Results of Proficiency Test
Ethanol/Gasoline mix
December 2014

CONTENTS

Appendices:

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. It was decided to continue this interlaboratory study in the 2014/2015 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 2014 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 a 100 ml bottle, labelled resp. #14240, #14241 and #14242). 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 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.

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
#14240	Ethanol/Gasoline	80 / 20 %V/V
#14241	Ethanol/Gasoline	60 / 40 %V/V
#14242	Ethanol/Gasoline	20 / 80 %V/V

Table 1: Homogeneity test results of subsamples #14240, #14241 and #14242.

Of each mixture a bulk amount of 5 liter 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 8 stratified random selected samples.

Sample	Density @ 15ºC in kg/L (sample #14240)	Density @ 15ºC in kg/L (sample #14241)	Density @ 15ºC in kg/L (sample #14242)
Sample 1	0.78255	0.77088	0.74828
Sample 2	0.78256	0.77090	0.74822
Sample 3	0.78256	0.77087	0.74840
Sample 4	0.78255	0.77091	0.74828
Sample 5	0.78258	0.77088	0.74829
Sample 6	0.78258	0.77085	0.74831
Sample 7	0.78257	0.77085	0.74829
Sample 8	0.78257	0.77094	0.74826

Table 2: Homogeneity test results of subsamples #14240, #14241, #14242

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 #14240)	Density @ 15ºC in kg/L (sample #14241)	Density @ 15ºC in kg/L (sample #14242)
r (Observed)	0.00003	0.00008	0.00014
reference method	ASTM D4052:11	ASTM D4052:11	ASTM D4052:11
0.3 * R (ref. method)	0.00023	0.00039	0.00060

Table 3: Repeatability of subsamples #14240, #14241 and #14242

The repeatabilities of the results from the homogeneity test for sample #14240, #14241 and #14242 were in agreement with the requirements of the standard.

To each of the participating laboratories 1 set of three amber glass bottles of 100ml (1 bottle of sample #14240, 1 bottle of sample #14241 and 1 bottle of sample #14242) was sent on November 12, 2014.

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 a given density.
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/. The detailed report form was also 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

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.

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 also the Horwitz equation can be used to estimate target reproducibility.

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. Two participants reported the results after the final reporting date and eight participants did not report any test result at all due to several reasons. Finally, the 10 reporting laboratories did send in 52 test results. No outlying results were observed. 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.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as "not OK" or "suspect". The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

Ethanol %M/M: This determination was very problematic for all three prepared
Ethanol/Gasoline mixtures. No statistical outliers were observed. All
calculated reproducibilities 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. No statistical
outliers were observed. All calculated reproducibilities are not in
agreement with the requirements of ASTM D5501:12. It is noticed that the
spreads found for all three samples are somewhat larger for %V/V then for
%M/M. This may be caused by the conversion from %M/M to %V/V. A
number of laboratories probably did not use the given density for
calculating the results in %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	10	80.83	3.55	1.13
Ethanol	%V/V	10	79.78	4.28	1.13

Table 4: Reproducibilities of sample #14240

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	8	61.82	4.59	1.32
Ethanol	%V/V	8	60.04	5.03	1.35

Table 5: Reproducibilities of sample #14241

Parameter	Unit	n	average	2.8 *sd_R	R (lit)
Ethanol	%M/M	8	22.31	7.29	2.44
Ethanol	%V/V	8	20.87	7.37	2.54

Table 6: Reproducibilities of sample #14242

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   EVALUATION OF THE PROFICIENCY TEST OF DECEMBER 2014 WITH PREVIOUS PTS

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

Table 7: 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 2014	December 2013
Gasoline/Ethanol (20:80)	--	--
Gasoline/Ethanol (40:60)	--	--
Gasoline/Ethanol (80:20)	--	--

Table 8: 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

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.
Furthermore, it was noticed that a number of laboratories (lab 131, 193, 311, 1067 and 1201) did not use the given density to calculate the Ethanol content in %V/V, but used a density of their own.
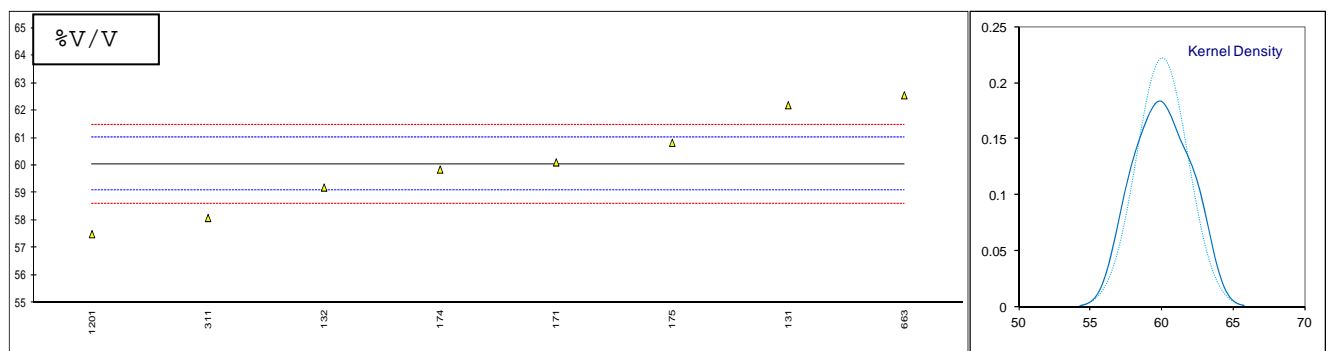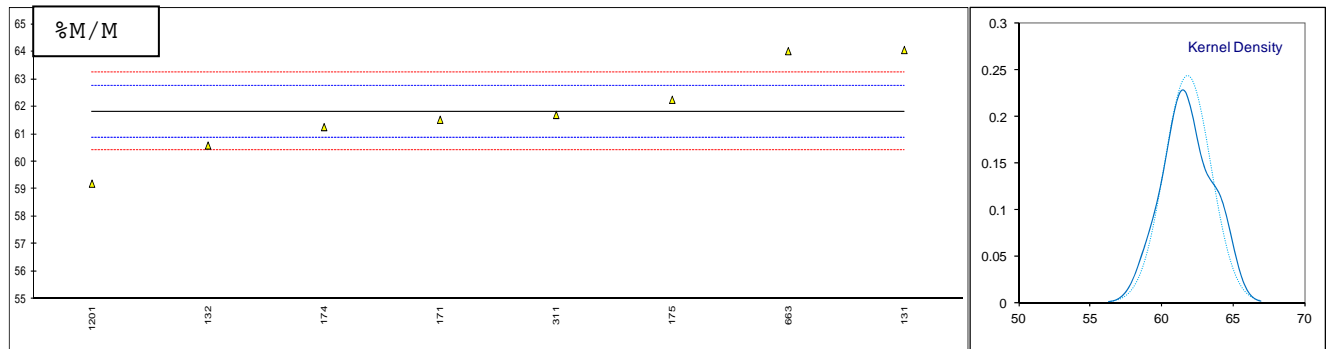
APPENDIX 1

Determination of Ethanol acc ASTM D5501:12 on sample #14240; results in %M/M and %V/V.

Lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120		-----		-----	-----		-----	
131	D5501	81.13		0.75	79.96		0.44	
132	D5501	80.232		-1.48	79.577		-0.51	
159		-----		-----	-----		-----	
171	D5501	80.7836		-0.11	80.1252		0.84	
174	D5501	80.976		0.37	80.316		1.31	
175	D5501	81.965		2.83	81.242		3.60	
193	D5501	79.65		-2.93	78.51		-3.14	
194		-----		-----	-----		-----	
311	D5501	80.52		-0.76	78.07		-4.23	
323		-----		-----	-----		-----	
340		-----		-----	-----		-----	
511		-----		-----	-----		-----	
663	D5501	83.412		6.43	82.732		7.27	
922		-----		-----	-----		-----	
1067	INH-GC	80.9		0.18	79.8		0.04	
1161		-----		-----	-----		-----	
1201	D5501	78.7		-5.29	77.5		-5.63	

normality	suspect		OK	
n	10		10	
outliers	0		0	
mean (n)	80.827		79.783	
st.dev. (n)	1.2674		1.5300	
R(calc.)	3.549		4.284	
R(D5501:12e1)	1.126		1.135	
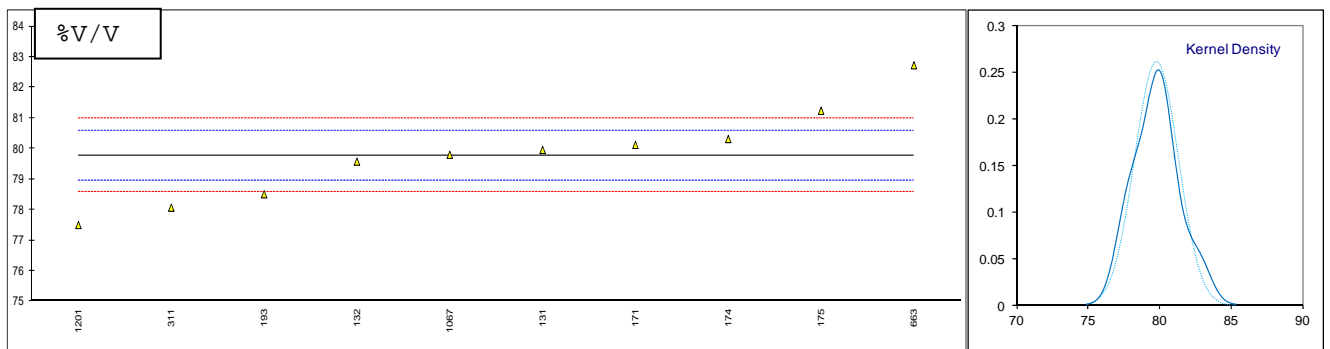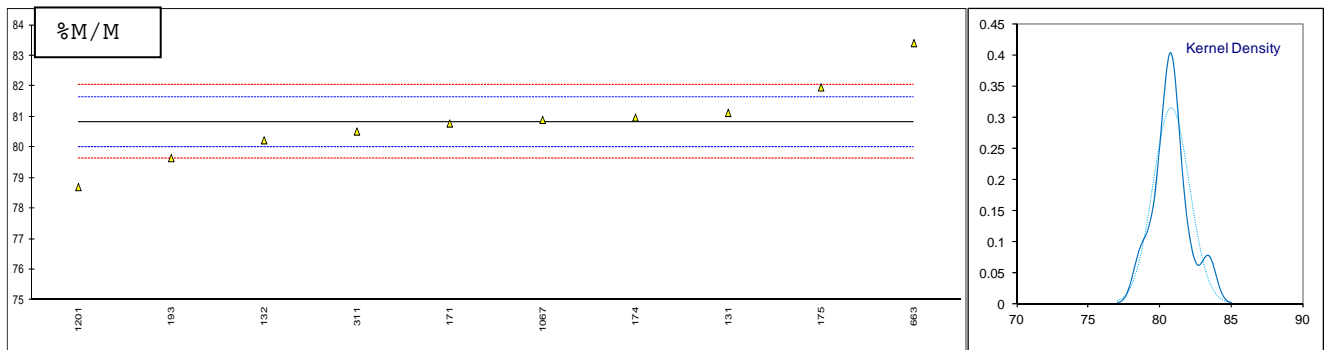
Determination of Ethanol acc ASTM D5501:12 on sample #14241; results in %M/M and %V/V.

lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120		-----		-----	-----		-----	
131	D5501	64.06		4.73	62.19		4.47	
132	D5501	60.587		-2.62	59.197		-1.75	
159		-----		-----	-----		-----	
171	D5501	61.5230		-0.64	60.1109		0.15	
174	D5501	61.256		-1.20	59.850		-0.39	
175	D5501	62.250		0.90	60.823		1.63	
193		-----		-----	-----		-----	
194		-----		-----	-----		-----	
311	D5501	61.70		-0.26	58.09		-4.05	
323		-----		-----	-----		-----	
340		-----		-----	-----		-----	
511		-----		-----	-----		-----	
663	D5501	64.020		4.65	62.551		5.23	
922		-----		-----	-----		-----	
1067		-----		-----	-----		-----	
1161		-----		-----	-----		-----	
1201	D5501	59.2	C	-5.56	57.5	C	-5.28	First reported 56.1 / 54.5

|					
normality	unknown			unknown	
n	8			8	
outliers	0			0	
mean (n)	61.824			60.039	
st.dev. (n)	1.6409			1.7947	
R(calc.)	4.594			5.025	
R(D5501:12e1)	1.323			1.346	

Determination of Ethanol acc ASTM D5501:12 on sample #14242; results in %M/M and %V/V.

lab	method	%M/M	mark	z(targ)	%V/V	mark	z(targ)	Remarks
120		-----		-----	-----		-----	
131	D5501	26.74		5.09	25.20		4.78	
132	D5501	21.923		-0.45	20.792		-0.09	
159		-----		-----	-----		-----	
171	D5501	21.6009		-0.82	20.4850		-0.43	
174	D5501	21.352		-1.10	20.250		-0.69	
175	D5501	21.478		-0.96	20.371		-0.55	
193		-----		-----	-----		-----	
194		-----		-----	-----		-----	
311	D5501	22.77		0.53	20.22		-0.72	
323		-----		-----	-----		-----	
340		-----		-----	-----		-----	
511		-----		-----	-----		-----	
663	D5501	24.733		2.78	23.457		2.85	
922		-----		-----	-----		-----	
1067		-----		-----	-----		-----	
1161		-----		-----	-----		-----	
1201	D5501	17.9	C	-5.07	16.2	C	-5.16	First reported 6 / 5.4
	normality	unknown			unknown			
	n	8			8			
	outliers	0			0			
	mean (n)	22.312			20.872			
	st.dev. (n)	2.6027			2.6311			
	R(calc.)	7.288			7.367			
	R(D5501:12e1)	2.438			2.537			
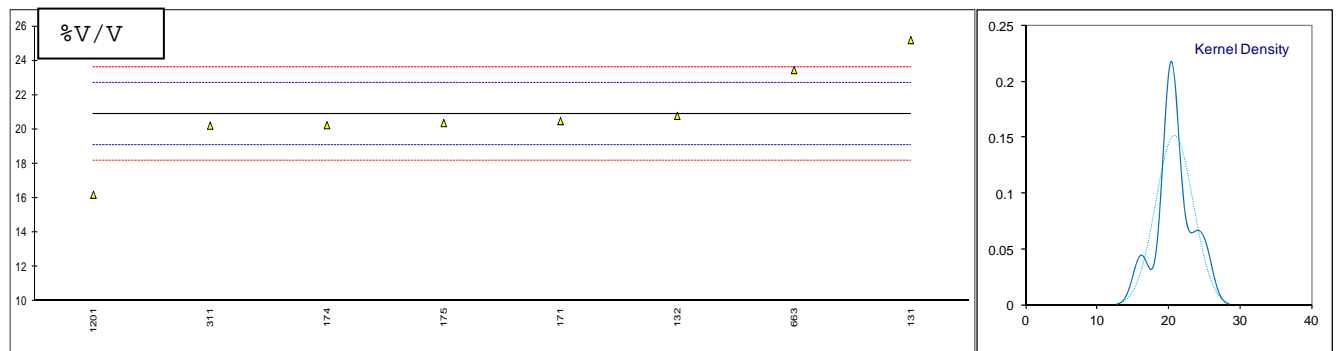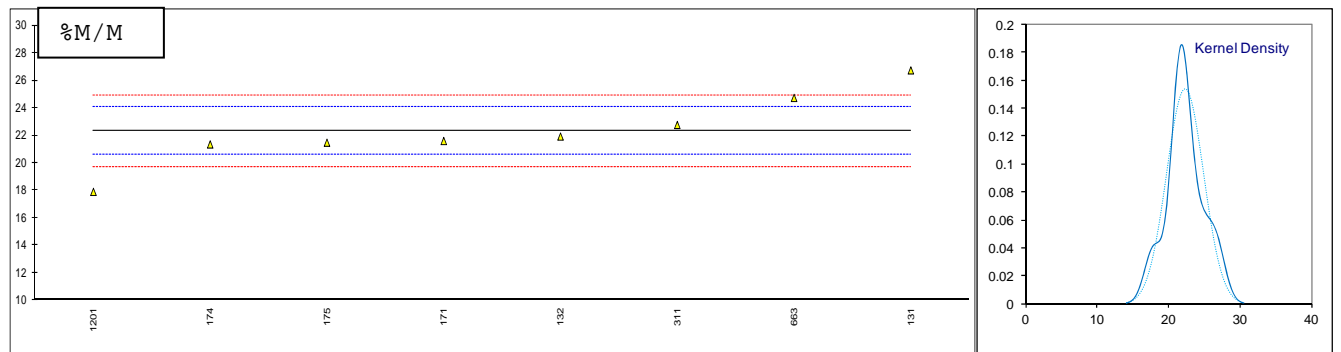
APPENDIX 2

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
> 1 lab in THAILAND
> 1 lab in TURKEY
> 9 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
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

Literature:

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