Results of Proficiency Test
Ethanol/Gasoline mix
December 2015

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

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1.   INTRODUCTION

Since 2013, the Institute for Interlaboratory Studies organises a proficiency test for the analysis of Ethanol/Gasoline mixtures every year. It was decided to continue this interlaboratory study in the 2015/2016 program. In this interlaboratory study, 18 laboratories in 8 different countries have participated. See appendix 2 for a list of number of participants per country. In this report the results of the 2015 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 to an accredited laboratory. It was decided to send three different samples of Ethanol/Gasoline mixtures (each one in a 100 ml bottle, labelled resp. #15233, #15234 and #15235). Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for the statistical evaluation.

2.1   QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on a 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' of April 2014 (iis-protocol, version 3.3). The protocol can be downloaded from iis website http://www.iisnl.com from the FAQ page.

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 (EN228) were obtained from the local market. The following three different mixtures were prepared:

Sample id	Mixture	approx. composition
#15233	Ethanol/Gasoline	80 / 20 %V/V
#15234	Ethanol/Gasoline	60 / 40 %V/V
#15235	Ethanol/Gasoline	20 / 80 %V/V

Table 1: Homogeneity test results of subsamples #15233, #15234 and #15235.

Of each mixture a bulk amount of 5 litre was prepared. Out of each mixture were after homogenisation, 40 amber glass bottles of 100 ml filled and labelled. The homogeneity of these subsamples was checked by determination of Density in accordance with ASTM D4052 on 5 stratified randomly selected samples.

Sample	Density at 15ºC in kg/L (sample #15233)	Density at 15ºC in kg/L (sample #15234)	Density at 15ºC in kg/L (sample #15235)
Sample 1	0.78505	0.77537	0.75509
Sample 2	0.78518	0.77530	0.75541
Sample 3	0.78507	0.77535	0.75518
Sample 4	0.78501	0.77544	0.75535
Sample 5	0.78522	0.77540	0.75519

Table 2: Homogeneity test results of subsamples #15233, #15234, #15235

From the test results of table 2, the repeatabilities were 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 at 15ºC in kg/L (sample #15233)	Density at 15ºC in kg/L (sample #15234)	Density at 15ºC in kg/L (sample #15235)
r (Observed)	0.00025	0.00015	0.00037
reference method	ASTM D4052:11	ASTM D4052:11	ASTM D4052:11
0.3 * R (ref. method)	0.00025	0.00035	0.00054

Table 3: Repeatability of subsamples #15233, #15234 and #15235

The repeatabilities of the results from the homogeneity test for sample #15233, #15234 and #15235 were in agreement with the requirements of the standard.

To each of the participating laboratories one set of three amber glass bottles of 100ml (1 bottle of sample #15233, 1 bottle of sample #15234 and 1 bottle of sample #15235) was sent on November 11, 2015.

2.5 STABILITY OF THE SAMPLES

The stability of the Ethanol/Gasoline mixtures, packed in brown 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 the samples: Ethanol content in %M/M and in %V/V, calculated by using the given densities, see paragraph 4.

To get comparable results a detailed report form, on which the units were prescribed as well as the required standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis/. 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 gathered via the data entry portal www.kpmd.co.uk/sgs-iis/. 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 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

The protocol followed in the organisation of this proficiency test is described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3).

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, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers,

this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

According to ISO 5725 the original results per determination were submitted to Dixon's and/or Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test (ref. 15). Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's 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 visualise 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 on 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 method is for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3; nos.13 and 14). Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

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.

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 whether the reported test result is fit-for-use.

The z-scores were calculated according to:

$z_{(target)}$ = (result - average of PT) / 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 no problems were encountered with despatch of the samples. Three participants reported the results after the final reporting date and three participants did not report any test result at all due to several reasons. Finally, the 15 reporting laboratories did send in 83 test results. Fifteen outlying results were observed, which is 18.1%. In proficiency studies, outlier percentages of 3% - 7.5% are normal. This higher outlier percentage could be caused by the fact that the analyses are not independent; an outlier in mass% will probably be an outlier in volume% as well. Also 29% of the results (mainly for volume%) were corrected because of calculation errors. Not all laboratories did correct the calculation, so some of the outliers may be caused by calculation errors.

The densities of the three different ethanol/gasoline mixtures to be used for the conversion of %M/M to %V/V during this round robin, as given by iis, are listed in the table below:

Sample id	Density in kg/L
#15233	0.78511
#15234	0.77542
#15235	0.75533

Table 4: Density given by iis of subsamples #15233, #15234 and #15235.

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.

All original data sets proved to have a normal Gaussian distribution.

Ethanol %M/M: This determination was not problematic for the 80/20 and 60/40, but was problematic for the 20/80 Ethanol/Gasoline mixtures. In total six statistical outliers were observed. The calculated reproducibilities after rejection of the statistical outliers were in agreement with the requirements of ASTM D5501:12e1 for the 80/20 and 60/40 Ethanol/Gasoline mixtures, but not in agreement with the requirements of ASTM D5501:12e1 for the 20/80 Ethanol/Gasoline mixture.
Since the water content was not requested in this PT, it was not clear if all the participants corrected the test results for water, as is stated in ASTM D5501. Therefore next year, the water content of the samples will be requested to be reported.

Ethanol %V/V: The reported test results for this determination are converted from %M/M to %V/V for all three Ethanol/Gasoline mixtures. Initially 10 out of 14 reporting participants did not calculate the %V/V according to ASTM D5501 equation 8. Several laboratories apparently did not use the density for each sample as given by iis or they did not use the density for Ethanol from ASTM D5501 Table 3. Others did not correct the %M/M test result for water content, but did do so with the corresponding %V/V test result. After implementing all corrections, this determination was not problematic for the 80/20 and 60/40, but it was problematic for the 20/80 Ethanol/Gasoline mixtures. In total 9 statistical outliers were observed. The calculated reproducibilities after rejection of the statistical outliers were in agreement with the requirements of ASTM D5501:12e1 for the 80/20 and 60/40 Ethanol/Gasoline mixtures, but not in agreement with the requirements of ASTM D5501:12e1 for the 20/80 Ethanol/Gasoline mixture.

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	12	81.42	1.14	1.12
Ethanol	%V/V	12	80.95	1.07	1.13

Table 5: Reproducibilities of sample #15233

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	10	62.86	0.64	1.31
Ethanol	%V/V	10	61.77	0.62	1.32

Table 6: Reproducibilities of sample #15234

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	12	24.78	2.71	2.29
Ethanol	%V/V	12	23.72	2.59	2.35

Table 7: Reproducibilities of sample #15235

Without further statistical calculations, it can be concluded that there is a good compliance of the group of participating laboratories with the target reproducibility.

4.3 EVALUATION OF THE PROFICIENCY TEST OF DECEMBER 2015 WITH PREVIOUS PTS

	December 2015	December 2014	December 2013
Number of rep. participants	15	10	12
Number of results reported	83	52	63
Number of statistical outliers	15	0	13
Percentage statistical outliers	18%	0%	21%

Table 8: Evaluation with previous proficiency tests.

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency test was compared against the requirements of the respective standards. The conclusions are given the following table:

	December 2015	December 2014	December 2013
Gasoline/Ethanol (20:80)	+/-	--	--
Gasoline/Ethanol (40:60)	++	--	--
Gasoline/Ethanol (80:20)	-	--	--

Table 9: Comparison determinations against the reference standards

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

5.   DISCUSSION

In previous PTs the calculations were not checked by iis, whereas in this PT all conversions from %M/M results to %V/V results were checked using ASTM D5501. For this conversion, the formula in paragraph 13.4 (equation 8) of ASTM D5501 was used. In the comments of this formula, it is mentioned that the density of ethanol is given in table 2, but this should be table 3. Thus the density at 20°C of ethanol as given in ASTM D5501 should be used and the density at 20°C of each of the samples was given by iis in the letter of instructions.

In total fifteen laboratories reported test results for all or either one of the three samples. One laboratory only reported the %V/V results. The test results for the remaining fourteen laboratories were re-calculated by iis. Only four laboratories calculated the %V/V correctly from the reported %M/M. The other laboratories were asked to check their results and conversion calculations. This took some time. Eventually eight laboratories reported revised test results. Various reasons were given for not having calculated the %V/V results correctly the first time. Some laboratories had not used the ethanol density as stated in ASTM D5501. One laboratory initially did report a mixture of single and duplicate measurements. One other laboratory had applied the water correction only on the %V/V results and not on the %M/M results. The other laboratories reported both revised %M/M and %V/V results without mentioning the reason for the revision.

Remarkably, the errors for the determination of Ethanol in Gasoline in this PT are not found in the method of analysis, but in the calculation of the results from this analysis. The calculation according to ASTM D5501 should have the attention of all laboratories measuring ethanol/gasoline mixtures. It appears to be a 'simple' calculation, but there are a lot of variables which may be chosen or measured differently, like density of the sample, density of ethanol, correction of the water content, etc.

The amount of outliers for this PT seems rather high as compared to last year. The explanation may be that in this PT more laboratories corrected their test results and therefore the normal distribution curves became smaller. Due to the smaller variation more outliers are observed. Last year, the dispersion of the test results was very high, resulting in broad distribution curves and therefore no outliers were detected.
Looking at table 9 however, it can be concluded that in this PT the final performance of the group (after all the corrections) significantly improved in comparison with the PTs of the years before.
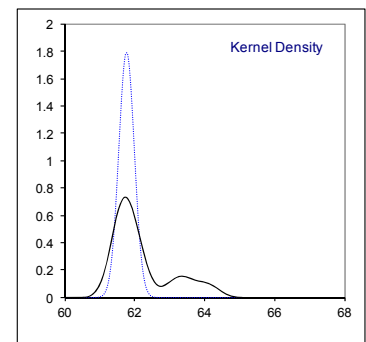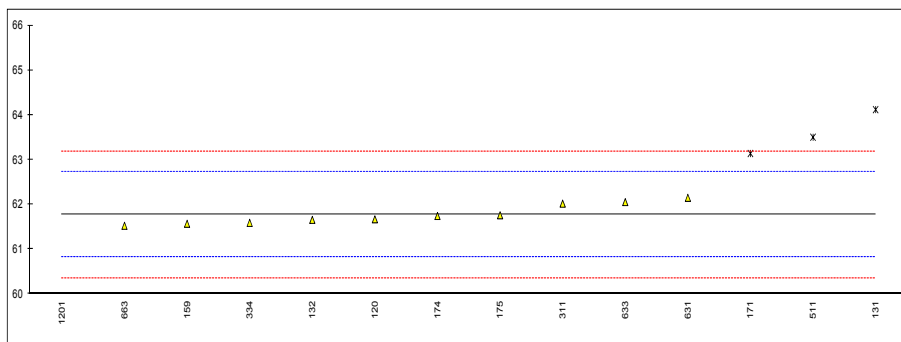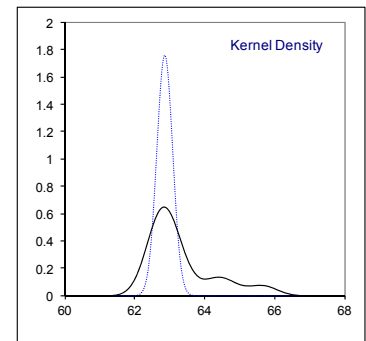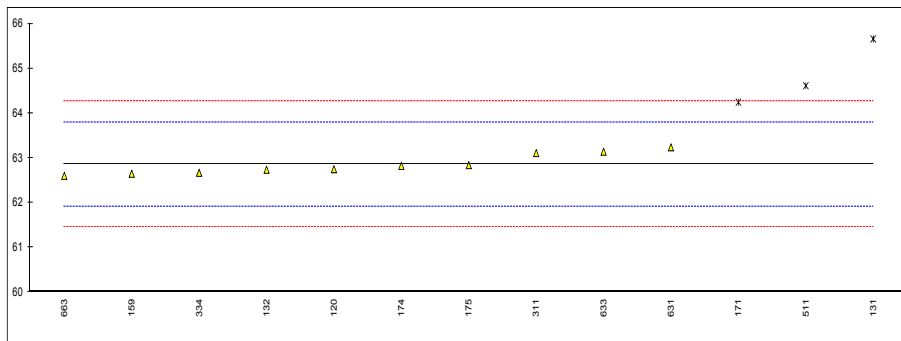
APPENDIX 1

Determination of Ethanol acc ASTM D5501 on sample #15233; results in %M/M and %V/V.

Lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120	D5501	81.42	C	0.01	81.02		0.19	first reported: 81.58%M/M
131	D5501	81.65		0.58	80.73	E	-0.54	iis calculated: 81.247%V/V
132	D5501	81.217		-0.50	80.816	C	-0.32	first reported: 79.8051%V/V
159	D5501	81.2684		-0.37	80.867	C	-0.19	first reported: 80.36%V/V
171	D5501	82.026		1.52	81.620		1.68	
174	D5501	81.290		-0.32	80.889		-0.14	
175	D5501	81.49		0.18	81.09	C	0.36	first reported: 80.58%V/V
194		-----		-----	-----		-----	
311	D5501	81.05		-0.92	80.65		-0.73	
323		-----		-----	-----		-----	
334	EN1601	85.04	G(0.01)	9.05	84.62	C,G(0.05)	9.15	first reported: 78.188%V/V
511	D5501	82.018		1.50	81.614		1.66	
631	D5501	81.00		-1.04	80.60	C	-0.86	first reported: 80.15%V/V
633	D5501	80.744		-1.68	80.346	C	-1.49	first reported: 80.300%V/V
663	D5501	79.074	C,G(0.01)	-5.85	78.684	C,G(0.01)	-5.63	fr: 78.328%M/M and 77.451%V/V
922		-----		-----	-----		-----	
1067	D5501	81.84		1.05	81.10	E	0.39	iis calculated: 81.437%V/V
1201		-----		-----	77.812	G(0.05)	-7.80	

|								
	normality	OK			OK			
	n	12			12			
	outliers	2			3			
	mean (n)	81.418			80.945			
	st.dev. (n)	0.4057			0.3803			
	R(calc.)	1.136			1.065			
	R(D5501:12e1)	1.121			1.125			
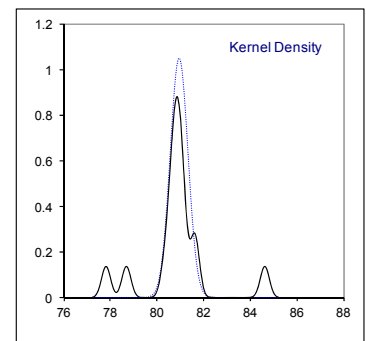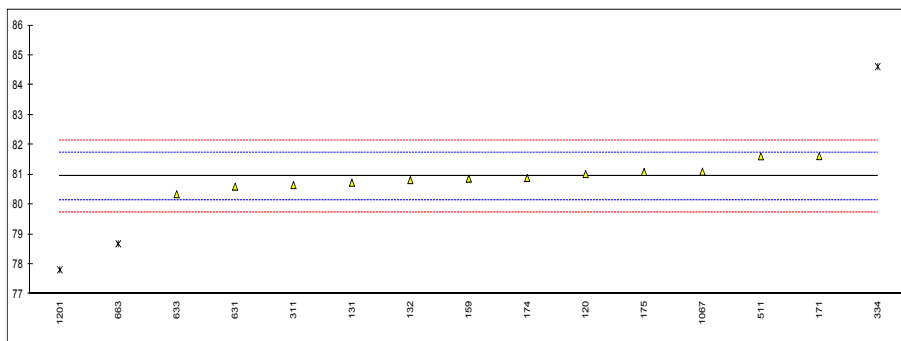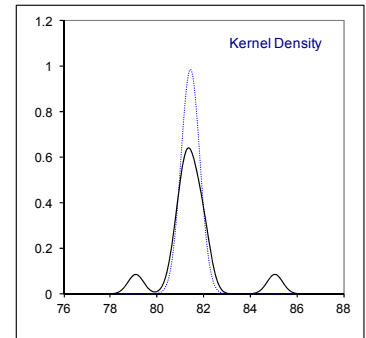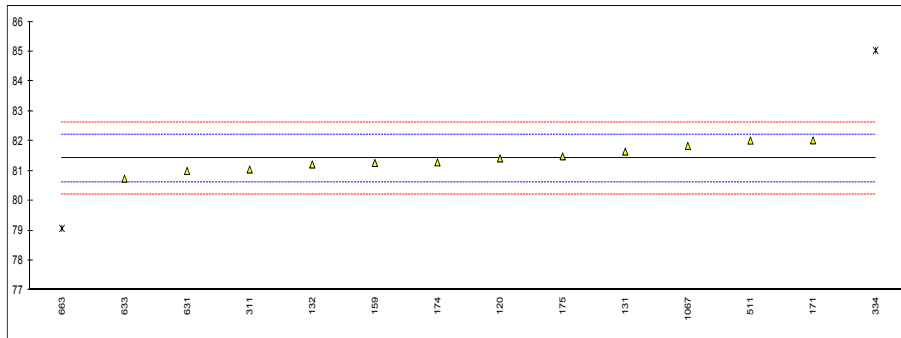
Determination of Ethanol acc ASTM D5501 on sample #15234; results in %M/M and %V/V.

lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120	D5501	62.75	C	-0.23	61.67		-0.22	first reported: 62.85%M/M
131	D5501	65.66	G(0.05)	6.00	64.12	DG(0.05),E	4.96	iis calculated: 64.530%V/V
132	D5501	62.737		-0.25	61.657	C	-0.25	first reported: 60.886%V/V
159	D5501	62.6482		-0.44	61.570	C	-0.43	first reported: 61.18%V/V
171	D5501	64.246	DG(0.01)	2.97	63.139	G(0.01)	2.89	
174	D5501	62.824		-0.07	61.743		-0.07	
175	D5501	62.84		-0.03	61.76	C	-0.03	first reported: 61.36%V/V
194		-----		-----	-----		-----	
311	D5501	63.11		0.54	62.02		0.52	
323		-----		-----	-----		-----	
334	EN1601	62.67		-0.40	61.59	C	-0.39	first reported: 61.51%V/V
511	D5501	64.614	DG(0.01)	3.76	63.503	DG(0.05)	3.66	
631	D5501	63.24		0.82	62.15	C	0.80	first reported: 61.80%V/V
633	D5501	63.141		0.61	62.054	C	0.59	first reported: 62.018%V/V
663	D5501	62.602	C	-0.54	61.525	C	-0.53	fr: 62.530%M/M and 61.067%V/V
922		-----		-----	-----		-----	
1067		-----		-----	-----		-----	
1201		-----		-----	53.33	G(0.01)	-17.87	

|				
normality	OK		OK	
n	10		10	
outliers	3		4	
mean (n)	62.856		61.774	
st.dev. (n)	0.2266		0.2220	
R(calc.)	0.635		0.622	
R(D5501:12e1)	1.310		1.323	

Determination of Ethanol acc ASTM D5501:12 on sample #15235; results in %M/M and %V/V.

lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120	D5501	23.86	C	-1.12	22.85		-1.03	first reported: 23.88%M/M
131	D5501	29.59	G(0.01)	5.89	28.15	G(0.01),E	5.28	iis calculated: 28.327%V/V
132	D5501	24.730		-0.06	23.675	C	-0.05	first reported: 23.378%V/V
159	D5501	23.3643		-1.73	22.367	C	-1.61	first reported: 22.23%V/V
171	D5501	24.480		-0.36	23.434		-0.34	
174	D5501	23.752		-1.25	22.738		-1.17	
175	D5501	23.88		-1.10	22.86	C	-1.02	first reported: 22.72%V/V
194		-----		-----	-----		-----	
311	D5501	25.95		1.44	24.84		1.34	
323		-----		-----	-----		-----	
334	EN1601	25.69		1.12	24.59	C	1.04	first reported: 24.46%V/V
511	D5501	25.563		0.96	24.474		0.90	
631	D5501	26.38		1.96	25.25	C	1.82	first reported: 25.11%V/V
633	D5501	25.054		0.34	23.985	C	0.32	first reported: 23.971%V/V
663	D5501	24.608	C	-0.21	23.558	C	-0.19	fr: 24.642%M/M and 23.442%V/V
922		-----		-----	-----		-----	
1067		-----		-----	-----		-----	
1201		-----		-----	5.40	G(0.01)	-21.83	

normality	OK		OK	
n	12		12	
outliers	1		2	
mean (n)	24.776		23.718	
st.dev. (n)	0.9669		0.9240	
R(calc.)	2.707		2.587	
R(D5501:12e1)	2.289		2.350	
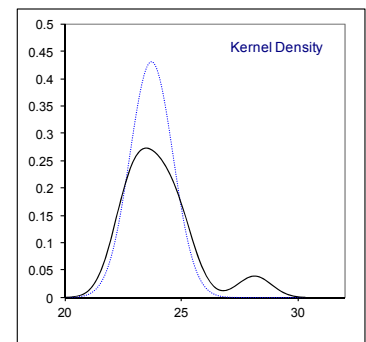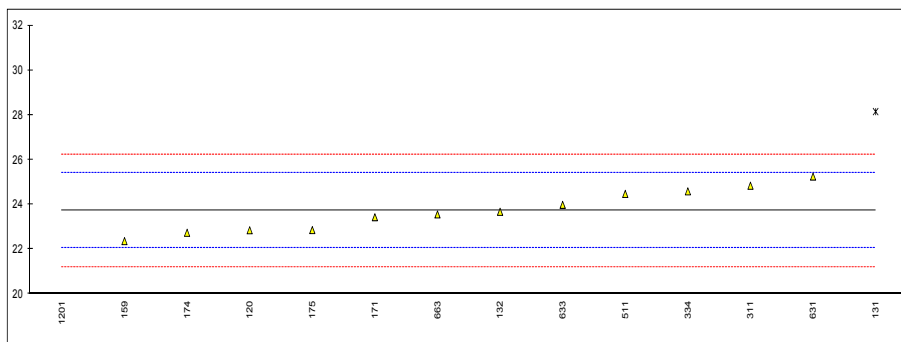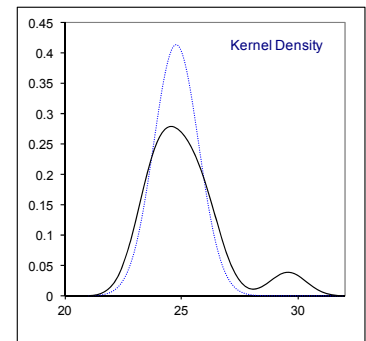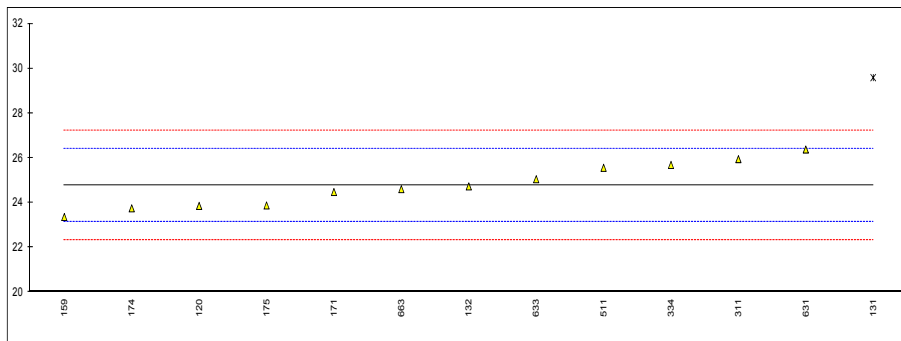
APPENDIX 2

Number of participants per country

　　　　1 lab in BELGIUM
　　　　1 lab in FRANCE
　　　3 labs in NETHERLANDS
　　　　1 lab in PAKISTAN
　　　　1 lab in PERU
　　　2 labs in PHILIPPINES
　　　　1 lab in THAILAND
　　　8 labs in UNITED STATES OF AMERICA

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
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
E	= error in calculations
ex	= excluded from calculations
n.a.	= not applicable
U	= unit error
SDS	= safety data sheet

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