Results of Proficiency Test
Ethanol/Gasoline mix
November 2013

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

Authors: ing. R.J. Starink
Correctors: dr. R.G. Visser & ing. L. Sweere

Report: iis13C20

February 2014

CONTENTS

1. INTRODUCTION

On request of several participants, the Institute for Interlaboratory Studies decided to organise a proficiency test for the analysis of Ethanol/Gasoline mixtures during the annual proficiency test program of 2013/2014. In this first international interlaboratory study 13 laboratories in 6 different countries have participated. See appendix 2 for a list of number of participants per country. In this report the results of the 2013 proficiency test are presented and discussed. This report is electronically available through the iis internet site www.iisnl.com.

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 three different samples of Ethanol/Gasoline mixtures (each one in an 8 ml vial, labelled resp. #13250, #13251 and #13252). 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 ISO17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Also 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 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' (iis-protocol, version 3.2) of January 2010.

2.3 CONFIDENTIALITY STATEMENT

All data presented 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 materials Fuel Ethanol (99%M/M) and Gasoline were obtained from the local market. The following three different mixtures were prepared:

Sample id	Mixture	approx. composition
#13250	Ethanol/Gasoline	80 / 20 %V/V
#13251	Ethanol/Gasoline	60 / 40 %V/V
#13252	Ethanol/Gasoline	20 / 80 %V/V

Table 1: sample Homogeneity test results of subsamples #12153

Of each mixture an amount of 250 ml was prepared. Each mixture was after homogenisation in 250 ml glass bottle, divided over 31 amber glass vials of 8 ml and labelled. The homogeneity of these subsamples was checked by determination of Density in accordance with ASTM D4052:11 on 8 stratified random selected samples, except for sample #13251 for which 7 samples were used.

Sample	*Density @ 15ºC in kg/L (sample #13250)*	*Density @ 15ºC in kg/L (sample #13251)*	*Density @ 15ºC in kg/L (sample #13252)*
Sample 1	0.78800	0.78106	0.76830
Sample 2	0.78783	0.78105	0.76844
Sample 3	0.78797	0.78135	0.76850
Sample 4	0.78810	0.78114	0.76825
Sample 5	0.78807	0.78101	0.76839
Sample 6	0.78792	0.78133	0.76835
Sample 7	0.78797	0.78116	0.76809
Sample 8	0.78799	-	0.76847

Table 2: Homogeneity test results of subsamples #12153

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:

Sample	*Density @ 15ºC in kg/L (sample #13250)*	*Density @ 15ºC in kg/L (sample #13251)*	*Density @ 15ºC in kg/L (sample #13252)*
r (Observed)	0.00023	0.00038	0.00038
reference method	ASTM D4052:11	ASTM D4052:11	ASTM D4052:11
0.3 * R (ref. method)	0.00023	0.00029	0.00041

Table 3: Repeatability of subsamples #13250, #13251 and #13252

The repeatabilities of the results from the homogeneity test for sample #13250 and #13252 were in agreement with the requirements of the respective standard. However, the repeatability of the results from the homogeneity test for sample #13251 is not in agreement with the respective standard, but is the same as for sample #13252. Therefore, homogeneity of all the prepared subsamples was assumed.

To each of the participating laboratories 1 set of three vials of 8 ml (1 vial of sample #13250, 1 vial of sample #13251 and 1 vial of sample #13252) was sent on October 30, 2013.

2.5 STABILITY OF THE SAMPLES

The stability of the Ethanol/Gasoline mixtures, packed in brown glass vials, 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 the samples: Ethanol content (in %M/M and in %V/V).
To get comparable results a detailed report form, on which the units were prescribed as well as some of the required standards and a letter of instructions were prepared and made available for download on the iis website (www.iisnl.com).
A SDS and a form to confirm receipt of the samples were added to the sample 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 ‘iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ (iis.-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.
For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

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 4, nos.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

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used this in order to evaluate the fit-for-useness of the reported test result.

4. EVALUATION

In this proficiency test no problems were encountered with despatch of the samples. Three participants reported the results after the final reporting date and one participant did not report any test result at all. Finally, the 12 reporting laboratories did send in 63 test results. Observed were 13 outlying results, which is 20.6%. 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 test methods used are listed in the tables together with the original data. The abbreviations, used in these tables, are listed in appendix 3.

For all tests normal distributions were found.

Ethanol %M/M: This determination was very problematic for all three prepared Ethanol/Gasoline mixtures. In total eight statistical outliers were observed. All calculated reproducibilities after rejection of the statistical outliers are not at all in agreement with the requirements of ASTM D5501:12. The large spreads found are not easily explained and may be caused by several issues like not correcting the final result for water, various calibration techniques used, linearity of the calibration curve and/or the zero point forcing.

Ethanol %V/V: The reported test results for this determination are converted from %M/M to %V/V for all three prepared Ethanol/Gasoline mixtures. In total five statistical outliers were observed. All calculated reproducibilities after rejection of the statistical outliers are not at all in agreement with the requirements of ASTM D5501:12. It is noticed that the spreads found for the samples #13250 and #13251 are larger for %V/V then for %M/M. This may be caused by not a proper conversion from %M/M to %V/V.

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 D5501:12) or previous proficiency tests are compared in the next table.

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	9	80.90	2.13	1.13
Ethanol	%V/V	6	80.11	2.86	1.13

Table 4: Reproducibilities of sample #13250

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	9	63.19	4.38	1.31
Ethanol	%V/V	7	62.44	5.34	1.31

Table 5: Reproducibilities of sample #13251

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	10	24.52	5.45	2.30
Ethanol	%V/V	8	23.59	5.18	2.36

Table 6: Reproducibilities of sample #13252

Without further statistical calculations, it can be concluded that there is not a good compliance of the group of participating laboratories with the target reproducibility.

4.3 COMPARISON OF THE PROFICIENCY TEST WITH PREVIOUS PTS

This proficiency test was organized for the first time by the Institute for Interlaboratory Studies. Therefore no comparison could be made with previous proficiency tests.
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

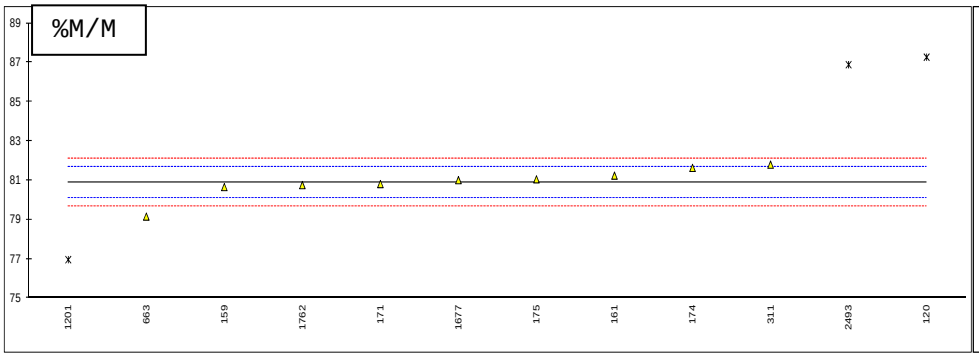
5 DISCUSSION

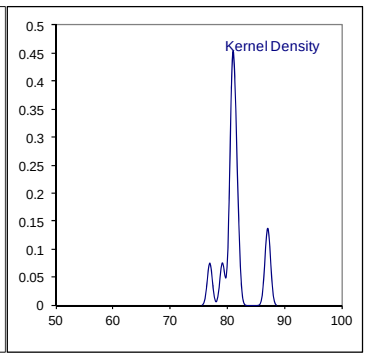
When from the pairs of reported results in %M/M and %V/V, the ratios %M/M : %V/V were calculated. It is expected that the ratio %/M/M : %V/V decreases when the percentage of Ethanol in the mixture decreases.
For all laboratories that reported %M/M as well as %V/V this decrease was visible, except for laboratory 174. For this laboratory the ratio %M/M : %V/V was constant.

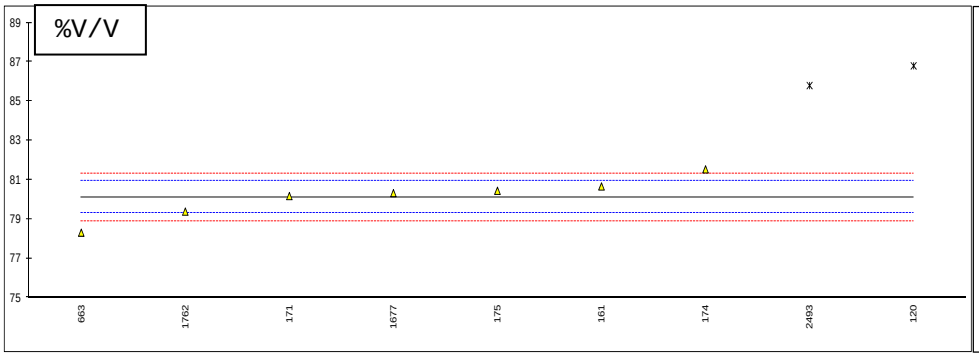
APPENDIX 1

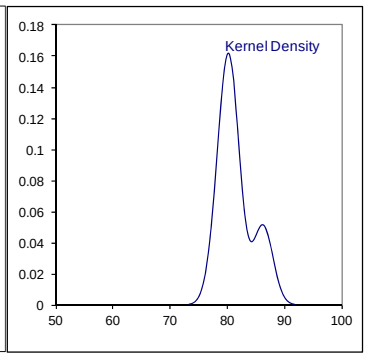
Determination of Ethanol acc ASTM D5501:12 on sample #13250; results in %M/M and %V/V.

Lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120	D5501	87.27	C,DG(0.01)	15.84	86.80	C,DG(0.05)	16.53	first.rep. 85.09 , 84.73
131		-----		-----	-----		-----	
159	D5501	80.6574		-0.61	-----		-----	
161	D5501	81.24		0.84	80.66		1.35	
171	D5501	80.811	C	-0.23	80.17	C	0.14	first rep. 80.95, 63.70
174	D5501	81.635	C	1.82	81.529	C, E	3.50	first rep. 85.200, 85.092
175	D5501	81.053		0.38	80.440		0.80	
311	D5501	81.80		2.23	-----		-----	
663	D5501	79.154		-4.35	78.306		-4.47	
1201	D5501	76.96	G(0.01)	-9.81	-----		-----	
1677	EN13132	81.01		0.27	80.32		0.51	
1762	D5501	80.756		-0.36	79.379	C	-1.82	first rep. 82.157
2493	D5501	86.888	DG(0.01)	14.89	85.797	DG(0.05)	14.05	
	normality	OK			OK			
	n	9			7			
	outliers	3			2			
	mean (n)	80.902			80.115			
	st.dev. (n)	0.7614			1.0215			
	R(calc.)	2.132			2.860			
	R(D5501:12)	1.126			1.132			



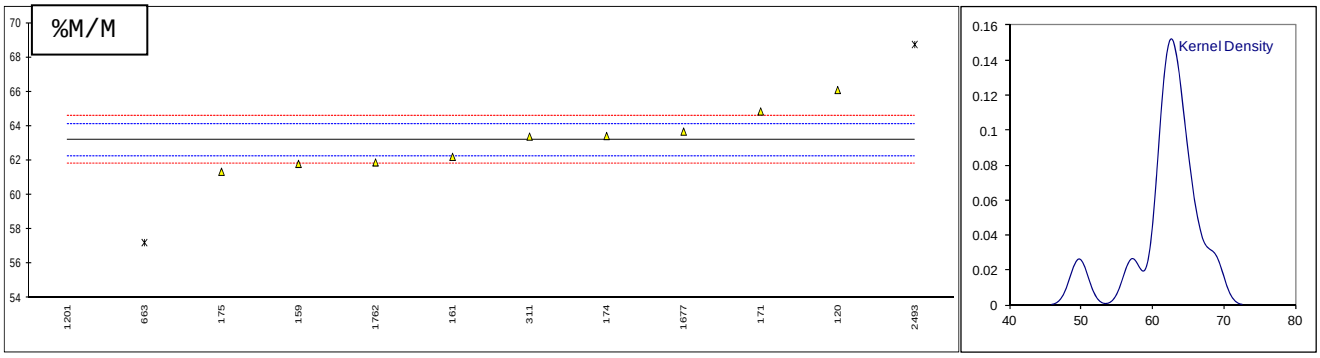


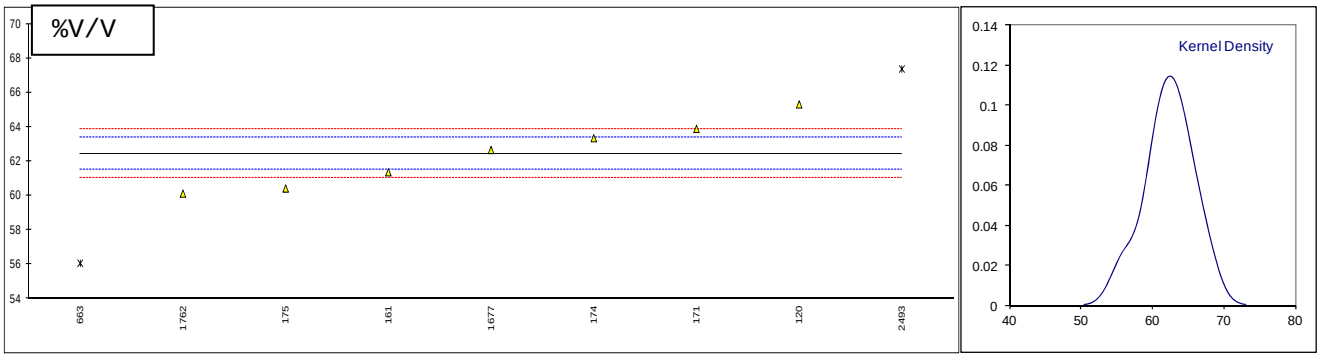




Determination of Ethanol acc ASTM D5501:12 on sample #13251; results in %M/M and %V/V.

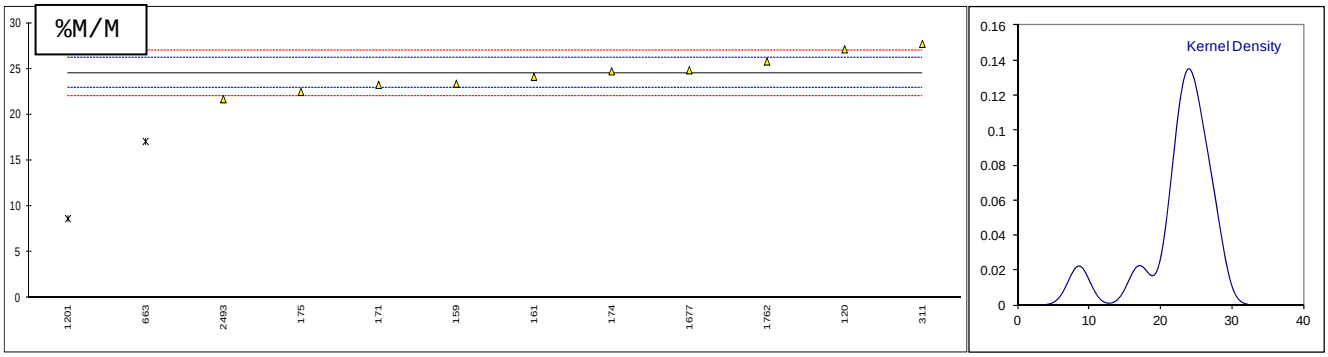
lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120	D5501	66.10		6.25	65.31		6.11	
131		-----		-----	-----		-----	
159	D5501	61.8031		-2.97	-----		-----	
161	D5501	62.21		-2.10	61.36		-2.30	
171	D5501	64.856	C	3.58	63.884	C	3.07	first rep. 62.08, 48.51
174	D5501	63.425	C	0.51	63.343	C, E	1.92	first rep. 68.634, 68.547
175	D5501	61.344		-3.96	60.417		-4.31	
311	D5501	63.39		0.43	-----		-----	
663	D5501	57.220	G(0.05)	-12.80	56.066	DG(0.05)	-13.58	
1201	D5501	49.81	G(0.01)	-28.70	-----		-----	
1677	EN13132	63.68		1.05	62.66		0.46	
1762	D5501	61.886		-2.79	60.121	C	-4.94	first rep. 63.702
2493	D5501	68.746	G(0.05)	11.92	67.372	G(0.05)	10.50	
	normality	OK			OK			
	n	9			7			
	outliers	3			2			
	mean (n)	63.188			62.442			
	st.dev. (n)	1.5641			1.9071			
	R(calc.)	4.379			5.340			
	R(D5501:12)	1.305			1.315			

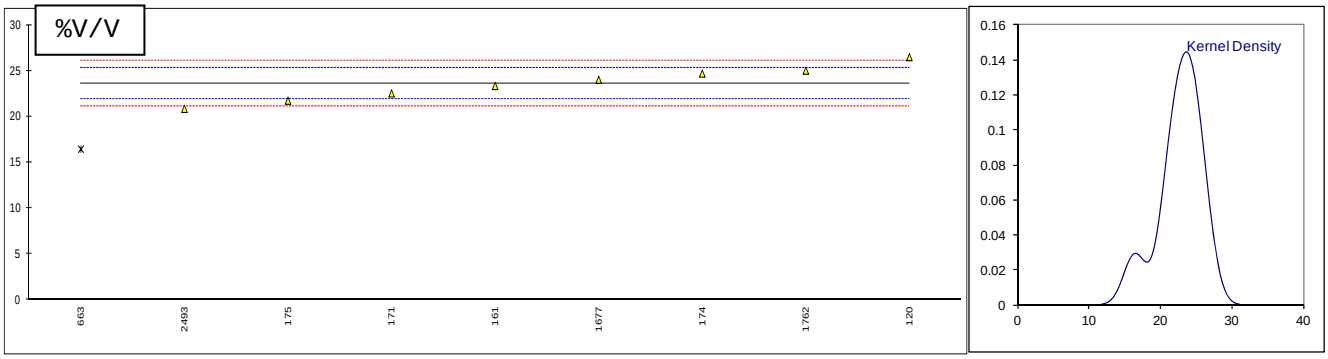




Determination of Ethanol acc ASTM D5501:12 on sample #13252; results in %M/M and %V/V.

lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120	D5501	27.13		3.17	26.49		3.44	
131		-----		-----	-----		-----	
159	D5501	23.3819		-1.38	-----		-----	
161	D5501	24.13		-0.47	23.35		-0.28	
171	D5501	23.251	C	-1.54	22.534	C	-1.25	first rep. 23.66, 18.19
174	D5501	24.730	C	0.26	24.698	C, E	1.32	first rep. 30.536, 30.497
175	D5501	22.479		-2.48	21.743		-2.19	
311	D5501	27.73		3.90	-----		-----	
663	D5501	17.080	G(0.05)	-9.04	16.445	G(0.05)	-8.49	
1201	D5501	8.65	G(0.01)	-19.29	-----		-----	
1677	EN13132	24.85		0.40	24.03		0.52	
1762	D5501	25.806		1.57	25.022	C	1.70	first rep. 26.615
2493	D5501	21.690		-3.44	20.851		-3.25	
	normality	OK			OK			
	n	10			8			
	outliers	2			1			
	mean (n)	24.518			23.590			
	st.dev. (n)	1.9481			1.8504			
	R(calc.)	5.455			5.181			
	R(D5501:12)	2.304			2.358			





APPENDIX 2

Number of participants per country

1 lab in HONG KONG
1 lab in HUNGARY
1 lab in THAILAND
2 labs in THE NETHERLANDS
7 labs in U.S.A.

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/)