Results of Proficiency Test
LIQUEURS
November 2010

Organised by: Institute for Interlaboratory Studies (iis)
Spijkenisse, the Netherlands

Authors: ing. R.J. Starink
Correctors: dr. R.G. Visser & ing. N. Boelhouwer

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CONTENTS

1. INTRODUCTION

Since 2009, a proficiency test for liqueurs is organised every year by the Institute for Interlaboratory Studies. During the planning of the annual proficiency testing program 2010/2011, it was decided to continue the proficiency test for the analysis of liqueurs. In this interlaboratory study, 21 laboratories in 10 different countries have participated. See appendix 2 for a list of number of participants per country. In this report, the results of the proficiency test are presented and discussed.

2 SET-UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test. Analysis for fit-for-use and homogeneity testing were subcontracted. It was decided to send two different samples of liqueur (1* 0.5 L of cream liqueur, labelled #1092 and 1* 0.5 L of spirit liqueur, labelled #1093). Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system on ISO guide 43, ILAC-G13:2007 and ISO17043:2010. This ensures 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' (i.i.s.-protocol, version 3.2) of January 2010.

2.3 CONFIDENTIALITY STATEMENT

All data present in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

The necessary bulk material (Cream Liqueur) for sample #1092 was obtained from a local producer. The approximately 30 litre bulk sample was, after homogenisation in a precleaned can, divided over 51 amber glass bottles of 0.5 L and labelled #1092. The homogeneity of these subsamples was checked by determination of Density in accordance with ASTM D4052:02e1 on 8 stratified random selected samples.

Sample	*Density @ 20ºC in kg/L*
Sample #1092-1	1.11746
Sample #1092-2	1.11746
Sample #1092-3	1.11747
Sample #1092-4	1.11746
Sample #1092-5	1.11746
Sample #1092-6	1.11746
Sample #1092-7	1.11748
Sample #1092-8	1.11746

table 1: Homogeneity test results of subsamples #1092

From the test results of table 1, the repeatability was calculated and compared with 0.3 times the corresponding target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Density @ 20ºC in kg/L
r (Observed)	0.00002
reference method	D4052:02e1
0.3 * R (ref. method)	0.00015

table 2: Repeatability of subsamples #1092

The necessary bulk material (Spirit Liqueur) for sample #1093 was obtained from a local producer. The approximately 25 litre bulk sample was, after homogenisation in a precleaned can, divided over 40 amber glass bottles of 0.5 L and labelled #1093. The homogeneity of these subsamples was checked by determination of Density in accordance with ASTM D4052:02e1 on 8 stratified random selected samples.

Sample	*Density @ 20ºC in kg/L*
Sample #1093-1	0.96231
Sample #1093-2	0.96230
Sample #1093-3	0.96230
Sample #1093-4	0.96231
Sample #1093-5	0.96229
Sample #1093-6	0.96227
Sample #1093-7	0.96232
Sample #1093-8	0.96232

table 3: Homogeneity test results of subsamples #1093

From the test results of table 3, the repeatability was calculated and compared with 0.3 times the corresponding target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Density @ 20ºC in kg/L
r (Observed)	0.00005
reference method	D4052:02e1
0.3 * R (ref. method)	0.00015

table 4: Repeatability of subsamples #1093

The repeatabilities of the results from the homogeneity test were in agreement with the requirements of the respective standards. Therefore, homogeneity of all the prepared subsamples was assumed.

To each of the participating laboratories 1*0.5 L bottle of sample #1092 and 1*0.5 L bottle of sample #1093 were sent on October 27, 2010.

2.5 STABILITY OF THE SAMPLES

The stability of liqueur, packed in the amber glass bottles, was checked. The material was found sufficiently stable for the period of the proficiency test.

2.6 ANALYSES

The participants were asked to determine on sample #1092 and #1093: Density @ 20^{o}C, pH and Strength (in %V/V).
To get comparable results a detailed report form, on which the units were printed, was sent together with each sample. In addition, a letter of instructions and a SDS were added to the package.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received. The original reported results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after deadline, a reminder fax was sent to those laboratories that had not yet reported any results at that moment.
Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected results are used for data analysis and original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' (i.i.s.-protocol, version 3.2) of January 2010.

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…' were not used in the statistical evaluation. First the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation should be used with due care.

In accordance with ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test. Both outliers and stragglers were not included in the calculations of averages and standard deviations. Finally, the reproducibilities were calculated from the standard deviations by multiplying these with a factor of 2.8.

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are under the X-axis.
The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.
Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3, nr.13-14).

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. ASTM reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study. The target standard deviation was calculated from the literature reproducibility by division with 2.8.

In case no literature reproducibility was available, other target values were used. In some cases, literature repeatability is available; in other cases, a reproducibility of a former iis proficiency test could be used and the Horwitz equation can be used to estimate target reproducibility.

The z-scores were calculated according to:

$$z_{(target)} = (\text{result} - \text{average of PT}) / \text{target standard deviation}$$

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The usual interpretation of z-scores is as follows:

| z | < 1	good
1 < | z | < 2	satisfactory
2 < | z | < 3	questionable
3 < | z |	unsatisfactory

4. EVALUATION

In this proficiency test, some problems were encountered with despatch of the samples. The laboratories in P.R. of China, Pakistan, Taiwan and Thailand did receive the samples very late. Four participants reported results after the final reporting date. Four other participants did not report any results at all. Not all laboratories were able to perform all analysis requested. Finally, the 17 reporting laboratories did send in 71 (numerical) results. Observed were 8 outlying results, which is 11.3%. In proficiency studies, outlier percentages of 3% - 7.5% are normal.

4.1 EVALUATION PER TEST

In this section, the results are discussed per test.
The methods, which are used by the various laboratories, are taken into account for explaining the observed differences when possible and applicable. These methods are also in the tables together with the original data. The abbreviations, used in these tables, are listed in appendix 3.

Not normal distribution was found for the following determination: Strenght (#1092). In this case the statistical evaluation should be used with due care.

Density: This determination was only problematic on the cream liqueur #1092. The determination on the spirit liqueur #1093 was not problematic. In total two statistical outliers were observed. The calculated reproducibility for sample #1092, after rejection of the statistical outlier, is not in agreement, while the calculated reproducibility of sample #1093 is in agreement with the requirements of ASTM D4052:02e1.

pH: This determination was not problematic for both samples. No statistical outliers were observed and both calculated reproducibilities are in agreement with the requirements of EN15490:07.

Strength (%V/V): This determination was very problematic for a number of laboratories. In total six statistical outliers were observed. Regretfully, no standard method with precision data exists.
When compared with the calculated reproducibilities of the previous proficiency test iis09C13c, the spread found for sample #1093 is in full agreement (0.148 vs 0.149), while the spread for sample #1092 is much larger (0.309 vs 0.202) than the spread on a similar sample in the previous PT.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard and the reproducibility as found for the group of participating laboratories. The average results per sample, calculated reproducibilities and reproducibilities derived from literature standards (in casu ASTM, EN standards) or previous proficiency tests are compared in the next table.

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Density @ 20°C	kg/L	13	1.11507	0.00073	0.00050
pH		8	7.28	0.16	0.69
Strength	%V/V	9	14.650	0.309	(0.202)

Table 5: Reproducibilities of sample #1092

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Density @ 20°C	kg/L	14	0.95931	0.00009	0.00050
pH		9	7.59	0.53	0.69
Strength	%V/V	10	34.962	0.148	(0.149)

Table 6: Reproducibilities of sample #1093

Results between brackets are compared with the spread of the previous proficiency test or estimated from target reproducibility

4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2010 WITH PREVIOUS PT'S

	November 2010	*December 2009*
Number of reporting labs	17	23
Number of results reported	71	92
Statistical outliers	8	11
Percentage outliers	11.3%	12.0%

table 7: comparison with previous proficiency tests.

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.
The performance of the determinations of the proficiency tests was compared against the requirements of the respective standards. The conclusions are given the following table:

Parameter	*November 2010*	*December 2009*
Cream liqueur		
Density @ 20^{o}C	--	++
pH	++	++
Strength	--	--
Spirit liqueur		
Density @ 20^{o}C	++	--
pH	++	+/-
Strength	+/-	--

Table 8: comparison determinations against the standard

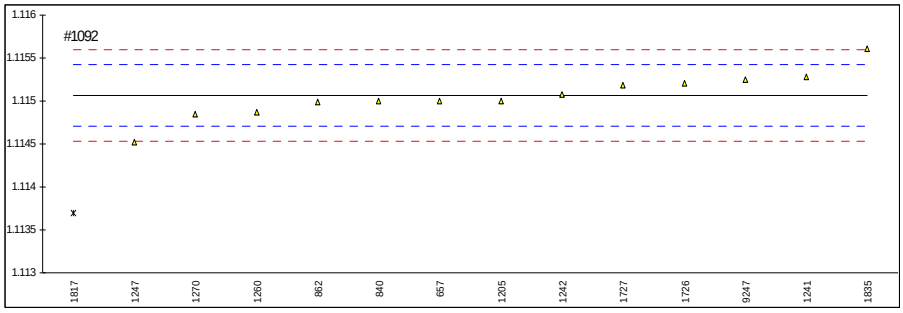
The performance of the determinations against the requirements of the respective standards is listed in the above table. The following performance categories were used:

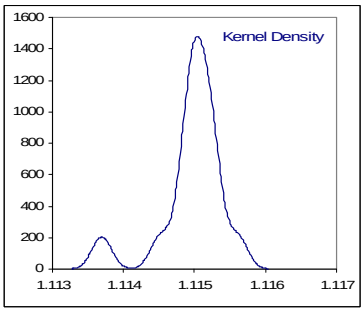
++: group performed much better than the standard
+ : group performed better than the standard
+/-: group performance equals the standard
- : group performed worse than the standard
-- : group performed much worse than the standard
n.e.: not evaluated

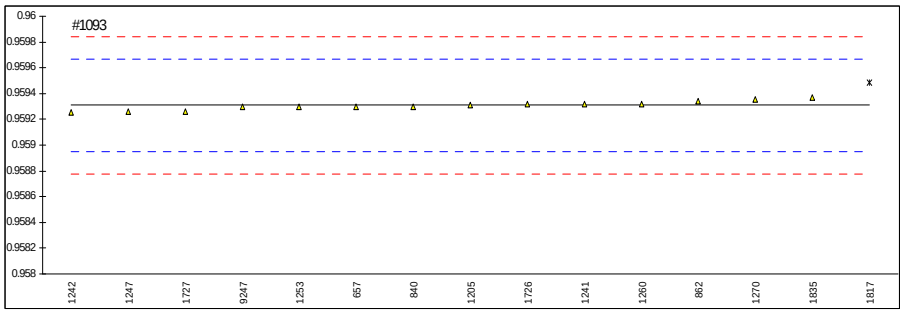
APPENDIX 1

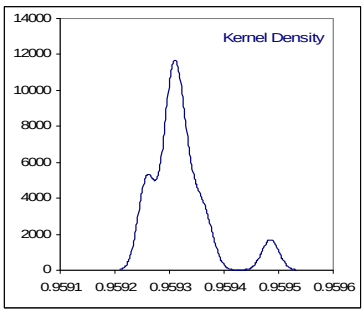
Determination of Density @ 20°C on sample #1092 and #1093; results in kg/L

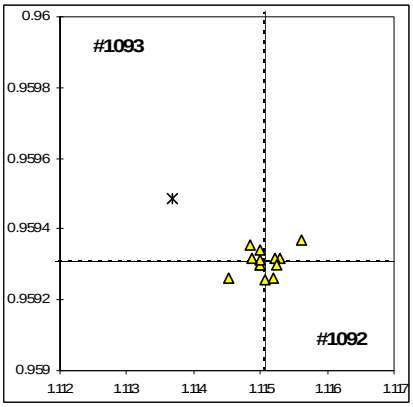
lab	method	#1092	mark	z(targ)	#1093	mark	z(targ)	remarks
657	D4052	1.1150		-0.36	0.9593		-0.05	
840	D4052	1.11500		-0.36	0.95930		-0.05	
862	D4052	1.11499		-0.42	0.95934		0.18	
867		-----		-----	-----		-----	
922		-----		-----	-----		-----	
1006		-----		-----	-----		-----	
1126		-----		-----	-----		-----	
1205	In house	1.115003		-0.35	0.959314		0.03	
1241	In house	1.11528		1.21	0.95932		0.07	
1242	D4052	1.115071		0.04	0.959256		-0.29	
1247	D4052	1.11452		-3.05	0.95926		-0.27	
1253		-----		-----	0.95930		-0.05	
1260	D4052	1.114872		-1.08	0.959320		0.07	
1270	D4052	1.114847		-1.22	0.959355		0.26	
1605		-----		-----	-----		-----	
1726	D4052	1.11521		0.81	0.95932		0.07	
1727	D4052	1.11519		0.70	0.95926	C	-0.27	First reported 0.95923
1817	In house	1.113694	G(0.01)	-7.68	0.959485	G(0.01)	0.99	
1835	D4052	1.11561		3.05	0.95937		0.35	
2160		-----		-----	-----		-----	
9247	D4052	1.11525		1.04	0.95930		-0.05	
	normality	OK			OK			
	n	13			14			
	outliers	1			1			
	mean (n)	1.11507			0.95931			
	st.dev. (n)	0.000260			0.000034			
	R(calc.)	0.00073			0.00009			
	R(D4052:02e1)	0.00050			0.00050			





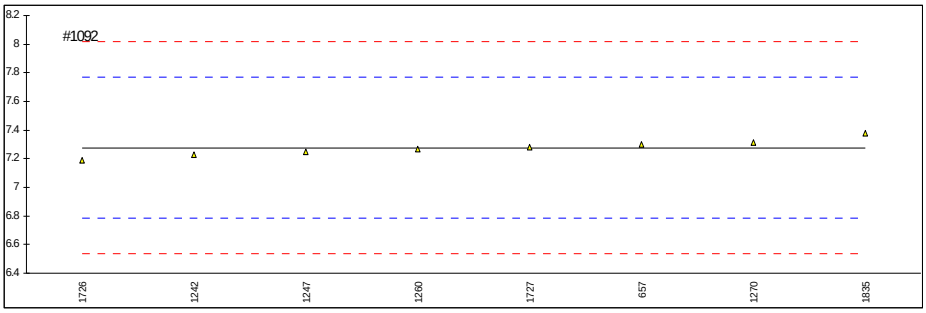


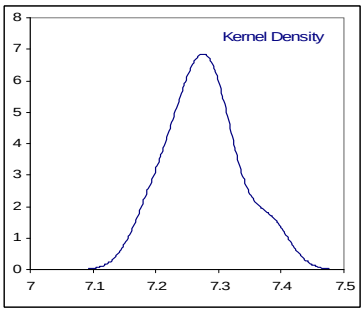


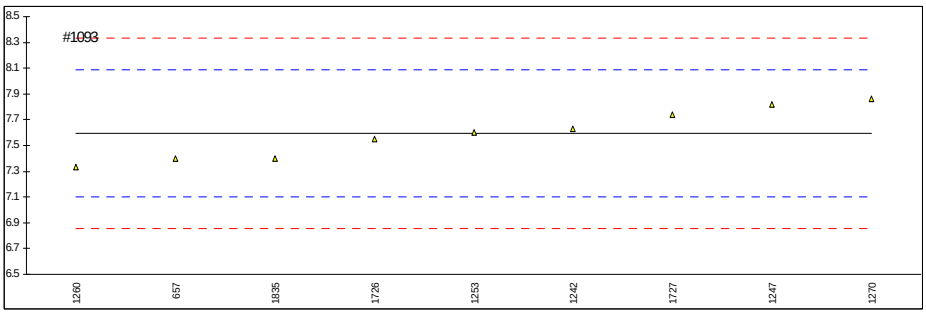


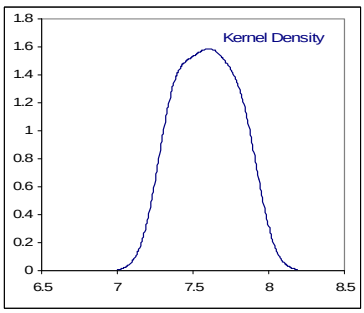
Determination of pH on sample #1092 and #1093;

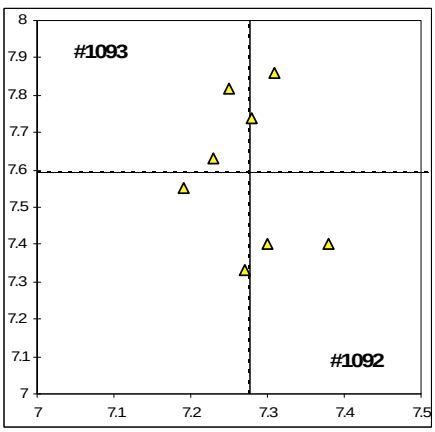
lab	method	#1092	mark	z(targ)	#1093	mark	z(targ)	remarks
657	INH-056	7.3		0.10	7.4		-0.78	
840		-----		-----	-----		-----	
862		-----		-----	-----		-----	
867		-----		-----	-----		-----	
922		-----		-----	-----		-----	
1006		-----		-----	-----		-----	
1126		-----		-----	-----		-----	
1205		-----		-----	-----		-----	
1241		-----		-----	-----		-----	
1242	EN15490	7.23		-0.19	7.63		0.15	
1247	EN15490	7.25		-0.11	7.82		0.92	
1253		-----		-----	7.6		0.03	
1260	EN15490	7.27		-0.03	7.33		-1.06	
1270	EN15490	7.31		0.14	7.86		1.09	
1605		-----		-----	-----		-----	
1726	EN15490	7.19		-0.35	7.55		-0.17	
1727	EN15490	7.28	C	0.02	7.74		0.60	First reported 7.54
1817		-----		-----	-----		-----	
1835	EN15490	7.38		0.42	7.40		-0.78	
2160		-----		-----	-----		-----	
9247		-----		-----	-----		-----	
	normality	OK			OK			
	n	8			9			
	outliers	0			0			
	mean (n)	7.28			7.59			
	st.dev. (n)	0.057			0.191			
	R(calc.)	0.16			0.53			
	R(EN15490:07)	0.69			0.69			





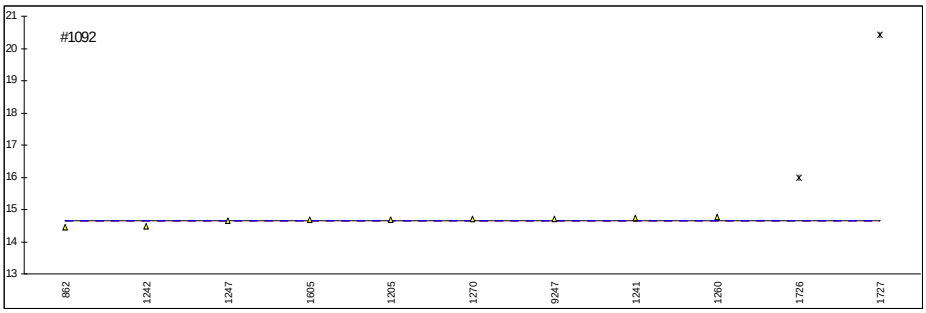


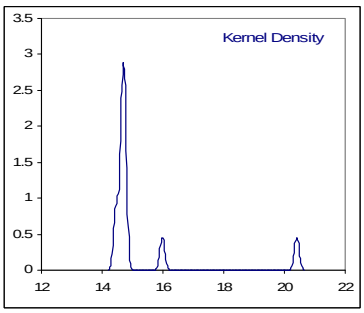


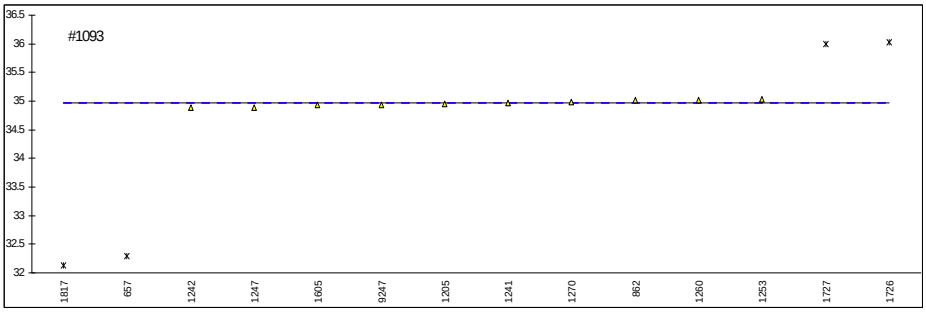


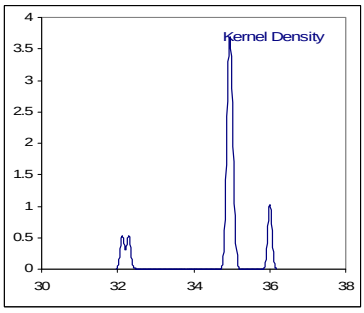
Determination of Strength on sample #1092 and #1093; results in %V/V

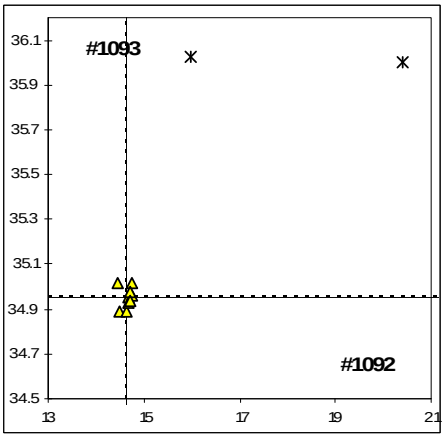
lab	method	#1092	mark	z(targ)	#1093	mark	z(targ)	remarks
657	OIML	-----		-----	32.30	DG(0.01)	-----	
840		-----		-----	-----		-----	
862	INH-15038	14.44		-----	35.02		-----	
867		-----		-----	-----		-----	
922		-----		-----	-----		-----	
1006		-----		-----	-----		-----	
1126		-----		-----	-----		-----	
1205	In house	14.68		-----	34.95		-----	
1241	distillation	14.737		-----	34.960		-----	
1242	distillation	14.492		-----	34.890		-----	
1247	distillation	14.65		-----	34.89		-----	
1253	distillation	-----		-----	35.04		-----	
1260	distillation	14.76		-----	35.02		-----	
1270	distillation	14.71		-----	34.98		-----	
1605		14.668		-----	34.930		-----	
1726	GC-FID	15.9788	G(0.01)	-----	36.0238	DG(0.01)	-----	
1727	GC	20.41	G(0.01)	-----	36.00	DG(0.01)	-----	
1817	AOAC 26.7.09	-----		-----	32.13	DG(0.01)	-----	
1835		-----		-----	-----		-----	
2160		-----		-----	-----		-----	
9247	distillation	14.71		-----	34.94		-----	
	normality	not OK			OK			
	n	9			10			
	outliers	2			4			
	mean (n)	14.650			34.962			
	st.dev. (n)	0.1102			0.0529			
	R(calc.)	0.309			0.148			
	R(lit)	unknown			unknown			
	R(iis09C13c)	0.202			0.149			











APPENDIX 2

List of number of participants per country

2 laboratories in	BELGIUM
2 laboratories in	P.R. of CHINA
1 laboratory in	PAKISTAN
1 laboratory in	SINGAPORE
3 laboratories in	SPAIN
1 laboratory in	TAIWAN ROC
1 laboratory in	THAILAND
8 laboratories in	THE NETHERLANDS
1 laboratory in	TURKEY
1 laboratory in	VIETNAM

APPENDIX 3

Abbreviations:

C	= final result after checking of first reported suspect result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
E	= error in calculations
ex	= excluded from calculations
n.a.	= not applicable
U	= unit error
SDS	= safety data sheet

Literature:

1 i.i.s. Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, January 2010

2 W. Horwitz and R. Albert, J. AOAC Int., Vol. 79, 3, p. 589, (1996)

3 ASTM E178-02

4 ASTM E1301-03

5 ISO13528-05

5 ISO 5725-86

6 ISO 5725, parts 1-6, 1994

7 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)

8 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)

9 IP 367/84

10 DIN 38402 T41/42

11 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)

12 J.N. Miller, Analyst, 118, 455, (1993)

13 Analytical Methods Committee Technical brief, No 4.January 2001

14 The Royal Society of Chemistry 2002, Analyst, 2002, 127, page 1359-1364, P.J. Lowthian and M. Thompson. (see http://www.rsc.org/suppdata/an/b2/b205600n/)