Short Report

Interlaboratory test on the method UN Test N.5 / EC A.12 “Substances which, in contact with water, emit flammable gases” 2007

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BAM Federal Institute for Materials Research and Testing

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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 2007 on the method UN Test N.5 “Test method for substances which in contact with water emit flammable gases” [1] / EC A.12 “Flammability (contact with water)” [2] which was organized by the Center for Quality Assurance for Testing of Dangerous Goods and Hazardous Substances.

In dependence on the chemical structure and/or the physical form and state (e.g. particle size) substances or mixtures may be able to react with water (even water damp / air humidity) under normal ambient temperature conditions. Sometimes this reaction can be violent and/or with significant generation of heat. Especially if gases are evolved this reaction may become dangerous. In addition, it is important to know whether a substance emits flammable gases due to contact with water because special precautions are necessary especially with regard to explosion protection.
The methods UN Test N.5 and EC A.12 are applied to characterize chemical substances or mixtures which in contact with water emit flammable gases. To differentiate between chemicals with these properties and chemicals which are not classified as hazardous / dangerous, the substance’s gas evolution rate is determined and compared to the classification criteria(s) in the last step of the test method. In the methods UN Test N.5 / EC A.12 no special laboratory apparatus / measuring technique to determine gas evolving flow is required.
However, practical experience shows that the testing procedure for substances and mixtures which in contact with water emit flammable gases is sensitive to a number of influencing factors.
Since the methods (UN N.5 / EC A.12) 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 2007 on the method UN Test N.5 / EC A.12 “Substances which, in contact with water, emit flammable gases” are:

1. **Assessment of the performance of the methods UN Test N.5 / EC A.12:**
   The current practical application of the method in different laboratories and the classification error were assessed by the interlaboratory test. For this purpose specific precision indicators (e.g. reproducibility, repeatability, probability of incorrect classification etc.) were generated.
2. **Assessment of other influencing 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.

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

3 Test material

3.1 Interlaboratory test sample "metal mixture powder"

"Metal mixture powder" (Zn and ZnO (< 87%), Al and Al_2O_3 (appr.9%), Mg and MgO (appr.3%)) was chosen as the interlaboratory test sample.

3.1.1 Preparation of the interlaboratory test samples

In February 2007 the original stock sample (16,6 kg) was divided into 64 sub-samples (interlaboratory test sample, approx. 250 g) by aid of a spinning (rotating) riffler (see Figure 3-1) [3].

Figure 3-1: Dividing of the 16.6 kg stock sample on a spinning (rotating) riffler at BAM right picture: the sample flows from the hopper to a vibrating chute and travels along the chute to the receivers (8 glass containers)

The homogenising procedure was performed in accordance with the principles of the cross-riffling-procedure [4] (see Figure 3-2).

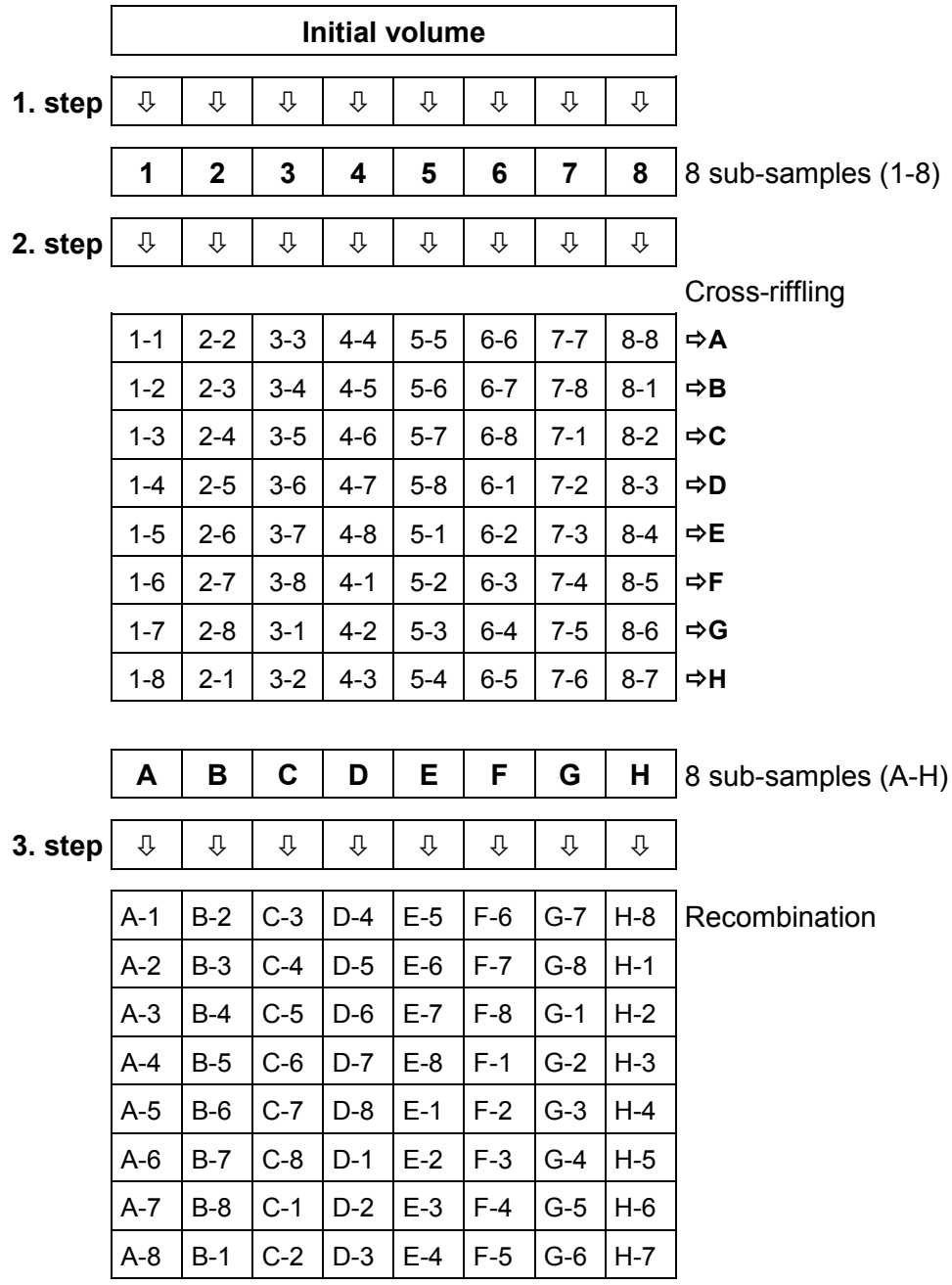

Figure 3-2: Division of the sample of the cross riffling procedure

The divided interlaboratory test samples were packed into transport containers and sent to the participants of the interlaboratory test.

3.1.2 Homogeneity and stability of the interlaboratory test samples

Based on experience with mixed metal powders and the interlaboratory test sample “Metal mixture powder” and the test methods the stock sample are known to be sufficiently homogeneous and stable within the testing time frame of the round robin test (June 2007 to September 2007).
In addition, tests of the homogeneity and stability were performed. For this purpose the gas evolution rate of several interlaboratory test samples was checked in the period from February 2007 until October 2007 (e.g. 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 Annex 8.1. The expected homogeneity and stability of the interlaboratory test samples were confirmed by the results of these additional tests.

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 “Metal mixture powder” together with a test instruction and the laboratory data input form (see Appendix 8.2 and 8.3), was distributed to 12 participating laboratories (see Table 4-1).

Table 4-1: Participating laboratories (n=12)

Laboratory / Agency	Country
AIST National Institute of Advanced Industrial Science and Technology	Japan
ALMAMET GmbH	Germany
AQura GmbH	Germany
BAM Federal Institute for Materials Research and Testing	Germany
BASF AG	Germany
Bayer Industry Services GmbH & Co. OHG	Germany
Chilworth Technology Ltd.	United Kingdom
Government Laboratory of Hong Kong HKSAR	China
Henkel AG & Co. KGaA	Germany
INERIS	France
Minton, Treharne & Davies Ltd.	United Kingdom
Siemens AG	Germany

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	May 2007
Order and registration	June 2007
Distribution of the test sample and the test instruction	June 2007
Laboratory testing period	July 2007 to September 2007 *
First statistical evaluation and draft report	November to December 2007 **
Distribution of the Certificates	December 2007

* ..... The testing period was prolonged from August 2007 to September 2007 because not all laboratories were able to perform the tests until August 2007 (as originally foreseen in June 2007).

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

4.2 Test procedure

The interlaboratory test was performed on the methods UN Test N.5 “Test method for substances which in contact with water emit flammable gases” and EC A.12 “Flammability (contact with water)” (see Table 4-3):

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

Test method	Source
UN Test N.5 “Test method for substances which in contact with water emit flammable gases”	United Nations: Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Fifth revised edition, United Nations, New York and Geneva, 2009 [1][1]
EC A.12 “Flammability (contact with water)”	European legislation: Council Regulation (EC) No 440/2008 of 30 May 2008 [2]

Both methods, UN Test N.5 and EC A.12, are comparable with regard to the general principles and the criteria for classification and non-classification.

In contrast to EC A.12, UN Test N.5 does not only distinguish between substances and mixtures which are classified as flammable and those that are not but it also divides classified substances and mixtures into three categories / packing groups (see Table 4-4).

[1] UN Test N.5 has not been changed compared to the Fourth revised edition of the UN Manual of Tests and Criteria which was effective at the time of the interlaboratory test.

Table 4-4: Scope of the methods

Method	Purpose
UN Test N.5 “Test method for substances which in contact with water emit flammable gases”	Decision on classification in accordance with - GHS: Classification in hazard class "Substances and mixtures which, in contact with water, emit flammable gases" and assignment of the appropriate category 3, 2 or 1 - TDG: Classification in Division 4.3 and assignment of the appropriate Packing group III, II or I
EC A.12 “Flammability (contact with water)”	Decision on classification as F; R15

4.2.1 Interlaboratory test instruction and laboratory data input form

The test instruction for the interlaboratory test (see Appendix 8.2) was distributed together with the test sample.

The test instruction is more detailed than the current description of UN Test N.5 and EC A.12 and included the following information:

- The interlaboratory test sample should be tested as received, i.e. according to the following instructions:
  - DO NOT treat the test sample by any mechanical method before testing (**no sieving, no grinding**).
  - In case that the test sample is slightly agglomerated, crush possible agglomerates only very gently (by hand).
- Preparation of test samples with a precision of **10.0 g ± 0.1 g.**
- Using of **distilled (or demineralized) water.**
- The amount of distilled (or demineralized) water per test shall be **20.0 ml ± 0.5 ml.**
- Performing of the procedure as prescribed in chapter 33.4.1.4.3.5 of UN Test Manual (4th rev. edition, 2003) or, respectively, in chapter 1.6.4 of the European method A.12.
- Performing the test **over a period of 8 hours after adding the water**, i.e. the rate of the evolution of gas should be calculated **over 7 hours at 1 hour** intervals.
- The test should be performed in **triplicate**.

Apart from that, the other details of the procedure were supposed to be applied as usual in the laboratory and in accordance with chapter 34.4.1.4.3.5 of the UN Manual of Tests and Criteria [1] or/and in chapter 1.6.4 of the European method EC A.12 [2].

Laboratory specific parameters and test conditions were enquired with the aid of the laboratory data input form (see Appendix 8.3).

5 Evaluation

5.1 Background

The evaluation of the data was performed using a specially modified version[2] of the software package ProLab Plus 2007 [5]. ProLab Plus is widely employed for the evaluation of interlaboratory tests and laboratory proficiency tests.

The method according to DIN 38402-45 [7] (=ISO/TS 20612) was applied for the statistical analysis of gas evolution rates (see remark below Figure 5-2). This method is a robust method and no outlier examination is required.

5.2 Quantity of test results

Measurements were conducted by 12 laboratories and all of them submitted results (see Table 4-1).

5.3 Plausibility check

To begin with, a first check of the plausibility of the data was performed. All results of the trials were considered as plausible regarding the gas evolution rate (e.g. with regard to completeness, consistency etc.).

5.4 Results and resulting classification of the interlaboratory test sample "Metal mixture powder"

The laboratory single values and the mean value of the gas evolution rate for the interlaboratory test sample are given in the following Table 5-1 and Table 5-2.

[2] 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: Results of the Laboratory – single values and laboratory mean value

Laboratory	Gas evolution rate [l / (kg x h)]			
	Value 1	Value 2	Value 3	Laboratory mean value
066	3.9	3.6	3.5	3.67
106	1.9	1.6	1.9	1.80
121	1.53	1.53	1.63	1.56
201	0.4	2.1	0.5	1.00
251	3.1	3.6	3.4	3.37
272	3.38	2.85	3.67	3.20
902	4.2	4.2	4.2	4.20
906	3.6	3.3	4.0	3.63
907	5.7	5.6	4.3	5.20
908	2.22	2.95	2.2	2.46
910	3.97	4.13	3.97	4.02
911	3.5	4.3	3.8	3.87

Note: The number of decimals was not prescribed by the interlaboratory test instruction and therefore are different between laboratories.

The laboratory single values of the gas evolution rate of the Interlaboratory test sample are shown in Figure 5-1.

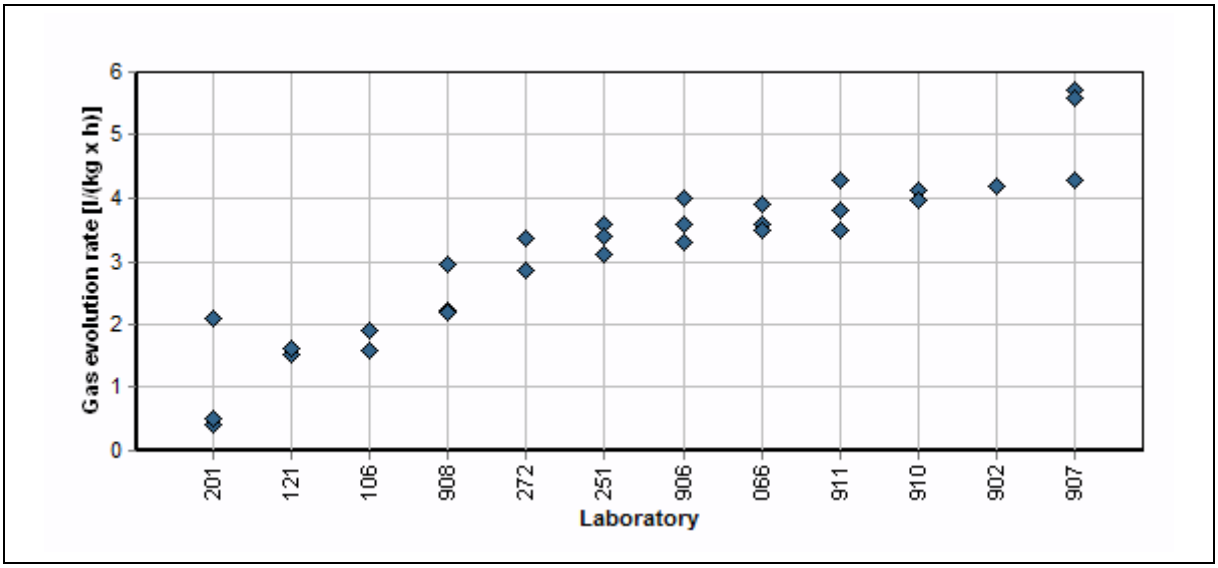

Figure 5-1: Gas evolution rates (singe values) of all laboratories

The robust mean value and standard deviation of the gas evolution rates over all laboratories is given in Table 5-2.

Table 5-2: Results of the Laboratory – Robust mean value and standard deviation over all laboratories (according to DIN 38402-45 [7])

Parameter	Value [gas evolution rate [l / (kg x h)]]
Robust mean value over all laboratories	3.18
Robust reproducibility s.d. over all laboratories	1.24

Based on these test results, the centrally distributed interlaboratory test sample “Metal mixture powder” would be classified by all laboratories in the same hazard class "Substances and mixtures which, in contact with water, emit flammable gases", category 3 and in the same division 4.3, packing group (PG III) (see Table 5-3).

Table 5-3: Classification results of the interlaboratory test sample “Metal mixture powder” according to the methods UN Test N.5 / EC A.12 based on the maximum value of the gas evolution rate (i.e. maximum of the three single values) (robust mean value and robust reproducibility s.d. according to DIN 38402-45 [7])

Laboratory / Kind of value	Maximum gas evolution rate [l /(kg x h)]	Classification result
066	3.9	Division 4.3, PG III / F; R15
106	1.9	Division 4.3, PG III / F; R15
121	1.63	Division 4.3, PG III / F; R15
201	2.1	Division 4.3, PG III / F; R15
251	3.6	Division 4.3, PG III / F; R15
272	3.38	Division 4.3, PG III / F; R15
902	4.2	Division 4.3, PG III / F; R15
906	4.0	Division 4.3, PG III / F; R15
907	5.7	Division 4.3, PG III / F; R15
908	2.95	Division 4.3, PG III / F; R15
910	4.13	Division 4.3, PG III / F; R15
911	4.3	Division 4.3, PG III / F; R15
Robust mean value of the maximum gas evolution rates	3.45 l / (kg x h)	
Robust reproducibility standard deviation of the maximum gas evolution rates	1.04 l / (kg x h)	

5.5 Kernel density estimation of single pressure rise times

An analysis of the underlying distribution of the single gas evolution rates was carried out by the so-called kernel density estimation in order to check the homogeneity. The following figure Figure 5-2 shows the results of the kernel density estimation for all single gas evolution rates.

The blue curve characterizes the distribution of single gas evolution rates obtained by the kernel density estimation.

The y-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 y-axis values are of interest, but only the shape of the curve.

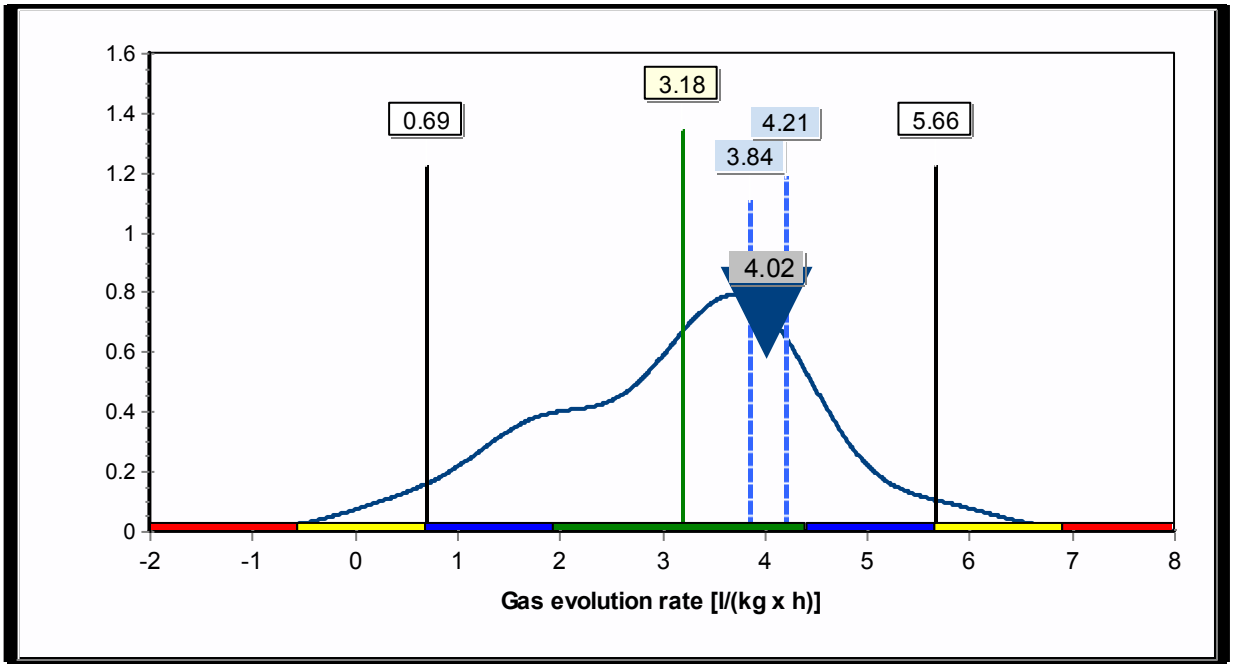

Figure 5-2: Kernel Density Estimation of the gas evolution rates (Reference value: 3.18 +/- 0.71) with:
bars denote the tolerance limits (|Z|=2) (as an example for laboratory 910)
triangle denotes the laboratory mean (as examples for laboratory 910)

Remark: According to the Kernel Density Plot the data are not normally distributed. Therefore DIN ISO 5725-2 cannot be applied. Even though the method according to DIN ISO 5725-5 is more robust than the method according to ISO 5725-2, the method described in DIN ISO 5725-5 is more sensitive to within-lab outliers than the method according to DIN 38402-45 [7]. Furthermore, in case the interlaboratory test is repeated, the method according DIN ISO 5725-5 is less efficient in terms of the reliability of the precision parameters (mean, standard deviation) than the method according to DIN 38402-45. Therefore DIN 38402-45 is used in this evaluation.

5.6 Performance of the method UN Test N.5 / EC A.12

5.6.1 Reproducibility, repeatability and classification error

A summary of the obtained mean values, repeatability and reproducibility standard deviations of the laboratory gas evolutions rates is shown in the following Figure 5-3.

In this figure, the size of the blue boxes symbolizes the laboratory's relative repeatability standard deviation. The horizontal line in the middle of the box indicates the laboratory's mean gas evolution rate. The figures also include the robust mean of the single gas evolution rates according to DIN 38402-45 (black line) as well as the limits of tolerance (red) – also according to DIN 38402-45.

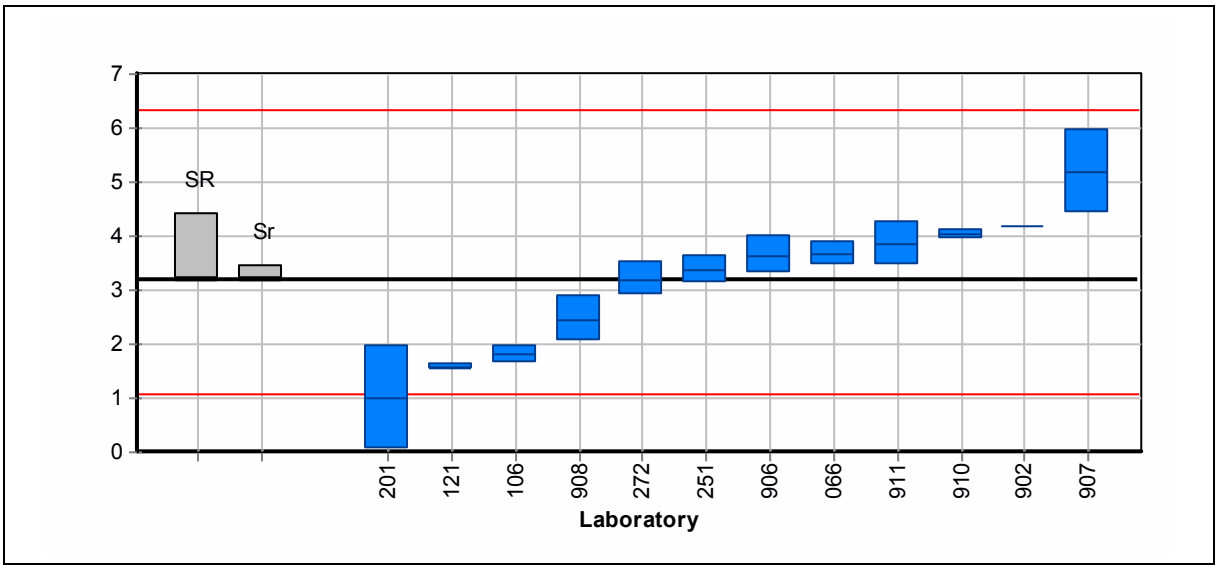

Figure 5-3: .. Analysis of gas evolutions rates of all laboratories with tolerance limits (red) and with: SR…reproducibility s.d., Sr….repeatability s.d.

The mean gas evolution rate of laboratory 201 is very low compared to other laboratories and below the lower tolerance.

5.6.1.1 Probability of incorrect classification for an arbitrary sample

False positive error of classification: 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.

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.

The probability of incorrect classification can also be predicted for an arbitrary test sample mixture, i.e. not only for the test sample which was used in the interlaboratory test. [3]

Figure 5-4 shows the probability of incorrect classification for an arbitrary test sample as tested under

the conditions of this interlaboratory test. Due to the form of the curve, such figures 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 positive classification (false positive error) as a function of the true gas evolution rate, i.e. the probability that the test sample is incorrectly classified in a lower packing group (of higher safety) than 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 negative classification (false negative error), i.e. the probability that the test sample is incorrectly classified in a higher packing group (of lower safety) than it correctly should be, based on its "true" pressure rise time (x-value).

In particular, this means:

Left arm of packing group III (increasing arm)	Probability that a laboratory classifies a test sample in PG III, although no classification would be correct (true) → **false positive classification**
Right arm of packing group III (decreasing arm)	Probability that a laboratory does not classify a test sample, although PG III would be necessary (true) → **false negative classification**

Read the Shark Profile as follows:

If for example the "true" gas evolution rate of an arbitrary test sample mixture amounts to 2.5 l / (kg x h), the probability for a false negative classification with regard to packing group III, i.e. the probability to not classify the test sample instead of the “true” packing group III, is about 9 %.

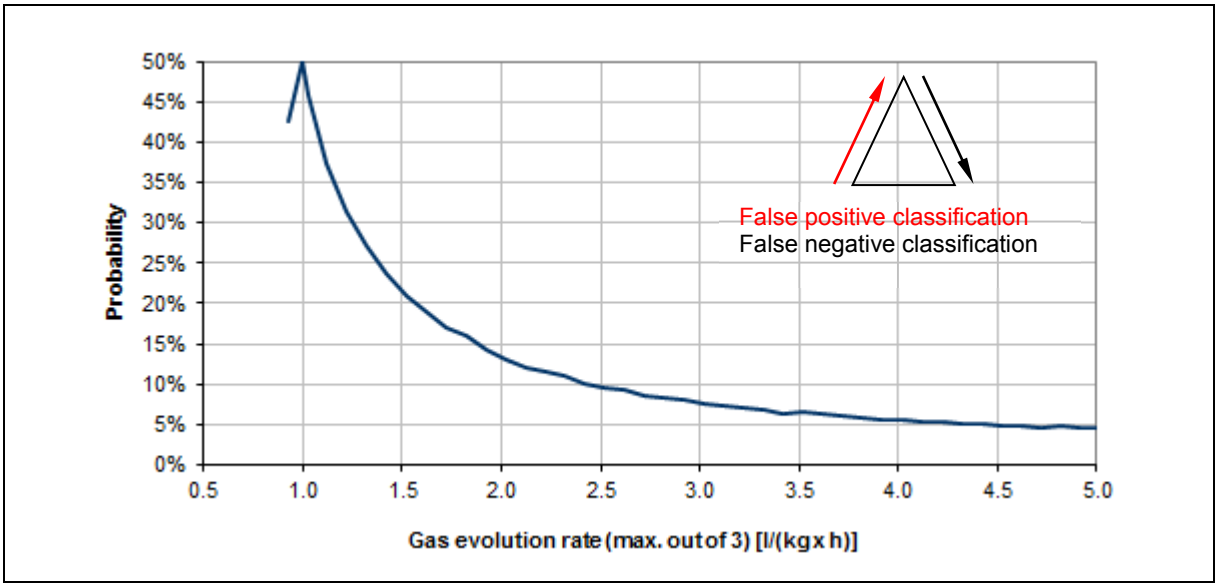

Figure 5-4: Shark profile – probability of incorrect classification in PG III or no classification as a function of the "true" gas evolution rate of an arbitrary sample

5.6.2 Z_u scores

The assessment of the laboratory's performance in determining the gas evolution rate of the laboratory test sample 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 over all laboratories (= robust mean value over all laboratories, see Table 5-2) 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 (= robust mean value over all laboratories, see Table 5-2).

In this interlaboratory test one of the z_u scores (laboratory 201) lies outside the limits of tolerance (see Table 5-4 and Figure 5-5).

Table 5-4: Z_u scores according to DIN 38402-45 / ISO/IEC 17043 of the laboratories

Laboratory	z_u score
066	0.31
106	-1.31
121	-1.53
201	-2.07
251	0.12
272	0.01
902	0.65
906	0.29
907	1.28
908	-0.68
910	0.54
911	0.44

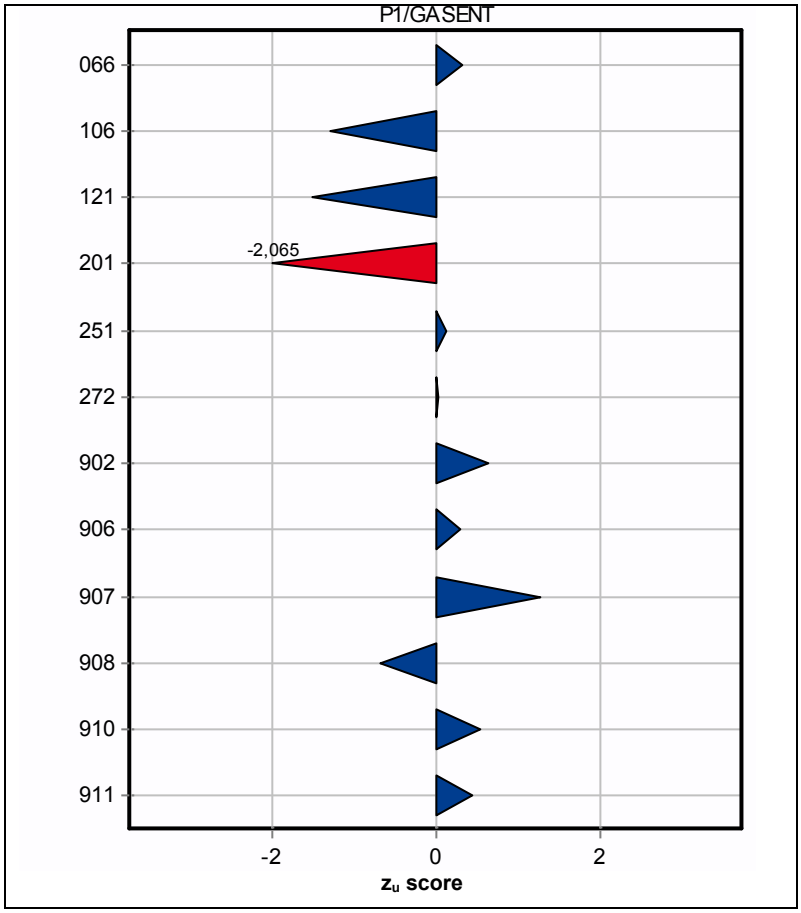

Figure 5-5: Overview of the z_U scores of the laboratories

5.8 Other influencing (disturbing) factors

An additional exploratory analysis of the gas evolution rates was conducted in order to find the reason for the broad spread of the results and the deviations between the laboratories.
Different measuring devices und techniques are used in the laboratories (see Figure 5-6).

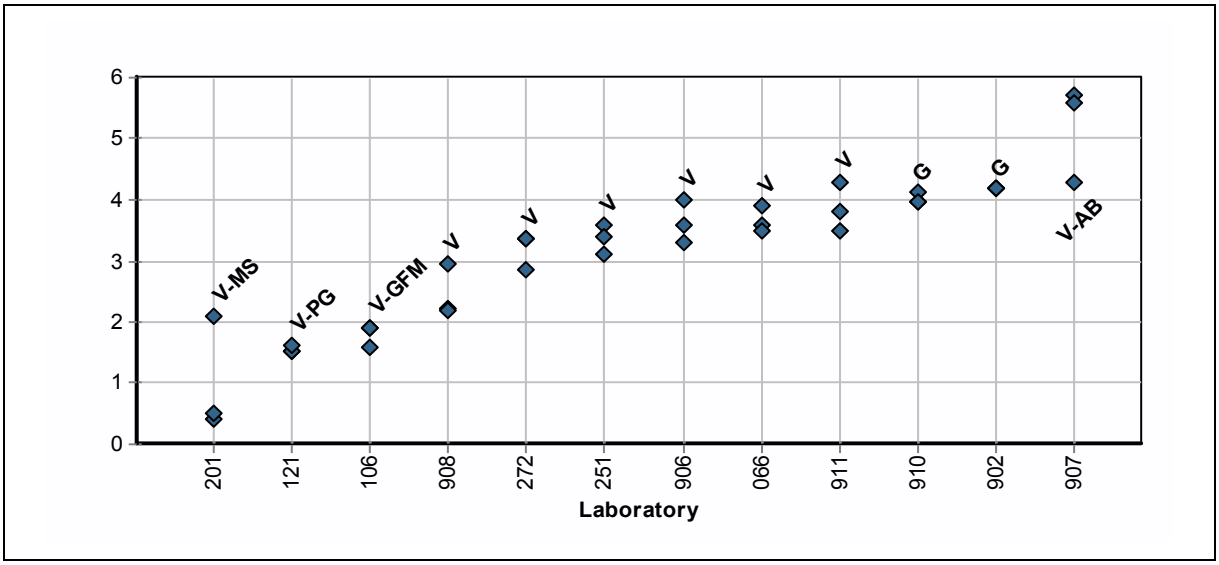

Figure 5-6: Gas evolution rate of laboratories with different measuring devices:

G	**Gravimetry**
V	**Volumetry**
V-MS	**Volumetry with magnetic stirrer**
V-PG	**Volumetry with a pressure gauge**
V-GFM	**Volumetry with gas flow meter**
V-AB	**Volumetry with automated gas burette**

Two laboratories have used a gravimetric detection technique. It is remarkable that the results of these two laboratories are very similar and have a comparatively high repeatability.
Very low gas evolution rates were determined by laboratory 201 which measures the gas evolution rate by volumetry and uses a magnetic stirrer in addition. It therefore might be concluded that the use of a stirrer considerably lowers the measured gas evolution rate.

Furthermore, the ambient room temperature in the laboratories was different (see Figure 5-7).

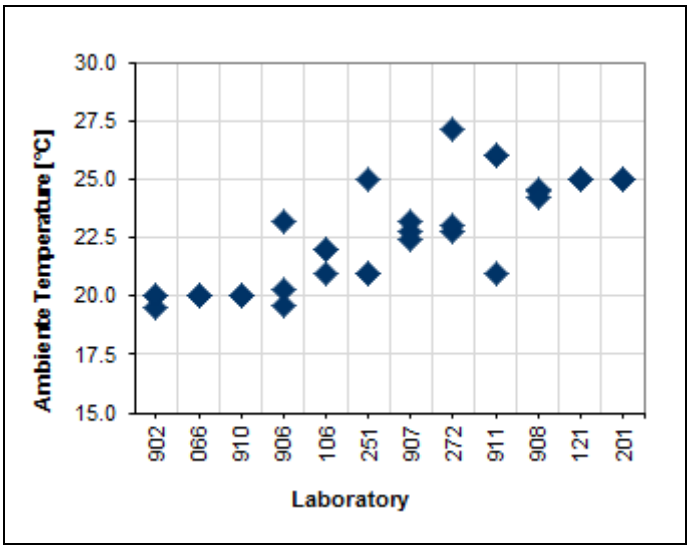

Figure 5-7: Ambient temperature during the detection of the gas evolution rate in different laboratories

The relationship between the gas evolution rate and the ambient temperature is shown in Figure 5-8 for those 6 laboratories using "Volumetry (V)".

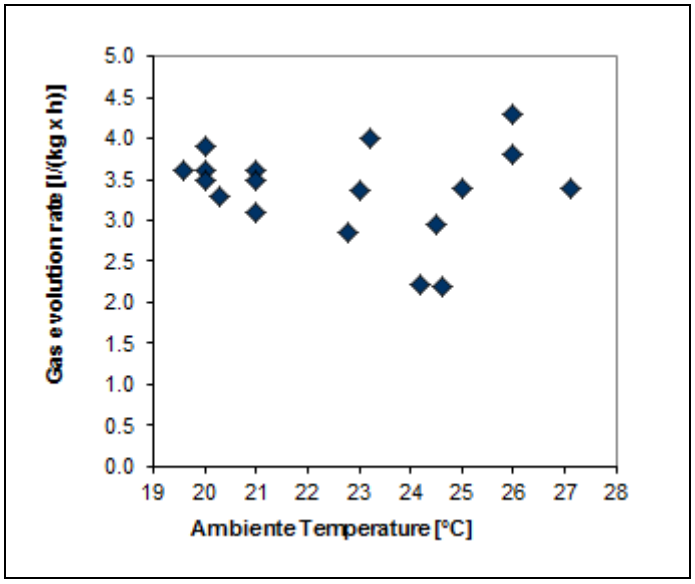

Figure 5-8: Relationship between the gas evolution rate and the ambient temperature of laboratories using “Volumetry (V)” (6 of 12 laboratories)

No significant relationship can be identified between the ambient temperature and the gas evolution rate for laboratories with comparable test techniques (Volumetry).

6 Summary and conclusions

The following conclusions can be drawn concerning the aim of this interlaboratory test.
The methods do not prescribe a certain procedure or apparatus for determining the gas evolution rate. As a result the laboratories use different procedures and equipment where the main difference is application of a volumetric or a gravimetric method. As demonstrated by this interlaboratory test the gas evolution rates measured by the different laboratories vary in a wide range.
Additionally, the test methods do not foresee the use of a reference material.
Therefore it is recommended that adequate quality control measures are consistently applied.

6.1 Performance of the methods UN Test N.5 / EC A.12

Even though the interlaboratory test sample “Metal mixture powder” would be classified by all laboratories in the same hazard class "Substances and mixtures which, in contact with water, emit flammable gases", category 3 and in the same division 4.3, packing group (PG III) (see Table 5-3), the gas evolution rates of the single values varied in a wide range from 0.4 to 5.7 l / (kg x h). However, it must be noted that the interlaboratory test on the method UN Test N.5 / EC A.12 shows significant differences in the determination of the gas evolution rates and a relatively high probability of incorrect classification (see chapter 5.6.1.1).

Further, it was observed that the participants of the interlaboratory test 2007 used different devices to measure the gas evolution rate like classical volumetric measuring devices (e.g. gas burette or automatic gas burette) as well as other measuring techniques / devices (e.g. pressure gauge or gas flow meter or gravimetric detection technique). It is remarkable that the results of the two laboratories which used a gravimetric detection technique are very similar and have a comparatively high repeatability. On the other hand, very low gas evolution rates were determined by the laboratory which measures the gas evolution rate by volumetry and uses a magnetic stirrer in addition. It therefore might be concluded that the use of a stirrer considerably lowers the measured gas evolution rate.

It is recommended that the reasons for these differences in the measured gas evolution rates when applying test method UN Test N.5 / EC A.12 are investigated in further and more specific investigations.

6.2 Influencing factors

An additional exploratory analysis of the gas evolution rates was conducted in order to find the reason for the broad spread of the results and the deviations between the laboratories.
Based on the results of one laboratory it might be concluded that the use of a stirrer considerably lowers the gas evolution rate.
It was found that ambient temperature has no influence of the gas evolution rate.

6.3 Recommendations for the participants of the interlaboratory test to improve 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 6-1).

Table 6-1: Recommendations to improve the execution of the method

Laboratory	Application recommendation
066	No additional recommendations.
106	Even though the result of laboratory 106 was "satisfactory" according to DIN 38402-45 the following recommendations are given: 1. Check the accuracy of the measuring device “Gas flow meter FM4 (SYSTAG SystemTechnik AG, Switzerland)” by comparison with an independent method (e.g. glass burette). 2. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
121	Even though the result of laboratory 121 was "satisfactory" according to DIN 38402-45 the following recommendations are given: 1. Check the accuracy of the measuring device “pressure gauge” by comparison with an independent method (e.g. glass burette). 2. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
201	1. Check the influence of the procedure stirring with “magnetic stirrer” by comparison with a test performed without stirring the sample. Remark: The method gives no recommendation to use a stirrer. 2. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
251	Even though the result of laboratory 251 was "satisfactory" according to DIN 38402-45 the following recommendation is given: 1. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
272	Even though the result of laboratory 272 was "satisfactory" according to DIN 38402-45 the following recommendation is given: 1. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
902	No additional recommendations.
906	Even though the result of laboratory 906 was "satisfactory" according to DIN 38402-45 the following recommendation is given: 1. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
907	Even though the result of laboratory 907 was "satisfactory" according to DIN 38402-45 the following recommendations are given: 1. Check the accuracy and the precision of the measuring device “automated gas burette system” by comparison with an independent method (e.g. glass burette). 2. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
908	Even though the result of laboratory 908 was "satisfactory" according to DIN 38402-45 the following recommendation is given: 1. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.
910	No additional recommendations.
911	Even though the result of laboratory 911 was "satisfactory" according to DIN 38402-45 the following recommendation is given: 1. Check compliance with the method with regard to the requirement that the test is to be performed at 20 °C.

It is recommended that quality control measures, which were applied to check the accuracy of the laboratory results, should be noted in the laboratory test reports.

6.4 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:
    - 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 Test N.5 / EC A.12
    - Identification of the causes for the differences between the laboratories with the aid of more specific investigations (cause study).
    - It should be considered to agree on a specific procedure and equipment for determination of the gas evolution rate and the methods UN Test N.5 / EC A.12 should be revised accordingly and 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.

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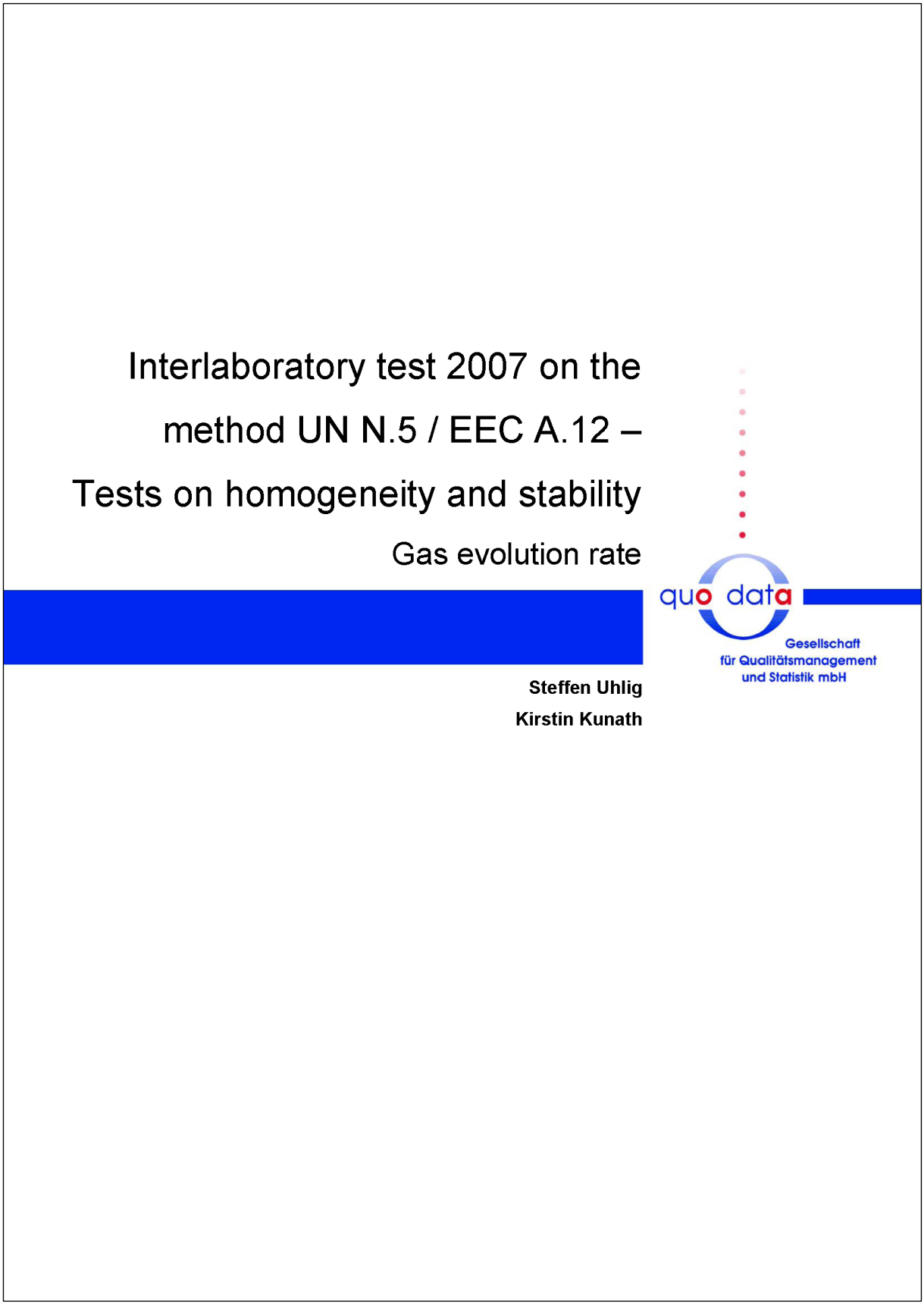
[6] Uhlig S, Lischer P (1998) Statistically-based performance characteristics in laboratory performance studies; Analyst, 123, 167-172.

[7] 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 of the homogeneity and stability



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1 Test on homogeneity

1.1 Data

For the test on homogeneity, 28 test portions have been chosen randomly and the gas evolution rate has been determined three times for each test portion (see Table 1-1).

Table 1-1: Overview of the data used for the test on homogeneity

Test portion	Sample	Gas evolution rate [l/kg/h] measurement value 1	Gas evolution rate [l/kg/h] measurement value 2	Gas evolution rate [l/kg/h] measurement value 3
1	A1	4.09	4.00	4.11
2	A1	4.16	4.15	4.12
3	A1	4.23	4.30	4.15
4	A1(Anl. 2)	4.22	3.69	3.89
5	A7	4.18	4.25	4.24
6	A7	4.15	4.24	4.06
7	A7	4.28	4.27	4.39
8	A7	4.14	4.15	3.96
9	B6	4.13	4.22	4.06
10	B6	3.51	3.67	3.65
11	B6	4.13	4.10	4.03
12	B6 (Anl.2)	4.32	4.22	4.41
13	C5	4.24	4.31	4.08
14	C5	4.20	4.21	4.14
15	C5	4.20	4.23	4.23
16	C5	3.99	3.92	3.99
17	D4 (Anl.2)	4.30	4.38	4.40
18	E3	4.06	4.14	4.04
19	E3	4.21	4.27	4.17
20	F2	4.42	4.23	4.03
21	F2	4.15	4.19	4.13
22	G1	4.30	4.24	4.25
23	G1 (Anl.2)	4.26	4.44	4.27
24	G8	4.07	4.11	4.06
25	G8	4.19	4.25	4.13
26	H7	4.17	4.27	4.08
27	H7	4.22	4.39	4.00
28	H7 (Anl.2)	4.14	4.10	0.68

1.2 Test on homogeneity

An analysis of variance is carried out which tests if the sampling variance (between-sample variance) differs significantly from zero. If there is a significant difference, the material exhibits heterogeneity.
A significance level smaller 5% indicates heterogeneous sample material.
The data described in Section 1.1 exhibits an empirical significance level of 13.4%.

Table 1-2: Statistical values over all test portions

Mean	abs. analytic s.d.	rel. analytic s.d.	abs. heterogeneity s.d.	rel. heterogeneity s.d.
4.111	0.39	9.43%	0.145	3.52%

According to ISO 13528 the samples are sufficiently homogenous.

2 Test on stability

2.1 Data

Day	Date	Gas evolution rate [l/kg/h] measurement value 1	Gas evolution rate [l/kg/h] measurement value 2	Gas evolution rate [l/kg/h] measurement value 3	comment
1	14.11.2005	5.41	5.22	5.61	with CaCl dissolution
2	21.11.2005	6.05	4.83	6.07	with CaCl dissolution
3	22.02.2007	3.75	3.77	3.65	
4	07.03.2007	4.01	2.81	4.72	
5	09.03.2007	4.05	3.98	3.30	
6	15.03.2007	4.08	4.03	4.17	
7	21.03.2007	3.99	4.16	3.57	
8	27.03.2007	4.12	3.93	4.84	
9	29.03.2007	3.96	4.74	4.31	
10	17.04.2007	4.41	4.10	4.30	
11	26.04.2007	4.20	4.47	4.45	
12	03.05.2007	4.23	4.82	4.09	
13	10.05.2007	0.76	3.62	4.42	
14	31.05.2007	4.13	4.24	4.21	
15	06.06.2007	4.14	4.38	4.21	
16	13.06.2007	4.46	3.63	4.68	
17	03.07.2007	4.35	3.90	4.14	
18	15.08.2007	4.46	6.76	4.58	
19	05.09.2007	4.14	3.50	3.28	
20	27.09.2007	3.63	3.52	3.88	
21	04.10.2007	4.06	3.76	3.71	

2.2 Results

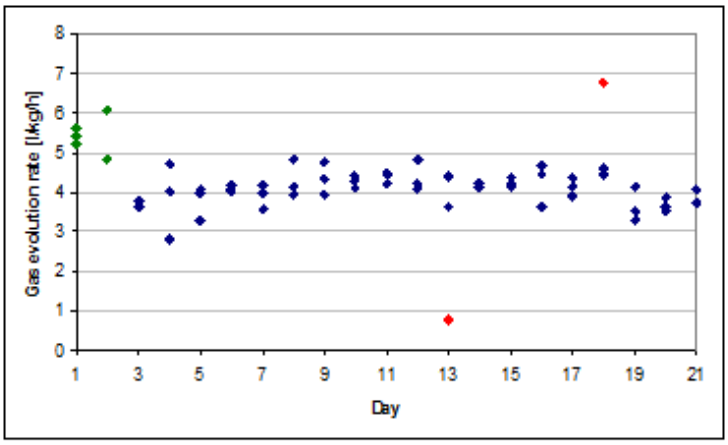


Figure 2-1: Relationship between the Gas evolution rate and the time (day)

Green marked measurements: with CaCl dissolution (not taken into account)

Red marked measurements: potential outliers (not taken into account)

Table 2-1: ANOVA table

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	3.73518	18	0.20751	1.44	0.1722
Within groups	5.18887	36	0.144135		
Total (Corr.)	8.92404	54			

Table 2-2: Linear model - No significant trend can be identified (p-value=0.9124 >0.05)

Parameter	Least Squares Estimate	Standard Error	T Statistic	P-Value
Intercept	4.06029	0.131347	30.9127	0
Slope	0.00110889	0.0100337	0.110517	0.9124

Table 2-3: ANOVA table corresponding to the linear model in Table 2-2

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	0.00205608	1	0.00205608	0.01	0.9124
Residual	8.92199	53	0.168339		
Total (Corr.)	8.92404	54			

8.2 Test instruction

Center for quality assurance for testing of dangerous goods and hazardous substances

Federal Institute for Materials Research and Testing (BAM)

Quality Management and Statistics GmbH

Physikalisch-Technische Bundesanstalt (PTB)

Round Robin Test on the method UN N.5 / EEC A.12 Instruction to perform the Round Robin Test

2007-06-26

Dear colleagues,

As announced at the last OECD-IGUS-EOS meeting in Delft (May 2007) 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 other) on the method UN N.5 / EEC A.12.
For this test the substance "metal mixture powder" was chosen as test substance.

11 laboratories did confirm to participate in this round robin test. Therefore we ask the participating laboratories to perform the UN N.5 / EEC A.12 test with this substance submitted to you by BAM according to the test procedure in the UN Test Manual (4th rev. edition, 2003, 33.4.1) or, respectively, to the European test method A.12 (see: http://ecb.jrc.it/testing-methods/). Please perform the test under the following special conditions and/or with the following exceptions:

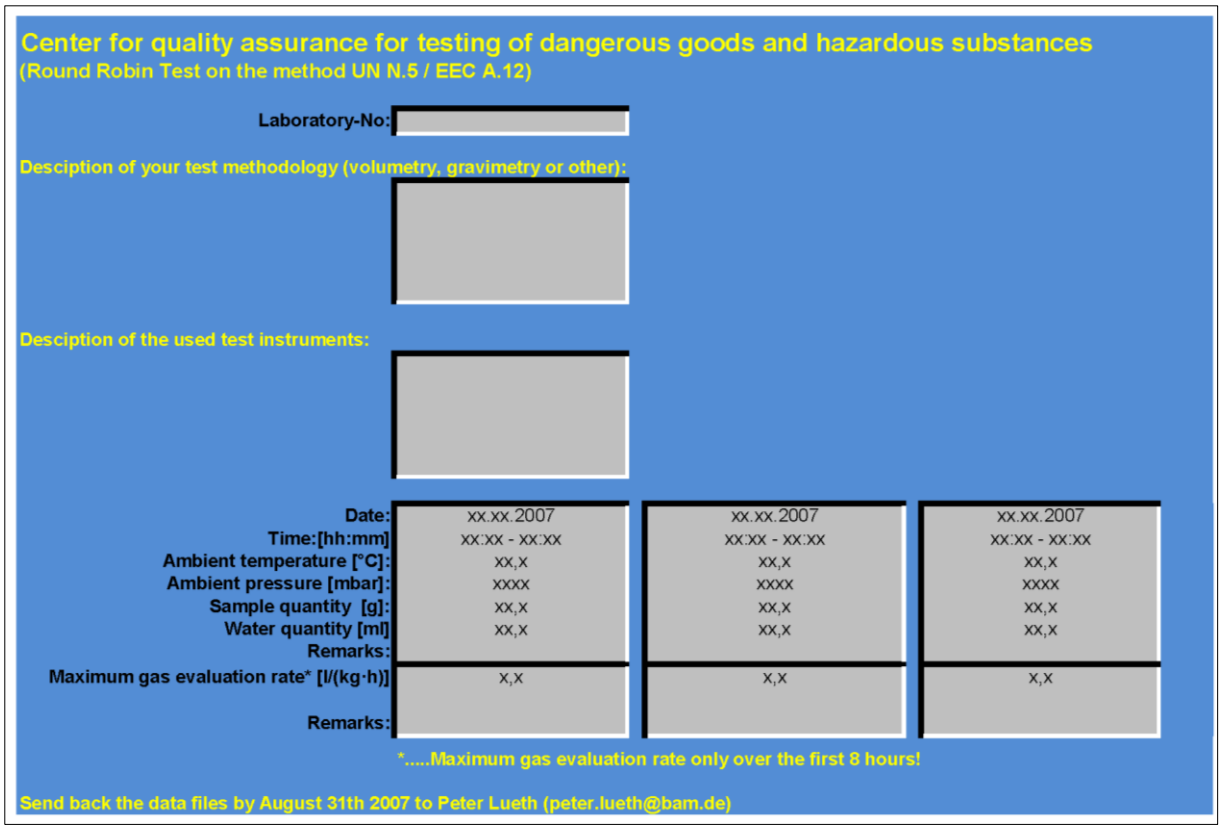
- Please perform **only the mean test** as prescribed in chapter 33.4.1.4.3.5 of UN Test Manual (4th rev. edition, 2003) or, respectively, in chapter 1.6.4 of the European method A.12. The test should be performed in **triplicate**.
- The substance should be tested in its commercial state, i.e. please DO NOT treat the test substance by any mechanical method before testing (**NO SIEVING, NO GRINDING**,...). In case that the substance is slightly agglomerated, please crush possible agglomerates only very gently (by hand). There should be no problems to obtain again a fluid powder thereby.
- Prepare **10.0± 0.1 g samples**.
- For the test use **20.0± 0.5 ml distilled (or demineralised) water.**
- The test should be preformed **only over 8 hours after adding the water**, i.e. the rate of the evolution of gas should be calculated **over 7 hours at 1 hour** intervals.

All the other procedures as prescribed in chapter 33.4.1.4.3.5 of UN Test Manual (4th rev. edition, 2003) or, respectively, in chapter 1.6.4 of the European method A.12. and should be applied as usual.

Together with the test substance "metal mixture powder" (appr. 250 g) you receive from BAM a prepared data file for the acquisition of your measurement data.
We ask you **to perform the tests by middle of August 2007** and to **send back the duly completed data file by August 31th 2007 to** Peter Lueth via email: **peter.lueth@bam.de**.
If you still have any questions, please do not hesitate to contact us.
We thank you for participating in this round robin test and wish you a successful performance. We are looking forward to discussing the results with you.

Peter Lueth (BAM)
June 2007

8.3 Laboratory data input form



Center for quality assurance for testing of dangerous goods and hazardous substances
(Round Robin Test on the method UN N.5 / EEC A.12)

Laboratory-No:			
Desciption of your test methodology (volumetry, gravimetry or other):			
Desciption of the used test instruments:			
Date:	xx.xx.2007	xx.xx.2007	xx.xx.2007
Time:[hh:mm]	xx:xx - xx:xx	xx:xx - xx:xx	xx:xx - xx:xx
Ambient temperature [°C]:	xx,x	xx,x	xx,x
Ambient pressure [mbar]:	xxxx	xxxx	xxxx
Sample quantity [g]:	xx,x	xx,x	xx,x
Water quantity [ml]	xx,x	xx,x	xx,x
Remarks:			
Maximum gas evaluation rate* [l/(kg·h)]	x,x	x,x	x,x
Remarks:			

*.....Maximum gas evaluation rate only over the first 8 hours!

Send back the data files by August 31th 2007 to Peter Lueth (peter.lueth@bam.de)