

Final Report
Evaluation of the
interlaboratory test on the
method UN O.2 / EC A.21
“Test for oxidizing liquids”
2009 – 2010



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Impressum

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Final Report

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Report

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1 Introduction

For the classification of chemicals, special standardized test procedures have been developed and are used world-wide. Safe handling and use of these chemicals depend on the correct classification which therefore must be based on the precise and correct execution of the tests and their evaluation. In this context interlaboratory tests (round robin tests, interlaboratory comparisons / intercomparisons) are a crucial element of a laboratory's quality system. Participation in interlaboratory tests is explicitly recommended by the standard ISO/IEC 17025.

The present document reports on the results of the interlaboratory test 2009/2010 on the test methods UN O.2 "Test for oxidizing liquids" [1] / EC A.21 "Oxidizing Properties (Liquids)" [2] which was organized by the Center for Quality Assurance for Testing of Dangerous Goods and Hazardous Substances.

The test methods UN O.2 and EC A.21 are applied to characterize the oxidizing properties of liquid chemical substances or mixtures. To differentiate between chemicals with hazardous / dangerous oxidizing properties and chemicals which are not classified as hazardous / dangerous, the substance's oxidizing properties are compared to those of a standard reference substance.

Since the methods (UN O.2 / EC A.21) were developed and came into force in the early nineties a systematic review concerning the practical application of the test method has not been carried out.

2 Aim

The aims of this interlaboratory test 2009/2010 on the method UN O.2 / EC A.21 "Test for oxidizing liquids" are:

1. **Assessment of the performance of the methods UN O.2 / EC A.21:**

The current practical application of the method in different laboratories and the classification error were assessed by the 1st part of the interlaboratory test (**test series 1**). For this purpose specific precision indicators (e.g. reproducibility, repeatability, probability of incorrect classification etc.) were generated.

2. **Assessment of the modified mixing procedure:**

The influence of the mixing procedure on the test results / classification was evaluated based on a 2nd, optional test (**test series 2**) the participating laboratories were requested to perform. The mixing procedure in this test series was standardized with regard to mixing equipment and mixing duration. The modification of the mixing procedure was based on a proposal by BAM [5].

3. **Assessment of other influencing (disturbing) factors:**

Other laboratory specific factors which possibly may have an influence on the test result / classification were evaluated with the aid of a further exploratory analysis.

4. **Recommendations for the participants of the interlaboratory test to improve the execution of the method:**

In view of the results of the interlaboratory test it was assessed which recommendations could be given to the participating laboratories to improve the execution of the method.

3 Test material

3.1 Interlaboratory test sample "aqueous solution of Sodium Nitrate"

"Aqueous solution of Sodium Nitrate" (concentration 44.6 % w/w (checked by gravimetry) / 44.7 % w/w to 45.0 % w/w (checked by ion chromatography)) was chosen as the interlaboratory test sample.

Sodium nitrate, 45 % aqueous solution is listed in Table 34.4.2.5 "Examples of result" of the method UN O.2 [1] as an example of an oxidizing liquid which must be classified in Division 5.1, PG III according to the UN Recommendations on the Transport of Dangerous Goods - Model Regulations.

3.1.1 Preparation of the interlaboratory test samples

In September/October 2009 the stock solution of the interlaboratory test sample "aqueous solution of Sodium Nitrate" was prepared by BAM from a batch of 2 kg (one container) of solid crystalline sodium nitrate (sodium nitrate cryst. extra pure FCC, E 251, Merck KGaA, Batch-no 716CC516035). The purity of the origin batch of solid sodium nitrate was checked by BAM with the aid of ion chromatography. Additionally, the moisture content was tested by BAM by coulometry.

In order to prepare the stock solution of the interlaboratory test sample "aqueous solution of Sodium Nitrate" 900.0 g of the origin solid crystalline Sodium Nitrate were added to / dissolved in 1100.0 g of distilled water under continuous stirring in a plastic flask. The concentration of the "aqueous solution of Sodium Nitrate" was 44.6 % w/w (checked by gravimetry) and 44.7 % w/w to 45.0 % w/w (checked by ion chromatography).

28 interlaboratory test samples were produced by decanting of 30 ml of the stock solution into a 50 ml plastic flask. The stock solution was stirred during decanting with the aid of a pipette.

Finally, the divided interlaboratory test samples (2 flasks at 30 ml for each laboratory) were packed into transport containers and sent to the participants of the interlaboratory test by BAM.

3.1.2 Homogeneity and stability of the interlaboratory test samples

Based on experience with the substance sodium nitrate and the oxidizer test methods the prepared stock solution and the interlaboratory test samples are known to be sufficiently homogeneous and stable within the testing time frame of the round robin test (November 2009 to March 2010) and no further tests to control the homogeneity and stability were performed.

In addition, tests of the concentration of the stock solution and the interlaboratory test samples (filled in the transport flasks (30 ml)) were performed before sending out the test samples, in the middle of the testing period and after the end of the testing period. The test results are listed in Table 3-1.

Table 3-1: Control of the concentration of sodium nitrate in the aqueous solution of the stock solution and the interlaboratory test sample

Date of control	Type of test sample	Concentration of sodium nitrate in the aqueous solution [% w/w]	
		by ion chromatography	by gravimetry
16.10.2009	Stock solution	44.7	44.6
28.01.2010	Stock solution	45.0	44.6
	Interlaboratory test sample	44.8	44.6
15.03.2010	Stock solution	45.0	-

The expected homogeneity and stability of the interlaboratory test samples were confirmed by the results of this additional test.

3.2 Further substances and mixtures required for the test method

The reference substances (see Table 4-4, page 5) and the cellulose which are necessary to perform the test UN O.2 / EC A.21 were not distributed by BAM. The reference substance mixtures were prepared by the laboratories themselves using the substances they normally use. The test sample mixture was also prepared by the laboratories using the distributed interlaboratory test sample.

In this interlaboratory test three different reference substance mixtures and one mixture of the interlaboratory test sample with cellulose were investigated (see Table 3-2):

Table 3-2: Mixtures which are prepared by the different laboratories

Name of the mixture (short name)	Composition of the mixture
Reference substance mixture for packing group I (PG I)	50 % perchloric acid : cellulose = 1:1
Reference substance mixture for packing group II (PG II)	40 % aqueous sodium chlorate solution : cellulose = 1:1
Reference substance mixture for packing group III (PG III)	65 % aqueous nitric acid : cellulose = 1:1
Test sample mixture (TS)	Interlaboratory test sample : cellulose = 1:1

4 Procedure of the interlaboratory test

4.1 Organisation

The interlaboratory test was organized by BAM Federal Institute for Materials Research and Testing, Berlin, in the frame of the interlaboratory test programme within the Center for Quality Assurance for Testing of Dangerous Goods and Hazardous Substances.

The interlaboratory test sample "aqueous solution of Sodium Nitrate" together with a test instruction and the laboratory data input form (see Appendix 8.1 and 8.2), was distributed to 11 participating laboratories (see Table 4-1) by BAM.

Table 4-1: List of all 11 participating laboratories (9 laboratories submitted data)

Laboratory / Agency	Country
AQura GmbH	Germany
BAM Federal Institute for Materials Research and Testing	Germany
BASF AG	Germany
Canadian Explosives Research Laboratory (CERL)	Canada
Chilworth Technology Ltd.	United Kingdom
Currenta GmbH & Co. OHG	Germany
Government Laboratory of Hong Kong HKSAR *	China
Henkel AG & Co. KGaA	Germany
LAUS GmbH	Germany
Siemens AG	Germany
Syngenta Hazards Group *	United Kingdom

*... Laboratories which have not submitted data during the testing period.

The following Table 4-2 shows the time schedule of the study.

Table 4-2: Time schedule of the interlaboratory test

Round Robin step	Time period
Public announcement	June 2009
Order and registration	September 2009
Distribution of the test sample and the test instruction	October 2009
Laboratory testing period	November 2009 to March 2010 *
First statistical evaluation and draft report	April to May 2010 **

*... The testing period was prolonged from December 2009 to March 2010 because not all laboratories were able to perform the tests until December 2009 (as originally foreseen in October 2009).

** . The statistical evaluation was postponed due to the prolonged testing period.

4.2 Test procedures

The interlaboratory test was performed on the test methods UN O.2 "Test for oxidizing liquids" and EC A. 21 "Oxidizing Properties (Liquids)" (see Table 4-3):

Table 4-3: Test methods of the Round Robin test

Test method	Source
UN O.2 "Test for oxidizing liquids"	United Nations: Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fifth revised edition, United Na- tions, New York and Geneva, 2009 [1]
EC A.21 "Oxidizing Properties (Liquids)"	European legislation: Council Regulation (EC) No 440/2008 of 30 May 2008 [2]

Both test methods, UN O.2 and EC A.21, are widely comparable and based on the same measuring principle. Due to the comparability and in accordance with chapter 1.1 of method EC A.21, the test method EC A.21 may not need to be performed when results for the test substance in the UN test O.2 for oxidizing liquids are already available. Furthermore, the UN test O.2 does not only distinguish between liquids which are classified as oxidizing and those that are not but it also divides oxidizing liquids into three categories / packing groups (see in Table 4-4).

Table 4-4: Reference substances to prepare the reference substance mixtures with cellulose (see Table 3-2):

Method	Reference substance	Purpose
UN O.2 "Test for oxidizing liquids"	65 % aqueous nitric acid	To classify in Class 5.1 and to differentiate between Packing group III, II and I
	40 % aqueous sodium chlorate solution	
	50 % perchloric acid	
EC A.21 "Oxidizing Properties (Liquids)"	65 % aqueous nitric acid	Decision whether hazardous properties or not.

The interlaboratory test was carried out with all reference substances listed in Table 4-4.

4.2.1 Interlaboratory test instruction and laboratory data input form

The test instruction for the interlaboratory test (see Appendix 8.1) which was distributed together with the test sample focuses on the specifics of the two different test series (see Table 4-5).

Table 4-5: Test series of the interlaboratory test

Test series	Method	Instruction for the mixing procedure (short description)
1	UN O.2 / EC A.21 (without modification)	No special recommendation* ("should be applied as usual in your laboratory")
2 (optional)	Modification of the method UN O.2 / EC A.21	Modified mixing procedure: 1. use a ceramic mortar and a pistil 2. homogenize with only very little force 3. homogenize within exactly 2 minutes

* ... Two laboratories have performed the test series 1 in the same way as it was recommended for test series 2.

The test instruction (which is more detailed than the current description of UN test O.2 and EC A.21) for both test series included:

- Preparation of a mixture with a precision of 2.50 g ± 0.01 g of the liquid (test sample or reference substance, respectively) and 2.50 g ± 0.01 g of the dried cellulose.
- Execution of one test series by one and the same laboratory assistant, otherwise it should be noted.
- Execution of the trials of one test series within one working day.
- Performance of the individual trials in a special sequence (order) (see Appendix 8.2 Laboratory data input form).

Apart from that the other details of the procedure were supposed to be applied as usual in the laboratory and in accordance with chapter 34.4.2 of the UN Manual of Tests and Criteria [1] or/and in chapter 1.6 of the European method EC A.21 [2].

Laboratory specific parameters and test conditions were enquired with the aid of the laboratory data input form (see Appendix 8.2).

Information on the diameter of the coil of the ignition wire and on the 40 % aqueous sodium chlorate solution / concentration are not available due to the unclear phrasing of the respective questions in the laboratory data input form. Obviously the wordings of these questions (description of the parameter) were not clear enough and too many laboratories have transmitted implausible data / specifications. The answers concerning all other parameters were plausible and could be used for the statistical evaluation.

5 Evaluation

5.1 Background

The evaluation of the data was performed using a specially modified version¹ of the software package ProLab Plus 2009 [3]. ProLab Plus is widely employed for the evaluation of interlaboratory tests and laboratory proficiency tests.

The following Table 5-1 gives an overview of the three types of data for the test sample mixture and the reference substance mixtures and for all combinations of the test sample mixture and the reference substance mixtures, respectively, which were analysed statistically as outlined in the following sections.

¹ The basic ProLab Plus version has been extended by additional tools taking into account the specific design of the intercomparison. These additional tools are in-house tools only.

Table 5-1: Overview of analysed data types

Data type	Evaluation according to	Elimination of outliers?	Background	Resulting in
single pressure rise times				<ul style="list-style-type: none"> → total mean of single pressure rise times ... → reproducibility standard deviation ... → repeatability standard deviation ... → 95 % confidence band of the total mean of single pressure rise times ... → limits of tolerance according to DIN 38402-45 (no outliers have been eliminated)
laboratory mean pressure rise times	DIN 38402-45 (robust method)	no	robust analysis because outliers are normally not eliminated systematically by the laboratories	<ul style="list-style-type: none"> → mean of laboratory mean pressure rise times ... → reproducibility standard deviation ... → 95 % confidence band of the mean of laboratory mean pressure rise ... → limits of tolerance according to DIN 38402-45 (no outliers have been eliminated)
ratios of laboratory mean pressure rise times				<ul style="list-style-type: none"> → mean of ratios of laboratory mean pressure rise times ... → reproducibility standard deviation ... → 95 % confidence band of the mean of ratios of laboratory mean ... → limits of tolerance according to DIN 38402-45 (no outliers have been eliminated)

Data type: single pressure rise times

The method according to DIN 38402-45 (=ISO/TS 20612) was applied for the statistical analysis of single pressure rise times. This method is a robust method and no outlier examination is required.

Data type: laboratory mean pressure rise times

There is no recommendation concerning the quality assurance in the UN-method UN O.2 ("Liquid Oxidizer"), i.e. no special requirements with regard to the validity of the single pressure rise times are given. Five trials have to be performed from which the average value is derived as the "simple" arithmetic mean value. Consequently, each measurement value is considered as valid even when the variability is comparatively high.

In contrast, in the European method EC A.21, which is completely equivalent with regard to the testing procedure itself, the following quality criterion is given (in section 1.5): "In a series of five trials on a single substance no results should differ by more than 30 % from the arithmetic mean. Results that differ by more than 30 % from the mean should be discarded, the mixing and filling procedure improved and the testing repeated."

For data that are based on testing according to UN-method UN O.2 (no special recommendations according the statistical handling of the single pressure rise times) the assumption of normal distribution is not necessarily valid for the laboratory mean pressure rise times. Furthermore, each laboratory provides only one laboratory mean pressure rise time of the respective reference substance mixtures and the test sample mixture, hence no replicates of the laboratory mean pressure rise time are available.

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

Data type: ratios of laboratory mean pressure rise times

According to UN O.2 / EC A.21 the laboratory mean pressure rise time of the test sample mixture is compared to those of the reference substance mixtures in order to decide whether a substance is classified as an oxidizing liquid and if so to which category (or packing group) it is assigned. Therefore, not only the pressure rise times but also their ratios were analysed and evaluated.

The ratios of laboratory mean pressure rise times for 9 combinations (6 in test series 1 and 3 in test series 2; see Table 5-2) of reference substance mixtures and the test sample mixture were considered in the statistical analysis. The ratios of laboratory mean pressure rise times were evaluated on the basis of the statistical method according to DIN 38402-45 (=ISO/TS 20612). This method is a robust method and no outlier examination is required.

Table 5-2: Considered ratios of laboratory mean pressure rise times

	Symbol	Description
Test series 1	PG II / PG I	Ratio of laboratory mean pressure rise times for PG II and PG I
	PG III / PG I	Ratio of laboratory mean pressure rise times for PG III and PG I
	PG III / PG II	Ratio of laboratory mean pressure rise times for PG III and PG II
	TS / PG I	Ratio of laboratory mean pressure rise times for TS and PG I
	TS / PG II	Ratio of laboratory mean pressure rise times for TS and PG II
	TS / PG III	Ratio of laboratory mean pressure rise times for TS and PG III
Test series 2 (optional)	PG III / PG II	Ratio of laboratory mean pressure rise times for PG III and PG II
	TS / PG II	Ratio of laboratory mean pressure rise times for TS and PG II
	TS / PG III	Ratio of laboratory mean pressure rise times for TS and PG III

For all three data types described above, the respective mean as well as the respective reproducibility standard deviation were calculated over all laboratories.

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

The repeatability standard deviation describes the variability of the data under repeatability conditions, i.e. independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. For determining the repeatability standard deviation, replicates of the measurements are necessary. Thus, for the two data types *laboratory mean pressure rise times* and *ratios of laboratory mean pressure rise times*, repeatability standard deviations cannot be obtained from the data as for each laboratory and sample only one "measurement value" (= laboratory mean value) is available. Therefore, the repeatability standard deviation was calculated only for the first data type (single pressure rise times). For the third data type (ratio of laboratory mean pressure rise times) it was predicted by means of error propagation methods.

5.2 Quantity of test results

Measurements were conducted by ten laboratories and nine of them submitted analytical results (see also Table 4-1). Seven out of these nine laboratories also submitted results for the optional test series 2.

5.3 Plausibility check

To begin with, a first check of the plausibility of the data was performed. All results of the trials – except for one – were considered as plausible regarding the single pressure rise times (e.g. with regard to completeness, consistency etc.). Only trial 5 for PG II in test series 1 of laboratory 261 was not considered as plausible due to irregular deviations as stated by the laboratory itself ("Result not consistent

with trials 1 to 4" / Pressure rise time in trial 5 was 4440 ms instead of the results in the range between 357 ms and 660 ms in trial 1 to 4.). This value was not considered in the statistical evaluation of the data.

Two laboratories (908 and 910) performed test series 1 in the same way as it was recommended for test series 2.

The laboratories were requested to perform the tests in a special sequence (order), laboratories 106 and 261 did not adhere to this order.

5.4 Results and resulting classification of the interlaboratory test sample "aqueous solution of Sodium Nitrate"

The laboratory mean pressure rise times for each reference substance mixture and test sample mixture of both test series are given in the following Table 5-3.

**Table 5-3: Laboratory mean pressure rise times [ms]
(grey cells: no measurements available)**

Laboratory	Test series 1				Test series 2		
	PG I	PG II	PG III	TS	PG II	PG III	TS
106	57	548	2250 ¹⁾	4395	454	2650 ¹⁾	3200
121	81	2068	3984	7421	729	3621	7188
127	138	2618	4231	2491			
201	65	1593 ¹⁾	3994	6619	816	4744	5295
251	152 ¹⁾	4000	4620	7500	2540 ¹⁾	5408 ¹⁾	7056 ¹⁾
261	88	528 ¹⁾	2425 ¹⁾	13250 ¹⁾	1524 ¹⁾	2475 ¹⁾	12712 ¹⁾
907	97	2542	4042	5453			
908	144	2017	3947	4832	1574	3810	4603
910	41	271	2746	2957	263	2527	3181

¹⁾ The quality criterion according to the European method EC A.21² is not fulfilled.

The test results for the reference substance mixtures and the test sample mixture are shown graphically in Figure 5-1 and Figure 5-2. The pressure rise time is given in Figure 5-1 in a "normal" scale, while in Figure 5-2 the measurements are diagrammed in a logarithmic scale to base 2.

The laboratory values are displayed in these figures in form of a box. The larger the box the larger is the laboratory's relative repeatability standard deviation. The laboratory mean pressure rise time is marked by a horizontal line within the boxes, while the single values are shown as diamonds. The two test series are shown next to each other for each laboratory: test series 1 on the left and test series 2 on the right.

² Quality criterion according to the European method EC A.21 (section 1.5): "In a series of five trials on a single substance no results should differ by more than 30 % from the arithmetic mean. Results that differ by more than 30 % from the mean should be discarded, the mixing and filling procedure improved and the testing repeated."

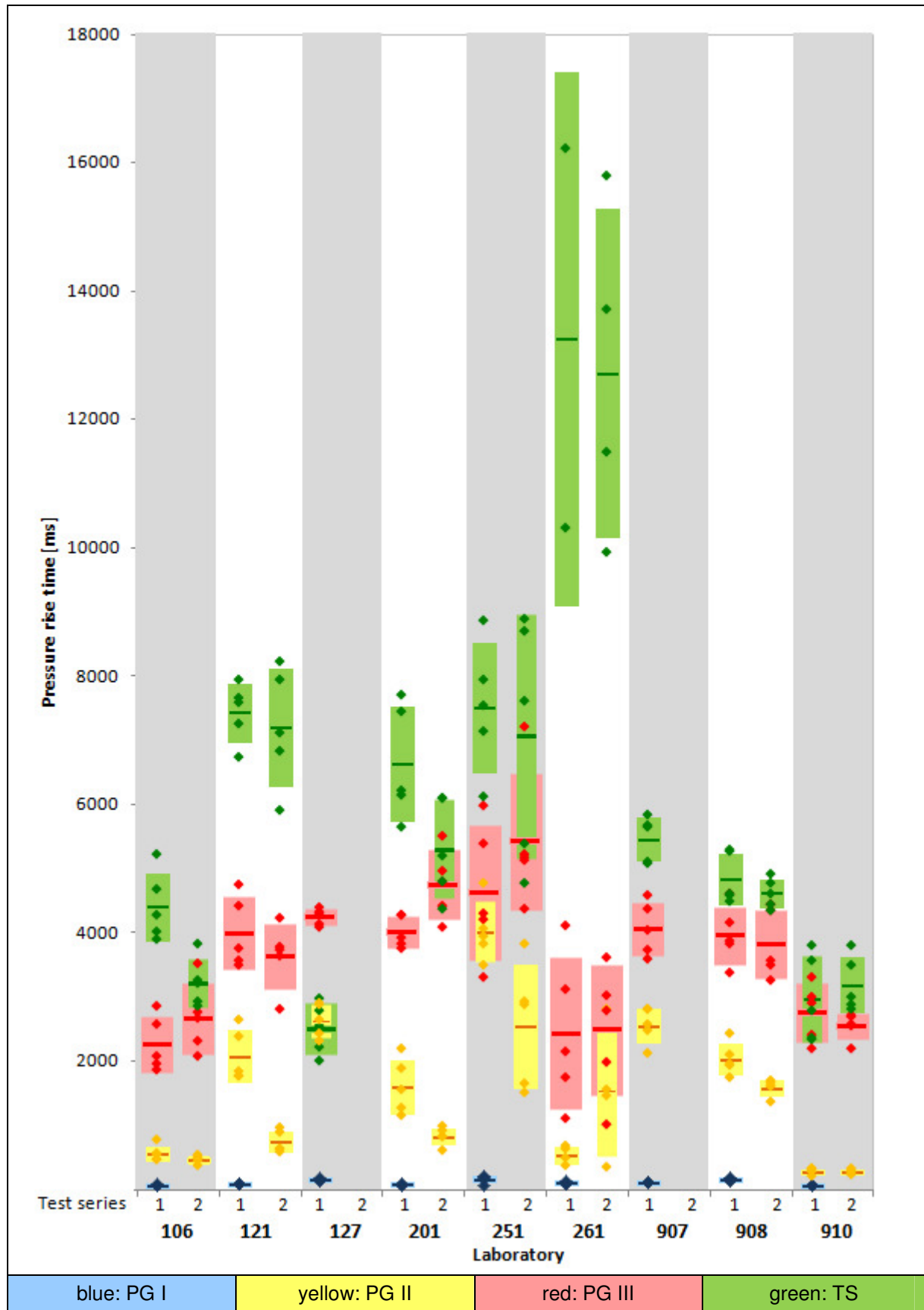


Figure 5-1: Test results of the laboratories

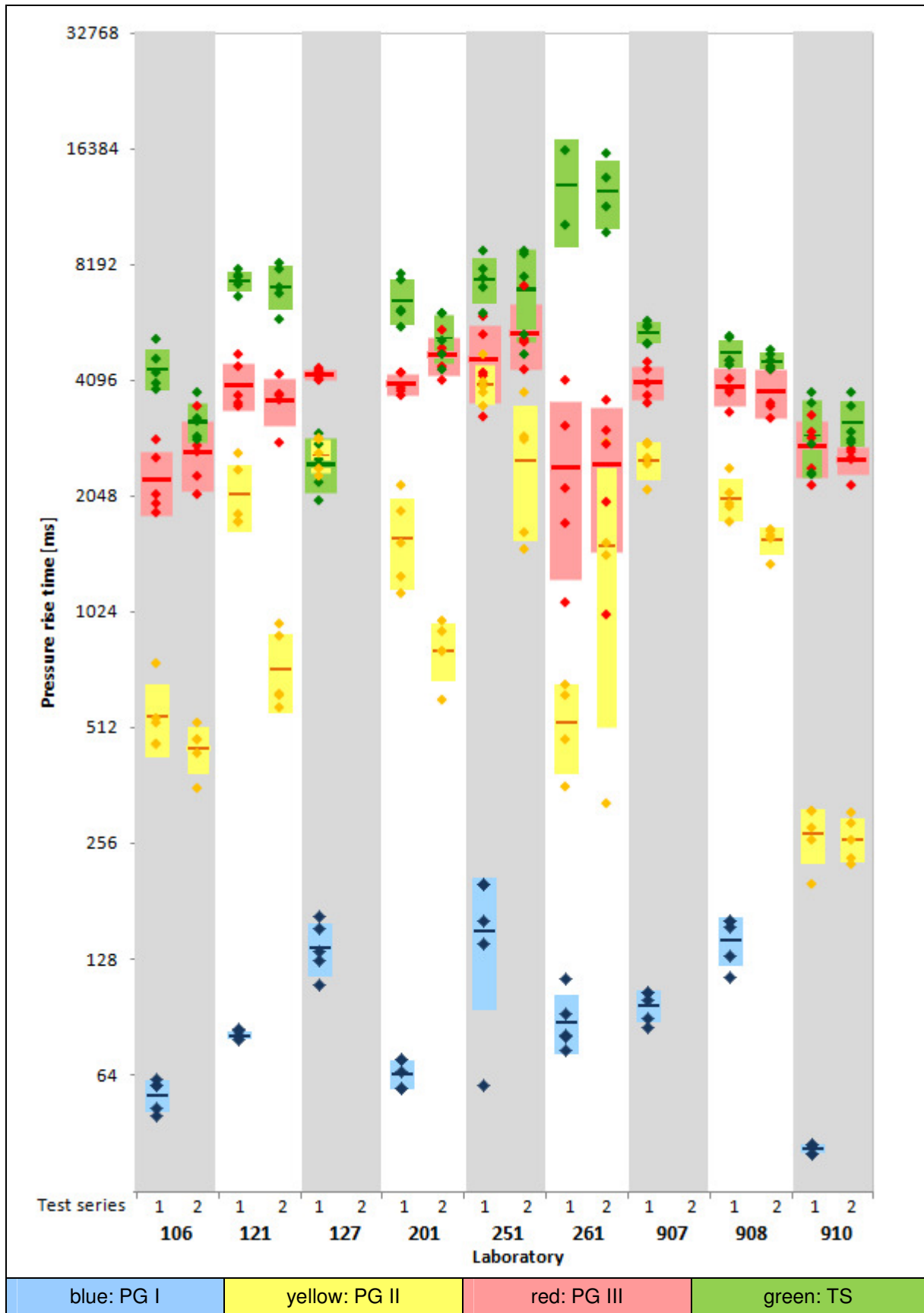


Figure 5-2: Test results of the laboratories – the y-axis (pressure rise time) is logarithmically scaled to base 2

Based on these test results, the centrally distributed interlaboratory test sample "aqueous solution of Sodium Nitrate" would not be classified as an oxidizing liquid except for one case (see Table 5-4).

Table 5-4: Classification results of the interlaboratory test sample "aqueous solution of Sodium Nitrate" according to the test methods UN O.2 "Test for oxidizing liquids" [1] / EC A.21 "Oxidizing Properties (Liquids)" [2] based on the laboratory mean pressure rise times

Laboratory	Classification result
106	-*
121	-*
127	Oxidizing liquid / class 5.1, PG II
201	-*
251	-*
261	-*
907	-*
908	-*
910	-*

*....not classified as oxidizing liquid

5.5 Kernel density estimation of single pressure rise times

An analysis of the underlying distribution of the single pressure rise times was carried out by the so-called kernel density estimation in order to check the homogeneity. The following figures (Figure 5-3 and Figure 5-4) show the results of the kernel density estimation for all considered reference substance mixtures and the test sample mixture for both test series.

The blue curve characterizes the distribution of single pressure rise times obtained by the kernel density estimation, where single pressure rise times are marked as small blue circles.

Modi (maxima) of the curves are marked by arrows and the respective value is given. Distributions with only one modus are called unimodal, while distributions with two or more modi are called bimodal or multimodal. Multimodal distributions indicate that there might be two or more groups of participants with clearly differing results. However, only a modus, which is based on at least 25 % of the measurement values by one group of participants, should be considered as forming a sub-group.

The left axis of the kernel density plot shows the probability density. This probability density is neither the probability nor the frequency. It indicates the relative frequency of values occurring at different points along the x-axis. Thereby not the values on the left axis are of interest, but the only the shape of the curve.

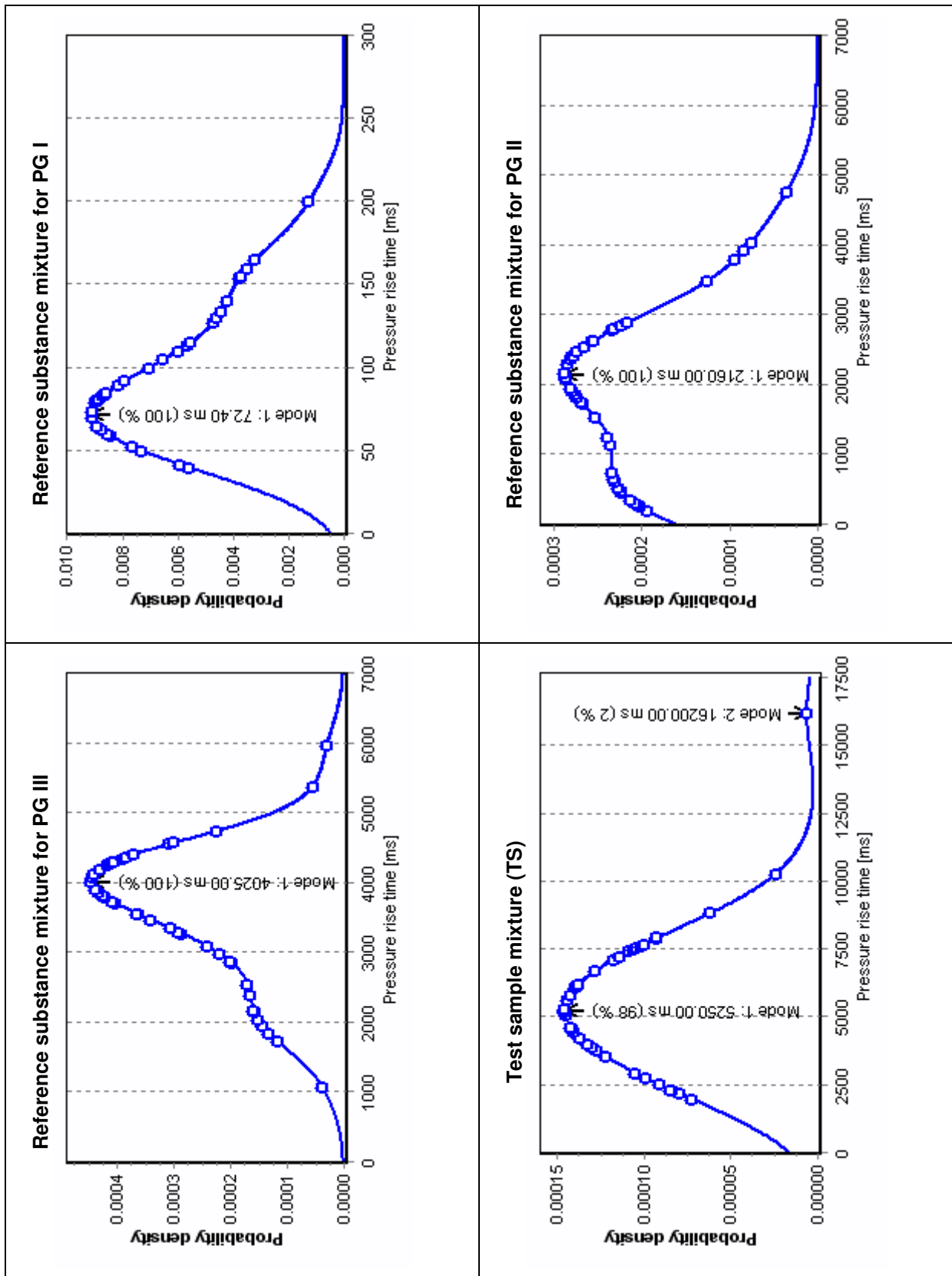


Figure 5-3: Kernel density estimation for the reference substance mixtures and the test sample mixture corresponding to test series 1

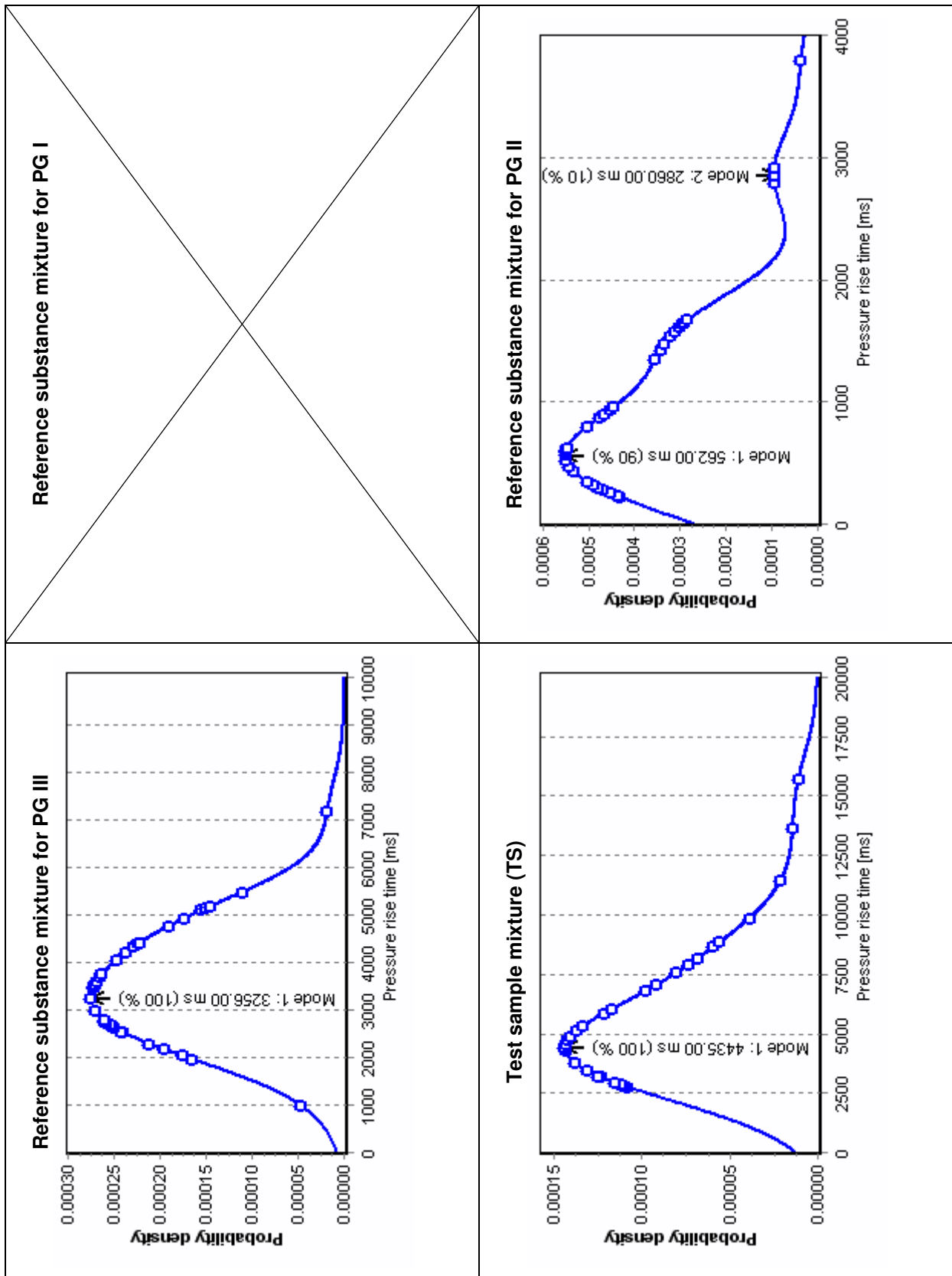


Figure 5-4: Kernel density estimation for the reference substance mixtures and the test sample mixture corresponding to test series 2

5.6 Performance of the method UN O.2 / EC A.21

5.6.1 Reproducibility, repeatability and classification error

A summary of the obtained mean values, relative repeatability and reproducibility standard deviations of the single pressure rise times and laboratory mean pressure rise times of all reference substance mixtures for packing groups PG I, PG II and PG III and the test sample mixture TS as well as for the ratios of laboratory mean pressure rise times of reference substance mixtures and test sample mixture is given in the following Table 5-5.

Table 5-5: Mean values and relative standard deviations for single pressure rise times, laboratory mean pressure rise times and ratios of laboratory mean pressure rise times evaluated according to DIN 38402-45

Test series	Mixture / Mixture ratio	Mean value	Relative reproducibility s. d.	Relative repeatability s. d.
Single pressure rise times				
1	PG I	96 ms *	49 %	10 %
	PG II	1782 ms *	77 %	15 %
	PG III	3582 ms *	27 %	15 %
	TS	5833 ms *	57 %	13 %
2	PG II	1084 ms *	70 %	13 %
	PG III	3605 ms *	43 %	19 %
	TS	5912 ms *	56 %	15 %
Laboratory mean pressure rise times				
1	PG I	96 ms **	46 %	n/a****
	PG II	1747 ms **	68 %	
	PG III	3717 ms **	14 %	
	TS	5879 ms **	61 %	
2	PG II	1129 ms **	87 %	
	PG III	3605 ms **	53 %	
	TS	6017 ms **	62 %	
Ratios of laboratory mean pressure rise times				
1	PG II / PG I	17.5 ***	51 %	13 %
	PG III / PG I	41.6 ***	43 %	10 %
	PG III / PG II	2.4 ***	48 %	24 %
	TS / PG I	71.5 ***	67 %	18 %
	TS / PG II	4.1 ***	86 %	55 %
	TS / PG III	1.4 ***	47 %	41 %
2	PG III / PG II	4.3 ***	45 %	13 %
	TS / PG II	7.1 ***	67 %	18 %
	TS / PG III	1.3 ***	16 %	16 %

* Total mean value of single pressure rise times

** Mean value of laboratory mean pressure rise times

*** Mean value of ratios of laboratory mean pressure rise times

**** n/a = not applicable

The reference substance mixture PG III in test series 1 exhibits the smallest relative reproducibility standard deviation of the single pressure rise times and of the laboratory mean pressure rise times, and the ratio PG III / PG II in test series 2 exhibits the smallest relative reproducibility standard deviation.

tion for the ratios of laboratory mean pressure rise times.

The relative reproducibility standard deviations of the ratios of laboratory mean pressure rise times are partly even higher than for the single pressure rise times. For example in test series 1, the relative reproducibility standard deviation of the laboratory mean pressure rise times amounts to 61 % for TS, to 68 % for PG II whereas it amounts to 86 % for the ratio TS/PG II. The relative reproducibility standard deviation of the ratio TS/PG II in test series 1 is extremely high (86 %) compared to those of the other ratios.

Normally, it might be expected that systematic effects could cancel out by building the ratios of the laboratory mean pressure rise times, however, this was not the case, i. e. the reproducibility standard deviations of the ratios of laboratory mean pressure rise time are not significantly smaller than those of the single pressure rise times. This might be caused by the fact that laboratories used different substances from different suppliers.

The relative repeatability standard deviations of the single pressure rise times lies between 10 % and 15 % in test series 1 and between 13 % and 19 % in test series 2 for all laboratories (see Table 5-5).

The relative repeatability standard deviations of the ratios of laboratory mean pressure rise times range between 10 % and 55 % in test series 1 and between 13 % and 18 % in test series 2.

5.6.1.1 Ratios of laboratory mean pressure rise times and classification

The test sample "aqueous solution of Sodium Nitrate" would not be classified as an oxidizing liquid based on the test results of most laboratories (see chapter 5.4, page 11). To characterize the differences, the ratios of the laboratory mean pressure rise times for each reference substance mixture and test sample mixture of both test series for each laboratory are given in the Table 5-6.

Table 5-6: Ratios of laboratory mean pressure rise times
(grey cells: no measurements available)

Laboratory	Test series 1						Test series 2		
	PG II / PG I	PG III / PG I	PG III / PG II	TS / PG I	TS / PG II	TS / PG III	PG III / PG II	TS / PG II	TS / PG III
106	9.6	39.5	4.1	77.1	8.0	2.0	5.8	7.1	1.2
121	25.4	48.9	1.9	91.2	3.6	1.9	5.0	9.9	2.0
127	19.0	30.7	1.6	18.0	1.0	0.6			
201	24.7	61.8	2.5	102.5	4.2	1.7	5.8	6.5	1.1
251	26.3	30.4	1.2	49.3	1.9	1.6	2.1	2.8	1.3
261	6.0	27.5	4.6	150.2	25.1	5.5	1.6	8.3	5.1
907	26.2	41.7	1.6	56.2	2.1	1.3			
908	14.0	27.4	2.0	33.6	2.4	1.2	2.4	2.9	1.2
910	6.6	66.6	10.1	71.8	10.9	1.1	9.6	12.1	1.3

The ratios of the laboratory mean pressure rise times of the test sample mixture and packing group III (TS / PG III) in test series 1 and of packing group III and packing group II are exemplarily shown in the following Figure 5-5 and Figure 5-6. For all other ratios please refer to Appendix 8.5.

In these figures, the size of the boxes symbolize the laboratory's relative repeatability standard deviation of the ratios of the respective pressure rise times, as estimated by means of error propagation methods. The horizontal line in the middle of the box indicates the ratio of the laboratory mean pressure rise times. The figures also include the 95 % confidence interval (green band) of the mean of the ratios of laboratory mean pressure rise times according to DIN 38402-45 (black line) as well as the limits of tolerance for the ratios of the laboratory mean pressure rise times (red lines) – also according to DIN 38402-45.

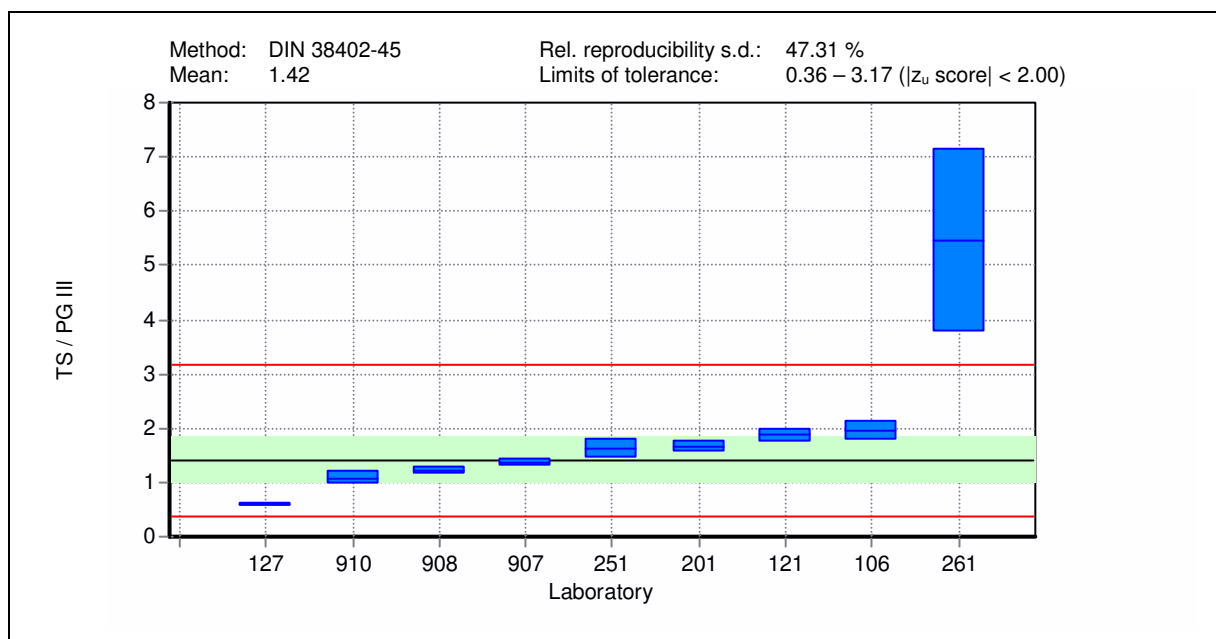


Figure 5-5: Analysis of ratios of laboratory mean pressure rise times – ratio TS / PG III in test series 1

In comparison to the other laboratories the ratio TS/PG III of laboratory 261 in test series 1 is very high and above the upper limit of tolerance (see Figure 5-5). The reason is the relatively long pressure rise time of the test sample mixture TS of laboratory 261.

The ratio PG III / PG II of laboratory 910 in test series 1 is very high compared to other ratios / laboratories and above the upper tolerance limit (see Figure 5-6 and Appendix 8.5). The reason is the relatively short pressure rise time of the reference substance mixture PG II of laboratory 910.

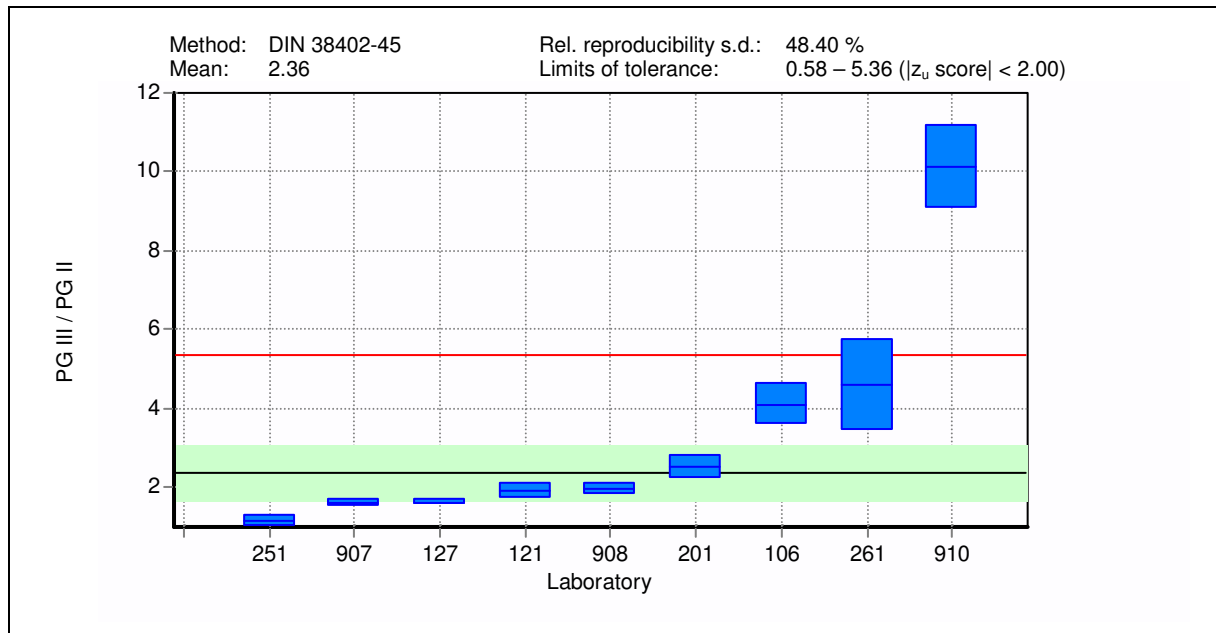


Figure 5-6: Analysis of ratios of laboratory mean pressure rise times – ratio PG III / PG II in test series 1

5.6.1.2 Probability of incorrect classification

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

The following calculations are based on the means of the ratios of the laboratory mean pressure rise times and the respective reproducibility standard deviations (see Table 5-5).

5.6.1.2.1 Distribution of the ratios of laboratory mean pressure rise times of the interlaboratory test

Figure 5-7 and Figure 5-8 show the probability density³ of the ratios of the laboratory mean pressure rise times of the test sample mixture and the reference substance mixtures – separately for PG III and PG II (depiction of PG I of test series 1 is not possible as the curve is close to 0). On the x-axis the ratios are displayed, and the y-axis shows the probability density of the ratios of laboratory mean pressure rise times of the test sample mixture and the respective reference substance mixture. This probability density is neither the probability nor the frequency. It can, however, be thought of as showing the relative frequency of values occurring at different points along the x-axis. These probability density curves are similar to the bell curve by Gauss. Thereby not the values on the left axis are of interest, but the position of the curve (Is the x-position of the maximum smaller than 1 or larger?) and the shape of the curve (Is it flat or steep, is it skewed?). As for all probability densities, the area beneath one curve equals 100 %.

³ based on the assumption that the ratios are normally distributed

In Figure 5-7 the probability densities for classification in PG II and PG III in test series 1 demonstrate that the distribution with respect to PG II is wider than for PG III, i.e. for PG II the laboratory results deviate more than for PG III. Furthermore, the x-position of the maximum is greater than 1 for both curves (located to the right of the black line). Generally, these figures can be interpreted as follows: A ratio of 1 corresponds to identical pressure rise times of the test sample mixture and the reference substance mixture of the respective packing group. The x-position of the maximum of a curve indicates the mean ratio of laboratory mean pressure rise times for the test sample mixture and the respective reference substance mixture and is regarded as "true" ratio. This "true" ratio is considered to be the factor from which the "true" pressure rise time for the test sample mixture may be derived. In test series 1 the mean ("true") ratio of the laboratory mean pressure rise times amounts to 4.1 for TS / PG II (red) and to 1.4 for TS / PG III (green), while it amounts to 71.5 for TS / PG I (not displayed because of the extremely flat shape) (see also Table 5-5).

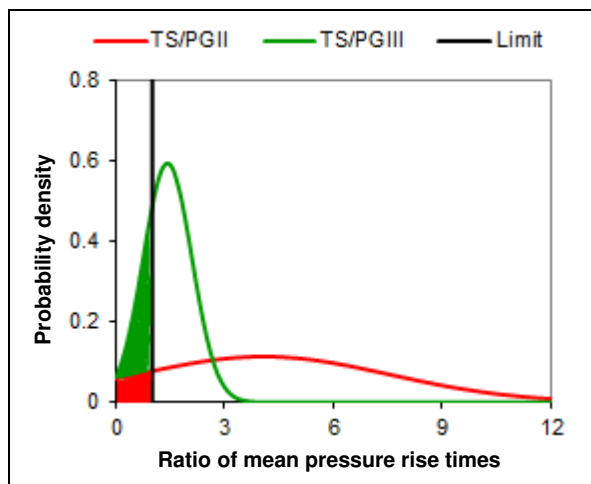


Figure 5-7: Probability density for the classification in PG II and PG III in test series 1 (depiction of PG I not possible as curve is close to 0)

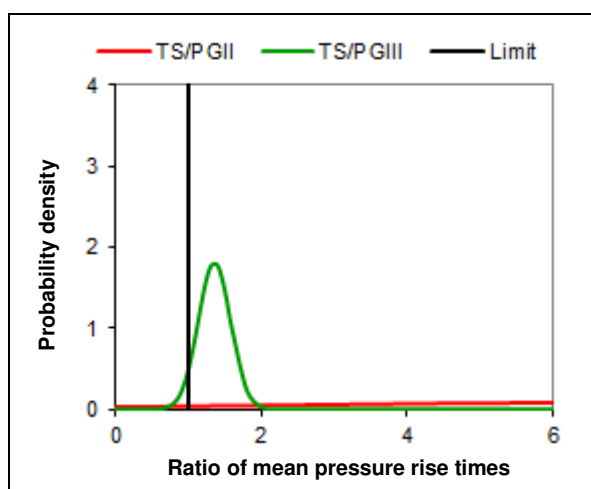


Figure 5-8: Probability density for the classification in PG II and PG III in test series 2

5.6.1.2.2 False positive and false negative error of classification

False positive error of classification: In the following it is assumed that a false positive error indicates that the test sample is classified by a laboratory to a lower packing group (of higher safety), although a higher packing group (of lower safety) would be correct because this is the "true" packing group. For example, a laboratory has classified the test sample in packing group PG I but the "true" packing group is PG II. That is, the laboratory's mean pressure rise time of the test sample mixture is shorter than the pressure rise time of the reference substance mixture for packing group I, although the "true" pressure rise time of the test sample mixture (derived from the "true" ratio) is longer. Expressed by ratios this means that the measured ratio is smaller than the limit 1, while the "true" ratio is larger than 1. The probability for such a false positive error can be derived from the distribution figures given in Figure 5-7 and Figure 5-8.

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

For packing group II in test series 1 the area equals 0.16 (the respective area is marked in red; see Figure 5-7), i.e. the probability for a false positive result $TS < PG II$ equals 19 %, while the true value of the test sample TS amounts to $TS = 4.1 \times PG II$.

The probabilities for false positive results with regard to all classifications / packing groups in both test series are given in Table 5-7.

Table 5-7: Probability for a false positive error for the classification in PG I, PG II and PG III depending on the test series

Test series	Packing group	False positive error of classification
1	PG I	7 %
	PG II	19 %
	PG III	27 %
2	PG II	10 %
	PG III	5 %

False negative error of classification: A false negative error indicates that the test sample is classified in a higher packing group (of lower safety), although a lower packing group (of higher safety) would be necessary. For example, a laboratory has classified the test sample in packing group PG III but the true packing group is PG II. That is, the laboratory's mean pressure rise time of the test sample mixture is longer than the pressure rise time of the reference substance mixture of packing group II, although the "true" pressure rise time of the test sample mixture (derived from the "true" ratio) is shorter. Expressed by ratios this means that the measured ratio is larger than 1, while the "true" ratio is smaller than 1. The probability for such a false negative error can again be derived from the distribu-

tion figures given in Figure 5-7 and Figure 5-8.

Again, the "true" ratio is given by the x-position of the maximum of a curve. Only if this "true" ratio is smaller than 1, a false negative error can occur. Then the probability for a false negative result is indicated by the area beneath the curve for ratios larger than 1, i.e. the area on the right side of the vertical black line.

However, all considered ratios are larger than 1 and consequently, no false negative error can occur.

The whole proceeding in the previous section 5.6.1.2.2 is similar to statistical testing with a null hypothesis ($TS > PG$) and an alternative hypothesis ($TS < PG$). Additionally, it is the intention to keep the probabilities of the positive and the negative result as small as possible in this application. It cannot be ensured though that the probabilities of the positive and the negative result are kept below a specific limit and consequently both probabilities may amount to 50 %.

5.6.1.3 Probability of incorrect classification for an arbitrary sample

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

For the calculation of the probability of incorrect classification the normal distribution is assumed as an approximation of the distribution of the ratios of pressure rise times (see section 5.6.1.2).

Figure 5-9 and Figure 5-10 shows the probability of incorrect classification for an arbitrary test sample as tested under the conditions of test series 1 and test series 2, respectively. For this purpose the relative standard deviation for an arbitrary "true ratio" was calculated by the aid of the functional relationship between the three relative standard deviations of the true ratios TS/PG I, TS/PG II and TS/PG III based on the result of this interlaboratory study."

Due to the form of the curves, Figure 5-9 and Figure 5-10 are also referred to as shark profiles. They can be interpreted as follows:

The increasing arm of a curve of the probability of incorrect classification with respect to a certain packing group indicates the probability of the false negative classification (false negative error) as a function of the true pressure rise time of a test sample mixture, i. e. the probability that the test sample is classified in a higher packing group (of lower safety) as it correctly should be, based on its "true" pressure rise time (x-value). On the other hand, the decreasing arm of a curve of one packing group indicates the probability of the false positive classification (false positive error), i. e. the probability that the test sample is classified in a lower packing group (of higher safety) as it correctly should be, based on its "true" pressure rise time (x-value).

In particular, this means:

Left arm of packing group I (red)	Probability that a laboratory classifies a test sample in PG II, although PG I would be necessary (true) → false negative classification
Right arm of packing group I (red)	Probability that a laboratory classifies a test sample in PG I, although PG II would be correct (true) → false positive classification
Left arm of packing group II (blue)	Probability that a laboratory classifies a test sample in PG III, although PG II would be necessary (true) → false negative classification
Right arm of packing group II (blue)	Probability that a laboratory classifies a test sample in PG II, although PG III would be correct (true) → false positive classification
Left arm of packing group III (green)	Probability that a laboratory does not classify a test sample, although PG III would be necessary (true) → false negative classification
Right arm of packing group III (green)	Probability that a laboratory classifies a test sample mixture in PG III, although no classification would be correct (true) → false positive classification

As long as the curves do not overlap, only one type of error (incorrect classification) can occur. In the range where two or more curves overlap more than one type of error have to be taken into account.

Read the Shark Profile as follows:

If for example in series 1 the "true" pressure rise time of an arbitrary test sample mixture equals 500 ms, the probability for a false positive classification with regard to packing group I, i.e. the probability to classify the test sample mixture to packing group I instead of the "true" packing group II, is about 30 % (value of red curve for 500 ms). At the same time, for a mean pressure rise time of 500 ms, there is the possibility for a false negative error of classification as well: The probability for a false negative classification, i.e. the probability to classify the test sample mixture to packing group III instead of "true" packing group II, is about 15 % (value of blue curve for 500 ms).

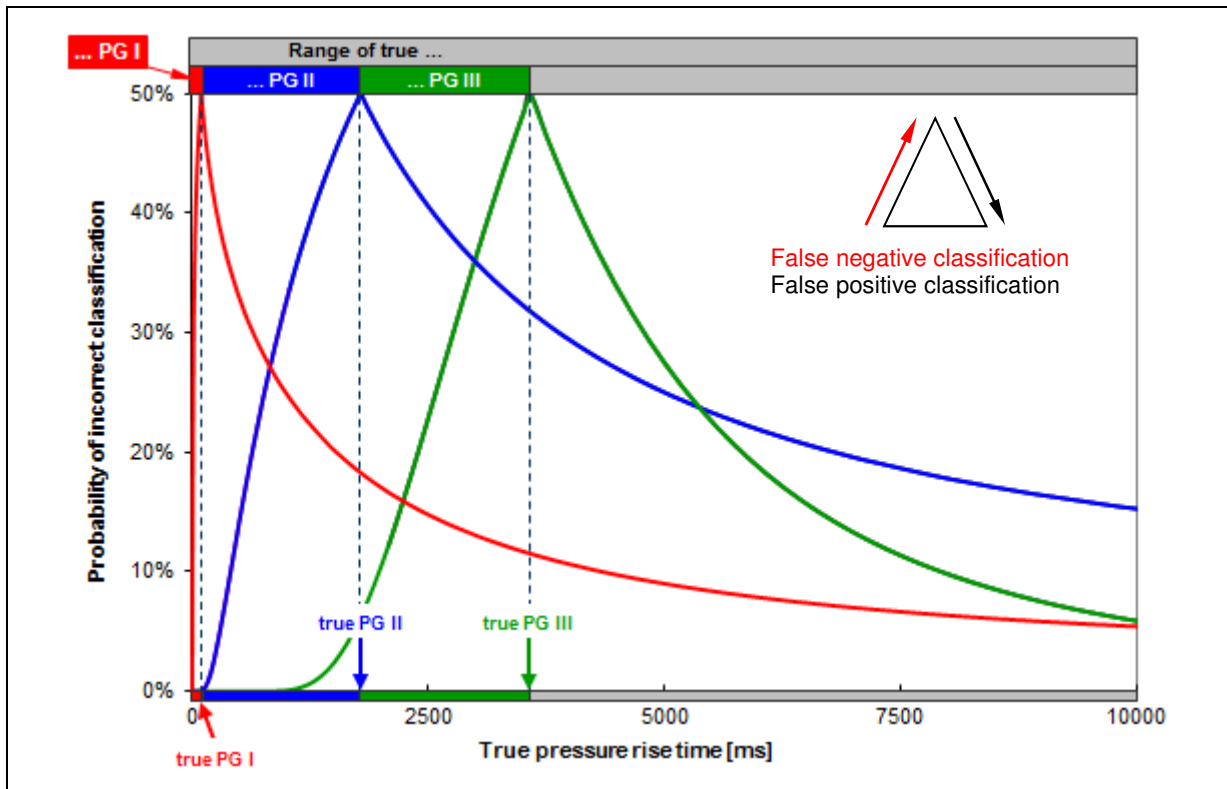


Figure 5-9: Shark profile for test series 1 – probability of incorrect classification in PG I, PG II or PG III or no classification as a function of the "true" pressure rise time of an arbitrary sample mixture (values of PG I, PG II and PG III see laboratory mean pressure rise times in Table 5-5)

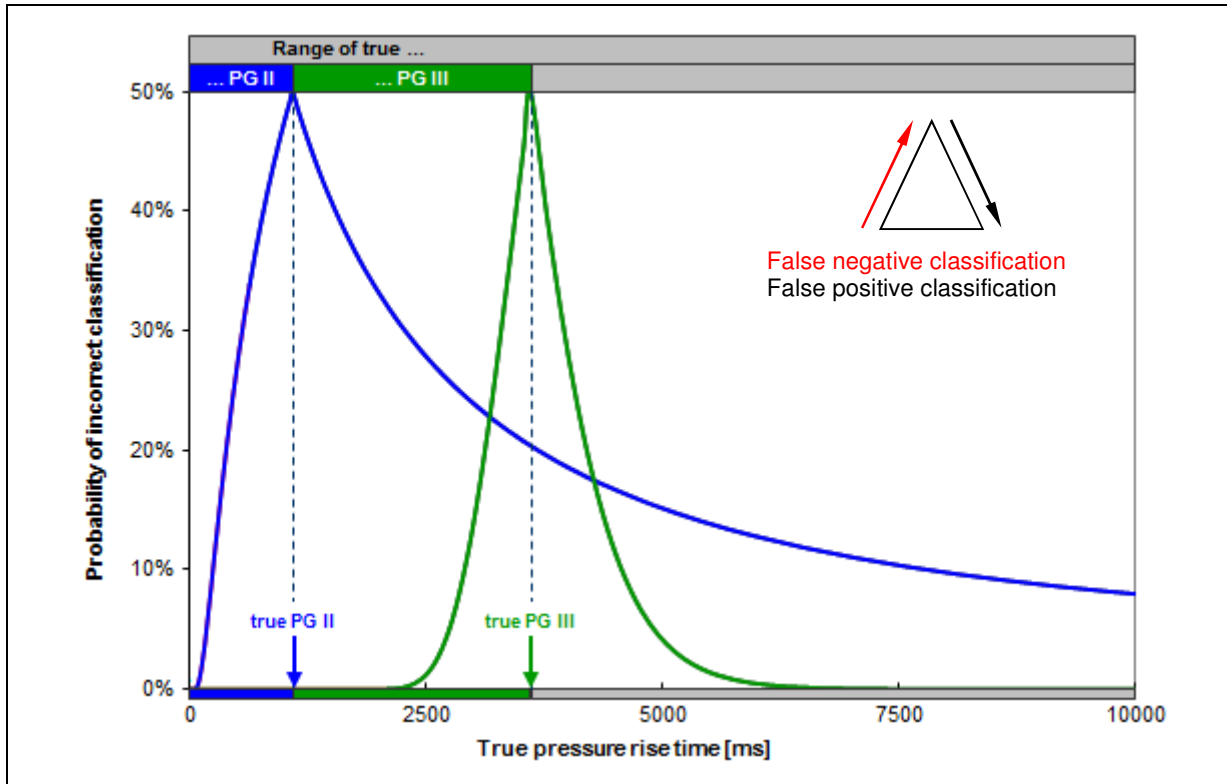


Figure 5-10: Shark profile for test series 2 – probability of incorrect classification in PG II or PG III or no classification as a function of the "true" pressure rise time of an arbitrary sample mixture (values of PG II and PG III see laboratory mean pressure rise times in Table 5-5)

5.6.2 Z_u scores

The assessment of the laboratory's performance in determining the pressure rise time of the test sample mixture and the reference substance mixtures was carried out using z_u scores according to DIN 38402-45 / ISO/IEC 17043. In general, z_u scores describe the standardised deviation of laboratory mean values from the total mean value under consideration that the lower limit of tolerance does not fall below zero. Under normal distribution, z_u scores lie within the limits -2 and 2 with probability 95 % and therefore if $|z_u \text{ score}| > 2$ holds, the quality criterion is not fulfilled.

Summarised, a laboratory's result is

- satisfactory if..... $|z_u \text{ score}| \leq 2$;
- questionable if $2 < |z_u \text{ score}| < 3$;
- unsatisfactory if..... $|z_u \text{ score}| \geq 3$.

In general, a z_u score smaller (greater) than zero means that the laboratory's mean is smaller (greater) than the total mean over all laboratories.

5.6.2.1 Z_u scores based on single pressure rise times

The z_u scores considered in this chapter are based on the single pressure rise times and were calculated using the respective total mean of the single pressure rise times (as assigned value) and the respective reproducibility standard deviation (as target standard deviation) according to DIN 38402-45 (see also Table 5-5).

In this interlaboratory test none of the z_u scores based on single pressure rise times lies outside the limits of tolerance.

Laboratories 106 and 910 exhibit only negative z_u scores, whereas laboratory 251 exhibits only positive z_u scores.

It has to be noted that in test series 1 laboratories 908 and 910 applied the mixing procedure as required for test series 2.

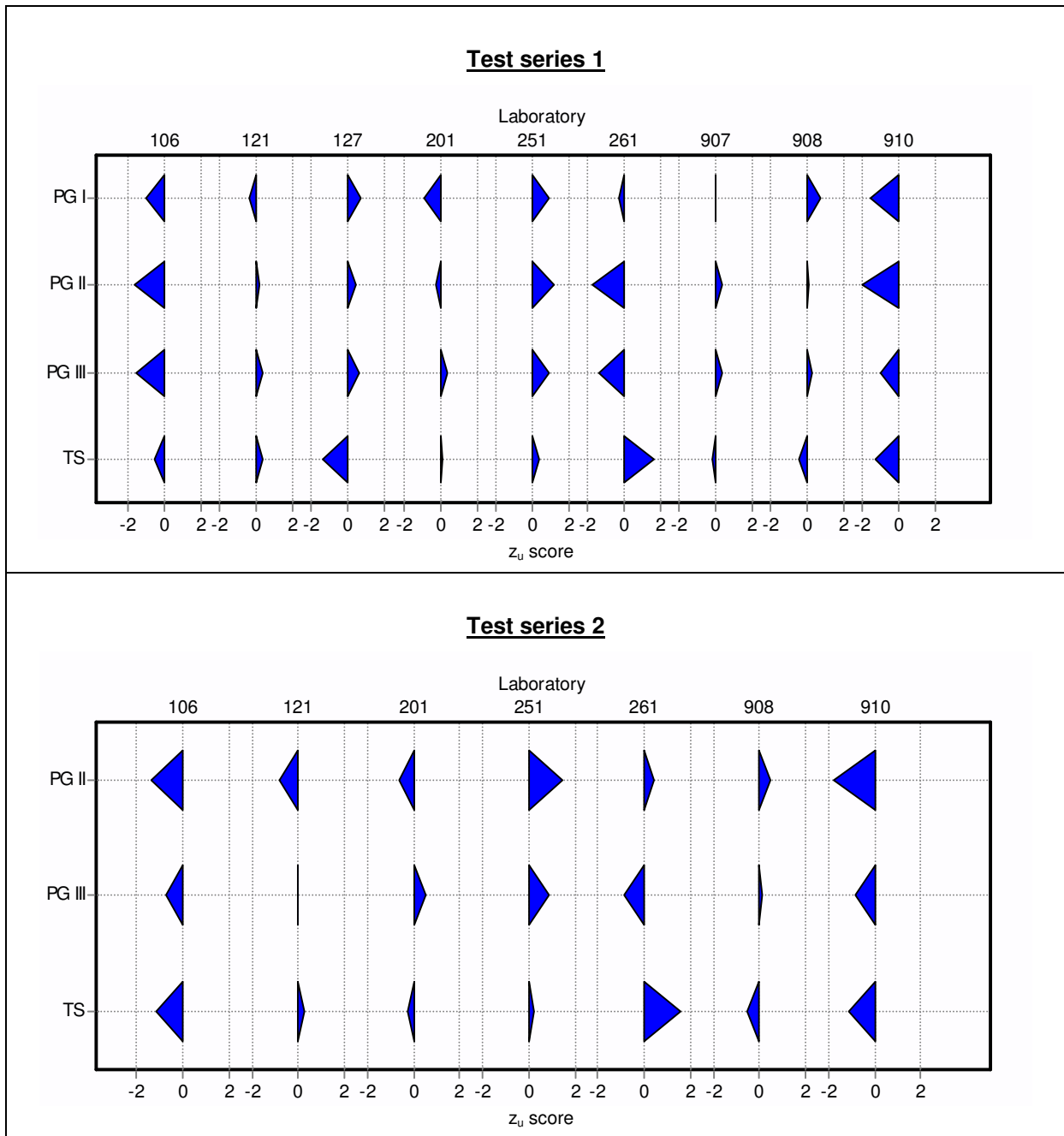


Figure 5-11: Z_u scores based on single pressure rise times – for each test series separately

5.6.2.2 Z_u scores based on laboratory mean pressure rise times

The Z_u scores considered in this chapter are based on the laboratory mean pressure rise times and were calculated using the respective mean of the ratios of of laboratory mean pressure rise times (as assigned value) and the respective reproducibility standard deviation (as target standard deviation) according to DIN 38402-45 (see also Table 5-5).

The quality criterion ($-2 \leq z_u \leq +2$) is not fulfilled by three laboratories in test series 1 as shown in the following Table 5-8 and in Figure 5-12.

Table 5-8: Laboratories and the respective laboratory mean pressure rise times for which the quality criterion is not fulfilled

Lab Code	Test series 1	Test series 2
106	PG II	-
261	PG III	-
910	PG III	-

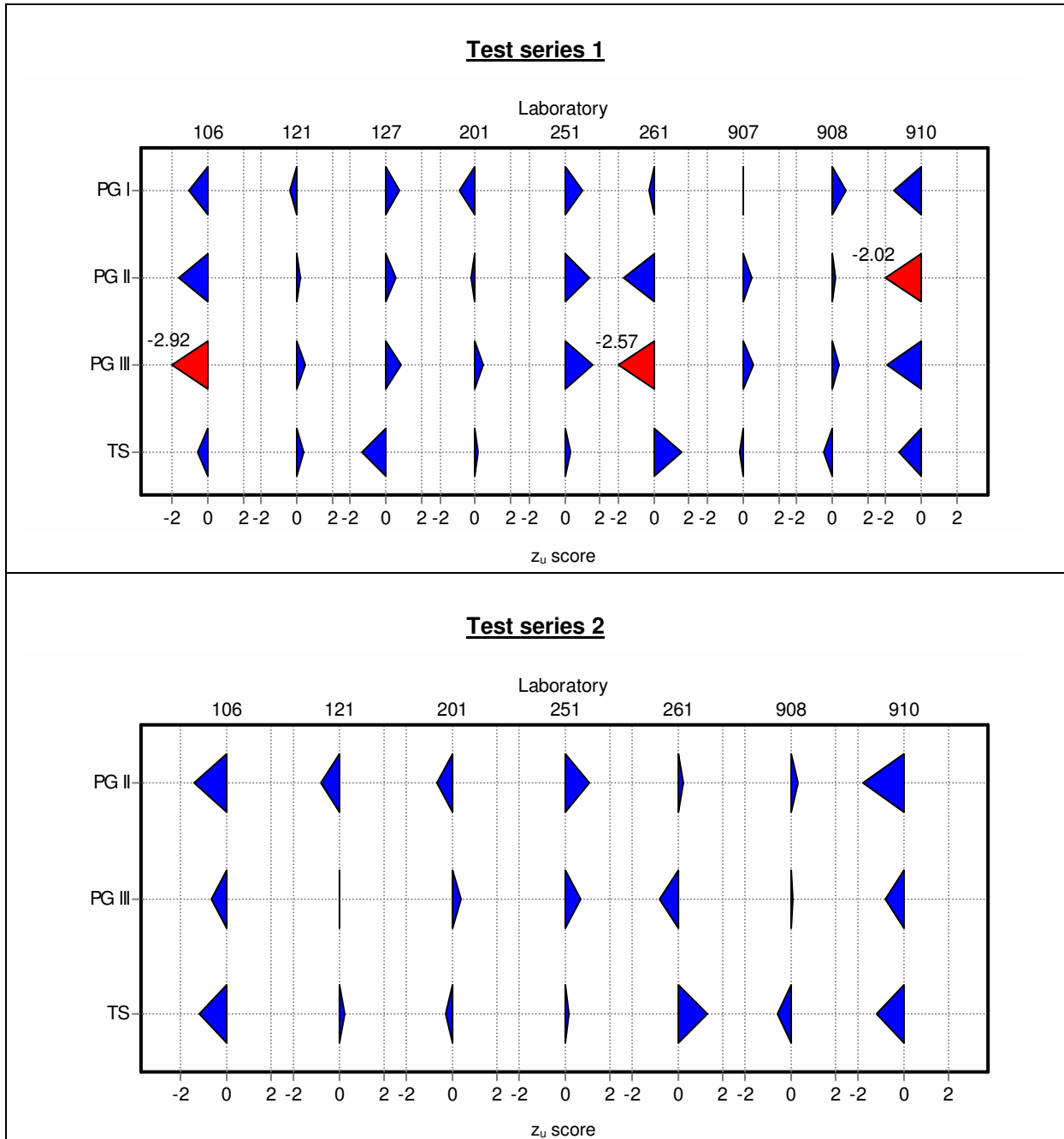


Figure 5-12: Z_u scores based on laboratory mean pressure rise times – for each test series separately (Note: The size of the triangles is limited to 2 even for $|z_u| > 2$ (for the lack of space), instead the respective triangles are coloured in red and the values are indicated next to them.)

5.6.2.3 Z_u scores based on ratios of laboratory mean pressure rise times

The z_u scores considered in this chapter are based on the ratios of laboratory mean pressure rise times and were calculated using the respective mean of the ratios of laboratory mean pressure rise times (as assigned value) and the respective reproducibility standard deviation (as target standard deviation) according to DIN 38402-45 (see also Table 5-5).

The quality criterion ($-2 \leq z_u \leq +2$) is not fulfilled by three laboratories as shown in the following Table 5-9 and in Figure 5-13. Especially laboratory 261 shows four out of nine z_u scores, which do not fulfil the quality criterion.

Table 5-9: Laboratories and the respective ratios of laboratory mean pressure rise times for which the quality criterion is not fulfilled

Lab Code	Test series 1	Test series 2
121	-	TS / PG III
910	PG III / PG II	PG III / PG II
261	TS / PG II; TS / PG III	PG III / PG II; TS / PG III

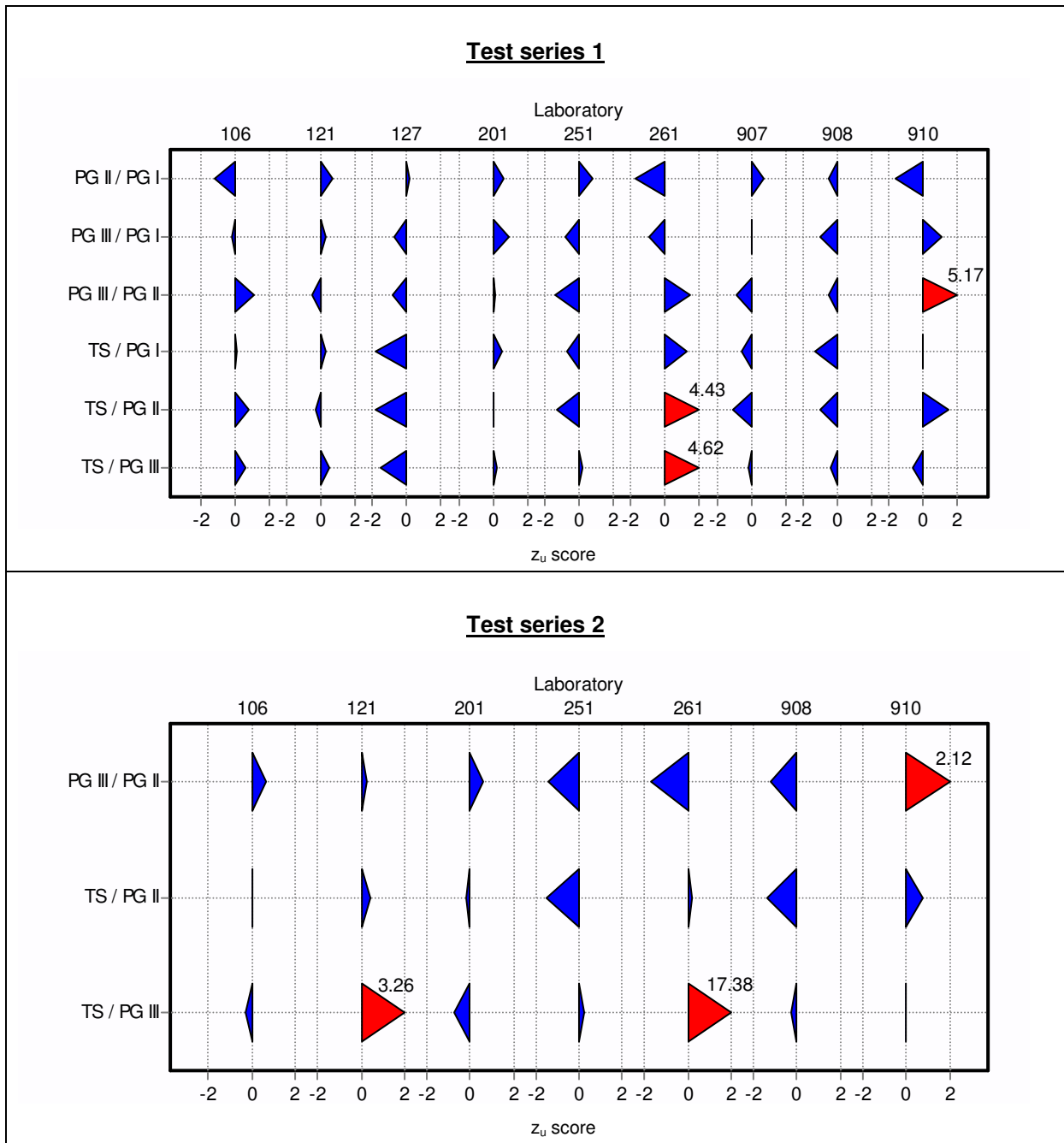


Figure 5-13: Z_u scores based on ratios of laboratory mean pressure rise times – for each test series separately

(Note: The size of the triangles is limited to 2 even for z_u scores with $|z_u| > 2$, instead the respective triangles are coloured in red and the values are indicated next to them)

There are two clear outlier results (i.e. z_u scores below -5 or above +5):

- laboratory 910 for the ratio PG III / PG II in test series 1 and
- laboratory 261 for the ratio TS / PG III in test series 2.

Combination scores based on ratios of laboratory mean pressure rise times

The combination scores of the systematic deviations (rescaled sum of z_u scores – RSZ) and the relative laboratory performance (RLP) was calculated for each laboratory from the z_u scores [4].

The **RSZ** is based on a standardized sum of all z_u scores. The standardization of the sum ensures that the RSZ can be interpreted as a single z_u score. As long as the RSZ is within the tolerance range of -2 to +2, the respective laboratory does not exhibit any significant systematic deviations.

The **RLP** is based on the quadratic mean of z_u scores of the test sample mixtures and different reference substance mixtures of the respective laboratory. A rough classification of the RLP values is:

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

RLP \approx 1: laboratory exhibits an average performance

RLP > 1.5: laboratory exhibits a performance below average with large measurement deviations⁴

The combination scores RSZ and RLP based on the ratios of laboratory mean pressure rise times are listed in the following Table 5-10.

Table 5-10: RSZ (rescaled sum of z_u scores) and RLP (relative laboratory performance) for each laboratory based on z_u scores for the ratios of laboratory mean pressure rise times

Laboratory	Test series 1		Test series 2	
	RSZ	RLP	RSZ	RLP
106	0.56	0.80	0.20	0.39
121	0.43	0.45	2.14	1.76
127	-2.70	1.30	-	-
201	0.96	0.49	-0.19	0.57
251	-1.28	0.93	-1.51	1.17
261	2.46	2.06	0.86	2.00
907	-0.76	0.68	-	-
908	-1.85	0.82	-1.65	1.08
910	1.34	1.60	1.68	1.31

red RSZ values: significant systematic deviations over all considered mixtures

red RLP values: laboratory exhibits a performance below average with large measurement deviations

The combination scores over all ratios of laboratory mean pressure rise times of the references substance mixtures and the test sample mixture are shown in the following Figure 5-14 separately for test series 1 and test series 2. The green square displays the tolerance range (between -2 and +2 for RSZ and below 1.5 for RLP).

⁴ The limit 1.5 is specified based on experience and theoretical considerations. These considerations show that an upper limit for the RLP should be above 1.4, but not be larger than 1.5. Therefore 1.5 is only a compromise, but it appears to be a very good compromise which is applied in many proficiency tests. See also [4]

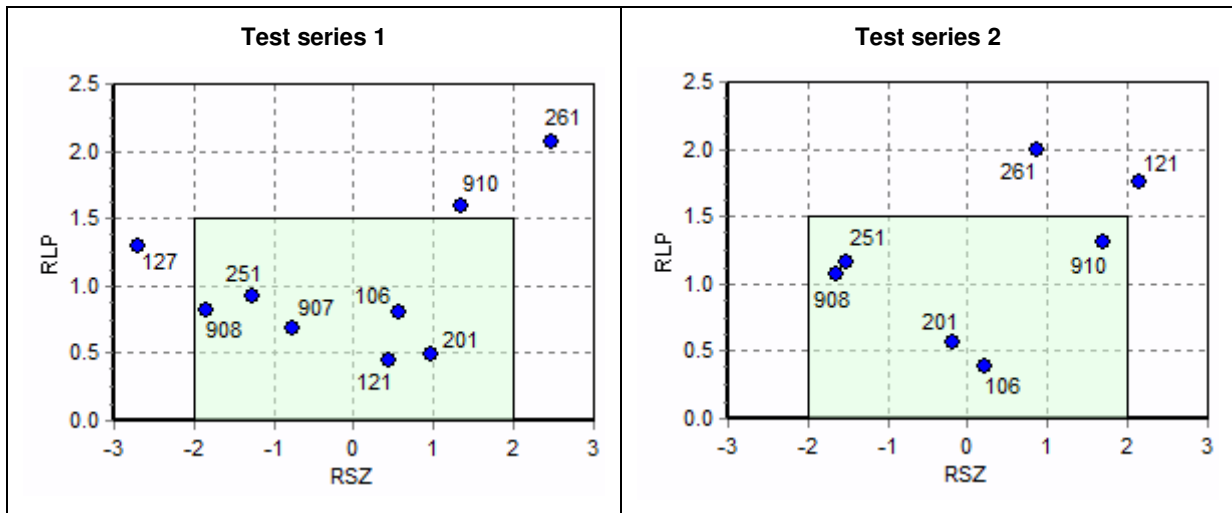


Figure 5-14: Combination scores over all ratios of laboratory mean combustion times – for each test series separately

The relative laboratory performance (RLP) based on the z_u scores of the ratios of laboratory mean pressure rise times varies in a relatively wide range in both test series, i.e. from 0.45 to 2.06 in test series 1 and from 0.39 to 2.00 in test series 2.

Laboratory 261 shows a RLP greater than 1.5 in both test series. The RSZ is greater than 2 in test series 1 – but not in test series 2. Therefore, it might be concluded that in laboratory 261 the different mixing procedures possibly result in systematic deviations.

In test series 1 the RSZ and RLP of laboratory 121 lie clearly within the tolerance limits. However, in test series 2 significant systematic effects ($RSZ > 2$) and a relative laboratory performance (RLP) greater than 1.5 are observed. Thus it might be concluded that in laboratory 121 the different mixing procedures possibly effect systematic deviations.

5.7 Effect of the mixing procedure – modified mixing procedure in test series 2

The single pressure rise times of the reference substance mixtures PG II and PG III and the test sample mixture TS were compared regarding the influence of the different mixing procedures of test series 1 and 2 (see Table 4-5).

The reference substance mixture PG I was tested only in test series 1 and therefore is not considered here.

Laboratory 127 and laboratory 907 are not taken into consideration because from these laboratories only measurements for test series 1 were available.

Laboratory 908 and laboratory 910 used the same mixing procedure in both test series. However, these values will be also considered as they may influence the reproducibility.

Details about the mixing duration and the mixing equipment are listed in Table 5-11. Laboratories that applied different mixing procedures in test series 1 and 2 are marked in blue and the two laboratories with the same mixing procedure in both test series are marked in red.

Table 5-11: Mixing duration and mixing equipment applied in test series 1 and test series 2

Laboratory	Mixing duration [min]		Mixing equipment	
	Test series 1	Test series 2	Test series 1	Test series 2
106	2	2	glass beaker with glass rod	mortar with pistil
121	1		glass beaker with plastic rod with rubber wiper	
201	2		glass beaker with glass rod	
251	1		glass beaker with glass rod	
261	PG II: 3 to 7 PG III: 3 TS: 1 to 5*		glass beaker with glass rod and spatula	
908	2		mortar with pistil	
910	2		mortar with pistil	

*...only 2 measurements available: lower value: 1 min; upper value: 4.6 min

A graphical comparison between the single pressure rise times, the laboratory mean pressure rise times and the laboratory standard deviation of the single pressure rise times of test series 1 and 2 is shown in the following three figures (PG II in Figure 5-15, PG III in Figure 5-16 and TS in Figure 5-17). The variability of the values is displayed in form of blue boxes (bottom diagram in the respective figure). The larger the box the larger is the laboratory standard deviation. The laboratory mean pressure rise times are marked by a horizontal line within each box, while the single pressure rise times are shown as small triangles. The relative standard deviations of the laboratories are shown in the upper part of the figures in form of grey bars.

Reference substance mixture for packing group II

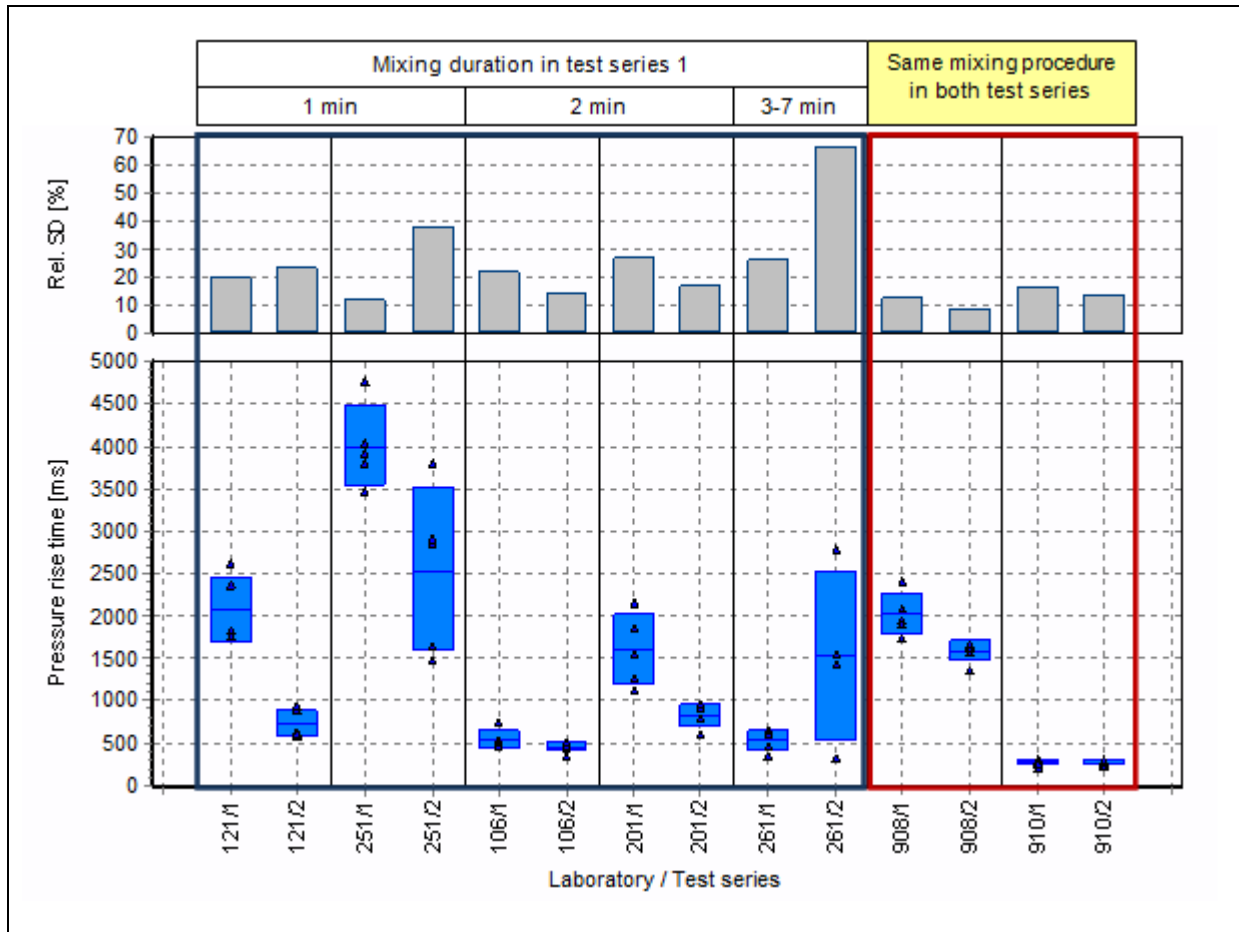


Figure 5-15: Comparison of the single pressure rise times for PG II

Significant differences between the results of the reference substance mixture for packing group II (laboratory mean pressure rise times) of test series 1 and 2 are observed in 5 from 7 laboratories.

The single pressure rise times of laboratories 106 and 910 exhibit no significant differences.

In all laboratories the laboratory mean pressure rise times of test series 1 are higher than the laboratory mean pressure rise times of test series 2.

The relative standard deviation between both test series is noticeably higher for laboratories 251 and 261.

Reference substance mixture of packing group III

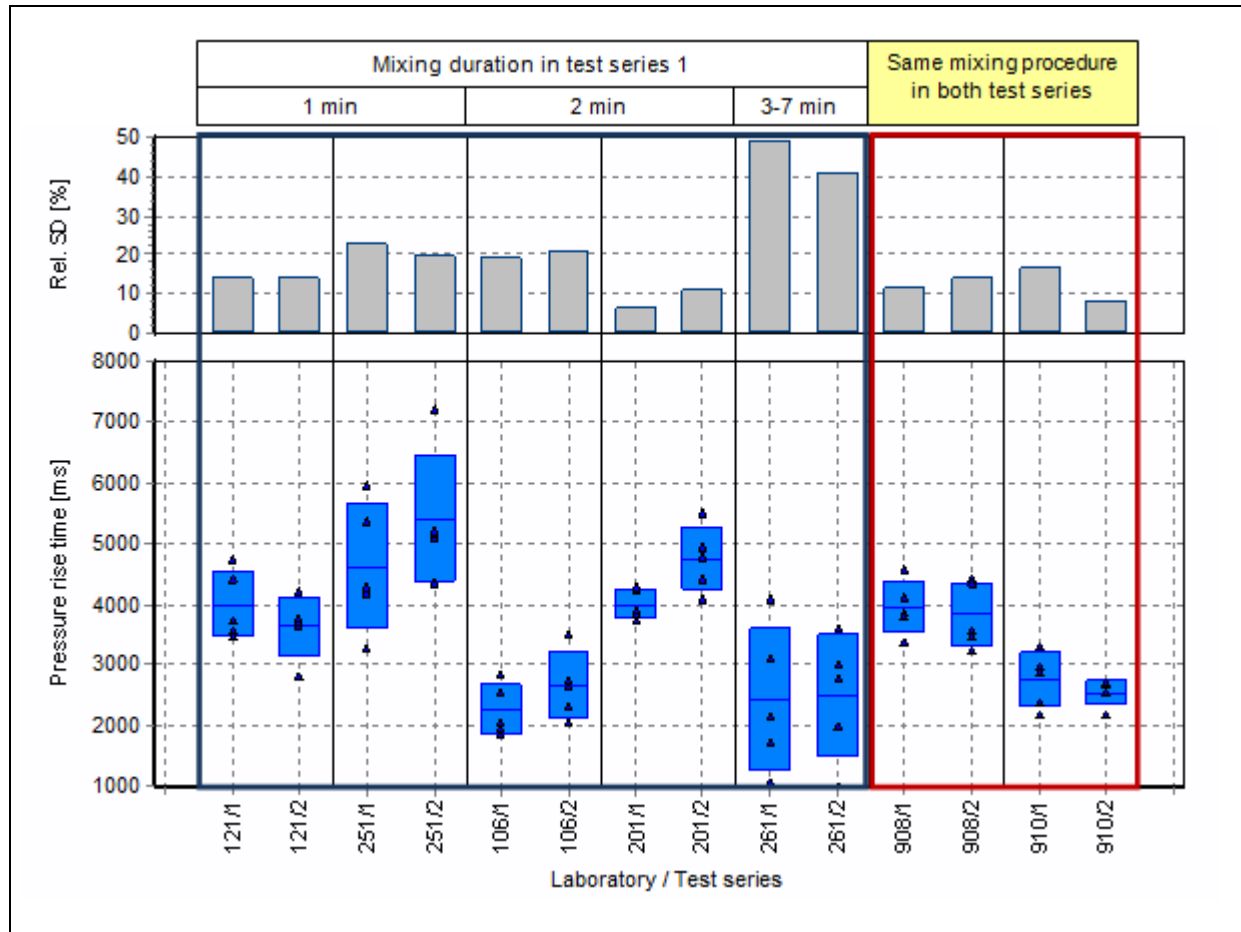


Figure 5-16: Comparison of the single pressure rise times for PG III

Significant differences between the results of the reference substance mixture of packing group III of test series 1 and 2 can be observed only in laboratory 201.

In contrast to packing group II, the laboratories' mean pressure rise times of test series 2 are more often higher than of test series 1.

Test sample mixture TS

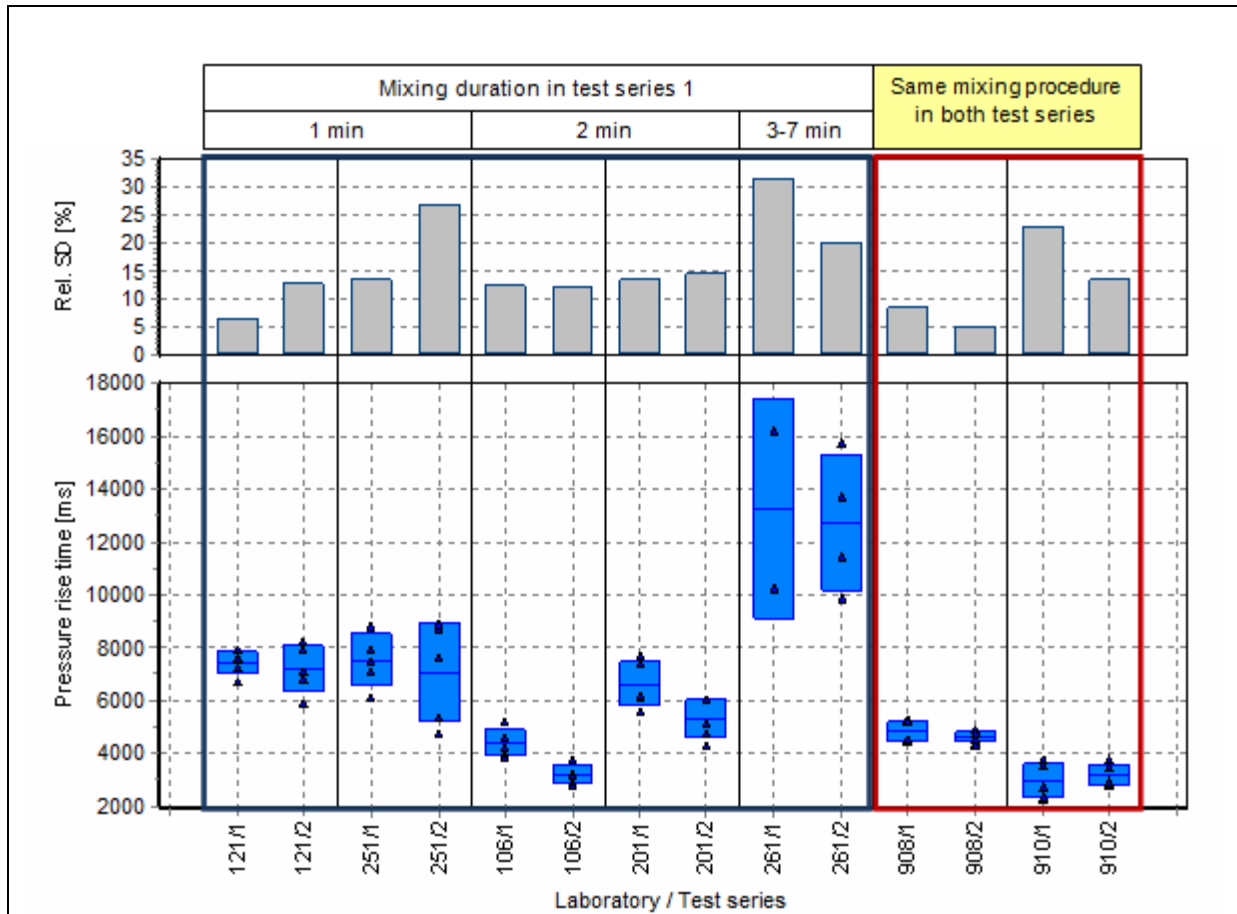


Figure 5-17: Comparison of the single pressure rise times for TS

Although the laboratories' mean pressure rise times of test series 1 are higher than of test series 2 for most of the laboratories, significant differences between the results of the test sample mixture TS of test series 1 and 2 can be observed only in the laboratories 106 and 201.

For laboratory 201 and laboratory 106 the only difference between test series 1 and 2 was the mixing equipment used. In test series 1 a glass beaker with glass rod was used while in test series 2 a mortar with pistil was used. All other factors were the same (i.e. have not been varied in both test series). Therefore it might be concluded that the mixing equipment is the reason for these differences.

5.8 Other influencing (disturbing) factors

The reason for the broad spread of the results and the deviations between the laboratories was analysed by an additional exploratory data analysis of the single pressure rise times of the laboratories (see chapter 2 Aim). However, the conclusiveness of the findings is limited because the aim of this interlaboratory test was mainly focussing on the mixing procedure and not on other factors.

5.8.1 Effect analysis of single pressure rise times based on laboratory-specific and trial-comprehensive test parameters

The effects of different laboratory-specific test parameters (e.g. parameters with regard to the cellulose, test equipment, mixing procedure) are shown in the following sections (for the respective single pressure rise times and more detailed data see chapter 8.3.1.1 - 8.3.1.7).

It has to be noted that these figures provide only a rough orientation and no statistically firm conclusions can be derived from them.

5.8.1.1 Reference substance – Supplier

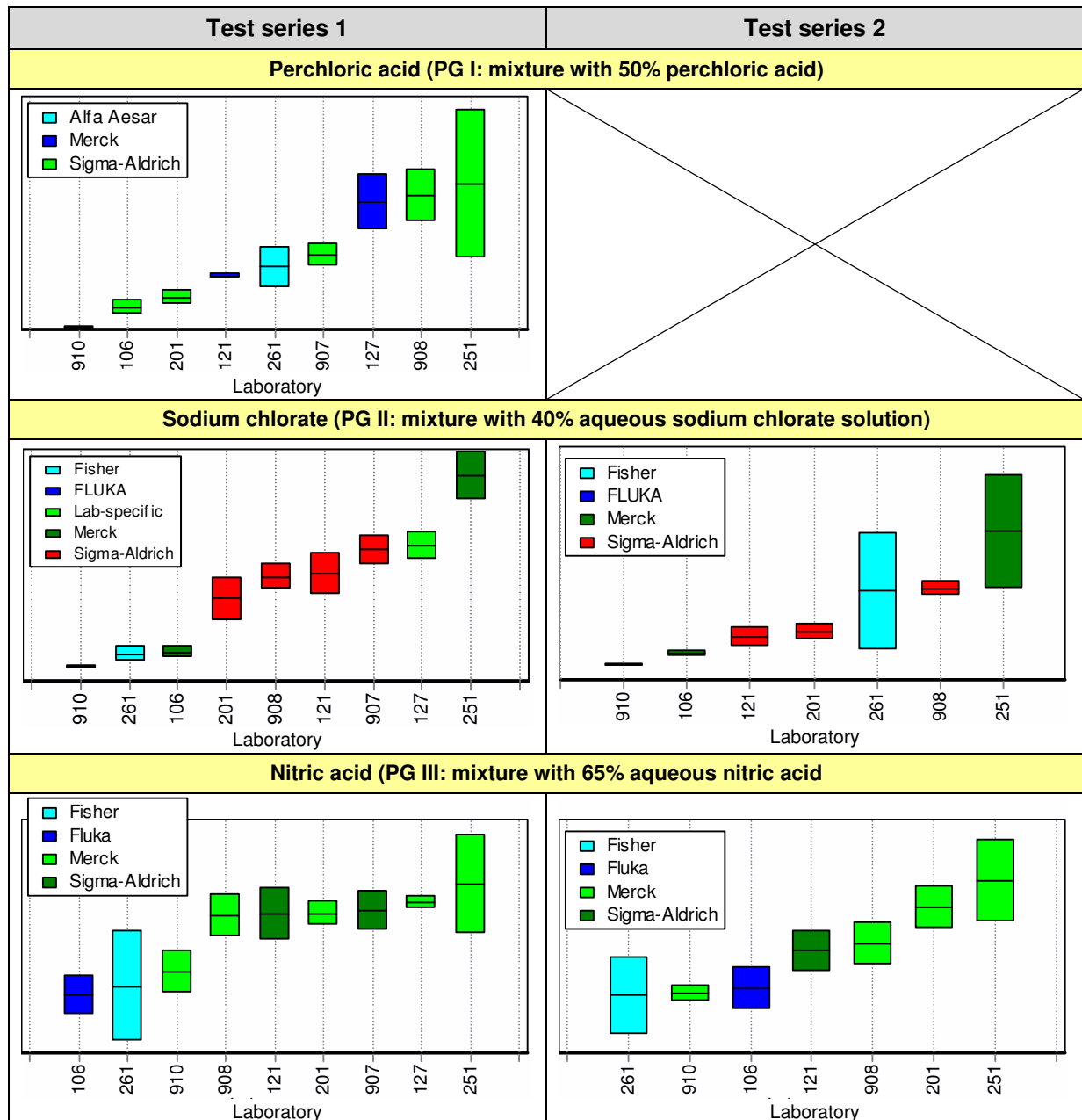


Figure 5-18: Influence of the supplier of the reference substance
(Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.2 Cellulose – Supplier

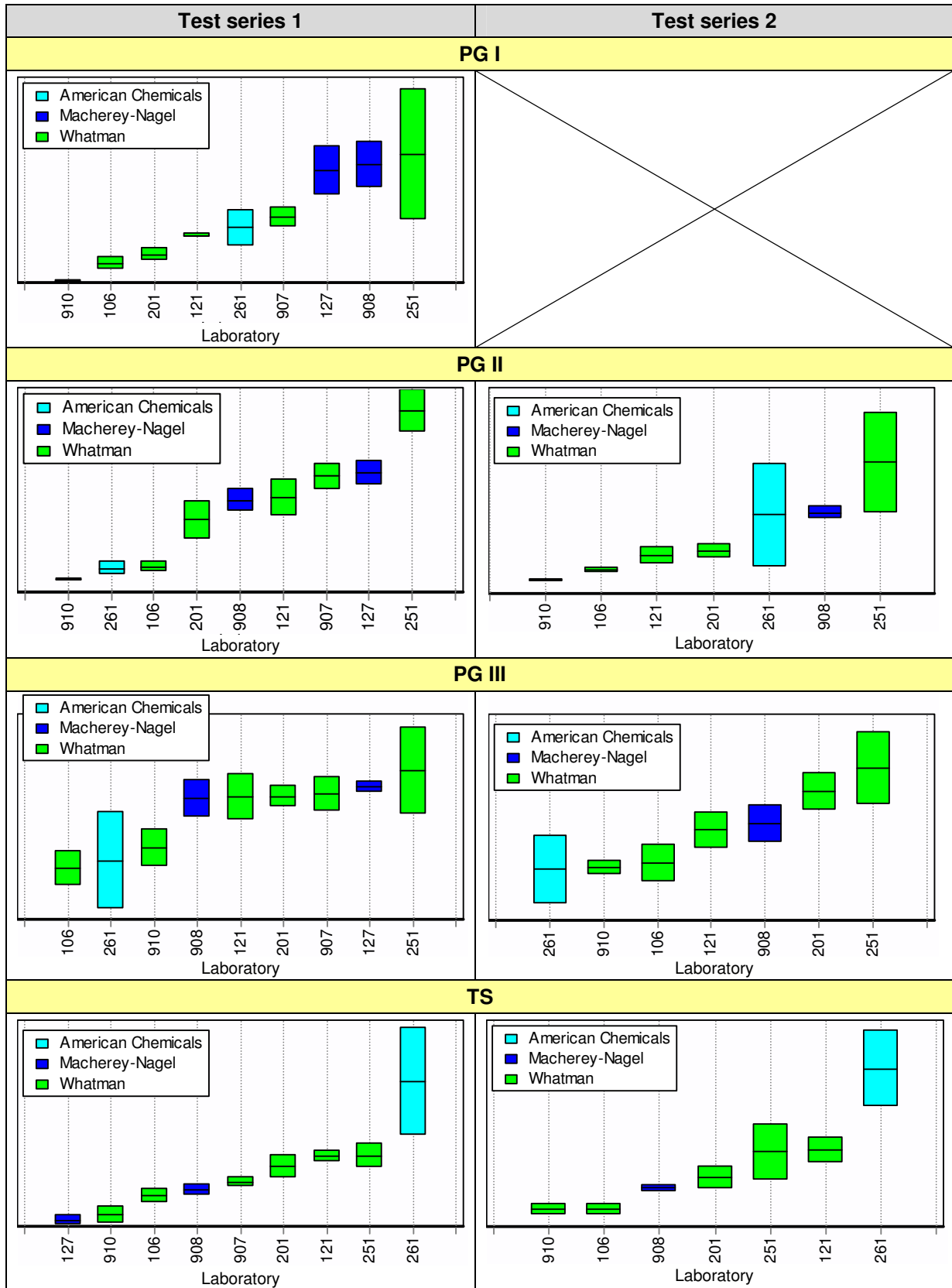


Figure 5-19: Influence of the supplier of the cellulose
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.3 Cellulose – Drying time

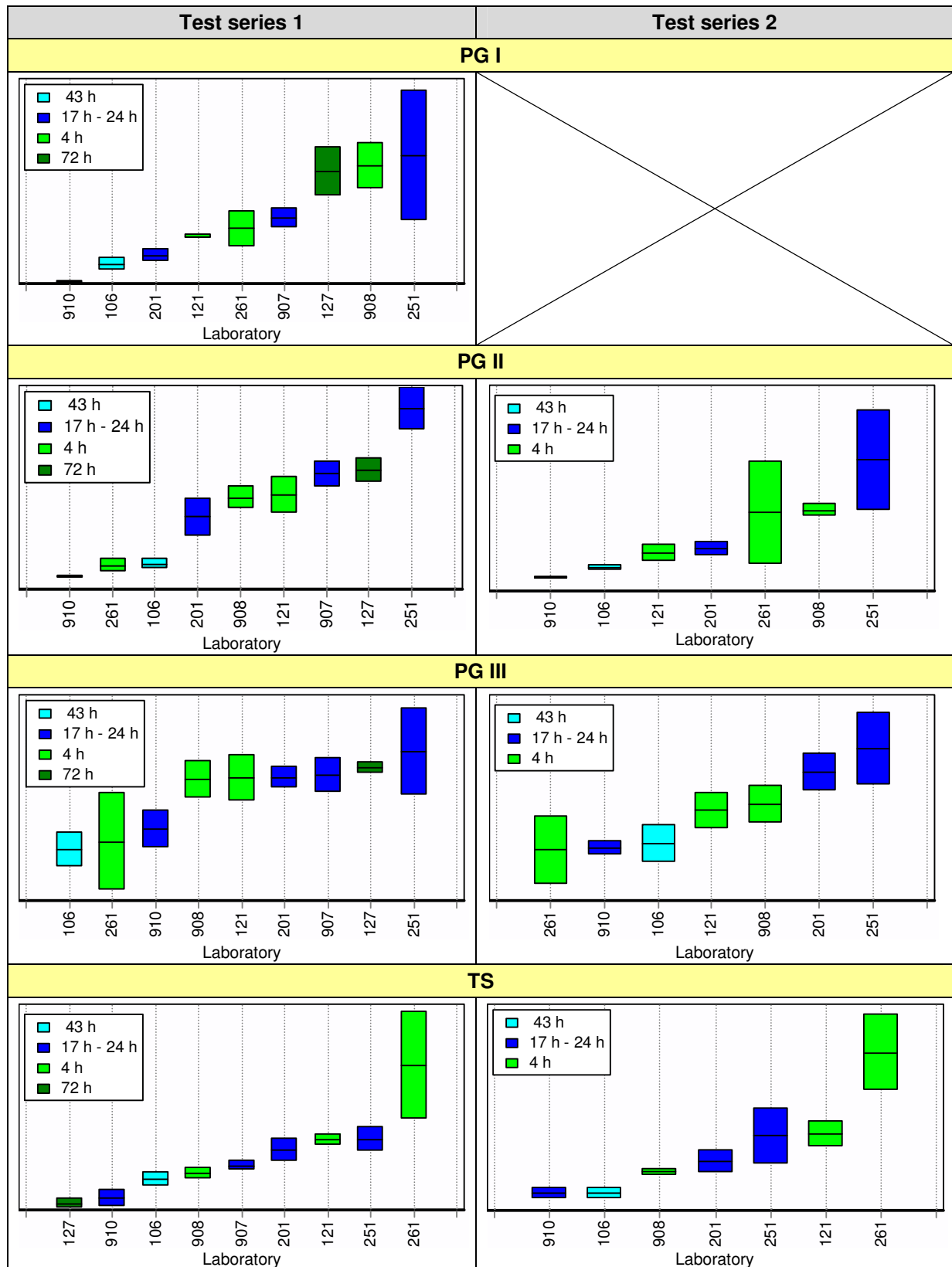


Figure 5-20: Influence of the drying time of the cellulose
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.4 Cellulose – Drying temperature

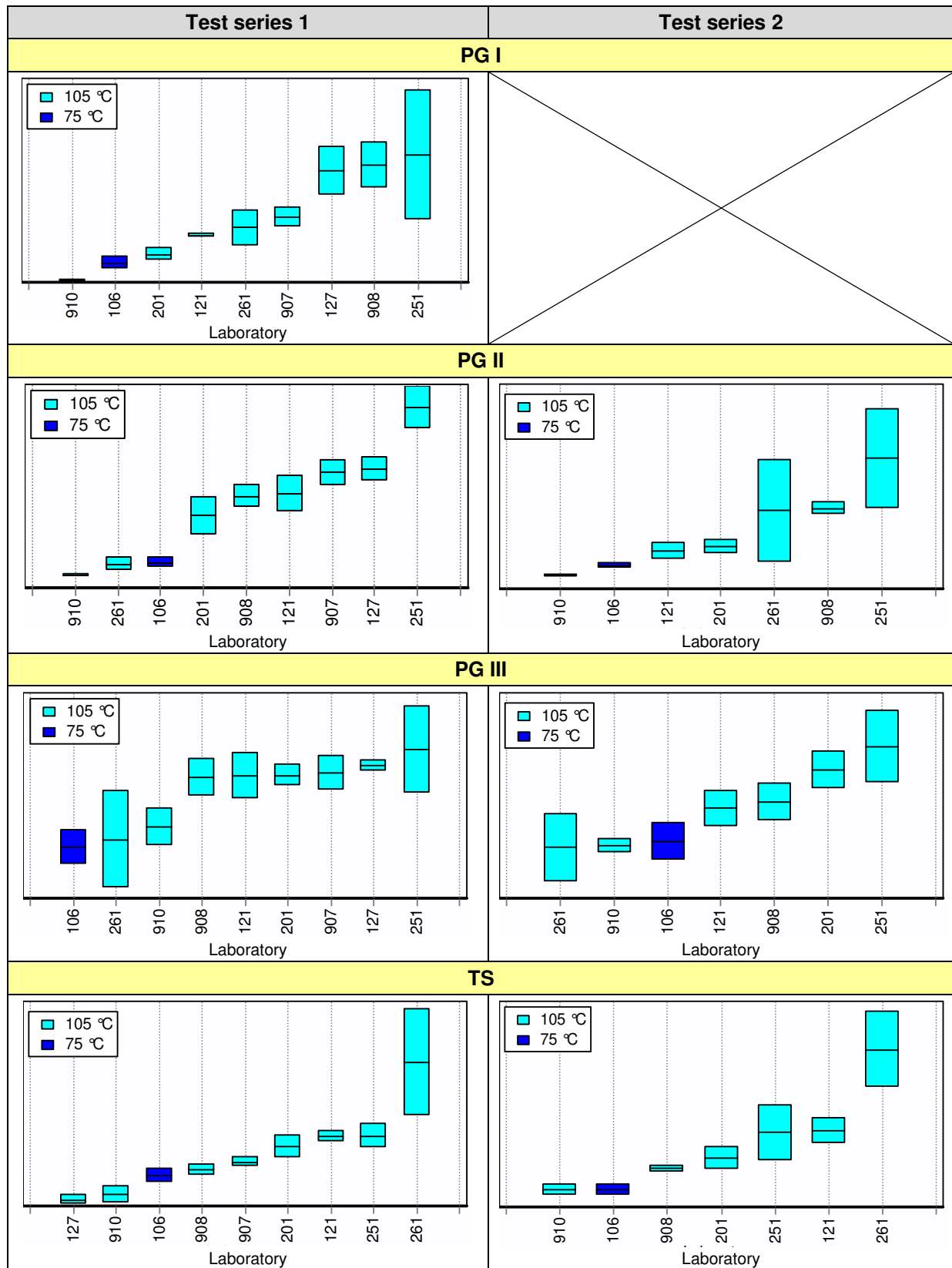


Figure 5-21: Influence of the drying temperature of the cellulose
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.5 Cellulose – Residual moisture

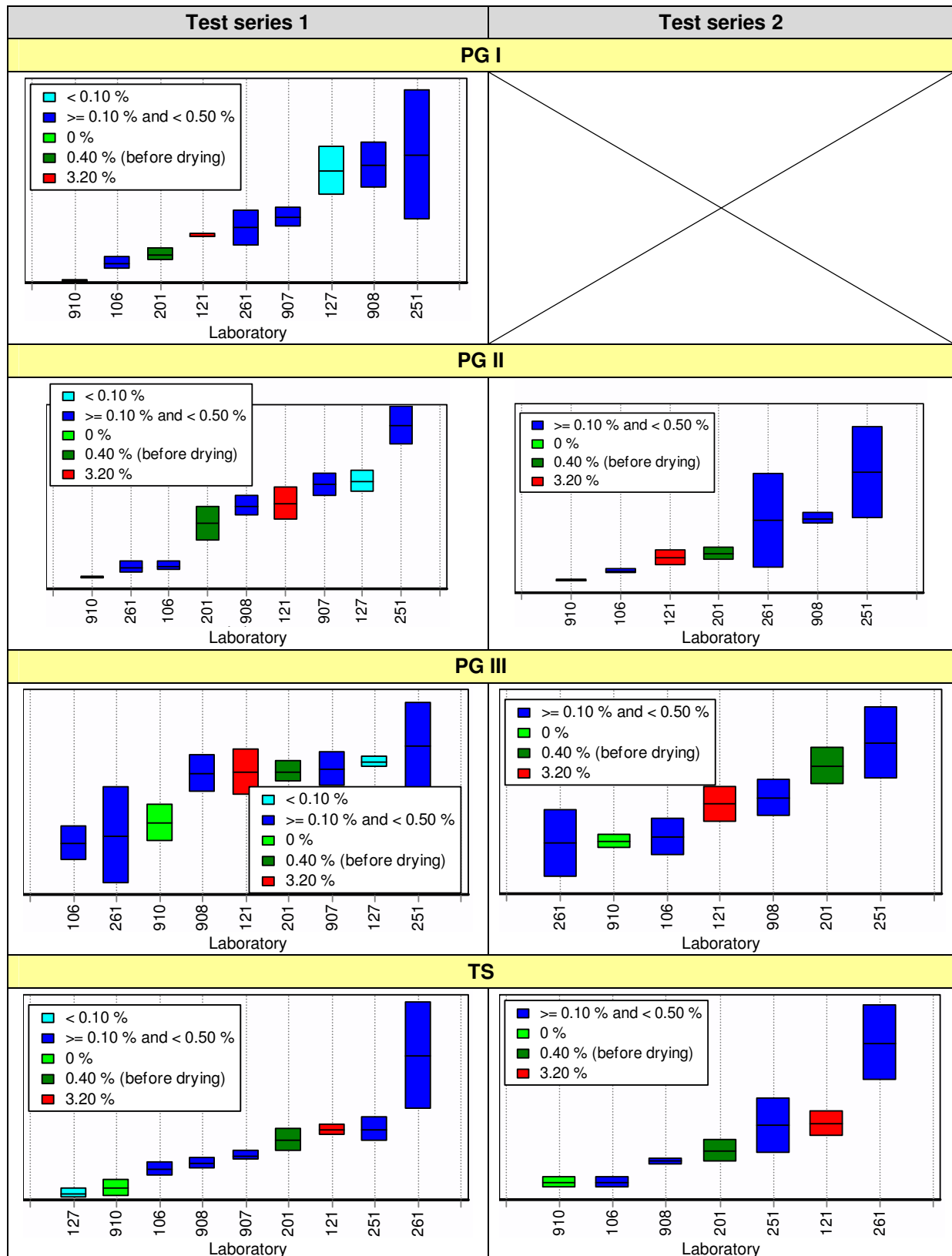


Figure 5-22: Influence of the residual moisture of the cellulose
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.6 Mixing procedure – Duration (varied only in test series 1)

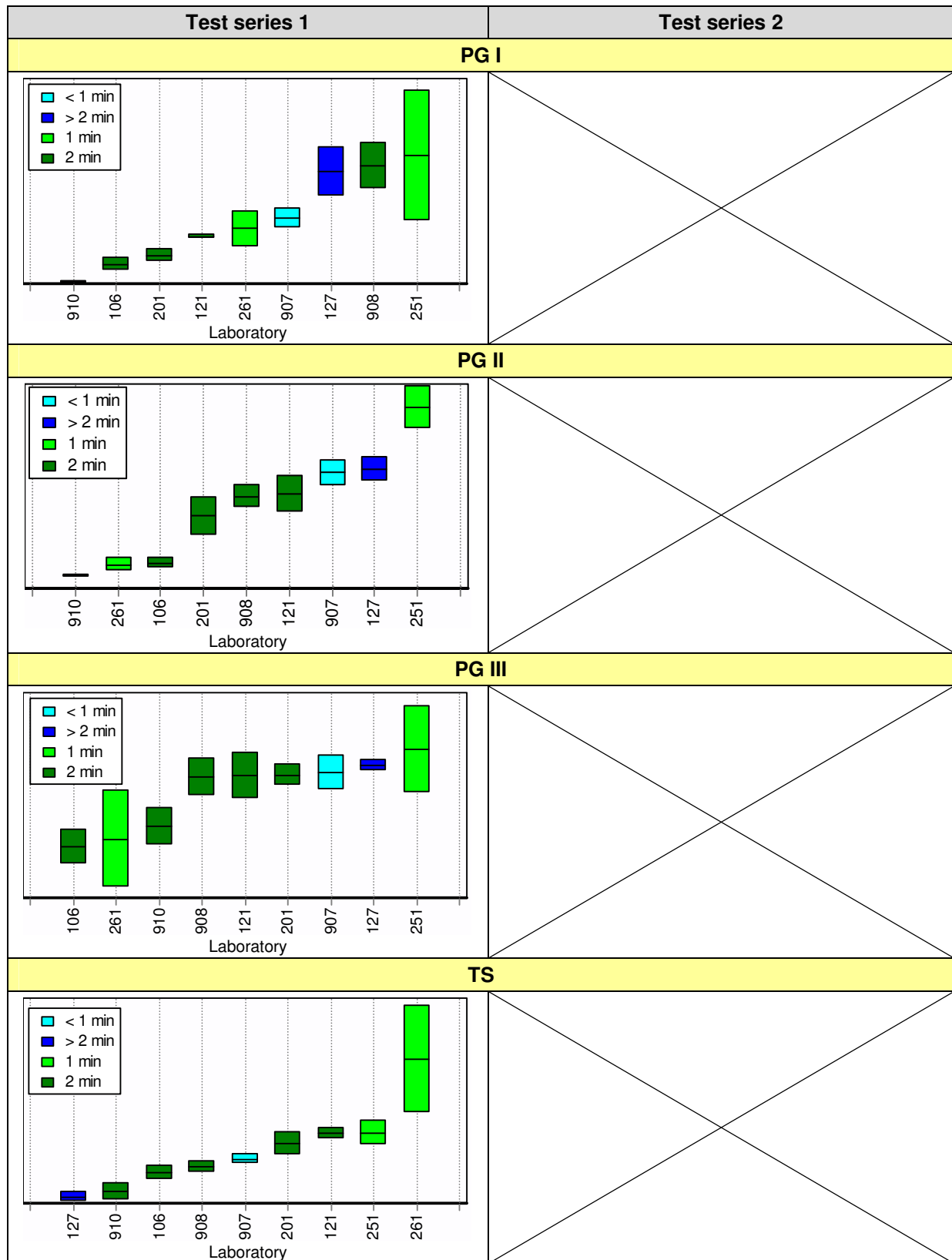


Figure 5-23: Influence of the duration of the mixing procedure
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.7 Mixing procedure – Equipment

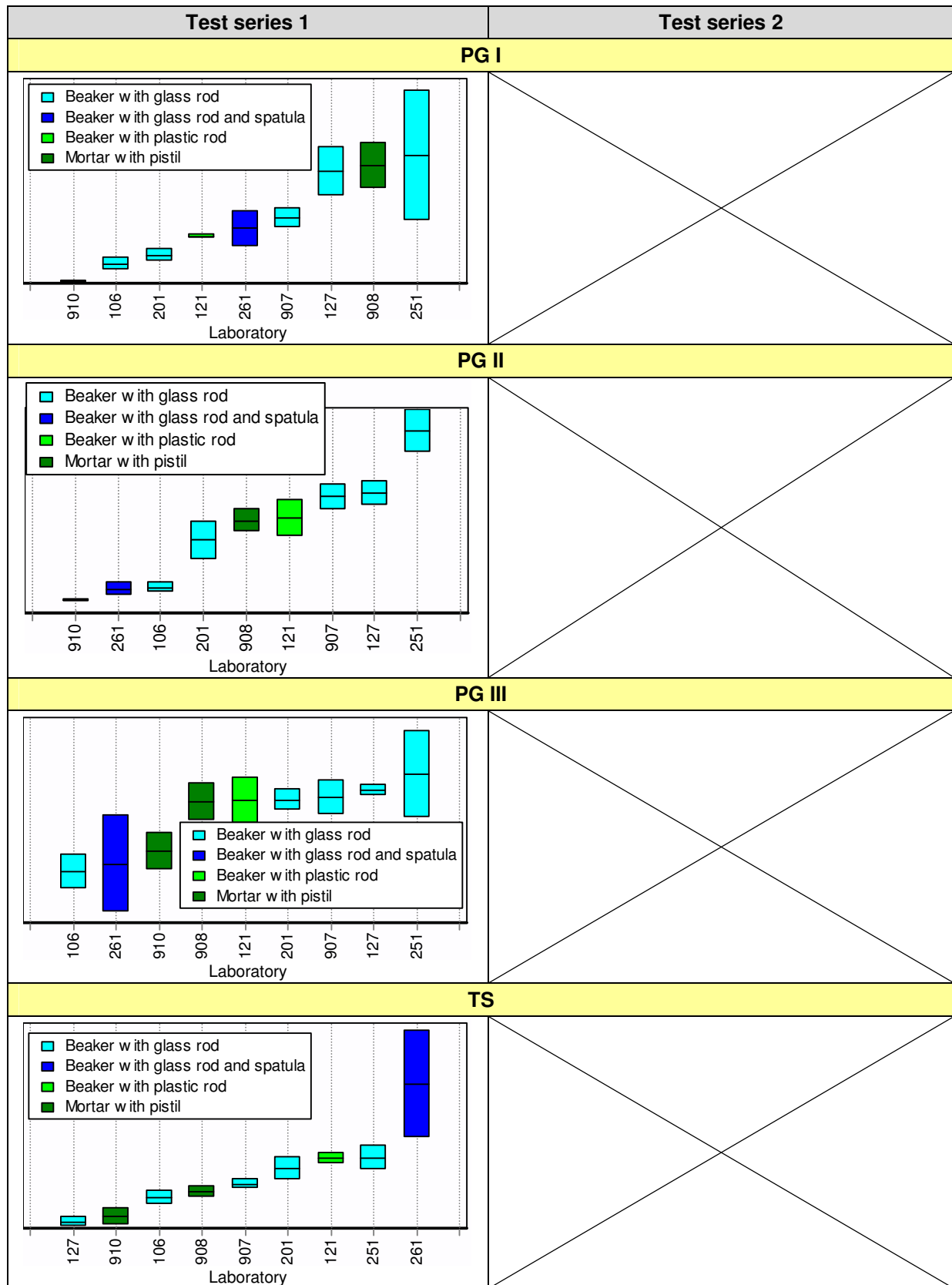


Figure 5-24: Influence of the equipment of the mixing procedure
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.1.8 Resistance of the ignition wire of the test equipment

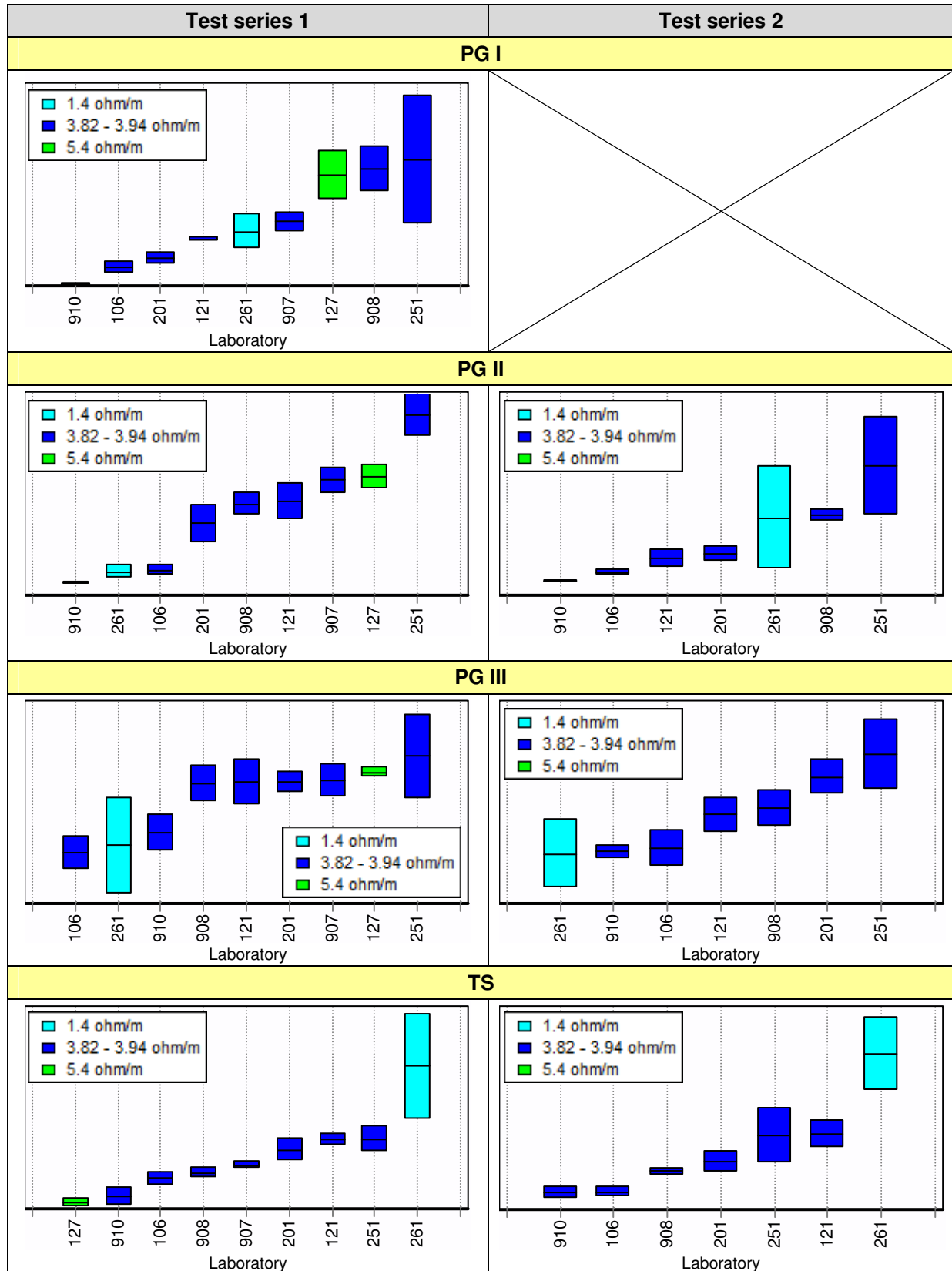


Figure 5-25: Influence of the resistance of the ignition wire of the test equipment
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on the figures in chapter 8.3.1, page 59)

5.8.2 Effect analysis of single pressure rise times based on trial-specific detailed information

In general, the following parameters may vary from trial to trial during the tests (see Table 5-12):

Table 5-12: Parameters, which may vary from trial to trial

Ambient pressure
Ambient relative air humidity
Ambient temperature
Mass of the cellulose
Mass of the liquid
Mixing duration (varied only in series 1)
Time from the start of mixing until ignition (switching the power)

The dependence of the pressure rise time on the different varying parameters (effect of the parameters on the pressure rise time) was investigated by the following analysis.

The single pressure rise times have been normalized by subtracting the respective total mean of single pressure rise times and dividing by the reproducibility standard deviation (see Table 5-5) in order to ensure a sample-comprehensive effect analysis. Hence, standardized single pressure rise times were obtained, for which an analysis of variance (ANOVA) was carried out (for detailed results see chapter 8.3.2, page 76).

Summarizing, the following parameters have a significant influence on the pressure rise time:

- Mass of the cellulose
- Mixing duration
- Time from the start of mixing until ignition (switching the power).

Furthermore, there are highly significant effects (i. e. there are systematic differences) between laboratories and between test series 1 and test series 2 regarding the obtained single pressure rise times.

It has to be noted that such an effect analysis is only possible for the single pressure rise times and only for the trial-specific detailed information which varies from trial to trial in some laboratories.

An effect analysis of the single pressure rise times regarding the lab-specific settings (laboratory specific parameters which are constant in all trial) was not carried out because of the small number of laboratories.

6 Summary and conclusions

The following conclusions can be drawn concerning the aim of this interlaboratory test.

6.1 Performance of the methods UN O.2 / EC A.21

The results of this interlaboratory test show a sufficiently clear picture concerning the application of the methods UN O.2 / EC A.21 in the laboratory practise.

The relative repeatability standard deviations of the single pressure rise times vary between 10 % and 15 % in test series 1 and between 13 % and 19 % in test series 2 (see Table 5-5). Those of the ratios of the laboratory mean pressure rise times range between 10 % (PG III / PG II) and 55 % (TS / PG II) in test series 1 and between 13 % (PG III / PG II) and 18 % (TS / PG II) in test series 2.

The relative reproducibility standard deviation of the ratio TS/PG II in test series 1 is extremely high (86 %) compared to the other ratios. The reference substance mixture PG III in test series 1 exhibits the smallest relative reproducibility standard deviation for the single pressure rise times as well the laboratory mean pressure rise times, and the ratio PG III / PG II in test series 2 exhibits the smallest relative reproducibility standard deviation for the ratios of laboratory mean pressure rise times.

The relative reproducibility standard deviations obtained for the ratios of laboratory mean pressure rise times are partly even higher than for the single pressure rise times. For example in test series 1, the relative reproducibility standard deviation for the laboratory mean pressure rise times of TS equals 61 %, for PG II equals 68 %, however, for the ratio TS/PG II it amounts to 86 %.

Normally, it might be expected that systematic effects could cancel out by building the ratios of the laboratory mean pressure rise times, however, this was not the case, i. e. the reproducibility standard deviations of the ratios of laboratory mean pressure rise time are not significantly smaller than those of the single pressure rise times. This might be caused by the fact that laboratories used different substances from different suppliers.

The relative laboratory performance (RLP) based on the z_u scores of the ratios of the laboratory mean pressure rise times varies in a relatively wide range in both test series. Furthermore significant systematic effects can be observed (rescaled sum of z_u scores (RSZ) > 2). All in all it can be summarized that:

- There are clear outliers regarding z_u scores of the laboratories, i.e. z_u scores below -5 or above +5.
- There are noticeable differences between the relative laboratory performance (RLP) of the laboratories.
- There are noticeable differences between the rescaled sum of z_u scores (RSZ) of the laboratories.

The reason might be that in some laboratories the different mixing procedures cause systematic deviations. It is recommended that the reasons leading to outliers and the noticeable differences of the results when applying this test method are investigated in further more specific investigations.

On the basis of the assessed precision indicators (reproducibility, repeatability and probability of incor-

rect classification) it can be concluded that the method and its application are not satisfactory, especially with regard to the following aspects and results:

- There is a high heterogeneity between the laboratories and also a high variability of the laboratory's performance with many outlier laboratories.
- Especially the single values of the test sample mixture and the reference substance mixture of PG II show an insufficient (multimodal) distribution (see kernel density estimation, chapter 5.5, page 14 et seqq.). In test series 1 there are two groups of laboratories with clearly differing results, for which no reason can be found in the laboratory's additional information.
- In 5 out of 7 cases regarding the single pressure rise times and in 6 out of 9 cases regarding the ratios of mean pressure rise times, the repeatability standard deviation is considerably smaller (considered as percentages) than the reproducibility standard deviation of the single pressure rise times (see Table 5-5). Hence, it can be concluded that systematic deviations between laboratories are the essential reason for the different ratios of the laboratory mean pressure rise times, the classification differences and the relatively moderate discriminatory power between the classification groups (see shark profiles in chapter 5.6.1.2, page 21).
- The determined shark profiles are rather stump, thus the classification error (probability of incorrect classification) seems to be relatively high and a clear separation of the packing groups with an acceptable certainty is not possible – for neither of the test series.
- It is noticeable that two laboratories (251 and 261) show a very broad distribution of the single pressure rise times (see figures of laboratory results in chapter 8.3.1, page 59 et seqq.). In these cases, the laboratory mean pressure rise times exhibit a high uncertainty. Hence, control limits regarding the variation of measurements (quality assurance) are recommended for these laboratories.

6.2 Modified mixing procedure in test series 2 in comparison to test series 1

The analysis of the single pressure rise times suggests that the time from the "start of mixing until ignition (switching the power)" and the mixing duration show a significant effect on the pressure rise time (see also chapter 5.8.2 on page 46 and appendix 8.3.2 (identifiable by the p-value, which is approximately 0.05). In general, the higher the mixing duration, the shorter the pressure rise time. This holds also for the time of the "start of mixing until ignition (switching the power)".

A further effect regarding the mixing procedure can be observed by comparing the reproducibility of both test series in the following Table 6-1.

Table 6-1: Reproducibility standard deviation of both test series in comparison

Relative reproducibility standard deviation according to DIN 38402-45		
	Test series 1 (based on 9 laboratories)	Test series 2 (based on 7 laboratories)
Single pressure rise times		
PG II	77 %	70 %
PG III	27 %	43 %
TS	57 %	56 %
Ratio of laboratory mean pressure rise times		
PG III / PG II	48 %	45 %
TS / PG II	86 %	67 %
TS / PG III	47 %	16 %

In almost all cases – except for the single pressure rise times corresponding to PG III – the relative reproducibility standard deviation is lower (considerably lower for TS / PG III and TS / PG II and slightly lower for PG II, TS and PG III / PG II) in test series 2 (with the same mixing equipment and a constant mixing duration for all laboratories) than in test series 1. While the difference of the relative reproducibility standard deviation for the single pressure rise times between test series 1 and 2 is marginal, the relative reproducibility standard deviations for the ratios TS / PG II and TS / PG III in test series 2 are considerably lower than the values of test series 1.

As the performance of the laboratories is insufficient, in test series 1 as well as in test series 2, an improvement of the execution of the method is highly recommended. Considering the results it can be recommended:

- to confirm the adequacy of the modified mixing procedure according to test series 2 with the aid of a more specific investigation and
- to describe the more standardized mixing procedure (e.g. mixing duration and mixing equipment) in the method UN O.2 / EC A.21 in a more detailed way.

However, it must be recognized that further measures / actions might be necessary in addition (see next chapter).

6.3 Other influencing (disturbing) factors

The reason for the broad spread of the results and the deviations between the laboratories was analysed by an additional exploratory data analysis of the single pressure rise times of the laboratories of both test series. It was found that the mixing procedure is not the only reason for the spread of the results. Possible further reasons might be:

- the resistance of the ignition wire,
- the drying time of the cellulose,

- the reference substance mixtures (different suppliers/manufacturers) or a combination of the reference substance mixtures and the mixing procedure.

With the aid of an analysis of variance (ANOVA) it was shown that the following parameters have a significant influence on the pressure rise time:

- mass of the cellulose,
- mixing duration,
- time from the start of mixing until ignition (switching the power).

However, the conclusiveness of the findings is limited because the aim and the testing concept of this interlaboratory test were mainly focussing on the mixing procedure and not on other possible factors. Therefore it is recommended

- to confirm these findings with the aid of more specific investigations and
- to determine their influence on the classification in the sense of the method UN O.2 / EC A.21.

6.4 Recommendations for the participants of the interlaboratory test to improve the execution of the method

In view of the results of the interlaboratory test the following recommendations for improving execution of the method can be given to the participating laboratories (see Table 6-2).

Table 6-2: Recommendations to improve the execution of the method

Laboratory	Recommendation
106	No additional recommendations.
121	No additional recommendations.
127	Even though in test series 1 the result of this laboratory was validated as "satisfactory" for ratio TS / PG III and TS / PG II according to DIN 38402-45, it is recommended to check the reason for the relatively short pressure rise time of TS: <ul style="list-style-type: none"> • Check the influence of the relatively long drying time of the cellulose (72 h). Check compliance with the method concerning the drying procedure of the cellulose (drying time). • Check the influence of the resistance of the ignition wire with regard to the required resistance of 3.85 ohm/m.
201	No additional recommendations.
251	No additional recommendations.
261	In test series 1 the result of this laboratory was validated as "unsatisfactory" for ratio TS / PG III and TS / PG II according to DIN 38402-45 based on the relatively long pressure rise time of TS. It is recommended to check the influence of the resistance of the ignition wire with regard to the required resistance of 3.85 ohm/m.
907	No additional recommendations.
908	No additional recommendations.
910	In test series 1 the result of this laboratory was validated as "unsatisfactory" for ratio PG III / PG II according to DIN 38402-45 based on the relatively short pressure rise time of the reference mixture PG II. On the basis of the currently available data of this laboratory we cannot give recommendations.

6.5 Recommendations to improve execution of the method

Based on the interlaboratory test, the experience gained and the actual results, the following measures / actions are recommended:

1. Training of personnel:

- A training video "Procedure of mixing and filling the mixture in the pressure vessel" should be produced.
- Special samples should be manufactured and distributed centrally that may be used by the laboratories for their internal quality control (e.g. RM (reference material) or CRM (certified reference material)).
- An appropriate proficiency test scheme should be developed in order to be used for regular external quality control.

2. Development of the method UN O.2 / EC A.21

- Verify of the causes of the differences between the laboratories with the aid of more specific investigations (cause study).
- The description of the UN O.2 / EC A.21 should be revised in order to give a clear and unmistakable description of the method.

7 References

- [1] Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fifth revised edition, United Nations, New York and Geneva, 2009.
- [2] 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), OJ L 142, 31.5.2008.
- [3] ProLab Plus 2009 – The software package for method interlaboratory tests and proficiency tests; specially modified version of the software package, QuoData GmbH, Dresden.
- [4] Uhlig S, Lischer P (1998), Statistically-based performance characteristics in laboratory performance studies; *Analyst*, 123, 167-172.
- [5] Lueth P (2005) Cut off limit for the Liquid Oxidizer Test (UN O.2) for diluted aqueous solutions of solid oxidizing substances. IGUS EOS: 5 to 7 April 2005; Washington DC.
- [6] DIN 38402-45: 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.

8 Appendix

8.1 Test instruction

Round Robin Test on the method UN O.2 / EC A.21 "Test for oxidizing liquids" Instruction to perform the Round Robin Test

2009-10-20

Dear colleagues,

As announced the *Center for quality assurance for testing of dangerous goods and hazardous substances* agreed to perform a standardized round robin test (according to the principles of ISO 5725-2 or DIN 38402 A 42, A 45 and others) on the method UN O.2 / EC A.21 "Test for oxidizing liquids".

11 laboratories did confirm to participate in this round robin test. For this test the substance "aqueous solution of Sodium Nitrate" was chosen as test substance.

Together with the test substance "aqueous solution of sodium nitrate" (approx. 60 ml) you receive from BAM a prepared data file for the acquisition of your measurement data.

Therefore we ask the participating laboratories to perform the UN O.2 / EC A.21 test with this substance submitted to you by BAM according to the test procedure in the UN Test Manual⁵ (4th rev. edition, 2003, Chapter 34.4.2) or, respectively, to the European test method A.21⁶ (see: <http://ecb.jrc.it/testing-methods/>).

We ask you to **perform the tests by end of December 2009** and to **send back the duly completed data file by January 4th 2010** to Peter Lueth via email: peter.lueth@bam.de.

1st Test series

Please perform the 1st Test series under the following special conditions:

- If possible, prepare a mixture with a precision of **2.50 g ± 0.01 g of the liquid** (test sample / reference substance) **and 2.50 g ± 0.01 g of the dried Cellulose**.
- The test should always be performed by one and the same laboratory assistant, otherwise it should be noted.
- If possible, perform the trials of this test series within one working day.
- For statistical purposes it is necessary to perform the tests in the following sequence (order):

1. Test reference mixture PG III:	Trial 1-3
2. Test reference mixture PG II:	Trial 1-3
3. Test reference mixture PG I:	Trial 1-3
4. Test sample:	Trial 1-3

⁵ Test methods for dangerous goods in the scope of the "United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fourth revised edition, 2003"

⁶ EC-Test methods – Commission regulation (EC) No 440/2008

5. Test reference mixture PG III:	Trial 4-5
6. Test reference mixture PG II:	Trial 4-5
7. Test reference mixture PG I:	Trial 4-5
8. Test sample:	Trial 4-5

All the other procedures as prescribed in chapter 34.4.2 of the UN Test Manual (4th rev. edition, 2003) or in chapter 1.6 of the European method A.21 should be applied as usual in your laboratory.

2nd Test series (additional, optional)

We additionally ask you to perform a 2nd **optional** Test series using the following modified mixing procedure:

Note 1.: Use a ceramic mortar and a pistil (e.g. porcelain) as shown in figure 1 instead of a glass beaker and a glass stirring rod as it is prescribed in paragraph 34.4.2.3.1 of the UN Test Manual.

Note 2.: Carefully homogenize the liquid and the cellulose by using the pistil by a mostly circular motion and with only very little force on the pistil. For this purpose use three fingers as demonstrated in figure 1.

Note 3.: Homogenize the liquid and the cellulose within exactly 2 minutes.



Fig. 1: Mixing by using a ceramic mortar and a pistil instead of a glass beaker and a glass stirring rod

If possible, perform the trials of 2nd Test series within one working day and within the same week as the 1st Test series.

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

1. Test reference mixture PG III:	Trial 1-3
2. Test reference mixture PG II:	Trial 1-3
3. Test sample:	Trial 1-3
4. Test reference mixture PG III:	Trial 4-5
5. Test reference mixture PG II:	Trial 4-5
6. Test sample:	Trial 4-5

Important:

The tests of the 2nd test series should be performed in the same way as in the 1st test series. Only the mixing procedure should be changed (see Note 1-3)!

If you have any questions or difficulties with the schedule, please do not hesitate to contact us.
We thank you for participating in this round robin test and wish you a successful performance.

Peter Lueth (BAM)

October 2009

8.2 Laboratory data input form

Center for quality assurance for testing of dangerous goods and hazardous substances
 Round Robin Test 2009 on the method UN O.2 / EC A.21 "Test for oxidizing liquids"
 Data input form for 2 test series

Please complete the grey fields.

Laboratory No:

Cellulose:

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

65% aqueous nitric acid:

Supplier:
 Name:
 Batch No.:
 Concentration according to certificate:
 Checked original concentration [%]:
 Adjusted concentration * [%]:
 Remarks:

*...if adjusted for using as a reference due to a deviation from the required 65% reference concentration.

40% aqueous sodium chlorate solution:

Supplier:
 Name:
 Batch No.:
 Concentration [%]:
 Remarks:

50% perchloric acid:

Supplier:
 Name:
 Batch No.:
 Concentration according to certificate:
 Checked original concentration [%]:
 Adjusted concentration * [%]:
 Remarks:

*...if adjusted for using as a reference due to a deviation from the required 50% reference concentration.

Description of the test equipment:

Name / type of ignition wire:
 Resistance of the ignition wire [ohm/m]:
 Diameter of the coil of the ignition wire [mm]:
 Name / type / material of the bursting disk:
 Name / type of the pressure-measuring device:

(Please fill out)
 Further description of the used test equipment:
 Oszilloskop / Firma: Hewlett Packard / Seriennummer: US 38310292
 Ladungsverstärker / Firma: Kistler / Seriennummer: BN 619077
 Druckaufnehmer 200 bar / Firma: Kistler / Seriennummer: 603 B/BN643200

Description of your procedure to fill the pressure vessel:

(Please fill out)
 Description of your procedure of filling the pressure vessel
 (number of portions, intensity of tapping, equipment (e.g. funnel, rod, brush), duration...):
 Das genau 2 Minuten lang gerührte Gemisch wurde über einen kleinen Plastiktrichter, mit Hilfe eines kleinen Metallspatels, in die Druckapparatur eingebracht (teilmweise gestopft).

Test series 1:
 Test substance / reference substances and cellulose
 mixed / treated according to paragraph 34.4.2 of the UN
 Test Manual

Description of your mixing procedure in Test series 1:

[Please fill out]
 Description of your mixing procedure
 (vessel, equipment, intensity, duration...):
 Nach der Einwaage von 2,5 g Cellulose und 2,5 Flüssigkeit wurden die beiden Komponenten in einem 50 ml Becherglas mit Hilfe eines Glasstabes, genau 2 Minuten lang gemischt. Als Zeitmessung wurde eine Stoppuhr benutzt. Danach wurden klebrige Substanzrückstände mit einem Metallspatel vom Glasrand gekratzt und eingefüllt.

Results

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

PG III (65% aqueous nitric acid : Cell. = 2,5 g : 2,5 g):

Order no:	1	2	3	13	14
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time: start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remarks:					

Mean pressure rise time of trial 1-5 [ms]:
 \$DIV0!

PG II (40% aqueous sodium chlorate solution : Cell. = 2,5 g : 2,5 g):

Order no:	4	5	6	15	16
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time: start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remarks:					

Mean pressure rise time of trial 1-5 [ms]:
 \$DIV0!

PG I (50% perchloric acid : Cell. = 2,5 g : 2,5 g):

Order no:	7	8	9	17	18
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time: start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remarks:					

Mean pressure rise time of trial 1-5 [ms]:
 \$DIV0!

Test Sample (RR test sample : Cell. = 2,5 g : 2,5 g):

Order no:	10	11	12	19	20
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remarks:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time: start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remarks:					

Mean pressure rise time of trial 1-5 [ms]:
 \$DIV0!

Test series 2 (additional):

Test substance and cellulose mixed by the modified mixing procedure

Modified mixing procedure in Test series 2:

Please perform all tests of the test series 2 using the modified mixing procedure:

1. Use a ceramic mortar and a pestle (e.g. porcelain) as shown in the right figure instead of a glass beaker and a glass stirring rod as it is prescribed in paragraph 24.4.2.3.1 of the UN Test Manual.

2. Carefully homogenize the liquid and the cellulose by using the pestle by a mostly circular motion and with only somewhat / very low force on the pestle (for this purpose use three fingers as demonstrated in the right figure).

3. Homogenize the liquid and the cellulose within exactly 2 minutes.



Results

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

PG III (65% aqueous nitric acid:Cell. = 2,5 g : 2,5 g):

Order no:	21	22	23	20	21
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remark:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remark:					

Mean pressure rise time of trial 1-5 [ms]:
\$DIV/0!

PG II (40% aqueous sodium chlorate solution : Cell. = 2,5 g : 2,5 g)

Order no:	24	25	26	22	23
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remark:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remark:					

Mean pressure rise time of trial 1-5 [ms]:
\$DIV/0!

Test Sample (RR test sample : Cell. = 2,5 g : 2,5 g)

Order no:	27	28	29	34	35
Date:					
Time [h:mm]:					
Laboratory assistant (name):					
Mass of the liquid [g] (2 decimal, e.g. 2,51):					
Mass of the cellulose [g] (2 decimal, e.g. 2,49):					
Ambient temperature [°C]:					
Ambient pressure [mbar]:					
Ambient relative air humidity [%]:					
Remark:					
Trial:	1	2	3	4	5
Pressure rise time [ms] (without decimal, e.g. 3789):					
Mixing duration [min] (1 decimal, e.g. 1,8):					
Time start mixing until switching the power [min] (1 decimal, e.g. 9,8):					
Remark:					

Mean pressure rise time of trial 1-5 [ms]:
\$DIV/0!

Please send back this completed data form by January 4th 2010 to Peter Lueth (peter.lueth@bam.de)

Additional remarks to the round robin test:

(Please fill out)
 Additional remarks / your opinion on the round robin test (schedule, costs, suggestion for improvement...):
 Aufgrund der technischen Zu- bzw. Abfuhr im Bunker änderten sich die Temperatur und Feuchtebedingungen.
 Es wurde ein Achat-Mörser und Achat-Pestil benutzt.

8.3 Analysis of single pressure rise times

8.3.1 Summary of single pressure rise times

8.3.1.1 Test series 1 – Reference substance mixture PG I

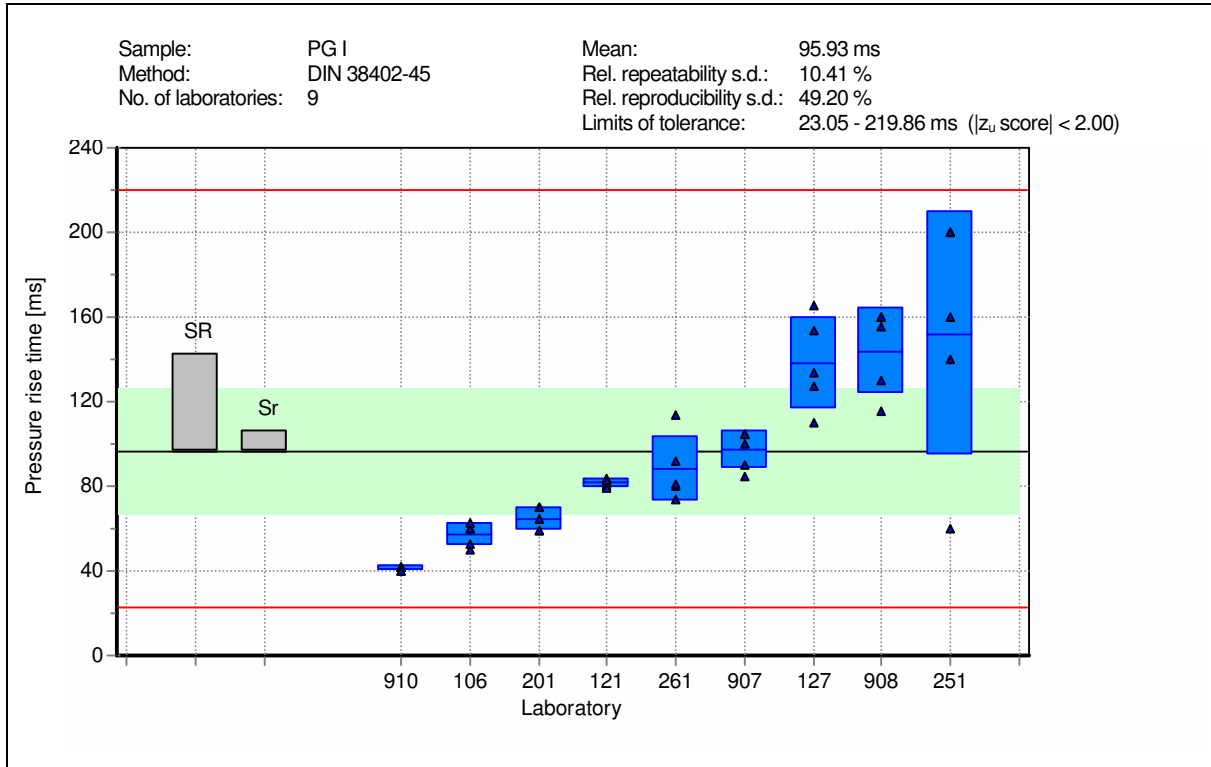


Figure 8-1: Analysis of single pressure rise times [ms] – PG I in test series 1

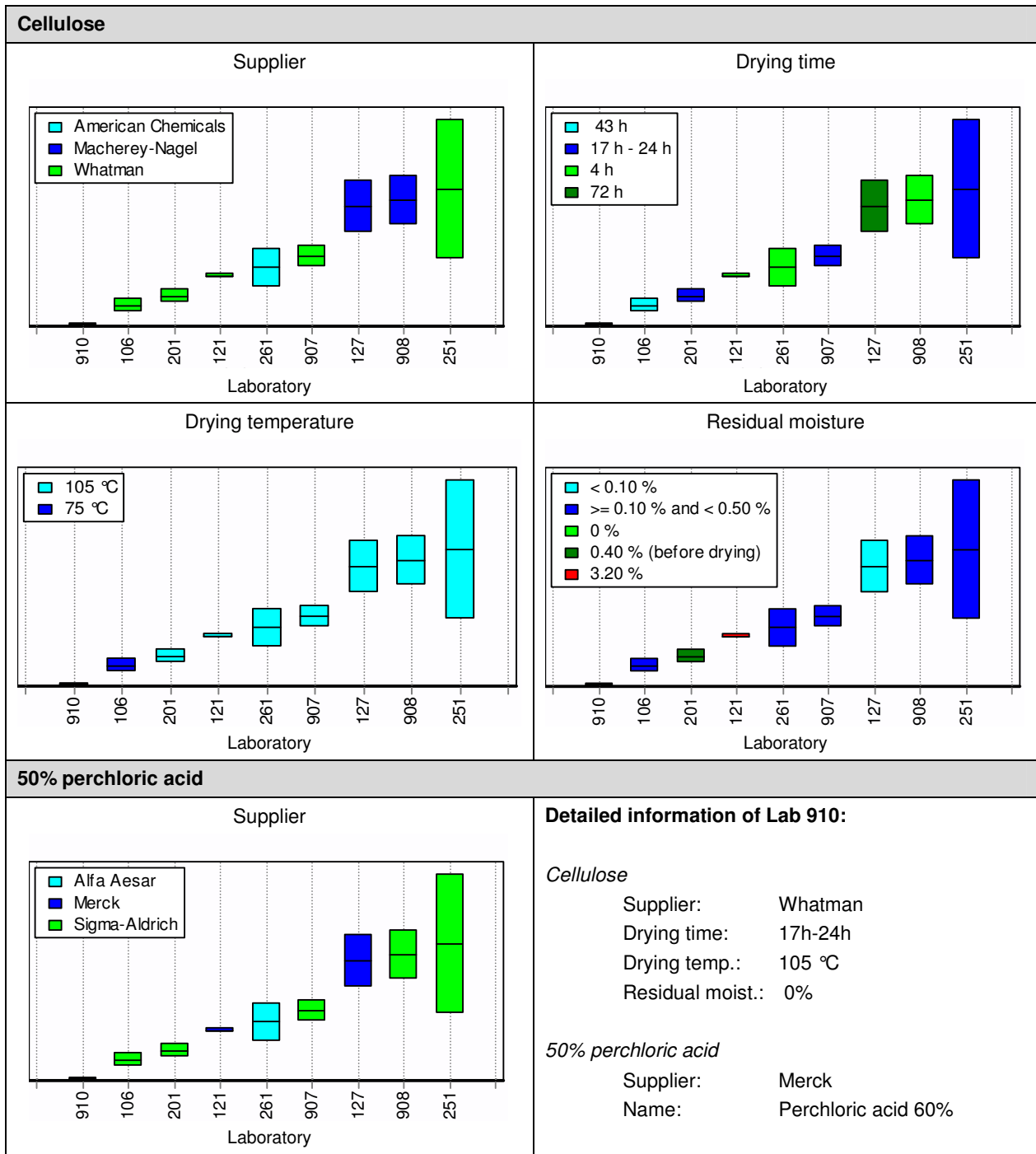


Figure 8-2: Pressure rise time in dependence on different laboratory specific parameters for PG I in test series 1
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-1)

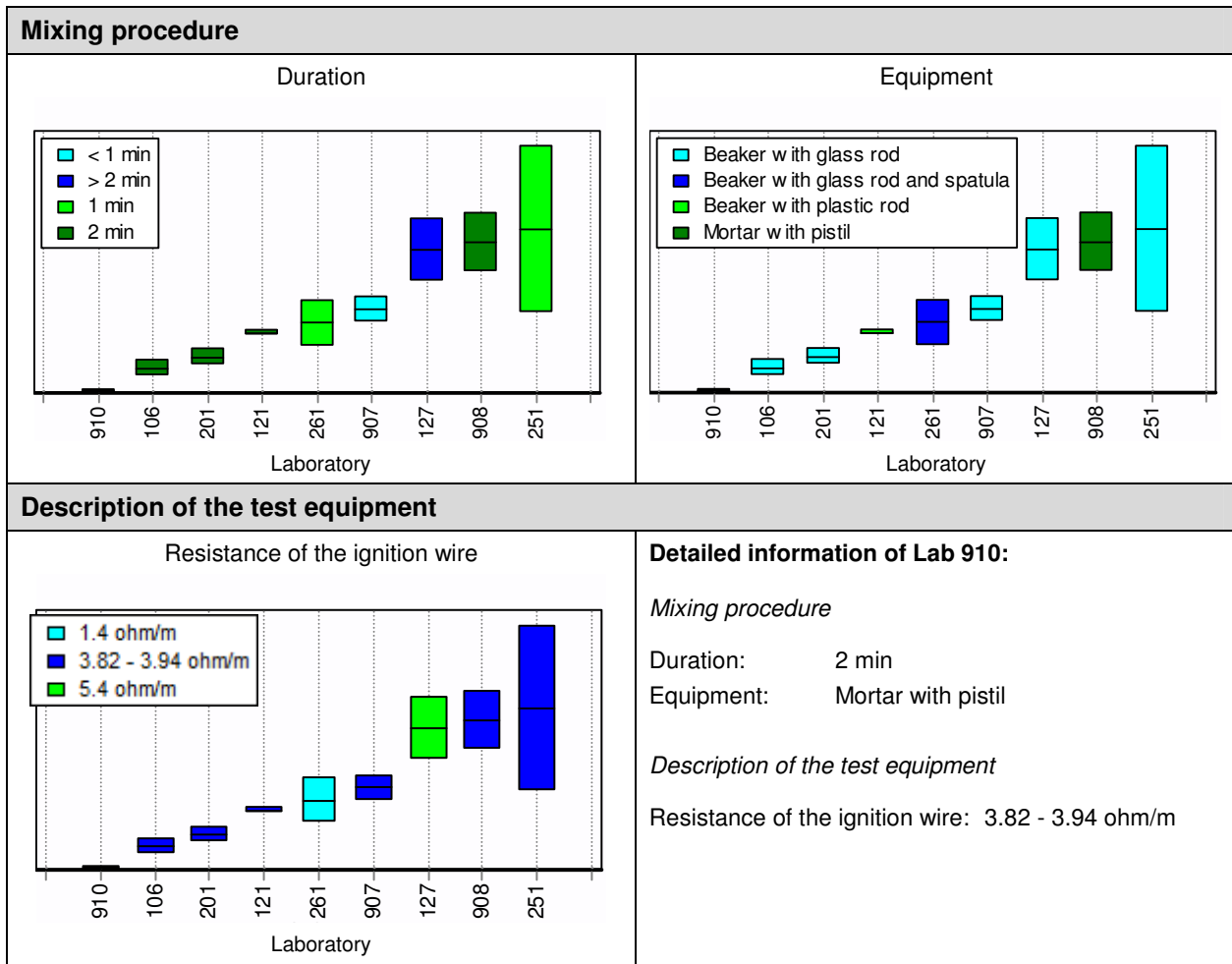


Figure 8-3: Pressure rise time in dependence on different laboratory specific parameters for PG I in test series 1
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-1)

8.3.1.2 Test series 1 – Reference substance mixture PG II

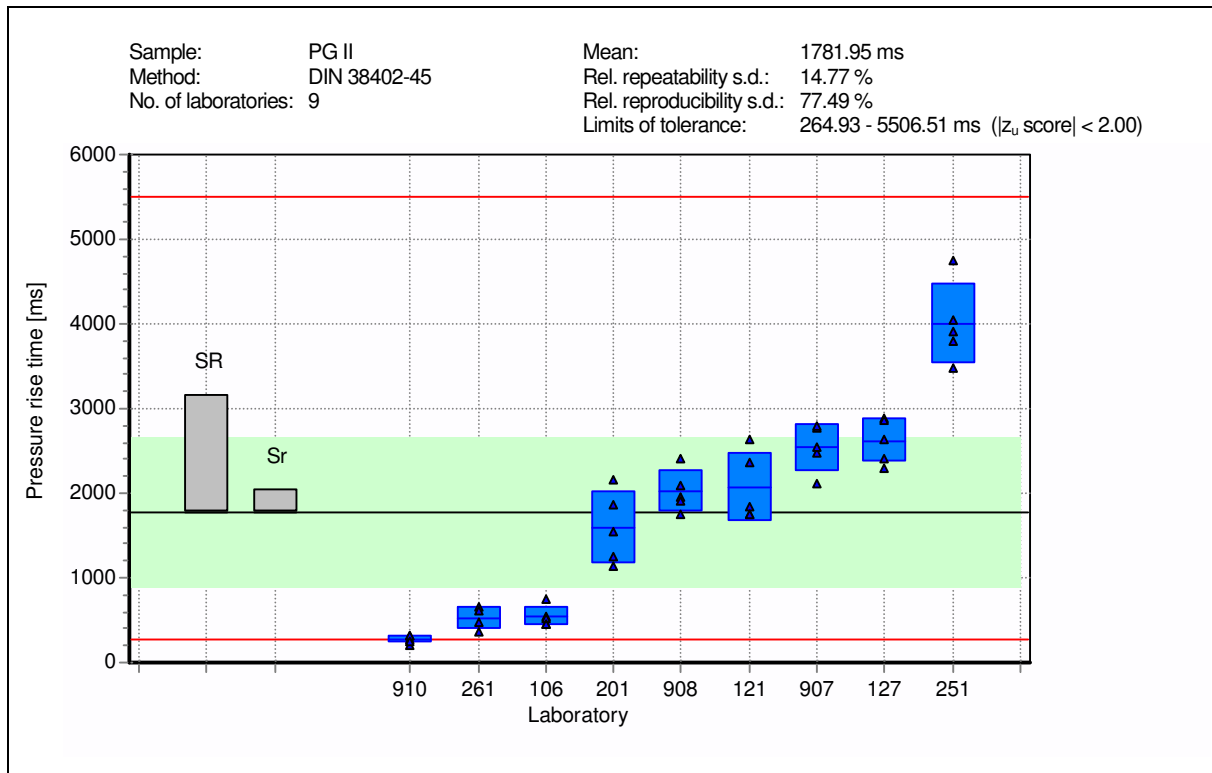


Figure 8-4: Analysis of single pressure rise times [ms] – PG II in test series 1

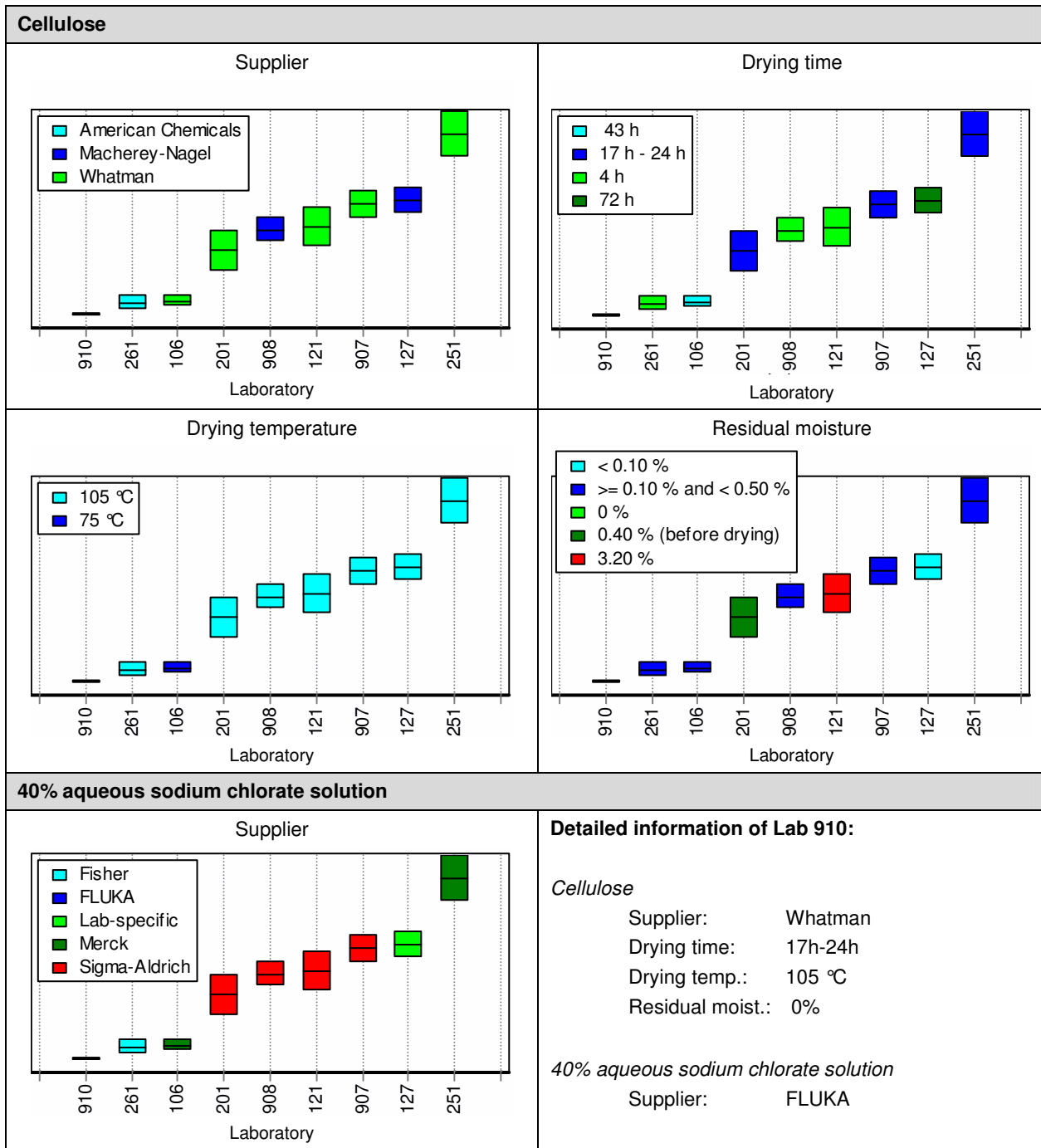


Figure 8-5: Pressure rise time in dependence on different laboratory specific parameters for PG II in test series 1
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-4)

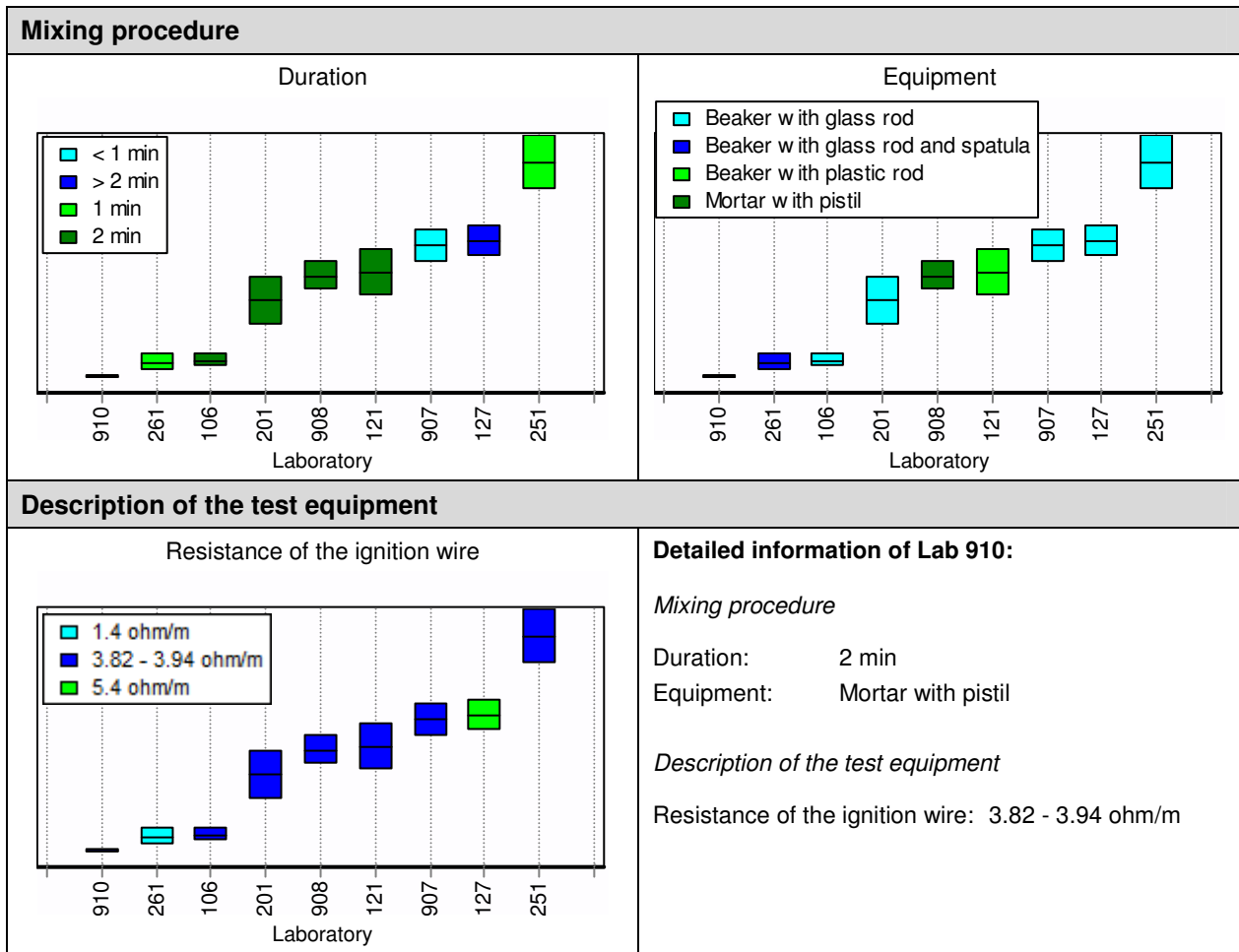


Figure 8-6: Pressure rise time in dependence on different laboratory specific parameters for PG II in test series 1
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-4)

8.3.1.3 Test series 1 – Reference substance mixture PG III

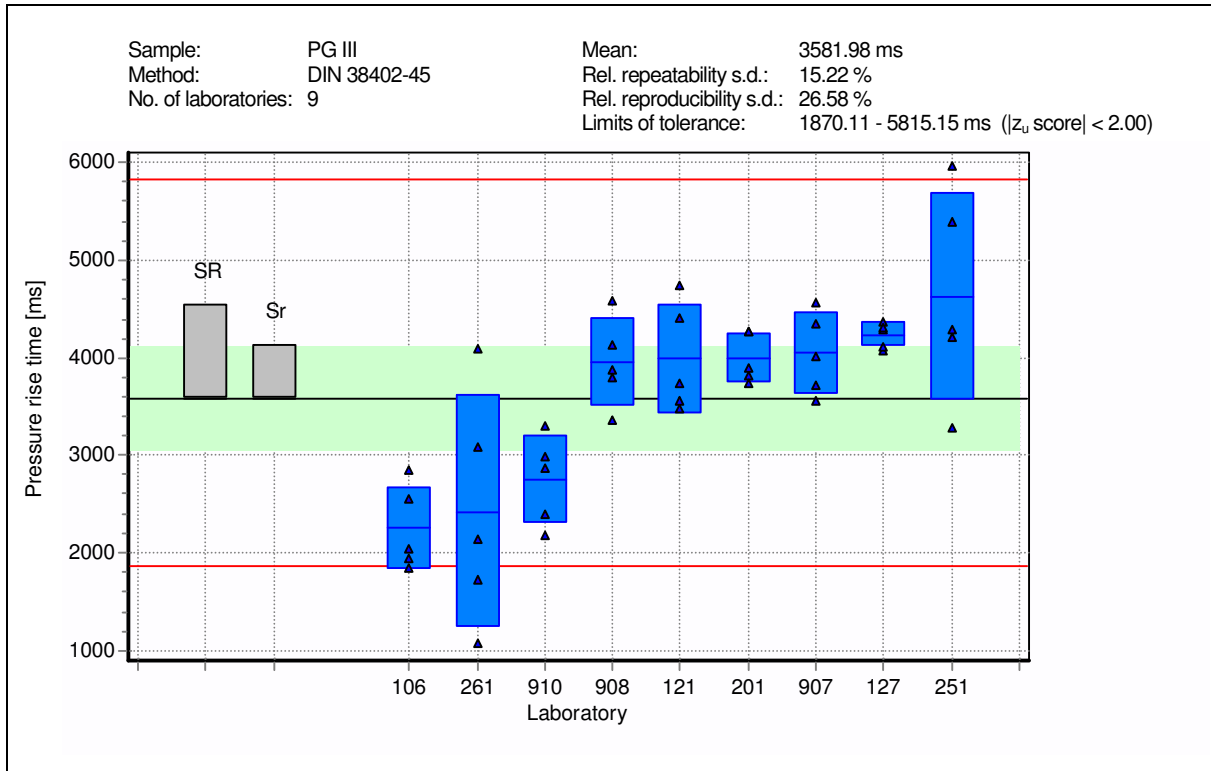


Figure 8-7: Analysis of single pressure rise times [ms] – PG III in test series 1

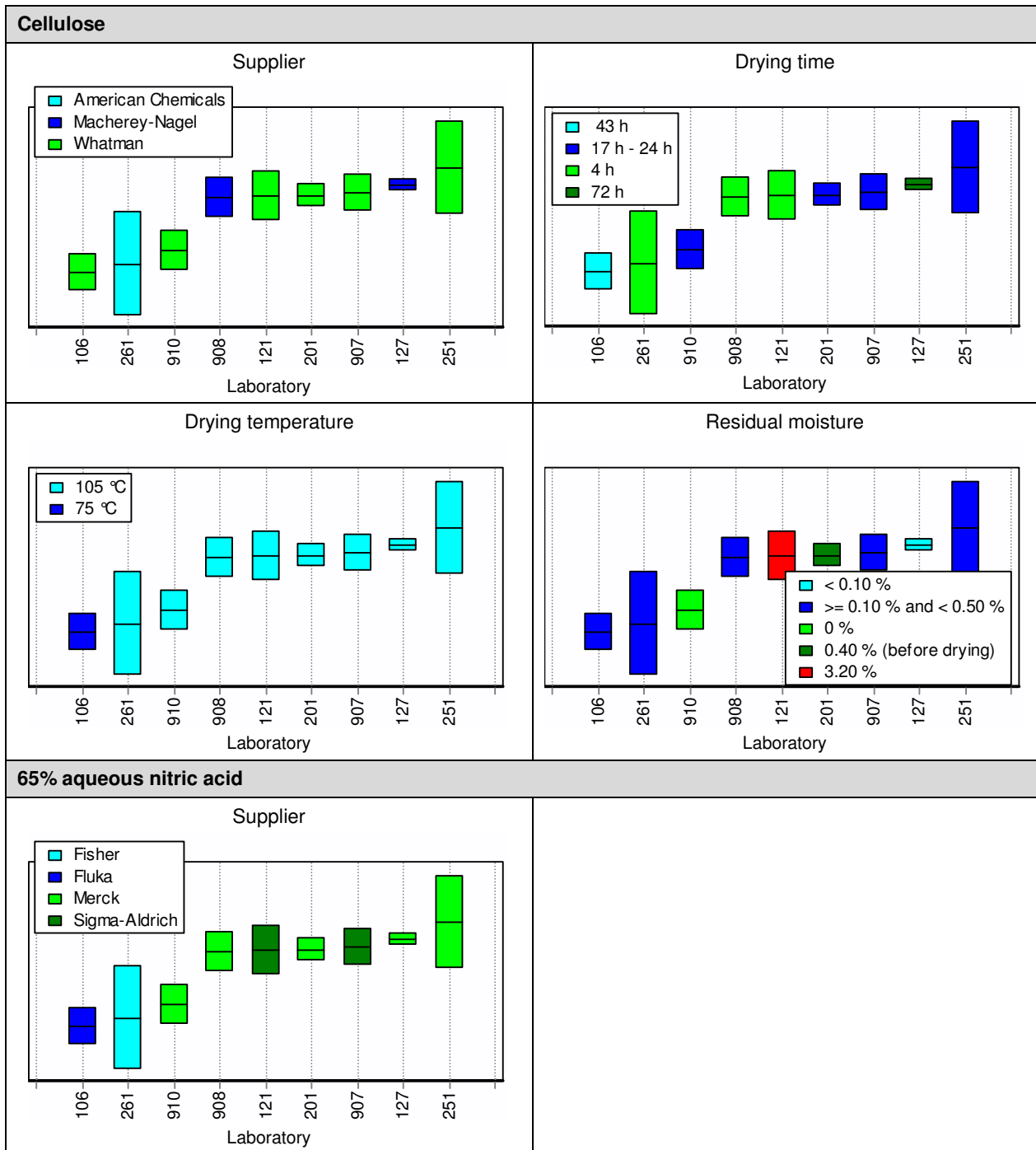


Figure 8-8: Pressure rise time in dependence on different laboratory specific parameters for PG III in test series 1 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-7)

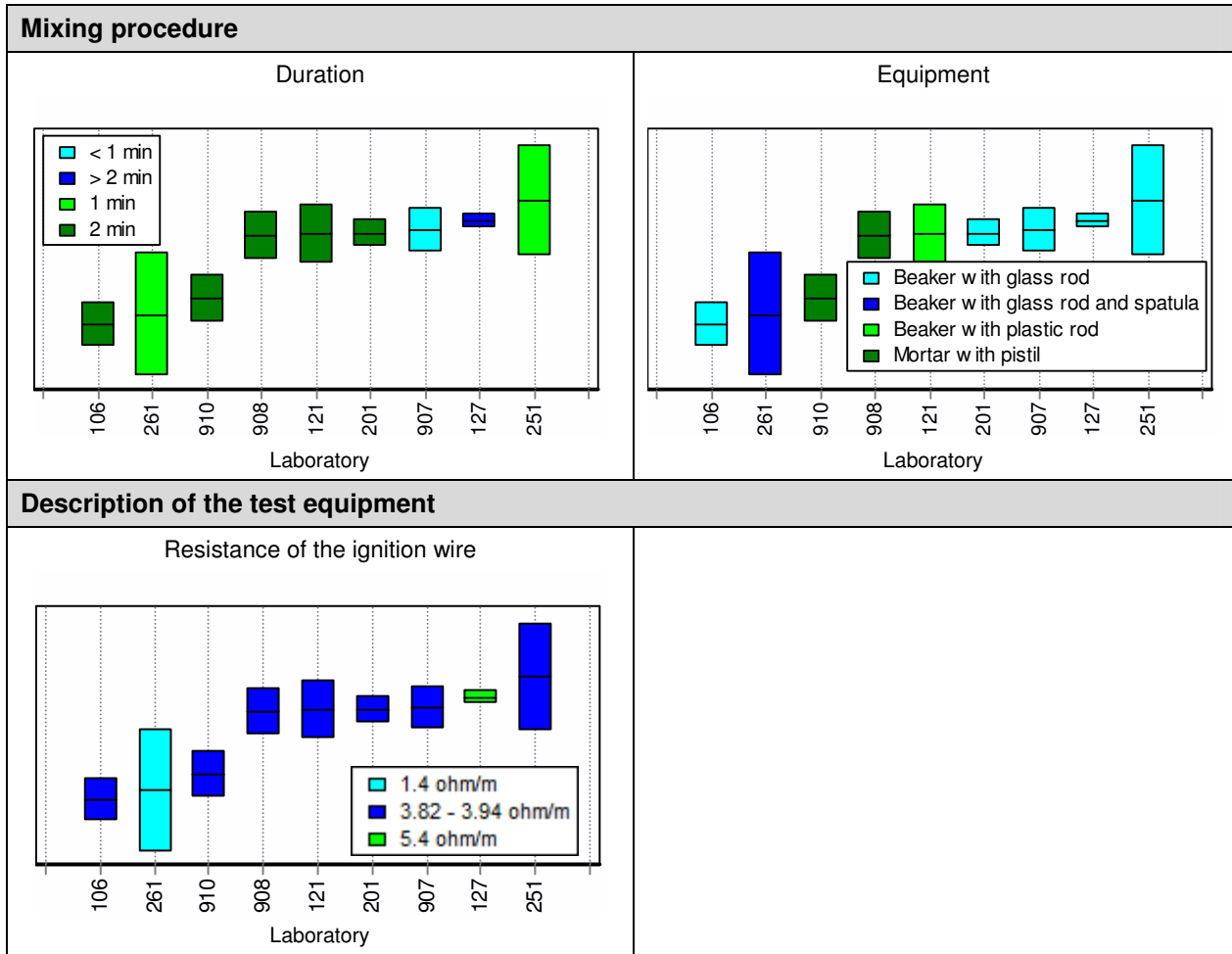


Figure 8-9: Pressure rise time in dependence on different laboratory specific parameters for PG III in test series 1
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-7)

8.3.1.4 Test series 1 – Test sample mixture TS

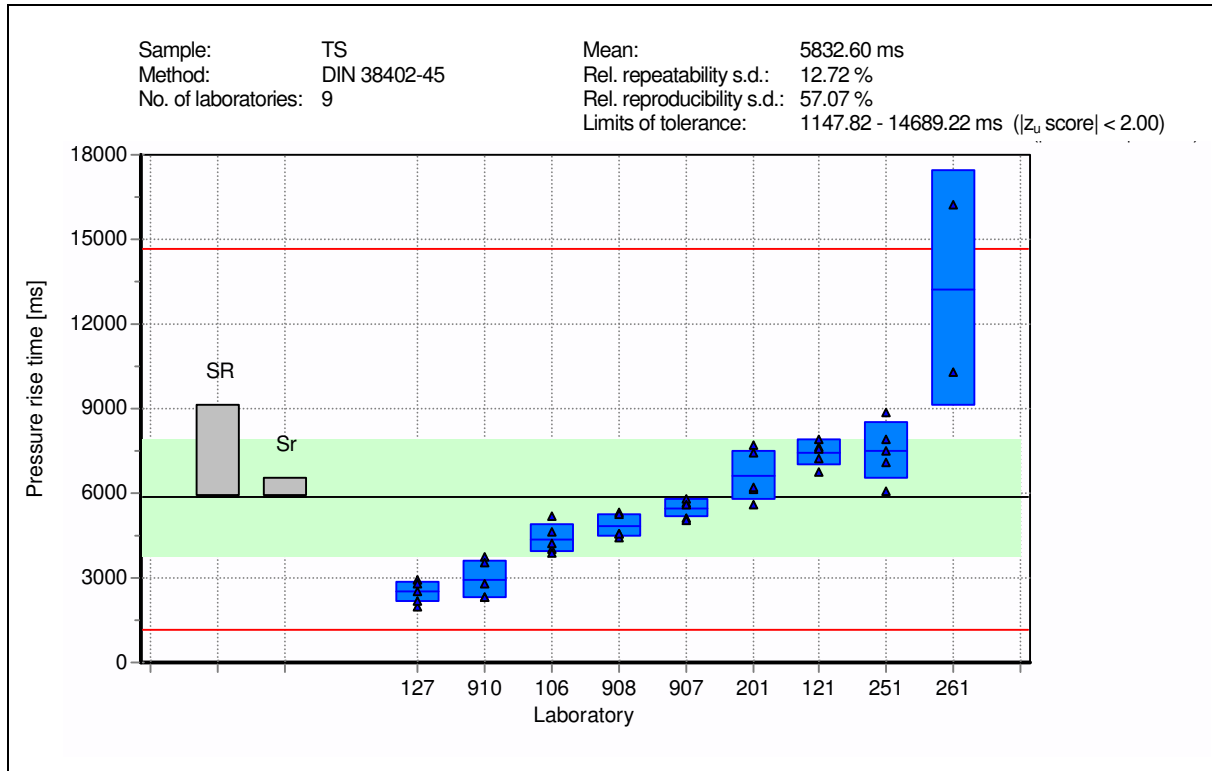


Figure 8-10: Analysis of single pressure rise times [ms] – TS in test series 1

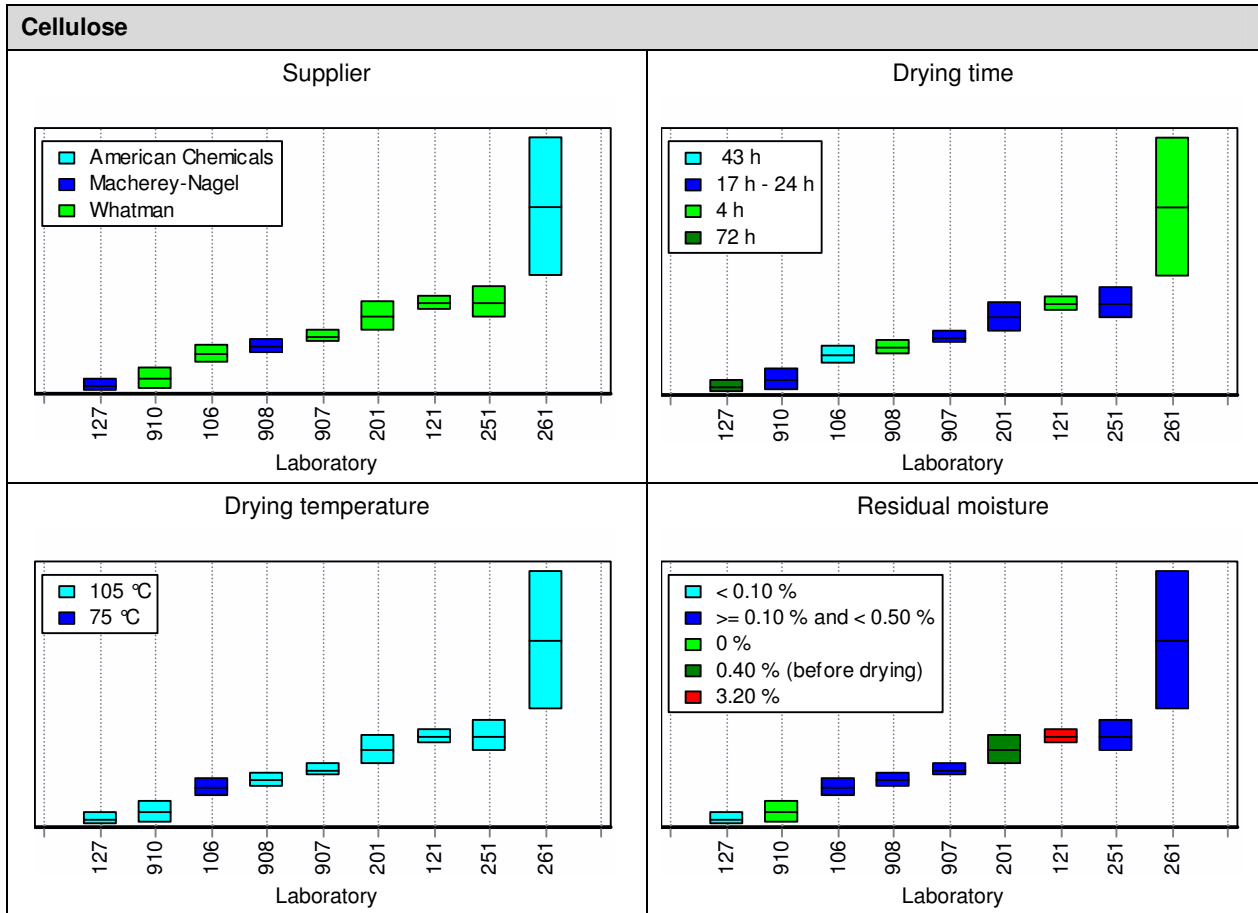


Figure 8-11: Pressure rise time in dependence on different laboratory specific parameters for TS in test series 1
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-10)

8.3.1.5 Test series 2 – Reference substance mixture PG II

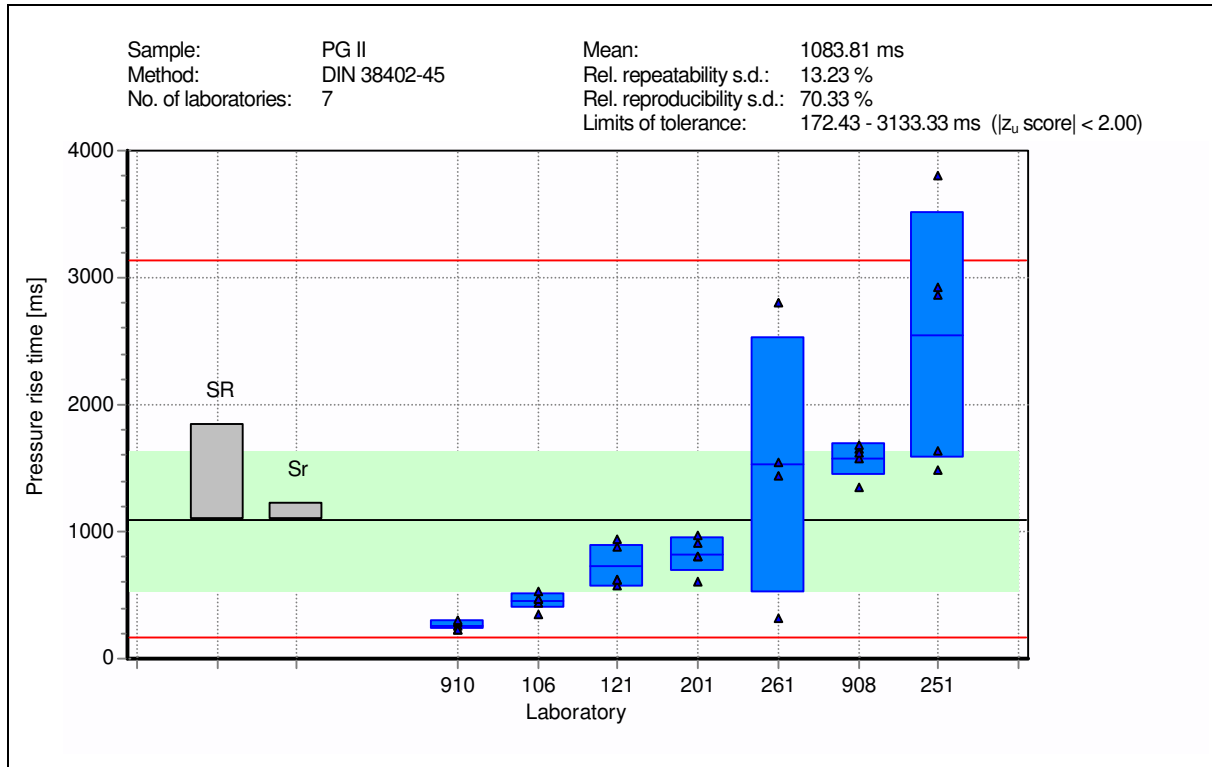


Figure 8-12: Analysis of single pressure rise times [ms] – PG II in test series 2

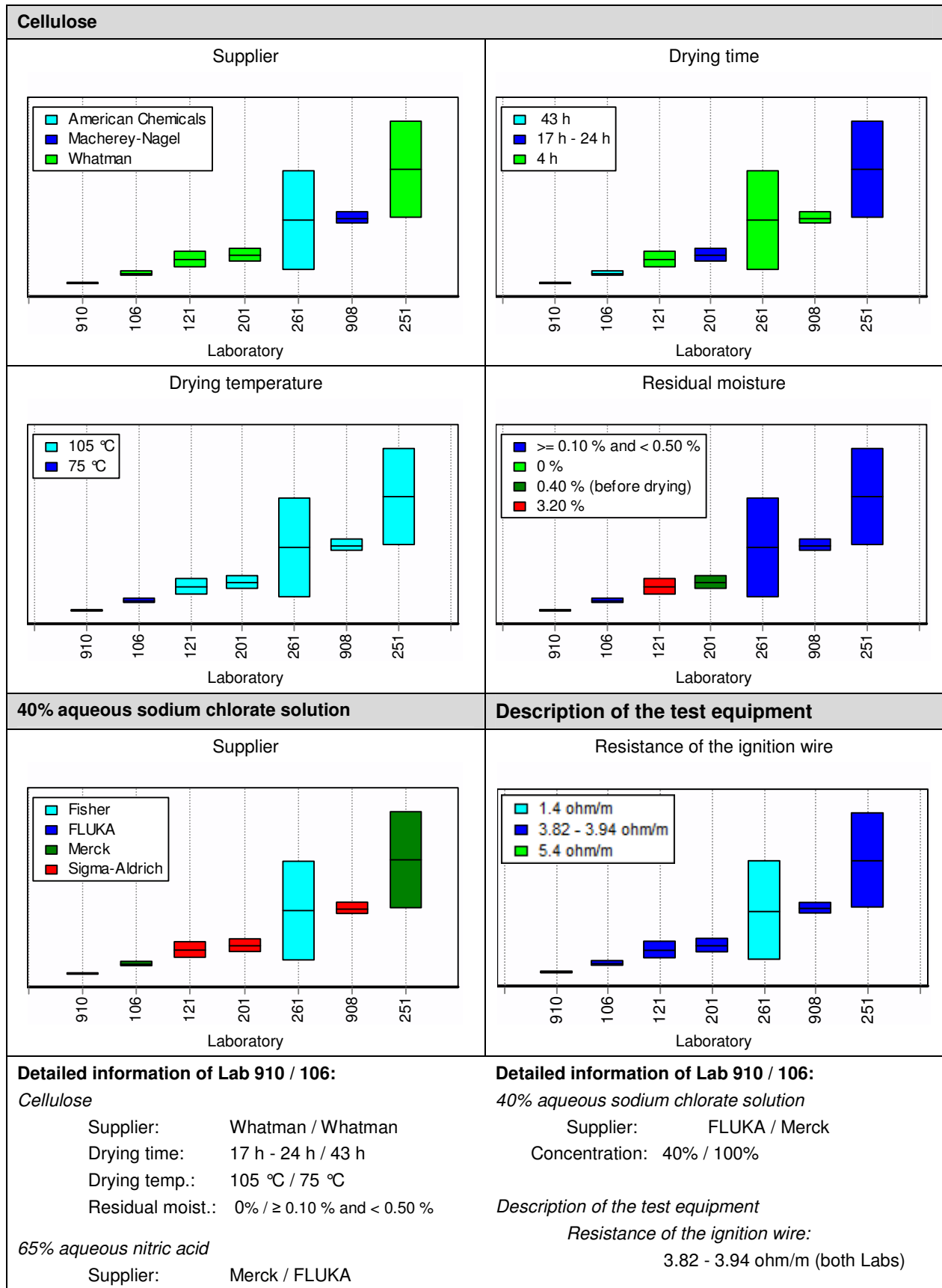


Figure 8-13: Pressure rise time in dependence on different laboratory specific parameters for PG II in test series 2
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-12)

8.3.1.6 Test series 2 – Reference substance mixture PG III

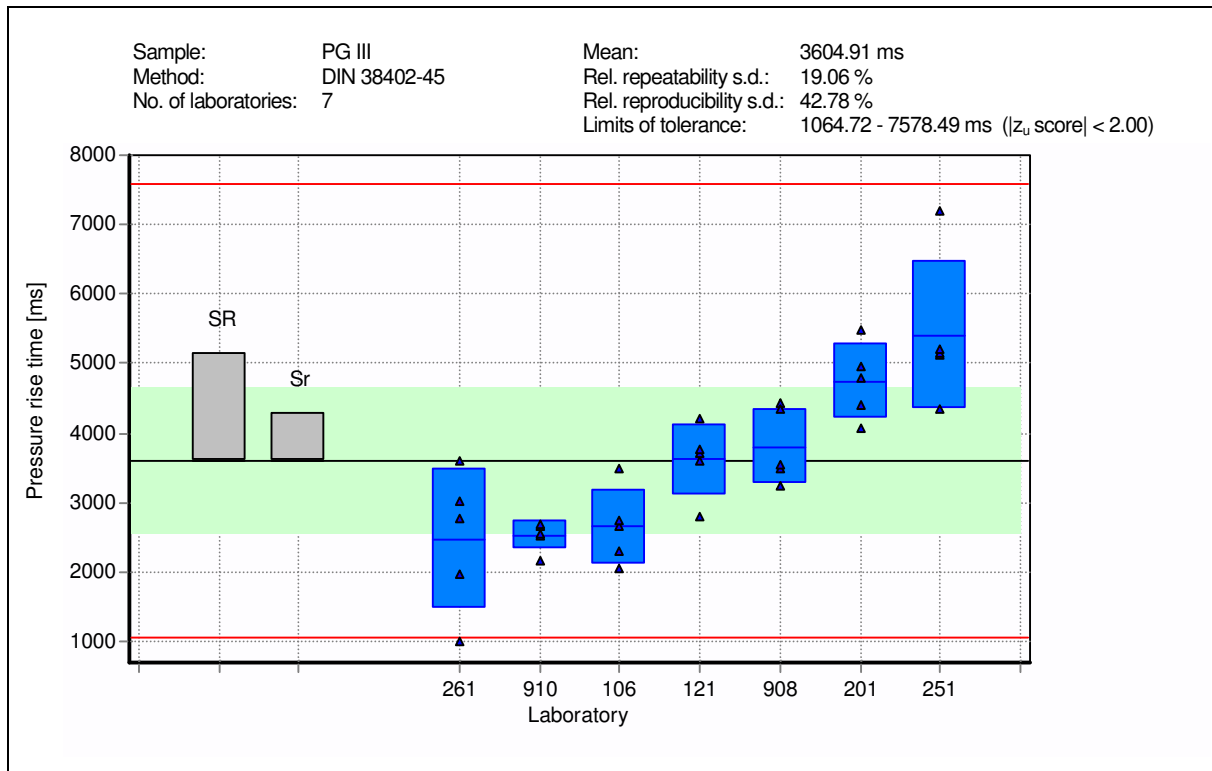


Figure 8-14: Analysis of single pressure rise times [ms] – PG III in test series 2

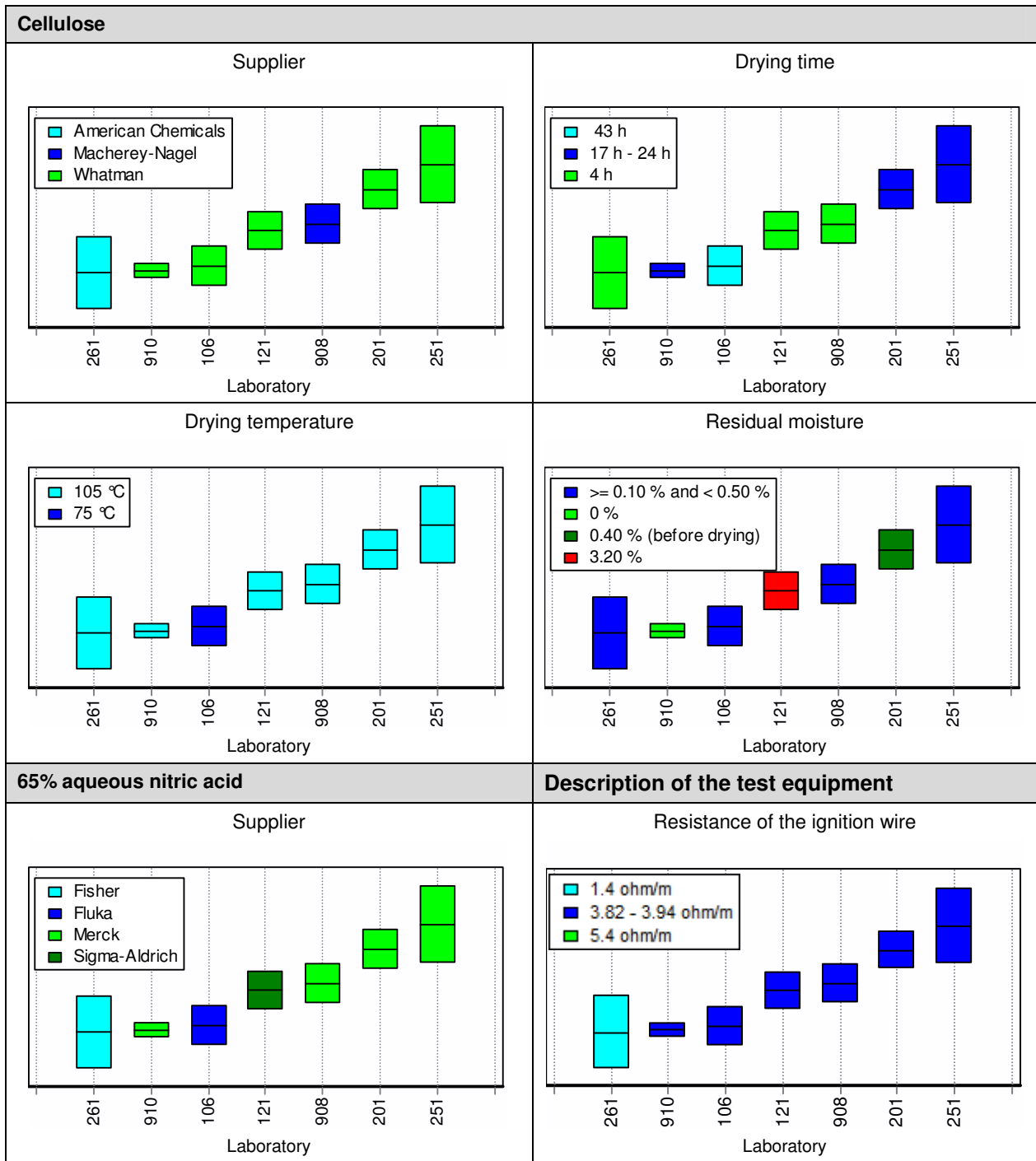


Figure 8-15: Pressure rise time in dependence on different laboratory specific parameters for PG III in test series 2
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-14)

8.3.1.7 Test series 2 – Test sample mixture TS

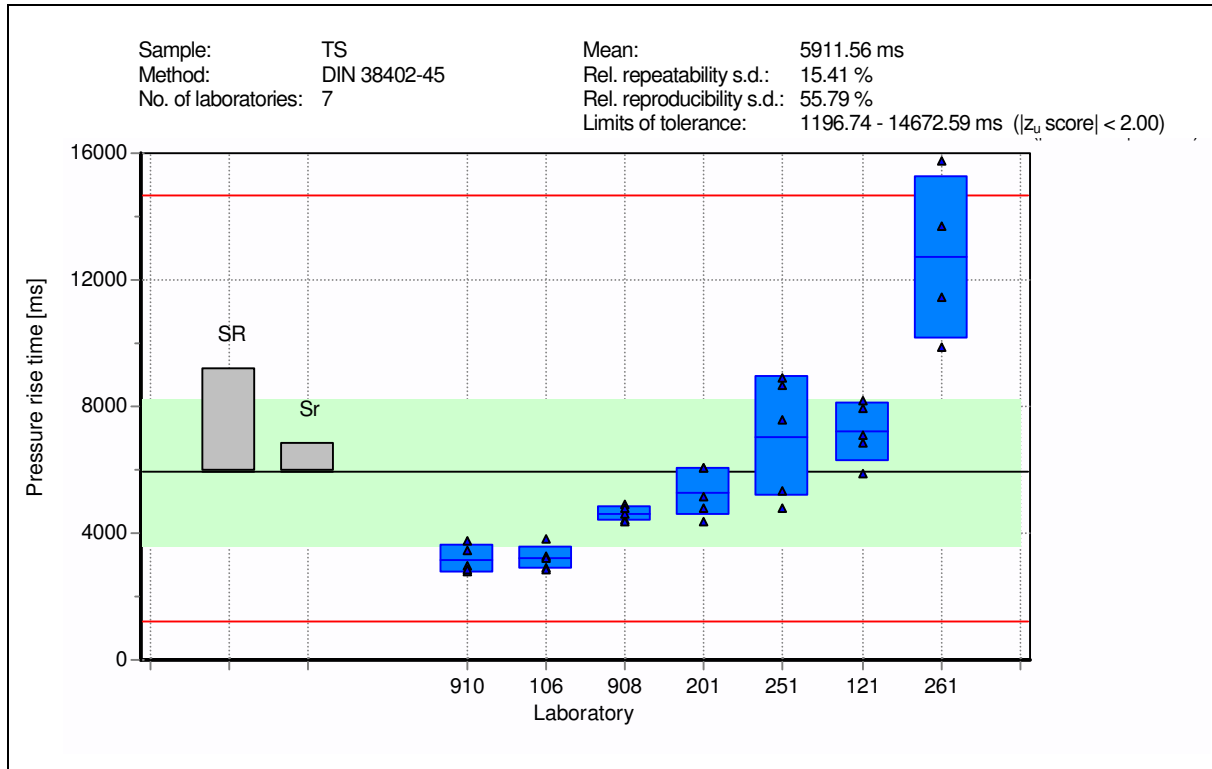


Figure 8-16: Analysis of single pressure rise times [ms] – TS in test series 2

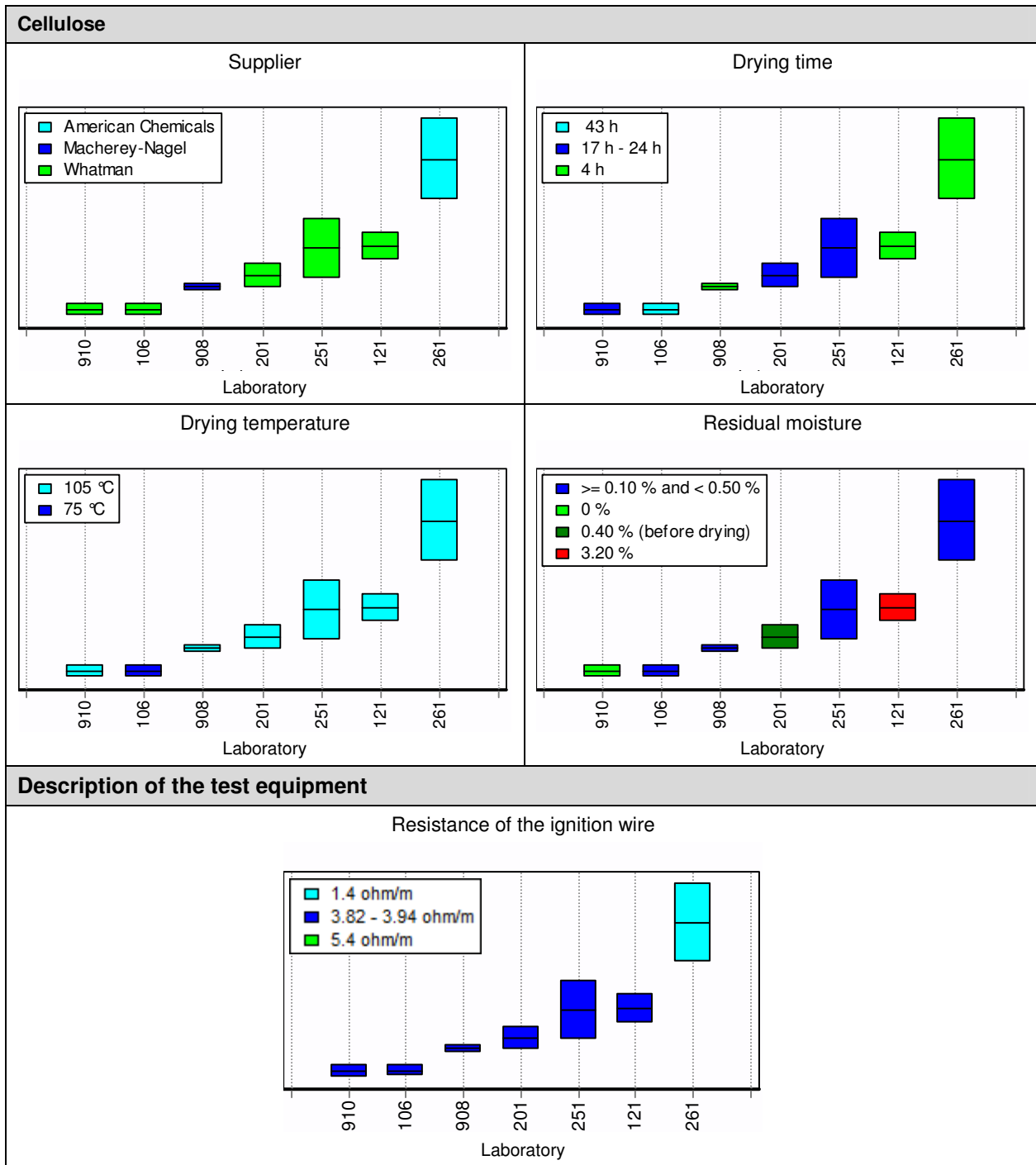


Figure 8-17: Pressure rise time in dependence on different laboratory specific parameters for TS in test series 2
 (Simplified view: proportional scaling of the ordinate (pressure rise time [ms]) based on Figure 8-16)

8.3.2 Detailed results of effect analysis of single pressure rise times based on trial-specific detailed information

Table 8-1: ANOVA table for standardized pressure rise time [in ms] (only significant effect are listed)

Effect	Sum of Squares	Df	Mean Square	F-Ratio	p-Value
Lab	101.447	8	12.681	28.1	0
Series	1.808	1	1.808	4.01	0.0463
Mass of the cellulose	4.328	1	4.328	9.6	0.0022
Mixing duration	1.731	1	1.731	3.8	0.0511
Time start mixing until switching the power	1.825	1	1.825	4.1	0.0453
Residuals	116.324	258	0.451		
Total (corrected)	230.267	270			

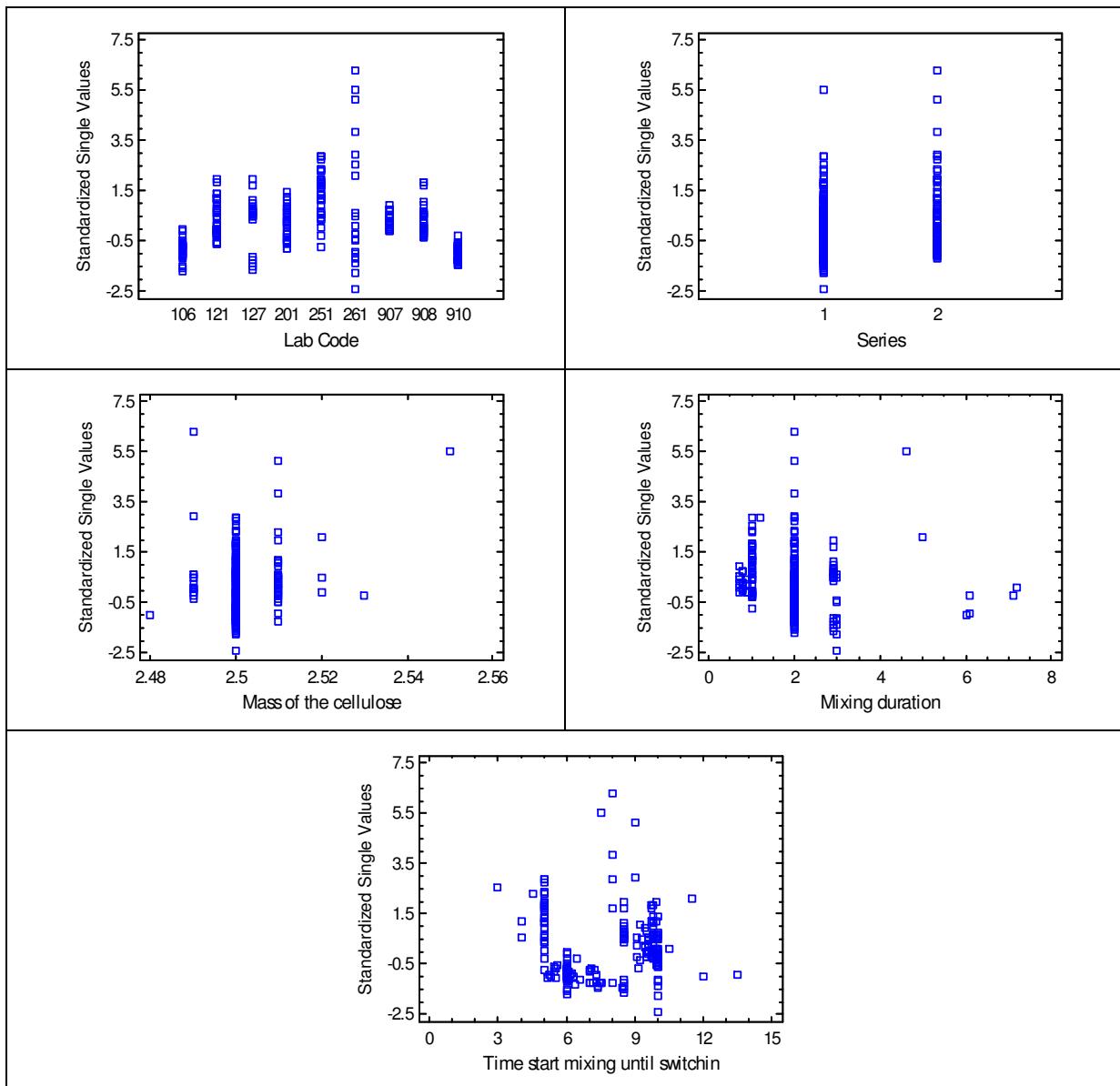


Figure 8-18: Dependence of standardized pressure rise time from significant parameters

8.4 Analysis of laboratory mean pressure rise times

8.4.1.1 Test series 1

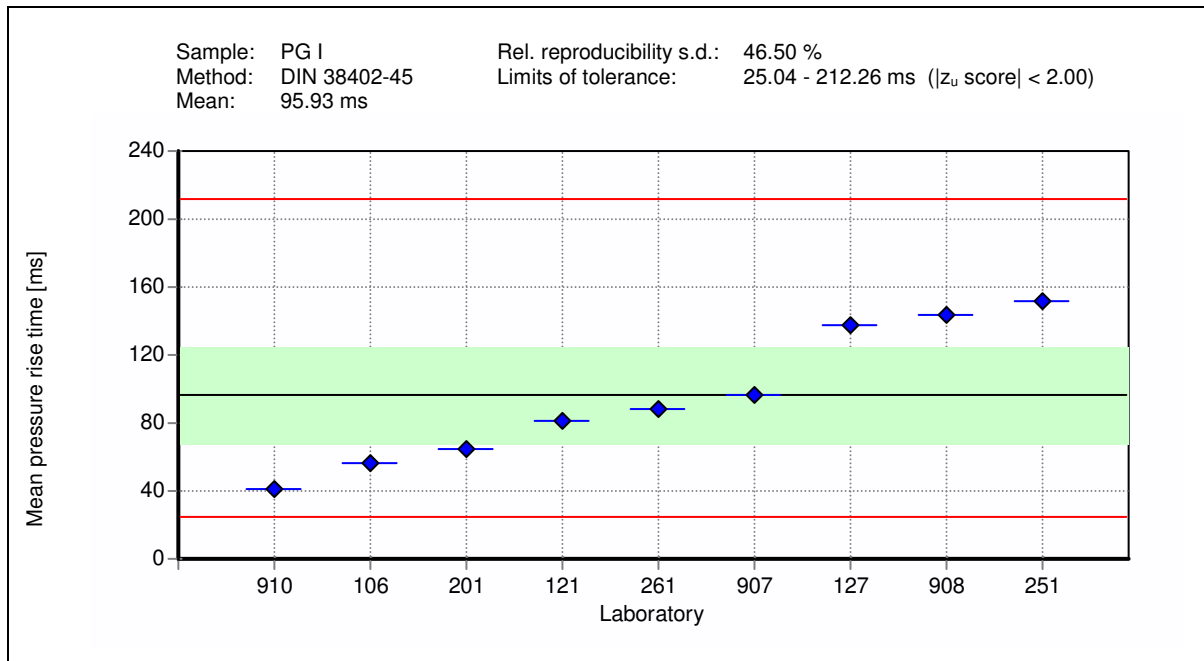


Figure 8-19: Analysis of laboratory mean pressure rise times [ms] – PG I in test series 1

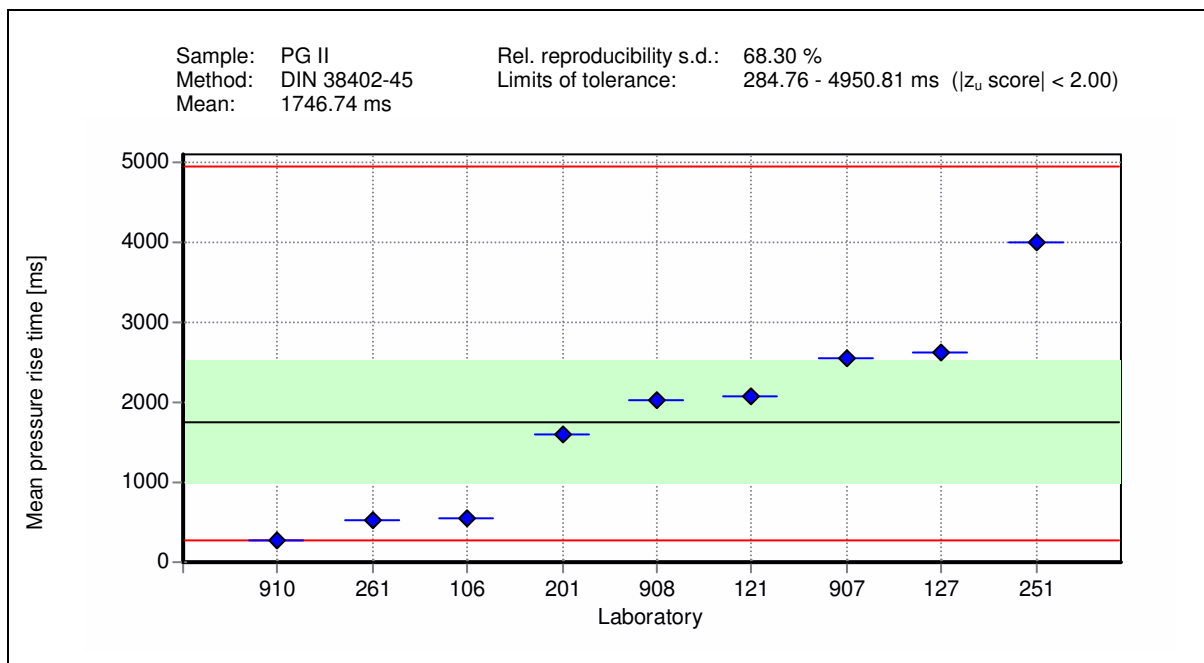


Figure 8-20: Analysis of laboratory mean pressure rise times [ms] – PG II in test series 1

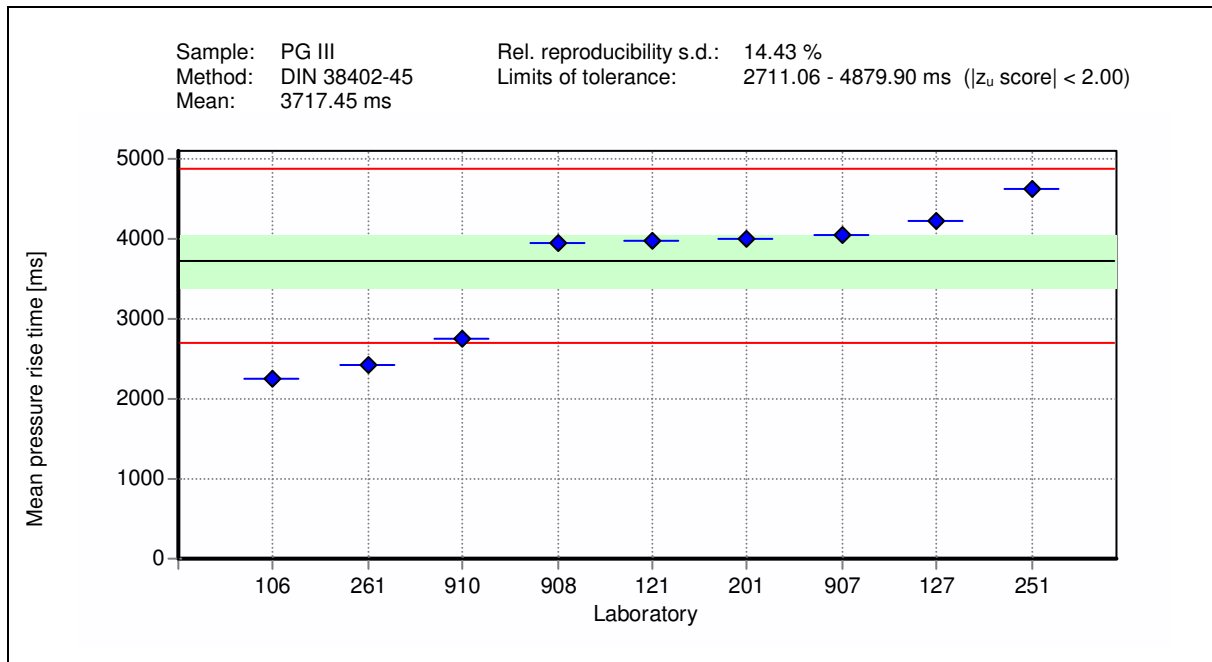


Figure 8-21: Analysis of laboratory mean pressure rise times [ms] – PG III in test series 1

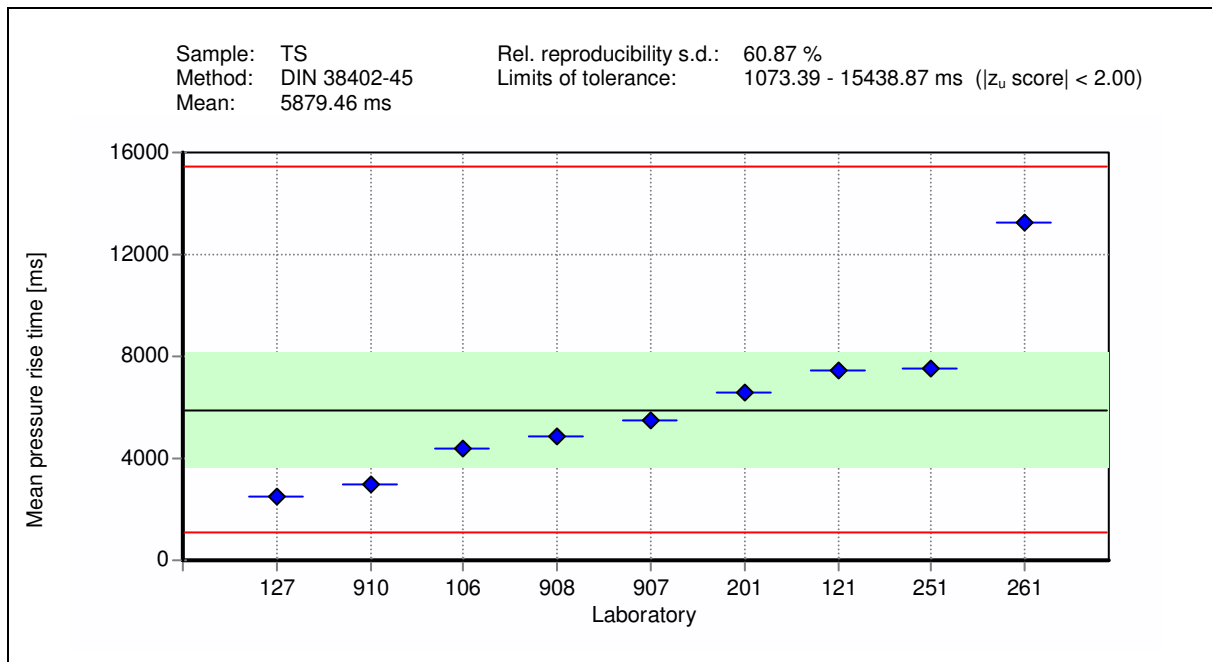


Figure 8-22: Analysis of laboratory mean pressure rise times [ms] – TS in test series 1

8.4.1.2 Test series 2

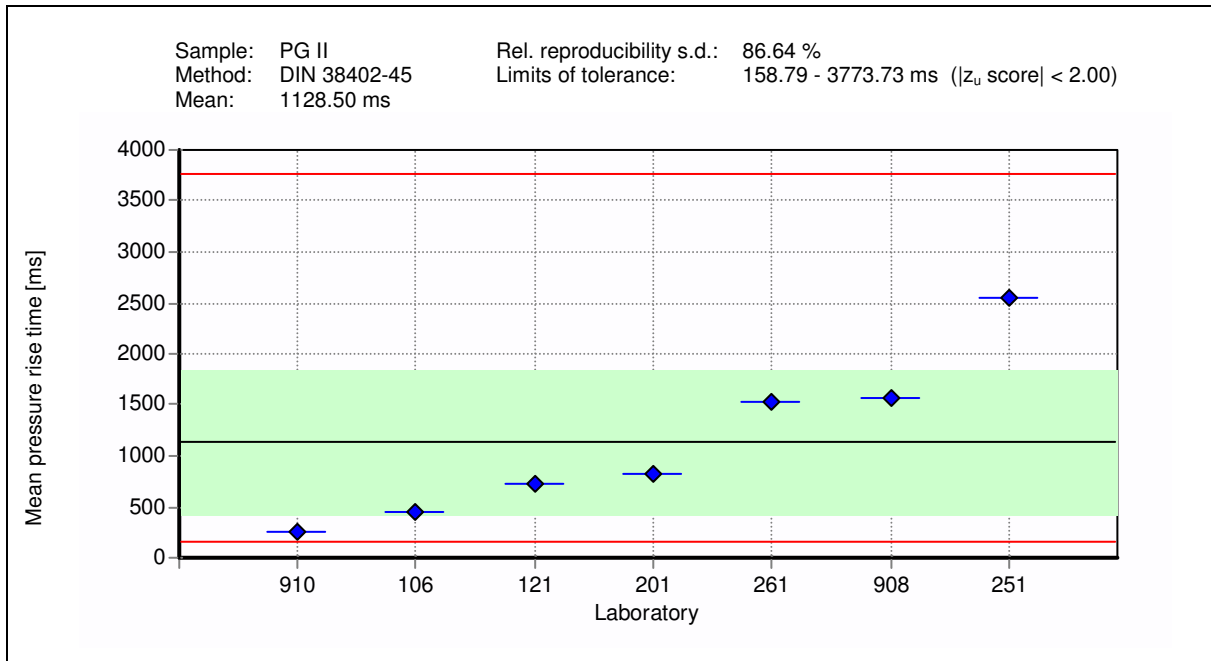


Figure 8-23: Analysis of laboratory mean pressure rise times [ms] – PG II in test series 2

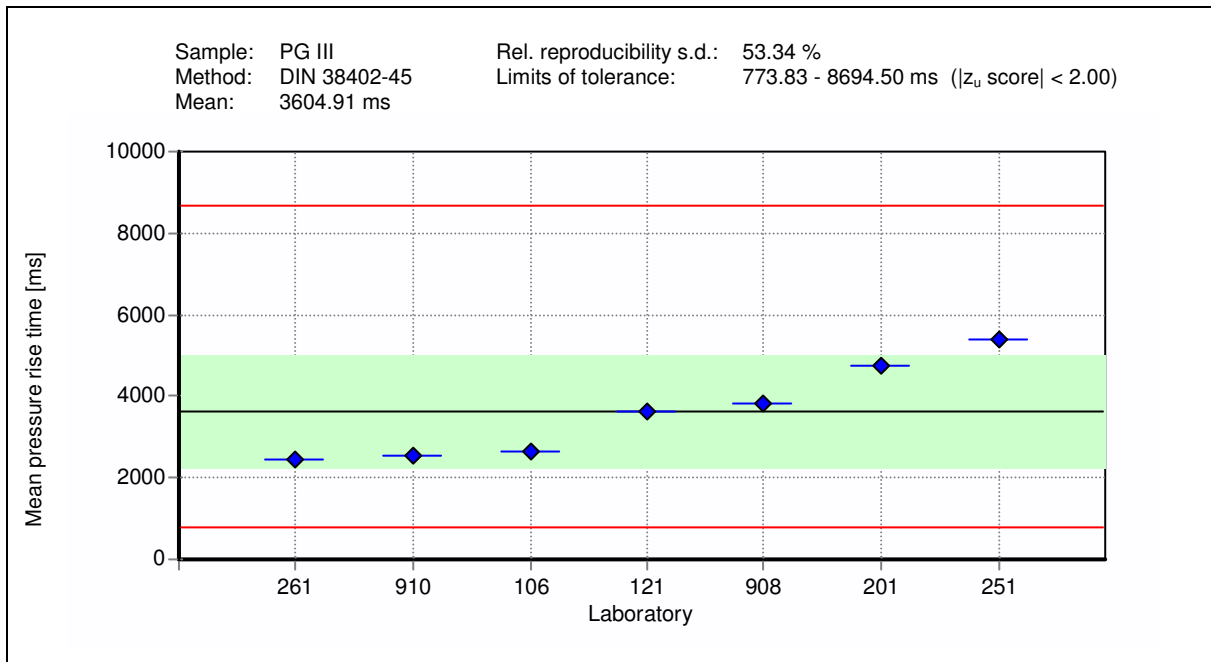


Figure 8-24: Analysis of laboratory mean pressure rise times [ms] – PG III in test series 2

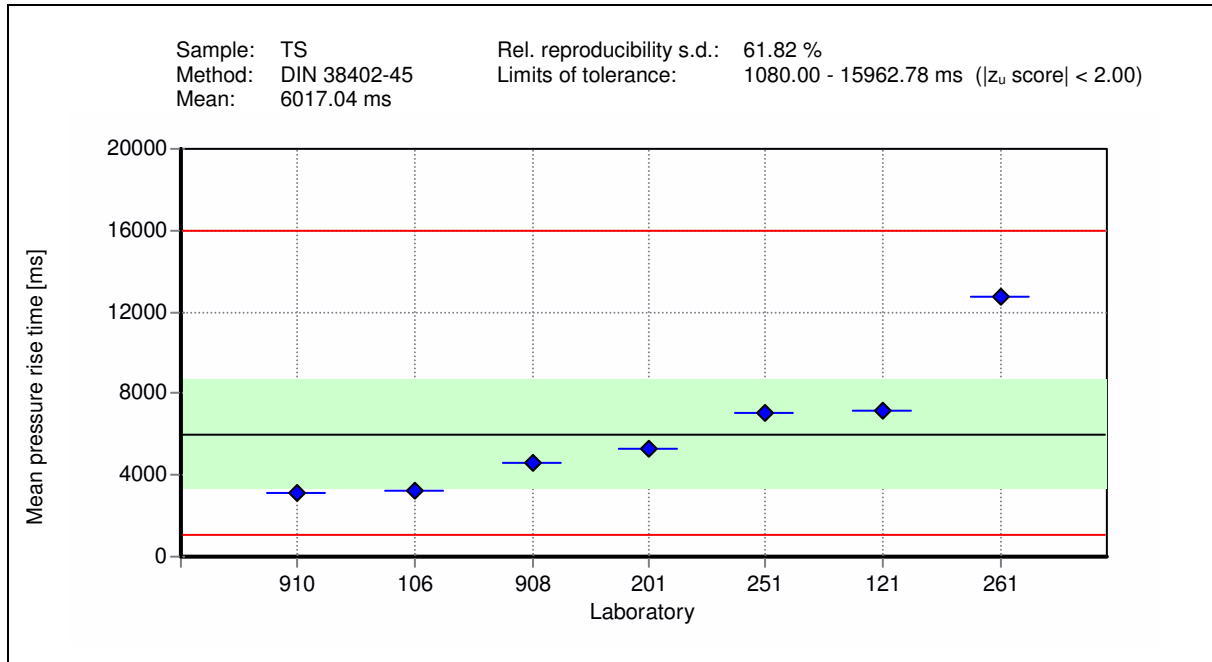


Figure 8-25: Analysis of laboratory mean pressure rise times [ms] – TS in test series 2

8.5 Analysis of ratios of laboratory mean pressure rise times

8.5.1 Test series 1

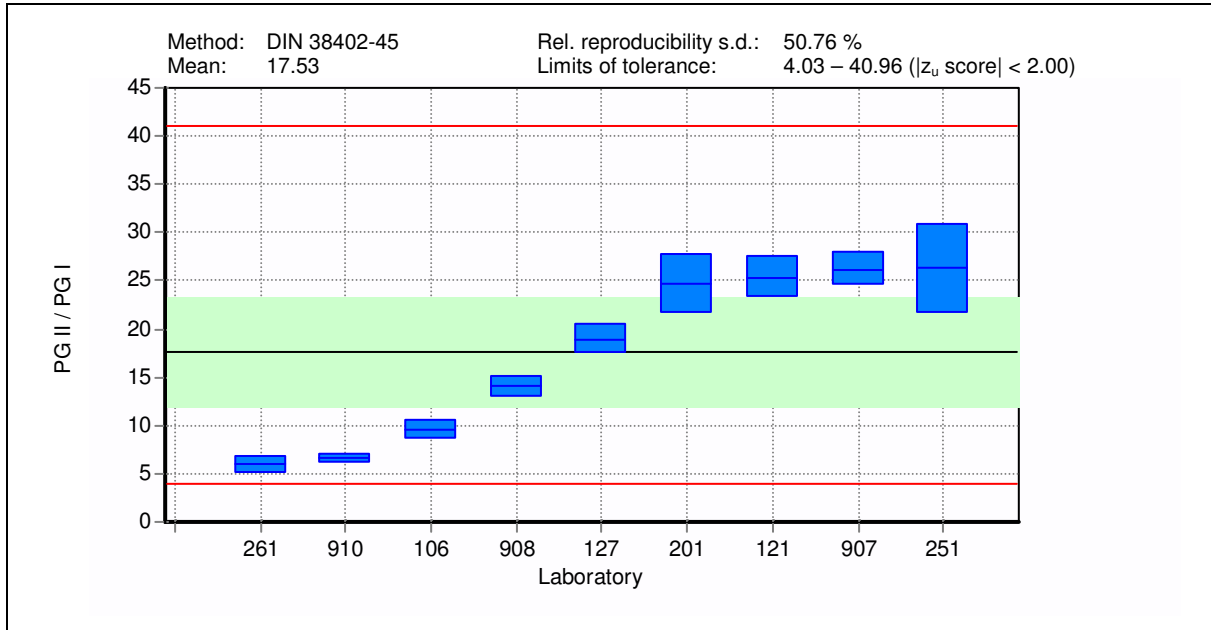


Figure 8-26: Analysis of ratios of laboratory mean pressure rise times – ratio PG II / PG I in test series 1

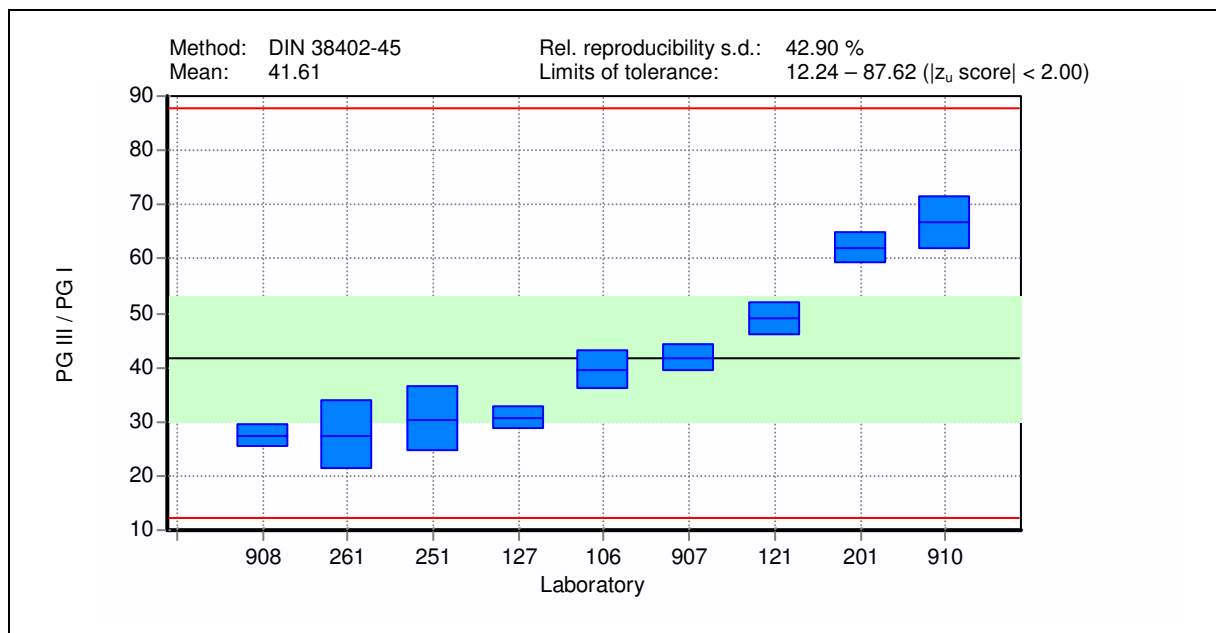


Figure 8-27: Analysis of ratios of laboratory mean pressure rise times – ratio PG III / PG I in test series 1

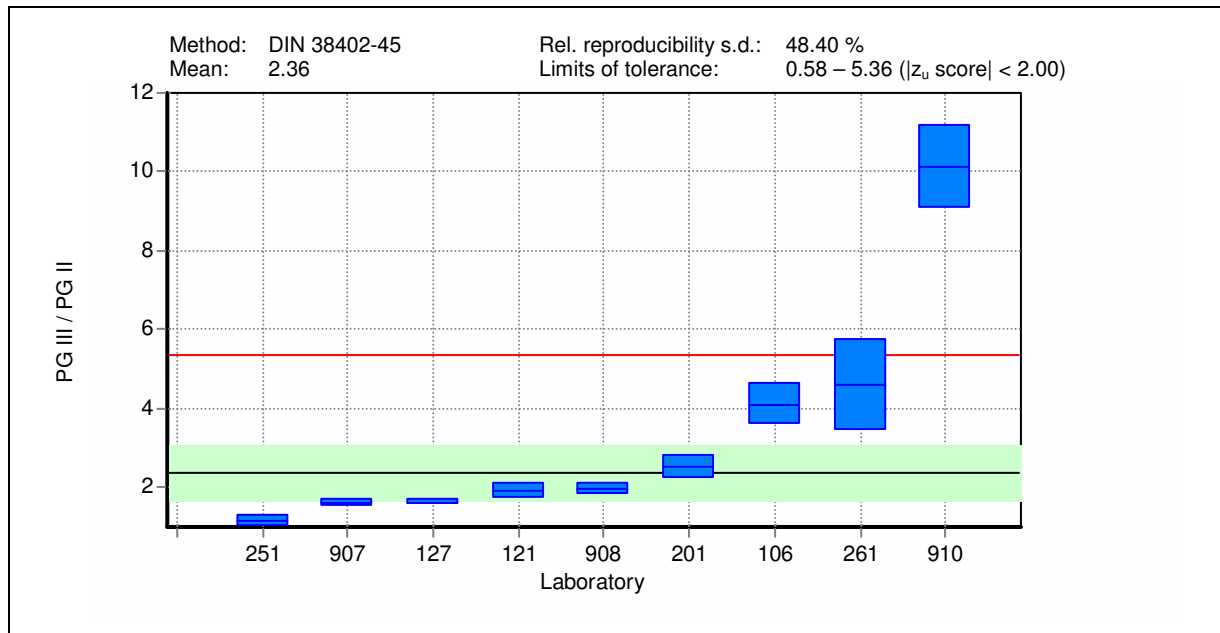


Figure 8-28: Analysis of ratios of laboratory mean pressure rise times – ratio PG III / PG II in test series 1

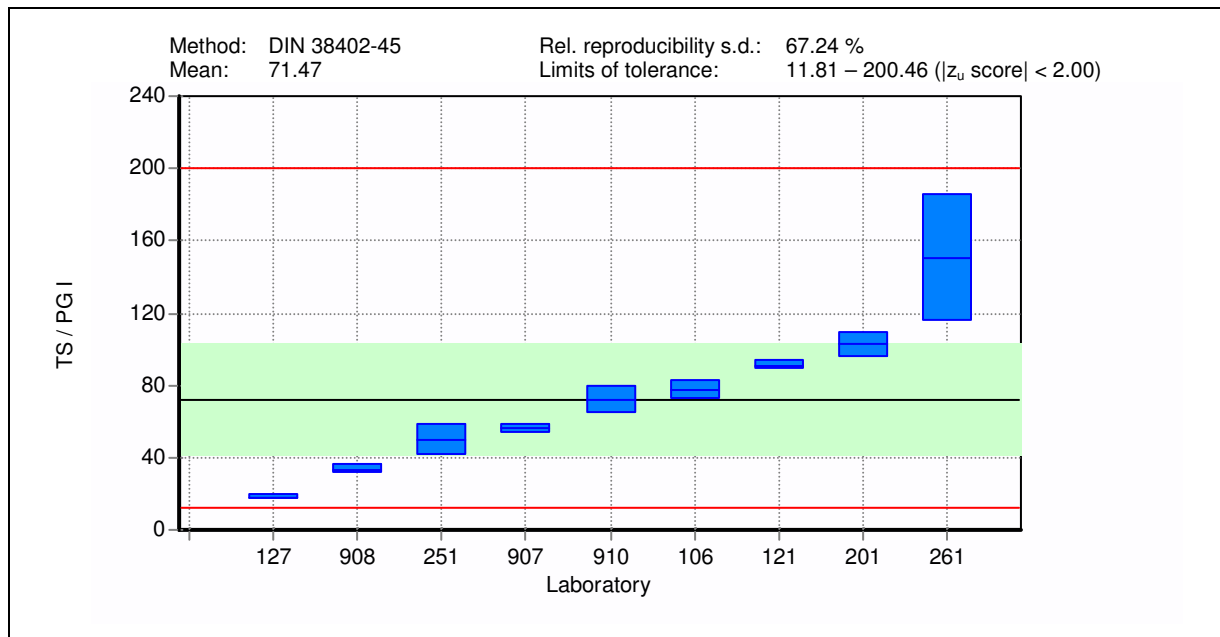


Figure 8-29: Analysis of ratios of laboratory mean pressure rise times – ratio TS / PG I in test series 1

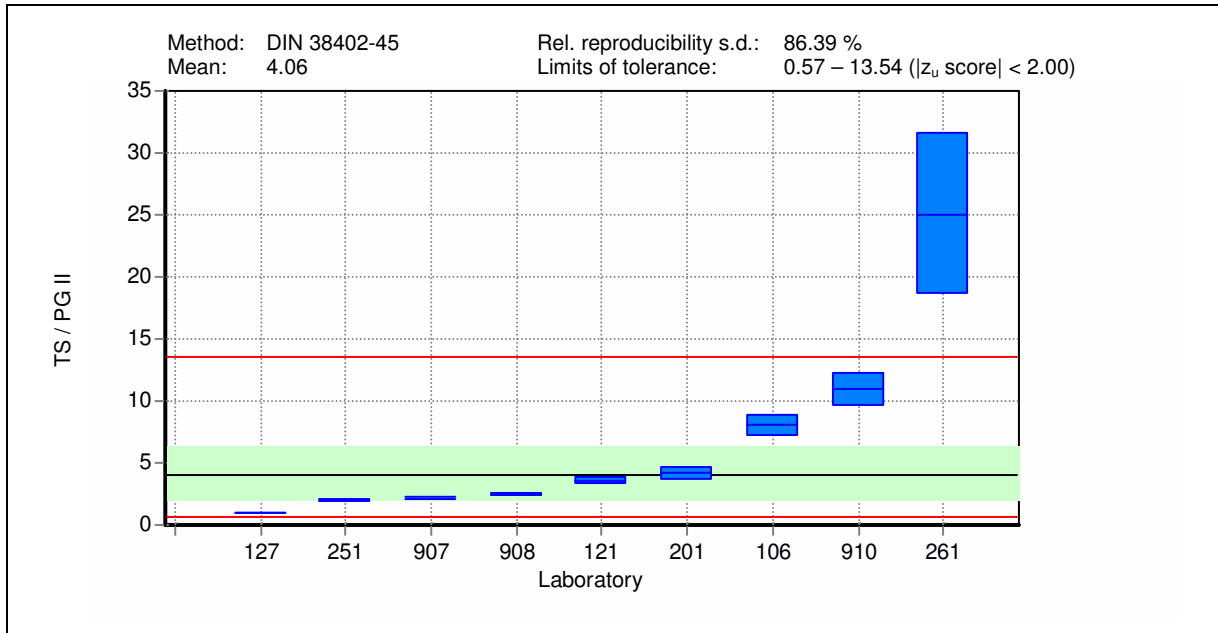


Figure 8-30: Analysis of ratios of laboratory mean pressure rise times – ratio TS / PG II in test series 1

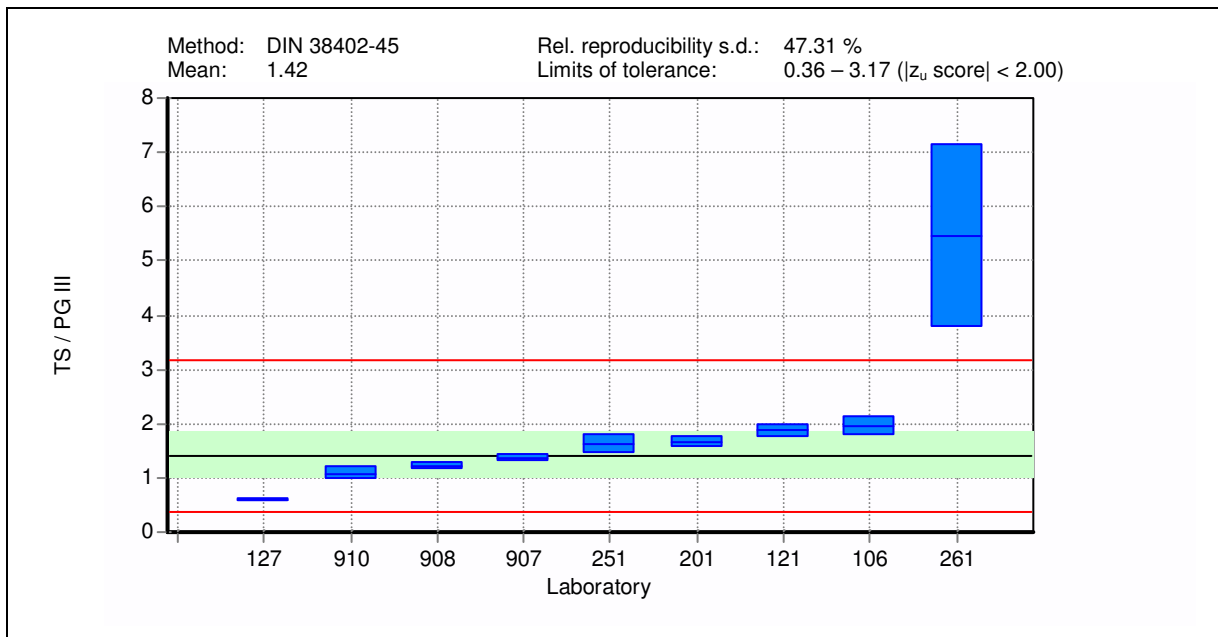


Figure 8-31: Analysis of ratios of laboratory mean pressure rise times – ratio TS / PG III in test series 1

8.5.1.1 Test series 2

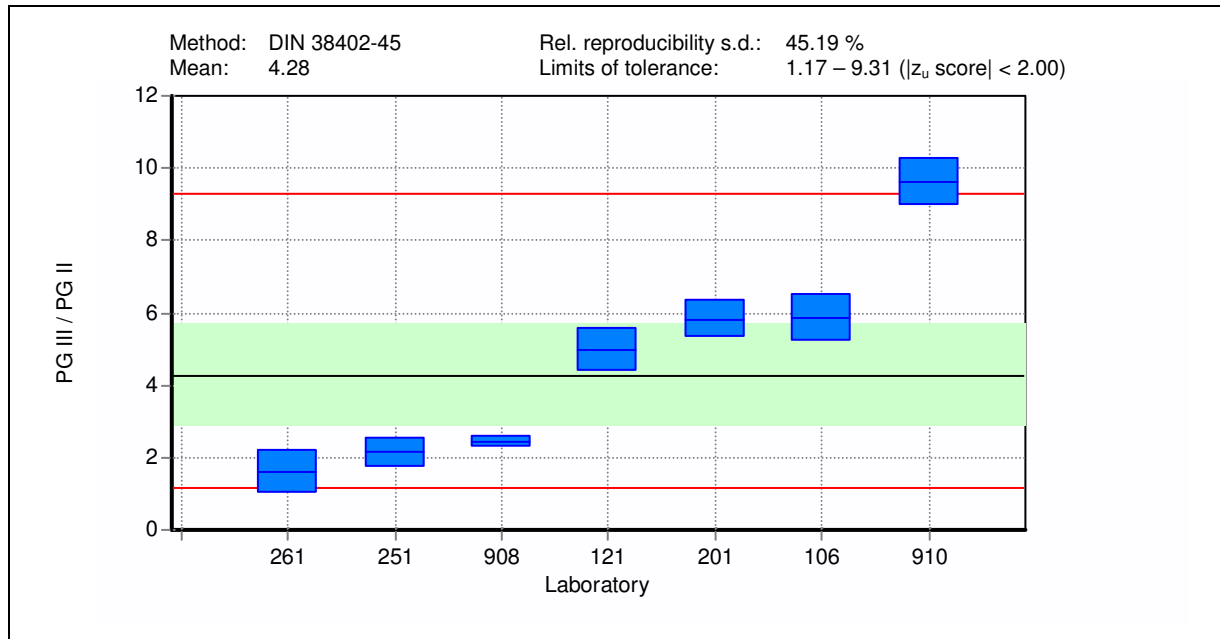


Figure 8-32: Analysis of ratios of laboratory mean pressure rise times – ratio PG III / PG II in test series 2

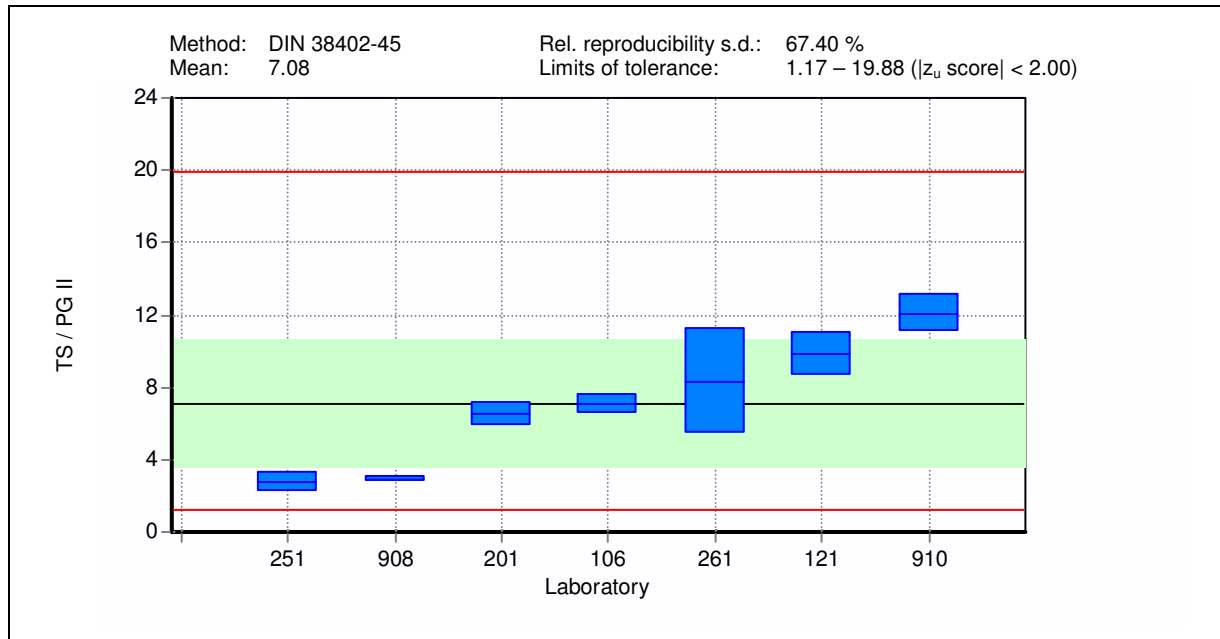


Figure 8-33: Analysis of ratios of laboratory mean pressure rise times – ratio TS / PG II in test series 2

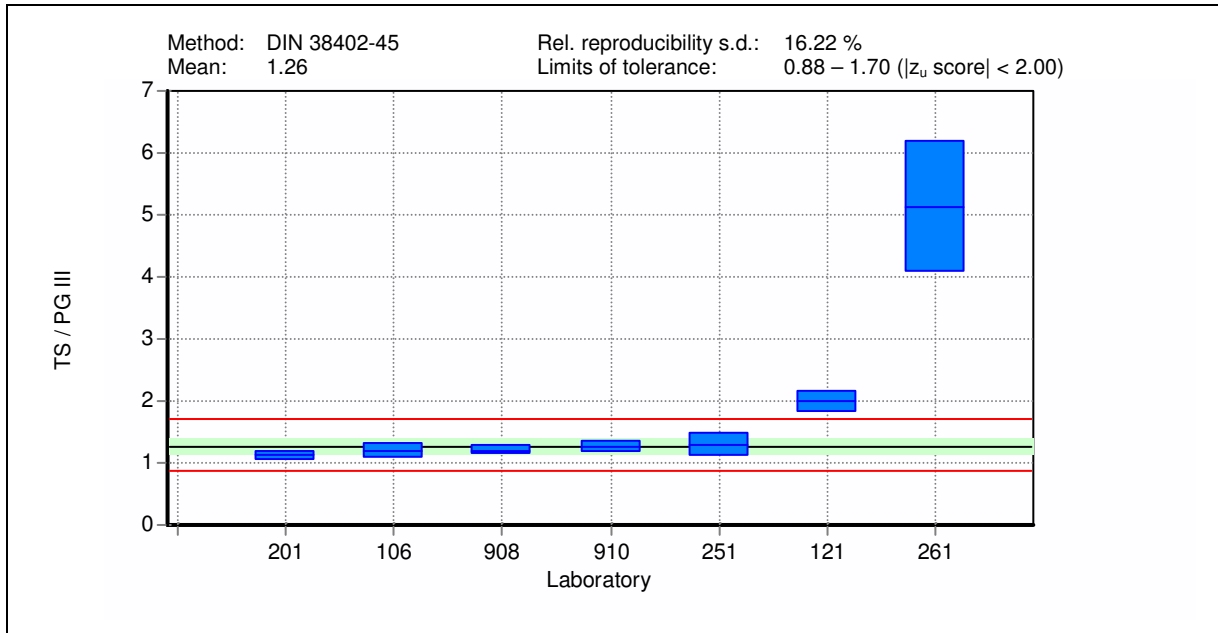


Figure 8-34: Analysis of ratios of laboratory mean pressure rise times – ratio TS / PG III in test series 2