Results of Proficiency Test
MTBE
February 2012

Organised by: Institute for Interlaboratory Studies
                Spijkenisse, the Netherlands

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Appendices:

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 2011/2012, it was decided to continue the round robin for the analyses of MTBE.
In this interlaboratory study for MTBE 20 laboratories in 14 different countries have participated. See appendix 2 for the number of participants per country. In this report, the results of the MTBE 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, depending on the registration, to send one sample of MTBE (0.5 litre bottle, labelled #12003) to the participants. Analyses for fit-four-use and homogeneity were subcontracted to an accredited laboratory. 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 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2   PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iiis-protocol, version 3.2).

2.3   CONFIDENTIALITY STATEMENT

All data, present 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 56 brown glass bottles of 500 mL and

labelled #12003. The homogeneity of the subsamples was checked by determination of Density @15˚C in accordance with ASTM D4052:02e1 and Water in accordance with ASTM E1064:05 on 7 stratified randomly selected samples:

	Density at 15˚C in kg/L	Water in mg/kg
sample #12003-1	0.74653	1180
sample #12003-2	0.74654	1190
sample #12003-3	0.74655	1180
sample #12003-4	0.74654	1190
sample #12003-5	0.74654	1190
sample #12003-6	0.74656	1200
sample #12003-7	0.74655	1200

table 1: homogeneity test results of subsamples #12003

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 15˚C in kg/L	Water in mg/kg
r (sample #12003)	0.00003	23
reference test method	ASTM D4052:02e1	ASTM E1064:05
0.3xR (reference test)	0.00015	58

table 2: repeatabilities of the subsamples #12003

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 #12003, was sent on on February 1, 2012.

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 #12003 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, was sent together with each set of samples. Also, a letter of instructions and a SDS were added to the 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 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers this check was repeated. In case a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

In accordance with ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test and by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test and by G(0.05) or DG(0.05) for the Grubbs 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 reproduciblities were calculated from the standard deviations by multiplying these with a factor of 2.8.

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis, the reported analysis results are plotted. The corresponding laboratory numbers are under the X-axis.
The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle. Furthermore, Kernel Density Graphs were made. This method is for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3; nr.13 and 14).

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. ASTM reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study. The target standard deviation was calculated from the literature reproducibility by division with 2.8.

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

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 Saudi Arabia and Turkey received the samples late or not at all due to problems at customs. From the 20 participants, 7 participants reported results after the deadline for reporting and 3 participants did not report any results at all. The 17 reporting laboratories submitted 178 numerical results. Observed were 16 outlying results, which is 9.0%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not for all determinations, a normal distribution was found. A not-normal distribution was found for: Methanol, 2,4,4-Trimethyl-2-pentene and Tert-butanol. The statistical evaluations for these determinations with anormal distributions should be used with care.

4.1   EVALUATION PER TEST

In this section, the results are discussed per test. The methods, which are used by the various laboratories, are taken into account for explaining the observed differences when possible and applicable. These methods are also in the tables together with the original data in appendix 1. The abbreviations, used in these tables, are listed in appendix 3.

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Appearance: No analytical problems were observed. All labs agreed about the appearance of sample #12003, which is pass, bright and clear, clear and free of particles or clear and free of suspended matter. The uniformity of reporting can be improved.
ASTM E2680 is available since 2009. According this method the appearance should be reported as 'pass' (or 'fail').

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

Refractive Index: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, in full agreement with the requirements of ASTM D1218:07.

Carbonyls: Only five participants reported a numerical result. Therefore, no significant conclusions were drawn. The five participants reported a result far above the application range (0.5-50 µg/g calculated as CO) of the ASTM E411:05.

Water: This determination was problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the

statistical outlier, not in agreement with the requirements of ASTM E1064:05.

Purity as received: This determination was problematic. One statistical outlier was observed. However, the calculated reproducibility is not in agreement with the requirements of ASTM D5441:08e1.
One laboratory reported a result for purity "as received" that was larger then purity result "on dry basis". This result was excluded from statistical evaluation.

Purity on dry basis: This determination was problematic. One statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, not in agreement with the requirements of ASTM D5441:08e1. It must be noted that a test result of D5441 will be on dry basis by definition due to the calculations used in this test method.
One laboratory reported a result for purity "on dry basis" that was smaller then purity result "as received". This result was excluded from statistical evaluation.

Methanol: This determination was problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of ASTM D5441:08e1.

Diisobutylene (=sum):   This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility in agreement with the estimated reproducibility limits, calculated using the Horwitz equation (n=2). When the results were evaluated after manual summation of the reported DIB's, it was observed that after rejection of one statistical outlier, the consensus value was the same, but the spread was much smaller.

2,4,4-Trime-1-pent.:   This determination was not problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, in agreement with the requirements of ASTM D5441:08e1.

2,4,4-Trime-2-pent.:   This determination was not problematic. Two statistical outliers were observed. However, the calculated reproducibility 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 a few numerical results were reported. Therefore, no significant conclusions were drawn.

Tert-butanol: This determination was not problematic. Only one statistical outlier was observed and the calculated reproducibility is, after rejection of the

statistical outlier, in good agreement with the requirements of ASTM D5441:08e1, although the concentration (0.355 %M/M) is outside the application range of the method (0.474 - 0.8763 %M/M).

C4-hydrocarbons: This determination was not problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, in full agreement with the requirements of ASTM D5441:08e1.

C5-hydrocarbons: This determination was very problematic. Two statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers, not at all in agreement with the requirements of ASTM D5441:08e1.

Other hydrocarb.+ Unknown Impurities:

Other hydrocarbons may be all components listed in table 2 of D5441:08e1 and not evaluated separately in this proficiency test.
For unknown impurities, it should be noticed that ASTM D5441:08e1 does not give a definition which "unknown impurities" might be present in MTBE. ASTM states however that for unknown contaminants a response factor of 1.00 should be used.
Only a few numerical results were reported for Other Hydrocarbons and Unknown impurities. Therefore, no significant conclusions were drawn.
In general, it is hard to judge a overall group performance, because ASTM D5441:08e1 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, ISO and EN standards, see tables in appendix 1).

	unit	n	average	R (Calc.)	R (lit)
Appearance		8	pass	n.a	n.a
Density @ 15°C	kg/L	14	0.74654	0.00036	0.00050
Refractive Index @ 20ºC		10	1.36950	0.00047	0.00050
Carbonyls	µg/g	4	336.9	n.a	n.a
Water	mg/kg	15	1214	202	193
Purity "as received"	%M/M	13	98.1216	0.4606	0.3034
Purity "on dry basis"	%M/M	11	98.2535	0.3650	0.3029
Methanol	%M/M	17	0.3616	0.1003	0.0771
Diisobutylene (=sum of 5)	% M/M	8	0.2365	0.0346	0.0465
2,4,4-Trimethyl-1-pentene	%M/M	10	0.1785	0.0248	0.0555
2,4,4-Trimethyl-2-pentene	%M/M	9	0.0499	0.0066	0.0088
Tert-butanol	%M/M	14	0.3549	0.0745	0.1320
C4 – hydrocarbons	%M/M	11	0.1314	0.0465	0.0436
C5 – hydrocarbons	%M/M	10	0.0724	0.0433	0.0290
Other hydrocarbons	%M/M	4	0.3550	n.a	unknown
Unknown impurities	%M/M	5	0.3449	n.a	unknown

table 3: performance evaluation of sample #12003

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 2012 WITH PREVIOUS PTS

A good comparison with the previous PT'S can not be made. The PT's from April 2007 to March 2010 also include the Ethyl Tertiary Butyl Ether (ETBE) data. This year the PT for ETBE has been cancelled because of too few participants.

	February 2012	March 2010	March 2008	April 2007
Number of reporting labs	17	33	23	19
Number of Results reported	178	305	400	364
Statistical outliers	16	22	38	19
Percentage outliers	9.0%	7.2%	9.5%	8.2%

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 samples of the proficiency test were compared against the requirements of the respective standards. The conclusions are given the following table:

Determination	February 2012	March 2010	March 2008	April 2007
Density @ 15°C	+	+	+	++
Refractive Index @ 20ºC	+/-	+	--	--
Carbonyls	n.e	n.e	n.e	n.e
Water	+/-	++	++	--
Purity as received	--	+	-	--
Purity on dry basis	-	+	-	--
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 only

*) 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 #12003;

lab	method	value	mark	z(targ)	remarks
171	E2680	C&F		-----	
311	E2680	pass		-----	
312		-----		-----	
323	E2680	CFSM		-----	
334		-----		-----	
357	E2680	pass		-----	
497	E2680	B&C		-----	
657	E2680	pass		-----	
663	E2680	B&C		-----	
862		-----		-----	
963	E2680	pass		-----	
1016		-----		-----	
1108		-----		-----	
1200		-----		-----	
1221		-----		-----	
1252		-----		-----	
1427		-----		-----	
1833		-----		-----	
1866		-----		-----	
1940		-----		-----	

C&F = Clear and Free of particles
B&C = Bright and clear
CFSM = Clear and Free of Suspended Matter

Determination of Density @ 15°C on MTBE sample #12003; results in kg/L

lab	method	value	mark	z(targ	remarks
171	D4052	0.7464		-0.80	
311	D4052	0.74654		-0.02	
312	D4052	0.7465	C	-0.24	first reported: 746.5
323	D4052	0.7465		-0.24	
334	D4052	0.74659		0.26	
357	D4052	0.7465		-0.24	
497	D4052	0.7466	C	0.32	first reported: 746.6
657	D4052	0.74652		-0.13	
663	D4052	0.7465		-0.24	
862	D4052	0.74671		0.94	
963	D4052	0.7458	G(0.01)	-4.16	
1016	D4052	0.7463		-1.36	
1108	D4052	0.74684		1.66	
1200		-----		-----	
1221	D4052	0.74655		0.04	
1252		-----		-----	
1427	D4052	0.74655		0.04	
1833		-----		-----	
1866	D4052	0.74787	G(0.01)	7.43	
1940		-----		-----	

normality	OK
n	14
outliers	2
mean (n)	0.74654
st.dev. (n)	0.000127
R(calc.)	0.00036
R(D4052:02e1)	0.00050
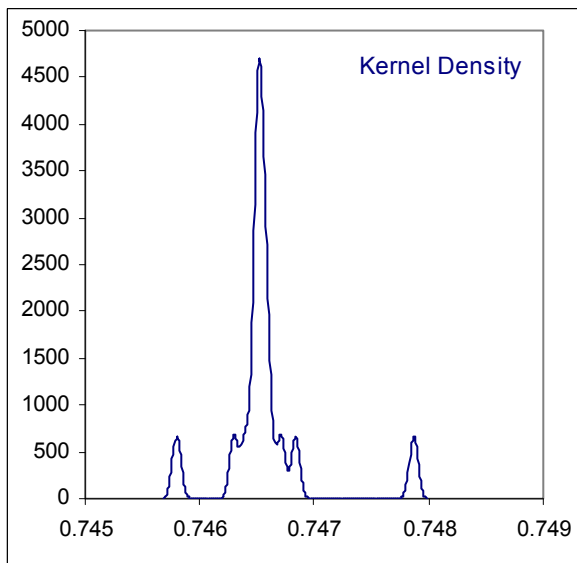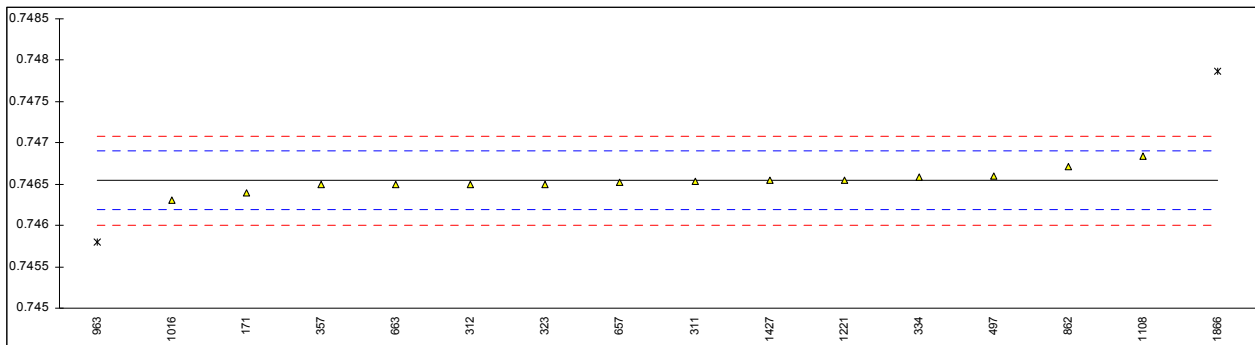
Determination of Refractive Index @ 20°C on MTBE sample #12003;

lab	method	value	mark	z(targ)	remarks
171	D1218	1.3697		1.10	
311	D1218	1.36941		-0.52	
312		-----		-----	
323	D1218	1.36952		0.10	
334		-----		-----	
357	D1218	1.3695		-0.02	
497	D1218	1.3694	C	-0.58	first reported: 1.3747
657	D1218	1.3695		-0.02	
663		-----		-----	
862	D1218	1.36940		-0.58	
963	D1218	1.3692		-1.70	
1016	D1218	1.3696		0.54	
1108	D1218	1.3698		1.66	
1200		-----		-----	
1221		-----		-----	
1252		-----		-----	
1427		-----		-----	
1833		-----		-----	
1866	D1218	1.3685	G(0.01)	-5.62	
1940		-----		-----	

normality	OK
n	10
outliers	1
mean (n)	1.36950
st.dev. (n)	0.000169
R(calc.)	0.00047
R(D1218:07)	0.00050
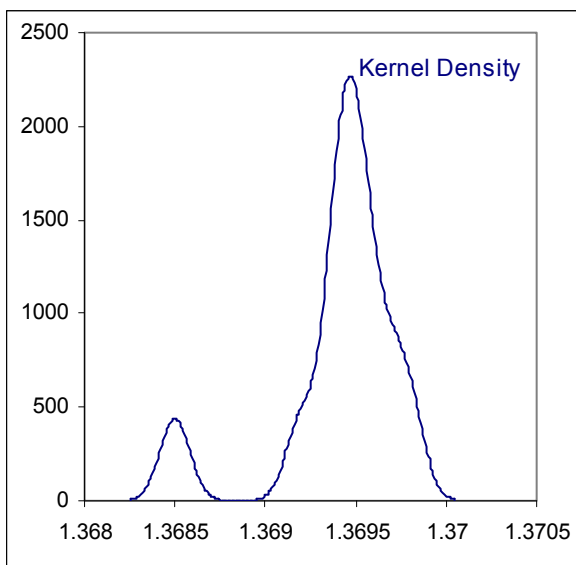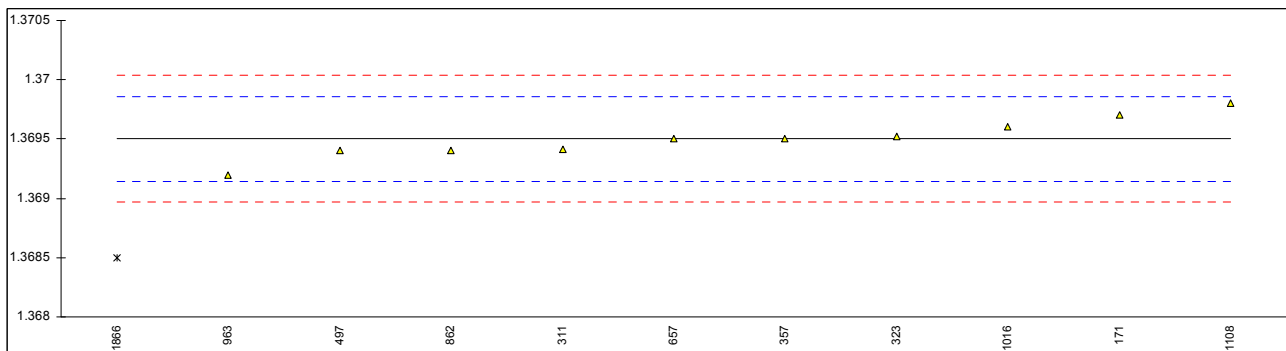
Determination of Carbonyls on MTBE sample #12003; results in µg/g

lab	method	value	mark	z(targ)	remarks
171	E411	411		-----	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
357		-----		-----	
497	E411	319.6		-----	
657	E411	279.1		-----	
663		-----		-----	
862	E411	338		-----	
963		-----		-----	
1016		-----		-----	
1108		-----		-----	
1200		-----		-----	
1221		-----		-----	
1252		-----		-----	
1427		-----		-----	
1833		-----		-----	
1866	E411	11.207	G(0.01)	-----	false negative?
1940		-----		-----	

normality	n.a	
n	4	
outliers	1	
mean (n)	336.92	
st.dev. (n)	n.a	
R(calc.)	n.a	
R(E411:05)	n.a	Application range : 0.5-50 µg/g calculated as CO
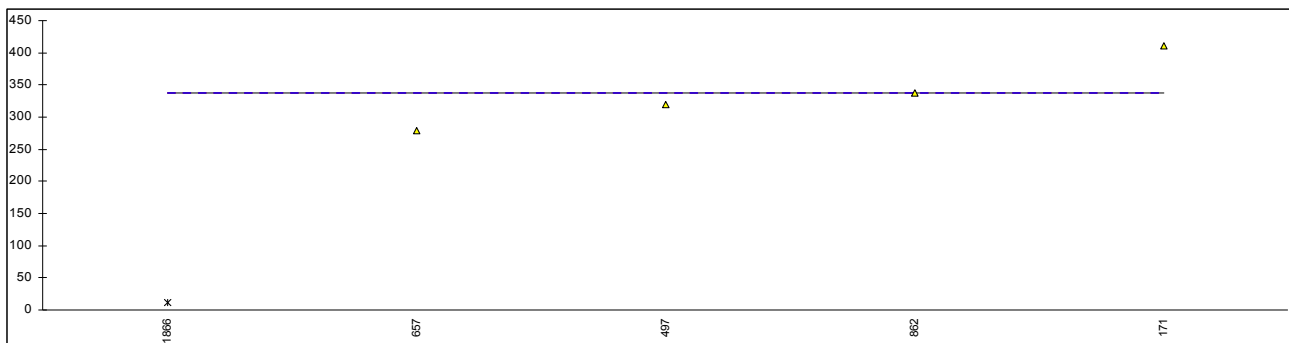
Determination of Water on MTBE sample #12003; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	E203	1134		-1.16	
311	E1064	1123		-1.32	
312	ISO12937	1160		-0.78	
323	E1064	1182		-0.46	
334	E1064	1230		0.23	
357	E1064	1360		2.12	
497	E1064	1175		-0.56	
657	E1064	1314.5		1.46	
663	E1064	1322		1.57	
862	E1064	1260		0.67	
963	E1064	1180		-0.49	
1016	D1364	1210		-0.06	
1108	E1064	1235		0.31	
1200		-----		-----	
1221	E1064	1176.47		-0.54	
1252		-----		-----	
1427	D1364	1146.66		-0.98	
1833		-----		-----	
1866	E1064	957	G(0.01)	-3.73	
1940		-----		-----	

normality	OK
n	15
outliers	1
mean (n)	1213.91
st.dev. (n)	72.284
R(calc.)	202.40
R(E1064:05)	193.01
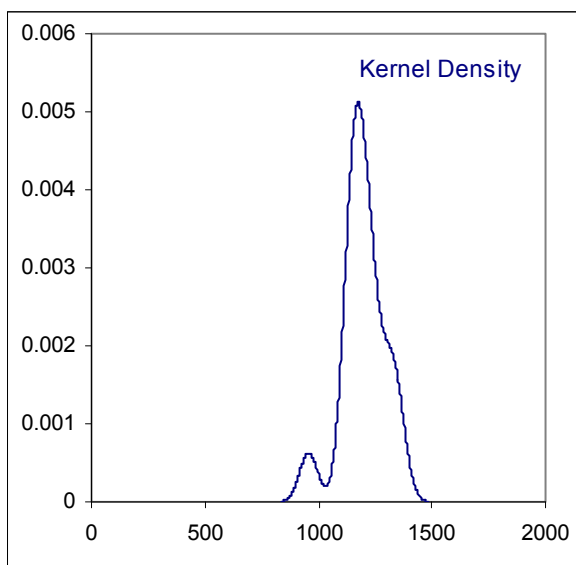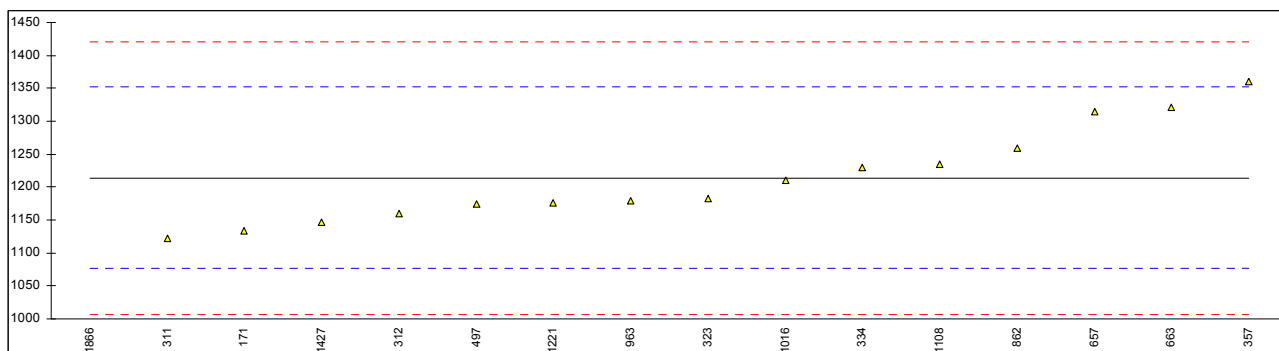
Determination of Purity "as received" of MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	98.114		-0.07	
311	D5441	98.34		2.02	
312	D5441	98.17		0.45	
323	D5441	98.14		0.17	
334	D5441	98.43		2.85	
357	D5441	98.098	ex	-0.22	result excluded; "as received" > purity "on dry basis"
497	D5441	97.6061	G(0.05)	-4.76	first reported: 98.4338
657	D5441	97.8909		-2.13	
663		-----		-----	
862	D5441	98.06		-0.57	
963	D5441	97.96		-1.49	
1016		-----		-----	
1108	D5441	98.24		1.09	
1200		-----		-----	
1221	D5441	98.169		0.44	
1252		-----		-----	
1427	D5441	98.204		0.76	
1833		-----		-----	
1866	D5441	97.914		-1.92	
1940	D5441	97.948484		-1.60	

|		
normality	OK	
n	14	
outliers	1	
mean (n)	98.1216	
st.dev. (n)	0.16452	
R(calc.)	0.4606	
R(D5441:08e1)	0.3034	estimated from reproducibility on dry basis *cfr* ASTM D5441
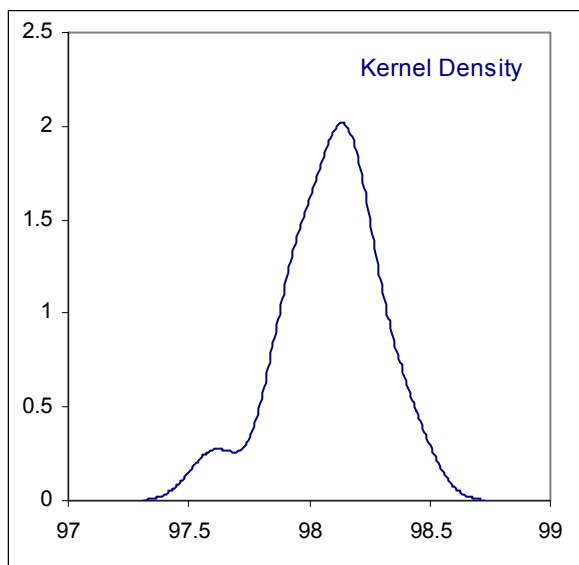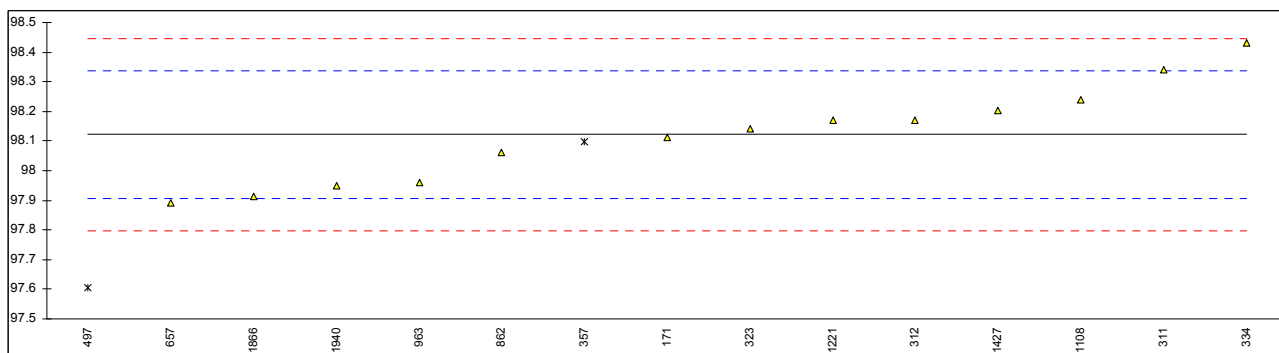
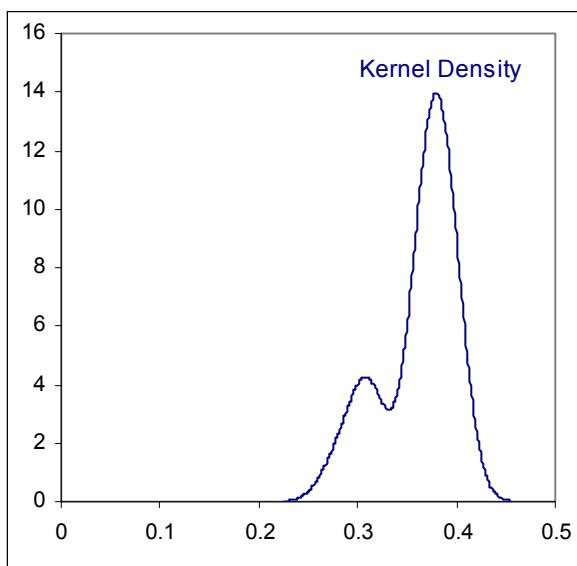Determination of Purity on dry basis on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	98.227		-0.24	
311	D5441	98.45		1.82	
312		-----		-----	
323	D5441	98.26		0.06	
334		-----		-----	
357	D5441	97.962	ex	-2.69	result excluded; "purity on dry basis" < "as received"
497	D5441	97.7236	C,G(0.05)	-4.90	first reported: 98.5513
657	D5441	98.0197		-2.16	
663		-----		-----	
862	D5441	98.19		-0.59	
963	D5441	98.08		-1.60	
1016	D5441	98.346	C	0.86	first reported: 99.336
1108	D5441	98.36		0.98	
1200		-----		-----	
1221	D5441	98.287		0.31	
1252		-----		-----	
1427	D5441	98.315		0.57	
1833		-----		-----	
1866		-----		-----	
1940		-----		-----	

normality	OK	
n	11	
outliers	1	
mean (n)	98.2535	
st.dev. (n)	0.13036	
R(calc.)	0.3650	
R(D5441:08e1)	0.3029	
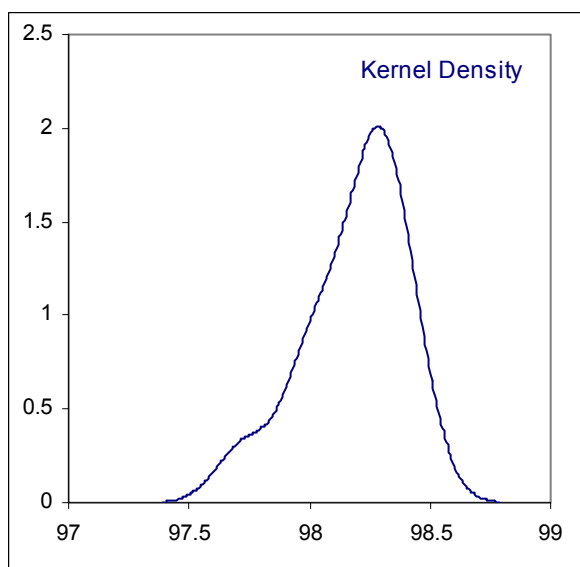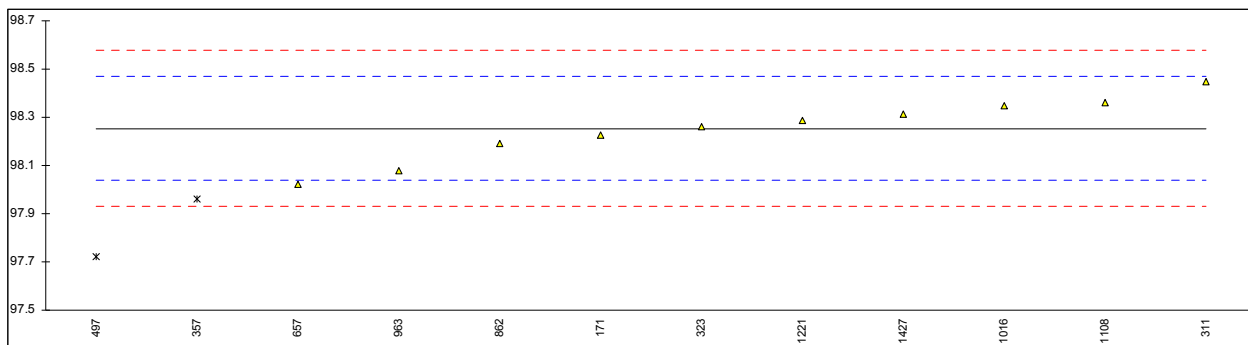
Determination of Methanol on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.387		0.92	
311	D5441	0.31		-1.87	
312	D5441	0.362		0.01	
323	D5441	0.31		-1.87	
334	D5441	0.37		0.30	
357	D5441	0.365		0.12	
497	D5441	0.3881		0.96	
657	D5441	0.390		1.03	
663	D5441	0.28		-2.96	
862	D5441	0.394		1.18	
963	D5441	0.40		1.39	
1016	D5441	0.376		0.52	
1108	D5441	0.375		0.49	
1200		-----		-----	
1221	D5441	0.366		0.16	
1252		-----		-----	
1427	D5441	0.311		-1.84	
1833		-----		-----	
1866	D5441	0.382		0.74	
1940	D5441	0.381235		0.71	

normality	not OK	
n	17	
outliers	0	
mean (n)	0.3616	
st.dev. (n)	0.03581	
R(calc.)	0.1003	
R(D5441:08e1)	0.0771	

Kernel Density
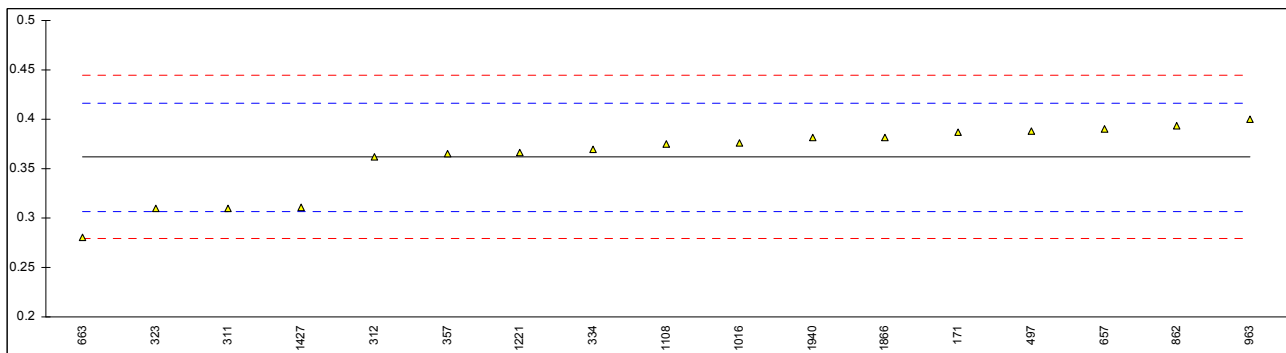
Determination of Diisobutylene (=sum 5 DIB's*) on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	value after manual summation	mark	z(targ)	remarks
171	D5441	0.232		-0.27	0.232		-0.07	
311		-----		-----	0.24		0.42	
312		-----		-----	0.213		-1.22	
323		-----		-----	-----		-----	
334		-----		-----	-----		-----	
357		-----		-----	0.228		-0.31	
497		-----		-----	0.4348	G(0.01)	12.29	
657	D5441	0.240		0.21	0.235		0.12	
663		-----		-----	-----		-----	
862	D5441	0.217		-1.17	-----		-----	
963	D5441	0.22		-0.99	0.22		-0.80	
1016		-----		-----	-----		-----	
1108	D5441	0.25		0.81	0.229		-0.25	
1200		-----		-----	-----		-----	
1221	D5441	0.242		0.33	0.242		0.54	
1252		-----		-----	-----		-----	
1427	D5441	0.248		0.69	0.249		0.97	
1833		-----		-----	-----		-----	
1866	D5441	0.243		0.39	0.243		0.60	
1940	D5441	0.183413	G(0.05)	-3.19	-----		-----	
	normality	OK			OK			
	n	8			10			
	outliers	1			1			
	mean (n)	0.2365			0.2331			
	st.dev. (n)	0.01238			0.01106			
	R(calc.)	0.0346			0.0310			
	R(Horwitz)	0.0465			0.0460			

* Sum of 5 DIB´s: 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.

only reported test results

Kernel Density

after manuel summation by iis

Kernel Density
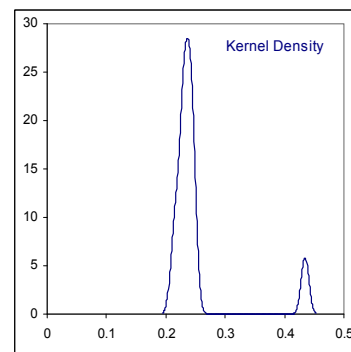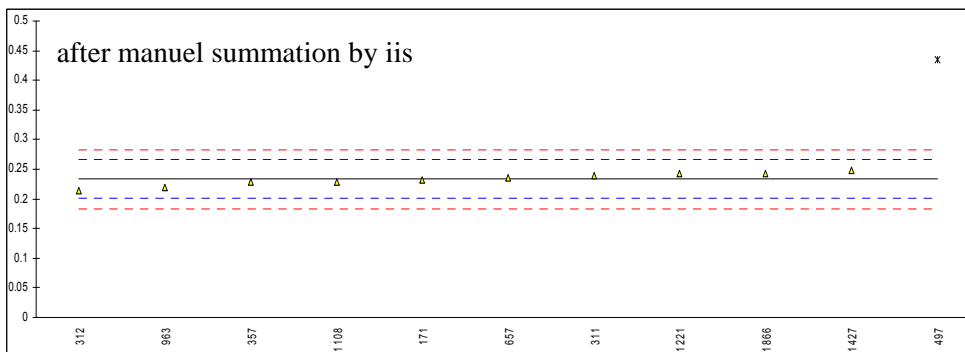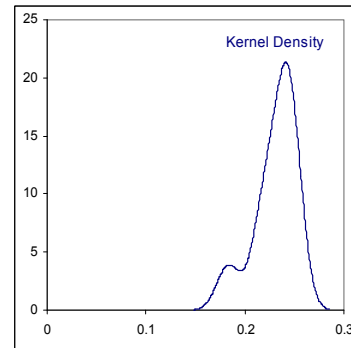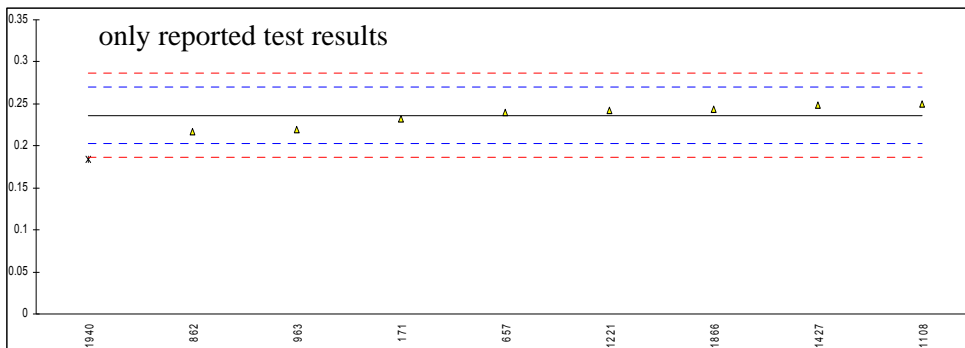
Determination of 2,4,4-Trimethyl-1-pentene on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.165		-0.68	
311	D5441	0.19		0.58	
312	D5441	0.167		-0.58	
323		-----		-----	
334		-----		-----	
357	D5441	0.177		-0.08	
497	D5441	0.3967	C,G(0.01)	11.01	first reported: 0.0354
657	D5441	0.183		0.23	
663		-----		-----	
862		-----		-----	
963	D5441	0.17		-0.43	
1016		-----		-----	
1108	D5441	0.179		0.03	
1200		-----		-----	
1221	D5441	0.190		0.58	
1252		-----		-----	
1427	D5441	0.180		0.08	
1833		-----		-----	
1866	D5441	0.184		0.28	
1940		-----		-----	

normality	OK
n	10
outliers	1
mean (n)	0.1785
st.dev. (n)	0.00886
R(calc.)	0.0248
R(D5441:08e1)	0.0555
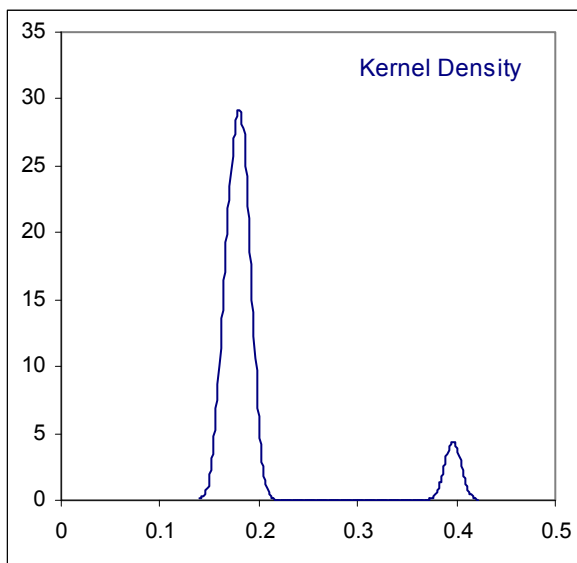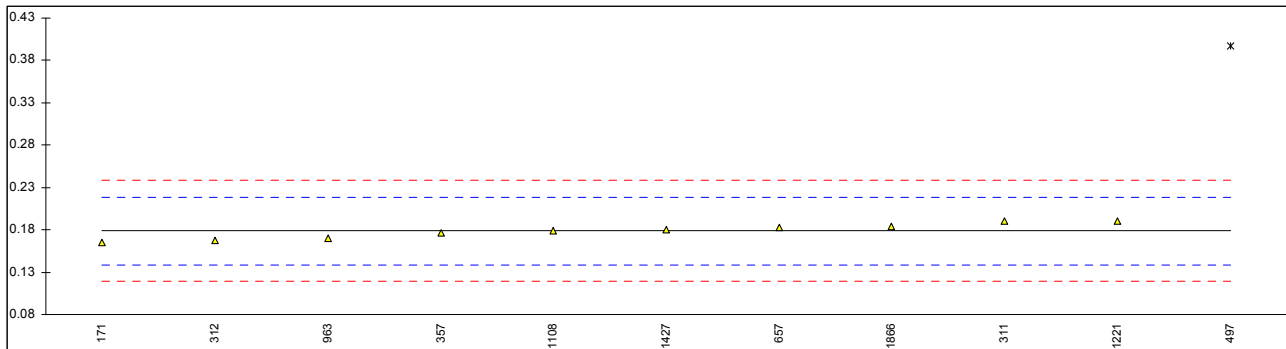
Determination of 2,4,4-Trimethyl-2-pentene on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.046		-1.24	
311	D5441	0.05		0.04	
312	D5441	0.046		-1.24	
323		-----		-----	
334		-----		-----	
357	D5441	0.051		0.35	
497	D5441	0.0381	C, G(0.05)	-3.76	first reported: 0.0150
657	D5441	0.052		0.67	
663		-----		-----	
862		-----		-----	
963	D5441	0.05		0.04	
1016		-----		-----	
1108	D5441	0.05		0.04	
1200		-----		-----	
1221	D5441	0.052		0.67	
1252		-----		-----	
1427	D5441	0.001	G(0.01)	-15.60	
1833		-----		-----	
1866	D5441	0.052		0.67	
1940		-----		-----	

normality	not OK
n	9
outliers	2
mean (n)	0.0499
st.dev. (n)	0.00237
R(calc.)	0.0066
R(Horwitz)	0.0088

Kernel Density
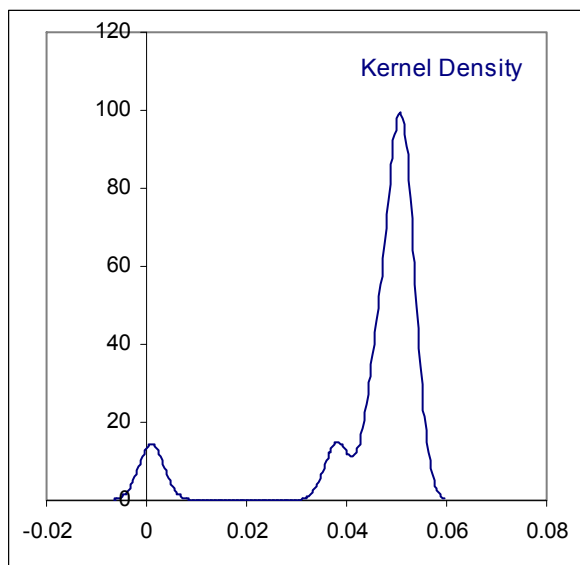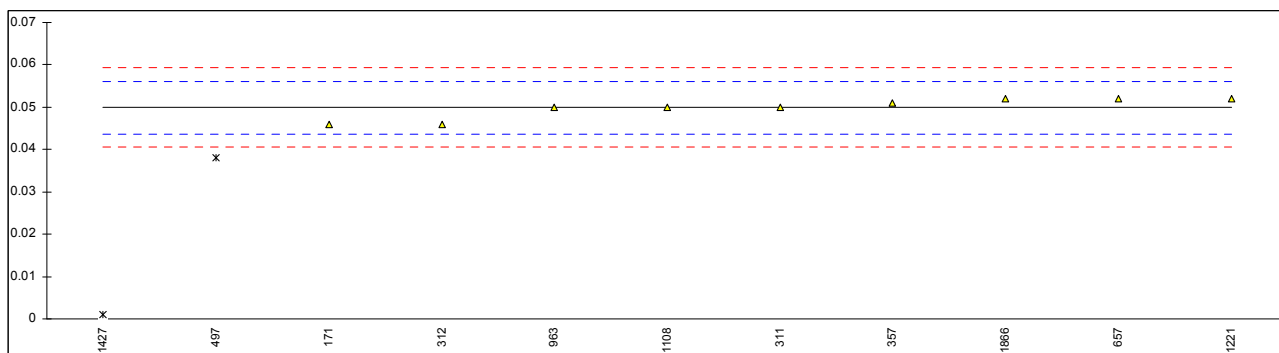
Determination of other individual diisobutylenes on MTBE sample #12003; results in %M/M

Lab	method	243T2P *)	mark	z(targ)	344T1P *)	mark	z(targ)	35D1H *)	mark	z(targ)	remarks
171	D5441	0.003		-----	0.018		-----	-----		-----	
311	D5441	-----		-----	-----		-----	-----		-----	
312	D5441	-----		-----	-----		-----	-----		-----	
323	D5441	-----		-----	-----		-----	-----		-----	
334	D5441	-----		-----	-----		-----	-----		-----	
357	D5441	-----		-----	-----		-----	-----		-----	
497	D5441	-----		-----	-----		-----	-----		-----	
657	D5441	<0.02		-----	<0.02		-----	<0.02		-----	
663		-----		-----	-----		-----	-----		-----	
862	D5441	-----		-----	-----		-----	-----		-----	
963	D5441	<0.02		-----	<0.02		-----	<0.02		-----	
1016	D5441	-----		-----	-----		-----	-----		-----	
1108	D5441	-----		-----	-----		-----	-----		-----	
1200	D5441	-----		-----	-----		-----	-----		-----	
1221	D5441	-----		-----	-----		-----	-----		-----	
1252	D5441	-----		-----	-----		-----	-----		-----	
1427	D5441	0.052	false pos?	-----	0.016		-----	<0.01		-----	
1833	D5441	-----		-----	-----		-----	-----		-----	
1866	D5441	-----		-----	0.007		-----	-----		-----	
1940	D5441	-----		-----	-----		-----	-----		-----	
	normality	n.a			n.a			n.a			
	n	2			3			0			
	outliers	0			0			0			
	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(Horwitz)	n.a			n.a			n.a			

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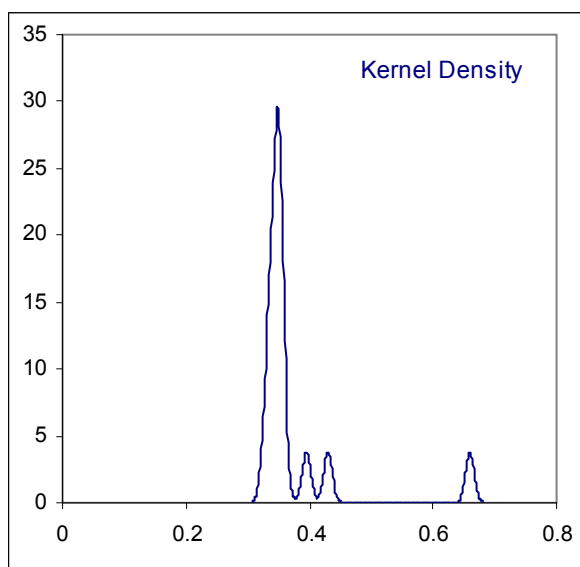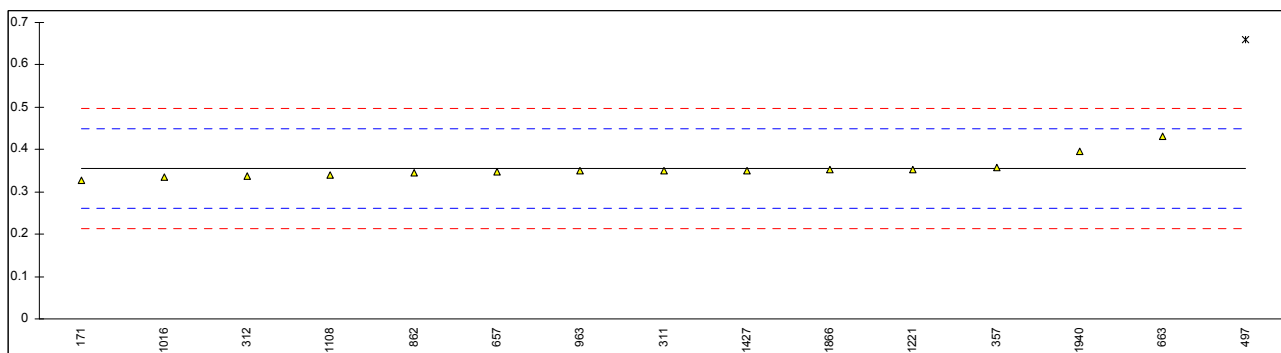*) 3,4,4-Trimethyl-1-pentene
*) 3,5-Dimethyl-1-hexene

Determination of Tert-butanol on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.328		-0.57	
311	D5441	0.35		-0.10	
312	D5441	0.337		-0.38	
323		-----		-----	
334		-----		-----	
357	D5441	0.358		0.06	
497	D5441	0.6600	C, G(0.01)	6.47	first reported: 0.2334
657	D5441	0.348		-0.15	
663	D5441	0.43		1.59	
862	D5441	0.344		-0.23	
963	D5441	0.35		-0.10	
1016	D5441	0.335		-0.42	
1108	D5441	0.34		-0.32	
1200		-----		-----	
1221	D5441	0.352		-0.06	
1252		-----		-----	
1427	D5441	0.350		-0.10	
1833		-----		-----	
1866	D5441	0.352		-0.06	
1940	D5441	0.395283		0.86	

|	
normality	not OK
n	14
outliers	1
mean (n)	0.3549
st.dev. (n)	0.02660
R(calc.)	0.0745
R(D5441:08e1)	0.1320

Application range: 0.474-0.8763 %M/M

Kernel Density

Determination of C4-hydrocarbons on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.136		0.30	
311	D5441	0.11		-1.37	
312		-----		-----	
323		-----		-----	
334		-----		-----	
357	D5441	0.125		-0.41	
497	D5441	0.1281	C	-0.21	first reported: 0.0642
657	D5441	0.163		2.03	
663		-----		-----	
862	D5441	0.133		0.10	
963	D5441	0.11		-1.37	
1016		-----		-----	
1108	D5441	0.144		0.81	
1200		-----		-----	
1221	D5441	0.120		-0.73	
1252		-----		-----	
1427	D5441	0.124		-0.47	
1833		-----		-----	
1866	D5441	0.152		1.32	
1940	D5441	0.049299	G(0.01)	-5.27	

normality	OK
n	11
outliers	1
mean (n)	0.1314
st.dev. (n)	0.01661
R(calc.)	0.0465
R(D5441:08e1)	0.0436
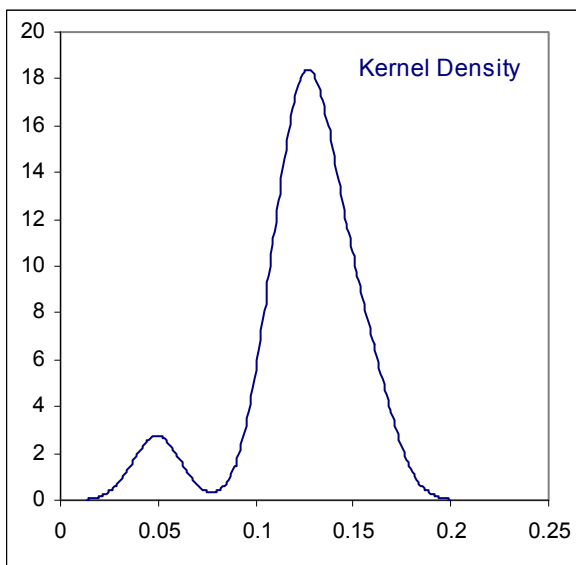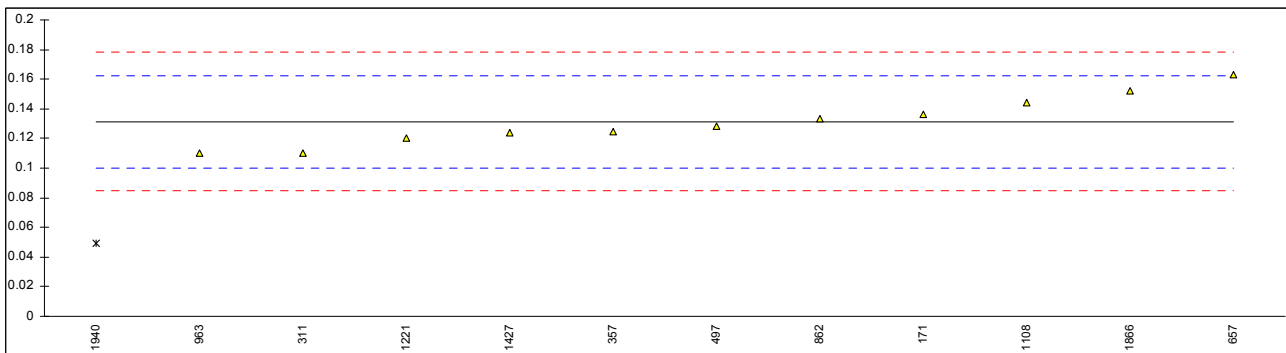
Determination of C5-hydrocarbons on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171	D5441	0.096		2.31	
311	D5441	0.06		-1.22	
312		-----		-----	
323		-----		-----	
334		-----		-----	
357	D5441	0.084		1.13	
497	D5441	0.0441	C	-2.77	first reported: 0.2392
657	D5441	0.075		0.25	
663		-----		-----	
862	D5441	0.150	DG(0.05)	7.60	
963	D5441	0.06		-1.22	
1016		-----		-----	
1108	D5441	0.09		1.72	
1200		-----		-----	
1221	D5441	0.067		-0.53	
1252		-----		-----	
1427	D5441	0.074		0.16	
1833		-----		-----	
1866	D5441	0.074		0.16	
1940	D5441	0.011777	DG(0.05)	-5.94	

|	
normality	OK
n	10
outliers	2
mean (n)	0.0724
st.dev. (n)	0.01546
R(calc.)	0.0433
R(D5441:08e1)	0.0290

Kernel Density
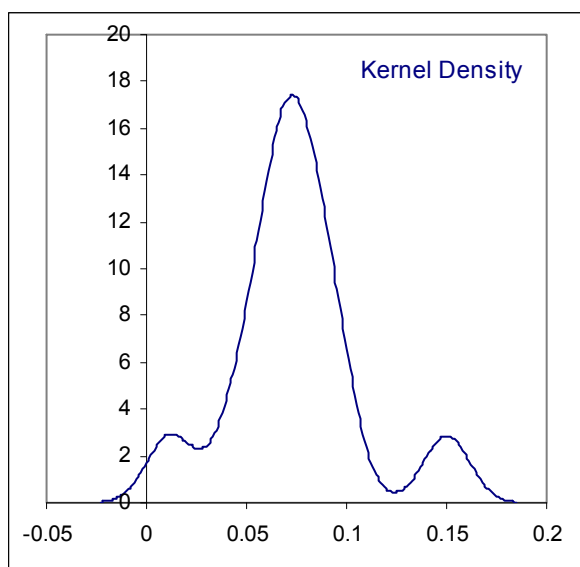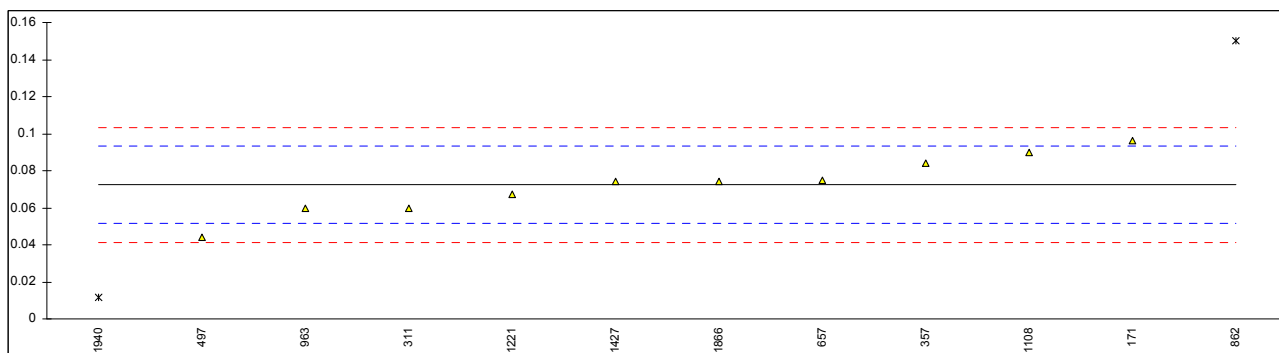
Determination of Other Hydrocarbons on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
357		-----		-----	
497	D5441	0.2988	C	-----	first reported: 0.1770
657	D5441	0.418		-----	
663		-----		-----	
862		-----		-----	
963		-----		-----	
1016		-----		-----	
1108		-----		-----	
1200		-----		-----	
1221		-----		-----	
1252		-----		-----	
1427	D5441	0.522		-----	
1833		-----		-----	
1866	D5441	0.181		-----	
1940	D5441	1.032891	ex	-----	Result excluded, 5 DIBs (0.183414 %M/M) is included in this result

normality	n.a
n	4
outliers	0
mean (n)	0.3550
st.dev. (n)	n.a
R(calc.)	n.a
R(lit.)	unknown
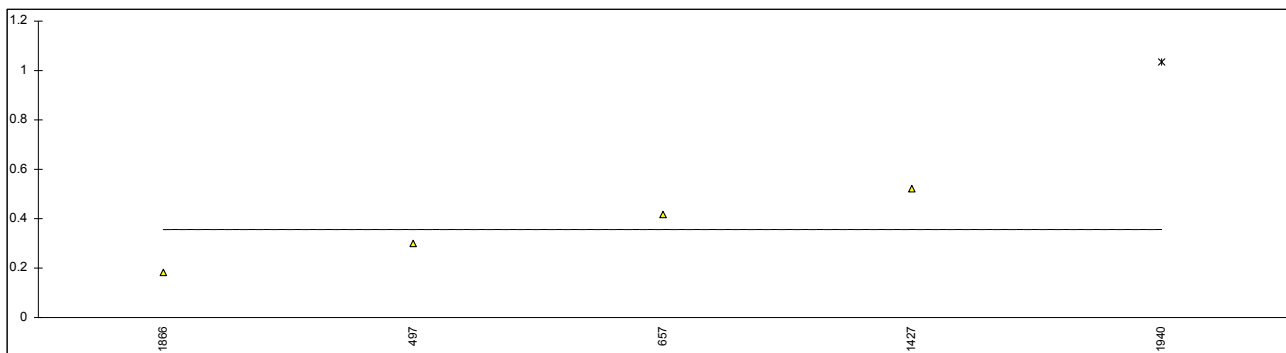
Determination of Unknown Impurities on MTBE sample #12003; results in %M/M

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
311		-----		-----	
312		-----		-----	
323		-----		-----	
334		-----		-----	
357		-----		-----	
497	D5441	0.3225	C	-----	first reported: 0.2464
657	D5441	0.343		-----	
663		-----		-----	
862		-----		-----	
963	D5441	0.34		-----	
1016		-----		-----	
1108	D5441	0.26		-----	
1200		-----		-----	
1221		-----		-----	
1252		-----		-----	
1427	D5441	0.053	G(0.05)	-----	
1833		-----		-----	
1866	D5441	0.459		-----	
1940		-----		-----	

	normality	OK
	n	5
	outliers	1
	mean (n)	0.3449
	st.dev. (n)	0.07204
	R(calc.)	0.2017
	R(lit.)	unknown
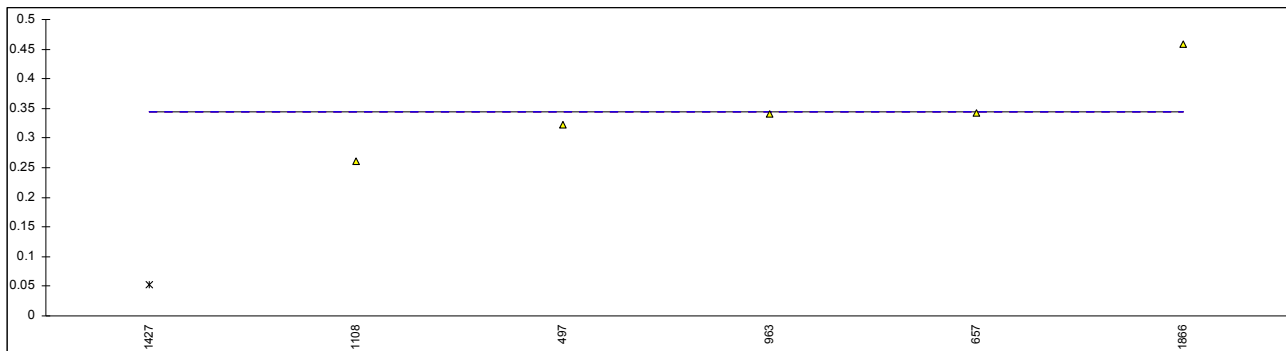
APPENDIX 2

Number of participating laboratories per country

1 lab in BELGIUM
1 lab in FINLAND
1 lab in FRANCE
1 lab in GERMANY
1 lab in GREECE
1 lab in P.R. of CHINA
1 lab in PORTUGAL
5 labs in SAUDI ARABIA
1 lab in SINGAPORE
1 lab in THAILAND
3 labs in THE NETHERLANDS
1 lab in TURKEY
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
ex	= excluded from calculations
S	= scope of the reported method is not applicable
n.a.	= not applicable
n.e.	= not evaluated
MSDS	= Material Safety Data Sheet
Fr.	= first reported
U	= reported in different unit
E	= possibly an error in the calculation

Literature:

1   iis Interlaboratory Studies. Protocol for the Organisation, Statistics and Evaluation, January 2010
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. First reported 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 (see http://www.rsc.org/suppdata/an/b2/b205600n)