

**Results of Proficiency Test
Dissolved Gas Analysis
November 2015**

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since 2007, the Institute for Interlaboratory Studies organizes a proficiency test for the analysis of Dissolved Gas Analysis (DGA) in Transformer Oil. During the annual proficiency testing program 2015/2016, it was decided to continue the round robin for Dissolved Gas Analysis (DGA) in Transformer Oil.

In this international interlaboratory study, 49 laboratories from 25 different countries have participated. See appendix 3 for the number of participants per country. In this report the results of the 2015 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, The Netherlands, was the organizer of this proficiency test. In total one batch of 67 certified syringes (of 50 mL) was prepared (lot RN192). The syringes were provided by Morgan Schaffer Inc, Quebec, Canada (True North). Each syringe was uniquely numbered and one syringe was sent to each participating laboratory, without the certificate provided by Morgan Schaffer Inc. Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires. Morgan Schaffer Inc. is ISO 9001:2008 certified and ISO/IEC17025:2005 accredited by SCC.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol is electronically available through the iis internet site www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

In this proficiency test only one sample was used. The 50 mL gas tight syringes with sample material were prepared and subsequently tested by Morgan Schaffer Inc. (Quebec, Canada) in accordance with principles outlined in ASTM Method D3612:01, Annex A2 (2001) and IEC 60567, clause 6.2 (2011).

In total one batch of 67 syringes was prepared (lot RN192). Each syringe was uniquely numbered and a certificate of analysis was provided by Morgan Schaffer Inc. These certificates were removed after receipt by iis prior to the forwarding of the samples to the participating laboratories.

The differences between the test results of each syringe are not statistically significant (see paragraph 4.4).

And for all components, the standard deviation is in agreement with 0.3 times the corresponding reproducibility of the target method according with the procedure of ISO 13528. Therefore, homogeneity of the samples was assumed.

To each of the participating laboratories one syringe of 50 mL (labelled #15226) was sent on November 4, 2015.

2.5 STABILITY OF THE SAMPLES

Morgan Schaffer declares that bulk storage prior to shipping has a shelf life of at least 6 months. This was assumed to be sufficient for the proficiency testing purposes.

2.6 ANALYSES

The participants were requested to determine on sample #15226: Hydrogen, Oxygen, Nitrogen, Carbon Monoxide, Carbon Dioxide, Methane, Ethane, Ethene, Ethyn, Propane and Propene. Also some method details were requested to be reported.

To get comparable results a detailed report form, on which the units were prescribed as well as the required standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis/.

A SDS and a form to confirm receipt of the samples were added to the sample package.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis/. The originally reported test results are tabulated per determination in the appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after deadline, a reminder was sent to those laboratories that did not report 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 raw data of these tests (no reanalysis). Additional or corrected results are used for data analysis and original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies-Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<...>' or '>...>' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

According to ISO 5725 the original results per determination were submitted to Dixon's and/or Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test (ref. 15). Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them 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 on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as an "x". 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; nos.13 and 14). Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

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

The z-scores were calculated in accordance with:

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

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.

The $Z_{(\text{target})}$ 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 major problems were encountered during execution. After receipt of the syringes from Morgan Schaffer Inc., it turned out that 5 syringes contained a large and significant air-bubble and were not suitable to be used in this round robin. These 5 syringes were replaced by new syringes of the same batch, which were received in good order. After dispatch of the samples, also a number of participants reported to have received syringes with an air-bubble, which were also replaced by syringes of the same batch. The dispatches of the replacement syringes did cause some delay in the reporting of test results by the participating laboratories and consequently also in the preparation of the PT report.

Six participants reported the results after the final reporting date and four participants did not report any test results at all. Not all labs were able to report all components requested. In total 45 participating laboratories reported 401 numerical results. Observed were 29 outlying results, which is 7.2% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER TEST

In this section the results are discussed per component.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care.

The test results of the laboratories 237, 912 and 6015 showed respectively 5, 3 and 3 outliers and 2, 6 and 3 false negative test results. As the nine test results are not independent, it was decided to reject all of the test results of these laboratories for the statistical evaluation.

Hydrogen: The determination of this component was very problematic. Two statistical outliers were observed and one other test result was excluded. The calculated reproducibility after rejection of suspect data is not at all in agreement with the strict requirements of IEC 60567:2011.

Oxygen: The determination of this component was very problematic. Two statistical outliers were observed and two other test results were excluded. The calculated reproducibility after rejection of suspect data is not at all in agreement with the requirements of IEC 60567:2011.

Nitrogen: The determination of this component was very problematic. Two statistical outliers were observed and two other test results were excluded. The calculated reproducibility after rejection of suspect data is not at all in agreement with the requirements of IEC 60567:2011.

Carbon Monoxide: The determination of this component was problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the requirements of IEC 60567:2011.

- Carbon Dioxide: The determination of this component was problematic. Two statistical outliers were observed and one other test result was excluded. The calculated reproducibility after rejection of suspect data is not in agreement with the requirements of IEC 60567:2011.
- Methane: The determination of this component was problematic. Five statistical outliers were observed and one other test result was excluded. The calculated reproducibility after rejection of suspect data is not in agreement with the strict requirements of IEC 60567:2011.
- Ethane: The determination of this component at the low level of 2 µL/L was very problematic. Four statistical outliers were observed and one test result was excluded. The calculated reproducibility after rejection of suspect data is not at all in agreement with the strict requirements of IEC 60567:2011.
- Ethene: The determination of this component was problematic. Five statistical outliers were observed and one test result was excluded. The calculated reproducibility after rejection of suspect data is not in agreement with the strict requirements of IEC 60567:2011.
- Ethyn: The determination of this component was problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the strict requirements of IEC 60567:2011.
- Propane: To few analytical test results were received to draw any significant conclusions.
- Propene: The determination of this component was very problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the strict requirements of IEC 60567:2011.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard and the reproducibility as found for the group of participating laboratories. The average results per component, calculated reproducibilities and reproducibilities from IEC 60567:2011 are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
Hydrogen H ₂	µl/L	40	15.15	8.98	3.03
Oxygen O ₂	µl/L	37	20229	10705	4046
Nitrogen N ₂	µl/L	37	57031	25970	11406
Carbon Monoxide CO	µl/L	42	171	51	34
Carbon Dioxide CO ₂	µl/L	42	1259	464	252
Methane CH ₄	µl/L	38	8.13	3.06	1.63
Ethane C ₂ H ₆	µl/L	38	2.28	1.08	0.46
Ethene C ₂ H ₄	µl/L	38	5.48	1.91	1.10
Ethyn C ₂ H ₂	µl/L	39	2.82	0.91	0.56
Propane C ₃ H ₈	µl/L	12	<1	n.a	n.a
Propene C ₃ H ₆	µl/L	10	3.58	2.60	0.72

Table 1: Performance of the group on sample #15226

Without further statistical calculations it can be concluded from the overview given in table 1 that there is not a compliance of the performance of the group of participating laboratories with the relevant standard IEC 60567:2011.

The problematic components have been discussed in paragraph 4.1.

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

	<i>November 2015</i>	<i>November 2014</i>	<i>November 2013</i>	<i>November 2012</i>	<i>November 2011</i>
Number of reporting labs	45	40	33	29	33
Number of results reported	401	358	293	265	299
Statistical outliers	29	10	10	15	18
Percentage outliers	7.2%	2.8%	3.4%	6.0%	6.0%

Table 2: Comparison of statistical summary parameters with previous proficiency tests

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

The performance of the determinations of the proficiency tests was determined by calculating the relative uncertainties. The conclusions are given the following table:

Determination	November 2015	November 2014	November 2013	November 2012	November 2011	IEC605671
Hydrogen H ₂	21%	24%	21%	20%	25%	7%
Oxygen O ₂	19%	18%	17%	16%	14%	7%
Nitrogen N ₂	16%	13%	19%	12%	12%	7%
Carbon Monoxide CO	11%	12%	12%	15%	14%	7%
Carbon Dioxide CO ₂	12%	17%	15%	14%	14%	7%
Methane CH ₄	13%	18%	19%	18%	19%	7%
Ethane C ₂ H ₆	17%	24%	23%	18%	25%	7%
Ethene C ₂ H ₄	12%	29%	17%	21%	18%	7%
Ethyn C ₂ H ₂	11%	35%	19%	20%	24%	7%
Propane C ₃ H ₈	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.
Propene C ₃ H ₆	26%	20%	n.e.	n.e.	n.e.	n.e.

Table 3: Comparison of the relative uncertainties on the various components

Comparing the results of the 2015 round robin to that of last year, the overall performance appears to be much better, except for Nitrogen and Propene.

4.4 DISCUSSION

The consensus values as determined in this PT are compared with the average values from the homogeneity testing by Morgan Schaffer in the following table. From this comparison it is clear that all consensus values as determined in this PT are very well in line with the values as determined by Morgan Schaffer after the preparation of the syringes.

Parameter	Average values by Morgan Schaffer in µ/L	Consensus values from participants results in µ/L	Absolute differences in µ/L
Hydrogen H ₂	13	15	+2
Oxygen O ₂	20500	20229	-271
Nitrogen N ₂	53200	57031	+3831
Carbon Monoxide CO	166	171	+5
Carbon Dioxide CO ₂	1310	1259	-51
Methane CH ₄	8.0	8.1	+0.1
Ethane C ₂ H ₆	2.4	2.3	-0.1
Ethene C ₂ H ₄	5.7	5.5	-0.2
Ethyn C ₂ H ₂	3.0	2.8	-0.2

Table 4: comparison of consensus values with values determined by Morgan Schaffer

In the 2012 round robin (iis12L06) a correlation could be found between the methods used by the laboratories and the reported results. The majority of the laboratories participating in the current round robin used a headspace method. Looking at the headspace results versus the other methods used, small differences were seen in the mean values and in the variations of the test results.

The target reproducibilities as required by IEC 60567 obviously appear to be very hard to meet, although the observed reproducibilities are decreasing during the subsequent annual PTs. Still, it is clear that the reproducibility requirements of IEC 60567 are quite strict as they are smaller than the reproducibilities estimated using the Horwitz equation for the majority of the components.

In order to evaluate whether the used test method has a significant influence on the test results, the headspace test results were evaluated separately, see appendix 1. From the evaluation is noted that for the majority of the components the consensus value for the headspace test results is slightly higher than the consensus value for all test results. However, for all components the precision of the headspace test results is clearly better than the precision for all test results, although the strict requirements of IEC 60567:2011 are still not met.

APPENDIX 1

Determination of Hydrogen on sample #15226; results in µ/L

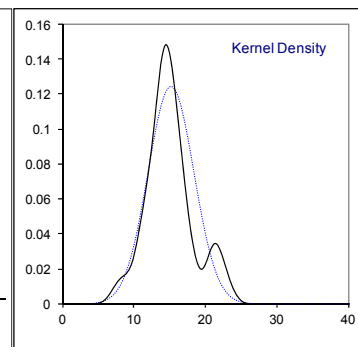
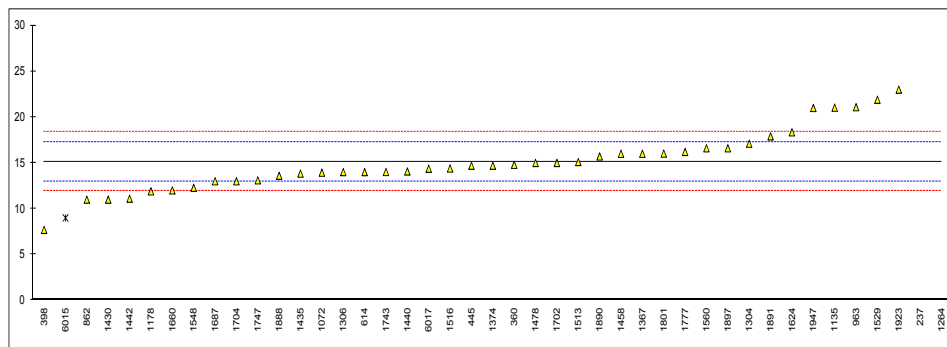
lab	method	value	mark	z(targ)	remarks
179	D3612	<13		----	
237	D3612	48.547	R(0.01)	30.85	
360	IEC60567	14.8		-0.33	
398	IEC60567	7.7		-6.89	
445	IEC60567	14.7		-0.42	
511		----		----	
614	IEC60567	14		-1.06	
862	IEC60567	11		-3.84	
912	D3612C	<10		<-4.76	False negative test result?
963	D3612C	21.08		5.48	
974		----		----	
1072	IEC60567	13.94		-1.12	
1135	IEC60567	21.03		5.43	
1178	IEC60567	11.9		-3.01	
1264	D3612	74.4	R(0.01)	54.74	
1304	INH-120	17.1		1.80	
1306	D3612	14		-1.06	
1367	IEC60567	16		0.78	
1374	D3612	14.7		-0.42	
1417		----		----	
1430	IEC60567	11		-3.84	
1435	IEC60567	13.84		-1.21	
1440	D3612	14.07		-1.00	
1442	IEC60567	11.1		-3.74	
1444		----		----	
1458	D3612	16		0.78	
1478	IEC60567	15.0		-0.14	
1513	IEC60567	15.1		-0.05	
1516	IEC60567	14.4		-0.70	
1529	IEC60567	21.9		6.23	
1548	IEC60567	12.29		-2.64	
1560	IEC60567	16.6		1.34	
1624	IEC60567	18.34		2.94	
1660	IEC60567	12		-2.91	
1687	IEC60567	13.00		-1.99	
1702	IEC60567	15		-0.14	
1704	IEC60567	13		-1.99	
1743	IEC60567	14.0108		-1.05	
1747	IEC60567	13.1		-1.90	
1777	IEC60567	16.2		0.97	
1801	IEC60567	16.02		0.80	
1888	IEC60567	13.6		-1.43	
1890	IEC60567	15.71		0.52	
1891	IEC60567	17.9		2.54	
1897	IEC60567	16.6		1.34	
1923	in house	23.00		7.25	
1947	IEC60567	21		5.40	
6015	IEC60567	9	ex	-5.68	Result excluded, see §4.1
6017	in house	14.372		-0.72	

normality OK
n 40
outliers 2 (+1 excl)
mean (n) 15.1526
st.dev. (n) 3.20819
R(calc.) 8.9829
R(IEC60567:11) 3.0305

Only Headspace results

OK
23
1 (+1 excl)
15.1210
2.79042
7.8132
3.0242

Compare R(Horwitz) = 4.5090



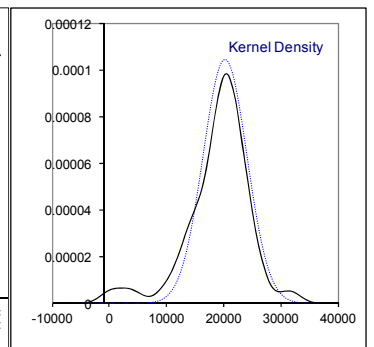
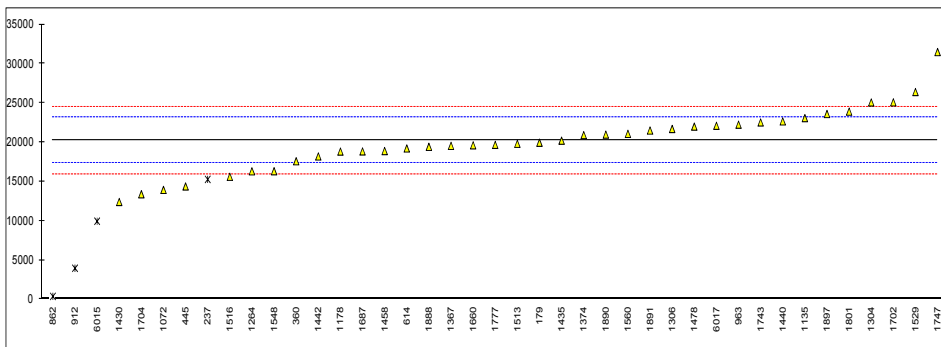
Determination of Oxygen on sample #15226; results in µl/L

lab	method	value	mark	z(targ)	remarks
179	D3612	19947		-0.20	
237	D3612	15279.314	ex	-3.43	Result excluded, see §4.1
360	IEC60567	17586.8		-1.83	
398		----		----	
445	IEC60567	14376		-4.05	
511		----		----	
614	IEC60567	19215.645		-0.70	
862	IEC60567	384	R(0.05)	-13.73	
912	D3612C	3964	R(0.05)	-11.26	
963	D3612C	22240.8		1.39	
974		----		----	
1072	IEC60567	13938.80		-4.35	
1135	IEC60567	23077.38		1.97	
1178	IEC60567	18822.9		-0.97	
1264	D3612	16309.20		-2.71	
1304	INH-120	25077.0		3.36	
1306	D3612	21700		1.02	
1367	IEC60567	19546		-0.47	
1374	D3612	20919		0.48	
1417		----		----	
1430	IEC60567	12400		-5.42	
1435	IEC60567	20204.8		-0.02	
1440	D3612	22663.5		1.68	
1442	IEC60567	18199.9		-1.40	
1444		----		----	
1458	D3612	18887		-0.93	
1478	IEC60567	21996.1		1.22	
1513	IEC60567	19810	C	-0.29	First reported 20810
1516	IEC60567	15610.2		-3.20	
1529	IEC60567	26400		4.27	
1548	IEC60567	16319.47		-2.71	
1560	IEC60567	21077		0.59	
1624		----		----	
1660	IEC60567	19619		-0.42	
1687	IEC60567	18841.60		-0.96	
1702	IEC60567	25092		3.37	
1704	IEC60567	13387		-4.74	
1743	IEC60567	22530.6152		1.59	
1747	IEC60567	31488.6		7.79	
1777	IEC60567	19675.4		-0.38	
1801	IEC60567	23905.18		2.54	
1888	IEC60567	19428		-0.55	
1890	IEC60567	20981		0.52	
1891	IEC60567	21500		0.88	
1897	IEC60567	23600		2.33	
1923		----		----	
1947		----		----	
6015	IEC60567	9949	ex	-7.11	Result excluded, see §4.1
6017	in house	22100		1.29	

Only Headspace results

normality	suspect	OK
n	37	22
outliers	2 (+2 excl)	1 (+2 excl)
mean (n)	20229.00	20554.97
st.dev. (n)	3823.252	3267.434
R(calc.)	10705.11	9148.82
R(IEC60567:11)	4045.80	4110.99

Compare R(Horwitz) = 2037.69



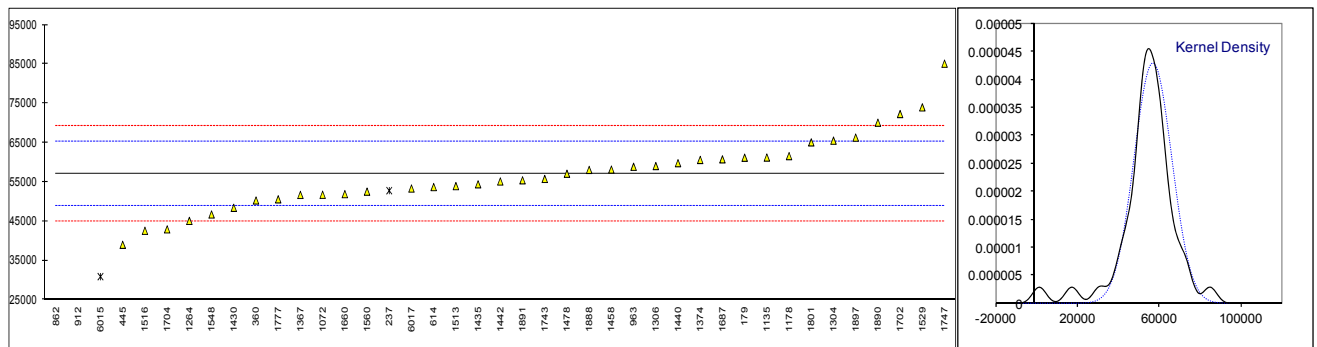
Determination of Nitrogen on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	61181		1.02	
237	D3612	52785.9	ex	-1.04	Result excluded, see §4.1
360	IEC60567	50299.3		-1.65	
398		----		----	
445	IEC60567	39012		-4.42	
511		----		----	
614	IEC60567	53709.590		-0.82	
862	IEC60567	1115	R(0.01)	-13.73	
912	D3612C	17138	R(0.05)	-9.79	
963	D3612C	58869.5		0.45	
974		----		----	
1072	IEC60567	51744.84		-1.30	
1135	IEC60567	61225.42		1.03	
1178	IEC60567	61588.4		1.12	
1264	D3612	45094.90		-2.93	
1304	INH-120	65519.5		2.08	
1306	D3612	59054		0.50	
1367	IEC60567	51702		-1.31	
1374	D3612	60617.0		0.88	
1417		----		----	
1430	IEC60567	48423		-2.11	
1435	IEC60567	54410.9		-0.64	
1440	D3612	59790.5		0.68	
1442	IEC60567	55135.9		-0.47	
1444		----		----	
1458	D3612	58162		0.28	
1478	IEC60567	57102.9		0.02	
1513	IEC60567	53950	C	-0.76	First reported 55950
1516	IEC60567	42572.2		-3.55	
1529	IEC60567	74000		4.17	
1548	IEC60567	46726.17		-2.53	
1560	IEC60567	52545		-1.10	
1624		----		----	
1660	IEC60567	51908		-1.26	
1687	IEC60567	60769.17		0.92	
1702	IEC60567	72298		3.75	
1704	IEC60567	42933		-3.46	
1743	IEC60567	55772.1250		-0.31	
1747	IEC60567	85118.9		6.90	
1777	IEC60567	50586.2		-1.58	
1801	IEC60567	65085.59		1.98	
1888	IEC60567	58073		0.26	
1890	IEC60567	70094		3.21	
1891	IEC60567	55433		-0.39	
1897	IEC60567	66300		2.28	
1923		----		----	
1947		----		----	
6015	IEC60567	30890	ex	-6.42	Result excluded, see §4.1
6017	in house	53336		-0.91	

Only Headspace results
 normality suspect
 n 37
 outliers 2 (+2 excl)
 mean (n) 57030.89
 st.dev. (n) 9274.979
 R(calc.) 25969.94
 R(IEC60567:11) 11406.18

OK
 22
 1 (+2 excl)
 57556.67
 7715.555
 21603.55
 11511.33

Compare R(Horwitz) = 4914.99



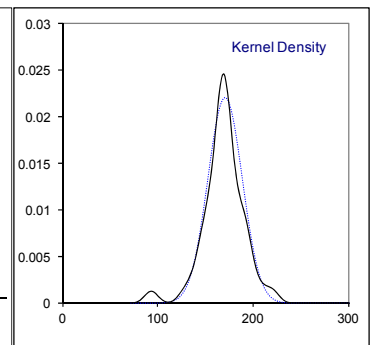
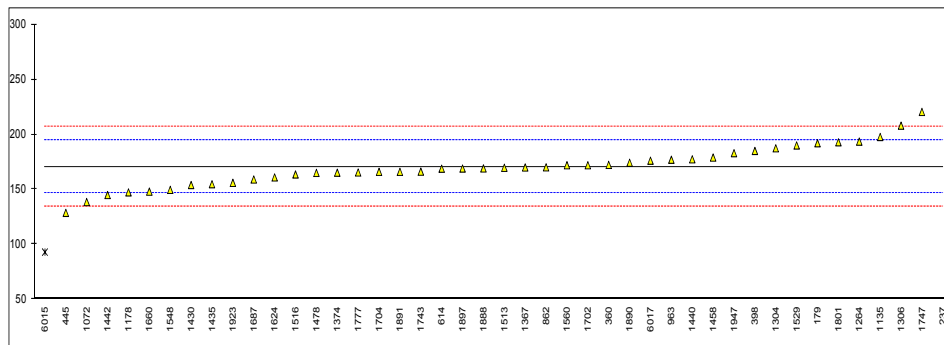
Determination of Carbon Monoxide on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	192		1.75	
237	D3612	519.699	R(0.01)	28.64	
360	IEC60567	172.3		0.14	
398	IEC60567	185		1.18	
445	IEC60567	128.7		-3.44	
511		----		----	
614	IEC60567	168.876		-0.14	
862	IEC60567	170.1		-0.04	
912	D3612C	<10		<-13.18	False negative test result?
963	D3612C	177.0		0.52	
974		----		----	
1072	IEC60567	138.55		-2.63	
1135	IEC60567	197.70		2.22	
1178	IEC60567	147.3		-1.91	
1264	D3612	193.5		1.88	
1304	INH-120	187.4		1.38	
1306	D3612	208		3.07	
1367	IEC60567	170		-0.05	
1374	D3612	165.2		-0.44	
1417		----		----	
1430	IEC60567	154		-1.36	
1435	IEC60567	154.74		-1.30	
1440	D3612	177.4		0.56	
1442	IEC60567	144.9		-2.11	
1444		----		----	
1458	D3612	179		0.69	
1478	IEC60567	165.0		-0.46	
1513	IEC60567	169.7		-0.08	
1516	IEC60567	163.6		-0.58	
1529	IEC60567	190		1.59	
1548	IEC60567	149.58		-1.73	
1560	IEC60567	172		0.11	
1624	IEC60567	160.92		-0.80	
1660	IEC60567	148		-1.86	
1687	IEC60567	159.06		-0.95	
1702	IEC60567	172		0.11	
1704	IEC60567	166		-0.38	
1743	IEC60567	166.1976		-0.36	
1747	IEC60567	220.45		4.09	
1777	IEC60567	165.42		-0.43	
1801	IEC60567	192.86		1.83	
1888	IEC60567	169.1		-0.12	
1890	IEC60567	174.28		0.30	
1891	IEC60567	166		-0.38	
1897	IEC60567	169		-0.13	
1923	in house	156.00		-1.20	
1947	IEC60567	183		1.02	
6015	IEC60567	93	R(0.01)	-6.37	
6017	in house	176.116		0.45	

Only Headspace results

normality	OK	OK
n	42	23
outliers	2	2
mean (n)	170.618	170.276
st.dev. (n)	18.1037	16.3330
R(calc.)	50.690	45.733
R(IEC60567:11)	34.124	34.055

Compare R(Horwitz) = 35.265

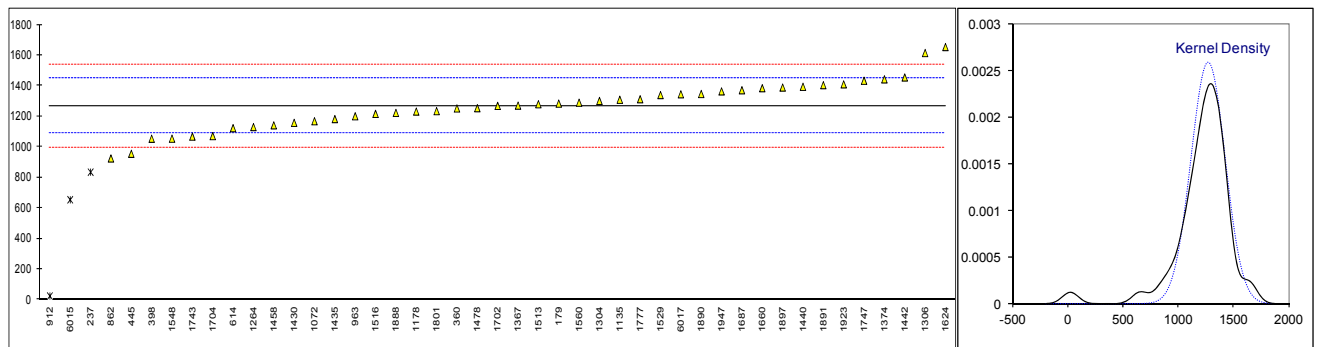


Determination of Carbon Dioxide on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	1284		0.16	
237	D3612	835.02	ex	-4.79	Result excluded, see §4.1
360	IEC60567	1252.4		-0.19	
398	IEC60567	1054		-2.38	
445	IEC60567	955.3		-3.46	
511		----		----	
614	IEC60567	1123.190		-1.61	
862	IEC60567	925		-3.80	
912	D3612C	24	R(0.01)	-13.74	
963	D3612C	1200.9		-0.76	
974		----		----	
1072	IEC60567	1168.42		-1.11	
1135	IEC60567	1309.32		0.44	
1178	IEC60567	1231.9		-0.41	
1264	D3612	1130.32		-1.53	
1304	INH-120	1301.3		0.35	
1306	D3612	1615		3.81	
1367	IEC60567	1271		0.02	
1374	D3612	1442.8		1.91	
1417		----		----	
1430	IEC60567	1158		-1.23	
1435	IEC60567	1182.65		-0.96	
1440	D3612	1394.0		1.37	
1442	IEC60567	1455.0	C	2.05	First reported 1812.5
1444		----		----	
1458	D3612	1142		-1.40	
1478	IEC60567	1254.1		-0.17	
1513	IEC60567	1280		0.12	
1516	IEC60567	1216.6		-0.58	
1529	IEC60567	1340		0.78	
1548	IEC60567	1054.47		-2.37	
1560	IEC60567	1290		0.23	
1624	IEC60567	1654.36		4.25	
1660	IEC60567	1385		1.28	
1687	IEC60567	1371.53		1.13	
1702	IEC60567	1269		0.00	
1704	IEC60567	1071		-2.19	
1743	IEC60567	1067.9789		-2.22	
1747	IEC60567	1433.5		1.81	
1777	IEC60567	1312.6		0.48	
1801	IEC60567	1234.72		-0.38	
1888	IEC60567	1223		-0.51	
1890	IEC60567	1346.88		0.85	
1891	IEC60567	1405		1.50	
1897	IEC60567	1389		1.32	
1923	in house	1410.00		1.55	
1947	IEC60567	1364		1.04	
6015	IEC60567	654	R(0.05)	-6.79	
6017	in house	1345.229		0.84	

		<u>Only Headspace results</u>
normality	OK	OK
n	42	23
outliers	2 (+1 excl)	2 (+1 excl)
mean (n)	1259.29	1322.40
st.dev. (n)	165.882	146.479
R(calc.)	464.47	410.14
R(IEC60567:11)	251.86	253.88

Compare R(Horwitz) = 193.97

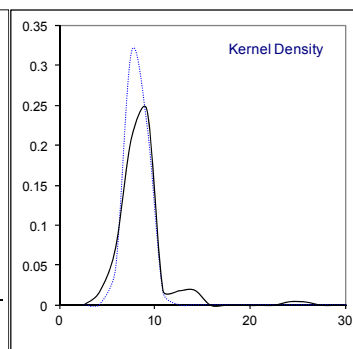
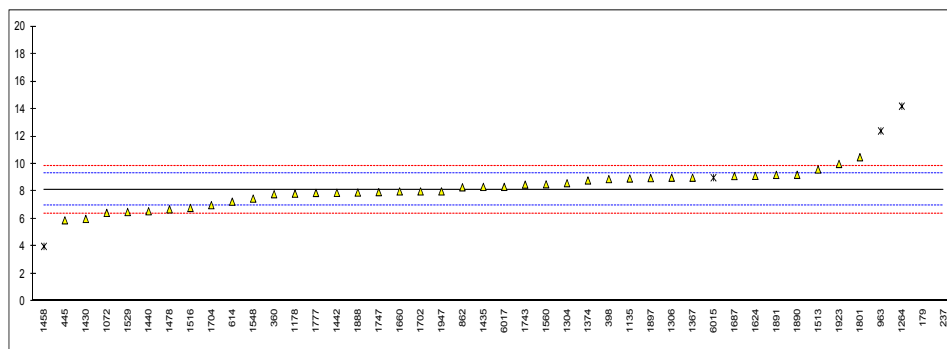


Determination of Methane on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	25	R(0.01)	29.06	
237	D3612	425.301	R(0.01)	718.53	
360	IEC60567	7.8		-0.57	
398	IEC60567	8.9		1.33	
445	IEC60567	5.9	C	-3.84	First reported 5
511		----		----	
614	IEC60567	7.255		-1.50	
862	IEC60567	8.3		0.30	
912	D3612C	<1		<-12.28	False negative test result?
963	D3612C	12.4	R(0.05)	7.36	
974		----		----	
1072	IEC60567	6.44		-2.91	
1135	IEC60567	8.94		1.40	
1178	IEC60567	7.84		-0.50	
1264	D3612	14.2	R(0.01)	10.46	
1304	INH-120	8.6		0.81	
1306	D3612	9		1.50	
1367	IEC60567	9		1.50	
1374	D3612	8.8		1.16	
1417		----		----	
1430	IEC60567	6		-3.67	
1435	IEC60567	8.33		0.35	
1440	D3612	6.56		-2.70	
1442	IEC60567	7.9		-0.39	
1444		----		----	
1458	D3612	4	R(0.05)	-7.11	
1478	IEC60567	6.7		-2.46	
1513	IEC60567	9.6		2.53	
1516	IEC60567	6.8		-2.29	
1529	IEC60567	6.5		-2.80	
1548	IEC60567	7.48		-1.12	
1560	IEC60567	8.52		0.67	
1624	IEC60567	9.13		1.73	
1660	IEC60567	8.0		-0.22	
1687	IEC60567	9.12		1.71	
1702	IEC60567	8		-0.22	
1704	IEC60567	7		-1.94	
1743	IEC60567	8.4973		0.64	
1747	IEC60567	7.95		-0.31	
1777	IEC60567	7.89		-0.41	
1801	IEC60567	10.49		4.07	
1888	IEC60567	7.92		-0.36	
1890	IEC60567	9.21	C	1.86	First reported 11.30
1891	IEC60567	9.2		1.85	
1897	IEC60567	8.97		1.45	
1923	in house	10.00		3.22	
1947	IEC60567	8		-0.22	
6015	IEC60567	9	ex	1.50	Result excluded, see §4.1
6017	in house	8.332		0.35	

	normality	OK	OK
	n	38	23
	outliers	5 (+1ex)	1 (+1 excl)
	mean (n)	8.1283	8.2861
	st.dev. (n)	1.09360	1.06887
	R(calc.)	3.0621	2.9928
	R(IEC60567:11)	1.6257	1.6572

Compare R(Horwitz) = 2.6565

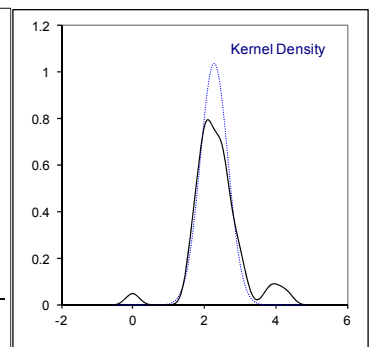
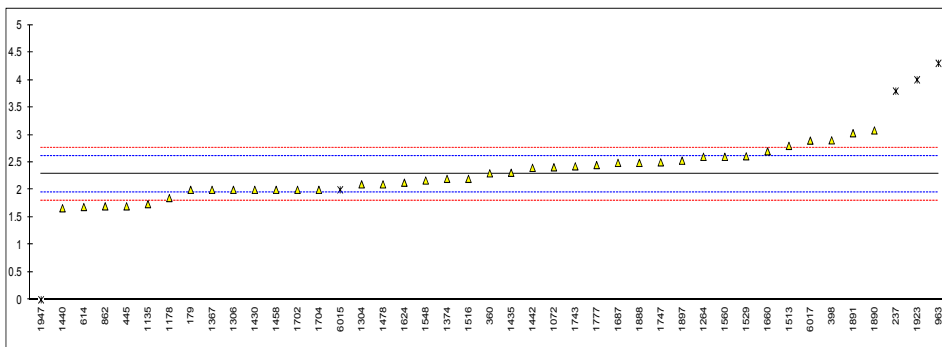


Determination of Ethane on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	2		-1.74	
237	D3612	3.795	R(0.05)	9.27	
360	IEC60567	2.3		0.10	
398	IEC60567	2.9		3.78	
445	IEC60567	1.7		-3.58	
511		----		----	
614	IEC60567	1.687		-3.66	
862	IEC60567	1.7		-3.58	
912	D3612C	<1		<-7.87	False negative test result?
963	D3612C	4.3	R(0.05)	12.37	
974		----		----	
1072	IEC60567	2.41		0.78	
1135	IEC60567	1.74	C	-3.33	First reported 5.32
1178	IEC60567	1.85		-2.66	
1264	D3612	2.6		1.94	
1304	INH-120	2.1		-1.12	
1306	D3612	2		-1.74	
1367	IEC60567	2		-1.74	
1374	D3612	2.2		-0.51	
1417		----		----	
1430	IEC60567	2		-1.74	
1435	IEC60567	2.31		0.16	
1440	D3612	1.665		-3.79	
1442	IEC60567	2.4		0.72	
1444		----		----	
1458	D3612	2		-1.74	
1478	IEC60567	2.1		-1.12	
1513	IEC60567	2.8		3.17	
1516	IEC60567	2.2		-0.51	
1529	IEC60567	2.61		2.00	
1548	IEC60567	2.17		-0.69	
1560	IEC60567	2.6		1.94	
1624	IEC60567	2.13		-0.94	
1660	IEC60567	2.7		2.56	
1687	IEC60567	2.49		1.27	
1702	IEC60567	2		-1.74	
1704	IEC60567	2		-1.74	
1743	IEC60567	2.4273		0.88	
1747	IEC60567	2.50		1.33	
1777	IEC60567	2.45		1.02	
1801	IEC60567	n.d		----	
1888	IEC60567	2.49		1.27	
1890	IEC60567	3.08		4.89	
1891	IEC60567	3.03		4.58	
1897	IEC60567	2.53		1.51	
1923	in house	4.00	R(0.05)	10.53	
1947	IEC60567	0	R(0.05)	-14.00	
6015	IEC60567	2	ex	-1.74	Result excluded, see §4.1
6017	in house	2.895		3.75	

	<u>Only Headspace results</u>
normality	OK
n	38
outliers	4 (+1 excl)
mean (n)	2.2833
st.dev. (n)	0.38722
R(calc.)	1.0842
R(IEC60567:11)	0.4567
	OK
	23
	1
	2.3247
	0.37365
	1.0462
	0.4694

Compare R(Horwitz) = 0.9034

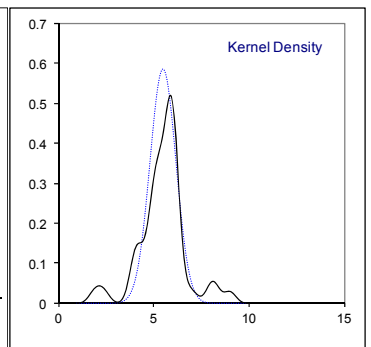
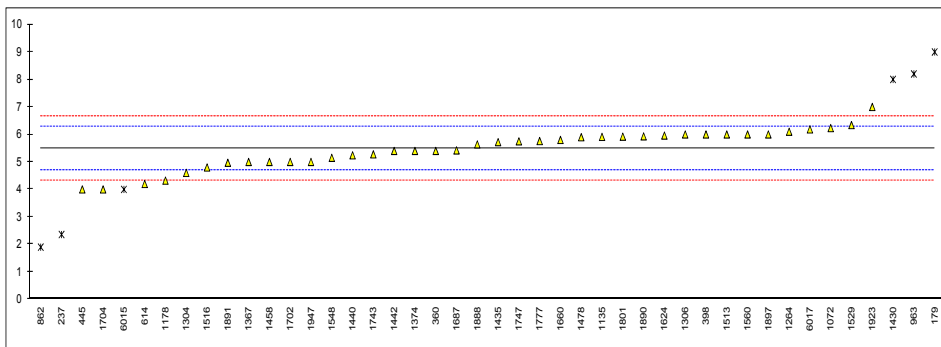


Determination of Ethene (ethylene) on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	9	R(0.05)	8.98	
237	D3612	2.360	R(0.05)	-7.97	
360	IEC60567	5.4		-0.21	
398	IEC60567	6.0		1.32	
445	IEC60567	4.0		-3.78	
511		----		----	
614	IEC60567	4.198		-3.28	
862	IEC60567	1.9	R(0.05)	-9.15	
912	D3612C	<1		<-11.45	False negative test result?
963	D3612C	8.2	R(0.05)	6.94	
974		----		----	
1072	IEC60567	6.23		1.91	
1135	IEC60567	5.91		1.09	
1178	IEC60567	4.32		-2.97	
1264	D3612	6.1		1.58	
1304	INH-120	4.6		-2.25	
1306	D3612	6		1.32	
1367	IEC60567	5		-1.23	
1374	D3612	5.4		-0.21	
1417		----		----	
1430	IEC60567	8	R(0.05)	6.43	
1435	IEC60567	5.72		0.61	
1440	D3612	5.24		-0.62	
1442	IEC60567	5.4		-0.21	
1444		----		----	
1458	D3612	5		-1.23	
1478	IEC60567	5.9		1.07	
1513	IEC60567	6.0		1.32	
1516	IEC60567	4.8		-1.74	
1529	IEC60567	6.34		2.19	
1548	IEC60567	5.15		-0.85	
1560	IEC60567	6		1.32	
1624	IEC60567	5.96		1.22	
1660	IEC60567	5.8		0.81	
1687	IEC60567	5.42		-0.16	
1702	IEC60567	5		-1.23	
1704	IEC60567	4		-3.78	
1743	IEC60567	5.2760		-0.53	
1747	IEC60567	5.75		0.68	
1777	IEC60567	5.76		0.71	
1801	IEC60567	5.92		1.12	
1888	IEC60567	5.64		0.40	
1890	IEC60567	5.93		1.14	
1891	IEC60567	4.97		-1.31	
1897	IEC60567	6.0		1.32	
1923	in house	7.00		3.88	
1947	IEC60567	5		-1.23	
6015	IEC60567	4	ex	-3.78	Result excluded, see §4.1
6017	in house	6.185		1.80	

	<u>Only Headspace results</u>
normality	OK
n	38
outliers	5 (+ 1 excl)
mean (n)	5.4821
st.dev. (n)	0.68161
R(calc.)	1.9085
R(IEC60567:11)	1.0964

Compare R(Horwitz) = 1.9011

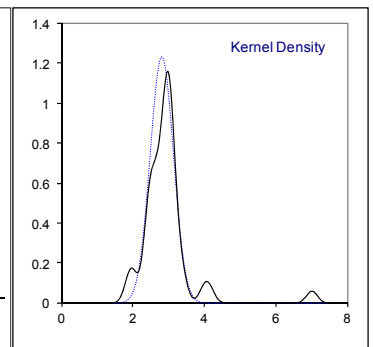
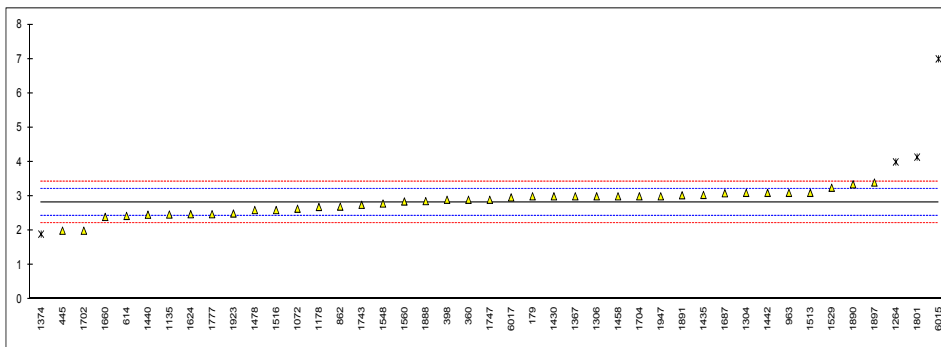


Determination of Ethyn (acetylene) on sample #15226; results in µ/L

lab	method	value	mark	z(targ)	remarks
179	D3612	3		0.90	
237	D3612	<1		<-9.03	False negative test result?
360	IEC60567	2.9		0.40	
398	IEC60567	2.9		0.40	
445	IEC60567	2.0		-4.07	
511		----		----	
614	IEC60567	2.430		-1.93	
862	IEC60567	2.7		-0.59	
912	D3612C	<1		<-9.03	False negative test result?
963	D3612C	3.1		1.40	
974		----		----	
1072	IEC60567	2.64		-0.89	
1135	IEC60567	2.47		-1.73	
1178	IEC60567	2.69		-0.64	
1264	D3612	4.0	R(0.05)	5.87	
1304	INH-120	3.1		1.40	
1306	D3612	3		0.90	
1367	IEC60567	3		0.90	
1374	D3612	1.9	R(0.05)	-4.56	
1417		----		----	
1430	IEC60567	3		0.90	
1435	IEC60567	3.04		1.10	
1440	D3612	2.465		-1.76	
1442	IEC60567	3.1		1.40	
1444		----		----	
1458	D3612	3		0.90	
1478	IEC60567	2.6	C	-1.09	First reported 4.6
1513	IEC60567	3.1		1.40	
1516	IEC60567	2.6		-1.09	
1529	IEC60567	3.25		2.14	
1548	IEC60567	2.79		-0.14	
1560	IEC60567	2.85		0.15	
1624	IEC60567	2.48		-1.68	
1660	IEC60567	2.4		-2.08	
1687	IEC60567	3.09		1.35	
1702	IEC60567	2		-4.07	
1704	IEC60567	3		0.90	
1743	IEC60567	2.7530		-0.33	
1747	IEC60567	2.90		0.40	
1777	IEC60567	2.48		-1.68	
1801	IEC60567	4.14	R(0.05)	6.56	
1888	IEC60567	2.86		0.20	
1890	IEC60567	3.35		2.64	
1891	IEC60567	3.03		1.05	
1897	IEC60567	3.4		2.89	
1923	in house	2.50		-1.58	
1947	IEC60567	3		0.90	
6015	IEC60567	7	R(0.01)	20.77	
6017	in house	2.968		0.74	

		<u>Only Headspace results</u>
normality	OK	OK
n	39	22
outliers	4	2
mean (n)	2.8189	2.8875
st.dev. (n)	0.32334	0.29769
R(calc.)	0.9054	0.8335
R(IEC60567:11)	0.5638	0.5775

Compare R(Horwitz) = 1.0805



Determination of Propane on sample #15226; results in µl/L

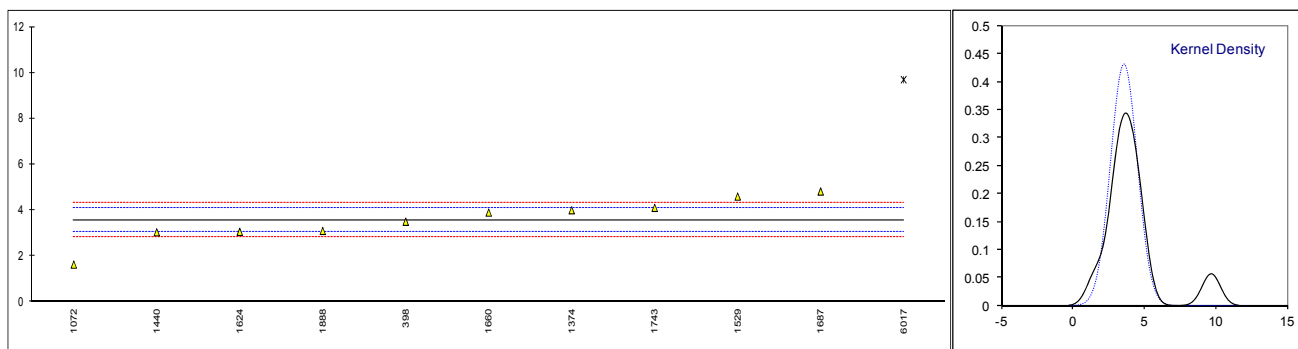
lab	method	value	mark	z(targ)	remarks
179		----		----	
237		----		----	
360		----		----	
398	IEC60567	<1		----	
445		----		----	
511		----		----	
614		----		----	
862		----		----	
912	D3612C	<1		----	
963		----		----	
974		----		----	
1072	D3612	<1		----	
1135		----		----	
1178		----		----	
1264		----		----	
1304		----		----	
1306		----		----	
1367		----		----	
1374	D3612	n.d.		----	
1417		----		----	
1430		----		----	
1435		----		----	
1440	D3612	0.00		----	
1442	IEC60567	<0.1		----	
1444		----		----	
1458		----		----	
1478		----		----	
1513		----		----	
1516		----		----	
1529	IEC60567	<0.1		----	
1548		----		----	
1560		----		----	
1624	IEC60567	<1		----	
1660	IEC60567	<0.5		----	
1687	IEC60567	<1		----	
1702		----		----	
1704		----		----	
1743	IEC60567	0		----	
1747		----		----	
1777		----		----	
1801		----		----	
1888	IEC60567	<1		----	
1890		----		----	
1891		----		----	
1897		----		----	
1923		----		----	
1947		----		----	
6015		----		----	
6017		----		----	
	n	12			
	mean (n)	<1			

Determination of Propene on sample #15226; results in µl/L

lab	method	value	mark	z(targ)	remarks
179		----		----	
237		----		----	
360		----		----	
398	IEC60567	3.5		-0.30	
445		----		----	
511		----		----	
614		----		----	
862		----		----	
912	D3612C	<1		<-10.09	False negative test result?
963		----		----	
974		----		----	
1072	D3612	1.63		-7.62	
1135		----		----	
1178		----		----	
1264		----		----	
1304		----		----	
1306		----		----	
1367		----		----	
1374	D3612	4.0		1.66	
1417		----		----	
1430		----		----	
1435		----		----	
1440	D3612	3.04		-2.10	
1442	IEC60567	<0,1		<-13.61	False negative test result?
1444		----		----	
1458		----		----	
1478		----		----	
1513		----		----	
1516		----		----	
1529	IEC60567	4.6		4.01	
1548		----		----	
1560		----		----	
1624	IEC60567	3.06		-2.02	
1660	IEC60567	3.9		1.27	
1687	IEC60567	4.82		4.87	
1702		----		----	
1704		----		----	
1743	IEC60567	4.1069		2.08	
1747		----		----	
1777		----		----	
1801		----		----	
1888	IEC60567	3.1		-1.86	
1890		----		----	
1891		----		----	
1897		----		----	
1923		----		----	
1947		----		----	
6015		----		----	
6017	in house	9.698	G(0.01)	23.97	

normality suspect
n 10
outliers 1
mean (n) 3.5757
st.dev. (n) 0.92709
R(calc.) 2.5959
R(IEC60567:11) 0.7151

Compare R(Horwitz) = 1.3224



APPENDIX 2**Extraction method used**

lab	Extraction method	remarks
179	Stripper Column (D3612B)	
237	Headspace	
360	Headspace	
398		
445		
511		
614	ToGas	
862		
912	Headspace	
963		
974		
1072	Toepler	
1135	Headspace	
1178	Toepler	
1264		
1304	Headspace	
1306	Headspace	
1367	Headspace	
1374	Headspace	
1417		
1430	Headspace	
1435	Headspace	
1440	Headspace	
1442	Headspace	
1444		
1458	Stripper Column (D3612B)	
1478	Toepler	
1513	Toepler	
1516	Headspace	
1529	Headspace	
1548	Headspace	
1560		
1624	Headspace	
1660	Headspace	
1687	Headspace	
1702		
1704	Multiple extraction system, toepler	
1743	Headspace	
1747	Toepler	
1777		
1801	Headspace	
1888	Headspace	
1890	Headspace	
1891	Headspace	
1897	Headspace	
1923		
1947	Mobile GC, extraction through shaking for 30s at room temp. Inside syringe	
6015	Headspace	
6017	Headspace	

APPENDIX 3

Number of participants per country

5 labs in AUSTRALIA
3 labs in BELGIUM
2 lab in BULGARIA
1 lab in CHINA, Peoples Republic of
1 lab in CROATIA
3 labs in FRANCE
4 labs in GERMANY
2 labs in INDIA
2 labs in ITALY
1 lab in MALAYSIA
1 lab in MOROCCO
2 labs in NETHERLANDS
1 lab in NIGERIA
1 lab in PERU
2 labs in PORTUGAL
1 lab in SAUDI ARABIA
1 lab in SERBIA
2 labs in SINGAPORE
1 lab in SLOVENIA
1 lab in SOUTH AFRICA
3 labs in SPAIN
1 labs in TURKEY
4 labs in UNITED ARAB EMIRATES
3 labs in UNITED KINGDOM
1 lab in UNITED STATES OF AMERICA

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
R(0.01)	= outlier in Rosner outlier test
R(0.05)	= straggler in Rosner outlier test
ex	= excluded from calculations
n.a.	= not applicable
n.d.	= not detected
W	= withdrawn on request of participant
U	= reported in deviating unit
E	= error in calculations
fr.	= first reported
SDS	= Safety Data Sheet

Literature:

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation, April 2014
- 2 prNEN 12766-2:2000.
- 3 ASTM E178-08
- 4 ASTM E1301-03
- 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 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), pp. 165-172, (1983)