Results of Proficiency Test
Biogasoline E85
May 2014

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

1 INTRODUCTION

On request of several participants, the Institute for Interlaboratory Studies decided to organise a proficiency test for the analysis of Biogasoline E85 during the annual proficiency testing program 2013/2014. In this interlaboratory study 16 laboratories in 12 different countries have participated. See appendix 2 for the number of participants per country. In this report, the results of the 2014 Biogasoline E85 proficiency test are presented and discussed. This report is also 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. It was decided to evaluate the E85 gasoline according the two different test scopes of ASTM D5798 and of prEN15293. The analyses for fit-for-use and homogeneity testing were subcontracted. In this proficiency test, the participants received one sample of Biogasoline E85.
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/IEC17043:2010. 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 a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded via the FAQ page of the iis website.

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 sample material of about 60 litres of Biogasoline E85 was purchased at a local pump station. After homogenisation, 60 brown glass bottles of 1 litre (labelled #14062) were filled. The homogeneity of the subsamples #14062 was checked by determination of Density @15^{o}C in accordance with ASTM D4052 on 8 stratified randomly selected samples.

	Density @ 15°C in kg/m^3
Sample #14062-1	780.88
Sample #14062-2	780.87
Sample #14062-3	780.88
Sample #14062-4	780.86
Sample #14062-5	780.92
Sample #14062-6	780.92
Sample #14062-7	780.89
Sample #14062-8	781.00

table 1: homogeneity test results of subsamples #14062

From the above test results, the repeatability was calculated and compared with 0.3 times the reproducibility of the reference test method which is in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Density @ 15 ^{o}C in kg/m^3
r (sample #14062)	0.13
reference test	ISO12185:96
0.3*R (reference test)	0.45

table 2: evaluation of repeatability of the subsamples #14062

The calculated repeatability is less than 0.3 times the reproducibility of the corresponding reference method. Therefore, homogeneity of the subsamples #14062 was assumed.

To each of the participants' one 1L bottle with sample #14062 was sent on April 23, 2014.

2.5 ANALYSIS

The participants were requested to determine on sample #14062: Acidity, Copper, Copper Corrosion, Density, Electric Conductivity, Existent Gum, Inorganic Chloride (mg/l and mg/kg), Oxidation Stability, pHe, Phosphorus, Sulphur, Water, Ethanol (%M/M and %V/V), Ethers (C5 – Higher), Methanol, Higher saturated monoalcohols (C3-C8), Total organic bound oxygen.

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 gathered. The original data are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers. Directly after the deadline, a reminder fax was sent to the laboratories that had not reported 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 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. In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon’s, Grubbs and Rosner 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 and by R(0.01) for the Rosner General ESD test (see appendix 3, no.17). Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test. Both outliers and stragglers were not included in the calculations of the averages and the 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 them 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 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. 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 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; nos.13 and 14). Also a normal Gauss curve was projected over the Kernel Density Graph.

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 in accordance with:

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

The $z_{(target)}$ scores are listed in the result tables in appendix 1.

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

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

4 EVALUATION

No problems were encountered during the execution of this proficiency test. Not all the laboratories were able to perform all requested analyses. Finally, 16 laboratories did report 126 numerical results. Observed were 2 outlying results, which is 1.6%. In proficiency tests, outlier percentages of 3 % - 7.5 % are quite normal.

4.1 EVALUATION PER TEST

In this section the results are discussed per test. For the determination of Copper, Inorganic Chloride (mg/L and mg/kg), Phosphorus, Sulphate, Methanol, Higher saturated monoalcohols (C3 – C5), Ethers and Total Organic Bound Oxygen too few test results were reported for a meaningful statistical evaluation.
The other data sets proved to have a normal distribution.

Total Acidity: This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the requirements of EN15491:07.

Copper as Cu: No significant conclusions were drawn. Two numerical results were reported and two other participants agreed on a value near or below the detection limit.

Copper corrosion: No problems have been observed. All reporting participants agreed on a result of 1 (or 1A).

Density @15ºC: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in good agreement with the requirements of ISO12185:96.

Electric Conductivity: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in agreement with the requirements of EN15938:10

Existent Gum: This determination was not problematic despite the low concentration level. No statistical outliers were observed and the calculated reproducibility is in agreement with the requirements of ISO6246:97.

Inorganic Chloride: No significant conclusions were drawn as for mg/L, only two test results and for mg/kg three test results were reported.

Oxidation stab.: In this determination no problems have been observed. All reporting participants agreed on a result above 360 minutes.

pHe: This determination was very problematic. No statistical outliers were observed. However, the calculated reproducibility is not at all in agreement with the requirements of EN15490:07.

Phosphorus: One false positive result was observed. Three other participants agreed on a value below the application range. Therefore no significant conclusions were drawn.

Sulphate: The three reporting participants agreed on a value below the detection limit. Therefore no significant conclusions were drawn.

Sulphur: This determination may be not problematic. No statistical outliers were observed. Although the consensus value is below the application range of EN15486:07 (5 – 20 mg/kg), the calculated reproducibility is in good agreement with the requirements estimated from EN15486:07.

Water: This determination was problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the requirements of EN15489:07.

Ethanol: This determination (%M/M and %V/V) was problematic. The calculated reproducibilities are both not in agreement with the requirements of ASTM D5501:12.

Organic oxygenate compounds according to EN1601:97

The gas chromatographic determination of Organic compounds according to EN1601:97 may not be optimized for Biogasoline E85. Oxygenated compounds with low content in diluted E85 fuel could not be identified with the regular test method. The determinations are still being investigated in terms of correct application and precision (see EN15293:11, p3,10).

Methanol: The reporting participants agreed on a value below the detection limit (<0.2%V/V). Therefore no significant conclusions were drawn.

Higher sat. alcohols: The reporting participants, except one, agreed on a value below the detection limit (<0.25%V/V). Therefore no significant conclusions were drawn.

Ethers (C5 – Higher): This determination may be problematic. Only five laboratories reported a test result (2 laboratories reported <0.3%V/V and 3 laboratories reported >0.5%V/V). Therefore no significant conclusions were drawn.

Tot. org. bound oxygen: Only four laboratories reported a test result. Therefore no significant conclusions were drawn.
When the theoretical values were estimated from the other reported test results, the determination appears to be problematic. The estimated reproducibility after rejection of one statistical outlier is not at all in agreement with the estimated requirements of EN1601:97.

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 assigned values, calculated reproducibilities and reproducibilities, derived from literature standards (in casu ASTM, ISO, EN standards) are compared in the next table.

Parameter	unit	n	mean	2.8 * sd	R (lit)
Acidity as acetic acid	%M/M	10	0.0020	0.0011	0.0014
Copper as Cu	mg/kg	4	n.e.	n.e.	n.e.
Copper corr. 3 hrs @ 50°C	-----	8	1 (1a)	n.e.	n.e.
Density @ 15°C	kg/m^3	14	781.0	0.4	0.5
Electric Conductivity	µS/cm	6	2.16	0.35	0.33
Existent Gum (washed)	mg/100mL	6	0.7	0.9	1.0
Inorganic Chloride	mg/L	2	0.9	n.e.	(0.4)
Inorganic Chloride	mg/kg	3	1.3	n.e.	(0.6)
Oxidation Stability	min.	8	>360	n.e.	n.e.
pHe		7	6.49	1.66	0.62
Phosphorus	mg/L	3	0.03	n.e.	(0.06)
Sulphate	mg/kg	3	<1.0	n.e.	n.e.
Sulphur	mg/kg	13	2.08	0.65	2.00
Water	%M/M	14	0.18	0.03	0.02
Ethanol	%M/M	10	81.67	1.84	1.12
Ethanol	%V/V	11	80.32	1.60	1.13
Organic oxygenate comp.					
- Methanol	%V/V	9	<0.2	n.e.	n.e.
- Higher saturated monoalc.	%V/V	4	<0.25	n.e.	n.e.
- Ethers (C5 – Higher)	%V/V	4	0.49	n.e.	(0.10)
-Total Organic Bound Oxygen	%M/M	4	28.6	0.6	1.9

table 3: performance evaluation sample #14062

Without further statistical calculations, it can be concluded that for several tests there is a good compliance of the group of participants with the relevant standards. The problematic tests have been discussed in paragraph 4.1.

4.3 COMPARISON OF PROFICIENCY TEST OF MAY 2014 WITH PREVIOUS PTS

Determination	May 2014	May 2013	May 2012	May 2011
Number of reporting labs	16	16	14	20
Number of results reported	126	110	103	155
Statistical outliers	2	5	3	8
Percentage outliers	1.6 %	4.5 %	2.9 %	5.2 %

table 4: 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:

Determination	May 2014	May 2013	May 2012	May 2011
Acidity as acetic acid	+	+/-	--	+/-
Copper as Cu	n.e.	n.e.	n.e.	n.e.
Copper corr. 3 hrs @ 50°C	++	++	++	++
Density @ 15°C	+	+/-	-	+/-
Electric Conductivity	+/-	-	n.e.	n.e.
Existent Gum (washed)	+	(+/-)*	(--)*	(+)*
Inorganic Chloride	n.e.	+	n.e.	++
Oxidation Stability	n.e.	n.e.	n.e.	n.e.
pHe	--	--	--	--
Phosphorous	n.e.	n.e.	n.e.	(-)*
Sulphate	n.e.	n.e.	n.e.	n.e.
Sulphur	++	++	++	++
Water	-	+/-	+/-	++
Ethanol	--	--	--	--
Organic oxygenate comp.				
-Ethers (C5 – Higher)	n.e.	--	n.e.	--
-Methanol	n.e.	n.e.	++	n.e.
-Higher saturated monoalc.	n.e.	n.e.	n.e.	n.e.
-Total organic bound oxygen	n.e.	n.e.	n.e.	+

table 5: comparison of the quality of the determinations against the respective standard requirements

*() = assigned value was near or below the detection limit

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

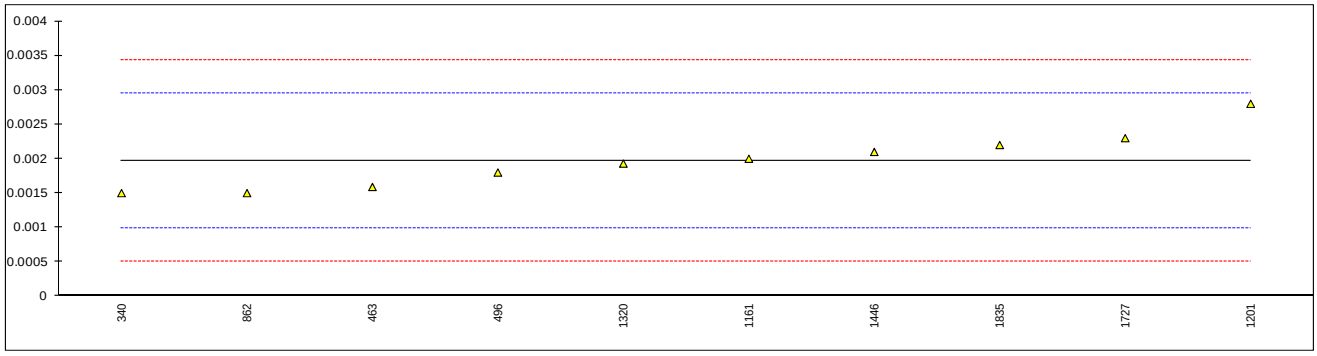
++: group performed much better than the standard
+ : group performed better than the standard
+/-: group performance equals the standard
- : group performed worse than the standard
-- : group performed much worse than the standard
n.e.: not evaluated

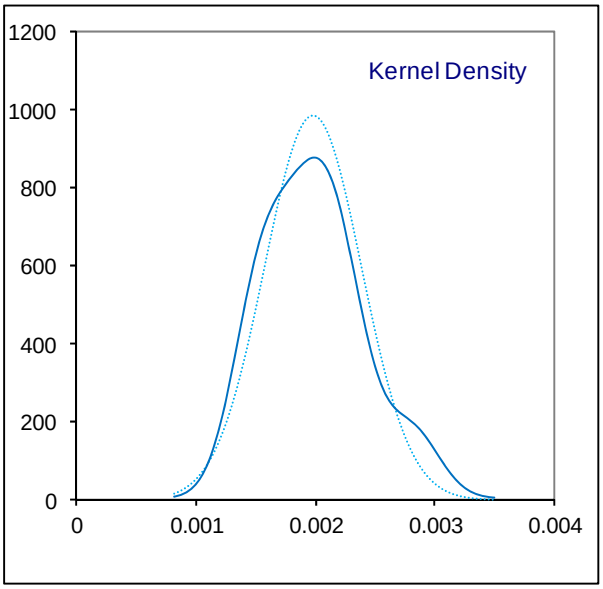
APPENDIX 1

Determination of Total Acidity as Acetic Acid on sample #14062; results in %M/M

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340	EN15491	0.0015		-0.96	
420		-----		-----	
447		-----		-----	
463	D1613	0.00159		-0.78	
496	EN15491	0.0018		-0.35	
862	EN15491	0.0015		-0.96	
1161	EN15491	0.002		0.06	
1201	EN15491/D7795	0.0028		1.69	
1320	EN15491	0.00193		-0.09	
1446	EN15491	0.0021		0.26	
1634		-----		-----	
1706		-----		-----	
1727	EN15491	0.0023		0.67	
1835	EN15491	0.0022		0.47	

normality	OK
n	10
outliers	0
mean (n)	0.00197
st.dev. (n)	0.000406
R(calc.)	0.00114
R(EN15491:07)	0.00137





Determination of Copper on sample #14062; results in mg/kg

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420	EN15488	<0.2		-----	
447		-----		-----	
463		-----		-----	
496		-----		-----	
862	EN15488	0.0013		-----	
1161		-----		-----	
1201	EN15488	<1		-----	
1320	EN15488	0.0029		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	
	normality	n.a.			
	n	4			
	outliers	n.a.			
	mean (n)	n.a.			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(EN15488:07)	n.a.			

Determination of Copper Corrosion 3hrs/50°C on sample #14062; rating

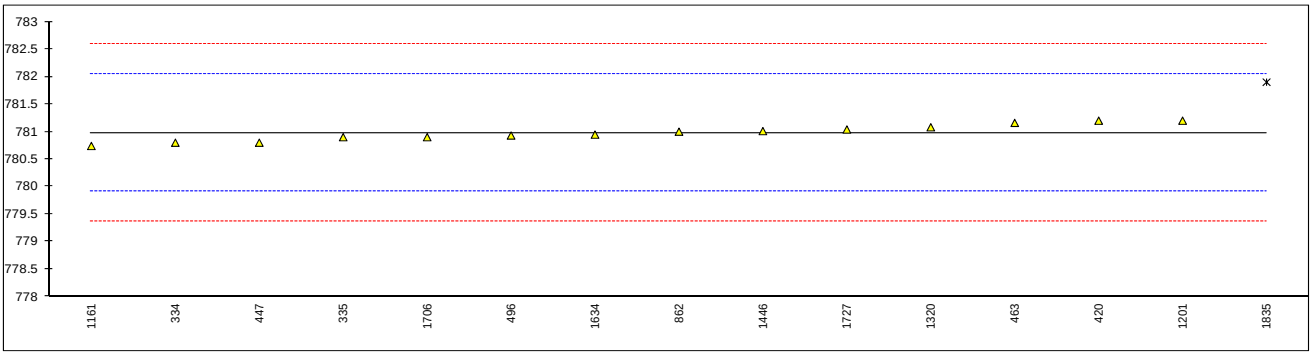
lab	method	value	mark	z(targ)	Remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420	ISO2160	1A		-----	
447	D130	1A		-----	
463	ISO2160	1A		-----	
496	D130	1A		-----	
862	D130	1A		-----	
1161	ISO2160/D130	1		-----	
1201	ISO2160/D130	1A		-----	
1320	ISO2160	1A		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	

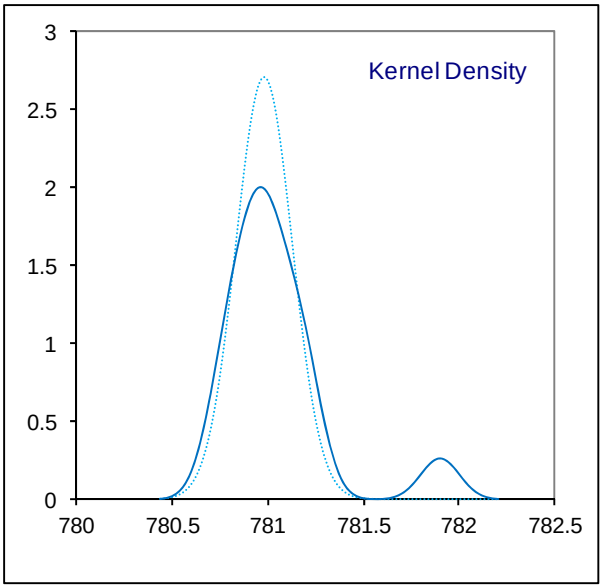
normality	n.a.
n	8
outliers	0
mean (n)	1 (1A)
st.dev. (n)	n.a.
R(calc.)	n.a.
R(ISO2160:98)	n.a.

Determination of Density @ 15°C on sample #14062; results in kg/m^3

lab	method	value	mark	z(targ)	remarks
334	ISO12185	780.8		-0.33	
335	ISO12185	780.9		-0.15	
340		-----		-----	
420	ISO12185	781.2		0.41	
447	ISO12185	780.8		-0.33	
463	ISO12185	781.16		0.34	
496	ISO12185	780.93		-0.09	
862	ISO12185	781.0		0.04	
1161	ISO12185	780.74		-0.45	
1201	ISO12185	781.2		0.41	
1320	ISO12185	781.08		0.19	
1446	ISO12185	781.01		0.06	
1634	ISO12185	780.947		-0.06	
1706	ISO12185	780.9		-0.15	
1727	D4052	781.04		0.11	
1835	D4052	781.9	G(0.01)	1.72	

normality	OK
n	14
outliers	1
mean (n)	780.98
st.dev. (n)	0.148
R(calc.)	0.41
R(ISO12185:96)	1.50

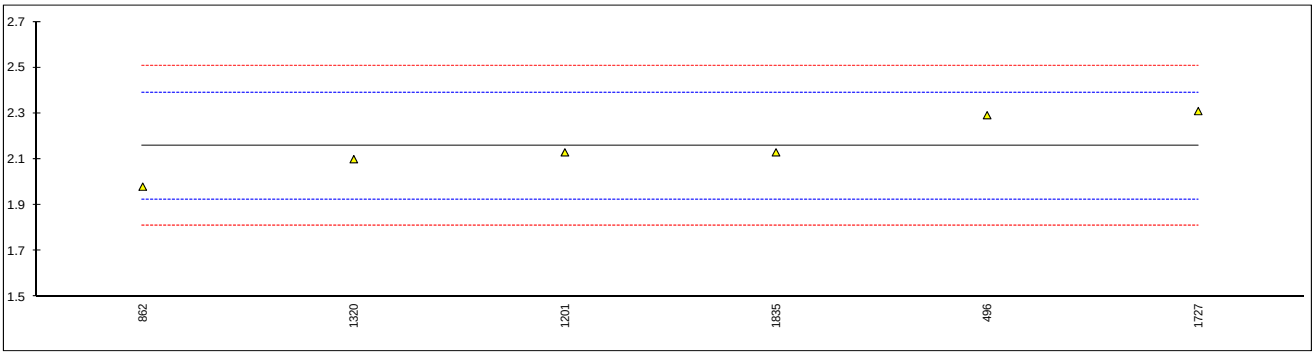




Determination of Electric Conductivity on sample #14062; results in µS/cm

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496	EN15938	2.292		1.16	
862	EN15938	1.980		-1.52	
1161		-----		-----	
1201	EN15938	2.13		-0.23	
1320	EN15938	2.1		-0.49	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727	EN15938	2.31		1.32	
1835	EN15938	2.13		-0.23	

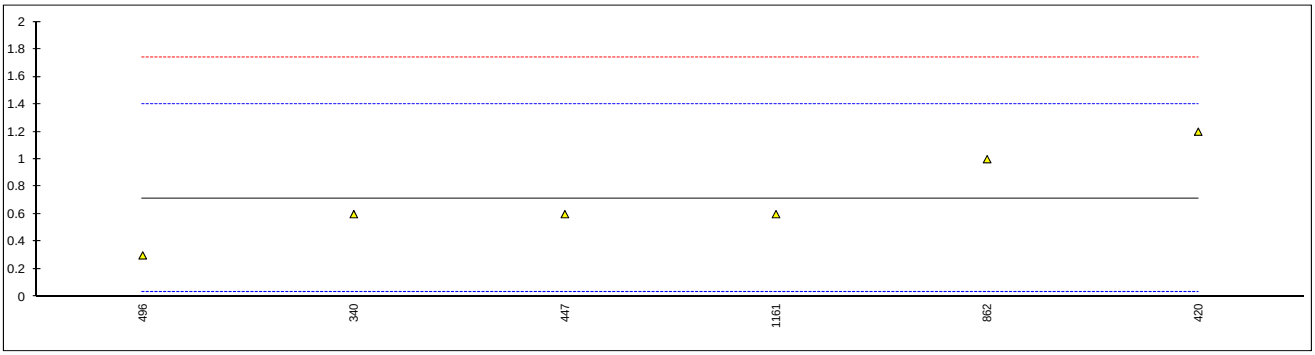
normality	unknown
n	6
outliers	0
mean (n)	2.157
st.dev. (n)	0.1246
R(calc.)	0.349
R(EN15938:10)	0.325



Determination of Existent Gum (washed) on sample #14062; results in mg/100ml

lab	method	value	mark	z(targ)	Remarks
334		-----		-----	
335		-----		-----	
340	D381	0.6		-0.34	
420	ISO6246	1.2		1.42	
447	D381	0.6		-0.34	
463	D381	<0.5		<-0.64	
496	ISO6246	0.3		-1.22	
862	D381	1.0		0.83	
1161	ISO6246/D381	0.6		-0.34	
1201	ISO6246/D381	<0.5		<-0.64	
1320	ISO6246	<0.2		<-1.51	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	

normality	unknown
n	6
outliers	0
mean (n)	0.72
st.dev. (n)	0.325
R(calc.)	0.91
R(ISO6246:97)	0.96



Determination of Inorganic Chloride on sample #14062; results in mg/L

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496		0.955		-----	
862		-----		-----	
1161		-----		-----	
1201		0.9		-----	
1320		-----		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	
	normality	n.a.			
	n	2			
	outliers	0			
	mean (n)	0.928			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(EN15492:08)	(0.410)			Application range: 0.8 – 2.0 mg/L

Determination of Inorganic Chloride on sample #14062; results in mg/kg

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496	EN15492	1.223		-----	
862		-----		-----	
1161		-----		-----	
1201	EN15492/D7328	1.2		-----	
1320		-----		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835	EN15492	1.37		-----	
	normality	n.a.			
	n	3			
	outliers	0			
	mean (n)	1.264			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(EN15492:12)	(0.595)			Application range: 1.0 – 2.5 mg/kg

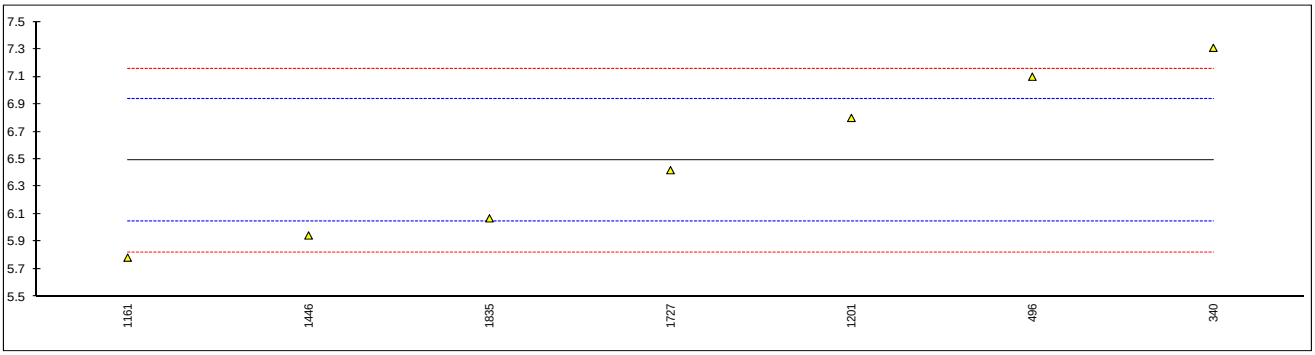
Determination of Oxidation Stability on sample #14062; results in minutes

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340	D525	>960		-----	
420	ISO7536	665		-----	
447		-----		-----	
463	D525	>360		-----	
496	ISO7536	>900		-----	
862	D525	>900		-----	
1161	ISO7536	>900		-----	
1201	ISO7536/D525	>360		-----	
1320	ISO7536	>1440		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	

normality	n.a.
n	8
outliers	>360
mean (n)	n.a.
st.dev. (n)	n.a.
R(calc.)	n.a.
R(ISO7536:94)	n.a.

Determination of pH_e on sample #14062;

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340	EN15490	7.31		3.69	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496	EN15490	7.100		2.74	
862		-----		-----	
1161	EN15490/D6423	5.784		-3.17	
1201	EN15490/D6423	6.8		1.39	
1320		-----		-----	
1446	EN15490	5.945		-2.45	
1634		-----		-----	
1706		-----		-----	
1727	EN15490	6.42		-0.31	
1835	EN15490	6.07		-1.89	
	normality	unknown			
	n	7			
	outliers	0			
	mean (n)	6.490			
	st.dev. (n)	0.5940			
	R(calc.)	1.663			
	R(EN15490:07)	0.623			



Determination of Phosphorus on #sample #14062; results in mg/L

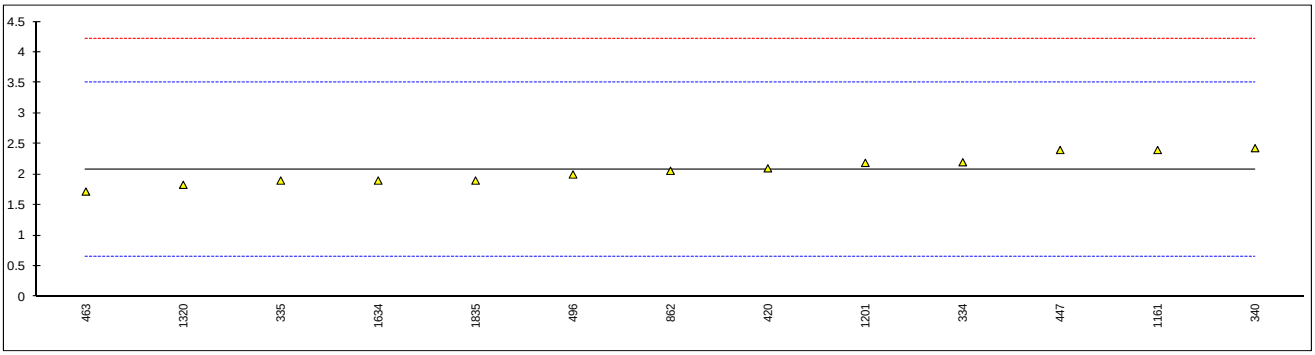
lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496	EN15487	0.027		-----	
862	EN15487	0.02		-----	
1161		-----		-----	
1201	EN15487	<1		-----	
1320	EN15487	0.032		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835	EN15487	0.27	G(0.01)	-----	False positive result?
	normality	n.a.			
	n	3			
	outliers	1			
	mean (n)	0.0263			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(EN15487:07)	(0.0624)			Application range: 0.15 – 1.50 mg/L

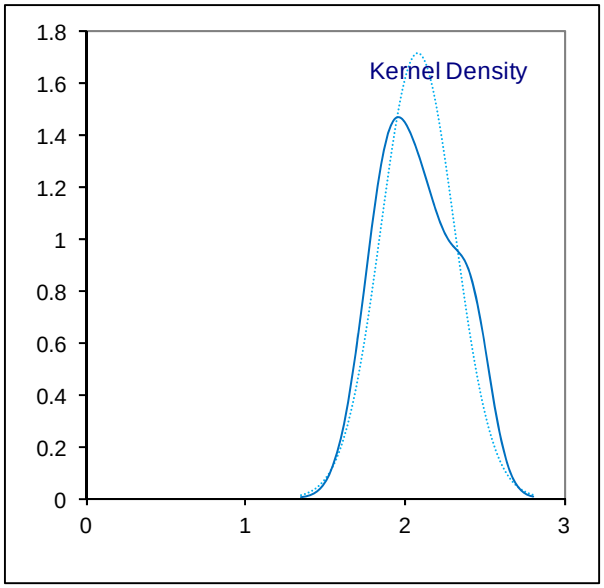
Determination of Sulphate on sample #14062; results in mg/kg

lab	method	value	mark	z(targ)	remarks
334		-----		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496	EN15492	0.141		-----	
862		-----		-----	
1161		-----		-----	
1201	EN15492/D7328	<0.15		-----	
1320		-----		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835	EN15492	<1.0		-----	
	normality	n.a.			
	n	3			
	outliers	0			
	mean (n)	<1.0			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(EN15492)	n.a.			

Determination of Sulphur on sample #14062; results in mg/kg

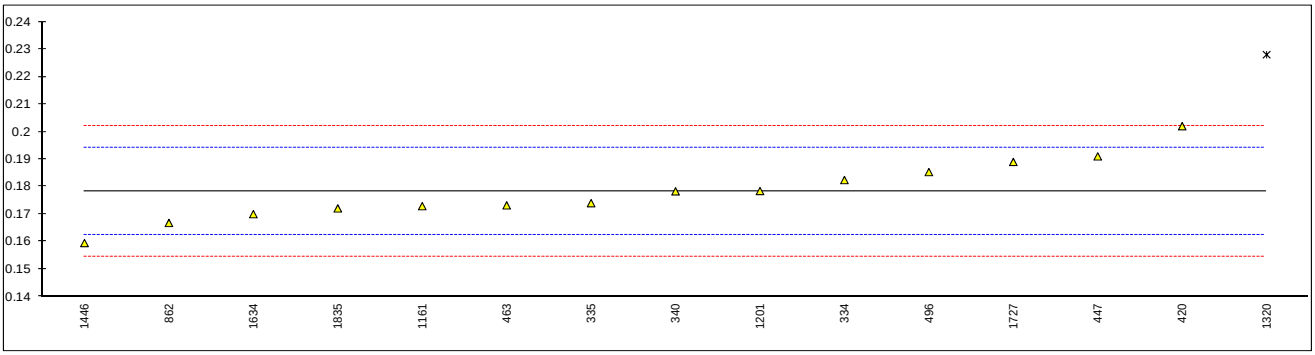
lab	method	value	mark	z(targ)	remarks
334	D5453	2.2		0.17	
335	EN15486/D5453	1.9		-0.25	
340	EN15486	2.43		0.49	
420	ISO20846	2.1		0.03	
447	D5453	2.4		0.45	
463	D5453	1.72		-0.50	
496	EN15486	2.00		-0.11	
862	D5453	2.06		-0.03	
1161	EN15486	2.4		0.45	
1201	EN15486/D5453	2.19		0.15	
1320	EN15486	1.83		-0.35	
1446		-----		-----	
1634	ISO20846	1.9		-0.25	
1706		-----		-----	
1727		-----		-----	
1835	EN15486	1.9		-0.25	
	normality	OK			
	n	13			
	outliers	0			
	mean (n)	2.079			
	st.dev. (n)	0.2328			
	R(calc.)	0.652			
	R(EN15486:07)	2.003			Application range: 5 – 20 mg/kg

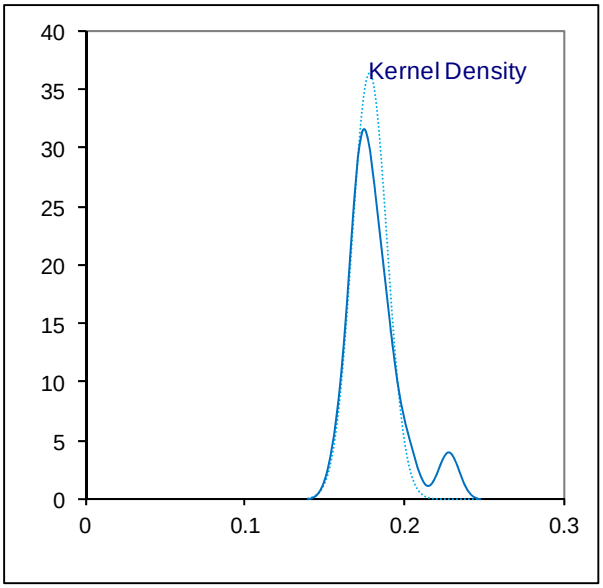




Determination of Water on sample #14062; results in %M/M

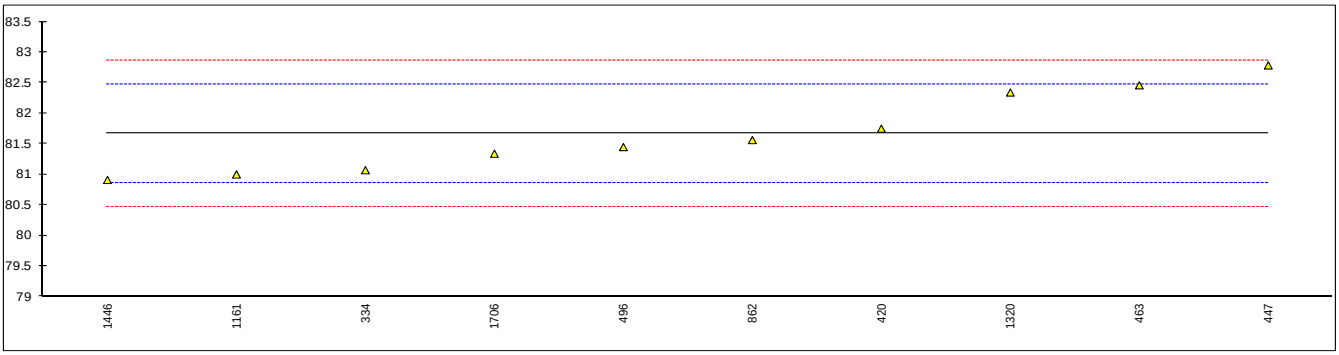
lab	method	value	mark	z(targ)	remarks
334	EN15489	0.1824		0.53	
335	EN15489	0.174		-0.53	
340	EN15489	0.1783		0.01	
420	EN15489	0.202		3.01	
447	IP438	0.191		1.62	
463	ISO12937	0.1732		-0.63	
496	EN15489	0.1853		0.90	
862	EN15489	0.1668		-1.44	
1161	EN15489	0.1729		-0.67	
1201	EN15489	0.1784		0.02	
1320	EN15489	0.228	G(0.01)	6.29	
1446	ISO760	0.1595		-2.36	
1634		0.170		-1.04	
1706		-----		-----	
1727	EN15489	0.1890		1.36	
1835	EN15489	0.1721		-0.77	
	normality	OK			
	n	14			
	outliers	1			
	mean (n)	0.1782			
	st.dev. (n)	0.01099			
	R(calc.)	0.0308			
	R(EN15489:07)	0.0222			

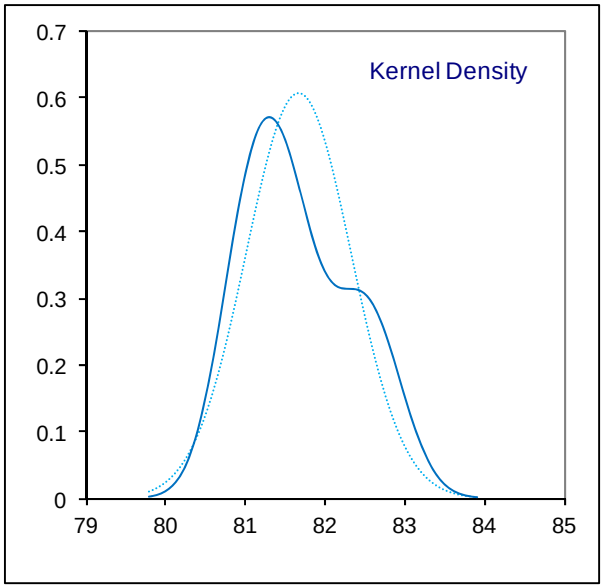




Determination of Ethanol content on sample #14062; results in %M/M

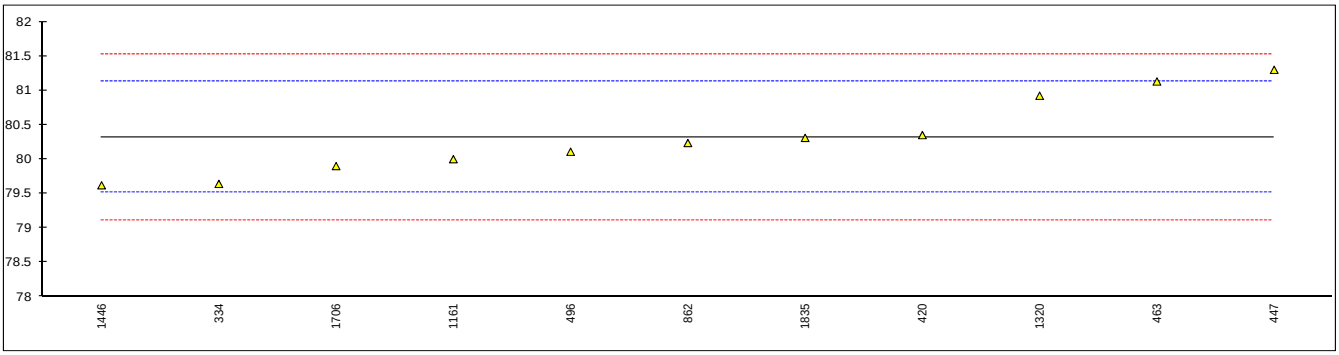
lab	method	value	mark	z(targ)	remarks
334	EN1601	81.07		-1.49	
335		-----		-----	
340		-----		-----	
420	EN13132	81.75		0.21	
447	IP466	82.785		2.80	
463	EN13132	82.46		1.98	
496	D5501	81.449		-0.55	
862	D5501	81.563		-0.26	
1161	EN13132	81.0		-1.67	
1201		-----		-----	
1320	D5501	82.342		1.69	
1446	EN1601/EN13132	80.91		-1.89	
1634		-----		-----	
1706	EN13132	81.34		-0.82	
1727		-----		-----	
1835		-----		-----	
	normality	OK			
	n	10			
	outliers	0			
	mean (n)	81.667			
	st.dev. (n)	0.6567			
	R(calc.)	1.839			
	R(D5501:12)	1.119			Application range: 20 – 100 %M/M

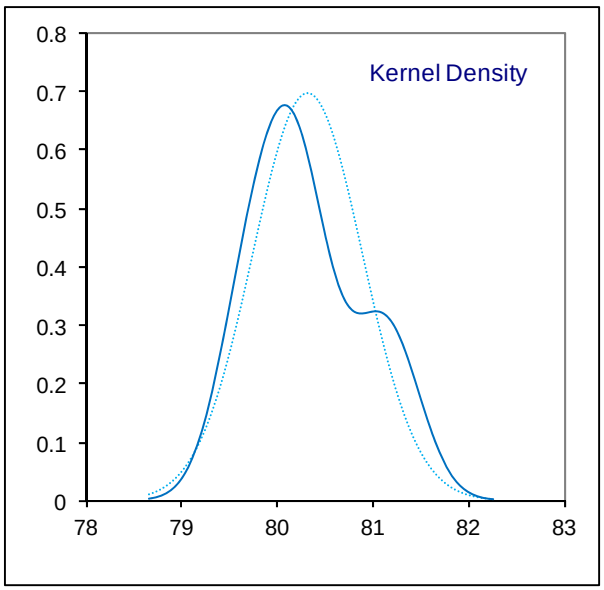




Determination of Ethanol content on sample #14062; results in %V/V

lab	method	value	mark	z(targ)	remarks
334	EN1601	79.64		-1.68	
335		-----		-----	
340		-----		-----	
420	EN13132	80.35		0.08	
447	IP466	81.3		2.43	
463	EN13132	81.13		2.01	
496	D5501	80.108		-0.52	
862	D5501	80.235		-0.21	
1161	EN13132	80.0		-0.79	
1201		-----	W	-----	Result withdrawn, first reported 78.5
1320	Calc.	80.923		1.49	
1446	EN1601/EN13132	79.62		-1.73	
1634		-----		-----	
1706	EN13132	79.9		-1.04	
1727		-----		-----	
1835	in house	80.31		-0.02	
	normality	OK			
	n	11			
	outliers	0			
	mean (n)	80.320			
	st.dev. (n)	0.5714			
	R(calc.)	1.600			
	R(D5501:12)	1.130			Application range: 20 – 100 %V/V





Determination of Methanol on sample #14062; results in %V/V

lab	method	value	mark	z(targ)	remarks
334	EN1601	<0.17		-----	
335		-----		-----	
340		-----		-----	
420	EN13132	<0.2		-----	
447	IP466	<0.2		-----	
463	EN13132	<0.2		-----	
496	EN1601	<0.1		-----	
862	D4815	<0.2		-----	
1161	EN13132	<0.2		-----	
1201	EN1601	0.08		-----	
1320	EN1601	0.06		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	

normality	n.a.
n	9
outliers	n.a.
mean (n)	<0.2
st.dev. (n)	n.a.
R(calc.)	n.a.
R(EN1601:97)	n.a.

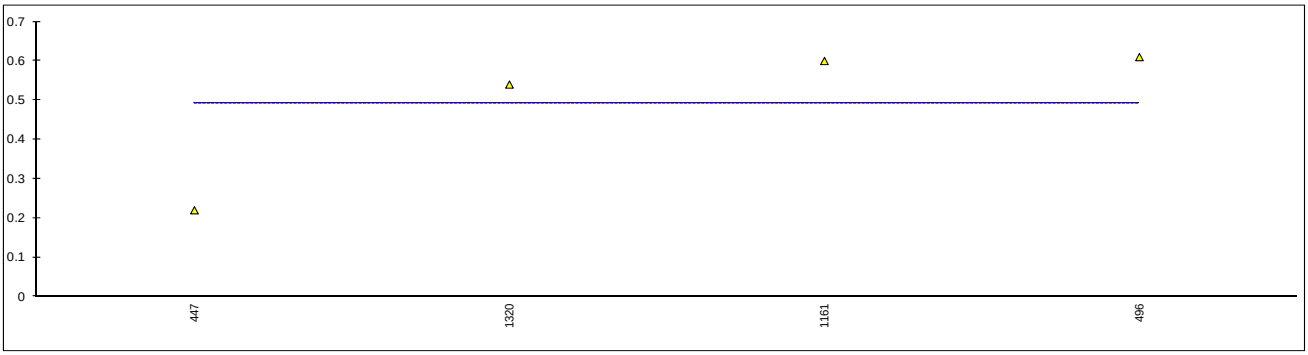
Determination of Higher saturated monoalcohols (C3-C5) on sample #14062; results in %V/V

lab	method	value	mark	z(targ)	remarks
334	EN1601	<0.17		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447		-----		-----	
463		-----		-----	
496	EN1601	0.23		-----	
862		-----		-----	
1161	EN13132	<0.2		-----	
1201	EN1601	1.5		-----	False positive result?
1320	EN1601	<0.01		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	
	normality	n.a.			
	n	4			
	outliers	1			
	mean (n)	<0.25			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(EN1601:97)	n.a.			

Determination of Ethers (C5 – Higher) on sample #14062; results in %V/V

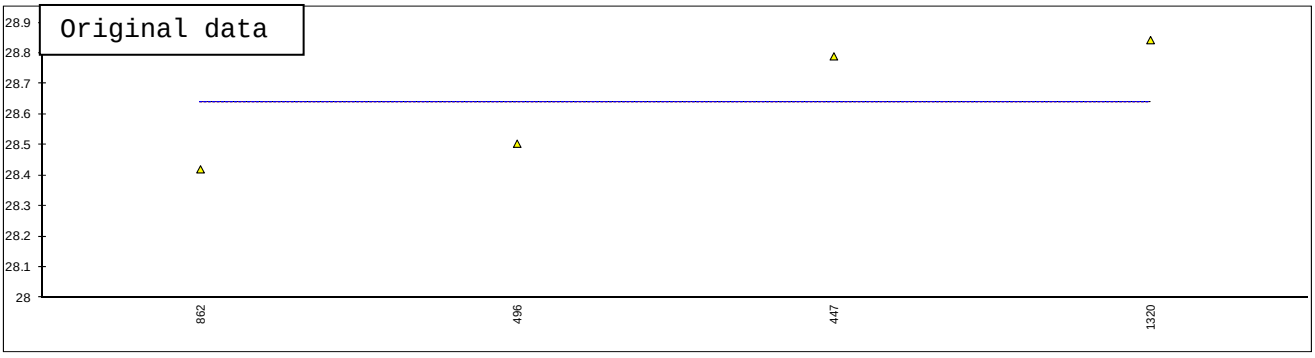
lab	method	value	mark	z(targ)	remarks
334	EN1601	<0.17		-----	
335		-----		-----	
340		-----		-----	
420		-----		-----	
447	IP466	0.22		-----	
463		-----		-----	
496	EN1601	0.61		-----	
862		-----		-----	
1161	EN13132	0.6		-----	
1201		-----		-----	
1320	EN1601	0.54		-----	
1446		-----		-----	
1634		-----		-----	
1706		-----		-----	
1727		-----		-----	
1835		-----		-----	

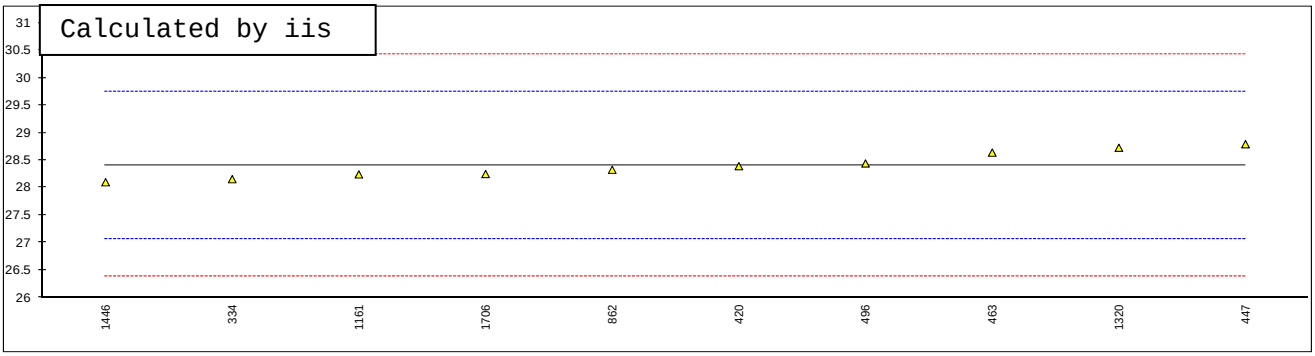
normality	unknown
n	4
outliers	0
mean (n)	0.493
st.dev. (n)	n.a.
R(calc.)	n.a.
R(EN1601:97)	(0.100)



Determination of Total Org Bound Oxygen on sample #14062; results in %M/M

lab	method	value	mark	z(targ)	remarks	Calc. by iis	Mark
334		-----		-----		28.155	
335		-----		-----		-----	
340		-----		-----		-----	
420		-----		-----		28.392	
447	IP466	28.79		-----		28.791	
463		-----		-----		28.638	
496	EN1601	28.504		-----		28.442	
862	D4815	28.42		-----		28.327	
1161		-----		-----		28.241	
1201		-----		-----		0.316	G(0.01)
1320	EN1601	28.843		-----		28.726	
1446		-----		-----		28.100	
1634		-----		-----		-----	
1706		-----		-----		28.249	
1727		-----		-----		-----	
1835		-----		-----		-----	
	normality	unknown				OK	
	n	4				10	
	outliers	0				1	
	mean (n)	28.639				28.406	
	st.dev. (n)	0.2086				0.2406	
	R(calc.)	0.584				0.674	
	R(EN1601:97)	(1.877)	Application range: 0.17 – 3.7 %M/M			(1.863)	





APPENDIX 2

Number of participants per country

1 lab in AUSTRIA
2 labs in CZECH REPUBLIC
3 labs in FRANCE
1 lab in GERMANY
1 lab in P.R. of CHINA
1 lab in PORTUGAL
1 lab in SLOVAKIA
2 labs in SPAIN
1 labs in SWEDEN
1 lab in THE NETHERLANDS
1 lab in TURKEY
1 lab in UNITED KINGDOM

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
ex	= excluded from calculations
E	= error in calculations
n.a.	= not applicable
n.e.	= not evaluated
W	= withdrawn
fr.	= first reported
U	= reported in different unit
SDS	= Safety Data Sheet

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014

2 ASTM E178-02

3 ASTM E1301-03

4 ISO 5725-86

5 ISO 5725, parts 1-6, 1994

6 ISO13528-05

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, No4 January 2001

14 The Royal Society of Chemistry 2002, Analyst 2002, 127 page1359-1364, P.J. Lowthian and M. Thompson. (see www.rsc.org/suppdata/an/b2/b205600n/)

15 EN15293:11

16 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, T*echnometrics*, 25(2), pp. 165-172, (1983)