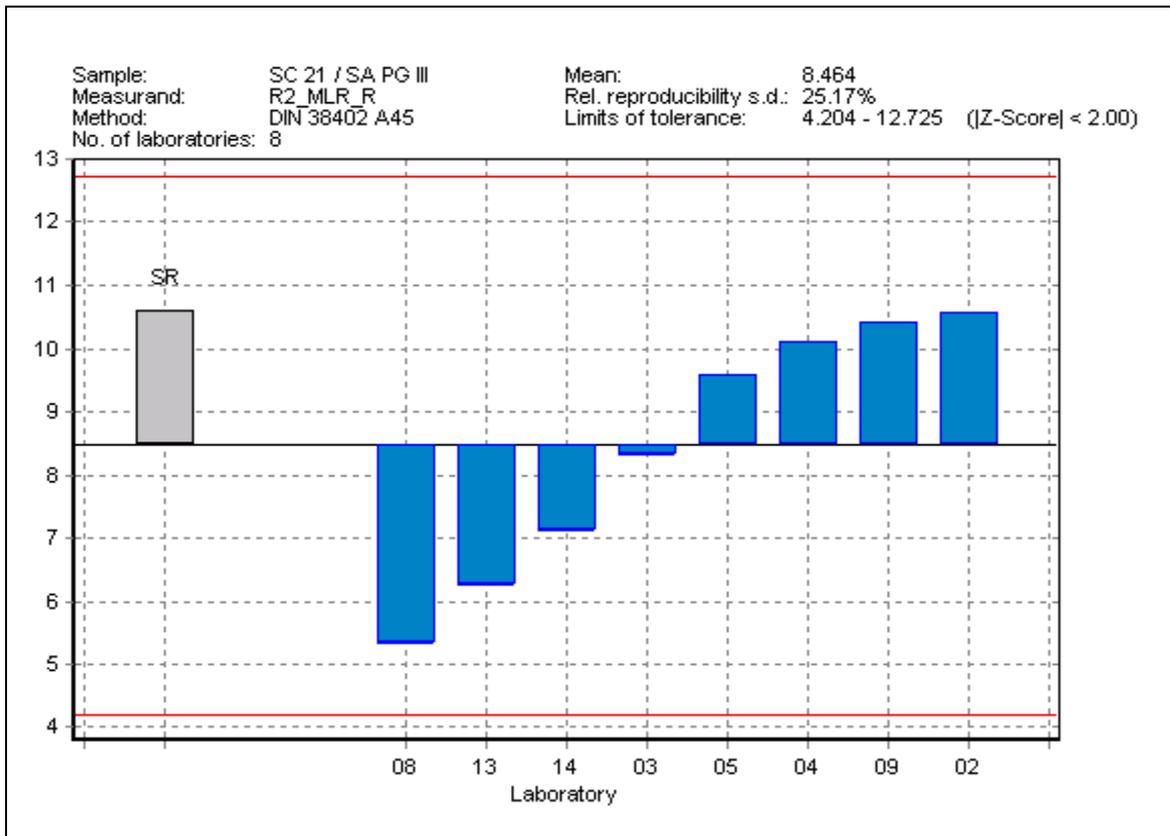


Figure 155: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SC 21 /SA PG III

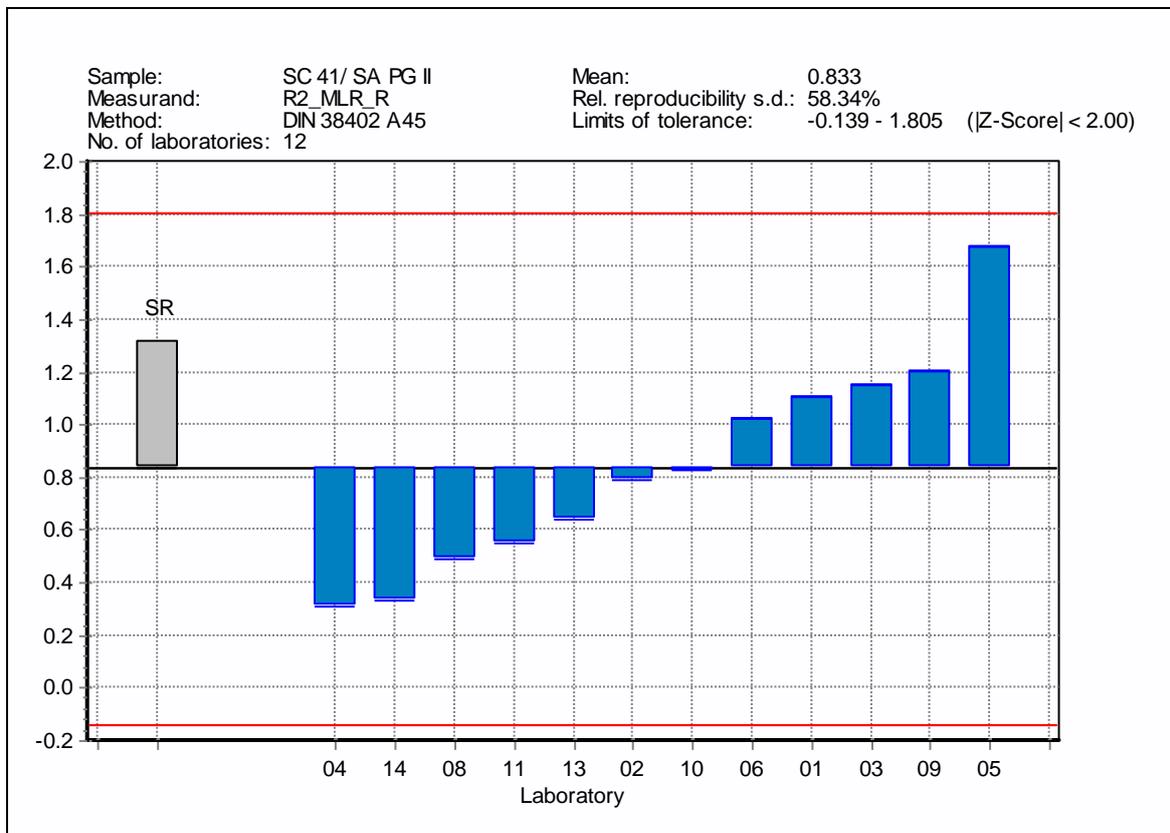


Figure 156: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SC 41 /SA PG II

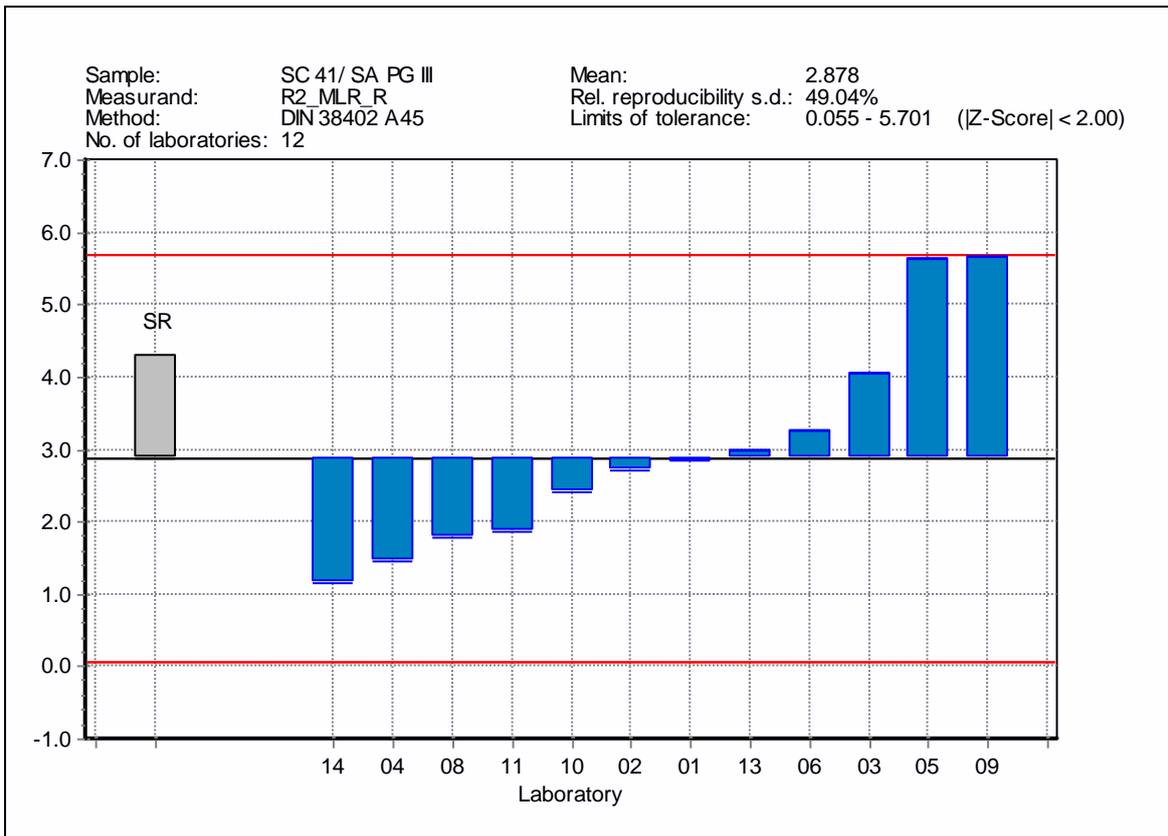


Figure 157: Laboratory results for mass loss rate by linear regression within 20 % to 80 % of total mass loss R^2 MLR₂₀₋₈₀ – ratio SC 41 /SA PG III

10.7 Consumption rate of 60 % of balanced combustible material

10.7.1 Outliers and stragglers

Table 55: Outliers and straggler for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ [g/s]

Sample	Lab code	Outlier test	Outlier/Straggler
SA PG II	04	Cochran	outlier
SA PG III	05	Cochran	outlier
SB 21	04	Cochran	outlier
SB 41	03	Cochran	straggler
SB 41	04	Grubbs	outlier
SC 21	04	Cochran	outlier

10.7.2 Analysis of single values

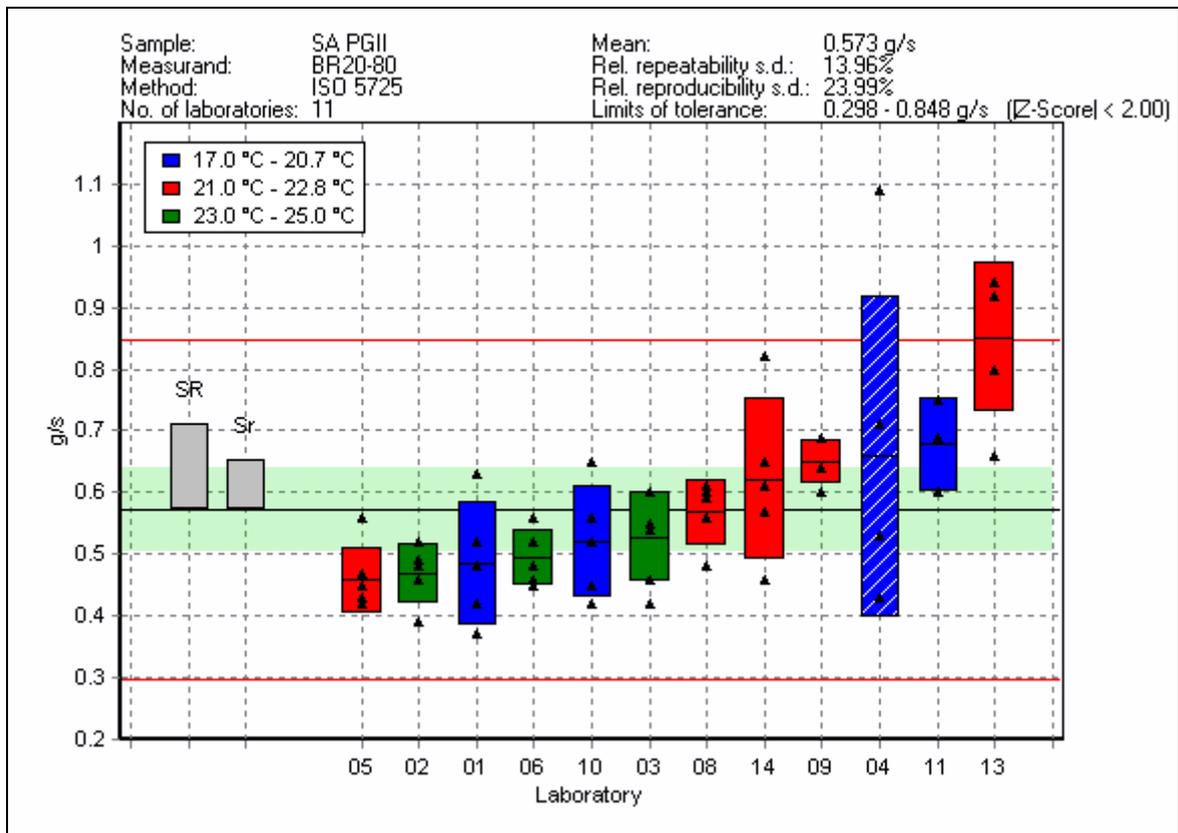


Figure 158: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SA PG II

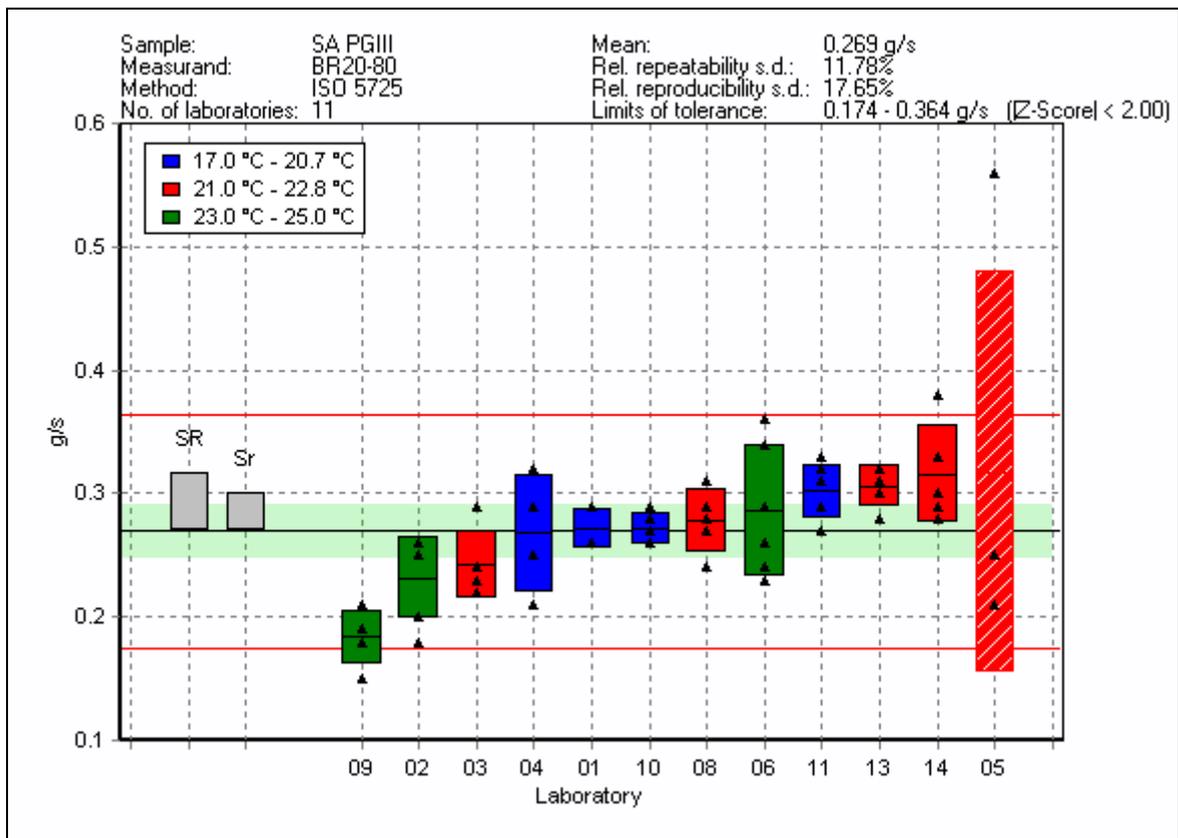


Figure 159: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SA PG III

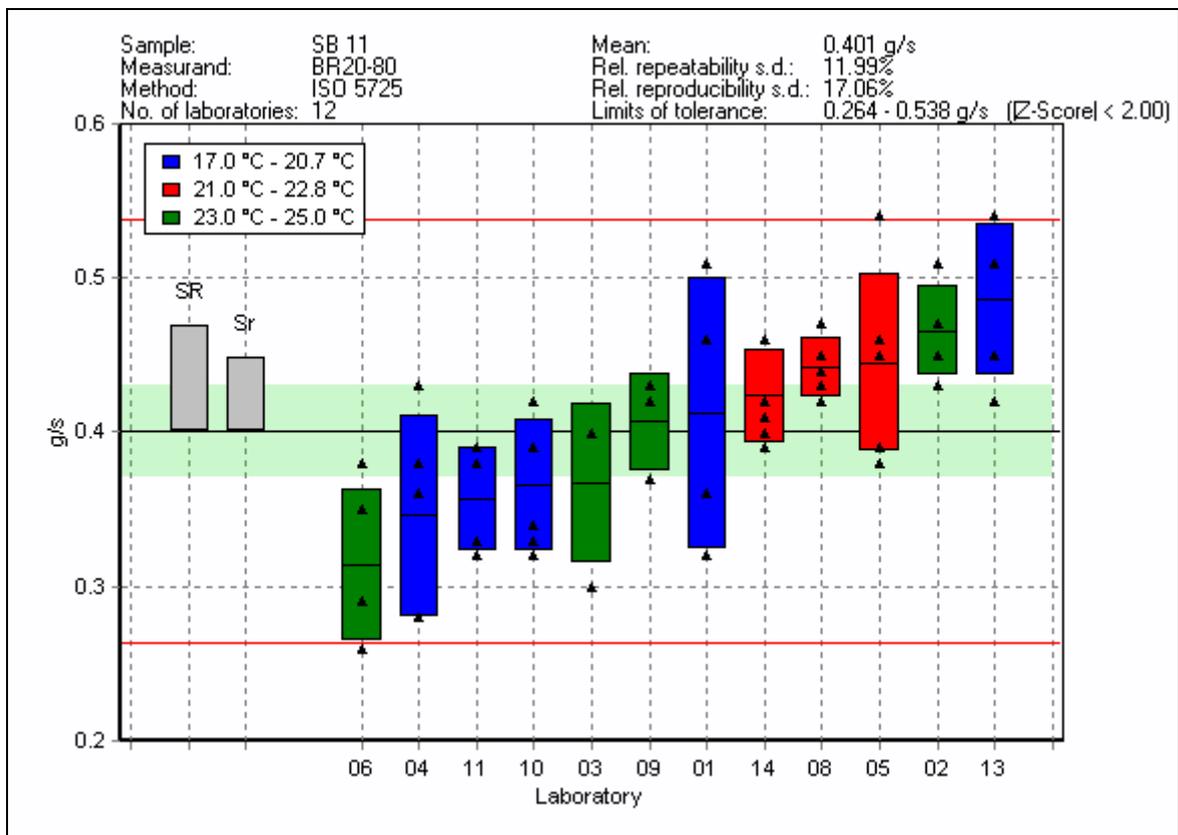


Figure 160: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SB 11

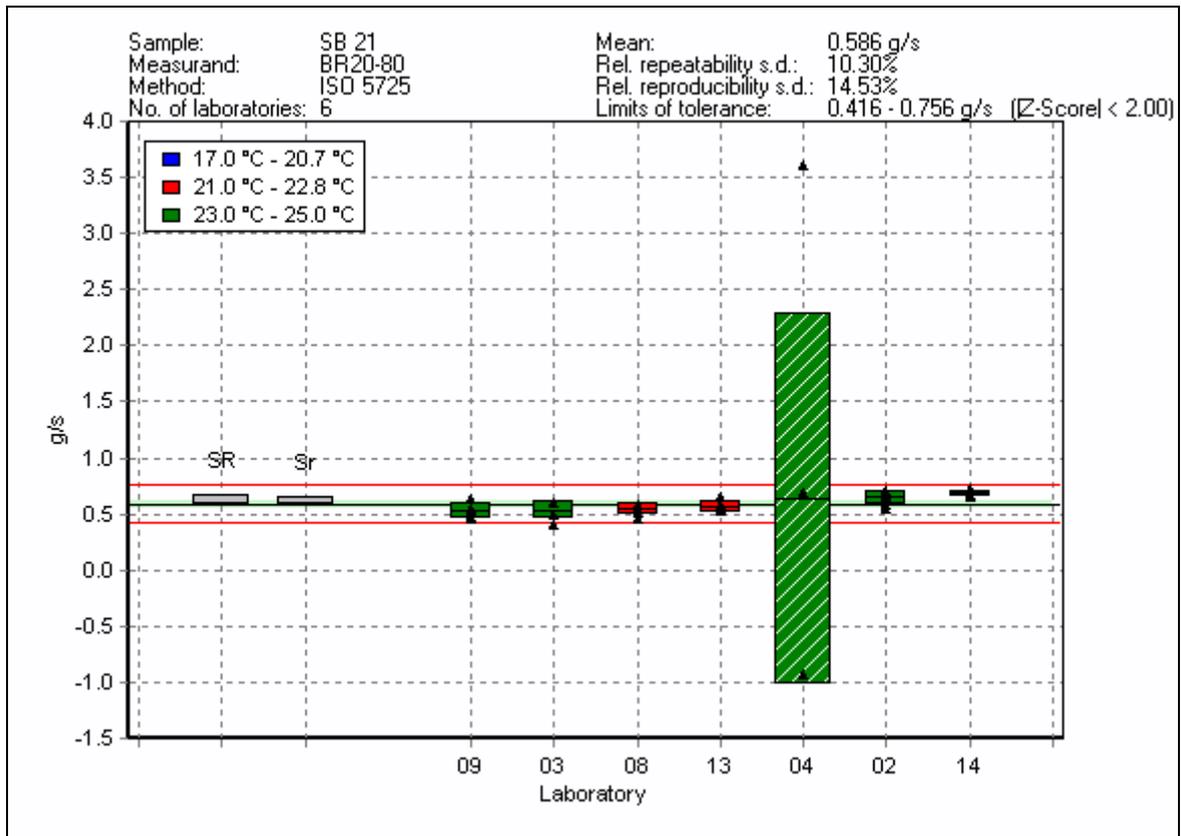


Figure 161: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SB 21

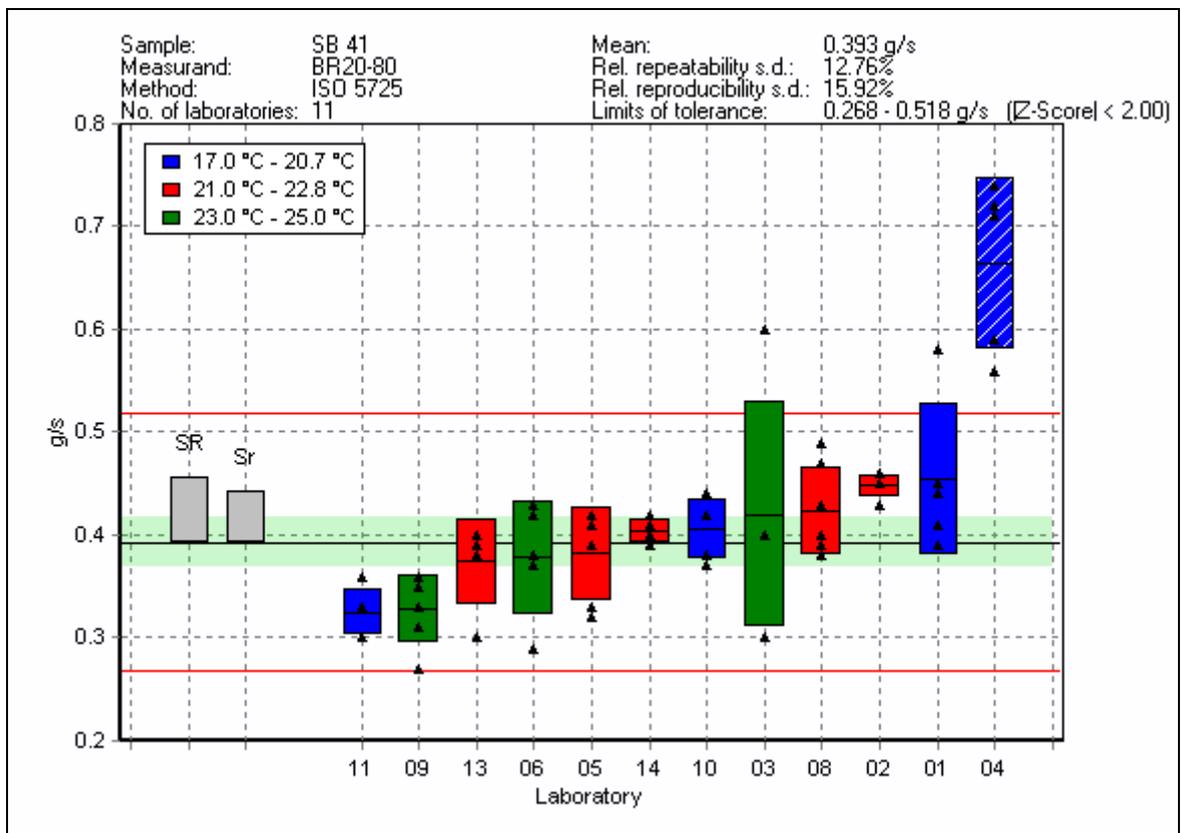


Figure 162: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SB 41

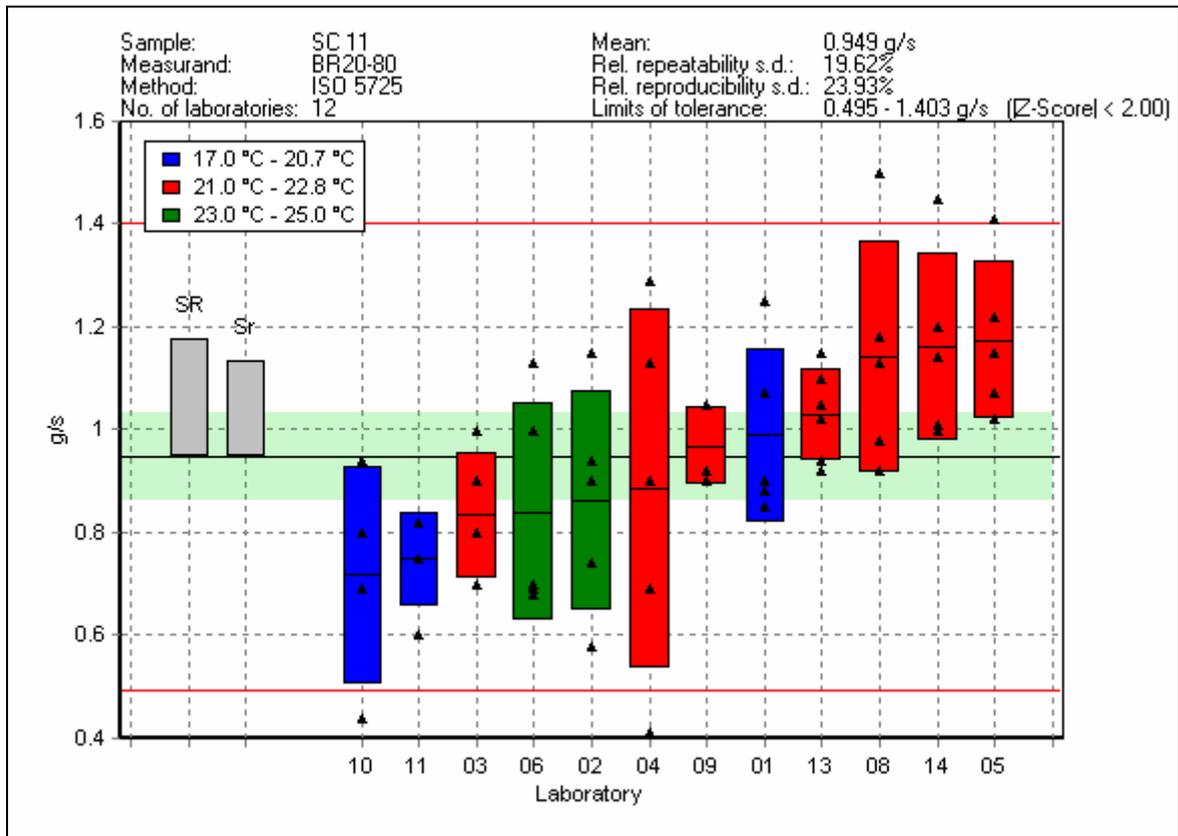


Figure 163: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SC 11

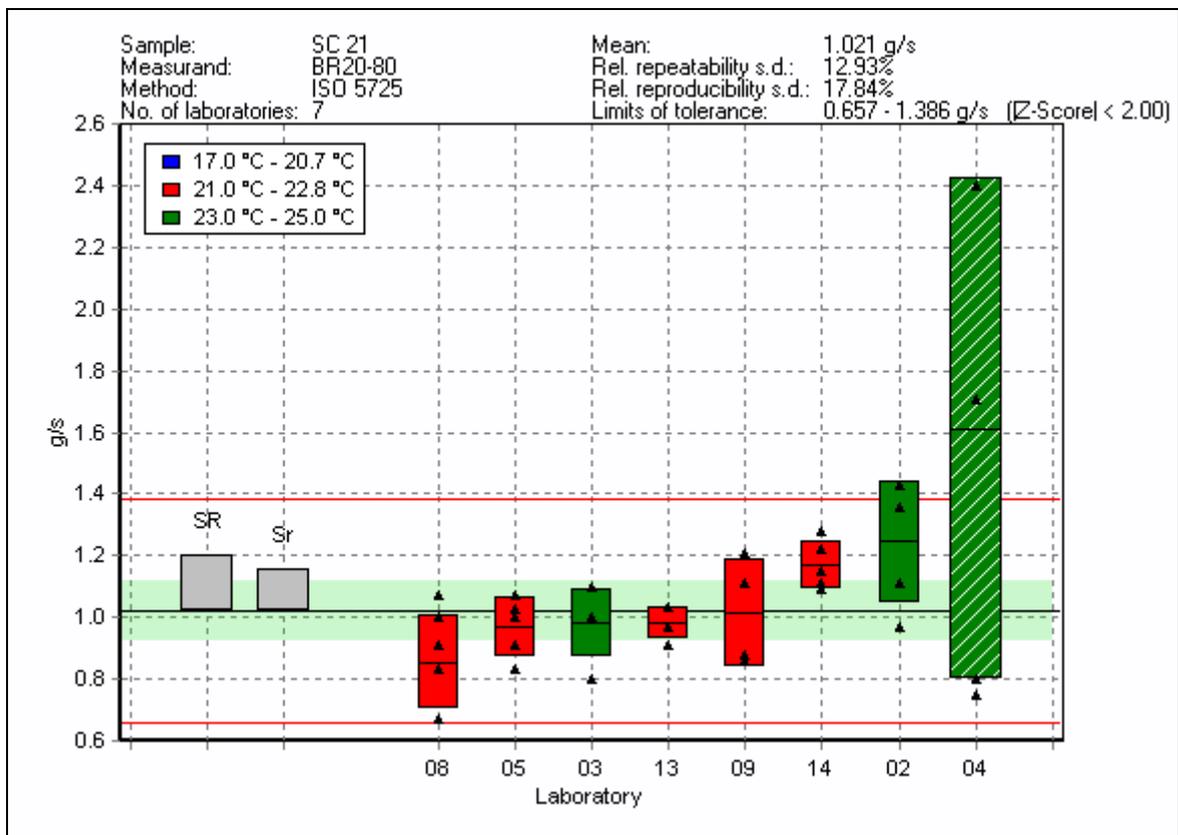


Figure 164: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SC 21

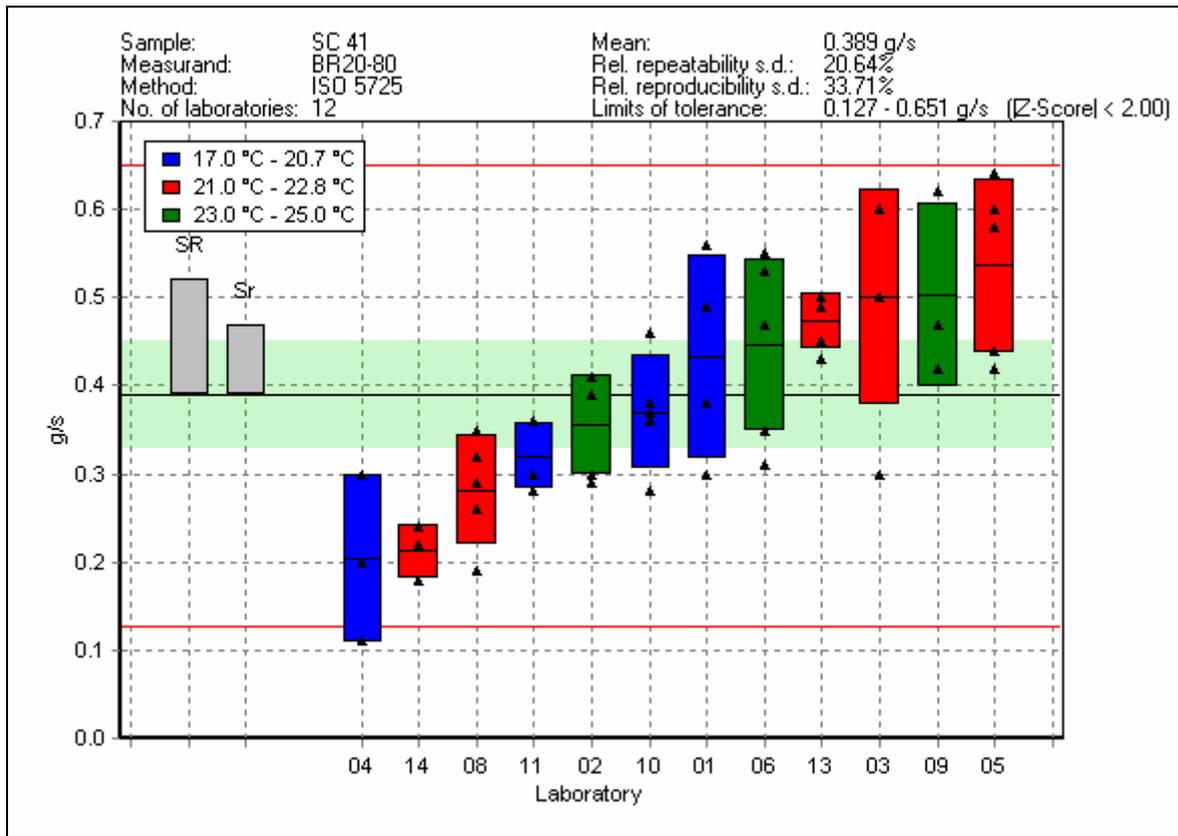


Figure 165: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – SC 41

10.7.3 Analysis of ratios

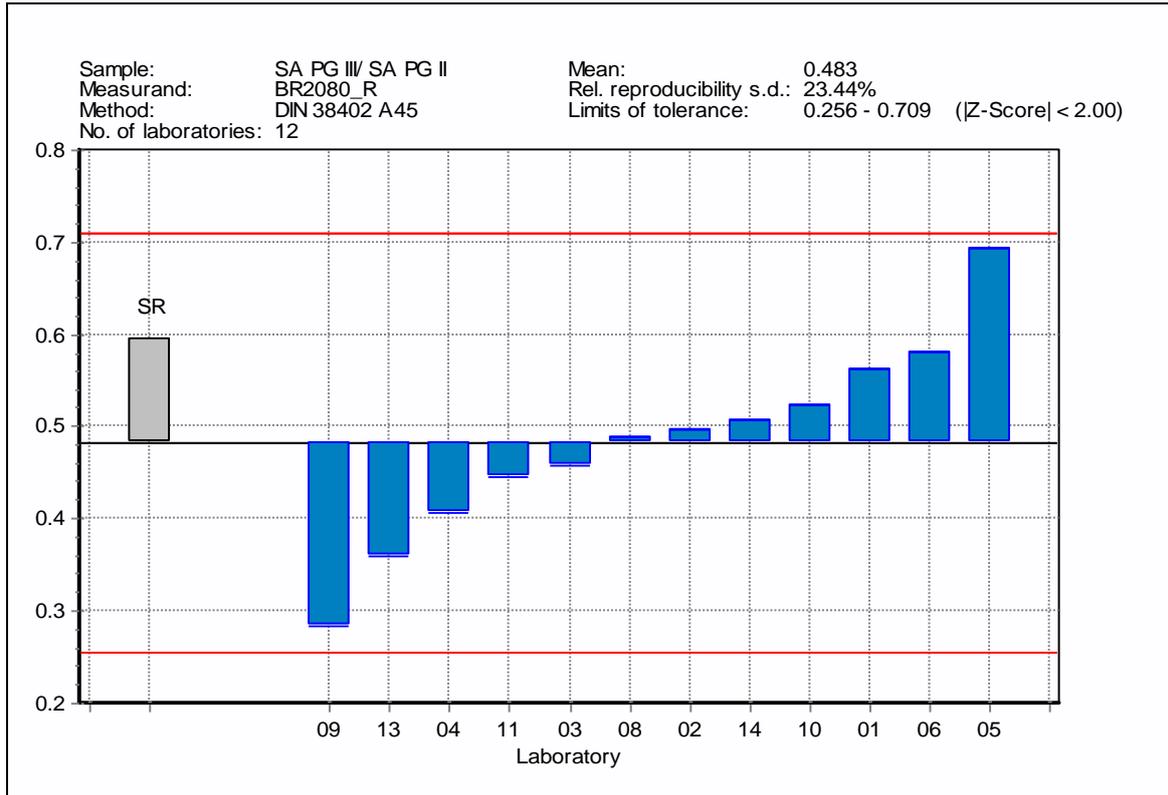


Figure 166: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SA PG III / SA PG II

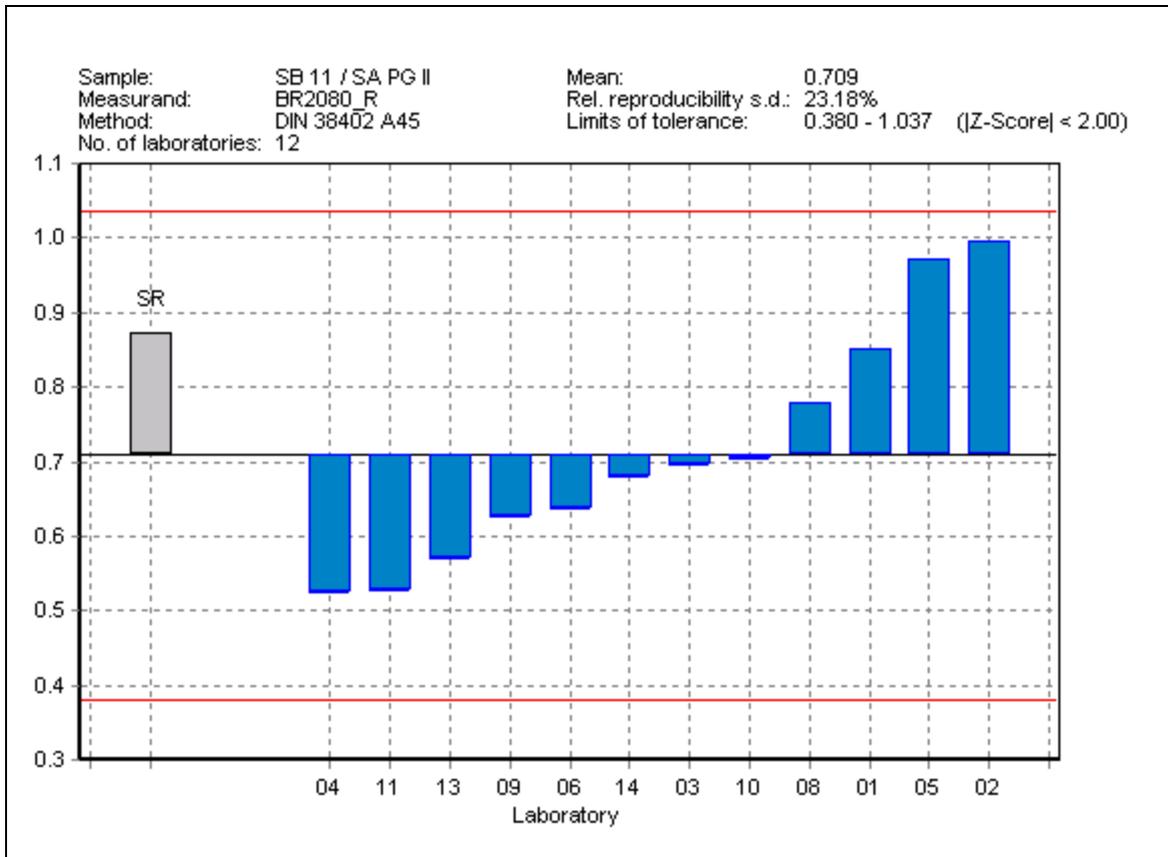


Figure 167: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SB 11 / SA PG II

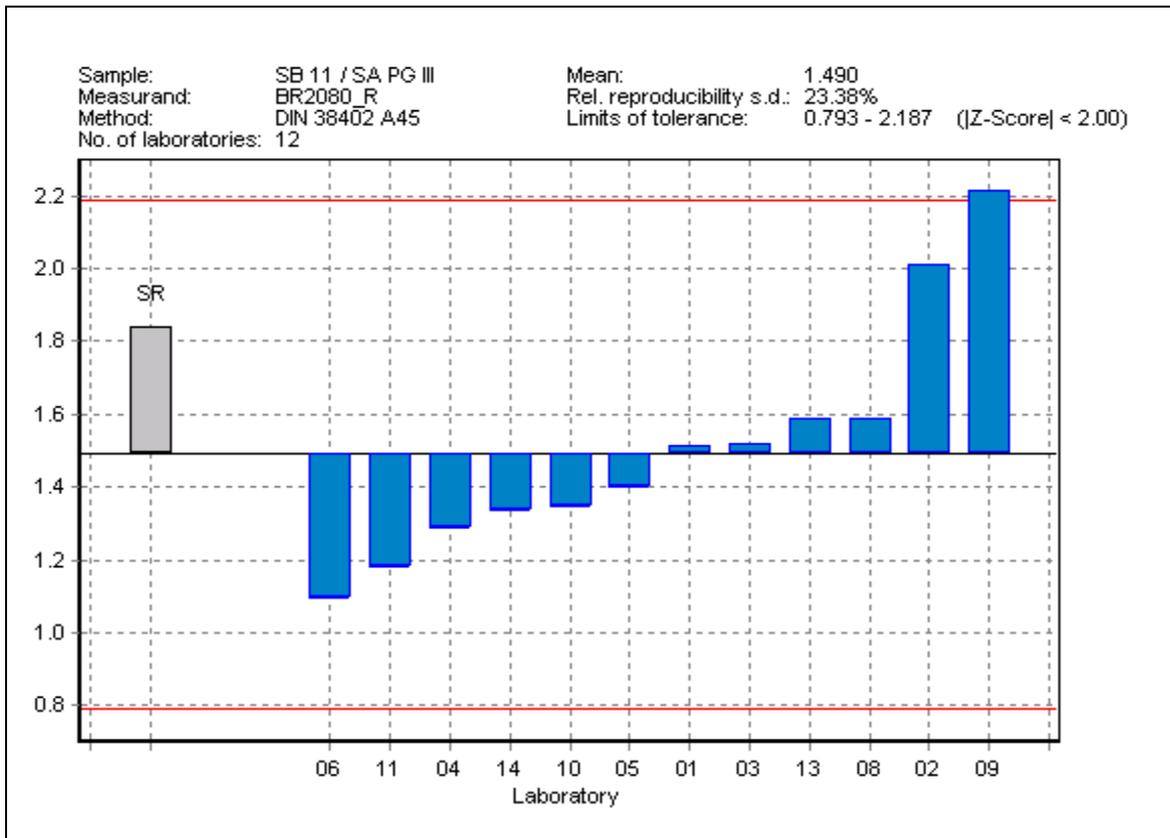


Figure 168: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SB 11 / SA PG III

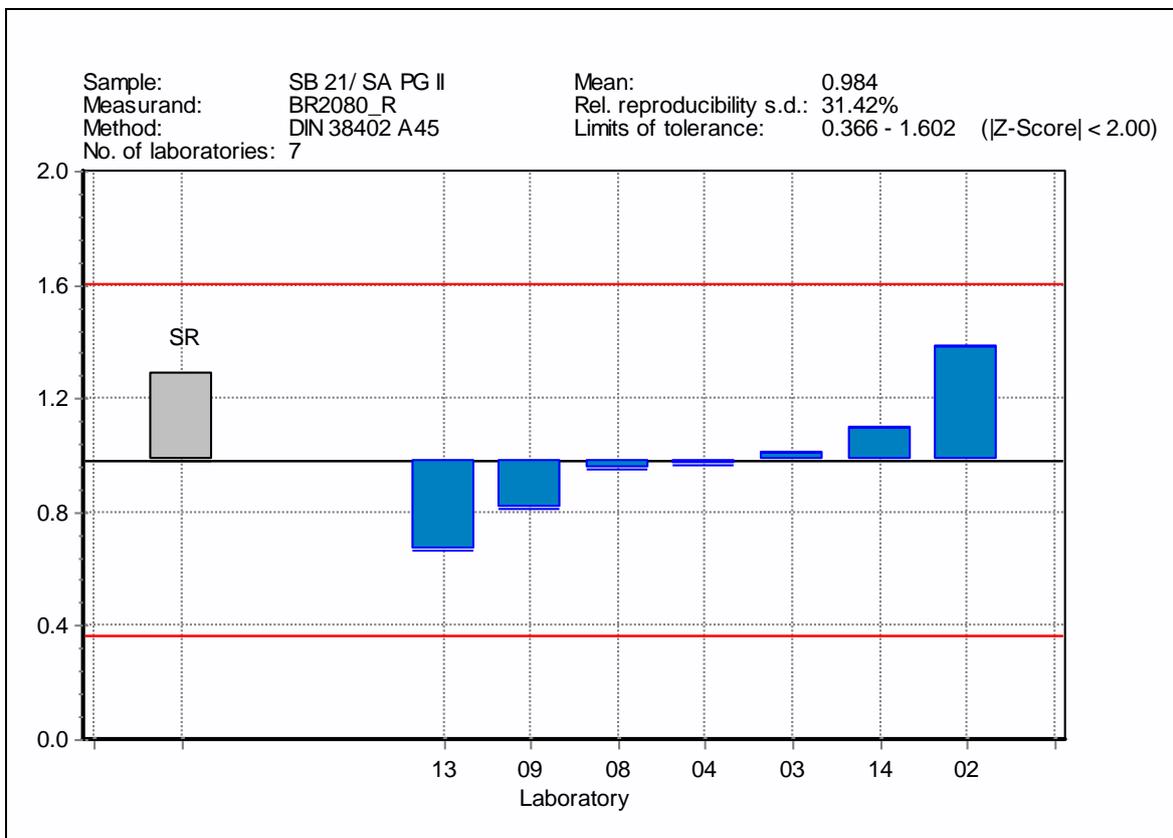


Figure 169: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SB 21 / SA PG II

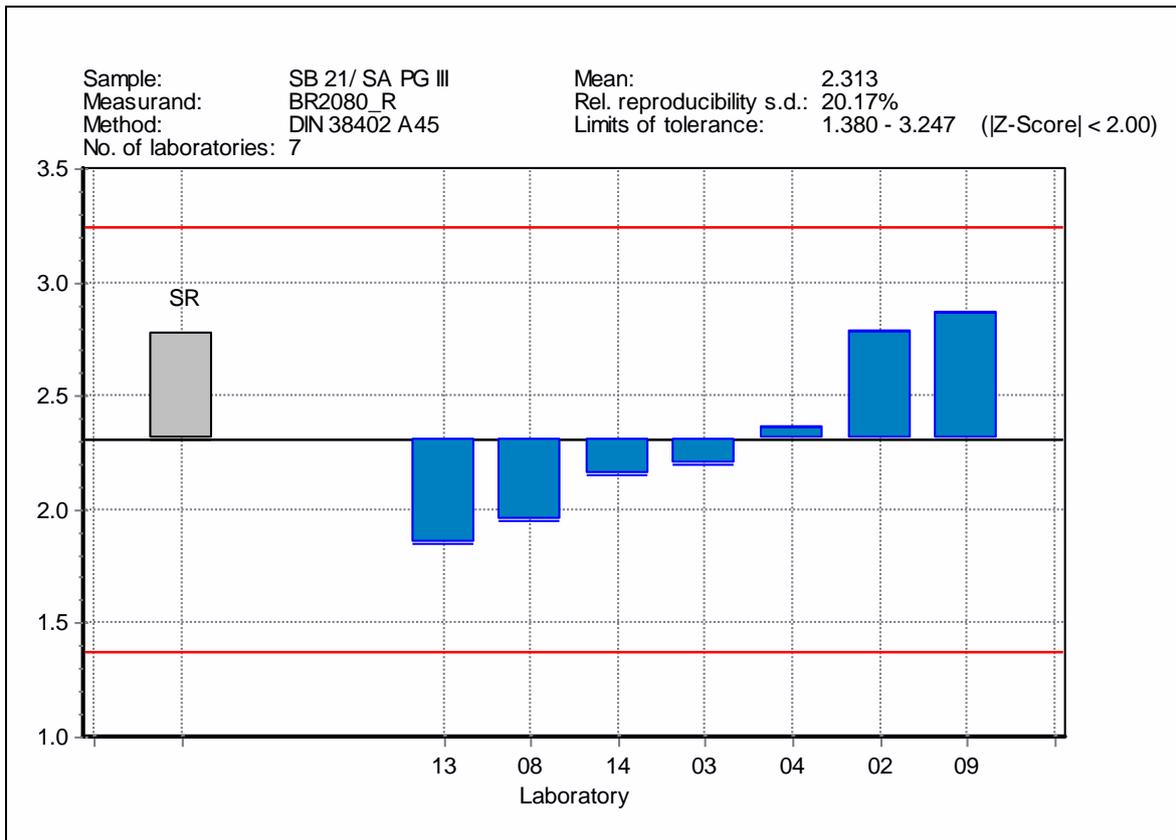


Figure 170: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SB 21 / SA PG III

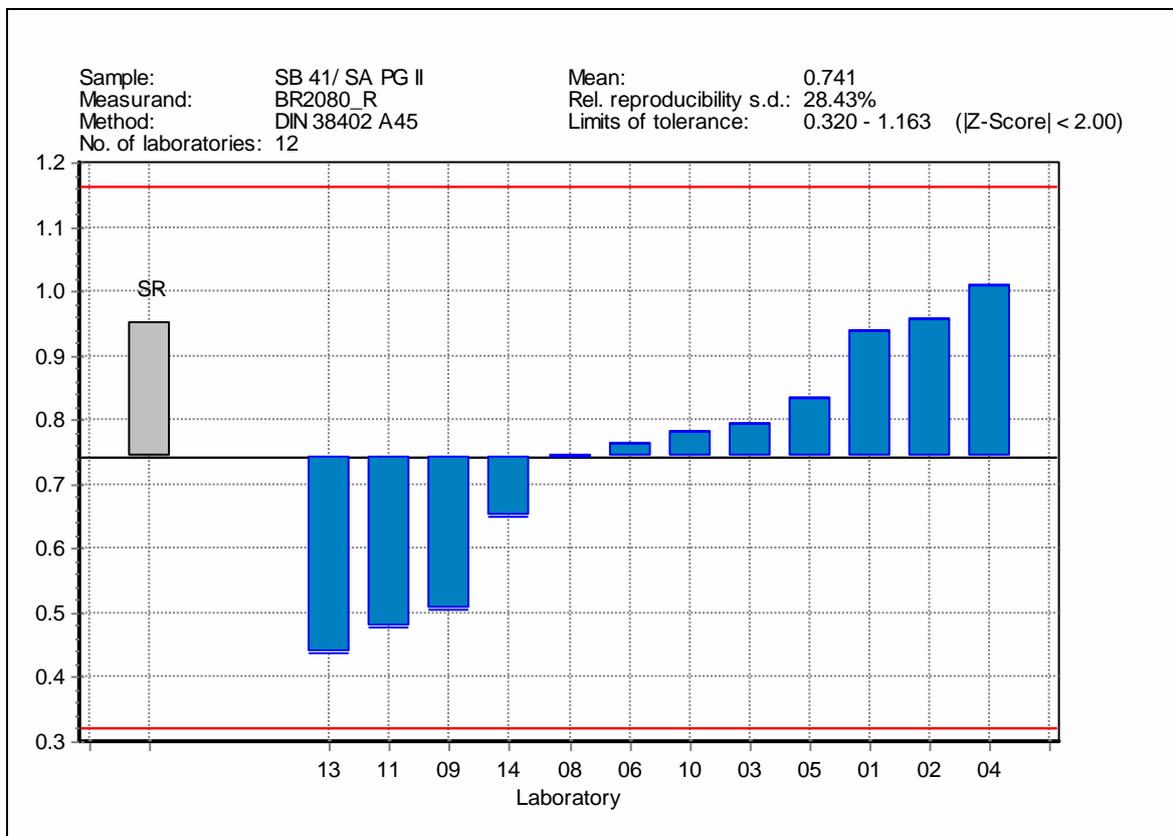


Figure 171: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SB 41 / SA PG II

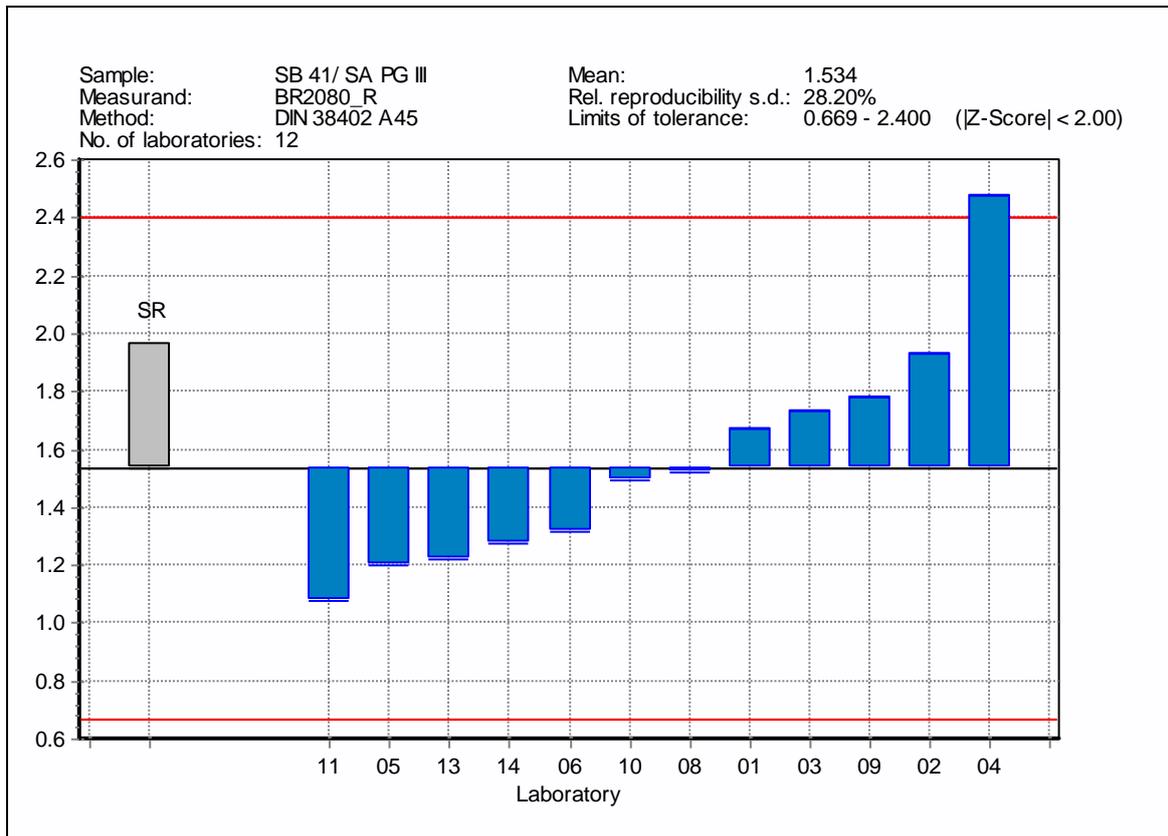


Figure 172: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SB 41 / SA PG III

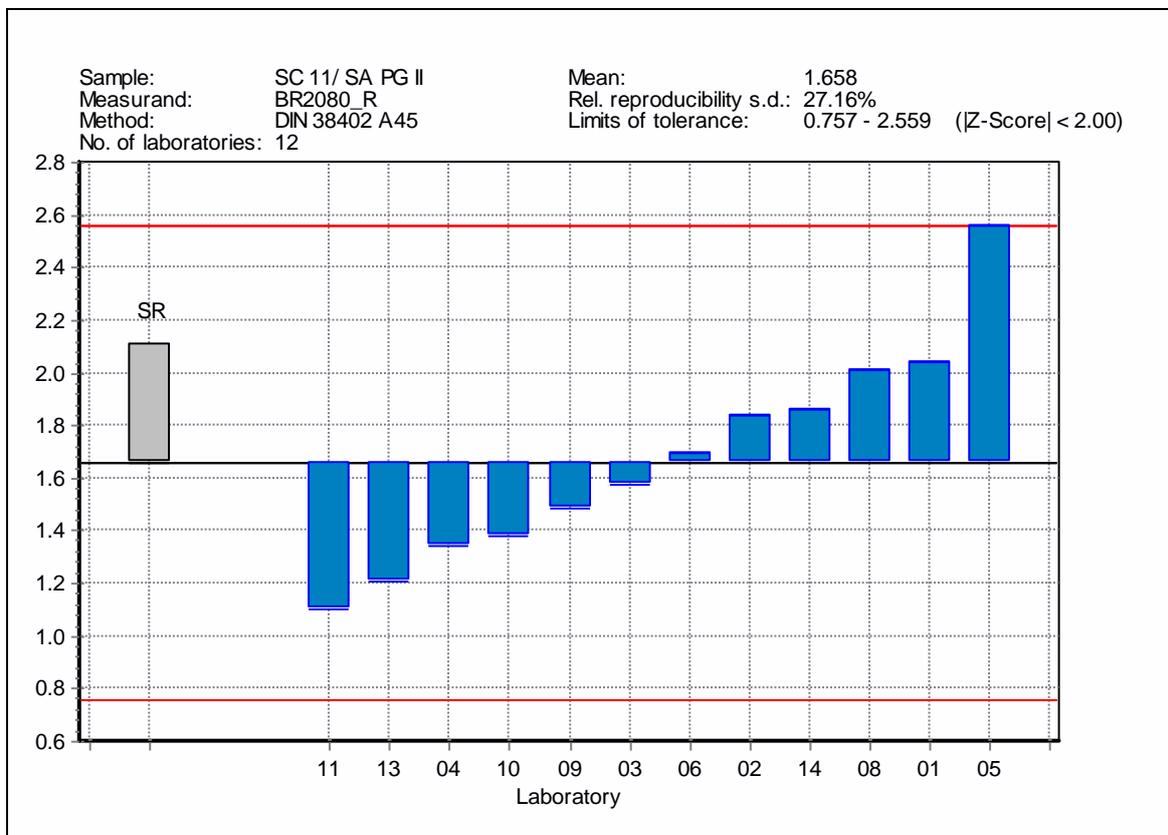


Figure 173: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SC 11 / SA PG II

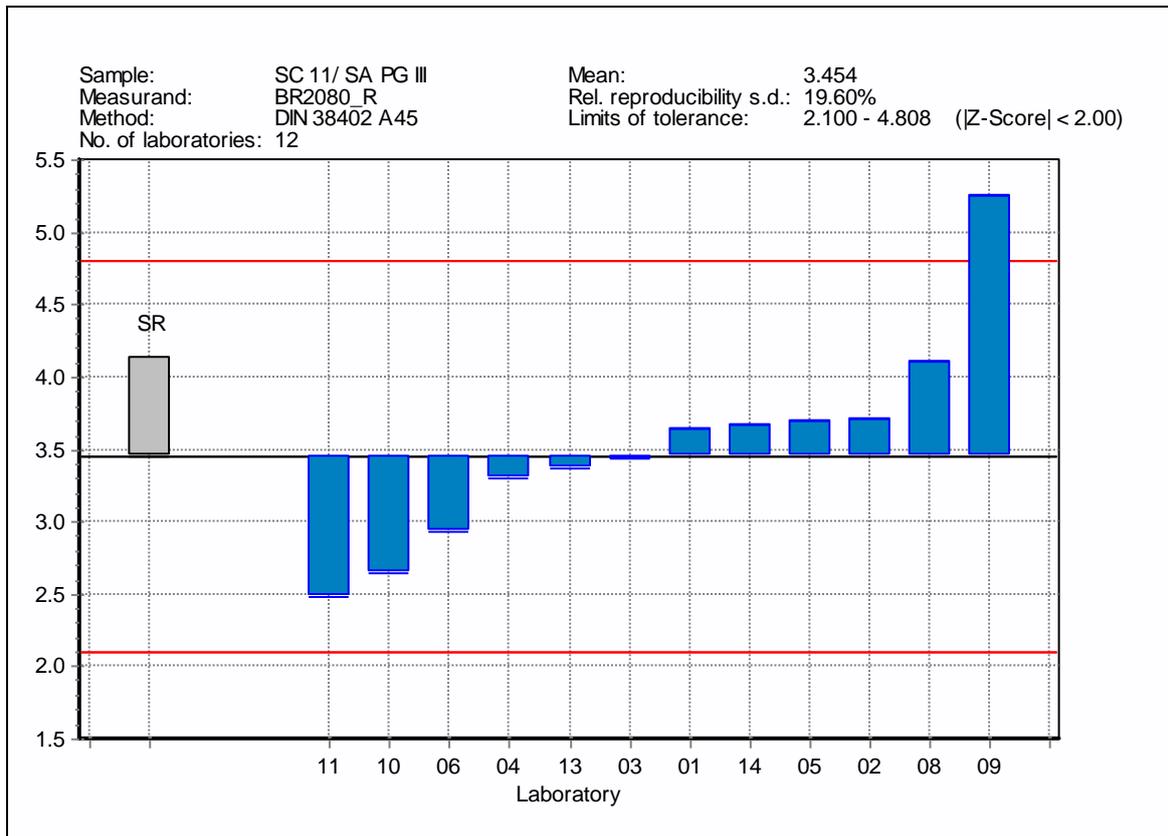


Figure 174: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SC 11 / SA PG III

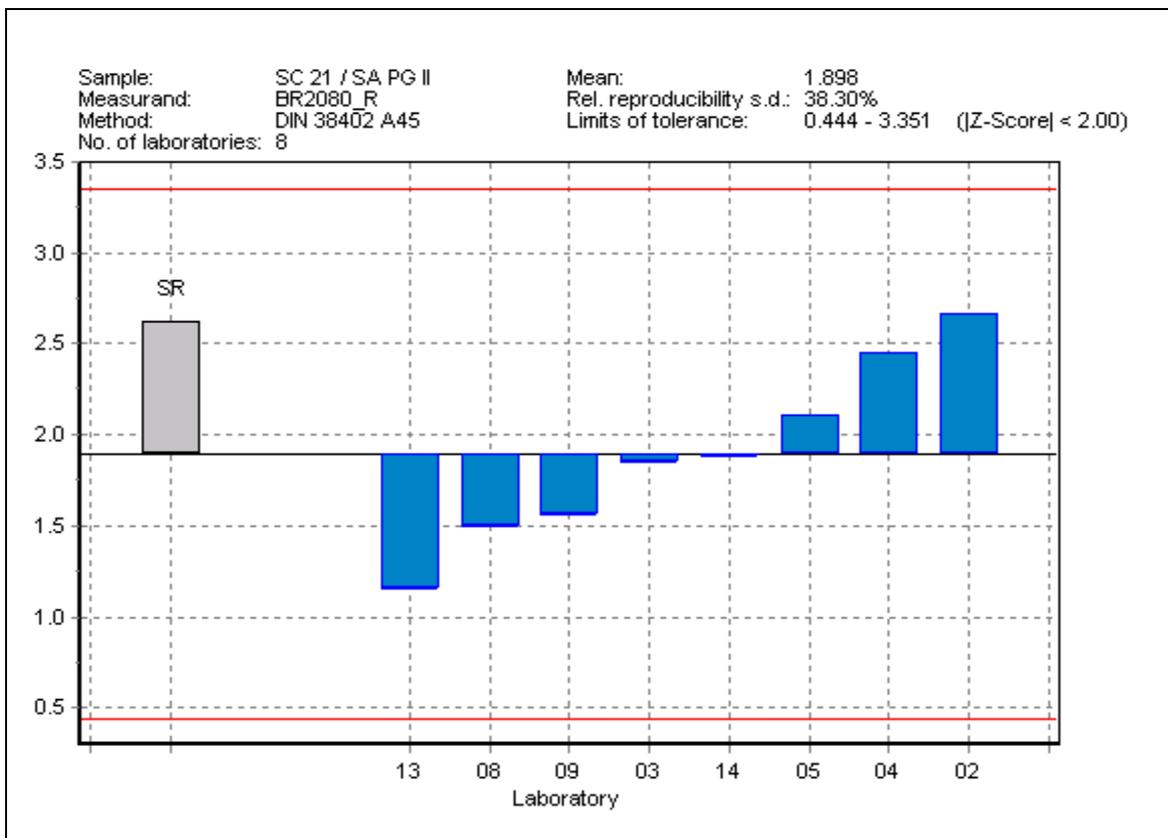


Figure 175: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SC 21 / SA PG II

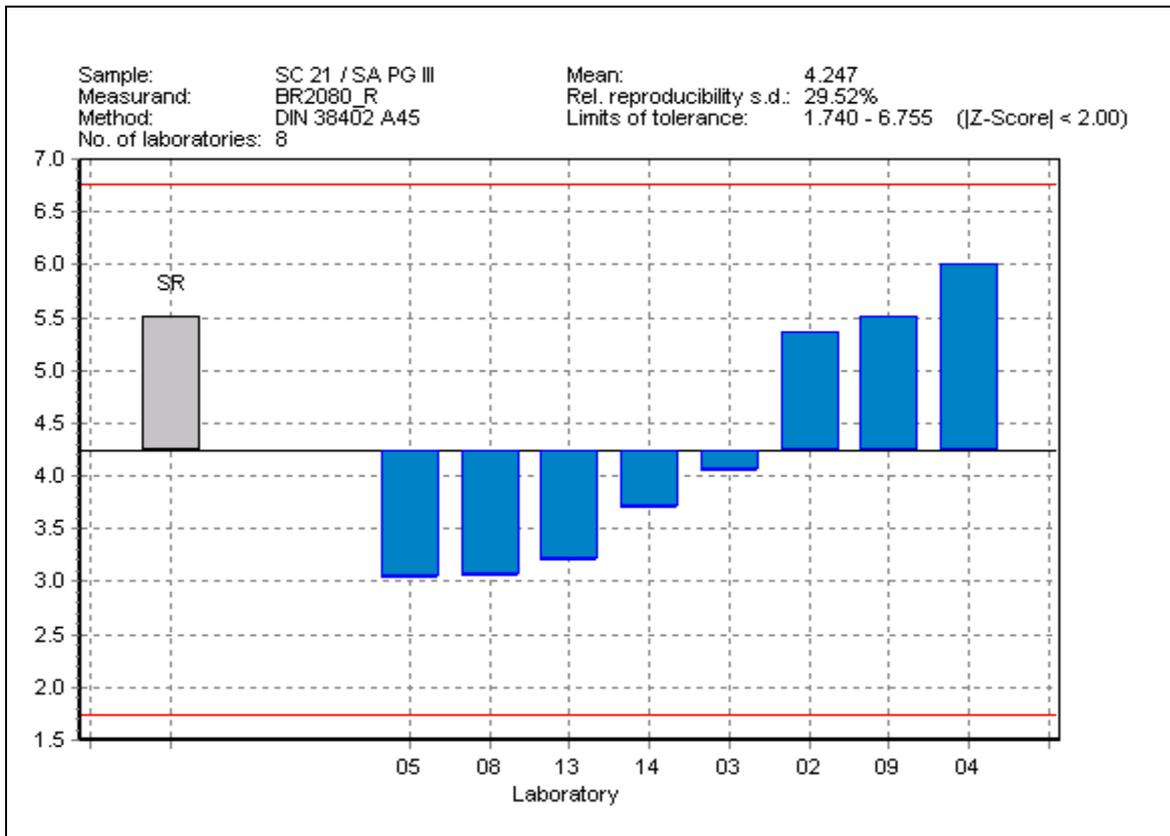


Figure 176: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SC 21 / SA PG III

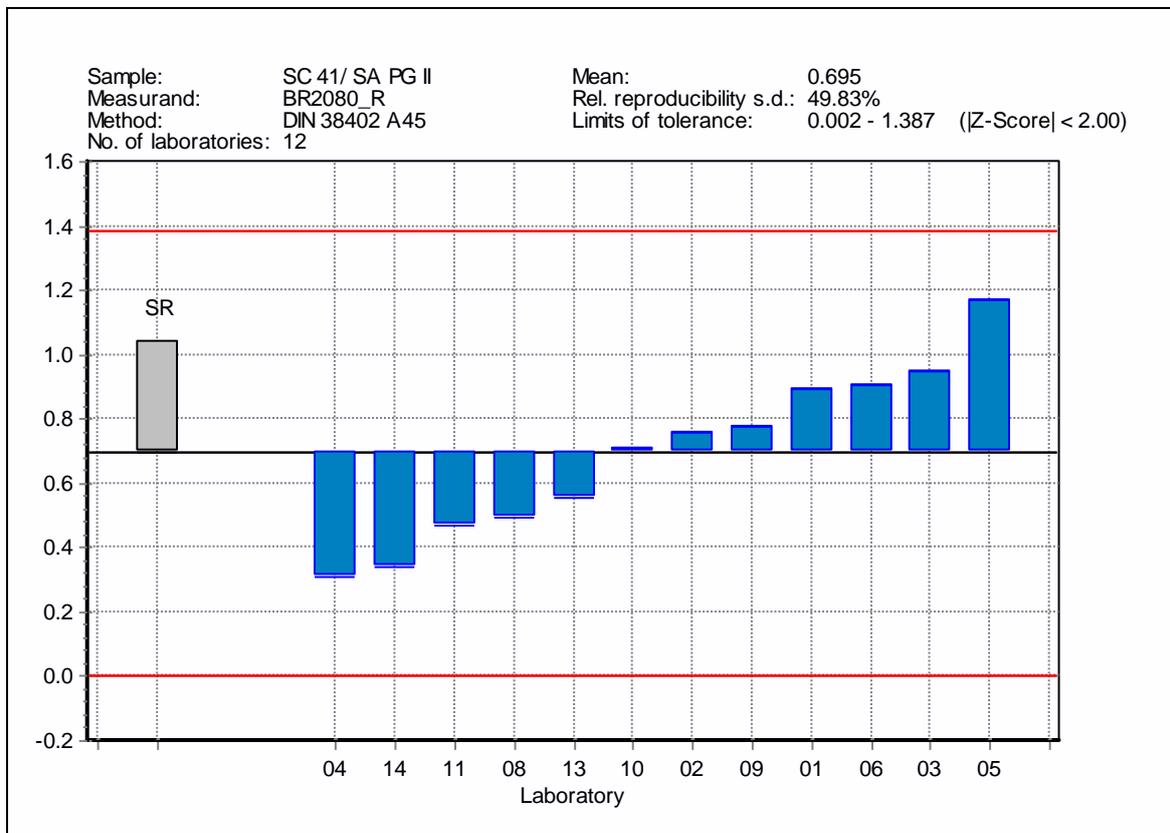


Figure 177: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SC 41 / SA PG II

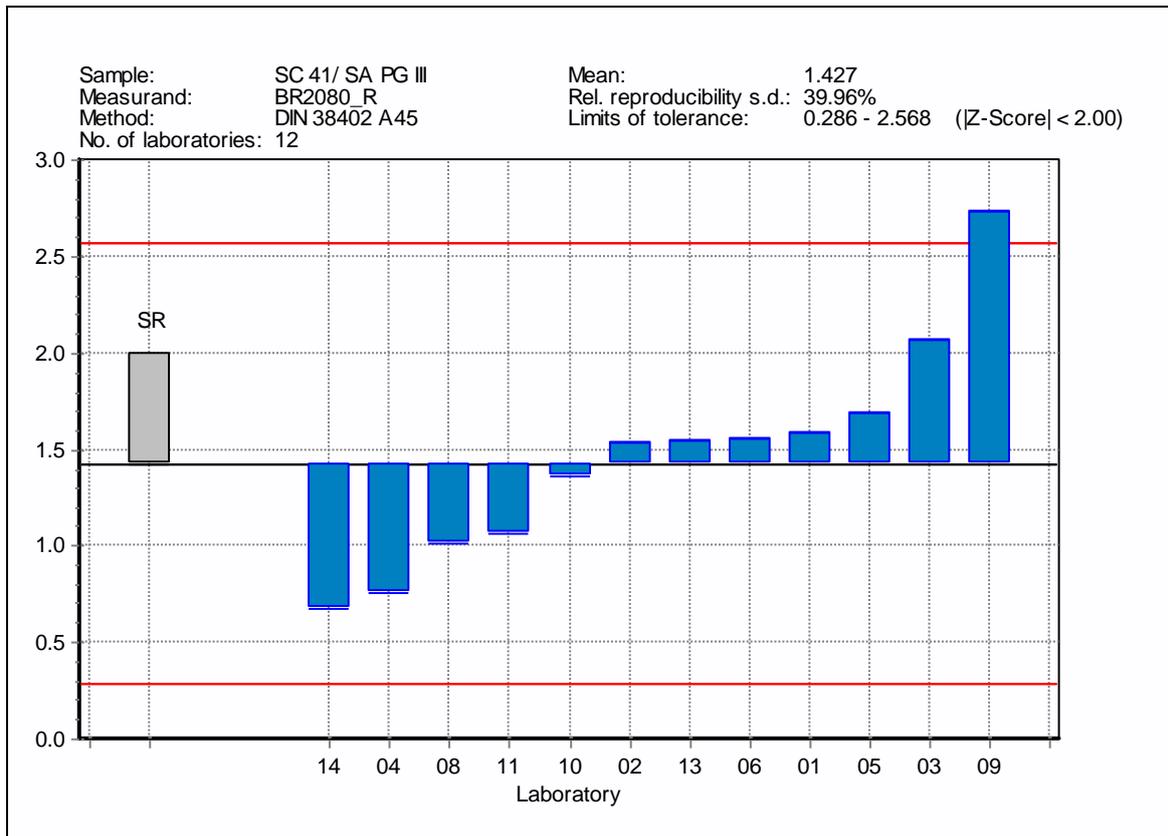


Figure 178: Laboratory results for consumption rate of 60 % of balanced combustible material BR₂₀₋₈₀ – ratio SC 41 / SA PG III