Results of Proficiency Test
Natural Gas Analysis
April 2011

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 inventarised. Most participants were very positive and therefore it was decided to repeat the PT in 2010 and 2011.

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 interlaboratory study 36 laboratories from 23 different countries participated. See appendix 3 for the number of participants in per country.
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 42 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, ISO17043:2010 and ILAC-G13:2007. This ensures 100% confidentially 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.
One batch of 42 cylinders was prepared (lot 82390) starting March 3, 2011. 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/lmol	r (abs, ISO6974-3) in %mol/lmol
Ethane	0.026	0.027	0.030
Propane	0.033	0.023	0.025
n-Butane	0.0054	0.0053	0.0089
iso-Butane	0.0031	0.0036	0.0060
Carbon dioxide	0.022	0.014	0.015
Nitrogen	0.027	0.027	0.030

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

From the above table it is clear that most repeatability values are less than 0.3 times the respective reproducibility of the reference method ISO6974-3 as well as less less than 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 April 6, 2011.

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:

	$\lvert z \rvert < 1$	good
$1 <$	$\lvert z \rvert < 2$	satisfactory
$2 <$	$\lvert z \rvert < 3$	questionable
$3 <$	$\lvert z \rvert$	unsatisfactory

4 EVALUATION

In this proficiency test several problems were encountered with customs clearance.
In total nine laboratories reported results after the final reporting date and three participants were not able to report any test results.
In total 33 participants reported 330 numerical results.
Observed were 16 outlying results, which is 4.8% 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: Methane, caloric value, density, rel. density and Wobbe index. In these cases the statistical evaluation should be used with due care, see also paragraph 4.4.
All test results reported by laboratory 529 were deviating, influenced by the very high n-butane and nitrogen results. Five of the seven test results appeared to be statistical outliers. As the seven test results are not independent, it was decided not to use any of the test results of this laboratory for the statistical evaluation.

Methane: The determination of this component is very problematic. Two 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.

Ethane: The determination of this component was not problematic. Only one statistical outlier was detected. And the calculated reproducibility after exclusion of the statistical outlier, is in good agreement with the requirements of both ISO6974-3:2000 and ASTM D1945:2003.

Propane: The determination of this component may be problematic for a number of participating laboratories, depending on the test method used by the laboratory. Only one statistical outlier was detected.
The calculated reproducibility after exclusion of the statistical outlier, is not in agreement with the strict 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 may be problematic for a number of participating laboratories, depending on the test method used by the

laboratory. Remarkably, three laboratories initially did mix-up the test results of n-butane and i-butane.
Three statistical outliers were detected. The calculated reproducibility after exclusion of the statistical outliers, is not (but almost) in agreement with the strict requirements of ISO6974-3:2000. However, the calculated reproducibility is in full agreement with the requirements of and ASTM D1945:2003.

i-Butane: The determination of this component may be problematic for a number of participating laboratories, depending on the test method used by the laboratory. Remarkably, three laboratories initially did mix-up the test results of n-butane and i-butane.
No statistical outliers were observed. The calculated reproducibility is not in agreement with the strict requirements of ISO6974-3:2000. However, the calculated reproducibility is in full agreement with the requirements of and ASTM D1945:2003.

Carbon Dioxide: The determination of this component may be problematic for a number of participating laboratories, depending on the test method used by the laboratory.
Three statistical outliers were detected. The calculated reproducibility after exclusion of the statistical outliers, is not in agreement with the strict requirements of ISO6974-3:2000. However, the calculated reproducibility is in full agreement with the requirements of and 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 40.879 MJ/m^3 and can be divided in two groups. No correlation with the methane concentration can be found. Probably not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.4.

Density: This calculated parameter is problematic. The reported results vary over a large range from 0.742073 up to 0.8136 kg/m^3 and can be divided in two groups. No correlation can be seen with the methane concentration. Probably not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.4.

Rel. density: This calculated parameter is problematic. The results vary over a large range from 0.619 up to 0.6466. Probably not all results were reported

using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.4.

Wobbe index: This calculated parameter is problematic. The reported results vary over a large range from 46.05 up to 51.58 MJ/m^3 and can be divided in two groups. No correlation can be seen with the methane concentration. Probably not all results were reported using the requested conditions, being 25°C and 101.325 KPa. See also the discussion in 4.4.

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.

	unit	n	cons. value	2.8 * sd	R(ISO6974-3)	R(D1945)
Methane	%mol/mol	31	89.458	0.268	0.179	0.150
Ethane	%mol/mol	32	3.020	0.068	0.091	0.100
Propane	%mol/mol	32	2.504	0.101	0.075	0.100
n-Butane	%mol/mol	30	0.301	0.021	0.018	0.070
iso-Butane	%mol/mol	32	0.200	0.016	0.012	0.070
Carbon dioxide	%mol/mol	29	1.509	0.062	0.045	0.100
Nitrogen	%mol/mol	29	3.000	0.132	0.090	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 APRIL 2011 WITH PREVIOUS PTS

	2011	2010	2009
Number of reporting labs	33	29	39
Number of results reported	330	280	381
Statistical outliers	16	25	30
Percentage outliers	4.8%	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. See the overview in the following table:

	2011 ISO6974-3	2011 D1945	2010 ISO6974-3	2010 D1945	2009 ISO6974-3	2009 D1945
Methane	--	--	--	--	--	--
Ethane	++	++	++	++	-	+
Propane	-	+/-	-	+	--	-
n-Butane	-	++	+/-	++	--	++
iso-Butane	-	++	+/-	++	--	++
Carbon dioxide	-	++	-	-	--	-
Nitrogen	--	-	--	-	--	--

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

From the above table it is clear that the performance of the group of participating laboratories is (slowly) improving. 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 ISO6974-3 and therefore it had to be concluded that, although a clear improvement was observed since the 2009 and 2010 PTs for Natural Gas, the determination of the composition of Natural Gas was still 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	89.48	89.458	-0.022
Ethane	3.002	3.020	+0.018
Propane	2.498	2.504	+0.006
n-Butane	0.297	0.301	-0.004
iso-Butane	0.200	0.200	+0.000
Carbon dioxide	1.512	1.509	-0.003
Nitrogen	3.010	3.000	-0.010

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

From the comparison in table 5 it is clear that the consensus values as determined in this PT are all very well in line with the values as determined during the preparation of the gas cylinders.

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 of the calculated parameters it is clear that not all results were calculated for the requested conditions, resulting in bimodal distributions of the reported results. Results calculated for different temperatures were reported. Five laboratories reported to have used 15°C, two 0°C and one 20°C for the calculation of the caloric value (see page 19).

Upon checking of all calculated parameters and comparison of the theoretical values with the reported test results, it became clear that also not all laboratories calculated the parameters for real gas.
Probably the following is the case:

2 labs may have reported the caloric value @15°C for ideal gas (& 10 labs for real gas);
3 labs may have reported the caloric value @25°C for ideal gas (& 5 labs for real gas);
3 labs may have reported the density @15°C for ideal gas (& 7 labs for real gas);
2 labs may have reported the density @25°C for ideal gas (but no labs for real gas);
6 labs may have reported the relative density for ideal gas (& 18 labs for real gas).

The instructions for the next PT obviously will have to be more clear and more detailed in order to improve the comparison of the calculated test results.

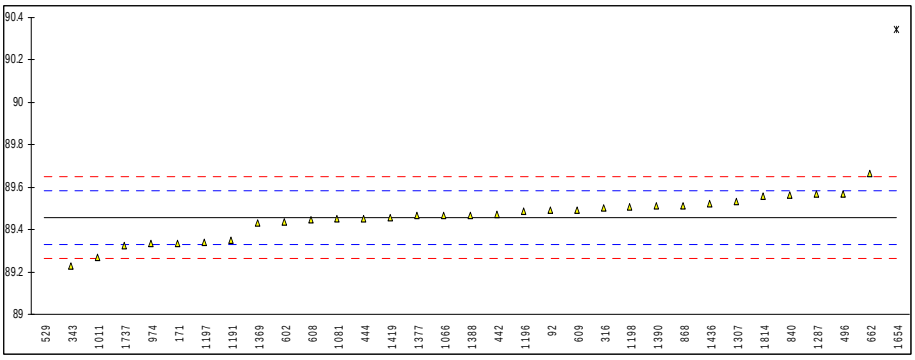
In order to get an impression of the spreads that can be reached when all laboratories will used the same combustion conditions and metering conditions, the theoretical values have been calculated from the reported compositions for a combustion temperature of 15°C and a metering temperature of 0°C for ideal gas. These theoretical values are given in appendix 1.

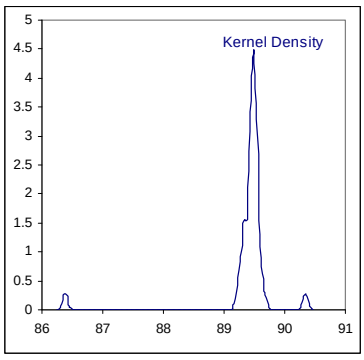
From the small spreads of the calculated theoretical values it can be concluded that the major part of the spreads in the reported results for the calculated parameters is not caused by the reported compositions, but rather by the use of different calculations!
For example for the Caloric Value (sup) of 39.495 ± 1.023 MJ/m^3 approx 95% of the spread is caused by calculation differences and only approx 5% by composition differences, as can be concluded from the small spread of the theoretical value of 38.686 ± 0.056 MJ/m^3, using an identical calculation for each composition.

APPENDIX 1

Determination of Methane on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	89.490		0.50	
171	D1945	89.336		-1.91	
225		-----		-----	
316	ISO6974-3	89.500		0.66	
343	CEA1624	89.228		-3.60	
399		-----		-----	
442	D1945	89.4734		0.24	
444	D1945	89.453		-0.08	
496	DIN51666	89.568		1.72	
529	D1945	86.382	G(0.01)	-48.14	
602	GPA2261	89.4343		-0.37	
608	GPA2261	89.444		-0.22	
609	GPA2261	89.4912		0.52	
662	D1945	89.662	C	3.19	first reported 89.729
840	D1945	89.5652		1.68	
868	GPA2261	89.514		0.88	
974	ISO6974	89.335		-1.92	
1011	UOP539	89.268		-2.97	
1066	ISO6974	89.466		0.13	
1081	in house	89.45		-0.13	
1191	UOP539	89.351		-1.67	
1196	GPA2261	89.4858		0.44	
1197	D1945	89.341		-1.83	
1198	D1945	89.509		0.80	
1287	ISO6974-3	89.566		1.69	
1307	Fast RGA	89.535		1.21	
1369	in house	89.431		-0.42	
1377	D1945	89.465		0.11	
1380		-----		-----	
1388	GPA2261	89.469		0.17	
1390	in house	89.5101		0.82	
1419	D1945	89.455		-0.05	
1436	ISO6974-3	89.523		1.02	
1654	D1945	90.345	C,G(0.01)	13.88	first reported 91.585
1737	in house	89.323		-2.11	
1814	D1945	89.556		1.53	
	normality	not OK			
	n	31			
	outliers	2			
	mean (n)	89.458			
	st.dev. (n)	0.0956			
	R(calc.)	0.268			
	R(ISO6974-3)	0.179			Compare R(ASTM D1945) = 0.150



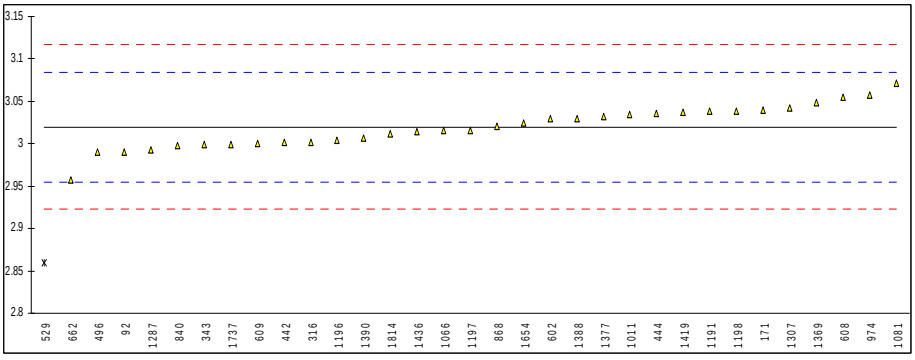


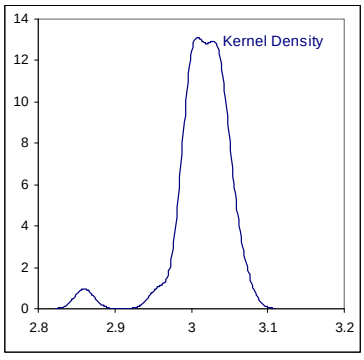
Determination of Ethane on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	2.990		-0.92	
171	D1945	3.040		0.63	
225		-----		-----	
316	ISO6974-3	3.002		-0.55	
343	CEA1624	2.999		-0.64	
399		-----		-----	
442	D1945	3.0017		-0.56	
444	D1945	3.036		0.50	
496	DIN51666	2.990		-0.92	
529	D1945	2.860	G(0.01)	-4.94	
602	GPA2261	3.0294		0.30	
608	GPA2261	3.055		1.09	
609	GPA2261	3.0001		-0.61	
662	D1945	2.957	C	-1.94	first reported 2.938
840	D1945	2.9983		-0.66	
868	GPA2261	3.021		0.04	
974	ISO6974	3.057		1.15	
1011	UOP539	3.034		0.44	
1066	ISO6974	3.015		-0.15	
1081	in house	3.071		1.59	
1191	UOP539	3.038		0.57	
1196	GPA2261	3.0048		-0.46	
1197	D1945	3.016		-0.11	
1198	D1945	3.038		0.57	
1287	ISO6974-3	2.993		-0.83	
1307	Fast RGA	3.042		0.69	
1369	in house	3.048		0.87	
1377	D1945	3.032		0.38	
1380		-----		-----	
1388	GPA2261	3.030		0.32	
1390	in house	3.0061		-0.42	
1419	D1945	3.037		0.53	
1436	ISO6974-3	3.014		-0.18	
1654	D1945	3.024	C	0.13	first reported 3.065
1737	in house	2.999		-0.64	
1814	D1945	3.012		-0.24	

	normality	OK
	n	32
	outliers	1
	mean (n)	3.0197
	st.dev. (n)	0.02414
	R(calc.)	0.0676
	R(ISO6974-3)	0.0906

Compare R(ASTM D1945) = 0.100



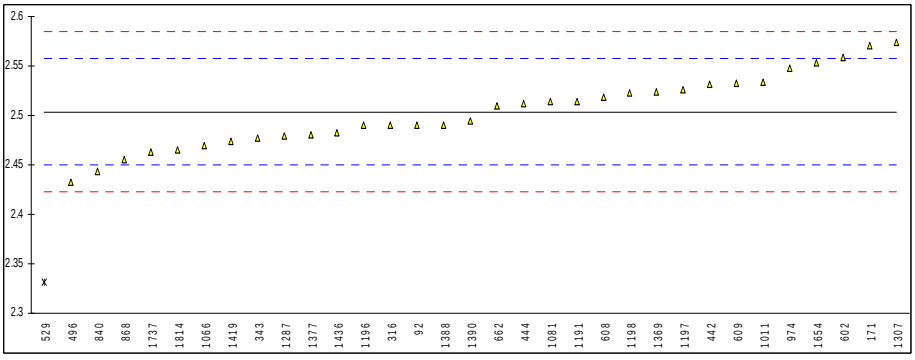


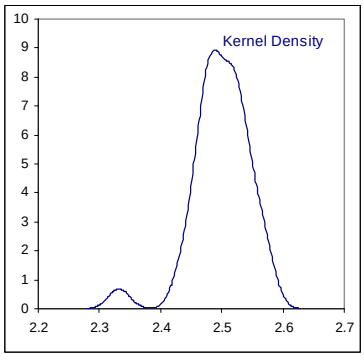
Determination of Propane on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	2.490		-0.51	
171	D1945	2.571		2.51	
225		-----		-----	
316	ISO6974-3	2.490		-0.51	
343	CEA1624	2.477		-1.00	
399		-----		-----	
442	D1945	2.5315		1.03	
444	D1945	2.512		0.31	
496	DIN51666	2.433		-2.64	
529	D1945	2.332	G(0.01)	-6.40	
602	GPA2261	2.5582		2.03	
608	GPA2261	2.519		0.57	
609	GPA2261	2.5324		1.07	
662	D1945	2.510	C	0.23	first reported 2.494
840	D1945	2.4435		-2.25	
868	GPA2261	2.455		-1.82	
974	ISO6974	2.548		1.65	
1011	UOP539	2.534		1.13	
1066	ISO6974	2.470		-1.26	
1081	in house	2.514		0.38	
1191	UOP539	2.514		0.38	
1196	GPA2261	2.4899		-0.52	
1197	D1945	2.526		0.83	
1198	D1945	2.523		0.72	
1287	ISO6974-3	2.479		-0.92	
1307	Fast RGA	2.574		2.62	
1369	in house	2.524		0.75	
1377	D1945	2.480		-0.89	
1380		-----		-----	
1388	GPA2261	2.490		-0.51	
1390	in house	2.4945		-0.35	
1419	D1945	2.474		-1.11	
1436	ISO6974-3	2.483		-0.77	
1654	D1945	2.553	C	1.83	first reported 2.597
1737	in house	2.463		-1.52	
1814	D1945	2.465		-1.45	

	normality	OK
	n	32
	outliers	1
	mean (n)	2.5038
	st.dev. (n)	0.03615
	R(calc.)	0.1012
	R(ISO6974-3)	0.0751

Compare R(ASTM D1945) = 0.100



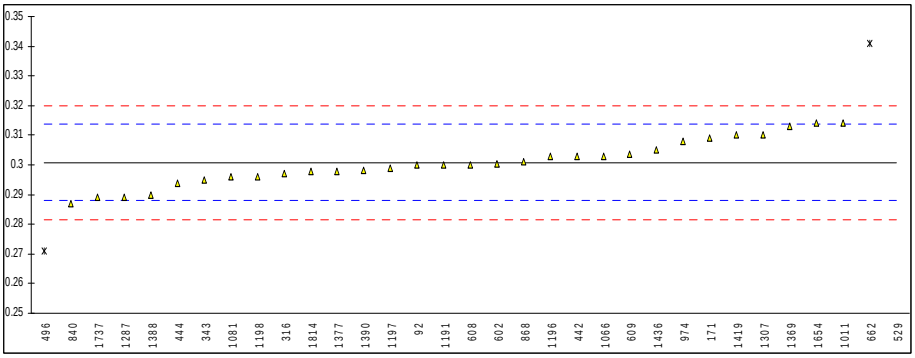


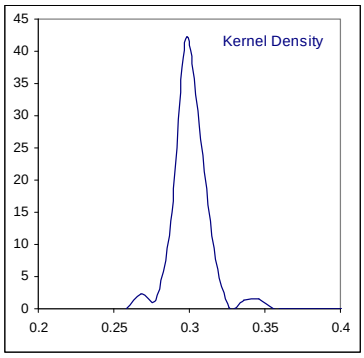
Determination of n-Butane on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	0.300		-0.12	
171	D1945	0.309		1.28	
225		-----		-----	
316	ISO6974-3	0.297		-0.58	
343	CEA1624	0.295		-0.89	
399		-----		-----	
442	D1945	0.3029		0.33	
444	D1945	0.294		-1.05	
496	DIN51666	0.271	C,G(0.05)	-4.62	first reported 0.189, result mixed up with i-butane result
529	D1945	2.716	G(0.01)	374.75	
602	GPA2261	0.3005		-0.04	
608	GPA2261	0.300		-0.12	
609	GPA2261	0.3037		0.46	
662	D1945	0.341	C,G(0.01)	6.24	first reported 0.339
840	D1945	0.2868	C	-2.17	first reported 0.2681
868	GPA2261	0.301		0.04	
974	ISO6974	0.308		1.12	
1011	UOP539	0.314		2.05	
1066	ISO6974	0.303		0.35	
1081	in house	0.296	C	-0.74	first reported 0.198, result mixed up with i-butane result
1191	UOP539	0.300		-0.12	
1196	GPA2261	0.3029		0.33	
1197	D1945	0.299		-0.27	
1198	D1945	0.296		-0.74	
1287	ISO6974-3	0.289		-1.83	
1307	Fast RGA	0.310		1.43	
1369	in house	0.313		1.90	
1377	D1945	0.298	C	-0.43	first reported 0.200, result mixed up with i-butane result
1380		-----		-----	
1388	GPA2261	0.290		-1.67	
1390	in house	0.2982		-0.40	
1419	D1945	0.310		1.43	
1436	ISO6974-3	0.305		0.66	
1654	D1945	0.314		2.05	
1737	in house	0.289		-1.83	
1814	D1945	0.298		-0.43	

	normality	OK
	n	30
	outliers	3
	mean (n)	0.3008
	st.dev. (n)	0.00739
	R(calc.)	0.0207
	R(ISO6974-3)	0.0180

Compare R(ASTM D1945) = 0.070



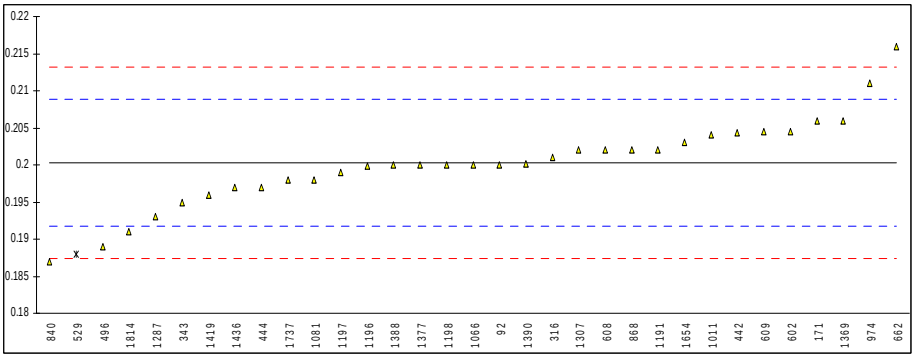


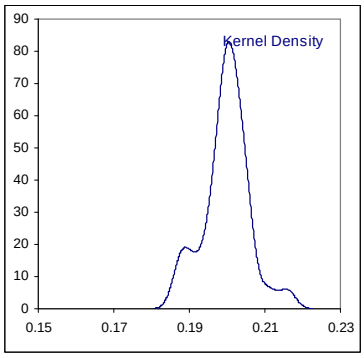
Determination of iso-Butane on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	0.200		-0.06	
171	D1945	0.206		1.34	
225		-----		-----	
316	ISO6974-3	0.201		0.17	
343	CEA1624	0.195		-1.23	
399		-----		-----	
442	D1945	0.2044		0.96	
444	D1945	0.197		-0.76	
496	DIN51666	0.189	C	-2.62	first reported 0.271, result mixed up with n-butane result
529	D1945	0.188	ex	-2.86	see §4.1
602	GPA2261	0.2045		0.99	
608	GPA2261	0.202		0.40	
609	GPA2261	0.2045		0.99	
662	D1945	0.216	C	3.67	first reported 0.214
840	D1945	0.1870		-3.09	
868	GPA2261	0.202		0.40	
974	ISO6974	0.211		2.50	
1011	UOP539	0.204		0.87	
1066	ISO6974	0.200		-0.06	
1081	in house	0.198	C	-0.53	first reported 0.296, result mixed up with n-butane result
1191	UOP539	0.202		0.40	
1196	GPA2261	0.1999		-0.08	
1197	D1945	0.199		-0.29	
1198	D1945	0.200		-0.06	
1287	ISO6974-3	0.193		-1.69	
1307	Fast RGA	0.202		0.40	
1369	in house	0.206		1.34	
1377	D1945	0.200	C	-0.06	first reported 0.298, result mixed up with n-butane result
1380		-----		-----	
1388	GPA2261	0.200		-0.06	
1390	in house	0.2001		-0.04	
1419	D1945	0.196		-0.99	
1436	ISO6974-3	0.197		-0.76	
1654	D1945	0.203		0.64	
1737	in house	0.198		-0.53	
1814	D1945	0.191		-2.16	

normality	OK
n	32
outliers	0
mean (n)	0.2003
st.dev. (n)	0.00578
R(calc.)	0.0162
R(ISO6974-3)	0.0120

Compare R(ASTM D1945) = 0.070

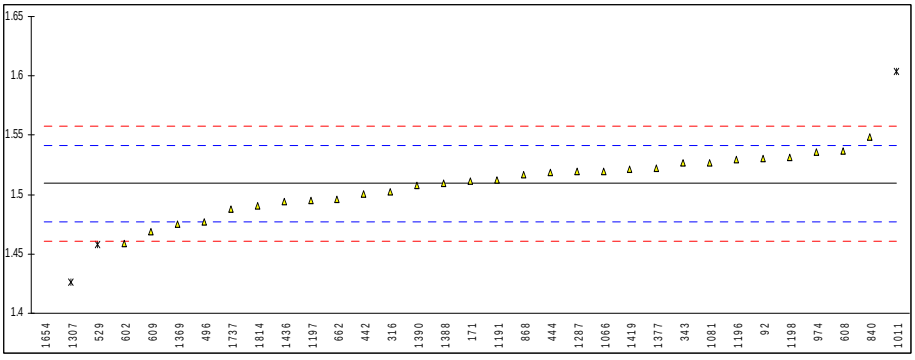


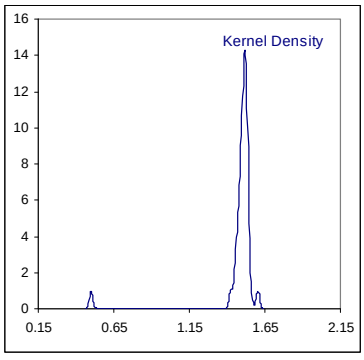


Determination of Carbon Dioxide on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	1.530		1.27	
171	D1945	1.511		0.10	
225		-----		-----	
316	ISO6974-3	1.502		-0.46	
343	CEA1624	1.527		1.09	
399		-----		-----	
442	D1945	1.5008		-0.53	
444	D1945	1.519		0.59	
496	DIN51666	1.477		-2.00	
529	D1945	1.458	ex	-3.18	see §4.1
602	GPA2261	1.4591		-3.11	
608	GPA2261	1.537		1.71	
609	GPA2261	1.4684		-2.53	
662	D1945	1.496	C	-0.83	first reported 1.486
840	D1945	1.5486		2.43	
868	GPA2261	1.517		0.47	
974	ISO6974	1.536		1.65	
1011	UOP539	1.604	G(0.05)	5.85	
1066	ISO6974	1.520		0.66	
1081	in house	1.527		1.09	
1191	UOP539	1.512		0.16	
1196	GPA2261	1.5296		1.25	
1197	D1945	1.495		-0.89	
1198	D1945	1.531		1.34	
1287	ISO6974-3	1.520		0.66	
1307	Fast RGA	1.426	G(0.05)	-5.16	
1369	in house	1.475		-2.13	
1377	D1945	1.522		0.78	
1380		-----		-----	
1388	GPA2261	1.510		0.04	
1390	in house	1.5076		-0.11	
1419	D1945	1.521		0.72	
1436	ISO6974-3	1.494		-0.95	
1654	D1945	0.500	C,G(0.01)	-62.42	first reported 0.735
1737	in house	1.488		-1.32	
1814	D1945	1.491		-1.14	

	normality	OK	
	n	29	
	outliers	3	
	mean (n)	1.5094	
	st.dev. (n)	0.02204	
	R(calc.)	0.0617	
	R(ISO6974-3)	0.0453	Compare R(ASTM D1945) = 0.100



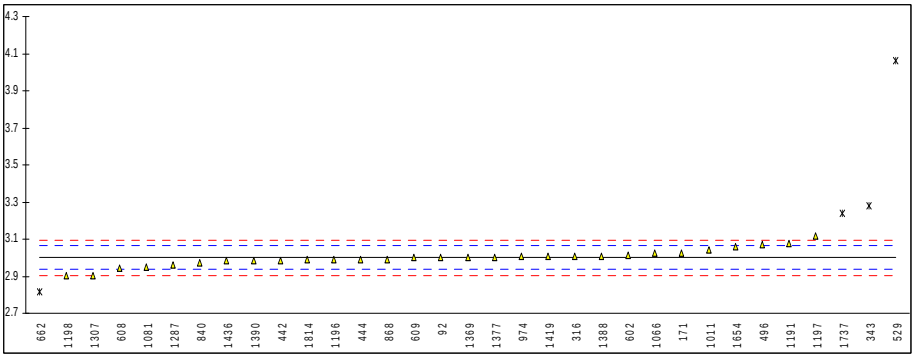


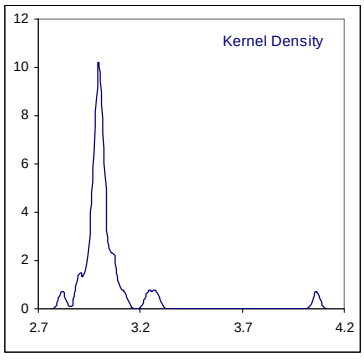
Determination of Nitrogen on sample #11024; results in %mol/mol

lab	method	value	mark	z(targ)	remarks
92	GPA2286	3.000		-0.01	
171	D1945	3.027		0.83	
225		-----		-----	
316	ISO6974-3	3.009		0.27	
343	CEA1624	3.279	G(0.05)	8.67	
399		-----		-----	
442	D1945	2.9853		-0.46	
444	D1945	2.989		-0.35	
496	DIN51666	3.072		2.23	
529	D1945	4.064	G(0.01)	33.09	
602	GPA2261	3.0140		0.43	
608	GPA2261	2.943		-1.78	
609	GPA2261	2.9996		-0.02	
662	D1945	2.818	C,G(0.05)	-5.67	first reported 2.800
840	D1945	2.9706		-0.92	
868	GPA2261	2.991		-0.29	
974	ISO6974	3.005	C	0.15	first reported 2.800
1011	UOP539	3.041		1.27	
1066	ISO6974	3.026		0.80	
1081	in house	2.947		-1.66	
1191	UOP539	3.078		2.42	
1196	GPA2261	2.9871		-0.41	
1197	D1945	3.120		3.73	
1198	D1945	2.900		-3.12	
1287	ISO6974-3	2.960		-1.25	
1307	Fast RGA	2.904		-2.99	
1369	in house	3.003		0.09	
1377	D1945	3.003		0.09	
1380		-----		-----	
1388	GPA2261	3.010		0.30	
1390	in house	2.9834		-0.52	
1419	D1945	3.007		0.21	
1436	ISO6974-3	2.983		-0.54	
1654	D1945	3.062	C	1.92	first reported 1.494
1737	in house	3.240	G(0.01)	7.46	
1814	D1945	2.987		-0.41	

normality	OK
n	29
outliers	4
mean (n)	3.0002
st.dev. (n)	0.04710
R(calc.)	0.1319
R(ISO6974-3)	0.0900

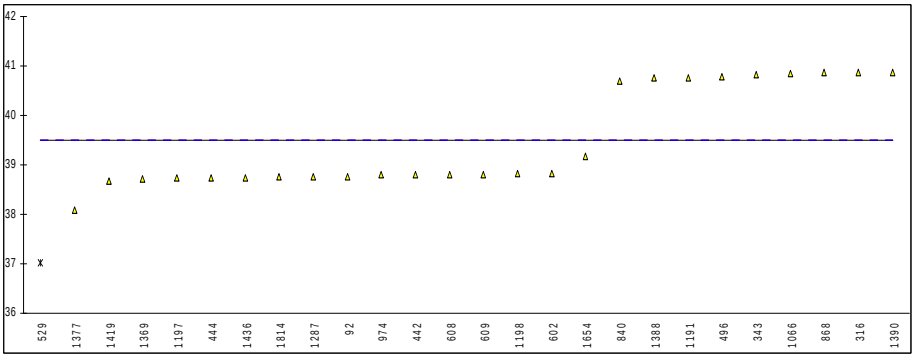
Compare R(ASTM D1945) = 0.100

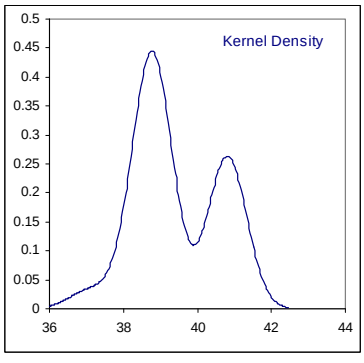


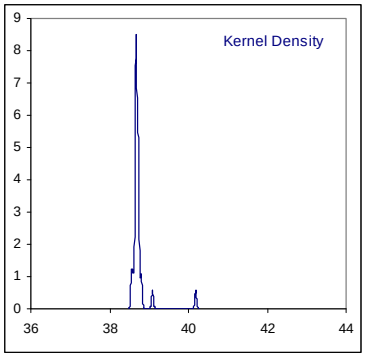


Determination of Caloric Value (sup) (@ 25°C and 101.325 kPa) on smpl #11024; results in MJ/m^3

lab	method	value	mark	z(targ)	remarks
92	AGA#5	38.76		-----	NB. Result was calculated @15° and 101.325 KPa
171		-----		-----	
225		-----		-----	
316	ISO6976	40.8730		-----	
343	CEA1624	40.834		-----	NB. Result was calculated @0° and 101.325 KPa
399		-----		-----	
442	ISO6976	38.81		-----	
444	ISO6976	38.74		-----	NB. Result was calculated @15° and 101.325 Kpa for real gas
496	DIN51857	40.786		-----	
529	ISO6976	37.03	ex	-----	see §4.1
602	ISO6976	38.833171		-----	NB. Result was calculated @15° and 101.325 KPa
608	ISO6976	38.8133		-----	NB. Result was calculated @15° and 101.325 KPa
609	ISO6976	38.8147		-----	NB. Result was calculated @15° and 101.325 KPa
662		-----		-----	
840	ISO6976	40.703		-----	NB. Result was calculated @0° and 101.325 Kpa for ideal gas
868	ISO6976	40.86		-----	
974	GPA2172	38.81		-----	
1011		-----		-----	
1066	ISO6976	40.8561		-----	
1081		-----		-----	
1191	ISO6976	40.762		-----	
1196		-----		-----	
1197	ISO6976	38.74		-----	
1198	ISO6976	38.82		-----	
1287	ISO6976	38.756	C	-----	first reported 3.756 (typing error)
1307		-----		-----	
1369	calc.	38.726		-----	
1377	ISO6976	38.0786		-----	NB. Result was calculated @20° and 101.325 KPa
1380		-----		-----	
1388	ISO6976	40.75484		-----	
1390	ISO6976	40.879		-----	
1419	ISO6976	38.68		-----	
1436	ISO6976	38.74217		-----	
1654	ISO6976	39.1813	C	-----	first reported 39.7308
1737		-----		-----	
1814	D3588	38.75388	C	-----	first reported 34.976
					Theor. results @15°C and 101.325 Kpa (ideal), see 4.1
	normality	not OK			not OK
	n	25			31
	outliers	0			2
	mean (n)	39.495			38.686
	st.dev. (n)	1.0227			0.0560
	R(calc.)	2.864			0.157
	R(lit.)	unknown			unknown

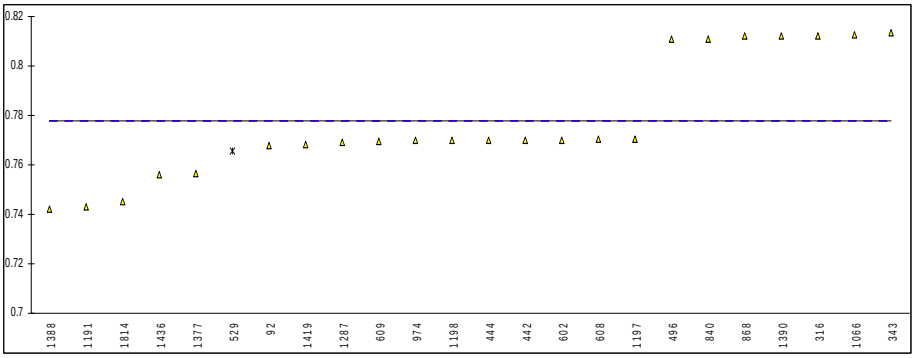


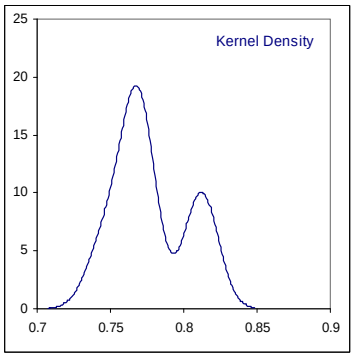


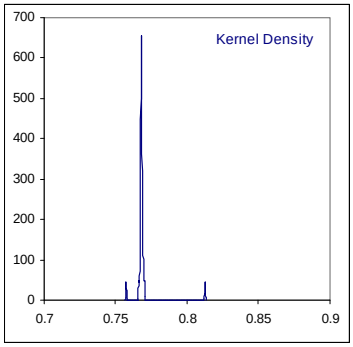


Determination of Density (@ 25°C and 101.325 kPa) on sample #11024; results in kg/m^3

lab	method	value	mark	z(targ)	remarks
92	GPA2286	0.768		-----	
171		-----		-----	
225		-----		-----	
316	ISO6976	0.8122		-----	
343	CEA1624	0.8136		-----	
399		-----		-----	
442	ISO6976	0.7701		-----	
444	ISO6976	0.7700		-----	
496	DIN51857	0.81069		-----	
529	ISO6976	0.7657	ex	-----	see §4.1
602	ISO6976	0.770153		-----	
608	ISO6976	0.770345		-----	
609	ISO6976	0.769764		-----	
662		-----		-----	
840	ISO6976	0.81100		-----	
868	ISO6976	0.8120		-----	
974	GPA2172	0.7699		-----	
1011		-----		-----	
1066	ISO6976	0.81242		-----	
1081		-----		-----	
1191	ISO6976	0.7431		-----	
1196		-----		-----	
1197	ISO6976	0.7705		-----	
1198	ISO6976	0.7699		-----	
1287	ISO6976	0.769		-----	
1307		-----		-----	
1369		-----		-----	
1377	ISO6976	0.756576		-----	
1380		-----		-----	
1388	ISO6976	0.742073		-----	
1390	ISO6976	0.8121		-----	
1419	ISO6976	0.7681		-----	
1436	ISO6976	0.756126		-----	
1654		-----		-----	
1737		-----		-----	
1814	ISO6976	0.745244		-----	
					Theor. results @15°C and 101.325 Kpa (ideal), see 4.1
	normality	not OK			OK
	n	23			31
	outliers	0			2
	mean (n)	0.77795			0.76810
	st.dev. (n)	0.024678			0.000758
	R(calc.)	0.06910			0.00212
	R(lit.)	unknown			unknown

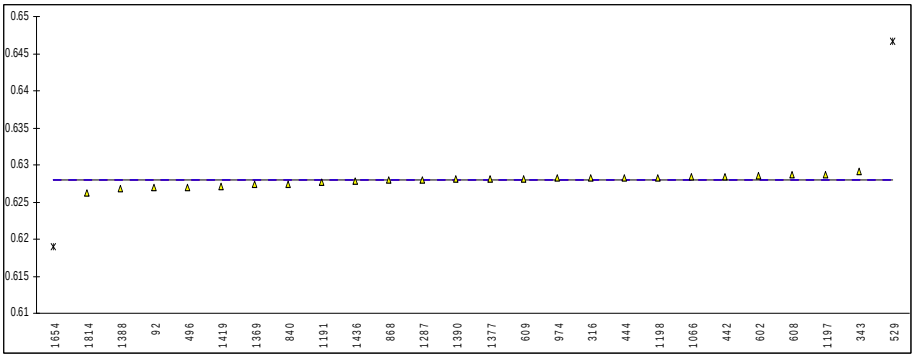


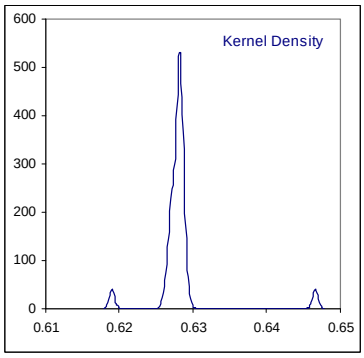


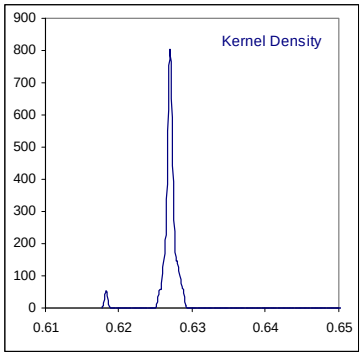


Determination of Relative Density (@ 25°C and 101.325 kPa) on sample #11024; results

lab	method	value	mark	z(targ)	remarks
92	GPA2286	0.627		-----	
171		-----		-----	
225		-----		-----	
316	ISO6976	0.6282		-----	
343	CEA1624	0.6292		-----	
399		-----		-----	
442	ISO6976	0.6284		-----	
444	ISO6976	0.6283		-----	
496	DIN51857	0.62702		-----	
529	ISO6976	0.6466	G(0.01)	-----	
602	ISO6976	0.628486		-----	
608	ISO6976	0.628643		-----	
609	ISO6976	0.628169		-----	
662		-----		-----	
840	ISO6976	0.62740		-----	
868	ISO6976	0.6280		-----	
974	GPA2172	0.6282		-----	
1011		-----		-----	
1066	ISO6976	0.62836		-----	
1081		-----		-----	
1191	ISO6976	0.6277		-----	
1196		-----		-----	
1197	ISO6976	0.6287		-----	
1198	ISO6976	0.6283		-----	
1287	ISO6976	0.628		-----	
1307		-----		-----	
1369	calc.	0.62733		-----	
1377	ISO6976	0.628152		-----	
1380		-----		-----	
1388	ISO6976	0.62685		-----	
1390	ISO6976	0.6281		-----	
1419	ISO6976	0.6271		-----	
1436	ISO6976	0.6277707		-----	
1654	ISO6976	0.619	G(0.01)	-----	
1737		-----		-----	
1814	ISO6976	0.62624		-----	
					Theor. results @15°C and 101.325 Kpa (ideal), see 4.1
	normality	not OK			OK
	n	24			31
	outliers	2			2
	mean (n)	0.62790			0.62707
	st.dev. (n)	0.000695			0.000619
	R(calc.)	0.00195			0.00173
	R(lit.)	unknown			unknown

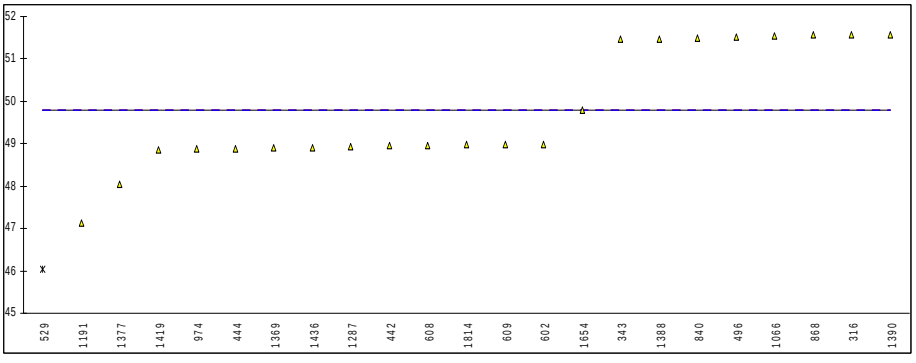


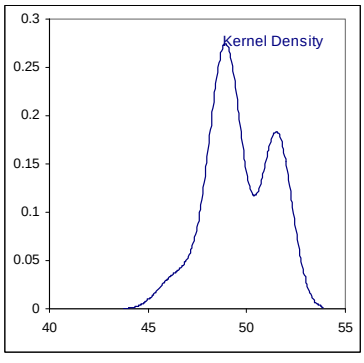


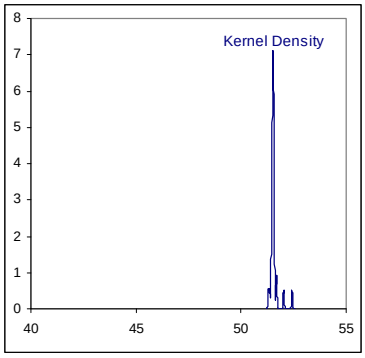


Determination of Wobbe Index (@ 25°C and 101.325 kPa) on sample #11024; results in MJ/m^3

lab	method	value	mark	z(targ)	remarks
92		-----		-----	
171		-----		-----	
225		-----		-----	
316	ISO6976	51.5707		-----	
343	CEA1624	51.466		-----	
399		-----		-----	
442	ISO6976	48.95		-----	
444	ISO6976	48.88		-----	
496	DIN51857	51.508		-----	
529	ISO6976	46.05	ex	-----	see §4.1
602	ISO6976	48.984096		-----	
608	ISO6976	48.9529		-----	
609	ISO6976	48.97325		-----	
662		-----		-----	
840	ISO6976	51.503		-----	
868	ISO6976	51.56		-----	
974	GPA2172	48.88		-----	
1011		-----		-----	
1066	ISO6976	51.5410		-----	
1081		-----		-----	
1191	ISO6976	47.134		-----	
1196		-----		-----	
1197		-----		-----	
1198		-----		-----	
1287	ISO6976	48.923		-----	
1307		-----		-----	
1369	calc.	48.894		-----	
1377	ISO6976	48.0451		-----	
1380		-----		-----	
1388	ISO6976	51.4751466		-----	
1390	ISO6976	51.580		-----	
1419	ISO6976	48.85		-----	
1436	ISO6976	48.897135		-----	
1654	ISO6976	49.782		-----	first reported 50.6241
1737		-----		-----	
1814	ISO6976	48.97164	C	-----	first reported 44.1597 Theor. results @15°C and 101.325 Kpa (ideal), see 4.1
	normality	not OK			OK
	n	22			31
	outliers	0			2
	mean (n)	49.79			51.52
	st.dev. (n)	1.422			0.075
	R(calc.)	3.98			0.21
	R(lit.)	unknown			unknown







APPENDIX 2

Details of the GC-configurations used

92	3 columns with switching/backflush (ISO 6974-5)
171	2 packed columns (ISO 6974-3 or ASTM D1945)
225	
316	2 packed columns (ISO 6974-3 or ASTM D1945)
343	3 columns with switching/backflush (ISO 6974-5)
399	
442	TCD channel (2 packed columns with switching) & FID channel (1 capillairy column)
444	TCD channel (2 packed columns with switching) & FID channel (1 capillairy column)
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	2 packed columns with switching/backflush to TCD1 & 2 packed columns to TCD2
609	3 columns with switching/backflush (ISO 6974-5)
662	
840	3 columns (2 packed & 1 capillairy) with switching/backflush
868	4 packed columns with switching/backflush (3 valves)
974	3 columns (2 packed & 1 capillairy) with dual TCD & FID
1011	
1066	2 packed columns (ISO 6974-3 or ASTM D1945)
1081	
1191	6 columns with switching/backflush (2xTCD + 1xFID)
1196	4 packed columns with switching/backflush (3 valves)
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 (ISO 6974-3 or ASTM D1945)
1307	Agilent fast RGA with 5 packed columns and 2 capillary colums
1369	3 packed columns (Molsieve 13X & 2x DC-200/500 Chrom PAW)
1377	2 packed columns (ISO 6974-3 or ASTM D1945)
1380	
1388	
1390	5 columns (1 capillairy to FID & 2 packed to TCD & 2 capillairy to TCD)
1419	HP6890 RGA 1058
1436	2 packed columns (ISO 6974-3 or ASTM D1945)
1654	3 capillairy columns with switching (ISO 6974-6)
1737	2 packed columns (Mol Sieve 13X & Charcoal) and one capillary column (Elite Alumina)
1814	2 columns (HP-Plot/Q & Molsieve X13)

APPENDIX 3

Number of participants per country

1 lab in	AUSTRALIA
2 labs in	BELGIUM
1 lab in	CANADA
1 lab in	CÔTE D'IVOIRE
1 lab in	FINLAND
1 lab in	FRANCE
1 lab in	GERMANY
1 lab in	HUNGARY
1 lab in	INDIA
2 labs in	ITALY
6 labs in	MALAYSIA
1 lab in	MEXICO
3 labs in	P.R. of CHINA
1 lab in	PORTUGAL
1 lab in	SLOVAK REPUBLIC
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.
3 labs in	UNITED KINGDOM
1 lab in	VIETNAM

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