

**Results of Proficiency Test  
Dissolved Gas Analysis  
November 2011**

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

**Author:** ing. L. Dijkstra  
**Corrector:** dr. R.G. Visser & ing. R. Starink  
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## **1 INTRODUCTION**

Since 2001, the Institute for Interlaboratory Studies organized a proficiency test for Transformer Oil every year. Since then several requests were received from laboratories to organize also a proficiency test for Dissolved Gas Analysis (DGA). The analytical test results of this DGA test are very important to evaluate the condition of a transformer oil. The first proficiency study for DGA was organized by iis in December 2007.

During the annual proficiency testing program 2011/2012, it was decided to continue the PT for Dissolved Gas Analysis.

In this international Interlaboratory study, 33 laboratories from 22 different countries have participated. See appendix 2 for the number of participants per country. In this report the results of the DGA proficiency test are presented and discussed.

## **2 SET UP**

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

In total one batch of 37 syringes (of 50 mL) was prepared (lot RN26) on October 26, 2011. The syringes were provided by Morgan Schaffer, Quebec, Canada (True North). Each syringe was uniquely numbered and one syringe was sent to each participating laboratory. Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

### **2.1 QUALITY SYSTEM**

The Institute for Interlaboratory Studies in Spijkensisse, the Netherlands, has implemented a quality system based on ISO guide 43, ILAC-G13:2007 and ISO17043:2010. This ensures 100% confidentiality of participant's data. Also customer's satisfaction is measured on regular basis by the distribution of questionnaires.

### **2.2 PROTOCOL**

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (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. The 50 mL gas tight syringes with sample material were prepared by Morgan Schaffer (Quebec, Canada) in accordance with principles outlined in ASTM Method D3612-01, Annex A2 (2001) and IEC 60567, clause 6.2 (1992). In total one batch of 37 syringes was prepared (lot RN26) on October 26, 2011. Each syringe was uniquely numbered and a certificate of analysis was provided by Morgan Schaffer. These certificates were removed after receipt by iis prior to the forwarding of the samples to the participating laboratories. The values, given on the Morgan Schaffer certificates are listed in below table:

	Syringe S/N	Ethane in µl/L	Ethylene in µl/L	CO <sub>2</sub> in µl/L	Oxygen in µl/L	Nitrogen in µl/L
sample #11107-1	8154	2.5	6.0	1350	22500	58300
sample #11107-2	8257	2.5	6.0	1350	22500	58300
sample #11107-3	8400	2.5	6.0	1350	22500	58300
sample #11107-4	8510	2.5	6.0	1350	22500	58300
sample #11107-5	8586	2.5	6.0	1350	22500	58300
sample #11107-6	8597	2.5	6.0	1350	22500	58300
sample #11107-7	8650	2.5	6.0	1350	22500	58300
sample #11107-8	8673	2.5	6.0	1350	22500	58300
sample #11107-9	8675	2.5	6.0	1350	22500	58300
sample #11107-10	8692	2.5	6.0	1350	22500	58300
sample #11107-11	8732	2.5	6.0	1350	22500	58300
sample #11107-12	8743	2.5	6.0	1350	22500	58300
sample #11107-13	8760	2.5	6.0	1350	22500	58300
sample #11107-14	8904	2.5	6.0	1350	22500	58300
sample #11107-15	8997	2.5	6.0	1350	22500	58300
sample #11107-16	9006	2.5	6.0	1350	22500	58300
sample #11107-17	9075	2.5	6.0	1350	22500	58300
sample #11107-18	9093	2.5	6.0	1350	22500	58300
sample #11107-19	9089	2.5	6.0	1350	22500	58300
sample #11107-20	9151	2.5	6.0	1350	22500	58300
sample #11107-21	9173	2.5	6.0	1350	22500	58300
sample #11107-22	9177	2.5	6.0	1350	22500	58300
sample #11107-23	9206	2.5	6.0	1350	22500	58300
sample #11107-24	9212	2.5	6.0	1350	22500	58300
sample #11107-25	9396	2.5	6.0	1350	22500	58300
sample #11107-26	9508	2.5	6.0	1350	22500	58300
sample #11107-27	9560	2.5	6.0	1350	22500	58300
sample #11107-28	9561	2.5	6.0	1350	22500	58300
sample #11107-29	9621	2.5	6.0	1350	22500	58300
sample #11107-30	9657	2.5	6.0	1350	22500	58300
sample #11107-31	9622	2.5	6.0	1350	22500	58300
sample #11107-32	9664	2.5	6.0	1350	22500	58300
sample #11107-33	9679	2.5	6.0	1350	22500	58300

sample #11107-34	9714	2.5	6.0	1350	22500	58300
sample #11107-35	9636	2.5	6.0	1350	22500	58300
sample #11107-36	9637	2.5	6.0	1350	22500	58300
sample #11107-37	9799	2.5	6.0	1350	22500	58300

Table 1: homogeneity test of sub samples #11107

From above data, the homogeneity of the prepared syringes was judged to be good for the proficiency test.

To each of the participating laboratories one syringe of 50 mL (labelled #11107) was sent on October 26, 2011.

## 2.5 STABILITY OF THE SAMPLES

Morgan Schaffer declare 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 #11107: 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, was sent together with each set of samples. Also a letter of instructions and a MSDS were added to the package as well as the Morgan Shaffer procedure how to deal with small gas bubbles in the syringe that may be present after transport.

## 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.

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.

### 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 results from a sample 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 3; nos.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 a target standard deviation, the z-scores were calculated using the IEC 60567 reproducibilities standard deviations. 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.

Absolute values for  $z < 2$  are very common and absolute values for  $z > 3$  are very rare. Therefore the usual interpretation of the 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 no problems were encountered during execution, except for one laboratory. This laboratory needed two more syringes to determine DGA. All participants did report one or more test results. In total 33 participating laboratories reported 299 numerical results. Observed were 18 outlying results, which is 6.0% 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.

All data sets proved to have a normal distribution. Two laboratories were excluded from the evaluation. One laboratory reported very low results for Hydrogen, Oxygen, Nitrogen, Carbon monoxide, Carbon dioxide and Methane. The other laboratory reported a very high results for Hydrogen and Carbon monoxide, Carbon dioxide, Methane and Ethene but very low result for Oxygen and Nitrogen. As the eight test results are not independent, it was decided not to use any of the eight test results of these two laboratories for the statistical evaluation.

- Hydrogen: The determination of this component was very problematic. Three statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers, not at all in agreement with the requirements of IEC 60657:2005.
- Oxygen: The determination of this component was problematic. Three statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers, not in agreement with the requirements of IEC 60657:2005.
- Nitrogen: The determination of this component was problematic. Five statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers not in agreement with the requirements of IEC 60657:2005.
- Carbon monoxide: The determination of this component was problematic. Three statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers not in agreement with the requirements of IEC 60657:2005.
- Carbon dioxide: The determination of this component was problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of IEC 60657:2005.
- Methane: The determination of this component was very problematic. No statistical outliers were observed. However, the calculated reproducibility is not at all in agreement with the requirements of IEC 60657:2005.
- Ethane: The determination of this component was very problematic. No statistical outliers were observed. However, the calculated reproducibility is not at all in agreement with the requirements of IEC 60657:2005.
- Ethene: The determination of this component was very problematic. Only one statistical outlier was observed. The calculated reproducibility is, after rejection of the statistical outlier, not at all in agreement with the requirements of IEC 60657:2005.
- Ethyn: The determination of this component was very problematic. Three statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers, not at all in agreement with the requirements of IEC 60657:2005.



Propane & Propene: To few analytical test results were received to draw any significant conclusions.

#### 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, derived from literature standards (in casu IEC 60657:2005) are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
Hydrogen H <sub>2</sub>	µl/L	28	23.9	16.7	4.8
Oxygen O <sub>2</sub>	mg/L	25	22.2	8.6	4.5
Nitrogen N <sub>2</sub>	mg/L	25	57.9	18.9	11.6
Carbon Monoxide CO	µl/L	29	173.8	67.6	34.7
Carbon Dioxide CO <sub>2</sub>	µl/L	31	1330.8	531.5	266.2
Methane CH <sub>4</sub>	µl/L	31	8.9	4.8	1.8
Ethane C <sub>2</sub> H <sub>6</sub>	µl/L	31	2.7	1.9	0.5
Ethene C <sub>2</sub> H <sub>4</sub>	µl/L	30	6.2	3.2	1.2
Ethyn C <sub>2</sub> H <sub>2</sub>	µl/L	27	2.5	1.7	0.5
Propane C <sub>3</sub> H <sub>8</sub>	µl/L	2	2.5	n.a	n.a
Propene C <sub>3</sub> H <sub>6</sub>	µl/L	7	4.1	n.a	n.a
Sum of Propane C <sub>3</sub> H <sub>8</sub> and Propene C <sub>3</sub> H <sub>6</sub>	µl/L	8	4.2	n.a	n.a

Table 2: Performance of the group on sample #11107

Without further statistical calculations it can be concluded from the overview given in table 2 that there is not a compliance of the performance of the group of participating laboratories with the relevant standard IEC 60657:2010.

The problematic components have been discussed in paragraph 4.1.

#### 4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2011 WITH PREVIOUS PTS

	November 2011	November 2010	November 2009	January 2009
Number of reporting labs	33	24	18	14
Number of results reported	299	218	182	140
Statistical outliers	18	10	9	8
Percentage outliers	6.0%	4.6%	5.0%	5.7%

Table 3: 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 compared against the requirements of the respective standards. The conclusions are given the following table:

Determination	November 2011	November 2010	November 2009	January 2009
Hydrogen H <sub>2</sub>	--	--	--	--
Oxygen O <sub>2</sub>	-	-	-	-
Nitrogen N <sub>2</sub>	-	-	--	--
Carbon Monoxide CO	-	-	--	--
Carbon Dioxide CO <sub>2</sub>	-	-	-	-
Methane CH <sub>4</sub>	--	-	--	-
Ethane C <sub>2</sub> H <sub>6</sub>	--	--	--	-
Ethene C <sub>2</sub> H <sub>4</sub>	--	-	--	-
Ethyn C <sub>2</sub> H <sub>2</sub>	--	--	--	-
Propane C <sub>3</sub> H <sub>8</sub>	n.e	n.e.	n.e	-
Propene C <sub>3</sub> H <sub>6</sub>	n.e	n.e.	n.e	-

Table 4: Comparison determinations against IEC 60657:2005

The performance of the determinations against the requirements of the respective standards is listed in the above table. The following performance categories were used:

- ++: group performed much better than the standard
- + : group performed better than the standard
- +/-: group performance equals the standard
- : group performed worse than the standard
- : group performed much worse than the standard
- n.e.: not evaluated

#### 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 µl/L	Consensus values from participants results in µl/L	Absolute differences in µl/L
Hydrogen H <sub>2</sub>	17	24	+7
Oxygen O <sub>2</sub>	22500	22267	-233
Nitrogen N <sub>2</sub>	58300	57892	-408
Carbon Monoxide CO	174	174	0
Carbon Dioxide CO <sub>2</sub>	1350	1331	-19
Methane CH <sub>4</sub>	8.5	8.9	+0.4
Ethane C <sub>2</sub> H <sub>6</sub>	2.5	2.7	+0.2
Ethene C <sub>2</sub> H <sub>4</sub>	6.0	6.2	+0.2
Ethyn C <sub>2</sub> H <sub>2</sub>	2.6	2.5	-0.1

Table 5: comparison of consensus values with values determined by Morgan Schaffer

No correlation could be found between the testing date and the reported results, see table 6:

laboratory	<i>actual testing date</i>	laboratory	<i>actual testing date</i>
398	unknown	1463	22 November 2011
445	18 November 2011	1473	12 November 2011
614	8 November 2011	1478	14 November 2011
963	unknown	1513	21 November 2011
1072	11 November 2011	1516	10 November 2011
1137	11 November 2011	1529	unknown
1178	4 November 2011	1626	unknown
1264	19 November 2011	1660	22 November 2011
1304	17 November 2011	1704	16 November 2011
1375	21 November 2011	1719	unknown
1435	3 November 2011	1801	9 November 2011
1439	20 November 2011	1923	14 November 2011
1440	4 November 2011	1924	8 November 2011
1442	4 November 2011	1925	7 November 2011
1452	4 November 2011	4445	17 November 2011
1453	7 November 2011	5445	17 November 2011
1458	19 November 2011		

Table 6: Actual testing dates

However, a correlation could be found between the methods used by the laboratories and the reported results. Seven laboratories (1072, 1178, 1452, 1478, 1513, 1516 and 1704) used the Toepler method (IEC 60567 clause 7.2), fifteen laboratories (445, 1137, 1264, 1304, 1375, 1435, 1439, 1440, 1442, 1453, 1473, 1626, 1660, 4445 and 5445) used the head-space method (IEC 60567 clause 7.5), three laboratories (1923, 1924 and 1925) used the Kelman method, one laboratory used partial extraction (1801) two laboratories (614, 1458) used the ToGas method, two laboratories (1463 and 1719) used the ASTM D3612-B stripper column extraction and three laboratories (398, 963 and 1529) did not report the extraction method that was used.

When the headspace method is compared with all other methods than it is noted that the results for headspace are higher for Oxygen, Carbon monoxide and Ethane. The results for Hydrogen, Nitrogen, Carbon dioxide, Methane, Ethene and Ethyn are lower for the headspace method than for all other methods.

The spread of the headspace results is larger than the spread of the results of the other test methods, except for Hydrogen, Nitrogen and Ethyn.

The three laboratories that did not report the used extraction method were excluded from the method comparison.

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 all smaller than the reproducibilities estimated using the Horwitz equation.

**APPENDIX 1**

Determination of Hydrogen on sample #11107; results in µl/L

lab	method	value	mark	z(targ)	remarks
398	EN60567	35.2		6.61	
445	IEC60567	16.7		-4.22	
614	IEC60567	30.629		3.94	
963	D3612C	12		-6.97	
1072	EN60567	23		-0.53	
1137	D3612	30.35786		3.78	
1178	IEC60567	35.52		6.80	
1264	D3612C	9.8	ex	-8.26	result excluded
1304	INH-120	27.644		2.19	
1375	IEC60567	44.4	DG(0.05)	12.00	
1430		----		----	
1435	IEC60567	24.20		0.17	
1439	IEC60567	29.47151		3.26	
1440	D3612-C	22.93		-0.57	
1442	IEC60567	18.382		-3.23	
1452	EN60567	64	G(0.01)	23.48	
1453	IEC60567	17.80		-3.58	
1458	D3612	26		1.23	
1463	D3612	25		0.64	
1473	IEC60567	22.73		-0.69	
1478	IEC60567	23.3		-0.35	
1513	IEC60567	24.8		0.52	
1516	IEC60567	28.9		2.92	
1529	IEC60567	25.4		0.88	
1626	IEC60567	45.1	DG(0.05)	12.41	
1660	IEC60567	30.8		4.04	
1702		----		----	
1704	IEC60567	n.d.		----	
1719	D3612B	25		0.64	
1801	EN60567	21.6		-1.35	
1923	in house	20		-2.29	
1924	in house	15		-5.22	
1925	in house	15		-5.22	
4445	IEC60567	24.4		0.29	
5445	IEC60567	17.6		-3.69	

normality OK  
n 28  
outliers 3  
mean (n) 23.906  
st.dev. (n) 5.9653  
R(calc.) 16.703  
R(IEC60567:05) 4.781

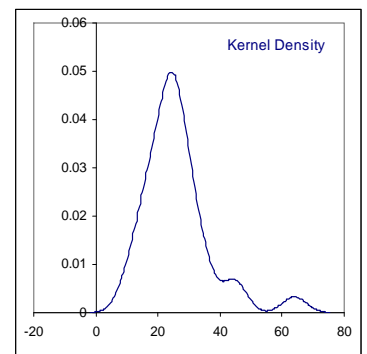
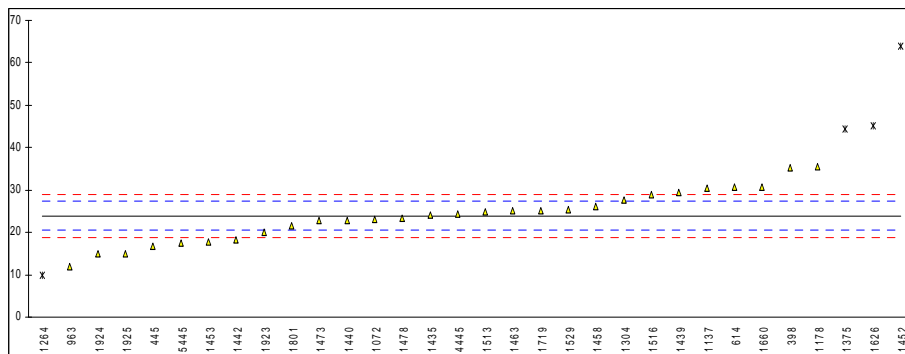
Only head space results:

OK  
12  
2  
23.585  
5.1788  
14.501  
4.781

All other results:

OK  
13  
1  
24.134  
5.7178  
16.010  
4.781

Compare R (Horwitz): 6.642



Determination of Oxygen on sample #11107; results in µl/L

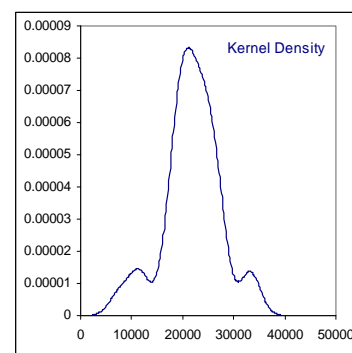
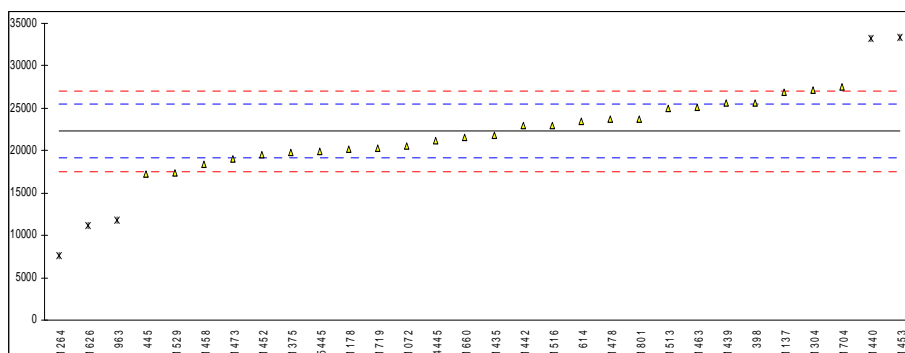
lab	method	value	mark	z(targ)	remarks
398	EN60567	25650		2.13	
445	IEC60567	17211.6		-3.18	
614	IEC60567	23512.12		0.78	
963	D3612C	11842	G(0.05)	-6.55	
1072	EN60567	20537		-1.09	
1137	D3612	26882.7		2.90	
1178	IEC60567	20189.1		-1.31	
1264	D3612C	7595	ex	-9.22	result excluded, see \$4.1
1304	INH-120	27180.38		3.09	
1375	IEC60567	19723		-1.60	
1430		----		----	
1435	IEC60567	21787.4		-0.30	
1439	IEC60567	25620.74		2.11	
1440	D3612-C	33254.01	G(0.05)	6.91	
1442	IEC60567	22925.500		0.41	
1452	EN60567	19586		-1.69	
1453	IEC60567	33300.35	G(0.05)	6.94	
1458	D3612	18401		-2.43	
1463	D3612	25118		1.79	
1473	IEC60567	19043.68		-2.03	
1478	IEC60567	23731		0.92	
1513	IEC60567	25000		1.72	
1516	IEC60567	23011.6		0.47	
1529	IEC60567	17400		-3.06	
1626	IEC60567	11122	ex	-7.01	result excluded, see \$4.1
1660	IEC60567	21521		-0.47	
1702		----		----	
1704	IEC60567	27458		3.26	
1719	D3612B	20277		-1.25	
1801	EN60567	23757.5		0.94	
1923		----		----	
1924		----		----	
1925		----		----	
4445	IEC60567	21211.6		-0.66	
5445	IEC60567	19941.1		-1.46	

normality OK  
n 25  
outliers 3  
mean (n) 22267.08  
st.dev. (n) 3057.821  
R(calc.) 8561.90  
R(IEC60567:05) 4453.42

Only head space results:  
OK  
11  
2  
22789.27  
4618.686  
12932.32  
4453.42

All other results:  
OK  
12  
0  
22548.19  
2721.449  
7620.06  
4453.42

Compare R (Horwitz): 2210.82



Determination of Nitrogen on sample #11107; results in µl/L

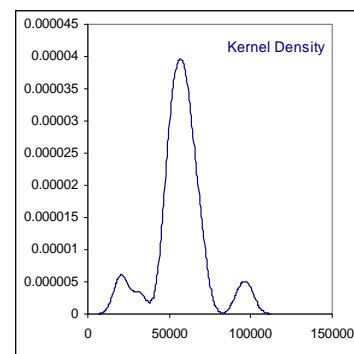
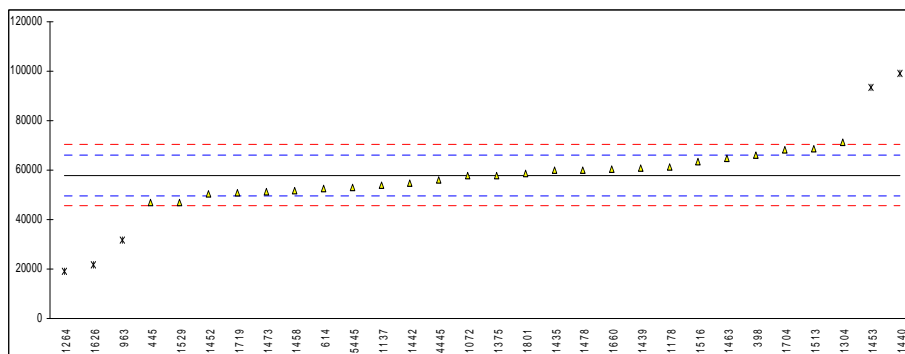
lab	method	value	mark	z(targ)	remarks
398	EN60567	65880		1.93	
445	IEC60567	46844.4		-2.67	
614	IEC60567	52490.53		-1.31	
963	D3612C	31685	G(0.05)	-6.34	
1072	EN60567	57695		-0.05	
1137	D3612	54022.5		-0.94	
1178	IEC60567	61324.3		0.83	
1264	D3612C	19014	DG(0.01)	-9.40	
1304	INH-120	71300.76		3.24	
1375	IEC60567	57718		-0.04	
1430		----		----	
1435	IEC60567	59870		0.48	
1439	IEC60567	60872.18		0.72	
1440	D3612-C	99147.93	DG(0.05)	9.98	
1442	IEC60567	54622.600		-0.79	
1452	EN60567	50353		-1.82	
1453	IEC60567	93555.36	DG(0.05)	8.62	
1458	D3612	51641		-1.51	
1463	D3612	64600		1.62	
1473	IEC60567	51451.69		-1.56	
1478	IEC60567	60076		0.53	
1513	IEC60567	68900		2.66	
1516	IEC60567	63284.9		1.30	
1529	IEC60567	47000		-2.63	
1626	IEC60567	21875	DG(0.01)	-8.71	
1660	IEC60567	60527		0.64	
1702		----		----	
1704	IEC60567	68312		2.52	
1719	D3612B	50869		-1.70	
1801	EN60567	58608.2		0.17	
1923		----		----	
1924		----		----	
1925		----		----	
4445	IEC60567	55890.0		-0.48	
5445	IEC60567	53140.3		-1.15	

normality OK  
n 25  
outliers 5  
mean (n) 57891.73  
st.dev. (n) 6748.849  
R(calc.) 18896.78  
R(IEC60567:05) 11578.35

Only head space results:  
OK  
11  
4  
56932.68  
6365.647  
17823.82  
11578.35

All other results:  
OK  
12  
0  
59012.83  
6607.642  
18501.40  
11578.37

Compare R (Horwitz): 4977.94

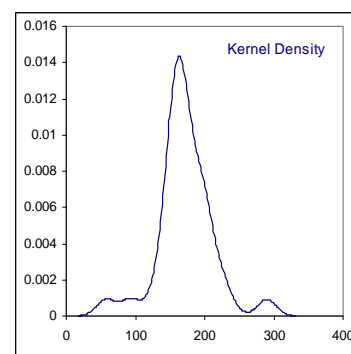
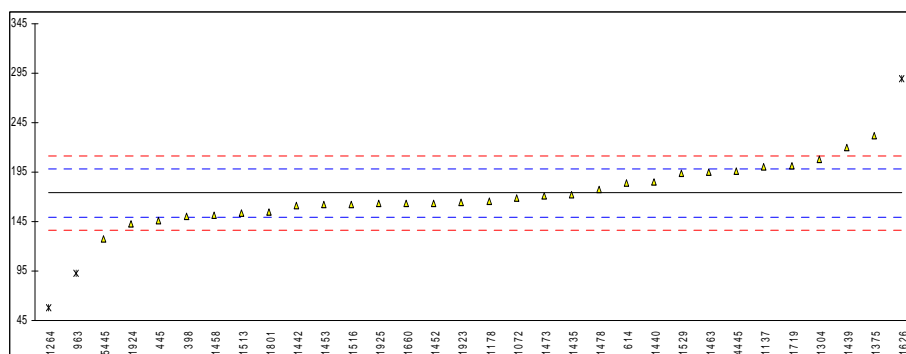


Determination of Carbon monoxide on sample #11107; results in µ/L

lab	method	value	mark	z(targ)	remarks
398	EN60567	150		-1.92	
445	IEC60567	146.5		-2.20	
614	IEC60567	184.356		0.85	
963	D3612C	93	D(0.05)	-6.51	
1072	EN60567	169		-0.39	
1137	D3612	200.2439		2.13	
1178	IEC60567	165.22		-0.69	
1264	D3612C	57.75	G(0.05)	-9.35	
1304	INH-120	208.214		2.77	
1375	IEC60567	232		4.69	
1430		-----		-----	
1435	IEC60567	171.72		-0.17	
1439	IEC60567	219.5392		3.68	
1440	D3612-C	185.76		0.96	
1442	IEC60567	160.941		-1.04	
1452	EN60567	164		-0.79	
1453	IEC60567	161.91		-0.96	
1458	D3612	152		-1.76	
1463	D3612	195		1.71	
1473	IEC60567	171.02		-0.23	
1478	IEC60567	178		0.34	
1513	IEC60567	153.8		-1.61	
1516	IEC60567	162.7		-0.90	
1529	IEC60567	194		1.62	
1626	IEC60567	290	G(0.05)	9.36	
1660	IEC60567	163.6		-0.82	
1702		-----		-----	
1704	IEC60567	n.d.		-----	
1719	D3612B	202		2.27	
1801	EN60567	154.8		-1.53	
1923	in house	165		-0.71	
1924	in house	143		-2.48	
1925	in house	163		-0.87	
4445	IEC60567	196.0		1.79	
5445	IEC60567	127.7		-3.72	

		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK	OK	OK
n	29	13	14
outliers	3	2	0
mean (n)	173.83	180.40	167.99
st.dev. (n)	24.154	29.898	16.632
R(calc.)	67.63	83.71	46.57
R(IEC60567:05)	34.77	34.77	34.77

Compare R (Horwitz): 35.83

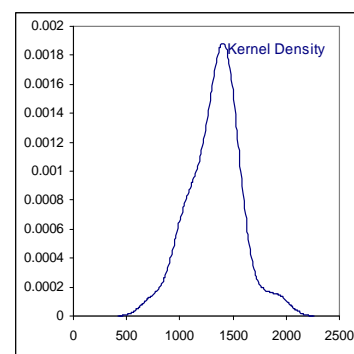
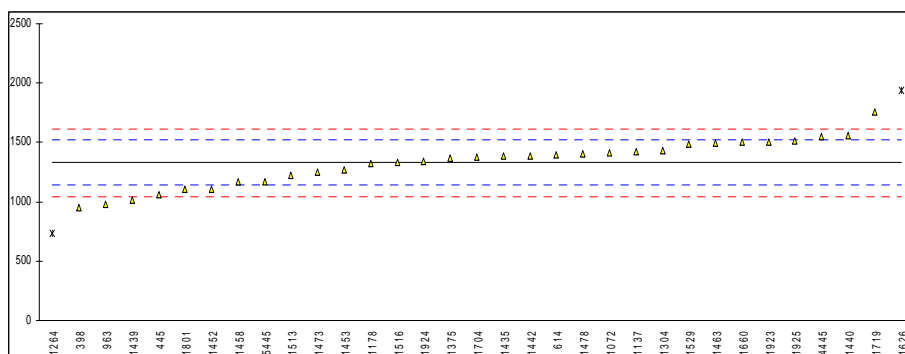


Determination of Carbon dioxide on sample #11107; results in µl/L

lab	method	value	mark	z(targ)	remarks
398	EN60567	952		-3.98	
445	IEC60567	1062.9		-2.82	
614	IEC60567	1397.293		0.70	
963	D3612C	981		-3.68	
1072	EN60567	1409		0.82	
1137	D3612	1426.545		1.01	
1178	IEC60567	1322.08		-0.09	
1264	D3612C	736.45	ex	-6.25	result excluded, see \$4.1 result
1304	INH-120	1427.38		1.02	
1375	IEC60567	1370		0.41	
1430		-----		-----	
1435	IEC60567	1388.49		0.61	
1439	IEC60567	1016.837		-3.30	
1440	D3612-C	1556.91		2.38	
1442	IEC60567	1388.652		0.61	
1452	EN60567	1105		-2.38	
1453	IEC60567	1268.27		-0.66	
1458	D3612	1171		-1.68	
1463	D3612	1494		1.72	
1473	IEC60567	1254.42		-0.80	
1478	IEC60567	1400		0.73	
1513	IEC60567	1220		-1.17	
1516	IEC60567	1332.8		0.02	
1529	IEC60567	1490		1.67	
1626	IEC60567	1940	ex	6.41	result excluded, see \$4.1 result result
1660	IEC60567	1505		1.83	
1702		-----		-----	
1704	IEC60567	1379		0.51	
1719	D3612B	1757		4.48	
1801	EN60567	1103.1		-2.40	
1923	in house	1506		1.84	
1924	in house	1340		0.10	
1925	in house	1510		1.89	
4445	IEC60567	1547.5		2.28	
5445	IEC60567	1172.4		-1.67	

		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK	OK	OK
n	31	13	15
outliers	0	0	0
mean (n)	1330.79	1337.33	1363.08
st.dev. (n)	189.829	173.147	171.945
R(calc.)	531.52	484.81	481.45
R(IEC60567:05)	266.16	266.16	266.16

Compare R (Horwitz): 201.91





Determination of Methane on sample #11107; results in µl/L

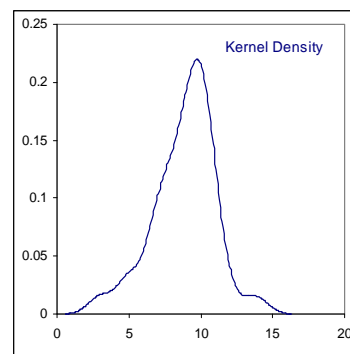
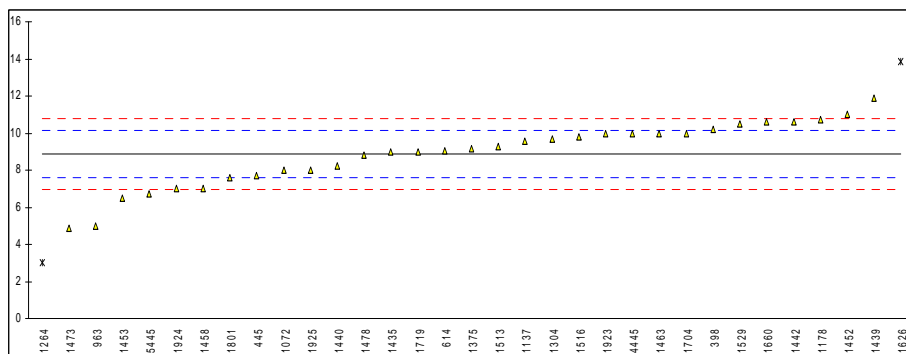
lab	method	value	mark	z(targ)	remarks
398	EN60567	10.2		2.07	
445	IEC60567	7.7		-1.87	
614	IEC60567	9.055		0.27	
963	D3612C	5		-6.12	
1072	EN60567	8		-1.40	
1137	D3612	9.5694		1.08	
1178	IEC60567	10.74		2.92	
1264	D3612C	3.0	ex	-9.27	result excluded, see \$4.1
1304	INH-120	9.669		1.23	
1375	IEC60567	9.15		0.42	
1430		-----		-----	
1435	IEC60567	8.98		0.15	
1439	IEC60567	11.86	C	4.69	first reported:9.807123
1440	D3612-C	8.22		-1.05	
1442	IEC60567	10.615		2.72	
1452	EN60567	11		3.33	
1453	IEC60567	6.52		-3.73	
1458	D3612	7		-2.97	
1463	D3612	10		1.76	
1473	IEC60567	4.88		-6.31	
1478	IEC60567	8.8		-0.14	
1513	IEC60567	9.3		0.65	
1516	IEC60567	9.8		1.44	
1529	IEC60567	10.5		2.54	
1626	IEC60567	13.85	ex	7.82	result excluded, see \$4.1
1660	IEC60567	10.6		2.70	
1702		-----		-----	
1704	IEC60567	10		1.76	
1719	D3612B	9		0.18	
1801	EN60567	7.6		-2.03	
1923	in house	10		1.76	
1924	in house	7		-2.97	
1925	in house	8		-1.40	
4445	IEC60567	10.0		1.76	
5445	IEC60567	6.7		-3.44	

normality OK  
n 31  
outliers 0  
mean (n) 8.89  
st.dev. (n) 1.712  
R(calc.) 4.79  
R(IEC60567:05) 1.78

Only head space results:  
OK  
13  
0  
8.80  
1.944  
5.44  
1.78

All other results:  
OK  
15  
0  
9.02  
1.275  
3.57  
1.78

Compare R (Horwitz): 2.86

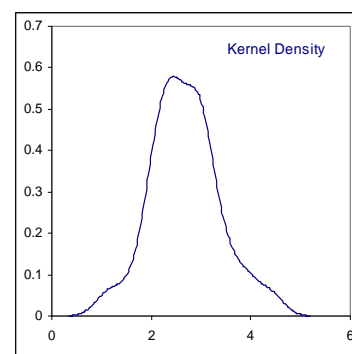
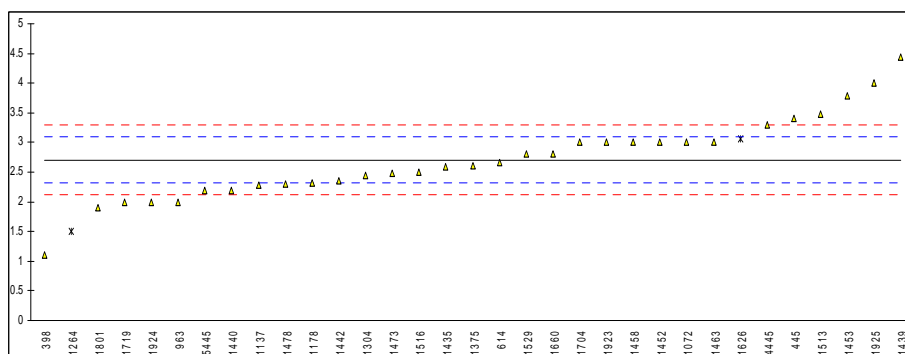


Determination of Ethane on sample #11107; results in µ/L

lab	method	value	mark	z(targ)	remarks
398	EN60567	1.1		-8.31	
445	IEC60567	3.4		3.58	
614	IEC60567	2.670		-0.20	
963	D3612C	2		-3.66	
1072	EN60567	3		1.51	
1137	D3612	2.28478		-2.19	
1178	IEC60567	2.32		-2.01	
1264	D3612C	1.51	ex	-6.19	result result excluded, see \$4.1
1304	INH-120	2.446		-1.36	
1375	IEC60567	2.61		-0.51	
1430		----		----	
1435	IEC60567	2.59		-0.61	
1439	IEC60567	4.43	C	8.90	first reported: 5.71843
1440	D3612-C	2.20		-2.63	
1442	IEC60567	2.357		-1.82	
1452	EN60567	3		1.51	
1453	IEC60567	3.79		5.59	
1458	D3612	3		1.51	
1463	D3612	3		1.51	
1473	IEC60567	2.48		-1.18	
1478	IEC60567	2.3		-2.11	
1513	IEC60567	3.48		3.99	
1516	IEC60567	2.5		-1.08	
1529	IEC60567	2.80		0.47	
1626	IEC60567	3.07	ex	1.87	result result excluded, see \$4.1
1660	IEC60567	2.8		0.47	
1702		----		----	
1704	IEC60567	3		1.51	
1719	D3612B	2		-3.66	
1801	EN60567	1.9		-4.18	
1923	in house	3		1.51	
1924	in house	2		-3.66	
1925	in house	4	C	6.68	first reported:7
4445	IEC60567	3.3		3.06	
5445	IEC60567	2.2		-2.63	

		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK	not OK	OK
n	31	13	15
outliers	0	0	0
mean (n)	2.71	2.84	2.74
st.dev. (n)	0.679	0.690	0.584
R(calc.)	1.90	1.93	1.64
R(IEC60567:05)	0.54	0.54	0.54

Compare R (Horwitz): 1.04

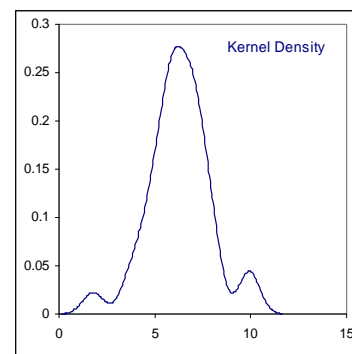
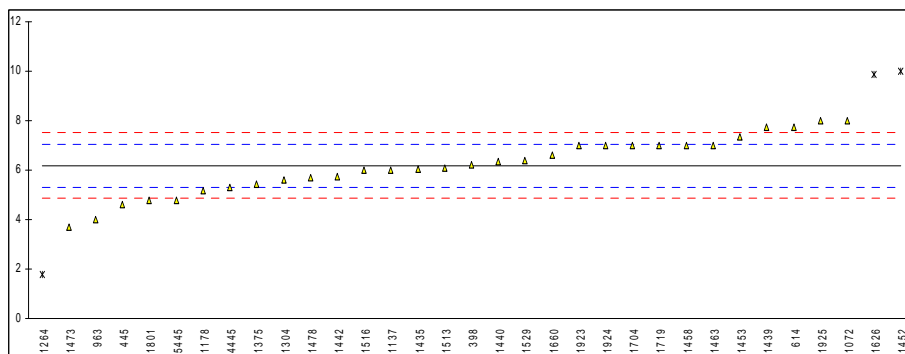


Determination of Ethene (ethylene) on sample #11107; results in µl/L

lab	method	value	mark	z(targ)	remarks
398	EN60567	6.2		0.05	
445	IEC60567	4.6		-3.58	
614	IEC60567	7.735		3.52	
963	D3612C	4		-4.94	
1072	EN60567	8		4.12	
1137	D3612	6.01833		-0.36	
1178	IEC60567	5.19		-2.24	
1264	D3612C	1.78	ex	-9.97	result result excluded, see \$4.1
1304	INH-120	5.617		-1.27	
1375	IEC60567	5.45		-1.65	
1430		-----		-----	
1435	IEC60567	6.04		-0.32	
1439	IEC60567	7.73	C	3.51	first reported 7.700631
1440	D3612-C	6.35		0.39	
1442	IEC60567	5.720		-1.04	
1452	EN60567	10	G(0.05)	8.66	
1453	IEC60567	7.36		2.67	
1458	D3612	7		1.86	
1463	D3612	7		1.86	
1473	IEC60567	3.68		-5.66	
1478	IEC60567	5.7		-1.09	
1513	IEC60567	6.1		-0.18	
1516	IEC60567	6.0		-0.41	
1529	IEC60567	6.39		0.48	
1626	IEC60567	9.85	ex	8.32	result result excluded, see \$4.1
1660	IEC60567	6.6		0.95	
1702		-----		-----	
1704	IEC60567	7		1.86	
1719	D3612B	7		1.86	
1801	EN60567	4.8		-3.13	
1923	in house	7		1.86	
1924	in house	7		1.86	
1925	in house	8		4.12	
4445	IEC60567	5.3		-1.99	
5445	IEC60567	4.8		-3.13	

		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK	OK	not OK
n	30	13	14
outliers	1	0	1
mean (n)	6.18	5.79	6.68
st.dev. (n)	1.138	1.101	0.989
R(calc.)	3.19	3.08	2.77
R(IEC60567:05)	1.24	1.24	1.24

Compare R (Horwitz): 2.10



Determination of Ethyn (acetylene) on sample #11107; results in µ/L

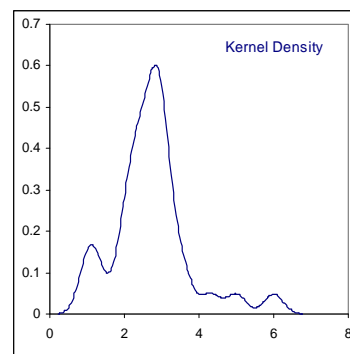
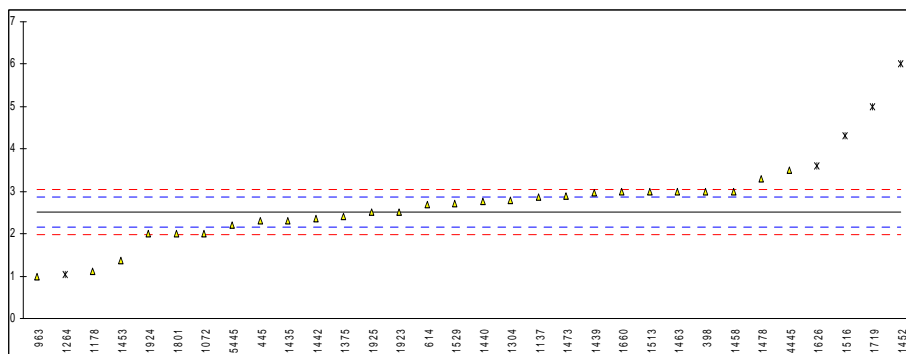
lab	method	value	mark	z(targ)	remarks
398	EN60567	3.0		2.78	
445	IEC60567	2.3		-1.13	
614	IEC60567	2.682		1.00	
963	D3612C	1		-8.41	
1072	EN60567	2		-2.81	
1137	D3612	2.86242		2.01	
1178	IEC60567	1.12		-7.73	
1264	D3612C	1.05	ex	-8.13	result result excluded, see \$4.1
1304	INH-120	2.791		1.61	
1375	IEC60567	2.42		-0.46	
1430		----		----	
1435	IEC60567	2.31		-1.08	
1439	IEC60567	2.96	C	2.56	first reported: 3.64988
1440	D3612-C	2.77		1.50	
1442	IEC60567	2.365		-0.77	
1452	EN60567	6	G(0.05)	19.56	
1453	IEC60567	1.38		-6.28	
1458	D3612	3		2.78	
1463	D3612	3		2.78	
1473	IEC60567	2.89		2.17	
1478	IEC60567	3.3		4.46	
1513	IEC60567	3.0		2.78	
1516	IEC60567	4.3	DG(0.05)	10.05	
1529	IEC60567	2.72		1.22	
1626	IEC60567	3.6	ex	6.14	result result excluded, see \$4.1
1660	IEC60567	3.0		2.78	
1702		----		----	
1704	IEC60567	n.d.		----	
1719	D3612B	5	DG(0.05)	13.97	
1801	EN60567	2.0		-2.81	
1923	in house	2.5		-0.01	
1924	in house	2.0		-2.81	
1925	in house	2.5		-0.01	
4445	IEC60567	3.5		5.58	
5445	IEC60567	2.2		-1.69	

normality OK  
n 27  
outliers 3  
mean (n) 2.50  
st.dev. (n) 0.619  
R(calc.) 1.73  
R(IEC60567:05) 0.500

Only head space results:  
OK  
13  
0  
2.60  
0.519  
1.45  
0.50

All other results:  
OK  
11  
3  
2.46  
0.637  
1.78  
0.50

Compare R (Horwitz): 0.98



## Determination of Propane and Propene on sample #11107; results in µl/L

lab	method	Propane	Propene	Sum of Propane & and Propene	remarks
398	EN60567	<1	<1	<1	
445		----	----	----	
614		----	----	----	
963	D3612C	n.d.	n.d.	n.d.	
1072		----	----	----	
1137	D3612	4.97254	----	4.97254	
1178		----	----	----	
1264	D3612C	2.6	0.0	2.6	results excluded, see § 4.1*
1304		----	----	----	
1375	IEC60567	<0.5	3.40	3.40	
1430		----	----	----	
1435		----	----	----	
1439		----	----	----	
1440	D3612-C	n.d.	3.81	3.81	
1442		----	1.743	1.743	
1452	EN60567	<1	6	6	
1453		----	----	----	
1458		----	----	----	
1463		----	----	----	
1473		----	----	----	
1478		----	----	----	
1513		----	----	----	
1516		----	4.2	4.2	
1529	IEC60567	0.11	4.5	4.61	
1626		----	----	----	
1660	IEC60567	<0.1	5.2	5.2	
1702		----	----	----	
1704		----	----	----	
1719	D3612B	n.d.	n.d.	n.d.	
1801		----	----	----	
1923		----	----	----	
1924		----	----	----	
1925		----	----	----	
4445		----	----	----	
5445		----	----	----	
	normality	not OK	OK	OK	
	n	2	7	8	
	outliers	0	0	0	
	mean (n)	2.54	4.12	4.24	
	st.dev. (n)	n.a	n.a	n.a	
	R(calc.)	n.a	n.a	n.a	
	R(IEC60567:05)	n.a	n.a	n.a	

## **APPENDIX 2**

### **Number of participants per country**

3 labs in AUSTRALIA  
1 lab in BELGIUM  
4 labs in BULGARIA  
1 lab in CANADA  
1 lab in CROATIA  
2 labs in FRANCE  
2 labs in GERMANY  
1 lab in INDIA  
1 lab in ISRAEL  
2 labs in ITALY  
1 lab in KINGDOM OF BAHRAIN  
1 lab in KOREA  
1 lab in MALAYSIA  
1 lab in NEW ZEALAND  
2 labs in PORTUGAL  
1 lab in SAUDI ARABIA  
1 lab in SLOVENIA  
3 labs in SPAIN  
1 lab in SWEDEN  
1 lab in THE NETHERLANDS  
1 lab in U.A.E.  
1 lab in UNITED KINGDOM

## APPENDIX 3

### Abbreviations:

C	= final result after checking of first reported suspect result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
ex	= excluded from calculations
n/a	= not applicable
W	= withdrawn on request participant
U	= reported in wrong unit
E	= error in calculations
SDS	= Safety Data Sheet

### Literature:

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