

**Results of Proficiency Test  
Natural Gas Analysis  
April 2010**

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

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## 1 INTRODUCTION

A first proficiency study for natural gas (composition only) was organised by iis in 2009. Afterwards the opinion of the participating laboratories was inventorised. Most participants were very positive and therefore it was decided to repeat the PT in 2010.

Because iis has limited gas-handling facilities in place to prepare gas samples, a co-operation with Scott Specialty Gases (Breda, the Netherlands) was set up. This company is fully equipped and has a broad experience in the preparation of synthetic natural gas samples for PT purposes. Scott Specialty Gases maintains an ISO17025 accreditation for the preparation of PT samples in homogeneous and stable batches and the analytical testing of these samples.

In this second Interlaboratory study 30 laboratories from 22 different countries participated. See appendix 3 for a list of participants in alphabetical country order. In this report the results of the proficiency test on natural gas are presented and discussed.

## 2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test.

To optimise the costs for the participating laboratories, it was decided to prepare one natural gas mixture. Samples were divided over a batch of 35 cylinders. The cylinder size is a cost-effective one-litre cylinder. Each cylinder was uniquely numbered. The limited cylinder size is chosen to optimise transport and handling costs.

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 guide 43 and ILAC-G13:2007. This ensures 100% confidentiality of participant's data. Also customer's satisfaction is measured on regular basis by the distribution of questionnaires.

Scott Specialty Gases Netherlands B.V is accredited for the preparation and testing of Natural Gas mixtures in accordance with ISO/IEC 17025, (K064) by the Dutch Accreditation Council RvA (Raad voor Accreditatie).

### 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 (iis-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

In this proficiency test only one sample was used. A batch of one litre cylinders with artificial natural gas mixture was prepared and tested for homogeneity by Scott Specialty Gases (Breda, the Netherlands) in conformance with ISO 6143 and ISO Guide 35.

In total one batch of 35 cylinders was prepared (lot 78131) on March 5, 2010. Each cylinder was uniquely numbered. The cylinders were all tested in fivefold to check the homogeneity of the batch. From ANOVA analysis on the test results in accordance with ISO 6143 the in-between bottle standard deviation was calculated. The repeatability values ( $r$ ) were calculated per component by multiplication of the respective standard deviation by 2.8. Subsequently, the calculated repeatabilities were compared with 0.3 times the reproducibility of the reference method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

Parameter	$r$ (abs, observed) in %mol/mol	0.3xR (abs, ISO6974-3) in %mol/mol	$r$ (abs, ISO6974-3) in %mol/mol
Ethane	0.006	0.039	0.043
Propane	0.017	0.023	0.023
n-Butane	0.0036	0.0019	0.0032
iso-Butane	0.0023	0.0020	0.0033
Carbon dioxide	0.033	0.034	0.037
Nitrogen	0.009	0.020	0.022

Table 1: evaluation of homogeneity test results against ISO6974-3 requirements

From the above table it is clear that almost all repeatability values are less than 0.3 times the reproducibility of the reference method ISO6974-3 as well as less than the respective repeatability of the reference method ISO6974-3.

Therefore, the homogeneity of the prepared cylinders was assumed.

To each of the participating laboratories one 1L gas cylinder was sent on March 30, 2010.

## 2.5 STABILITY OF THE SAMPLES

Scott Specialty Gases (Breda, the Netherlands) declares that the prepared gas cylinders have a shelf life of at least 6 months. This is sufficient for the proficiency testing purposes.

## 2.6 ANALYSES

The participants were asked to determine: Methane, Ethane, Propane, n-Butane, iso-Butane, Carbon dioxide, Nitrogen, Caloric Value (sup), Density, Relative Density and Wobbe index. Also some method details were requested to be reported. 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 gathered. The original results are tabulated per determination in the appendix 1 of this report. The laboratories are presented by their code numbers.

Directly 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 data are put under 'Remarks' in the result tables in appendix 1. Results that came in after deadline were not taken into account in the screening for suspect data and thus these participants were not requested for checks.

### 3.1 STATISTICS

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 (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.

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 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 4; 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 target standard deviation was calculated from the literature reproducibility by division with 2.8. The z-scores were calculated according to:

$$z(\text{target}) = (\text{result} - \text{average of PT}) / \text{target standard deviation}$$

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 is as follows:

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

## 4 EVALUATION

In this proficiency test several problems were encountered with sample transport. Also several laboratories reported after receipt of the gas cylinder that they could not sample the gas cylinder due to the lack of a proper connection.

In total eleven laboratories reported results after the final reporting date and one participant was not able to report any test results. One laboratory was not able to test and report carbon dioxide. Because this laboratory reported normalized results, all original results of this laboratory were relatively high. Therefore these results were corrected manually with the average PT carbon dioxide concentration before use in the statistical evaluation.

In total 29 participants reported 280 numerical results.

Observed were 25 outlying results, which is 8.9% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

### 4.1 EVALUATION PER TEST/COMPONENT

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

Not all original data sets proved to have a normal distribution. Non-Gaussian distributions were found for the following parameters: caloric value, density and Wobbe index. In these cases the statistical evaluation should be used with due care.

Methane: The determination of this component is very problematic. Three statistical outliers were detected and the calculated reproducibility after exclusion of the statistical outliers, is not at all in agreement with the requirements of ISO6974-3:2000, nor with ASTM D1945:2003.

Ethane: The determination of this component may only be problematic for a number of participating laboratories. Four statistical outliers were detected. However, the calculated reproducibility after exclusion of the statistical outliers, is in good agreement with the requirements of ISO6974-3:2000 and of ASTM D1945:2003.

Propane: The determination of this component may only be problematic for a number of participating laboratories, depending on the test method used by the laboratory. Two statistical outliers were detected. The calculated reproducibility after exclusion of the statistical outliers, is not in agreement with the requirements of ISO6974-3:2000. However, the calculated reproducibility is in full agreement with the requirements of and ASTM D1945:2003.

n-Butane: The determination of this component was not problematic. Two statistical outliers were detected, after exclusion of one test result that

was rounded to one significant figure. The calculated reproducibility after exclusion of the suspect test results, is in good agreement with the requirements of ISO6974-3:2000 and of ASTM D1945:2003.

i-Butane: The determination of this component was not problematic. Two statistical outliers were detected, after exclusion of one test result that was rounded to one significant figure. One other test result was excluded from the calculations because all other test results of this laboratory proved to be statistical outliers. The calculated reproducibility after exclusion of the suspect test results is in good agreement with the requirements of ISO6974-3:2000 and of ASTM D1945:2003.

Carbon Dioxide: The determination of this component is problematic. Three statistical outliers were detected and the calculated reproducibility after exclusion of the statistical outliers, is not in agreement with the requirements of ISO6974-3:2000, nor with ASTM D1945:2003.

Nitrogen: The determination of this component is problematic. Four statistical outliers were detected and the calculated reproducibility after exclusion of the statistical outliers, is not in agreement with the requirements of ISO6974-3:2000, nor with ASTM D1945:2003.

Caloric Value: This calculated parameter is problematic. The reported results vary over a large range from 37.0 up to 40.57 MJ/m<sup>3</sup> and can be divided in several groups. No correlation with the methane concentration can be found. Possibly not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.3.

Density: This calculated parameter is problematic. The reported results vary over a large range from 0.7407 up to 0.8395 kg/m<sup>3</sup> and can be divided in several groups. No correlation can be seen with the methane concentration. Possibly not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.3.

Rel. density: This calculated parameter is problematic. The results vary over a large range from 0.6150 up to 0.6493. Possibly not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.3.

Wobbe index: This calculated parameter is problematic. The reported results vary over a large range from 46.0 up to 51.2 MJ/m<sup>3</sup> and can be divided in several groups. No correlation can be seen with the methane concentration. Obviously not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.3.



## 4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

The average results per component, observed reproducibilities and target reproducibilities, derived from the standard methods ISO 6974-3 and ASTM D1945 are compared in the next table.

Component	unit	n	cons. value	2.8 * sd	R(ISO6974-3)	R(D1945)
Methane	%mol/mol	26	86.990	0.356	0.174	0.150
Ethane	%mol/mol	25	4.319	0.067	0.130	0.100
Propane	%mol/mol	27	2.506	0.094	0.075	0.100
n-Butane	%mol/mol	26	0.108	0.007	0.006	0.070
iso-Butane	%mol/mol	25	0.108	0.007	0.006	0.070
Carbon dioxide	%mol/mol	25	3.718	0.136	0.112	0.100
Nitrogen	%mol/mol	25	2.237	0.133	0.067	0.100

Table 2: Performance of the group in comparison with the target reproducibilities

Without further statistical calculations it can be concluded that for many components there is not a good compliance of the group of participating laboratories with the relevant standard. The problematic components have been discussed in paragraph 4.1.

## 4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2010 WITH PREVIOUS PT

	2010	2009
Number of reporting labs	29	39
Number of results reported	280	381
Statistical outliers	25	30
Percentage outliers	8.9%	7.9%

table 3: Comparison with previous proficiency tests

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

The performances of the determinations in the proficiency tests for NG were compared against the requirements of the two often used standard test methods in the following table:

Component	2010 ISO6974-3	2010 ASTM D1945	2009 ISO6974-3	2009 ASTM D1945
Methane	--	--	--	--
Ethane	++	++	-	+
Propane	-	+	--	-
n-Butane	+/-	++	--	++
iso-Butane	+/-	++	--	++
Carbon dioxide	-	-	--	-
Nitrogen	--	-	--	--

table 4: comparison of observed precision with precision of ISO6974-3 / ASTM D1945

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

#### 4.4 DISCUSSION

Many of the observed reproducibilities are larger than the reproducibility requirements of the test methods used and therefore it had to be concluded that, although a clear improvement was observed since the 2009 PT for NG, the determination of the composition of Natural Gas was problematic for a significant number of participating laboratories.

However, it is to be expected that the performance of many laboratories will further improve during the next PTs for Natural Gas.

The consensus values as determined in this PT are compared with the average values from the homogeneity testing by Scott Specialty Gases in the following table.

Parameter	Average values by Scott Specialty Gases in %mol/mol	Consensus values from participants results in %mol/mol	Absolute differences in %mol/mol
Methane	87.010	86.990	-0.014
Ethane	4.302	4.319	+0.017
Propane	2.502	2.506	+0.004
n-Butane	0.109	0.108	-0.001
iso-Butane	0.108	0.108	+0.000
Carbon dioxide	3.723	3.718	-0.010
Nitrogen	2.246	2.237	-0.011

Table 5: comparison of consensus values with values determined by Scott Specialty Gases

From the above comparison it is clear that the consensus values as determined in this PT are all in line with the values as determined during the preparation of the gas cylinders.

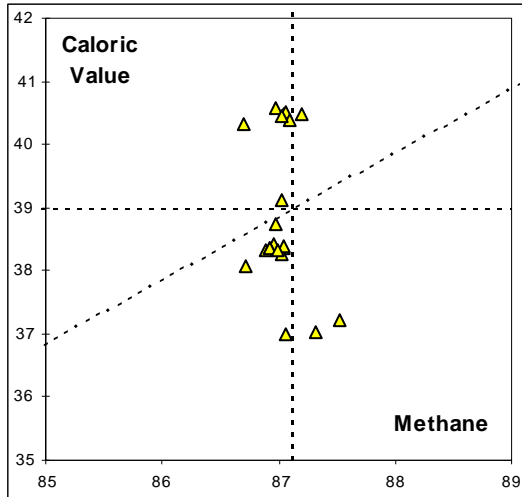
From the results of the calculated parameters it is clear that not all results were calculated for the requested conditions, resulting in trimodal distributions of the reported results. Probably many results calculated for different temperatures were reported.

It was the intention to request to report the ideal-gas superior caloric value on a volumetric basis in accordance with equation 8 of ISO 6976:1995 @**25**°C and 101.325 kPa (using table 4 of ISO6976:1995), and using the metering reference condition **0**°C and 101.325 kPa (see table 5 of ISO6976:1995).

From the reported results it was clear that not all laboratories used the intended conditions (**25**°C and 101.325 kPa) to calculate the caloric value results. Several laboratories did remark that the metering reference conditions **15**°C and 101.325 kPa were used.

Also for the other calculated parameters results were reported calculated using various conditions, at least 15°C and 25 °C.

The fact that no correlation can be seen between Caloric Value results and the methane concentration, but 3 groups of results in stead is in agreement with above conclusion.



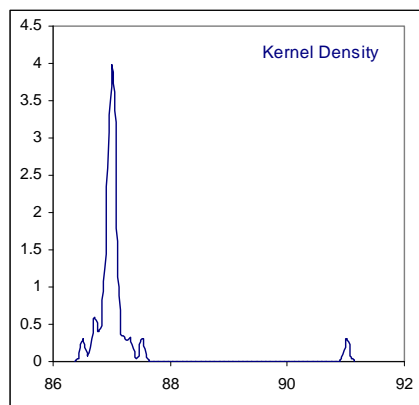
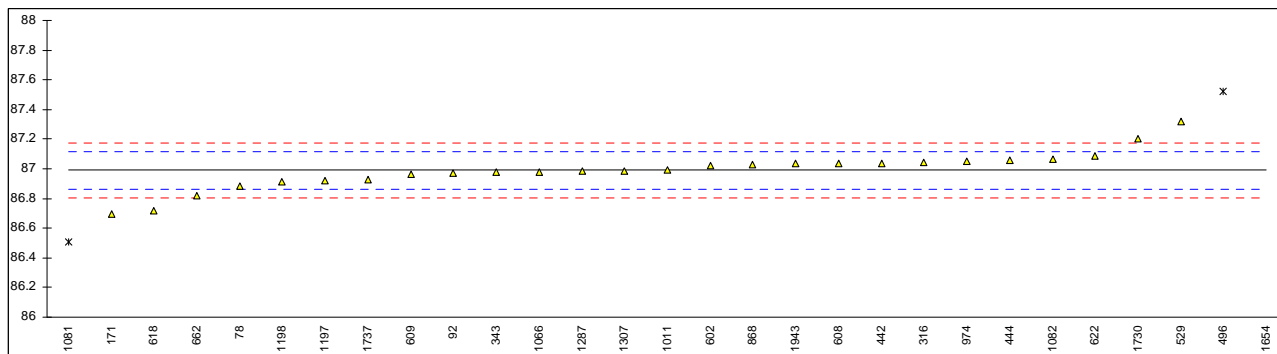
**APPENDIX 1**

Determination of Methane on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	86.887		-1.66	
92	GPA2286	86.970		-0.32	
171	D1945mod	86.696		-4.73	
225		-----			
316	ISO6974-3	87.046		0.90	
343	CEA1624	86.98		-0.16	
442	D1945	87.035		0.72	
444	D1945	87.059		1.11	
496	DIN51666	87.524	G(0.05)	8.59	
529	D1945	87.317		5.26	
602	GPA2261	87.025		0.56	
608	GPA2261	87.035		0.72	
609	GPA2261	86.962		-0.45	
618	GPA2261	86.720		-4.35	
622	D1945	87.089		1.59	
662	D1945	86.822		-2.70	
868	GPA2261	87.031		0.66	
974	ISO6974	87.0526		1.01	
1011	UOP539	86.99		0.00	
1066	ISO6974	86.981		-0.14	
1081	in house	86.51	G(0.05)	-7.73	
1082	UOP539	87.064		1.19	
1197	D1945	86.918		-1.16	
1198	D1945	86.916		-1.19	
1287	ISO6974-3	86.986		-0.06	
1307	RGA	86.989		-0.02	
1654	D1945	91.017	C,G(0.01)	64.81	first reported 80.490
1730	UOP539	87.206		3.48	
1737	in house	86.93		-0.97	
1943	ISO6974-3	87.03368		0.70	reported normalized result 90.395

normality OK  
n 26  
outliers 3  
mean (n) 86.9900  
st.dev. (n) 0.12702  
R(calc.) 0.3557  
R(ISO6974-3) 0.1740

Compare R(D1945) = 0.1500

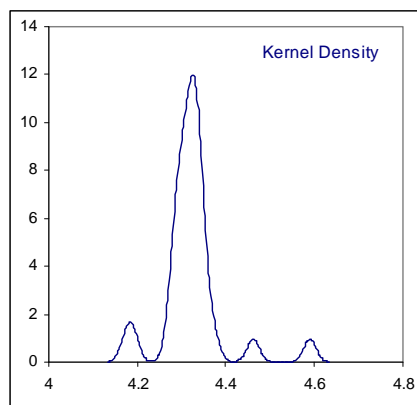
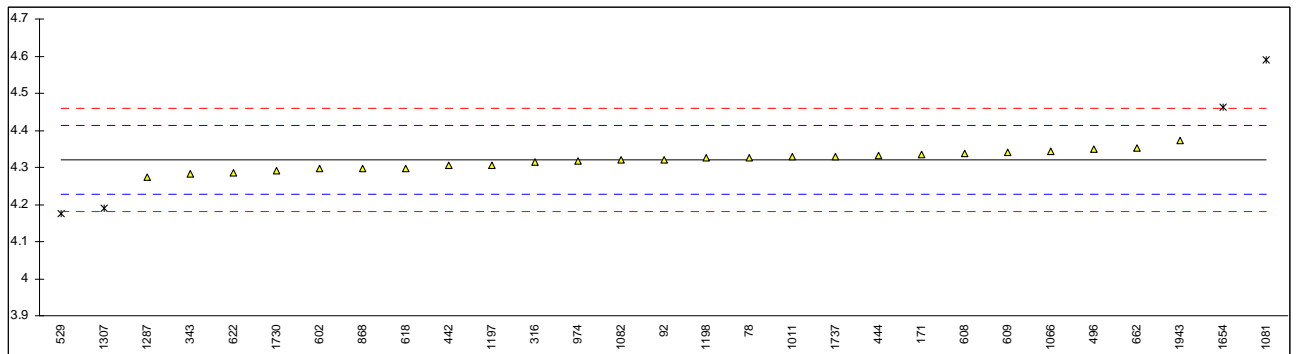


Determination of Ethane on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	4.326		0.15	
92	GPA2286	4.320		0.02	
171	D1945mod	4.335		0.34	
225		-----		-----	
316	ISO6974-3	4.314		-0.11	
343	CEA1624	4.283		-0.78	
442	D1945	4.306		-0.29	
444	D1945	4.331		0.25	
496	DIN51666	4.350		0.66	
529	D1945	4.176	G(0.05)	-3.10	
602	GPA2261	4.297		-0.48	
608	GPA2261	4.338		0.40	
609	GPA2261	4.340		0.45	
618	GPA2261	4.297		-0.48	
622	D1945	4.286		-0.72	
662	D1945	4.351		0.69	
868	GPA2261	4.297		-0.48	
974	ISO6974	4.3160		-0.07	
1011	UOP539	4.33		0.23	
1066	ISO6974	4.344		0.53	
1081	in house	4.59	G(0.01)	5.85	
1082	UOP539	4.319		-0.01	
1197	D1945	4.307		-0.27	
1198	D1945	4.325		0.12	
1287	ISO6974-3	4.275		-0.96	
1307	RGA	4.191	G(0.01)	-2.77	
1654	D1945	4.462	C,G(0.05)	3.08	first reported 3.952
1730	UOP539	4.292		-0.59	
1737	in house	4.33		0.23	
1943	ISO6974-3	4.373107		1.16	reported normalized result 4.542

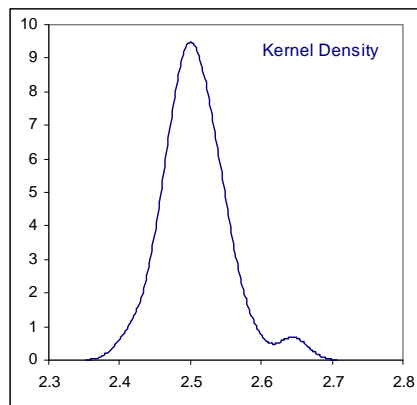
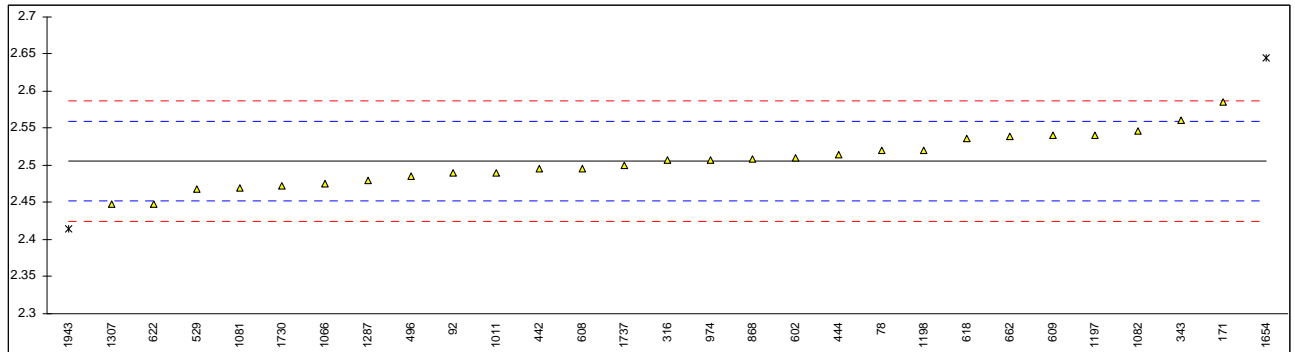
normality OK  
n 25  
outliers 4  
mean (n) 4.3193  
st.dev. (n) 0.02408  
R(calc.) 0.0674  
R(ISO6974-3) 0.1296

Compare R(D1945) = 0.1000



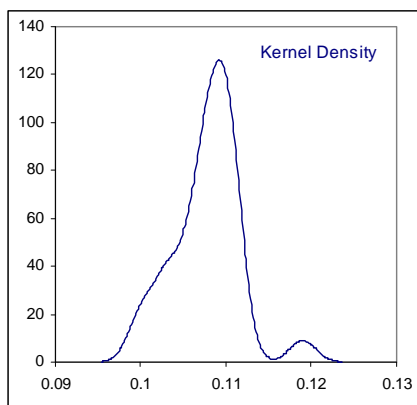
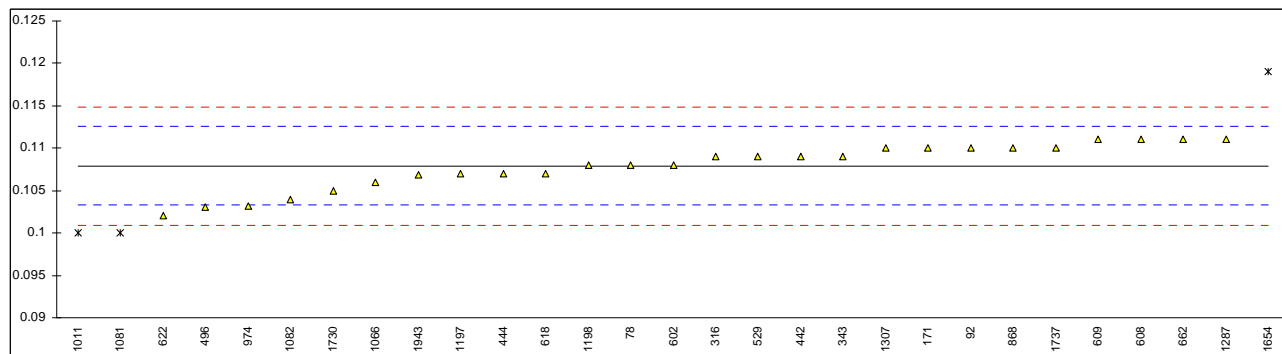
Determination of Propane on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	2.520		0.53	
92	GPA2286	2.490		-0.59	
171	D1945mod	2.585		2.95	
225		-----		-----	
316	ISO6974-3	2.507		0.04	
343	CEA1624	2.561		2.05	
442	D1945	2.496		-0.37	
444	D1945	2.515		0.34	
496	DIN51666	2.486		-0.74	
529	D1945	2.468		-1.41	
602	GPA2261	2.510		0.15	
608	GPA2261	2.496		-0.37	
609	GPA2261	2.540		1.27	
618	GPA2261	2.536		1.12	
622	D1945	2.448		-2.15	
662	D1945	2.539		1.24	
868	GPA2261	2.509		0.12	
974	ISO6974	2.5077		0.07	
1011	UOP539	2.49		-0.59	
1066	ISO6974	2.475		-1.15	
1081	in house	2.47		-1.33	
1082	UOP539	2.547		1.53	
1197	D1945	2.541		1.31	
1198	D1945	2.521		0.56	
1287	ISO6974-3	2.480		-0.96	
1307	RGA	2.448		-2.15	
1654	D1945	2.645	G(0.05)	5.18	first reported 2.345
1730	UOP539	2.472		-1.26	
1737	in house	2.50		-0.22	
1943	ISO6974-3	2.413778	G(0.05)	-3.43	reported normalized result 2.507
normality		OK			
n		27			
outliers		2			
mean (n)		2.5058			
st.dev. (n)		0.03355			
R(calc.)		0.0939			
R(ISO6974-3)		0.0752			Compare R(D1945) = 0.1000



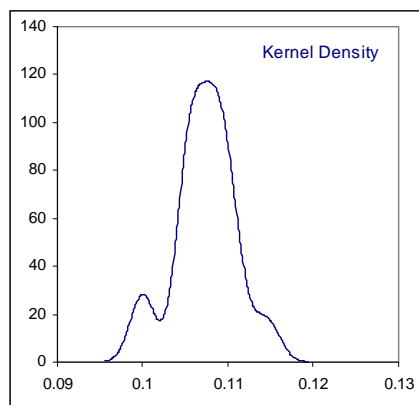
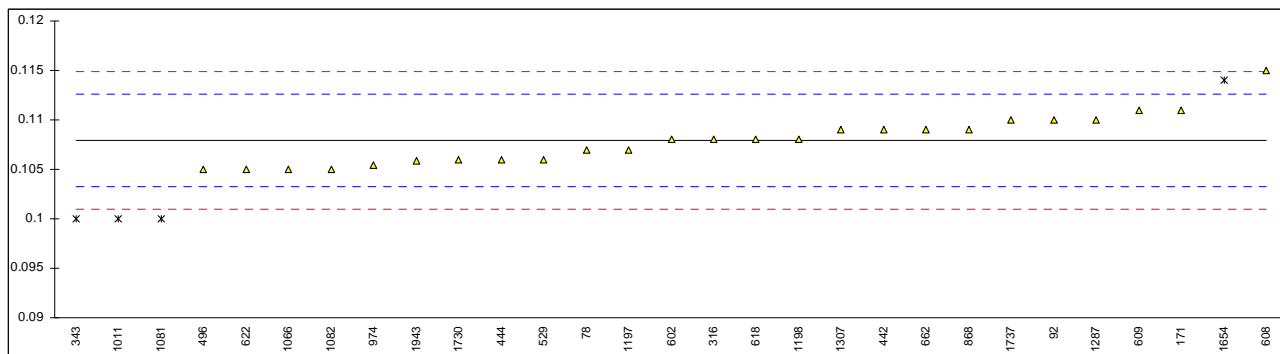
Determination of n-Butane on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	0.108		0.05	
92	GPA2286	0.110		0.91	
171	D1945mod	0.110		0.91	
225		-----		-----	
316	ISO6974-3	0.109		0.48	
343	CEA1624	0.109		0.48	
442	D1945	0.109		0.48	
444	D1945	0.107		-0.38	
496	DIN51666	0.103		-2.11	
529	D1945	0.109		0.48	
602	GPA2261	0.108		0.05	
608	GPA2261	0.111		1.35	
609	GPA2261	0.111		1.35	
618	GPA2261	0.107		-0.38	
622	D1945	0.102		-2.55	
662	D1945	0.111		1.35	
868	GPA2261	0.110		0.91	
974	ISO6974	0.1032		-2.03	
1011	UOP539	0.10	DG(0.05)	-3.41	
1066	ISO6974	0.106		-0.82	
1081	in house	0.1	ex	-3.41	excluded result rounded to one significant figure
1082	UOP539	0.104		-1.68	
1197	D1945	0.107		-0.38	
1198	D1945	0.108		0.05	
1287	ISO6974-3	0.111		1.35	
1307	RGA	0.110		0.91	
1654	D1945	0.119	C,D(0.05)	4.81	first reported 0.106
1730	UOP539	0.105		-1.25	
1737	in house	0.11		0.91	
1943	ISO6974-3	0.106872		-0.44	reported normalized result 0.111
normality		OK			
n		26			
outliers		2			
mean (n)		0.1079			
st.dev. (n)		0.00266			
R(calc.)		0.0075			
R(ISO6974-3)		0.0065			Compare R(D1945) = 0.0700



Determination of iso-Butane on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	0.107		-0.40	
92	GPA2286	0.110		0.89	
171	D1945mod	0.111		1.33	
225		-----		-----	
316	ISO6974-3	0.108		0.03	
343	CEA1624	0.100	D(0.05)	-3.43	
442	D1945	0.109		0.46	
444	D1945	0.106		-0.84	
496	DIN51666	0.105		-1.27	
529	D1945	0.106		-0.84	
602	GPA2261	0.108		0.03	
608	GPA2261	0.115		3.06	
609	GPA2261	0.111		1.33	
618	GPA2261	0.108		0.03	
622	D1945	0.105		-1.27	
662	D1945	0.109		0.46	
868	GPA2261	0.109		0.46	
974	ISO6974	0.1054		-1.09	
1011	UOP539	0.10	D(0.05)	-3.43	
1066	ISO6974	0.105		-1.27	
1081	in house	0.1	ex	-3.43	excluded result rounded to one significant figure
1082	UOP539	0.105		-1.27	
1197	D1945	0.107		-0.40	
1198	D1945	0.108		0.03	
1287	ISO6974-3	0.110		0.89	
1307	RGA	0.109		0.46	
1654	D1945	0.114	ex, C	2.62	first reported 0.101
1730	UOP539	0.106		-0.84	
1737	in house	0.11		0.89	
1943	ISO6974-3	0.106		-0.87	reported normalized result 0.110
normality		OK			
n		25			
outliers		2			
mean (n)		0.1079			
st.dev. (n)		0.00245			
R(calc.)		0.0069			
R(ISO6974-3)		0.0065			Compare R(D1945) = 0.0700



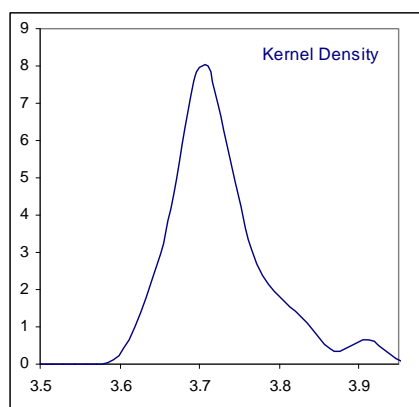
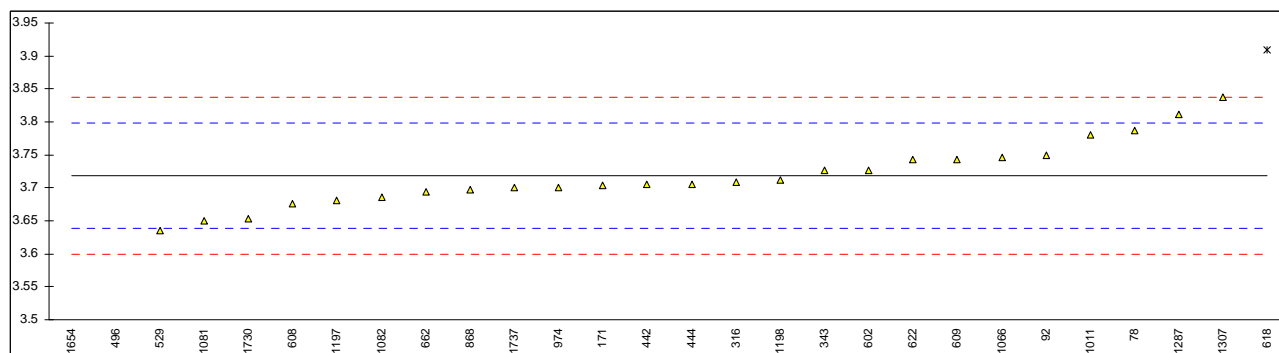


Determination of Carbon Dioxide on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	3.787		1.72	
92	GPA2286	3.750		0.79	
171	D1945mod	3.703		-0.39	
225		-----		-----	
316	ISO6974-3	3.709		-0.24	
343	CEA1624	3.727		0.21	
442	D1945	3.705		-0.34	
444	D1945	3.706		-0.31	
496	DIN51666	3.225	G(0.01)	-12.39	
529	D1945	3.636		-2.07	
602	GPA2261	3.727		0.21	
608	GPA2261	3.676		-1.07	
609	GPA2261	3.743		0.62	
618	GPA2261	3.909	G(0.05)	4.78	
622	D1945	3.743		0.62	
662	D1945	3.694		-0.61	
868	GPA2261	3.698		-0.51	
974	ISO6974	3.7009		-0.44	
1011	UOP539	3.78		1.54	
1066	ISO6974	3.746		0.69	
1081	in house	3.65		-1.72	
1082	UOP539	3.686		-0.82	
1197	D1945	3.681		-0.94	
1198	D1945	3.712		-0.16	
1287	ISO6974-3	3.812		2.35	
1307	RGA	3.837		2.97	
1654	D1945	0.491	C,G(0.01)	-81.01	first reported 11.158
1730	UOP539	3.653		-1.64	
1737	in house	3.70		-0.46	
1943		-----		-----	

normality OK  
 n 25  
 outliers 3  
 mean (n) 3.7185  
 st.dev. (n) 0.04865  
 R(calc.) 0.1362  
 R(ISO6974-3) 0.1116

Compare R(D1945) = 0.1000

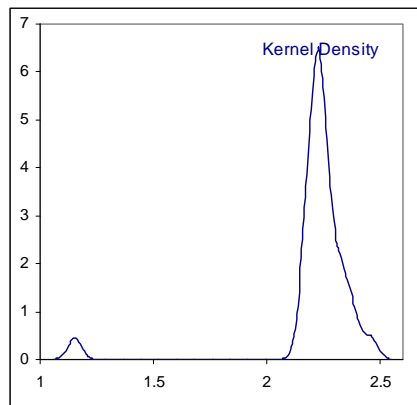
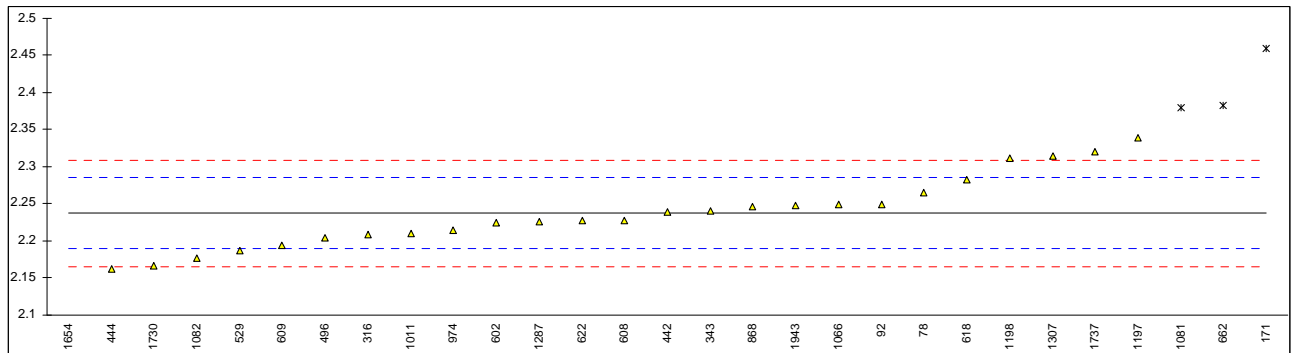


Determination of Nitrogen on sample #10ME; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
78	GPA2286	2.265		1.16	
92	GPA2286	2.250		0.53	
171	D1945mod	2.459	DG(0.05)	9.25	
225		-----		-----	
316	ISO6974-3	2.208		-1.22	
343	CEA1624	2.240	C	0.11	first reported 2.070
442	D1945	2.239		0.07	
444	D1945	2.162		-3.14	
496	DIN51666	2.205		-1.35	
529	D1945	2.187		-2.10	
602	GPA2261	2.224		-0.55	
608	GPA2261	2.228		-0.39	
609	GPA2261	2.194		-1.80	
618	GPA2261	2.282		1.87	
622	D1945	2.227		-0.43	
662	D1945	2.382	DG(0.05)	6.04	
868	GPA2261	2.246		0.36	
974	ISO6974	2.2142		-0.96	
1011	UOP539	2.21		-1.14	
1066	ISO6974	2.249		0.49	
1081	in house	2.38	D(0.05)	5.95	
1082	UOP539	2.177		-2.51	
1197	D1945	2.339		4.24	
1198	D1945	2.311		3.08	
1287	ISO6974-3	2.226		-0.47	
1307	RGA	2.315		3.24	
1654	D1945	1.152	CG(0.01)	-45.27	first reported 1.848
1730	UOP539	2.166		-2.97	
1737	in house	2.32		3.45	
1943	ISO6974-3	2.247211		0.42	reported normalized result 2.334

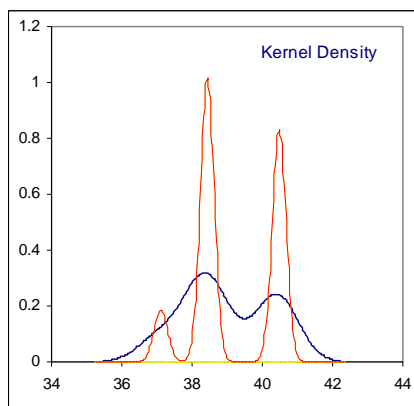
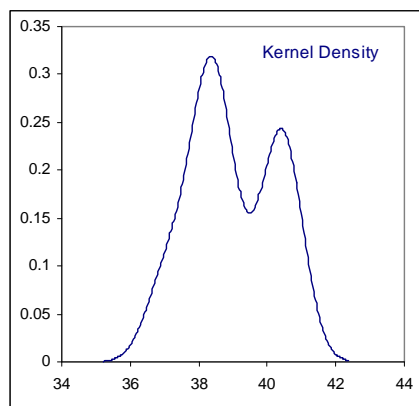
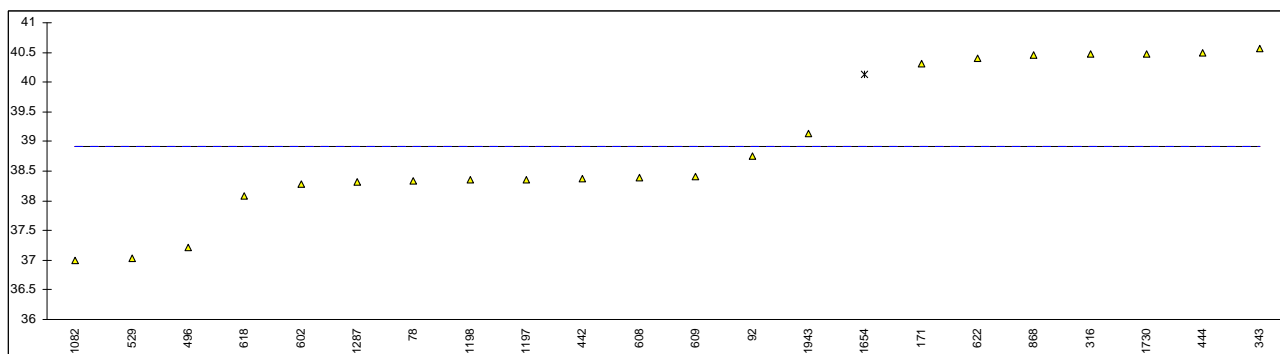
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n 25  
outliers 4  
mean (n) 2.2373  
st.dev. (n) 0.04760  
R(calc.) 0.1333  
R(ISO6974-3) 0.0671

Compare R(D1945) = 0.1000



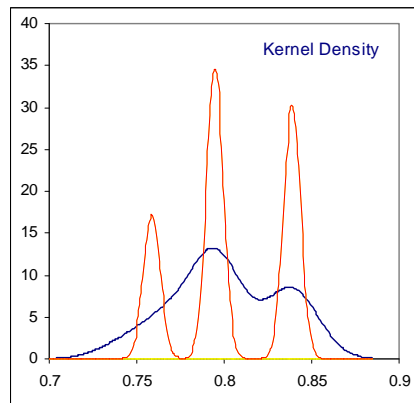
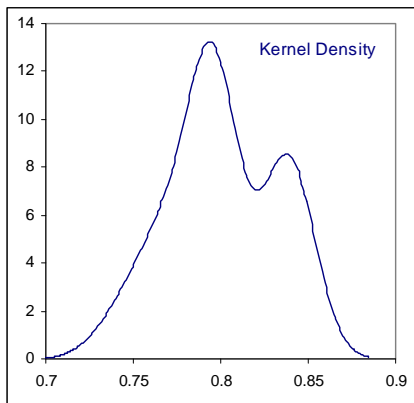
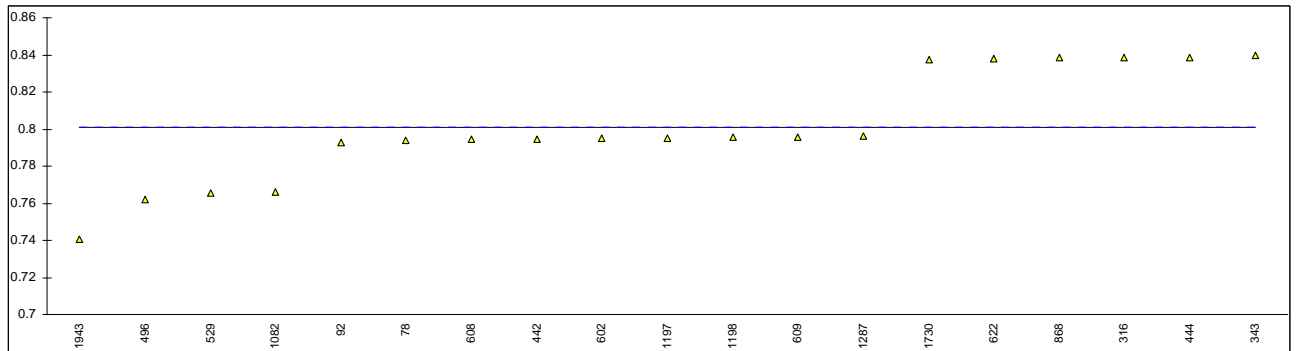
Determination of Caloric Value (sup) (@ 25°C and 101.325 kPa) on smpl #10ME; results in MJ/m<sup>3</sup>

lab	method	value	mark	z(targ)	remarks	
78	AGA#5	38.340		----	calculated @15°C and 101.325 as per AGA#5	
92	AGA#5	38.75		----	calculated @15°C and 101.325 as per AGA#5	
171	ISO6976	40.31		----		
225		----		----		
316	ISO6976	40.4730		----		
343		40.57199		----		
442	D1945	38.369		----		
444	ISO6976	40.50		----		
496	DIN51857	37.220		----		
529	ISO6976	37.03		----		
602	ISO6976	38.27431		----	calculated @15°C and 101.325	
608	ISO6976	38.39854		----	calculated @15°C and 101.325	
609	ISO6976	38.40727		----	calculated @15°C and 101.325	
618		38.08		----		
622	ISO6976	40.3984		----		
662		----		----		
868	ISO6976	40.45		----		
974		----		----		
1011		----		----		
1066		----		----		
1081		----		----		
1082	ISO6976	37.0051		----		
1197	ISO6976	38.35		----		
1198	ISO6976	38.35		----		
1287	ISO6976	38.316		----		
1307		----		----		
1654	ISO6976	40.132	ex,C	----	first reported 29.882	
1730	ISO6976	40.478		----		
1737		----		----		
1943	ISO6976	39.132		----		
	normality	not OK		<u>Group 1:</u>	<u>Group 2:</u>	<u>Group 3:</u>
	n	21		n/a	not OK	OK
	outliers	0		3	11	7
	mean (n)	38.9145		0	0	0
	st.dev. (n)	38.9145		37.085	38.4334	40.4545
	R(calc.)	1.22551		0.1175	0.279453	0.08248
	R(lit)	3.4314		0.3291	0.7825	0.2309
		n/a		n/a	n/a	n/a



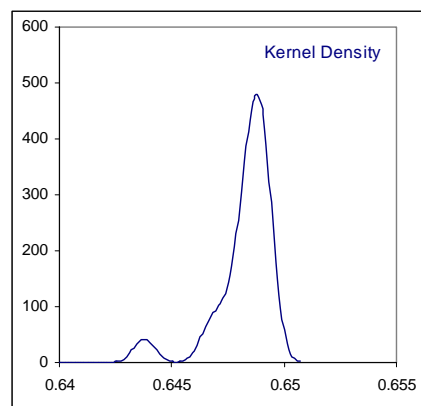
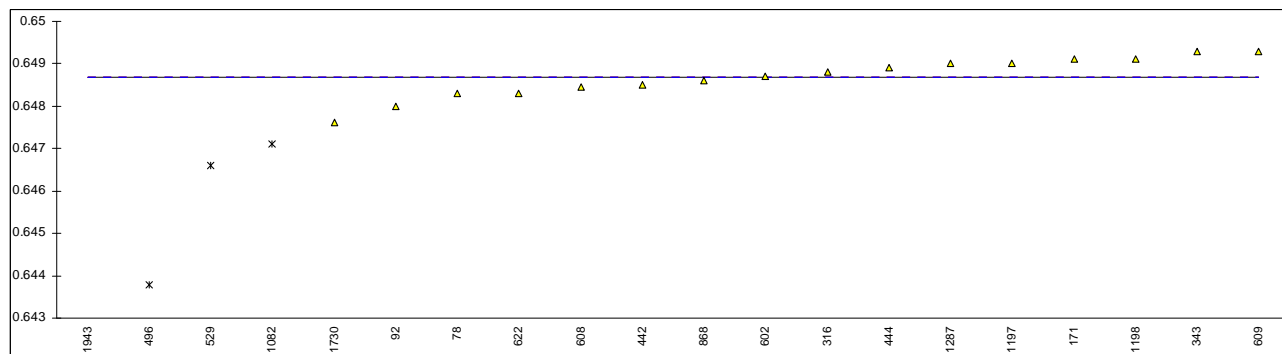
Determination of Density (@ 25°C and 101.325 kPa) on sample #10ME; results in kg/m<sup>3</sup>

lab	method	value	mark	z(targ)	remarks	
78	GPA2145	0.7941		----		
92	GPA2286	0.793		----		
171		----		----		
225		----		----		
316	ISO6976	0.8388		----		
343		0.8395		----		
442	D1945	0.7947		----		
444	ISO6976	0.8388		----	reported result for Real gas	
496	DIN51857	0.76212		----		
529	ISO6976	0.7657		----		
602	ISO6976	0.794945		----	calculated @15°C and 101.325	
608	ISO6976	0.794606		----	calculated @15°C and 101.325	
609	ISO6976	0.795662		----	calculated @15°C and 101.325	
618		----		----		
622	ISO6976	0.8382		----		
662		----		----		
868	ISO6976	0.8386		----		
974		----		----		
1011		----		----		
1066		----		----		
1081		----		----		
1082	ISO6976	0.7661		----		
1197	ISO6976	0.7953		----		
1198	ISO6976	0.7955		----		
1287	ISO6976	0.796		----		
1307		----		----		
1654		----		----		
1730	ISO6976	0.83763		----		
1737		----		----		
1943	ISO6976	0.7407		----		
	normality	not OK		<u>Group 1:</u>	<u>Group 2:</u>	<u>Group 3:</u>
	n	19		n/a	not OK	OK
	outliers	0		4	9	6
	mean (n)	0.80105		0	0	0
	st.dev. (n)	0.030218		0.75866	0.79487	0.83859
	R(calc.)	0.08461		0.012103	0.000914	0.000631
	R(lit)	n/a		0.03389	0.00256	0.00177
				n/a	n/a	n/a



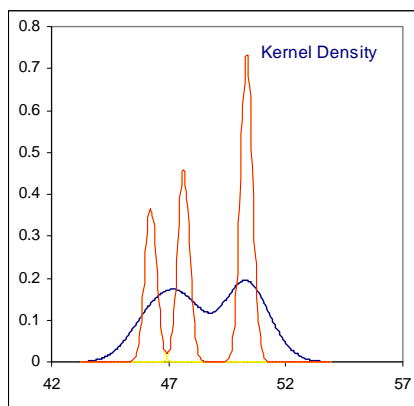
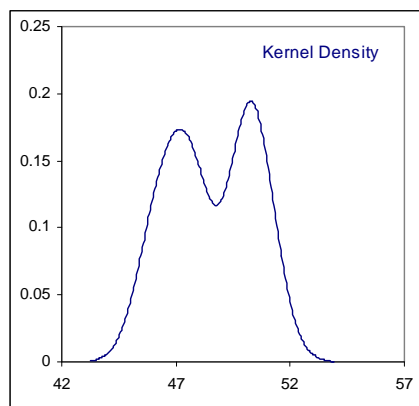
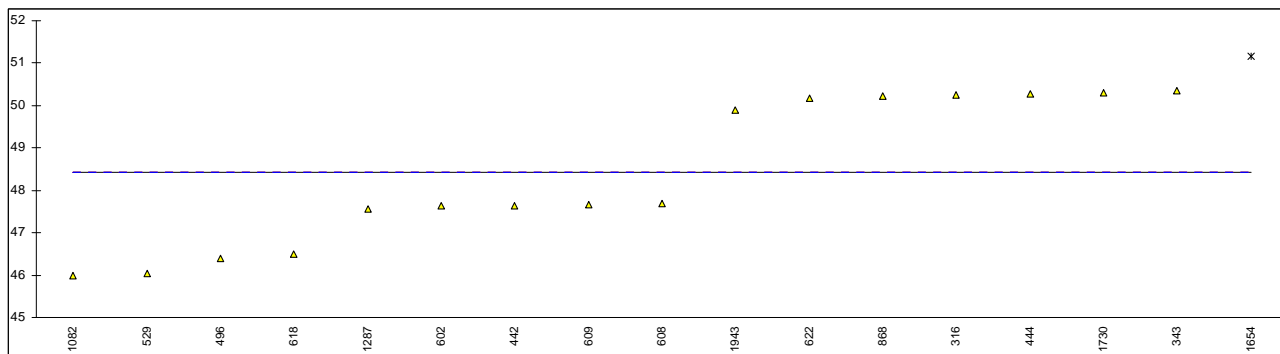
Determination of Relative Density (@ 25°C and 101.325 kPa) on sample #10ME; results

lab	method	value	mark	z(targ)	remarks
78	GPA2145	0.6483		----	
92	GPA2286	0.648		----	
171	D3588	0.6491		----	
225		----		----	
316	ISO6976	0.6488		----	
343		0.6493		----	
442	D1945	0.6485		----	
444	ISO6976	0.6489		----	reported result for Real gas
496	DIN51857	0.64379	G(0.01)	----	
529	ISO6976	0.6466	DG(0.05)	----	
602	ISO6976	0.648717		----	
608	ISO6976	0.648441		----	
609	ISO6976	0.649303		----	
618		----		----	
622	ISO6976	0.6483		----	
662		----		----	
868	ISO6976	0.6486		----	
974		----		----	
1011		----		----	
1066		----		----	
1081		----		----	
1082	ISO6976	0.6471	DG(0.05)	----	
1197	ISO6976	0.6490		----	
1198	ISO6976	0.6491		----	
1287	ISO6976	0.649		----	
1307		----		----	
1654		----		----	
1730	ISO6976	0.64761		----	
1737		----		----	
1943	ISO6976	0.6150	G(0.01)	----	
normality		OK			
n		16			
outliers		4			
mean (n)		0.64869			
st.dev. (n)		0.000475			
R(calc.)		0.00133			
R(lit)		n/a			



Determination of Wobbe Index (@ 25°C and 101.325 kPa) on sample #10ME; results in MJ/m<sup>3</sup>

lab	method	value	mark	z(targ)	remarks	
78		----		----		
92		----		----		
171		----		----		
225		----		----		
316	ISO6976	50.2490		----		
343		50.34959		----		
442	D1945	47.65		----		
444	ISO6976	50.28		----		
496	DIN51857	46.388		----		
529	ISO6976	46.05		----		
602	ISO6976	47.638		----	calculated @15°C and 101.325	
608	ISO6976	47.68475		----	calculated @15°C and 101.325	
609	ISO6976	47.664		----	calculated @15°C and 101.325	
618		46.5		----		
622	ISO6976	50.1741		----		
662		----		----		
868	ISO6976	50.23		----		
974		----		----		
1011		----		----		
1066		----		----		
1081		----		----		
1082	ISO6976	46.0002		----		
1197		----		----		
1198		----		----		
1287	ISO6976	47.555		----		
1307		----		----		
1654	ISO6976	51.163	ex,C	----	first reported 35.318	
1730	ISO6976	50.299		----		
1737		----		----		
1943	ISO6976	49.900		----		
	normality	not OK		<u>Group 1:</u>	<u>Group 2:</u>	<u>Group 3):</u>
	n	16		n/a	n/a/	OK
	outliers	0		4	5	7
	mean (n)	48.413		0	0	0
	st.dev. (n)	48.413		0.2470	47.638	50.212
	R(calc.)	1.7312		0.691	0.0497	0.1481
	R(lit)	4.847		n/a	0.139	0.415
		n/a		n/a	n/a	n/a



## APPENDIX 2

### Details of the GC-configurations used

78	3 columns with switching/backflush (Mol Sieve/TCD + Hayesep N/TCD + capillary/FID)
92	3 columns with switching/backflush (ISO 6974-5)
171	2 packed columns with switching/backflush
225	---
316	2 packed columns with switching/backflush
343	2 packed columns with switching/backflush
442	2 packed columns
444	2 packed columns with switching/backflush (D1945)
496	4 micropacked columns+2 capillary columns (1xFID & 2xTCD) with switching/backflush
529	3 columns with switching/backflush (Mol Sieve 13X + Hayesep + capillary CP-Sil 5CB)
602	3 columns with switching/backflush (ISO 6974-5)
608	3 packed columns with switching/backflush to TCD1 & 2 packed columns to TCD2
609	3 columns with switching/backflush (ISO 6974-5)
618	2 packed columns
622	3 packed columns (Mol Sieve 13X + Hayesep T + Hayesep Q) and one capillary column (CP-Sil 5CB)
662	---
868	4 packed columns with switching/backflush
974	4 columns (13X, 5A, Hayesep Q, CP Sil 5CB) with dual TCD & FID
1011	---
1066	2 packed columns
1081	---
1082	6 columns with switching/backflush (2xTCD + 1xFID)
1197	4 columns with switching/backflush (DC200, UCW 982, Hayesep Q, Mol Sieve)
1198	4 columns with switching/backflush (DC200, UCW 982, Hayesep Q, Mol Sieve)
1287	2 packed columns
1307	Agilent RGA with 5 packed columns and 2 capillary columns
1654	2 packed columns
1730	---
1737	2 packed columns (Mol Sieve 13X & Charcoal) and one capillary column (Elite Alumina)
1943	2 packed columns

## **APPENDIX 3**

### **List of participants**

- 1 lab in AUSTRALIA
- 1 lab in BELGIUM
- 2 labs in CANADA
- 1 lab in CÔTE D'IVOIRE
- 1 lab in FINLAND
- 1 lab in FRANCE
- 1 lab in GERMANY
- 1 lab in GREECE
- 1 lab in INDONESIA
- 1 lab in ITALY
- 1 lab in LATVIA
- 5 labs in MALAYSIA
- 1 lab in MEXICO
- 1 lab in P.R. of CHINA
- 1 lab in PORTUGAL
- 1 lab in SPAIN
- 1 lab in THAILAND
- 3 labs in THE NETHERLANDS
- 1 lab in TURKEY
- 1 lab in U.A.E.
- 1 lab in U.S.A.
- 2 labs in UNITED KINGDOM



## APPENDIX 4

### 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
n/a	= not applicable
W	= withdrawn on request participant
U	= reported in wrong unit
E	= error in calculations
SDS	= Safety Data Sheet

### Literature:

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation, January 2010
- 2 ISO 6974, Natural Gas – Determination of composition with defined uncertainty by GC
- 3 ASTM E178-89
- 4 ASTM E1301-89
- 5 ISO 5725-86
- 6 ISO 5725, parts 1-6, 1994
- 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 page1359-1364, P.J. Lowthian and M. Thompson. (see <http://www.rsc.org/suppdata/an/b2/b205600n/>)
- 15 ASTM D1945, Standard test method for Analysis of Natural Gas by GC