Results of Proficiency Test
MTBE
February 2015

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report no. iis15C03

April 2015

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1 INTRODUCTION

Since 1995, the Institute for Interlaboratory Studies organizes a proficiency test for the analysis of Methyl Tertiary Butyl Ether (MTBE). During the annual proficiency testing program 2014/2015, it was decided to continue the round robin for the analyses of MTBE.
In this interlaboratory study for MTBE 23 laboratories in 13 di fferent countries have participated. See appendix 2 for the number of participants per country. In this report, the results of the 2015 proficiency test are presented and discussed. This report is also electronically available through the iis internet site ww.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test. It was decided to send one sample of MTBE (0.5 litre bottle, labelled #15006) to the participants. Analyses for fit-for-use and homogeneity were subcontracted. 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.

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 25 litres of MTBE bulk material were obtained from a local producer. After homogenisation, the bulk material was transferred into 50 brown glass bottles of 500 mL and labelled #15006. The homogeneity of the subsamples was checked by determination of Density @20˚C in accordance with ASTM D4052 and Water in accordance with ASTM D1364 on 8 stratified randomly selected samples:

	Density at 20˚C in kg/L	Water in mg/kg
sample #15006-1	0.74065	76
sample #15006-2	0.74065	82
sample #15006-3	0.74065	79
sample #15006-4	0.74065	80
sample #15006-5	0.74065	76
sample #15006-6	0.74065	82
sample #15006-7	0.74065	90
sample #15006-8	0.74065	78

Table 1: homogeneity test results of subsamples #15006

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities of the target methods or with the reproducibility calculate using the Horwitz equation in agreement with the procedure of ISO 13528, Annex B2 in the next table;

	Density at 20˚C in kg/L	Water in mg/kg
r (sample #15006)	0.00000	12.7
reference test method	ASTM D4052:02e1	ASTM D1364:12
0.3xR (reference test)	0.00015	16.1

Table 2: repeatabilities of the subsamples #15006

The calculated repeatabilities were in agreement with 0.3 times the corresponding target reproducibility. Therefore, homogeneity of the samples was assumed.

To each of the participating laboratories one bottle of 500 ml, labelled #15006 was sent on January 21, 2015.

2.5 STABILITY OF THE SAMPLES

The stability of Methyl Tertiary Butyl Ether, packed in the brown glass bottles was checked. The material has been found stable for the period of the proficiency test.

2.6 ANALYSES

The participants were asked to determine on sample #15006 containing MTBE: Appearance, Density @15°C, Refractive index @ 20°C, Carbonyls, Water, Purity (both on as received and on dry basis), Methanol, and some GC-impurities (Sum of Diisobutylenes [2,4,4-Trimethyl-1-pentene; 2,4,4-Trimethyl-2-pentene; 2,3,4-Trimethyl-2-pentene; 3,4,4-Trimethyl-1-pentene and 3,5-Dimethyl-1-hexene], tert-Butylalcohol, Hydrocarbons (C4- and C5), Other hydrocarbons and Unknown impurities.
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, some problems were encountered during the execution. Participants in Brazil, Saudi Arabia and Venezuela received the samples late or not at all due to problems at customs. From the 23 participants, 5 participants reported results after the deadline for reporting and 6 participants did not report any results at all.
The 17 reporting laboratories submitted 159 numerical results. Observed were 13 outlying results, which is 8.2%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER TEST

In this section, the reported results are discussed per test.
Unfortunately, a suitable standard test method, providing the precision data, is not available for all determinations. For the tests, that have no available precision data, the spreads were compared against the spreads estimated from the Horwitz equation.
In the iis PT reports, ASTM methods are referred to with a number (e.g. D2086) and an added designation for the year that the method was adopted or revised (e.g. D2086-08). If applicable, a designation in parentheses is added to designate the year of reapproval (e.g. D2086-08 (2013)). In the results tables of Appendix 1 only the method number and year of adoption or revision will be used.

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.

Appearance: No analytical problems were observed. All labs agreed about the appearance of sample #15006, which is pass or bright and clear.

Carbonyls: Only two laboratories reported a test result, therefore, no analytical conclusions were drawn.

Density @ 15°C: This determination was not problematic. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in good agreement with the requirements of ASTM D4052:02e1. The current version of this method ASTM D4052:11 only give reproducibilities for gasoline, distillates, base stocks and lubricating oils. Therefore this 2011 version may not be applicable for MTBE.

Refractive Index: This determination was problematic for two laboratories. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in full agreement with the requirements of ASTM D1218:12.

Water: This determination was not problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in good agreement with the requirements of ASTM D1364:12.

Purity: This determination was problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the requirements of ASTM D5441:98(2008e1).

Methanol: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in full agreement with the requirements of ASTM D5441:98(2008e1).

Diisobutylene (=sum): This determination is not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the requirements of ASTM D5441:98(2008e1).

2,4,4-Trime-1-pent.: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of ASTM D5441:98(2008e1).

2,4,4-Trime-2-pent.: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in agreement with the estimated reproducibility limits, calculated using the Horwitz equation.

Other DIB.'s: It should be noticed that for the other DIB's, method D5441:08e1 is applicable for concentrations >0.02 %M/M. Only few numerical results were reported. Therefore, no significant conclusions were drawn.

Tert-butanol: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of statistical outlier is in good agreement with the requirements of ASTM D5441:98(2008e1), although the concentration (0.216 %M/M) is outside the application range of the test method (0.474 - 0.8763 %M/M).

C4-hydrocarbons: 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 ASTM D5441:98(2008e1).

C5-hydrocarbons: This determination was problematic for a number of laboratories. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in good agreement with the requirements of ASTM D5441:98(2008e1).

Other Impurities: Other impurities may be all components listed in table 2 of D5441:98(2008e1) and not evaluated separately in this proficiency test. No statistical outliers were observed. No significant conclusions were drawn as ASTM D5441:98(2008e1) does not specify requirements for the reproducibility for these components.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard and these parameters as found for the group of participating laboratories. The average results and the calculated reproducibilities are compared in the next tables with the reproducibilities, derived from literature standards (in casu the ASTM standards, see tables in appendix 1).

	Unit	n	average	R (Calc.)	R (lit)
Appearance		14	pass	n.a.	n.a.
Carbonyls	µg/g	2	n.a.	n.a.	n.a.
Density @ 15°C	kg/L	14	0.7459	0.0002	0.0005
Refractive Index @ 20ºC		6	1.3692	0.0004	0.0005
Water	mg/kg	15	96.1	24.2	58.8
Purity	%M/M	17	98.546	0.493	0.382
Methanol	%M/M	15	0.406	0.079	0.079
Diisobutylene (=sum of 5)	% M/M	8	0.173	0.052	0.054
2,4,4-Trimethyl-1-pentene	%M/M	9	0.139	0.039	0.046
2,4,4-Trimethyl-2-pentene	%M/M	6	0.039	0.006	0.007
Tert-butanol	%M/M	15	0.216	0.053	0.132
C4 – hydrocarbons	%M/M	12	0.390	0.221	0.126
C5 – hydrocarbons	%M/M	10	0.043	0.017	0.020
Other impurities	%M/M	9	0.295	0.434	unknown

Table 3: performance evaluation of sample #15006

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

4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2015 WITH PREVIOUS PTS

	February 2015	February 2013	February 2012	March 2010
Number of reporting labs	17	16	17	33
Number of Results reported	159	154	178	305
Statistical outliers	13	16	16	22
Percentage outliers	8.2%	10.4%	9.0%	7.2%

Table 4: comparison with previous proficiency tests.

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

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

Determination	February 2015	February 2013	February 2012	March 2010
Carbonyls	n.e.	--	n.e	n.e
Density @ 15°C	++	++	+	+
Refractive Index @ 20ºC	+	+	+/-	+
Water	++	--	+/-	++
Purity	--	+	--	+
Methanol	+/-	--	-	+
2,4,4-Trimethyl-1-pentene	+	+/-	++	++
2,4,4-Trimethyl-2-pentene	+ *)	- *)	+ *)	-- *)
Tert-butanol	(++)	(++)	(++)	(++)
C4 – hydrocarbons	--	(-)	+/-	--
C5 – hydrocarbons	+	++	--	++

Table 5: comparison determinations against the standard for MTBE

*) compared against the strict Horwitz equation

Result between brackets is an estimate, as the assigned value is below or 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 Appearance on MTBE sample #15006;

lab	method	value	mark	z(targ)	remarks
171	E2680	Pass		-----	
311	E2680	Pass		-----	
312	E2680	Pass		-----	
323	E2680	Pass		-----	
334		-----		-----	
347	E2680	Pass		-----	
555		-----		-----	
657	E2680	Pass		-----	
862	E2680	Pass		-----	
963	E2680	Pass		-----	
1120	E2680	Pass		-----	
1200		-----		-----	
1201	Visual	C&B		-----	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	Visual	C&B		-----	
1459		-----		-----	
1586	Visual	C&B		-----	
1653		-----		-----	
1788	Visual	C&B		-----	
1866		Pass		-----	
1940		-----		-----	

normality	n.a.
n	14
outliers	0
mean (n)	Pass
st.dev. (n)	n.a.
R(calc.)	n.a.
R()	n.a.

C&B = Clear and bright

Determination of Carbonyls as CO on MTBE sample #15006; results in µg/g

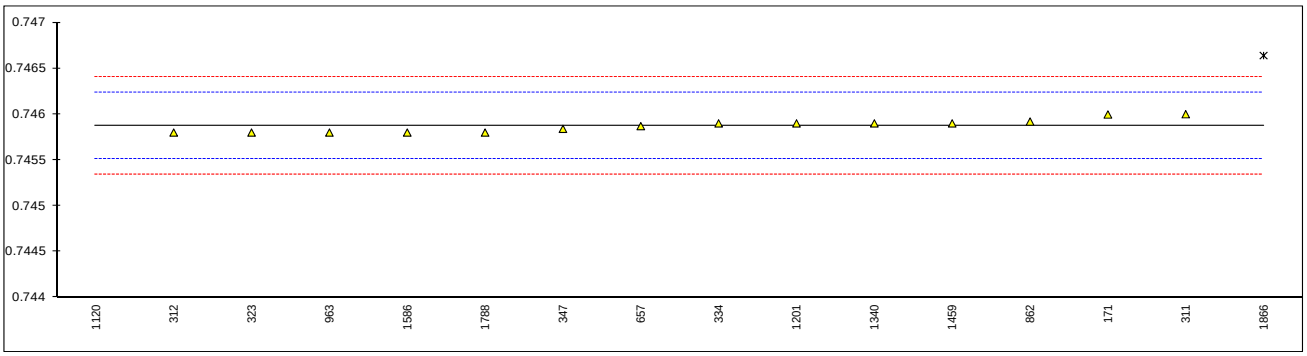
lab	method	value	mark	z(targ)	remarks
171	E411	528.3		-----	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347		-----		-----	
555		-----		-----	
657	E411	1013.2		-----	
862		-----		-----	
963		-----		-----	
1120		-----		-----	
1200		-----		-----	
1201		-----		-----	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340		-----		-----	
1459		-----		-----	
1586		-----		-----	
1653		-----		-----	
1788		-----		-----	
1866		-----		-----	
1940		-----		-----	

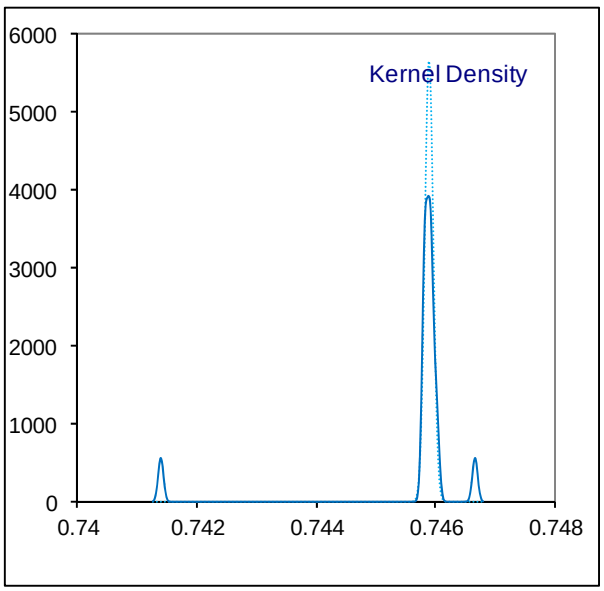
normality	n.a.
n	2
outliers	0
mean (n)	n.a.
st.dev. (n)	n.a.
R(calc.)	n.a.
R(E411:12)	n.a.

Determination of Density at 15°C on MTBE sample #15006; results in kg/L

lab	method	value	mark	z(targ)	remarks
171	D4052	0.745997		0.69	
311	D4052	0.7460		0.71	
312	D4052	0.7458		-0.41	
323	D4052	0.7458		-0.41	
334	D4052	0.7459		0.15	
347	D4052	0.74584		-0.19	
555		-----		-----	
657	D4052	0.74587		-0.02	
862	D4052	0.74592		0.26	
963	D4052	0.7458		-0.41	
1120	D4052	0.7414	G(0.01)	-25.05	
1200		-----		-----	
1201	D4052	0.7459		0.15	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	ISO12185	0.7459		0.15	
1459	ISO12185	0.7459		0.15	
1586	D4052	0.7458		-0.41	
1653		-----		-----	
1788	D4052	0.7458		-0.41	
1866	D4052	0.74664	G(0.01)	4.29	
1940		-----		-----	

normality	OK
n	14
outliers	2
mean (n)	0.74587
st.dev. (n)	0.000070
R(calc.)	0.00020
R(D4052:02e1)	0.00050

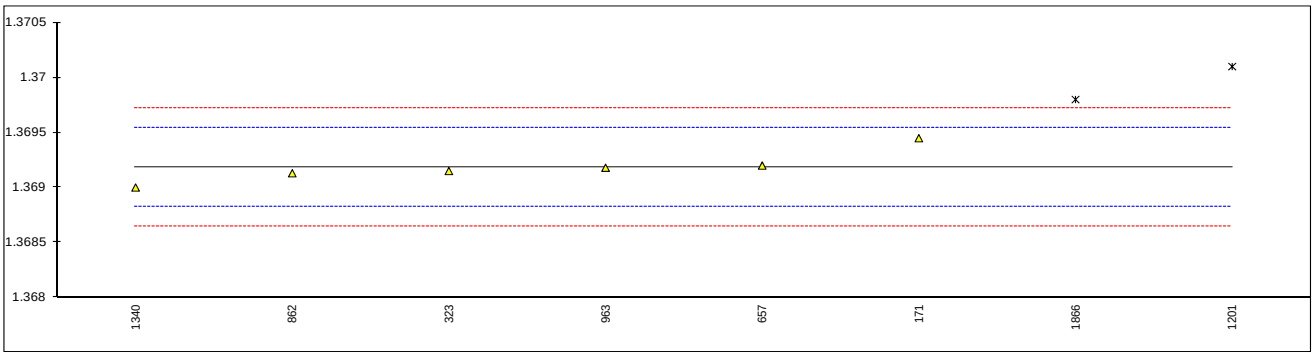


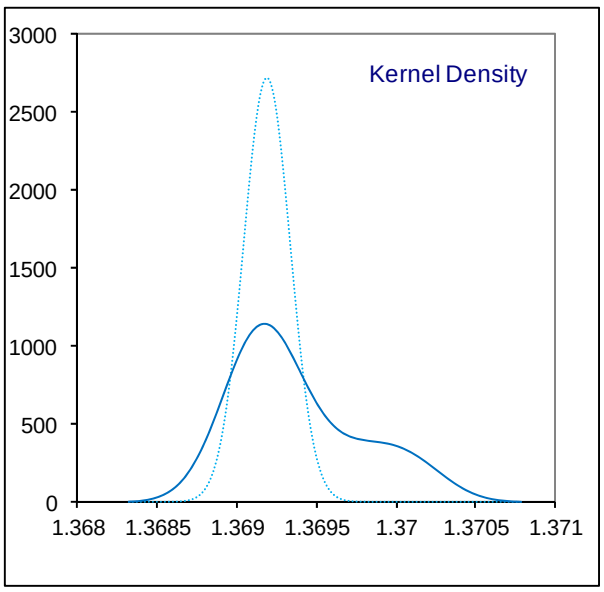


Determination of Refractive Index at 20°C on MTBE sample #15006;

lab	method	value	mark	z(targ)	remarks
171	D1218	1.3694483		1.48	
311		-----		-----	
312		-----		-----	
323	D1218	1.36915		-0.20	
334		-----		-----	
347		-----		-----	
555		-----		-----	
657	D1218	1.3692		0.08	
862	D1218	1.36913		-0.31	
963	D1218	1.36918		-0.03	
1120		-----		-----	
1200		-----		-----	
1201	D1218	1.3701	DG(0.05)	5.12	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D1218	1.3690		-1.04	
1459		-----		-----	
1586		-----		-----	
1653		-----		-----	
1788		-----		-----	
1866	D1218	1.3698	DG(0.05)	3.44	
1940		-----		-----	

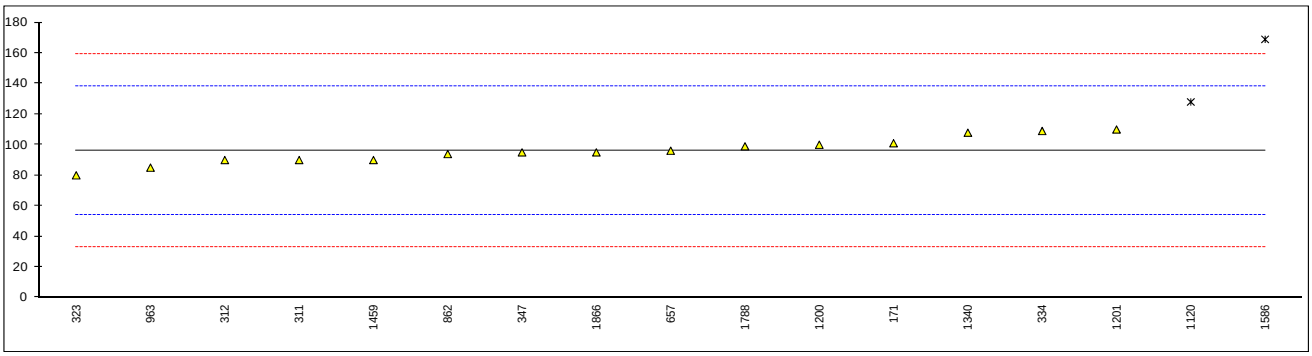
normality	unknown
n	6
outliers	2
mean (n)	1.36918
st.dev. (n)	0.000147
R(calc.)	0.00041
R(D1218:12)	0.00050

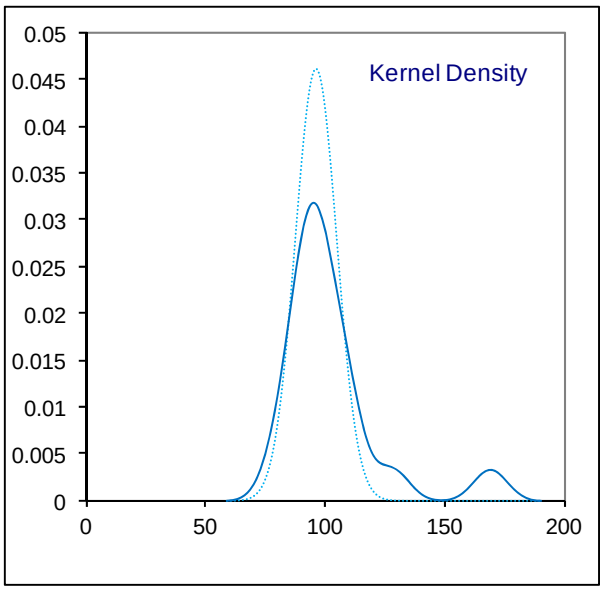




Determination of Water on MTBE sample #15006; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	E203	101		0.23	
311	E1064	90		-0.29	
312	E1064	90		-0.29	
323	E1064	80		-0.77	
334	D1364	109		0.61	
347	E1064	95		-0.05	
555		-----		-----	
657	E1064	96.1		0.00	
862	D6304	93.9		-0.11	
963	D1364	85	C	-0.53	First reported 60
1120	D1364	128	G(0.05)	1.52	
1200	E1064	100		0.18	
1201	D1364	110		0.66	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	ISO12937	107.9		0.56	
1459	ISO12937	90		-0.29	
1586	E1064	169	G(0.01)	3.47	
1653		-----		-----	
1788	D1364	99		0.14	
1866	D1364	95		-0.05	
1940		-----		-----	
	normality	OK			
	n	15			
	outliers	2			
	mean (n)	96.13			
	st.dev. (n)	8.651			
	R(calc.)	24.22			
	R(D1364:12)	58.83			Compare R(E1064) = 15.28

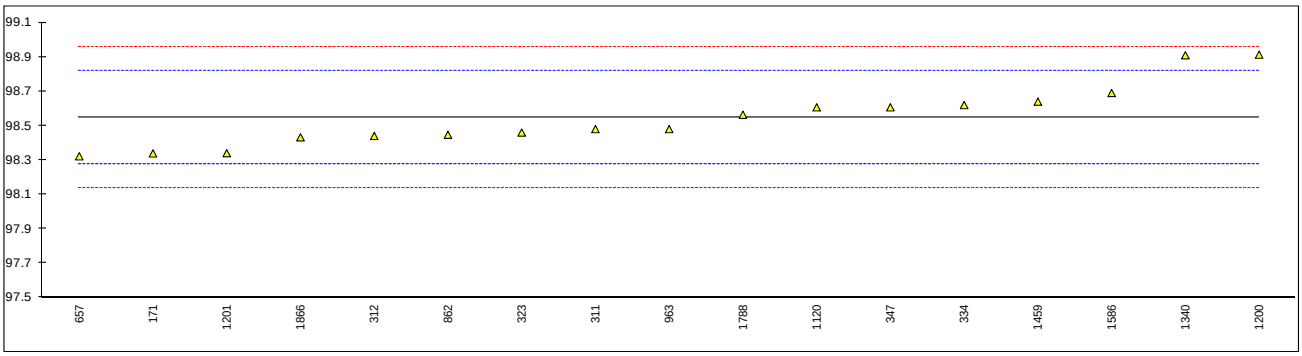


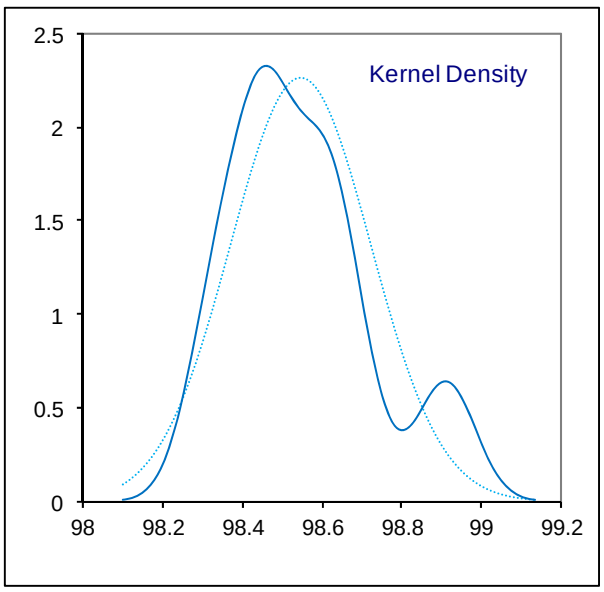


Determination of Purity by GC of MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	98.338628		-1.52	
311	D5441	98.48		-0.49	
312	D5441	98.44		-0.78	
323	D5441	98.46		-0.63	
334	D5441	98.62		0.54	
347	D5441	98.607		0.44	
555		-----		-----	
657	D5441	98.3218		-1.65	
862	D5441	98.447		-0.73	
963	D5441	98.480		-0.49	
1120	D5441	98.6066		0.44	
1200	D5441	98.9132		2.69	
1201	D5441	98.34		-1.51	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	98.91		2.67	
1459	D5441	98.64		0.69	
1586	D5441	98.69		1.05	
1653		-----		-----	
1788	D5441	98.5636		0.13	
1866	D5441	98.432		-0.84	
1940		-----		-----	

normality	OK
n	17
outliers	0
mean (n)	98.5465
st.dev. (n)	0.17606
R(calc.)	0.4930
R(D5441:98)	0.3816

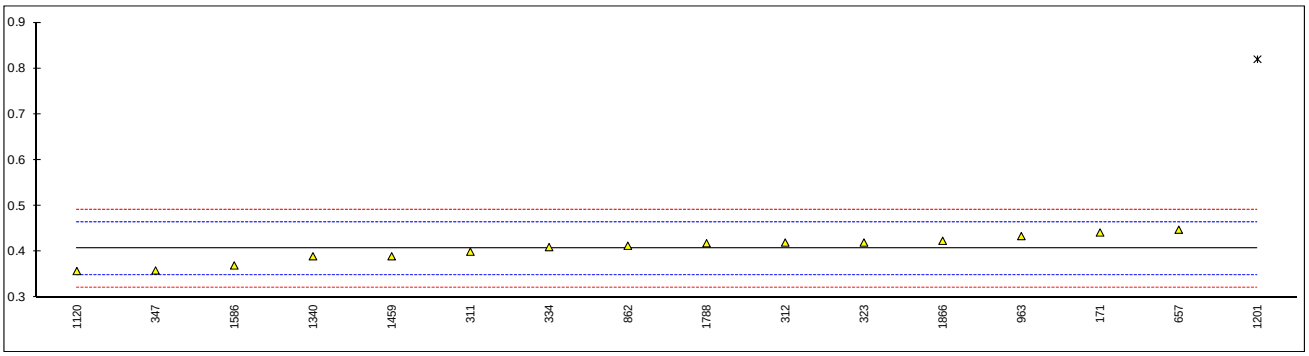


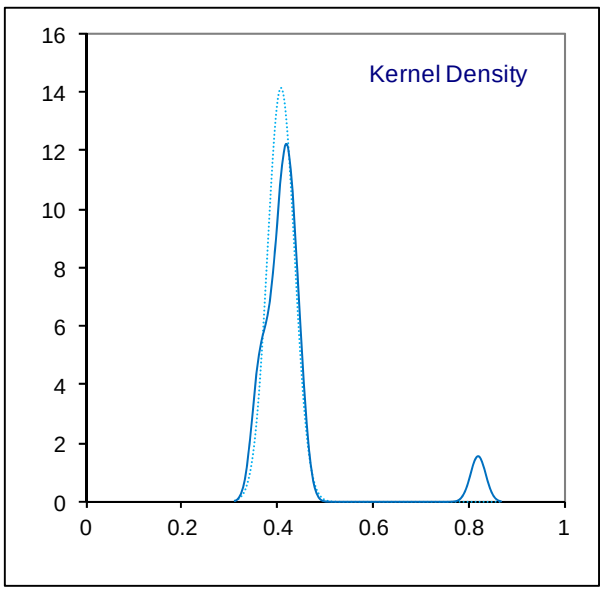


Determination of Methanol on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.441861		1.25	
311	D5441	0.40		-0.23	
312	D5441	0.42		0.48	
323	D5441	0.42		0.48	
334	D5441	0.41		0.13	
347	D5441	0.359	C	-1.67	First reported 0.287
555		-----		-----	
657	D5441	0.448		1.47	
862	D5441	0.413		0.23	
963	D5441	0.434		0.97	
1120	D5441	0.3577		-1.72	
1200		-----		-----	
1201	D5441	0.82	G(0.01)	14.59	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	0.390		-0.58	
1459	D5441	0.39		-0.58	
1586	D5441	0.37		-1.28	
1653		-----		-----	
1788	D5441	0.4184		0.42	
1866	D5441	0.4238		0.61	
1940		-----		-----	

normality	OK
n	15
outliers	1
mean (n)	0.4064
st.dev. (n)	0.02822
R(calc.)	0.0790
R(D5441:98)	0.0794



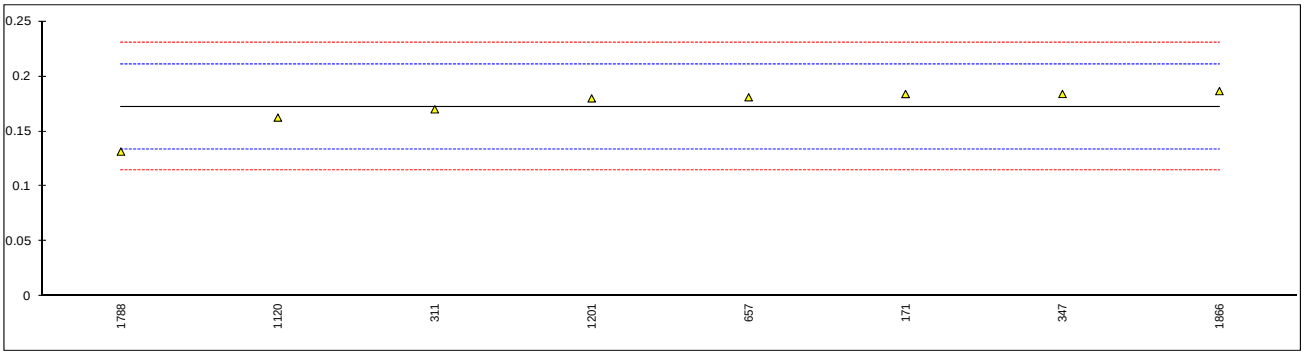


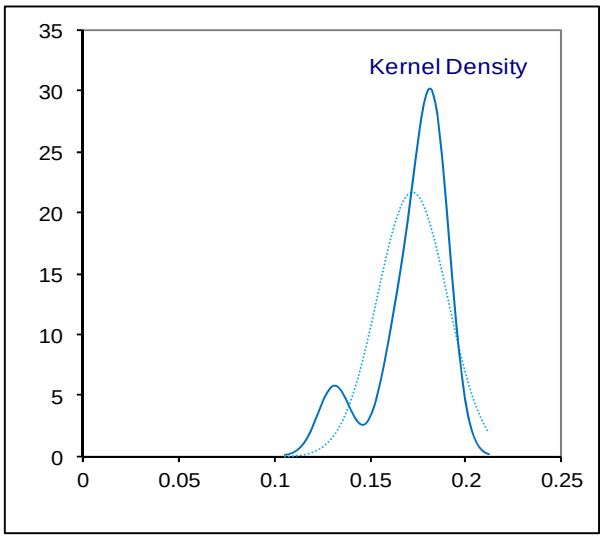
Determination of Diisobutylene (=sum 5 DIB*) on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171		0.18396		0.60	
311		0.17		-0.13	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347	D5441	0.184		0.60	
555		-----		-----	
657		0.181		0.44	
862		-----		-----	
963		-----		-----	
1120	D5441	0.1625		-0.52	
1200		-----		-----	
1201	D5441	0.18		0.39	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340		-----		-----	
1459		-----		-----	
1586		-----		-----	
1653		-----		-----	
1788		0.1316		-2.12	
1866	D5441	0.1866		0.73	
1940		-----		-----	

normality	unknown
n	8
outliers	0
mean (n)	0.1725
st.dev. (n)	0.01840
R(calc.)	0.0515
R(D5441:98)	0.0540

* Sum of 5 DIB: 2,4,4-Trimethyl-1-pentene; 2,4,4-Trimethyl-2-pentene; 2,3,4-Trimethyl-2-pentene; 3,4,4-Trimethyl-1-pentene and 3,5-Dimethyl-1-hexene.

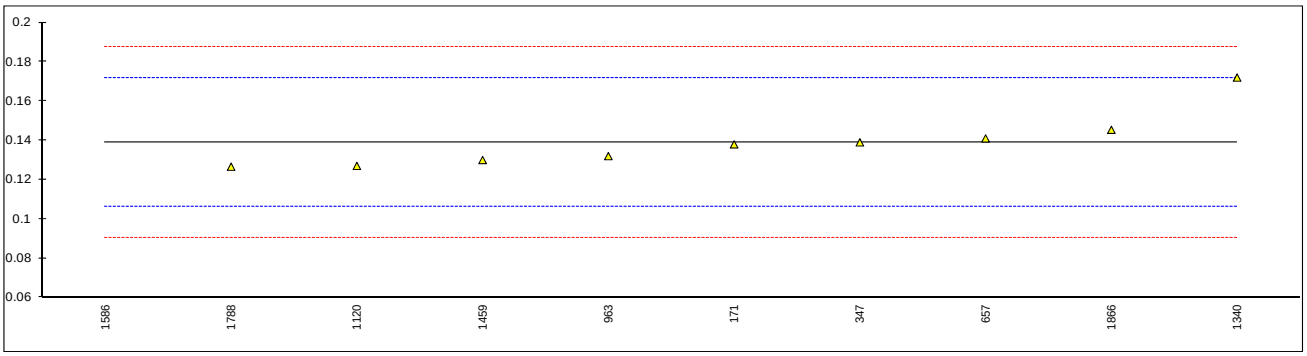


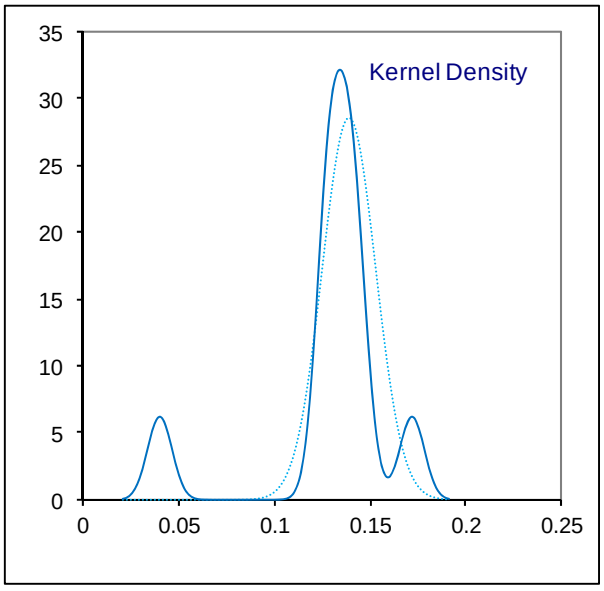


Determination of 2,4,4-Trimethyl-1-pentene on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.137969		-0.06	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347	D5441	0.139		0.00	
555		-----		-----	
657	D5441	0.141		0.12	
862		-----		-----	
963	D5441	0.132		-0.43	
1120	D5441	0.1270		-0.74	
1200		-----		-----	
1201		-----		-----	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	0.172		2.03	
1459	D5441	0.13		-0.55	
1586	D5441	0.04	G(0.01)	-6.09	
1653		-----		-----	
1788	D5441	0.1266		-0.76	
1866	D5441	0.1454		0.39	
1940		-----		-----	

normality	not OK
n	9
outliers	1
mean (n)	0.1390
st.dev. (n)	0.01398
R(calc.)	0.0391
R(D5441:98)	0.0455

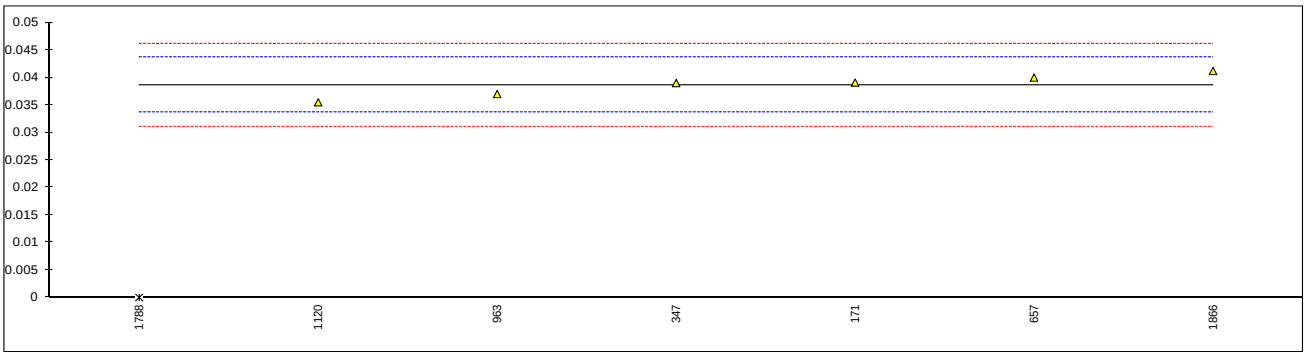




Determination of 2,4,4-Trimethyl-2-pentene on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.039088		0.18	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347	D5441	0.039		0.15	
555		-----		-----	
657	D5441	0.040		0.54	
862		-----		-----	
963	D5441	0.037		-0.65	
1120	D5441	0.0355		-1.24	
1200		-----		-----	
1201		-----		-----	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340		-----		-----	
1459		-----		-----	
1586		-----		-----	
1653		-----		-----	
1788	D5441	0.00	G(0.01)	-15.32	
1866	D5441	0.0412		1.02	
1940		-----		-----	

normality	unknown
n	6
outliers	1
mean (n)	0.0386
st.dev. (n)	0.00206
R(calc.)	0.0058
R(Horwitz)	0.0071



Determination of other individual diisobutylenes on MTBE sample #15006; results in %M/M

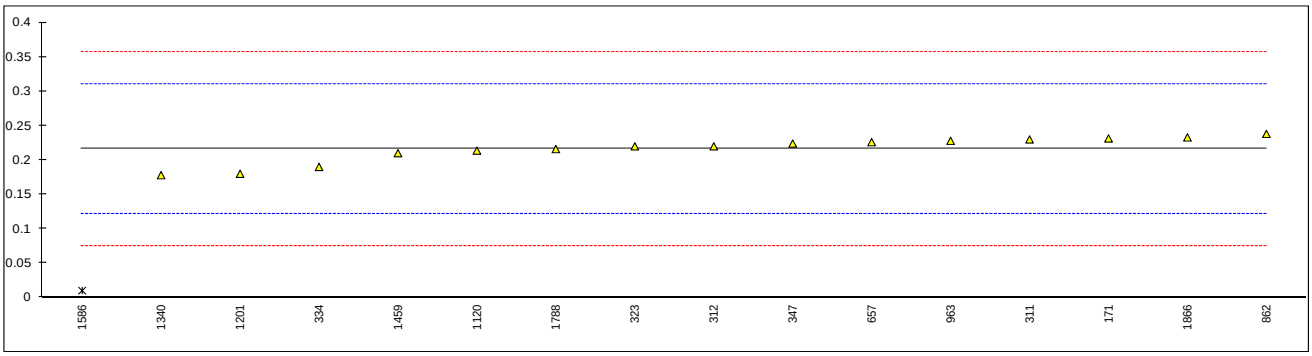
Lab	method	243T2P *)	mark	z(targ)	344T1P *)	mark	z(targ)	35D1H *)	mark	z(targ)	remarks
171	D5441	0.000816		-----	-----		-----	0.000875		-----	
311		-----		-----	-----		-----	-----		-----	
312		-----		-----	-----		-----	-----		-----	
323		-----		-----	-----		-----	-----		-----	
334		-----		-----	-----		-----	-----		-----	
347		-----		-----	-----		-----	-----		-----	
555		-----		-----	-----		-----	-----		-----	
657	D5441	<0.02		-----	<0.02		-----	<0.02		-----	
862		-----		-----	-----		-----	-----		-----	
963		-----		-----	-----		-----	-----		-----	
1120		-----		-----	-----		-----	-----		-----	
1200		-----		-----	-----		-----	-----		-----	
1201		-----		-----	-----		-----	-----		-----	
1221		-----		-----	-----		-----	-----		-----	
1252		-----		-----	-----		-----	-----		-----	
1261		-----		-----	-----		-----	-----		-----	
1340		-----		-----	-----		-----	-----		-----	
1459		-----		-----	-----		-----	-----		-----	
1586		-----		-----	-----		-----	-----		-----	
1653		-----		-----	-----		-----	-----		-----	
1788	D5441	0.00		-----	0.00		-----	0.0050		-----	
1866		-----		-----	-----		-----	-----		-----	
1940		-----		-----	-----		-----	-----		-----	
	normality	n.a.			n.a.			n.a.			
	n	3			2			3			
	outliers	n.a.			n.a.			n.a.			
	mean (n)	<0.02			<0.02			<0.02			
	st.dev. (n)	n.a.			n.a.			n.a.			
	R(calc.)	n.a.			n.a.			n.a.			
	R(lit)	n.a.			n.a.			n.a.			

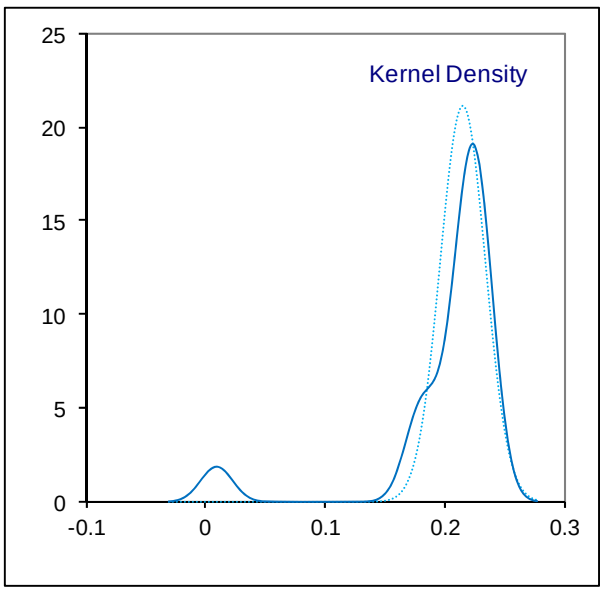
*) 2,4,3-Trimethyl-2-pentene
*) 3,4,4-Trimethyl-1-pentene
*) 3,5-Dimethyl-1-hexene

Determination of Tert-Butanol on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.231443		0.33	
311	D5441	0.23		0.30	
312	D5441	0.22		0.09	
323	D5441	0.22		0.09	
334	D5441	0.19		-0.55	
347	D5441	0.224		0.17	
555		-----		-----	
657	D5441	0.226		0.22	
862	D5441	0.238		0.47	
963	D5441	0.228		0.26	
1120	D5441	0.2137		-0.05	
1200		-----		-----	
1201	D5441	0.18		-0.76	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	0.178		-0.80	
1459	D5441	0.21		-0.12	
1586	D5441	0.01	G(0.01)	-4.37	
1653		-----		-----	
1788	D5441	0.2159		0.00	
1866	D5441	0.2329		0.36	
1940		-----		-----	

normality	OK
n	15
outliers	1
mean (n)	0.2159
st.dev. (n)	0.01890
R(calc.)	0.0529
R(D5441:98)	0.1320

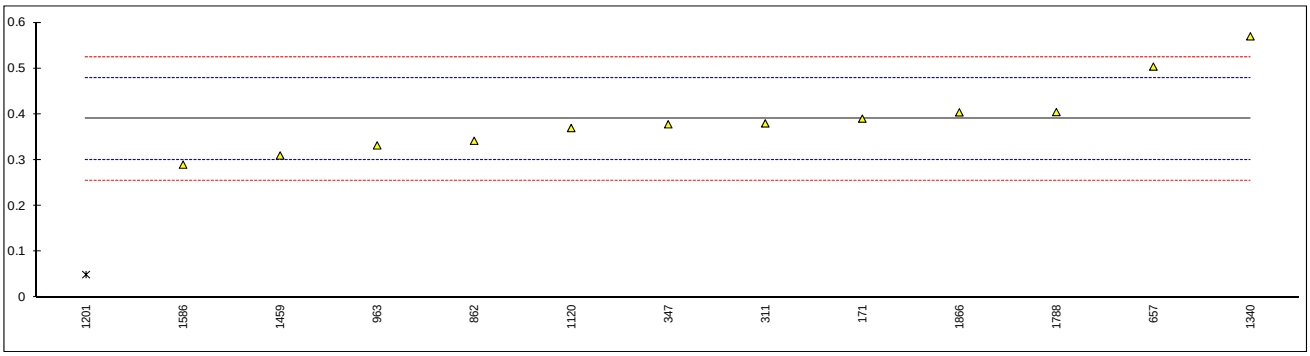


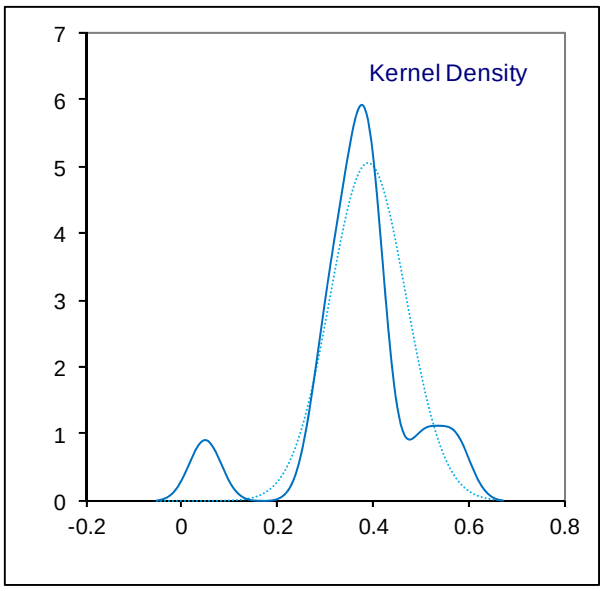


Determination of C4-hydrocarbons on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.39044		0.02	
311	D5441	0.38		-0.21	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347	D5441	0.378		-0.26	
555		-----		-----	
657	D5441	0.504		2.54	
862	D5441	0.342		-1.06	
963	D5441	0.332		-1.28	
1120	D5441	0.3699		-0.44	
1200		-----		-----	
1201	D5441	0.05	G(0.05)	-7.53	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	0.57		4.00	
1459	D5441	0.31		-1.77	
1586	D5441	0.29		-2.21	
1653		-----		-----	
1788	D5441	0.4048		0.34	
1866	D5441	0.4041		0.32	
1940		-----		-----	

normality	not OK
n	12
outliers	1
mean (n)	0.3896
st.dev. (n)	0.07893
R(calc.)	0.2210
R(D5441:98)	0.1262

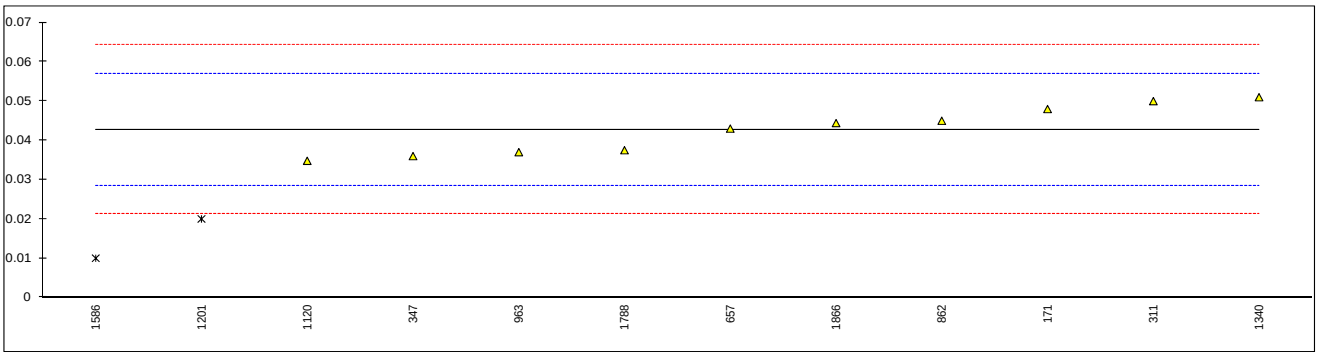


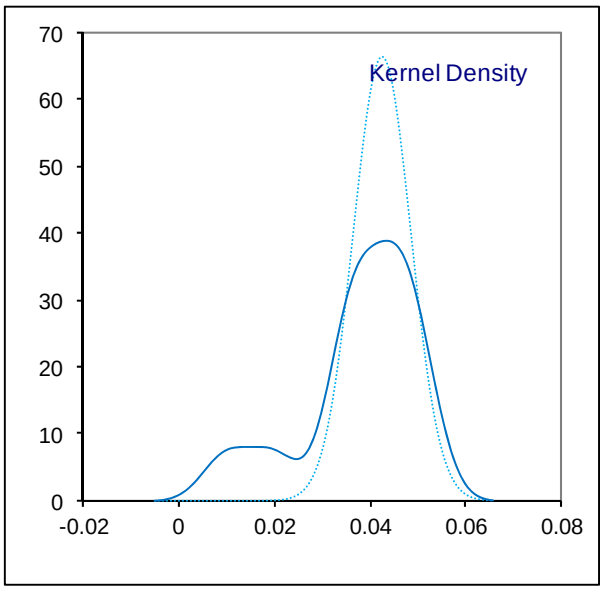


Determination of C5-hydrocarbons on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.047984		0.74	
311	D5441	0.05		1.02	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347	D5441	0.036		-0.93	
555		-----		-----	
657	D5441	0.043		0.05	
862	D5441	0.045		0.32	
963	D5441	0.037		-0.79	
1120	D5441	0.0348		-1.10	
1200		-----		-----	
1201	D5441	0.02	DG(0.05)	-3.16	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	0.051		1.16	
1459		-----		-----	
1586	D5441	0.01	DG(0.05)	-4.55	
1653		-----		-----	
1788	D5441	0.0375		-0.72	
1866	D5441	0.0444		0.24	
1940		-----		-----	

normality	OK
n	10
outliers	2
mean (n)	0.0427
st.dev. (n)	0.00601
R(calc.)	0.0168
R(D5441:98)	0.0201

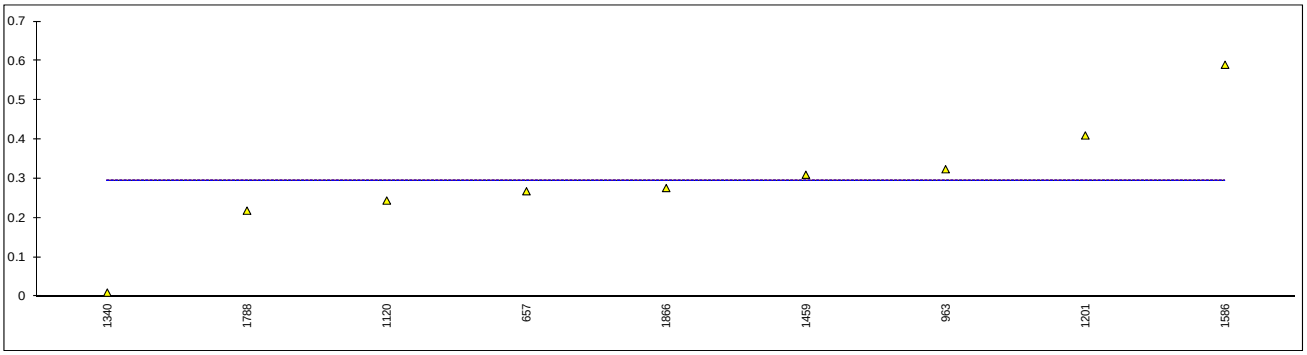


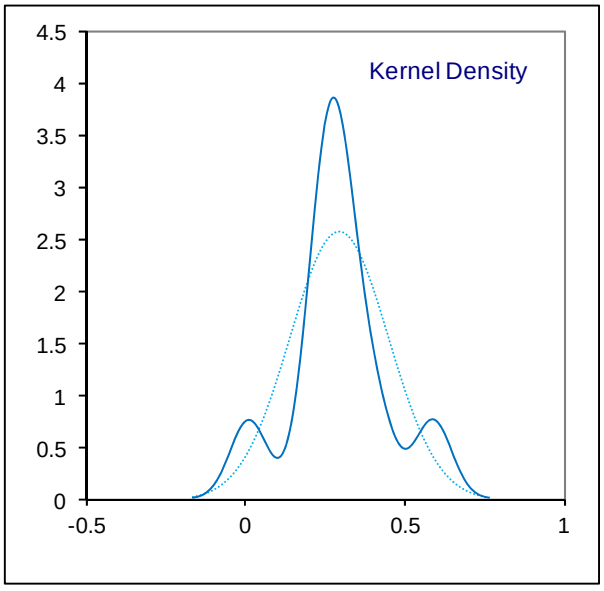


Determination of Other Impurities on MTBE sample #15006; results in %M/M

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
347		-----		-----	
555		-----		-----	
657	D5441	0.268		-----	
862		-----		-----	
963	D5441	0.324		-----	
1120	D5441	0.2443		-----	
1200		-----		-----	
1201	D5441	0.41		-----	
1221		-----		-----	
1252		-----		-----	
1261		-----		-----	
1340	D5441	0.01		-----	
1459	D5441	0.31		-----	
1586	D5441	0.59		-----	
1653		-----		-----	
1788	D5441	0.2185		-----	
1866	D5441	0.2762		-----	
1940		-----		-----	

normality	not OK
n	9
outliers	0
mean (n)	0.2946
st.dev. (n)	0.15494
R(calc.)	0.4338
R(lit.)	Unknown





APPENDIX 2

Number of participating laboratories per country

1 lab in BELGIUM
1 lab in BOSNIA and HERZEGOVINA
2 labs in BRAZIL
1 lab in CHINA, People's Republic
2 labs in FRANCE
1 lab in MALTA
3 labs in NETHERLANDS
1 lab in PORTUGAL
7 labs in SAUDI ARABIA
1 lab in SINGAPORE
1 lab in SPAIN
1 lab in U.S.A.
1 lab in VENEZUELA

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 outlier test
R(0.05)	= straggler in Rosner outlier test
E	= error in calculations
U	= error in reporting unit
ex	= excluded from calculations
n.a.	= not applicable
wd	= withdrawn method

Literature:

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

2 ASTM E178:89

3 ASTM E1301:89

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 page 1359-1364, P.J. Lowthian and M. Thompson

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