

**Results of Proficiency Test
Dissolved Gas Analysis
November 2009**

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

1	INTRODUCTION.....	3
2	SET UP.....	3
2.1	QUALITY SYSTEM.....	3
2.2	PROTOCOL.....	3
2.3	CONFIDENTIALITY STATEMENT.....	4
2.4	SAMPLES.....	4
2.5	STABILITY OF THE SAMPLES.....	5
2.6	ANALYSES.....	5
3	RESULTS.....	5
3.1	STATISTICS.....	5
3.2	GRAPHICS.....	6
3.3	Z-SCORES.....	6
4	EVALUATION.....	7
4.1	EVALUATION PER TEST.....	7
4.2	PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES.....	9
4.3	COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2009 WITH PREVIOUS PTS.....	9
4.4	DISCUSSION.....	10

Appendices:

1.	Data and statistical results.....	12
2.	List of participants.....	22
3.	Abbreviations and literature.....	23

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. 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 2009/2010, it was decided to continue the PT for Dissolved Gas Analysis.

In this international Interlaboratory study, 18 laboratories from 11 different countries have participated. See appendix 3 for a list of 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 Spijkenisse, The Netherlands, was the organizer of this proficiency test.

One batch of 50 mL DGA syringes to be used was prepared by Morgan Schaffer, Quebec, Canada (True North). Each syringe was uniquely numbered and per syringe a certificate of analysis was provided by Morgan Schaffer.

Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

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

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 November 2008 (iis-protocol, version 3.1).

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 of 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 necessary 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 21 syringes was prepared (lot BG32) on October 18, 2009. 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 syringes to the participating laboratories.

The values, given on the Morgan and Schaffer certificates are listed in below table:

	Syringe	Ethane in $\mu\text{L/L}$	Ethylene in $\mu\text{L/L}$	CO ₂ in $\mu\text{L/L}$	Oxygen in $\mu\text{L/L}$	Nitrogen in $\mu\text{L/L}$
sample #09DGA-1	3429	2.6	6.3	1390	21400	54300
sample #09DGA-2	4198	2.6	6.3	1390	21400	54300
sample #09DGA-3	4251	2.6	6.3	1390	21400	54300
sample #09DGA-4	4288	2.6	6.3	1390	21400	54300
sample #09DGA-5	4323	2.6	6.3	1390	21400	54300
sample #09DGA-6	4486	2.6	6.3	1390	21400	54300
sample #09DGA-7	4514	2.6	6.3	1390	21400	54300
sample #09DGA-8	4543	2.6	6.3	1390	21400	54300
sample #09DGA-9	4572	2.6	6.3	1390	21400	54300
sample #09DGA-10	4601	2.6	6.3	1390	21400	54300
sample #09DGA-11	4603	2.6	6.3	1390	21400	54300
sample #09DGA-12	4607	2.6	6.3	1390	21400	54300
sample #09DGA-13	4627	2.6	6.3	1390	21400	54300
sample #09DGA-14	4673	2.6	6.3	1390	21400	54300
sample #09DGA-15	4770	2.6	6.3	1390	21400	54300
sample #09DGA-16	4771	2.6	6.3	1390	21400	54300
sample #09DGA-17	4797	2.6	6.3	1390	21400	54300
sample #09DGA-18	4807	2.6	6.3	1390	21400	54300
sample #09DGA-19	4812	2.6	6.3	1390	21400	54300
sample #09DGA-20	4819	2.6	6.3	1390	21400	54300
sample #09DGA-21	4823	2.6	6.3	1390	21400	54300

Table 1: homogeneity test of subsamples #09DGA

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

To each of the participating laboratories one syringe of 50 mL (labelled #09DGA) was sent on October 26, 2009.

2.5 STABILITY OF THE SAMPLES

Morgan and Schaffer declare that bulk storage prior to shipping has a shelf life of at least 12 months. Shelf life of the samples is at least 1 month from date of delivery.

This was assumed to be sufficient for the proficiency testing purposes.

2.6 ANALYSES

The participants were asked to determine on sample #09DGA: Hydrogen, Oxygen, Nitrogen, Carbon Monoxide, Carbon Dioxide, Methane, Ethane, Ethene, Ethyn, Propane and Propene. Also the limit of detection and 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 as well as the Morgan and 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 November 2008 (iis-protocol, version 3.1).

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 G(0.01) for the Dixon test and by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by G(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 3; nr.13 and 14).

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against a target standard deviation, the z-scores were calculated using the IEC 60567 reproducibility 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 standard uncertainty (u_x) was calculated from the (target) standard deviation in accordance with ISO13528, paragraph 5.6 (see appendix 3, nr. 15):

$$u_x = 1.23 * (\text{st.dev} (n)) / \sqrt{n}$$

In ISO13528 [5] is stated that if $u_x \geq 0.3 * \text{standard deviation}$ for proficiency testing, the uncertainty of the assigned value is not negligible and need to be included in the interpretation of the results of the proficiency test. Therefore in these cases (hydrogen,

nitrogen, carbon monoxide, methane, ethane, ethylene, acetylene) z'-scores were calculated in stead of the usual z-scores.

The z-scores were calculated in accordance with:

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

The $z'_{(\text{target})}$ were calculated in accordance with ISO13528 paragraph 7.6:

$$z'_{(\text{target})} = (\text{result} - \text{mean of PT}) / \sqrt{((\text{target standard deviation})^2 + (u_x)^2)}$$

Absolute values for $z < 2$ are very common and absolute values for $z > 3$ are very rare. The evaluation of $z'_{(\text{target})}$ is not different as for common z-scores and both are evaluated as follows:

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

4 EVALUATION

No problems were encountered during execution. All syringes arrived at the participating laboratories in good order. Two laboratories reported a small air bubble present upon arrival. In total 18 participants reported 182 numerical results.

Observed were 9 outlying results, which is 5.0 % 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. The methods, which are used by the various laboratories, are taken into account for explaining the observed differences when possible and applicable. These methods are also in the tables together with the original data. The abbreviations, used in these tables, are listed in appendix 3.

All original data sets proved to have a normal distribution.

Hydrogen: The determination of this component is problematic. No statistical outliers were detected, but the calculated reproducibility is not at all in agreement with the requirements of IEC 60567:2005.

Oxygen: The determination of this component is problematic. Three statistical outliers were detected and the calculated reproducibility is, even after exclusion of the statistical outliers, not in agreement with the requirements of IEC 60567:2005.

Nitrogen: The determination of this component is problematic. Only one statistical outlier was detected, but the calculated reproducibility is, after exclusion of the statistical outlier, not at all in agreement with the requirements of IEC 60567:2005. The data is clearly bimodally divided with maxima at 38.4 mg/L and 66.6 mg/L.

Carbon monoxide: The determination of this component is problematic. No statistical outliers were detected, but the calculated reproducibility is not at all in agreement with the requirements of IEC 60567:2005.

Carbon dioxide: The determination of this component is problematic. Three statistical outliers were detected and the calculated reproducibility is, even after exclusion of the statistical outliers, not in agreement with the requirements of IEC 60567:2005.

Methane: The determination of this component is problematic. Only one statistical outlier was detected, but the calculated reproducibility is, after exclusion of the statistical outlier, not at all in agreement with the requirements of IEC 60567:2005.

Ethane: The determination of this component is problematic. No statistical outliers were detected, but the calculated reproducibility is not at all in agreement with the requirements of IEC 60567:2005.

Ethene: The determination of this component is problematic. No statistical outliers were detected, but the calculated reproducibility is not at all in agreement with the requirements of IEC 60567:2005.

Ethyn: The determination of this component is problematic. Only one statistical outlier was detected, but the calculated reproducibility is, after exclusion of the statistical outlier, not at all in agreement with the requirements of IEC 60567:2005.

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 sample, calculated reproducibilities and reproducibilities, derived from literature standards (in casu IEC 60567:2005) are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
Hydrogen H ₂	µL/L	18	18.5	15.9	5.9
Oxygen O ₂	mL/L	15	21.99	11.50	4.40
Nitrogen N ₂	mL/L	17	54.47	42.21	16.65
Carbon Monoxide CO	µL/L	18	161	159	56.2
Carbon Dioxide CO ₂	µL/L	15	1360	484	272
Methane CH ₄	µL/L	17	8.5	7.3	2.8
Ethane C ₂ H ₆	µL/L	17	2.4	2.4	0.9
Ethene C ₂ H ₄	µL/L	18	5.7	6.0	2.1
Ethyn C ₂ H ₂	µL/L	15	2.9	2.8	1.1
Propane C ₃ H ₈	µL/L	3	n/a	n/a	n/a
Propene C ₃ H ₆	µL/L	4	n/a	n/a	n/a
Sum of Propane C ₃ H ₈ and Propene C ₃ H ₆	µL/L	5	5.1	3.8	n/a

Table 2: Performance of the group for sample #09DGA

Without further statistical calculations it can be concluded that for most 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 NOVEMBER 2009 WITH PREVIOUS PTS

	<i>November 2009</i>	<i>January 2009</i>	<i>December 2007</i>
Number of reporting labs	18	14	13
Number of results reported	182	140	129
Statistical outliers	9	8	7
Percentage outliers	5.0%	5.7%	5.4%

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	<i>November 2009</i>	<i>January 2009</i>	<i>December 2007</i>
Hydrogen H ₂	--	--	--
Oxygen O ₂	-	-	--
Nitrogen N ₂	--	--	--
Carbon Monoxide CO	--	--	--
Carbon Dioxide CO ₂	-	-	--
Methane CH ₄	--	-	--
Ethane C ₂ H ₆	--	-	--
Ethene C ₂ H ₄	--	-	--
Ethyn C ₂ H ₂	--	-	--
Propane C ₃ H ₈	n.e.	-	--
Propene C ₃ H ₆	n.e.	-	--

table 4: comparison determinations against IEC 60567:2005

In 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 and Schaffer in the following table. From this comparison it is clear that all consensus values as determined in this PT are well in line with the values as determined during the preparation of the syringes.

Parameter	Average values by Morgan and Schaffer in $\mu\text{L/L}$	Consensus values from participants results in $\mu\text{L/L}$	Absolute differences in $\mu\text{L/L}$
Hydrogen H_2	14	18.5	+4.5
Oxygen O_2	21.40	21.99	+0.59
Nitrogen N_2	54.30	54.47	+0.17
Carbon Monoxide CO	177	161	-16
Carbon Dioxide CO_2	1390	1360	-30
Methane CH_4	9.2	8.5	-0.7
Ethane C_2H_6	2.6	2.4	-0.2
Ethene C_2H_4	6.3	5.7	-0.6
Ethyn C_2H_2	3.1	2.9	-0.2

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

No correlation could be found between the testing date and the reported results, see table 4:

laboratory	<i>actual testing date</i>
398	unknown
445	20 November 2009
614	13 November 2009
963	30 November 2009
1072	03 November 2009
1152	02 November 2009
1304	14 November 2009
1430	11 November 2009
1435	06 November 2009
1505	12 November 2009
1513	20 November 2009
1516	09 November 2009
1529	06 November 2009
1660	16 November 2009
1702	11 November 2009
1719	unknown
1801	13 November 2009
9445	20 November 2009

table 6: actual testing dates

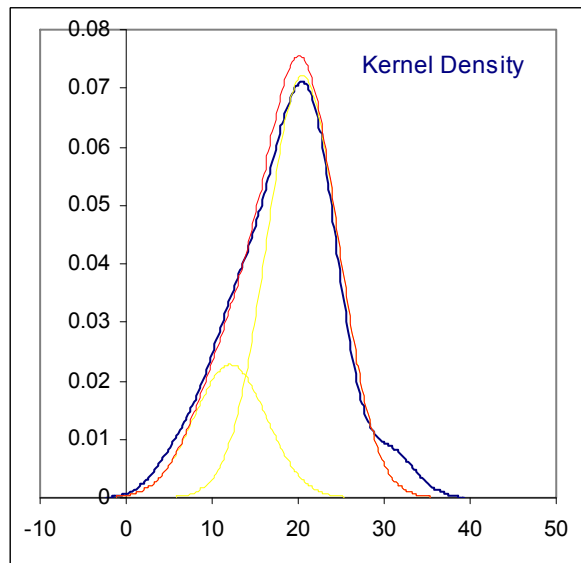
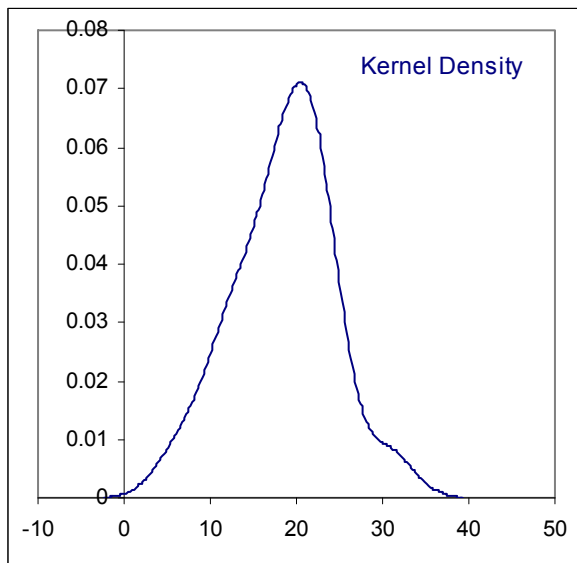
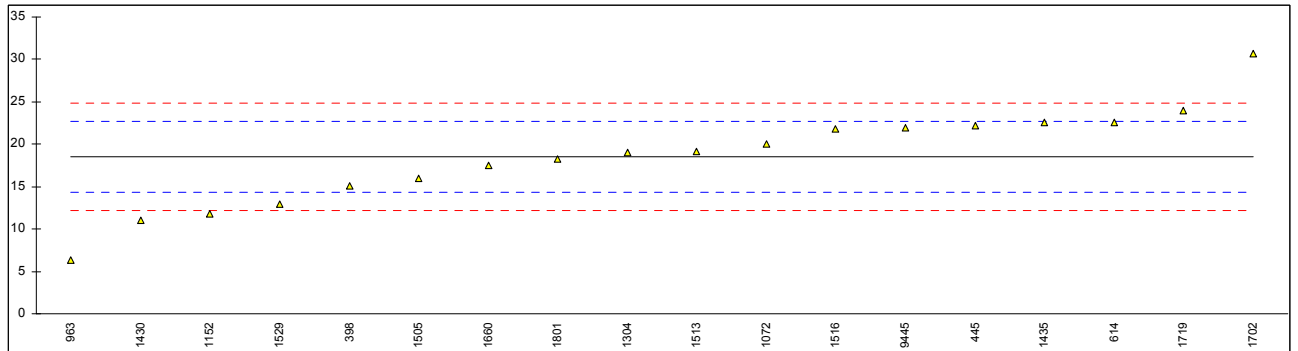
However, a correlation could be found between the methods used by the laboratories and the reported results. Four laboratories (1072, 1513, 1516 and 1702) used the Toepler method (IEC 60567 clause 7.2), ten laboratories (398, 445, 963, 1152, 1430, 1435, 1505, 1529, 1660 and 9445) used the head-space method (IEC 60567 clause 7.5), two laboratories used partial extraction (1304 and 1801), one laboratory (1719) used ASTM D3612-B stripper column extraction and one laboratory did not report the extraction method used. It is remarkable to note that the headspace results are the lowest observed for all components. The spread of the 10 headspace results is larger than the spread of the 8 results of the other test methods, again for all components. For several components a bimodal data distribution was clearly observed.

APPENDIX 1

Determination of Hydrogen on sample #09DGA; results in µL/L

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	15.1		-1.61	
445	IEC60567	22.2		1.75	
614	IEC60567	22.59		1.94	
963	ASTM D3612C	6.4		-5.72	
1072	EN60567	20		0.71	
1152	ASTM D3612	11.7756		-3.18	
1304	ACM120	19		0.24	
1430	IEC60567	11		-3.55	
1435	IEC60567	22.58		1.93	
1505	ASTM D3612C	16.0		-1.18	
1513	IEC60567	19.21		0.34	
1516	IEC60567	21.8		1.56	
1529	IEC60567	12.9		-2.65	
1660	IEC60567	17.5		-0.47	
1702	IEC60567	30.72		5.78	
1719	ASTM D3612B	24		2.60	
1801	IEC60567	18.2		-0.14	
9445	IEC60567	22.0		1.66	

		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	18	10	8
outliers	0	0	0
mean (n)	18.50	15.75	21.94
st.dev. (n)	5.693	5.424	4.064
R(calc.)	15.94	15.19	11.38
R(IEC60567)	3.70	3.15	4.39
U(mean)	1.65		
R'(IEC60567)	5.92		
		Compare R(Horwitz) = 5.34	



Determination of Oxygen on sample #09DGA; results in µL/L

lab	method	value	mark	z(target)	remarks
398	IEC60567	3100	DG(0.05)	-12.03	
445	IEC60567	22672.1		0.43	
614	IEC60567	25227.01		2.06	
963	ASTM D3612C	5982	DG(0.05)	-10.19	
1072	EN60567	24680		1.71	
1152	ASTM D3612	16050.87		-3.78	
1304	ACM120	24005		1.28	
1430	IEC60567	15984		-3.82	
1435	IEC60567	23037		0.67	
1505	ASTM D3612C	11485.1	G(0.05)	-6.69	
1513	IEC60567	24723		1.74	
1516	IEC60567	25343.4		2.13	
1529	IEC60567	15500		-4.13	
1660	IEC60567	19565		-1.54	
1702	IEC60567	21880.39		-0.07	
1719	ASTM D3612B	17683		-2.74	
1801	IEC60567	29076		4.51	
9445	IEC60567	24447		1.56	

normality OK
 n 15
 outliers 3
 mean (n) 21991.6
 st.dev. (n) 4107.55
 R(calc.) 11501.1
 R(IEC60567) 4398.3

 U(mean) 1304.5
 R'(IEC60567) n/a

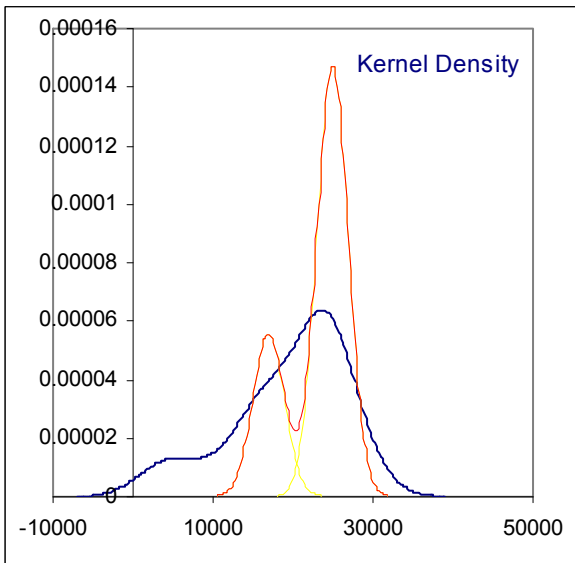
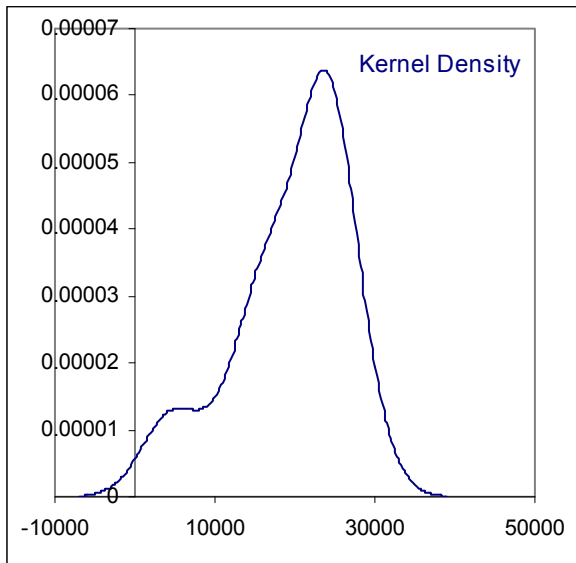
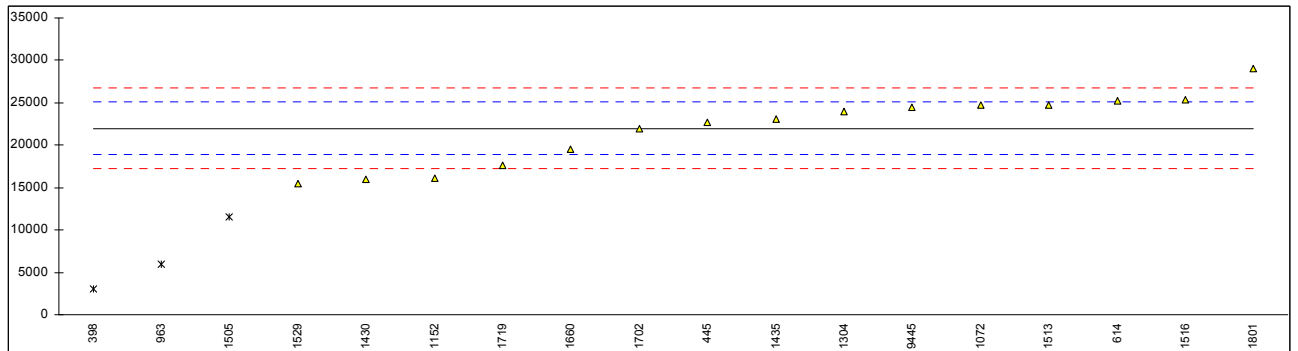
Only head space results:

10
 0
 15782.3
 7188.19
 20126.9
 3156.5

All other results:

8
 0
 24077.2
 2360.38
 9129.1
 4815.4

Compare R(Horwitz) = 2187.6



Determination of Nitrogen on sample #09DGA; results in µL/L

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	30150		-4.09	
445	IEC60567	57662.1		0.54	
614	IEC60567	66215.14		1.98	
963	ASTM D3612C	12910	G(0.05)	-6.99	
1072	EN60567	57619		0.53	
1152	ASTM D3612	37097.49		-2.92	
1304	ACM120	62802		1.40	
1430	IEC60567	32356		-3.72	
1435	IEC60567	45832		-1.45	
1505	ASTM D3612C	37940.1		-2.78	
1513	IEC60567	65952		1.93	
1516	IEC60567	65771.8		1.90	
1529	IEC60567	41000		-2.26	
1660	IEC60567	43987		-1.76	
1702	IEC60567	75279.98		3.50	
1719	ASTM D3612B	74929		3.44	
1801	IEC60567	69167		2.47	
9445	IEC60567	62206		1.30	

normality OK
n 17
outliers 1
mean (n) 54468.6
st.dev. (n) 15074.81
R(calc.) 42209.5
R(IEC60567) 10893.7

U(mean) 4497.1
R'(IEC60567) 16650.2

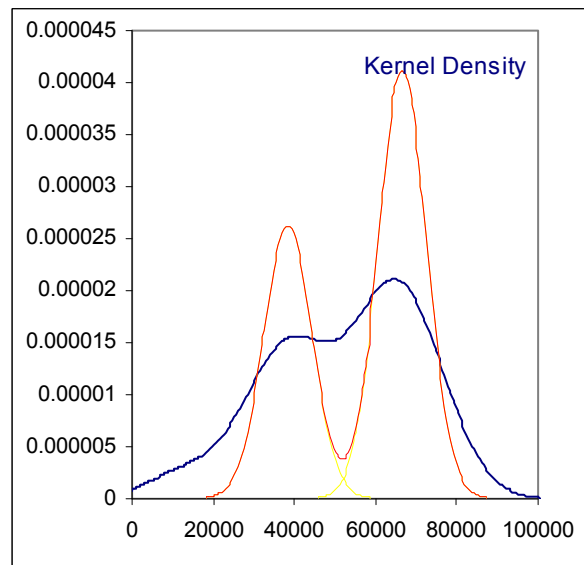
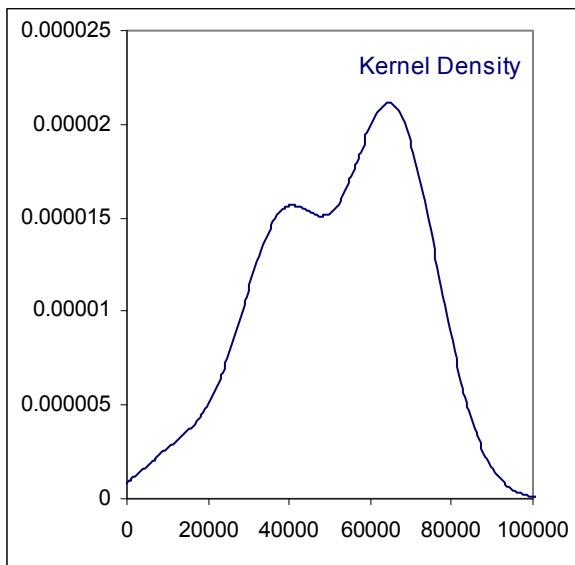
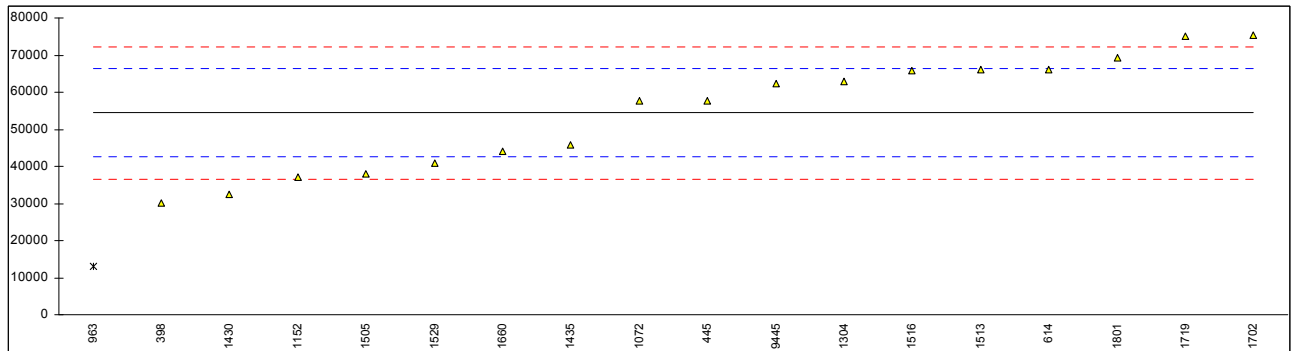
Only head space results:

9
1
40144.1
13975.47
39131.3
8028.8

All other results:

8
0
67217.0
5911.19
16551.3
13443.4

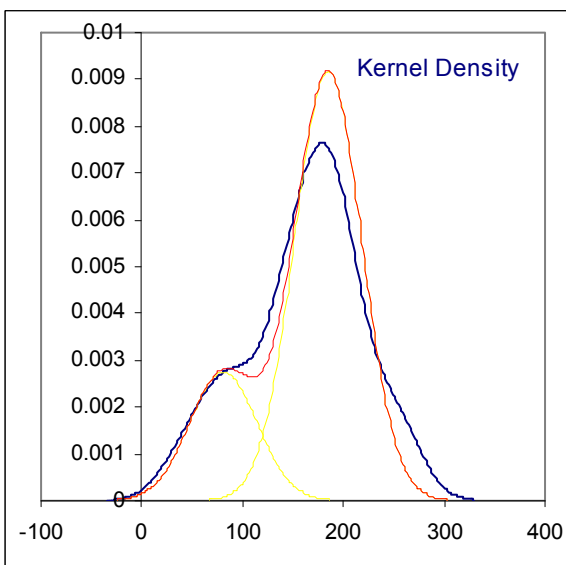
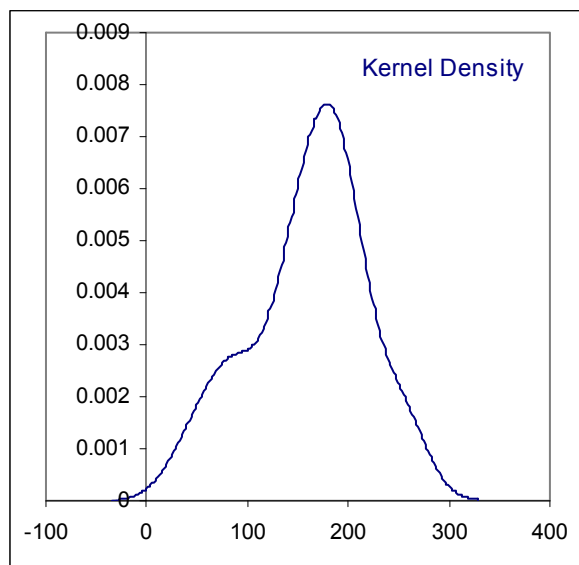
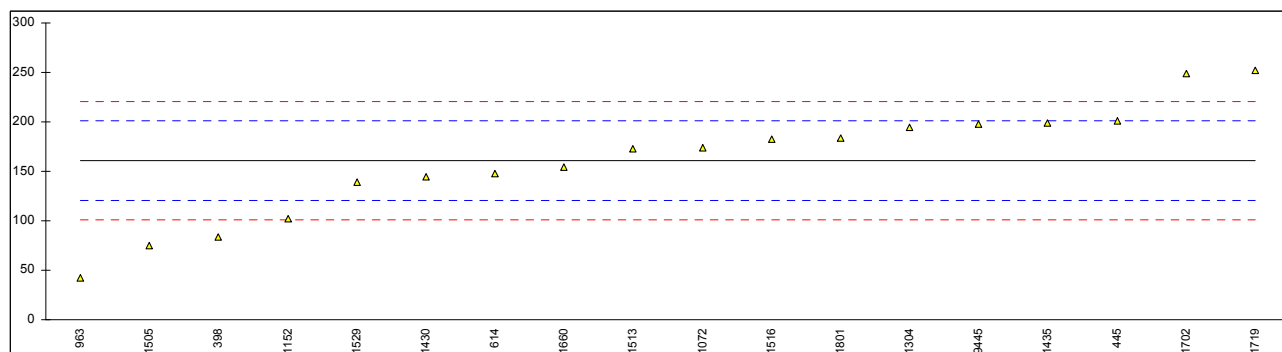
Compare R(Horwitz) = 4726.8



Determination of Carbon monoxide on sample #09DGA; results in µL/L

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	83.2		-3.87	
445	IEC60567	200.7		1.99	
614	IEC60567	148.25		-0.63	
963	ASTM D3612C	42.7		-5.89	
1072	EN60567	174		0.65	
1152	ASTM D3612	102.5456		-2.91	
1304	ACM120	195		1.70	
1430	IEC60567	145		-0.79	
1435	IEC60567	198.55		1.88	
1505	ASTM D3612C	75.1		-4.28	
1513	IEC60567	172.79		0.59	
1516	IEC60567	182.4		1.07	
1529	IEC60567	139		-1.09	
1660	IEC60567	154.1		-0.34	
1702	IEC60567	249.16		4.40	
1719	ASTM D3612B	252		4.54	
1801	IEC60567	183.4		1.12	
9445	IEC60567	197.9		1.85	

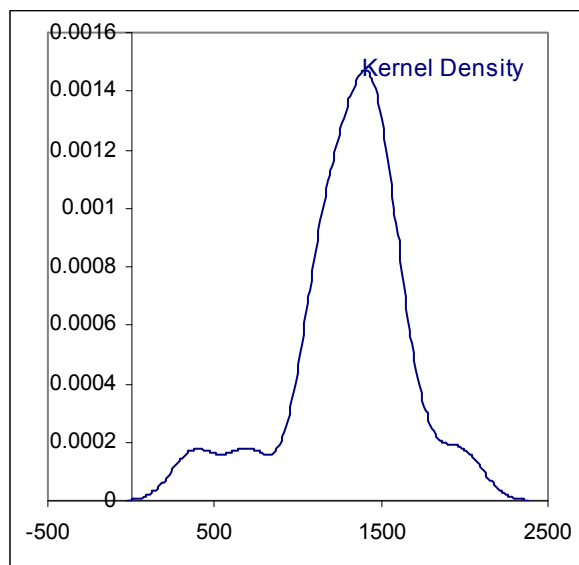
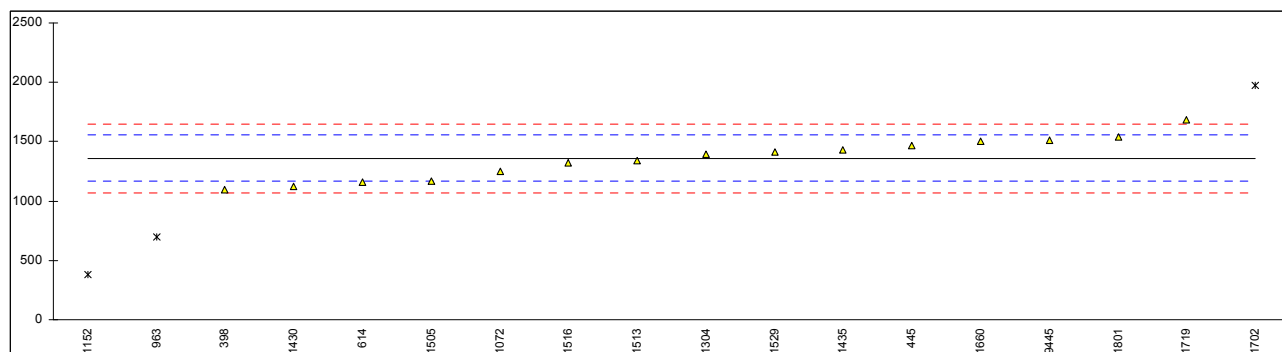
		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	18	10	8
outliers	0	0	0
mean (n)	160.88	133.88	194.63
st.dev. (n)	56.682	56.395	37.022
R(calc.)	158.71	157.91	103.66
R(IEC60567)	32.18	26.78	38.93
U(mean)	16.43		
R'(IEC60567)	56.15		
		Compare R(Horwitz) = 33.55	



Determination of Carbon dioxide on sample #09DGA; results in µL/L

lab	method	value	mark	z(targ)	remarks
398	IEC60567	1100		-2.68	
445	IEC60567	1462.9		1.06	
614	IEC60567	1161.24		-2.05	
963	ASTM D3612C	701.5	DG(0.05)	-6.78	
1072	EN60567	1252		-1.12	
1152	ASTM D3612	376.4863	DG(0.05)	-10.13	
1304	ACM120	1396		0.37	
1430	IEC60567	1120		-2.47	
1435	IEC60567	1435.56		0.77	
1505	ASTM D3612C	1166.0		-2.00	
1513	IEC60567	1336.8		-0.24	
1516	IEC60567	1322.8		-0.39	
1529	IEC60567	1410		0.51	
1660	IEC60567	1501		1.45	
1702	IEC60567	1978.85	G(0.05)	6.36	
1719	ASTM D3612B	1682		3.31	
1801	IEC60567	1544.2		1.89	
9445	IEC60567	1515		1.59	

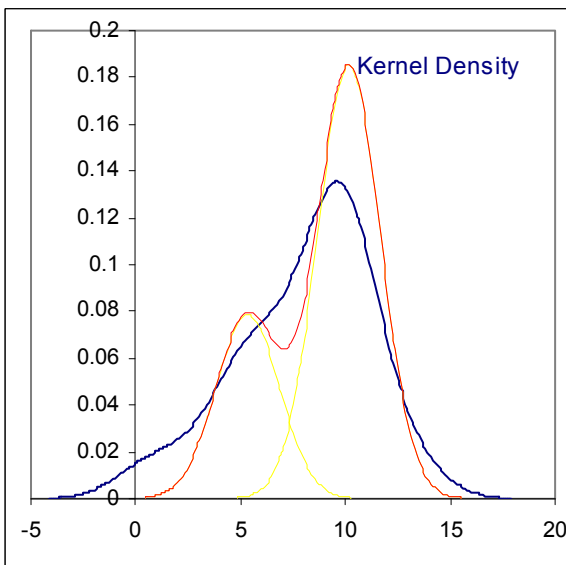
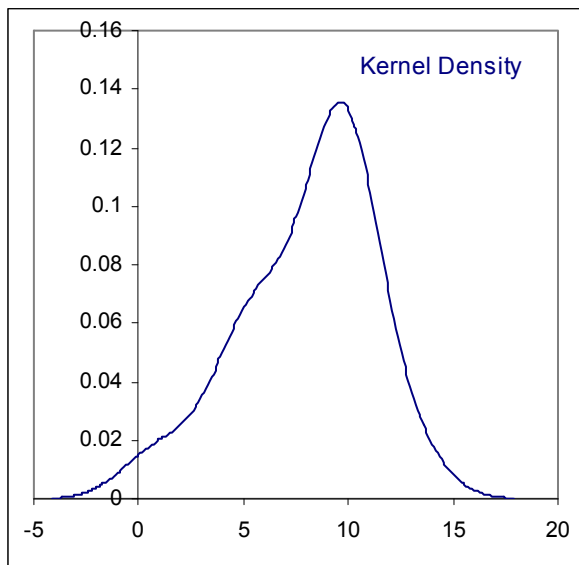
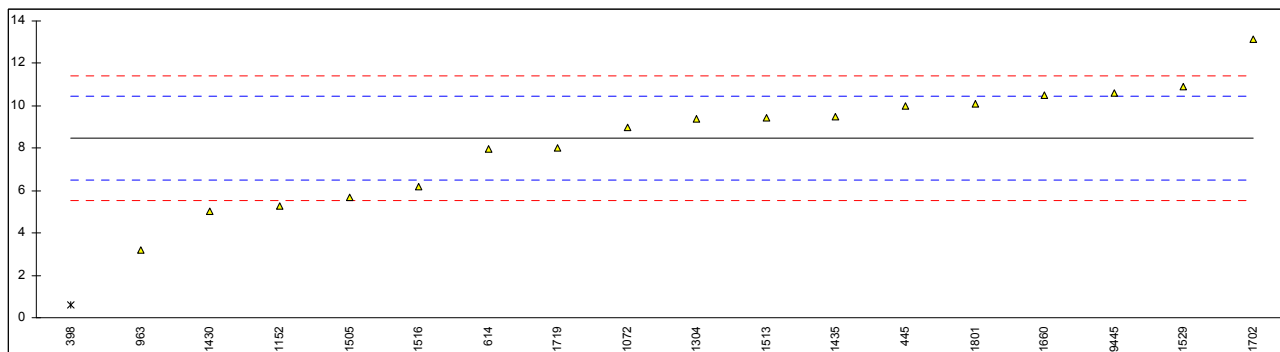
		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	15	8	7
outliers	3	2	1
mean (n)	1360.37	1338.81	1385.01
st.dev. (n)	172.697	178.064	176.835
R(calc.)	483.55	498.58	495.14
R(IEC60567)	272.07	267.76	277.00
U(mean)	54.85		
R'(IEC60567)	n/a	Compare R(Horwitz) = 205.72	



Determination of Methane on sample #09DGA; results in µL/L

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	0.6	G(0.05)	-8.00	
445	IEC60567	10.0		1.56	
614	IEC60567	7.94		-0.53	
963	ASTM D3612C	3.2		-5.36	
1072	EN60567	9		0.54	
1152	ASTM D3612	5.2768		-3.24	
1304	ACM120	9.4		0.95	
1430	IEC60567	5		-3.53	
1435	IEC60567	9.51		1.06	
1505	ASTM D3612C	5.7		-2.81	
1513	IEC60567	9.44		0.99	
1516	IEC60567	6.2	C	-2.30	first reported 10.2
1529	IEC60567	10.9		2.48	
1660	IEC60567	10.5		2.07	
1702	IEC60567	13.15		4.77	
1719	ASTM D3612B	8		-0.47	
1801	IEC60567	10.1		1.66	
9445	IEC60567	10.6		2.17	

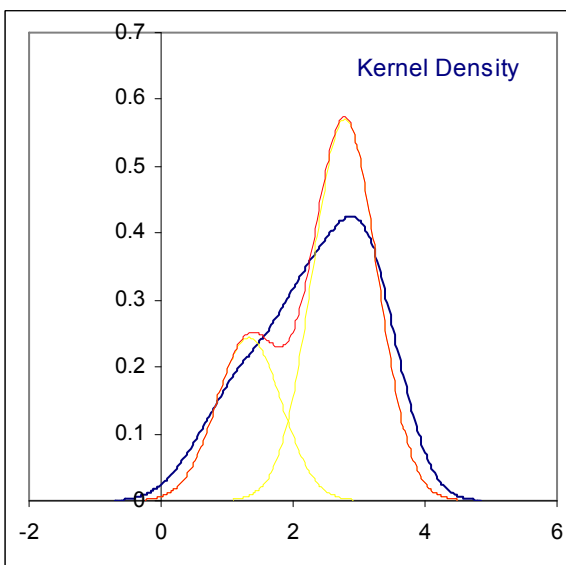
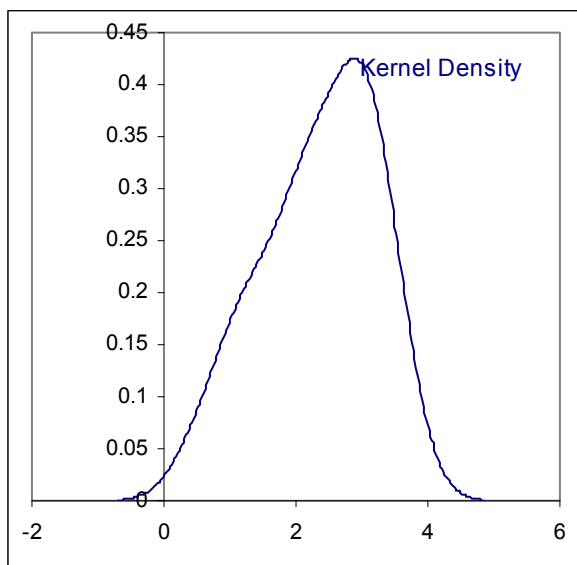
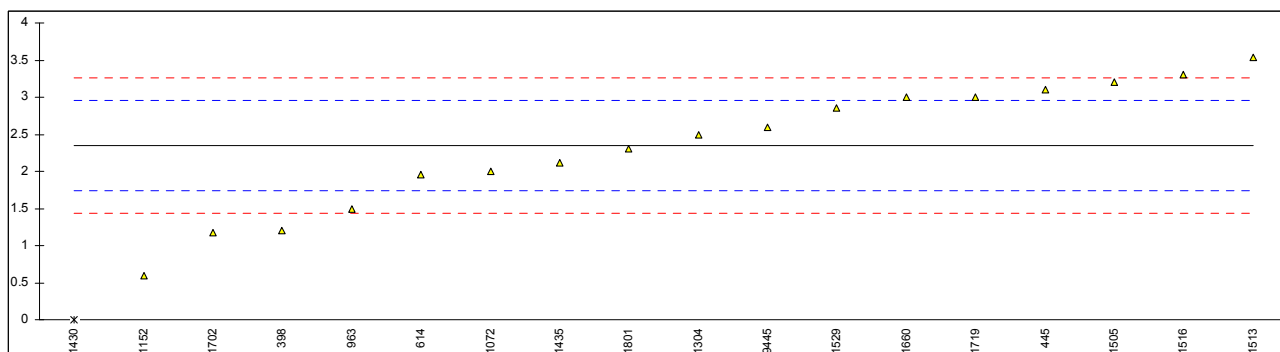
		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	17	9	8
outliers	1	1	0
mean (n)	8.47	7.85	9.15
st.dev. (n)	2.598	3.005	2.020
R(calc.)	7.27	8.41	5.66
R(IEC60567)	1.69	1.57	1.83
U(mean)	0.77		
R'(IEC60567)	2.75	Compare R(Horwitz) = 2.75	



Determination of Ethane on sample #09DGA; results in $\mu\text{L/L}$

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	1.2		-3.78	
445	IEC60567	3.1		2.46	
614	IEC60567	1.96		-1.28	
963	ASTM D3612C	1.5		-2.79	
1072	EN60567	2		-1.15	
1152	ASTM D3612	0.5993		-5.75	
1304	ACM120	2.5		0.49	
1430	IEC60567	0	ex	-7.72	zero is not a real value
1435	IEC60567	2.12		-0.76	
1505	ASTM D3612C	3.2		2.79	
1513	IEC60567	3.54		3.91	
1516	IEC60567	3.3		3.12	
1529	IEC60567	2.86		1.67	
1660	IEC60567	3.0		2.13	
1702	IEC60567	1.18		-3.84	
1719	ASTM D3612B	3		2.13	
1801	IEC60567	2.3		-0.17	
9445	IEC60567	2.6		0.82	

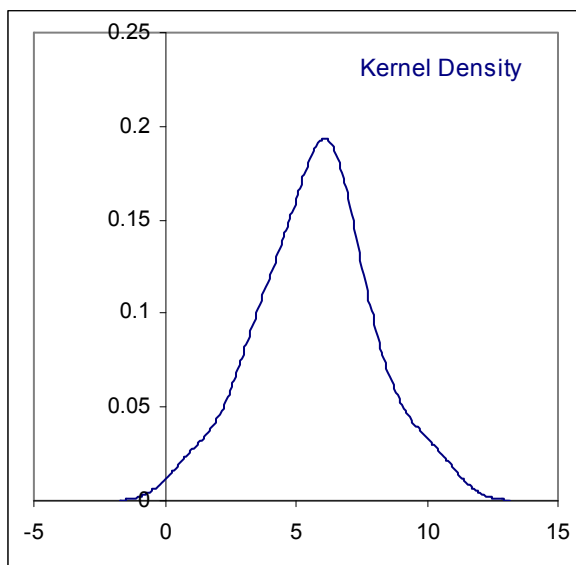
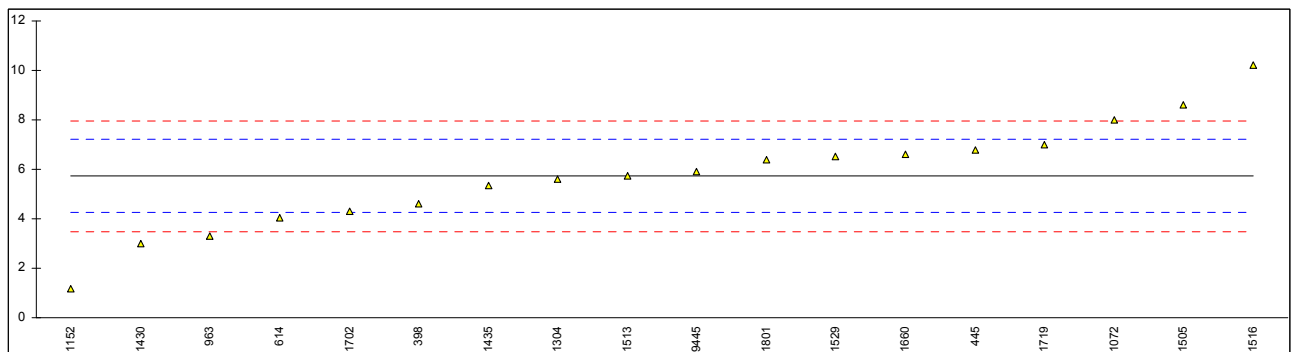
		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	17	9	8
outliers	0	0	0
mean (n)	2.35	2.24	2.47
st.dev. (n)	0.852	0.941	0.783
R(calc.)	2.38	2.64	2.19
R(IEC60567)	0.47	0.45	0.49
U(mean)	0.25		
R'(IEC60567)	0.85	Compare R(Horwitz) = 0.93	



Determination of Ethene (ethylene) on sample #09DGA; results in $\mu\text{L/L}$

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	4.6		-1.52	
445	IEC60567	6.8		1.43	
614	IEC60567	4.05		-2.26	
963	ASTM D3612C	3.3		-3.27	
1072	EN60567	8		3.05	
1152	ASTM D3612	1.1897		-6.10	
1304	ACM120	5.6		-0.18	
1430	IEC60567	3		-3.67	
1435	IEC60567	5.36		-0.50	
1505	ASTM D3612C	8.6		3.85	
1513	IEC60567	5.76		0.04	
1516	IEC60567	10.2		6.00	
1529	IEC60567	6.51		1.04	
1660	IEC60567	6.6		1.17	
1702	IEC60567	4.31		-1.91	
1719	ASTM D3612B	7		1.70	
1801	IEC60567	6.4		0.90	
9445	IEC60567	5.9		0.23	

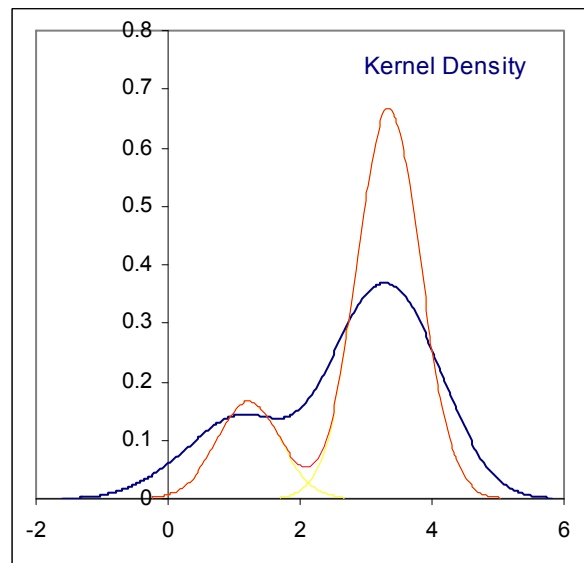
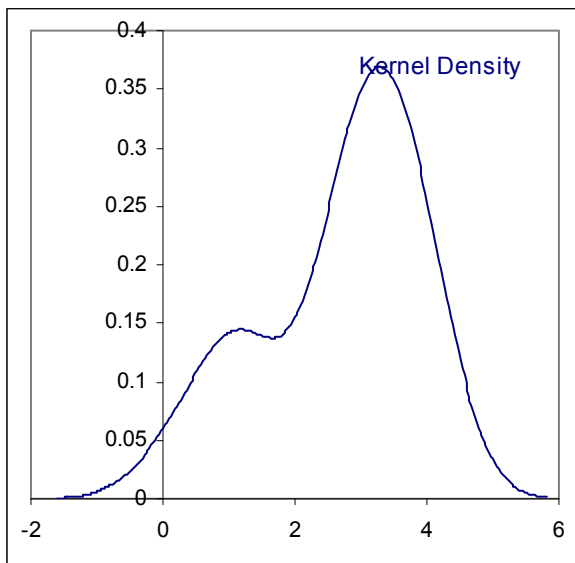
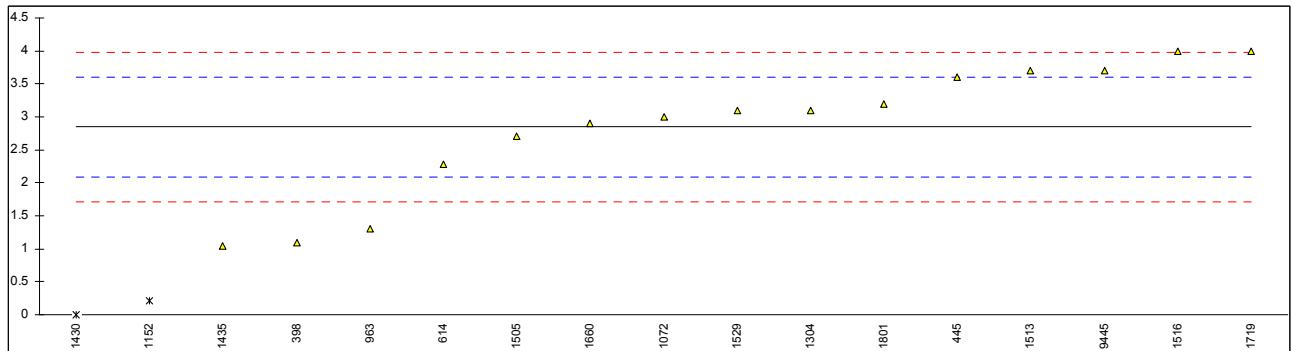
		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	18	10	8
outliers	0	0	0
mean (n)	5.73	5.19	6.42
st.dev. (n)	2.145	2.191	2.011
R(calc.)	6.01	6.13	5.63
R(IEC60567)	1.15	1.04	1.28
U(mean)	0.62		
R'(IEC60567)	2.08	Compare R(Horwitz) = 1.98	



Determination of Ethyn (acetylene) on sample #09DGA; results in µL/L

lab	method	value	mark	z'(targ)	remarks
398	IEC60567	1.1		-4.64	
445	IEC60567	3.6		1.99	
614	IEC60567	2.29		-1.48	
963	ASTM D3612C	1.3		-4.11	
1072	EN60567	3		0.40	
1152	ASTM D3612	0.2185	G(0.05)	-6.98	
1304	ACM120	3.1		0.67	
1430	IEC60567	0	ex	-7.56	zero is not a real value
1435	IEC60567	1.05		-4.77	
1505	ASTM D3612C	2.7		-0.39	
1513	IEC60567	3.70		2.26	
1516	IEC60567	4.0		3.06	
1529	IEC60567	3.09		0.64	
1660	IEC60567	2.9		0.14	
1702	IEC60567	n.d.		----	
1719	ASTM D3612B	4		3.06	
1801	IEC60567	3.2		0.93	
9445	IEC60567	3.7		2.26	

		<u>Only head space results:</u>	<u>All other results:</u>
normality	OK		
n	15	7	7
outliers	1	1	0
mean (n)	2.85	2.43	3.33
st.dev. (n)	0.999	1.112	0.619
R(calc.)	2.80	3.11	1.73
R(IEC60567)	0.57	0.49	0.67
U(mean)	0.32		
R'(IEC60567)	1.06	Compare R(Horwitz) = 1.98	



Determination of Propane and Propene on sample #09DGA; results in µL/L

lab	method	Propane	Propene	Sum of Propane& Propene	remarks
398	IEC60567	3.1	0.6	3.7	
445		----	----	----	
614		----	----	----	
963	ASTM D3612C	<1	<1	<1	
1072		----	----	----	
1152		----	----	----	
1304		----	----	----	
1430		----	----	----	
1435		----	----	----	
1505	ASTM D3612C	<0.07	6.4	6.4	
1513		----	----	----	
1516	IEC60567	0.1	3.9	4	
1529	IEC60567	<0.1	4.7	4.7	
1660	IEC60567	6.6	----	6.6	
1702		----	----	----	
1719		----	----	----	
1801		----	----	----	
9445		----	----	----	
	normality	unknown	unknown	unknown	
	n	3	4	5	
	outliers	n/a	n/a	n/a	
	mean (n)	n/a	n/a	5.08	
	st.dev. (n)	n/a	n/a	1.348	
	R(calc.)	n/a	n/a	3.77	
	R(IEC60567:05)	n/a	n/a	n/a	

APPENDIX 2

List of participants

- 2 labs in AUSTRALIA
- 1 lab in BELGIUM
- 1 lab in GREECE
- 2 labs in ITALY
- 2 labs in MALAYSIA
- 1 lab in NEW ZEALAND
- 2 labs in PORTUGAL
- 1 lab in SAUDI ARABIA
- 3 labs in SPAIN
- 1 lab in THE NETHERLANDS
- 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
SDS	= Safety Data Sheet

Literature:

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation, November 2008
- 2 prNEN 12766-2:2000.
- 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 ISO 15328-05