Results of Proficiency Test
Dissolved Gas Analysis
November 2013

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Appendices:

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 2013/2014, 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 2013 proficiency test are presented and discussed. This report is also electronically available through the iis web site http://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 41 certified syringes (of 50 mL) was prepared (lot RN108) on October 3, 2013. Each syringe was certified. 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 ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially 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 January 2010 (iis-protocol, version 3.2).

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 41 syringes was prepared (lot RN108) on October 3, 2013. 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. 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 #13209) was sent on October 23, 2013.

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 #13209: 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 some of the required standards, and a letter of instructions were prepared and made available for download on the iis website (www.iisnl.com).
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. 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 IEC60567 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 ia as follows:

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

4 EVALUATION

In this proficiency test no problems were encountered during execution, except for two laboratories. These laboratories needed two more syringes to determine DGA. Six participants reported the results after the final reporting date and one participant did not report any test results at all. Not all labs were able to report all components requested.

In total 33 participating laboratories reported 293 numerical results. Observed were 10 outlying results, which is 3.4% 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 distribution. A not normal distribution was found for the following determinations: Methane and Ethene. In these cases the statistical evaluation should be used with due care.

Hydrogen: 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 requirements of IEC 60567:2011.

Oxygen: 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 requirements of IEC 60567:2011.

Nitrogen: The determination of this component was very problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the requirements of IEC 60567:2011.

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

Carbon dioxide: 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 60567:2011.

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 60567:2011.

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 60567:2011.

Ethene: 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 60567:2011.

Ethyn: 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 requirements of IEC 60567:2011.

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 from IEC 60567:2011 are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
Hydrogen H_2	µl/L	30	16.316	9.627	3.263
Oxygen O_2	µl/L	30	21404.1	10352.2	4280.8
Nitrogen N_2	µl/L	27	57116.5	16806.9	11423.3
Carbon Monoxide CO	µl/L	30	173.002	57.414	34.600
Carbon Dioxide CO_2	µl/L	32	1316.60	544.10	263.32
Methane CH_4	µl/L	32	8.384	4.412	1.677
Ethane C_2H_6	µl/L	31	2.470	1.581	0.494
Ethene C_2H_4	µl/L	32	5.835	2.726	1.167
Ethyn C_2H_2	µl/L	31	2.711	1.453	0.542
Propane C_3H_8	µl/L	n.a.	n.a	n.a	n.a
Propene C_3H_6	µl/L	6	3.487	2.937	0.697

Table 1: Performance of the group on sample #13209

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 60567:2011.

The problematic components have been discussed in paragraph 4.1.

4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2013 WITH PREVIOUS PTS

	November 2013	*November 2012*	*November 2011*	*November 2010*
Number of reporting labs	33	29	33	24
Number of results reported	293	265	299	218
Statistical outliers	10	15	18	10
Percentage outliers	3.4%	6.0%	6.0%	4.6%

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 2013*	*November 2012*	*November 2011*	*November 2010*
Hydrogen H_2	21%	20%	25%	28%
Oxygen O_2	17%	16%	14%	21%
Nitrogen N_2	19%	12%	12%	20%
Carbon Monoxide CO	12%	15%	14%	16%
Carbon Dioxide CO_2	15%	14%	14%	11%
Methane CH_4	19%	18%	19%	18%
Ethane C_2H_6	23%	18%	25%	26%
Ethene C_2H_4	17%	21%	18%	18%
Ethyn C_2H_2	19%	20%	24%	22%
Propane C_3H_8	n.e	n.e	n.e	n.e.
Propene C_3H_6	n.e	n.e	n.e	n.e.

Table 3: Comparison of the relative uncertainties on determinations

Comparing the results of the 2013 round robin to that of last year, the performance appears to be similar (some better, some worse). In comparison with the earlier PTs on DGA (like 2010), the current PT shows a slightly improved performance.

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_2	14	16	+2
Oxygen O_2	21100	21404	+304
Nitrogen N_2	54000	57117	+3117
Carbon Monoxide CO	174	173	-1
Carbon Dioxide CO_2	1340	1317	-23
Methane CH_4	8.5	8.4	-0.1
Ethane C_2H_6	2.5	2.5	0.0
Ethene C_2H_4	6.1	5.8	-0.3
Ethyn C_2H_2	2.9	2.7	-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 were performing a headspace method. Looking at the headspace results versus the other methods used, differences were seen in mean values and spread of the test results.

In this round robin, twenty laboratories (360, 398, 445, 963, 1264, 1304, 1306, 1367, 1374, 1435, 1440, 1442, 1505, 1560, 1626, 1660 1687, 1743, 1777 and 8445) used the head-space method (IEC 60567 clause 7.5), five laboratories (1072, 1178, 1478, 1513 and 1702) used the Toepler method (IEC 60567 clause 7.2), two laboratories (614, 1801) used the ToGas method and one laboratory (1747) used the ASTM D3612-B stripper column extraction. Four laboratories (1430, 1529, 1548, 2125) did not report the extraction method that was used. Since more laboratories used the headspace method, this was evaluated separately (see extra column in Appendix 1).

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.

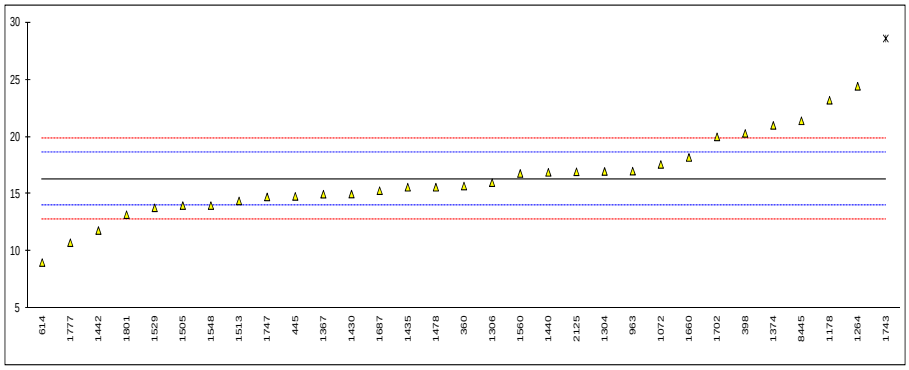
In order to evaluate whether the used test method has a significant influence on the test results, the headspace test results were evaluated separately, see appendix 2. From the evaluation is noted that for the majority of the components the consensus value for the headspace test results is slightly 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. The observed reproducibility for the Oxygen head space test results is almost in agreement with the IEC60567 requirements.

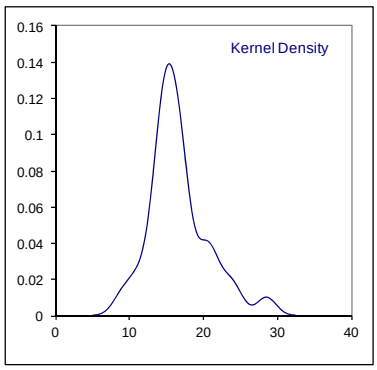
APPENDIX 1

Determination of Hydrogen on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	15.7		-0.53	
398	IEC60567	20.3		3.42	
445	IEC60567	14.8		-1.30	
614	IEC60567	9.025		-6.26	
963	D3612	17		0.59	
1072	IEC60567	17.59		1.09	
1178	IEC60567	23.2		5.91	
1264	D3612	24.4192		6.95	
1304	INH-120	16.98		0.57	
1306	IEC60567	16		-0.27	
1367	IEC60567	14.99		-1.14	
1374	D3612	21		4.02	
1430	IEC60567	15		-1.13	
1435	IEC60567	15.60		-0.61	
1440	D3612	16.9		0.50	
1442	IEC60567	11.82		-3.86	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	15.6		-0.61	
1505	D3612	14		-1.99	
1513	IEC60567	14.4		-1.64	
1529	IEC60567	13.8		-2.16	
1548		14		-1.99	
1560	IEC60567	16.8		0.42	
1626		-----		-----	
1660	IEC60567	18.2		1.62	
1687	IEC60567	15.3		-0.87	
1702	IEC60567	20	C	3.16	First reported: 24
1743	IEC60567	28.59	C,G(0.05)	10.53	First reported: 60.197
1747	IEC60567	14.75438		-1.34	
1777	D3612	10.756		-4.77	
1801	IEC60567	13.2		-2.67	
2125	IEC60567	16.95		0.54	
8445	IEC60567	21.4		4.36	
					Only headspace results:
	normality	OK			OK
	n	30			17
	outliers	1			2
	mean (n)	16.3162			16.3262
	st.dev. (n)	3.43827			2.86425
	R(calc.)	9.6272			8.0199
	R(IEC60567:11)	3.2632			3.2652

Compare R(Horwitz): 4.8015

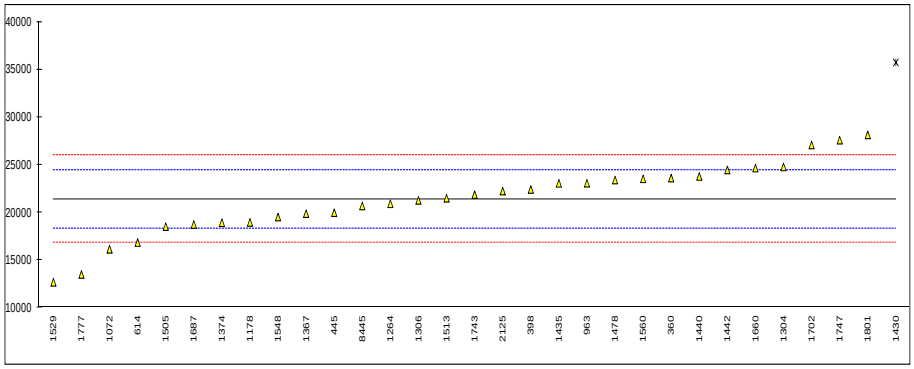


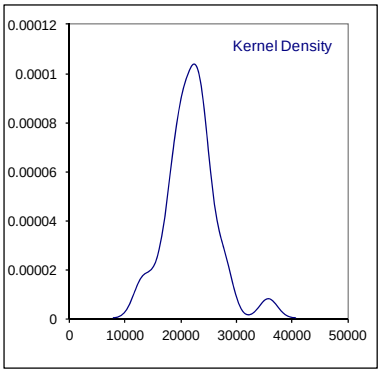


Determination of Oxygen on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	23621		1.45	
398	IEC60567	22421		0.67	
445	IEC60567	19990		-0.92	
614	IEC60567	16863.036		-2.97	
963	D3612	23075		1.09	
1072	IEC60567	16155.86		-3.43	
1178	IEC60567	18975		-1.59	
1264	D3612	20925.50	C	-0.31	First reported: 2.09255 µl/L
1304	INH-120	24784		2.21	
1306	IEC60567	21288		-0.08	
1367	IEC60567	19888		-0.99	
1374	D3612	18945		-1.61	
1430	IEC60567	35745	G(0.05)	9.38	
1435	IEC60567	23070.65		1.09	
1440	D3612	23792.3		1.56	
1442	IEC60567	24472		2.01	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	23418.6		1.32	
1505	D3612	18530		-1.88	
1513	IEC60567	21500		0.06	
1529	IEC60567	12700		-5.69	
1548		19534		-1.22	
1560	IEC60567	23541		1.40	
1626		-----		-----	
1660	IEC60567	24667		2.13	
1687	IEC60567	18756.9		-1.73	
1702	IEC60567	27093		3.72	
1743	IEC60567	21891		0.32	
1747	IEC60567	27593.87104		4.05	
1777	D3612	13515.97		-5.16	
1801	IEC60567	28151.7		4.41	
2125	IEC60567	22261		0.56	
8445	IEC60567	20703.4		-0.46	
					Only headspace results:
	normality	OK			OK
	n	30			18
	outliers	1			1
	mean (n)	21404.13			21908.99
	st.dev. (n)	3697.202			2104.140
	R(calc.)	10352.17			5891.59
	R(IEC60567:11)	4280.83			4381.80

Compare R(Horwitz): 2137.82

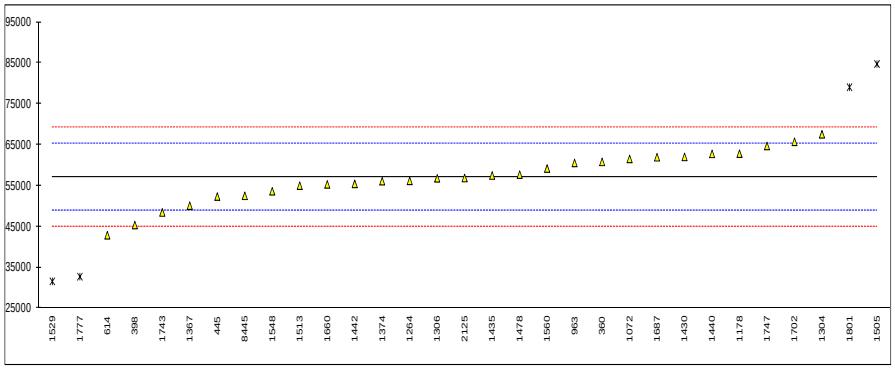


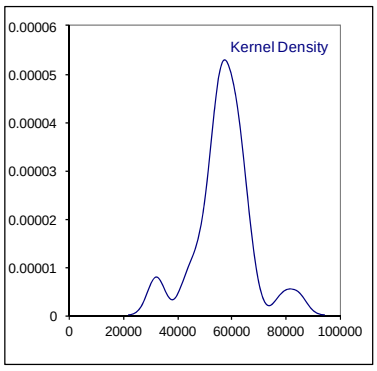


Determination of Nitrogen on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	60821		0.91	
398	IEC60567	45377		-2.88	
445	IEC60567	52359		-1.17	
614	IEC60567	42887.694		-3.49	
963	D3612	60569		0.85	
1072	IEC60567	61552.51		1.09	
1178	IEC60567	62830.3		1.40	
1264	D3612	56199.70	C	-0.22	First reported: 5.6199 µl/L
1304	INH-120	67574		2.56	
1306	IEC60567	56812		-0.07	
1367	IEC60567	50124		-1.71	
1374	D3612	56099		-0.25	
1430	IEC60567	62042		1.21	
1435	IEC60567	57492.2		0.09	
1440	D3612	62779.6		1.39	
1442	IEC60567	55454		-0.41	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	57721.3		0.15	
1505	D3612	84752	D(0.05)	6.77	
1513	IEC60567	55000		-0.52	
1529	IEC60567	31600	DG(0.05)	-6.25	
1548		53643		-0.85	
1560	IEC60567	59202		0.51	
1626		-----		-----	
1660	IEC60567	55318		-0.44	
1687	IEC60567	61960.45		1.19	
1702	IEC60567	65750		2.12	
1743	IEC60567	48456		-2.12	
1747	IEC60567	64720.8515		1.86	
1777	D3612	32750.42	DG(0.05)	-5.97	
1801	IEC60567	79077.9	G(0.05)	5.38	
2125	IEC60567	56872		-0.06	
8445	IEC60567	52529.3		-1.12	
					Only headspace results:
	normality	OK			OK
	n	27			17
	outliers	4			2
	mean (n)	57116.52			56419.19
	st.dev. (n)	6002.451			5590.839
	R(calc.)	16806.86			15654.35
	R(IEC60567:11)	11423.30			11283.83

Compare R(Horwitz): 4921.25

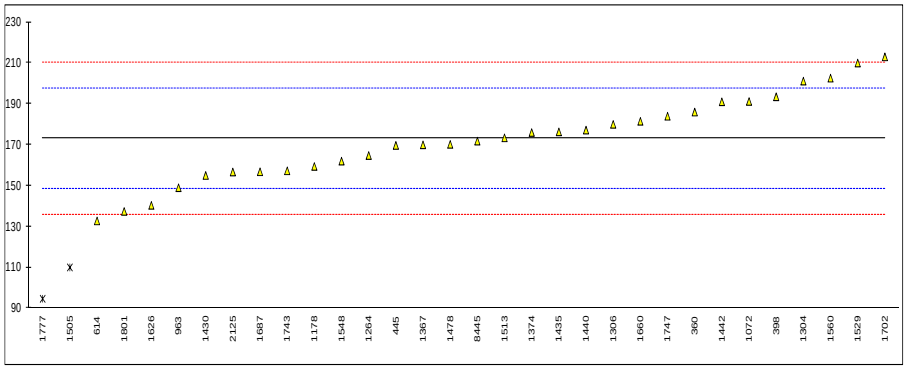


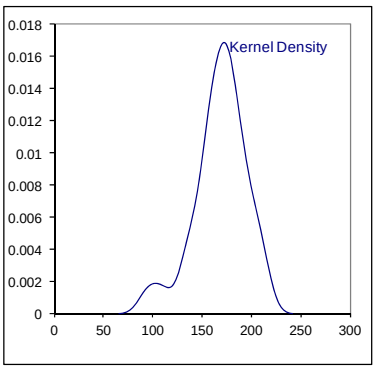


Determination of Carbon monoxide on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	186		1.05	
398	IEC60567	193.5		1.66	
445	IEC60567	169.7		-0.27	
614	IEC60567	132.763		-3.26	
963	D3612	149		-1.94	
1072	IEC60567	191.20		1.47	
1178	IEC60567	159.4		-1.10	
1264	D3612	164.7639		-0.67	
1304	INH-120	201.16		2.28	
1306	IEC60567	180		0.57	
1367	IEC60567	170		-0.24	
1374	D3612	176		0.24	
1430	IEC60567	155		-1.46	
1435	IEC60567	176.32		0.27	
1440	D3612	177.2		0.34	
1442	IEC60567	191.05		1.46	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	170.2		-0.23	
1505	D3612	110	DG(0.05)	-5.10	
1513	IEC60567	173.4		0.03	
1529	IEC60567	210		2.99	
1548		162		-0.89	
1560	IEC60567	202.6		2.40	
1626	IEC60567	140.37		-2.64	
1660	IEC60567	181.5		0.69	
1687	IEC60567	156.8		-1.31	
1702	IEC60567	213		3.24	
1743	IEC60567	157.2699		-1.27	
1747	IEC60567	183.9588		0.89	
1777	D3612	94.68	DG(0.05)	-6.34	
1801	IEC60567	137.4		-2.88	
2125	IEC60567	156.7		-1.32	
8445	IEC60567	171.8		-0.10	
					Only headspace results:
	normality	OK			OK
	n	30			18
	outliers	2			2
	mean (n)	173.0019			174.7241
	st.dev. (n)	20.50503			17.02828
	R(calc.)	57.4141			47.6792
	R(IEC60567:11)	34.6004			34.9448

Compare R(Horwitz): 35.684

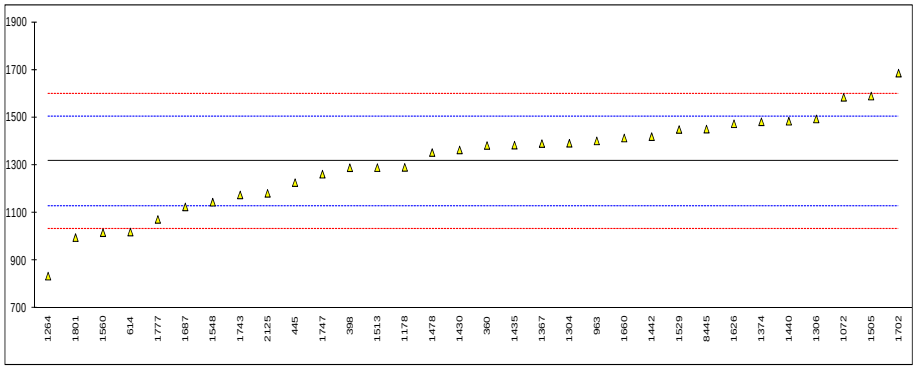


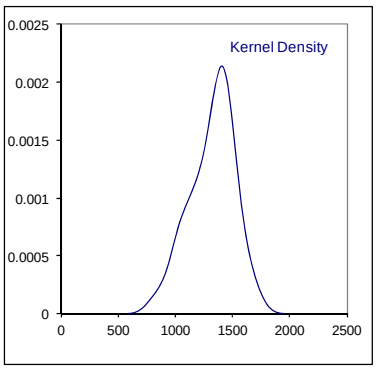


Determination of Carbon dioxide on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	1383		0.71	
398	IEC60567	1289.8		-0.28	
445	IEC60567	1227.2		-0.95	
614	IEC60567	1019.915		-3.15	
963	D3612	1402		0.91	
1072	IEC60567	1584.95		2.85	
1178	IEC60567	1291.2		-0.27	
1264	D3612	834.9878		-5.12	
1304	INH-120	1392.1		0.80	
1306	IEC60567	1494		1.89	
1367	IEC60567	1391		0.79	
1374	D3612	1482		1.76	
1430	IEC60567	1364		0.50	
1435	IEC60567	1384.04		0.72	
1440	D3612	1484.6		1.79	
1442	IEC60567	1420		1.10	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	1353.3		0.39	
1505	D3612	1590		2.91	
1513	IEC60567	1290		-0.28	
1529	IEC60567	1450		1.42	
1548		1145		-1.82	
1560	IEC60567	1017.1		-3.18	
1626	IEC60567	1473.91		1.67	
1660	IEC60567	1414.1		1.04	
1687	IEC60567	1125.3		-2.03	
1702	IEC60567	1686		3.93	
1743	IEC60567	1175.6		-1.50	
1747	IEC60567	1262.38048		-0.58	
1777	D3612	1073.02		-2.59	
1801	IEC60567	996.7		-3.40	
2125	IEC60567	1182.4		-1.43	
8445	IEC60567	1451.6		1.44	
					Only headspace results:
	normality	OK			not OK
	n	32			20
	outliers	0			0
	mean (n)	1316.600			1325.268
	st.dev. (n)	194.3216			191.5479
	R(calc.)	544.101			536.334
	R(IEC60567:11)	263.320			265.054

Compare R(Horwitz): 200.082

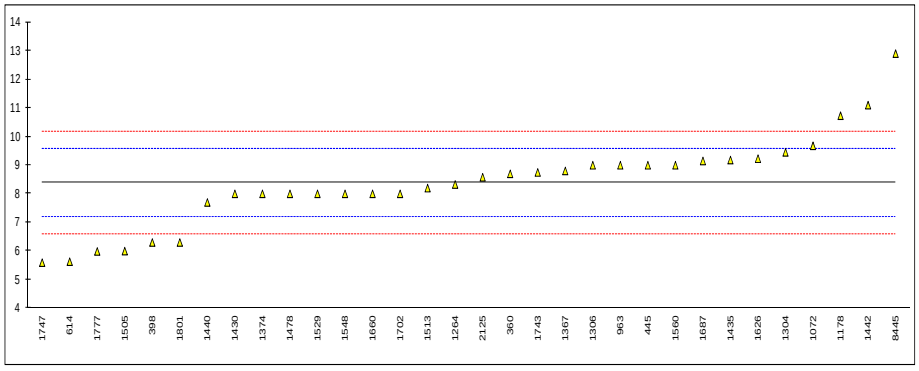


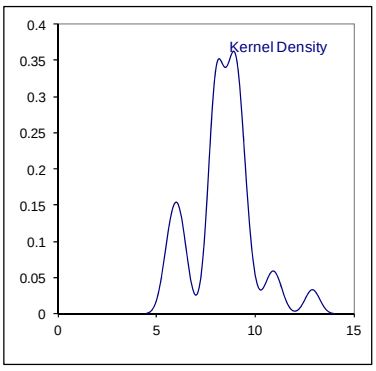


Determination of Methane on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	8.7		0.53	
398	IEC60567	6.3		-3.48	
445	IEC60567	9.0		1.03	
614	IEC60567	5.631		-4.60	
963	D3612	9		1.03	
1072	IEC60567	9.68		2.16	
1178	IEC60567	10.73		3.92	
1264	D3612	8.3284		-0.09	
1304	INH-120	9.45		1.78	
1306	IEC60567	9		1.03	
1367	IEC60567	8.8		0.69	
1374	D3612	8		-0.64	
1430	IEC60567	8		-0.64	
1435	IEC60567	9.18		1.33	
1440	D3612	7.7		-1.14	
1442	IEC60567	11.10		4.53	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	8.0		-0.64	
1505	D3612	6		-3.98	
1513	IEC60567	8.2		-0.31	
1529	IEC60567	8.0		-0.64	
1548		8		-0.64	
1560	IEC60567	9.0		1.03	
1626	IEC60567	9.23		1.41	
1660	IEC60567	8.0		-0.64	
1687	IEC60567	9.15		1.28	
1702	IEC60567	8	C	-0.64	First reported: 12
1743	IEC60567	8.7486		0.61	
1747	IEC60567	5.5956		-4.66	
1777	D3612	5.99		-4.00	
1801	IEC60567	6.3		-3.48	
2125	IEC60567	8.58		0.33	
8445	IEC60567	12.9		7.54	
					Only headspace results:
	normality	not OK			not OK
	n	32			19
	outliers	0			1
	mean (n)	8.3842			8.4567
	st.dev. (n)	1.57583			1.26482
	R(calc.)	4.4123			3.5415
	R(IEC60567:11)	1.6768			1.6913

Compare R(Horwitz): 2.727

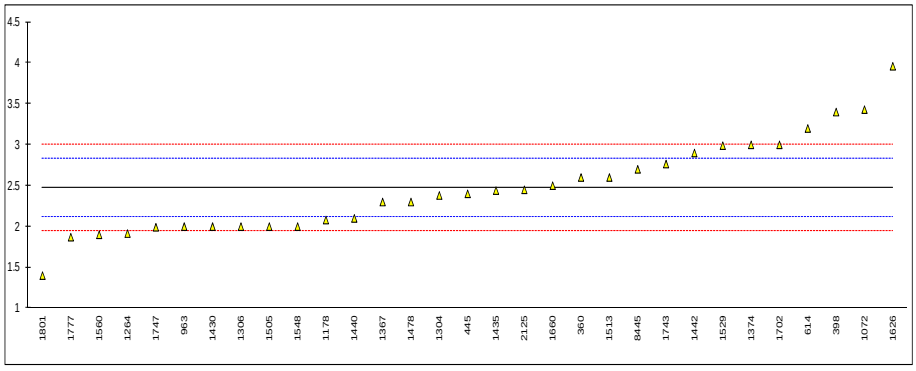


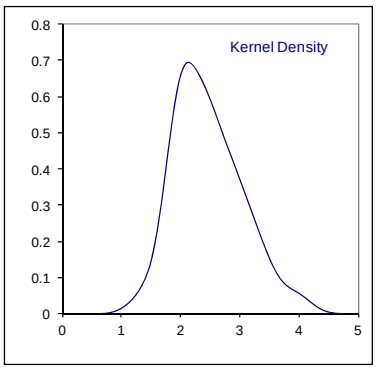


Determination of Ethane on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	2.6		0.74	
398	IEC60567	3.4		5.27	
445	IEC60567	2.4		-0.40	
614	IEC60567	3.2000		4.14	
963	D3612	2		-2.66	
1072	IEC60567	3.43		5.44	
1178	IEC60567	2.08		-2.21	
1264	D3612	1.9146		-3.15	
1304	INH-120	2.38		-0.51	
1306	IEC60567	2		-2.66	
1367	IEC60567	2.3		-0.96	
1374	D3612	3		3.00	
1430	IEC60567	2		-2.66	
1435	IEC60567	2.44		-0.17	
1440	D3612	2.1		-2.10	
1442	IEC60567	2.90		2.44	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	2.3		-0.96	
1505	D3612	2		-2.66	
1513	IEC60567	2.6		0.74	
1529	IEC60567	2.99		2.95	
1548		2		-2.66	
1560	IEC60567	1.9		-3.23	
1626	IEC60567	3.96		8.45	
1660	IEC60567	2.5		0.17	
1687	IEC60567	<1		< -8.33	False negative?
1702	IEC60567	3		3.00	
1743	IEC60567	2.7650		1.67	
1747	IEC60567	1.99148		-2.71	
1777	D3612	1.87		-3.40	
1801	IEC60567	1.4		-6.06	
2125	IEC60567	2.45		-0.11	
8445	IEC60567	2.7		1.30	
					Only headspace results:
	normality	OK			OK
	n	31			17
	outliers	0			2
	mean (n)	2.4700			2.3394
	st.dev. (n)	0.56463			0.36821
	R(calc.)	1.5810			1.0310
	R(IEC60567:11)	0.4940			0.4679

Compare R(Horwitz): 0.966

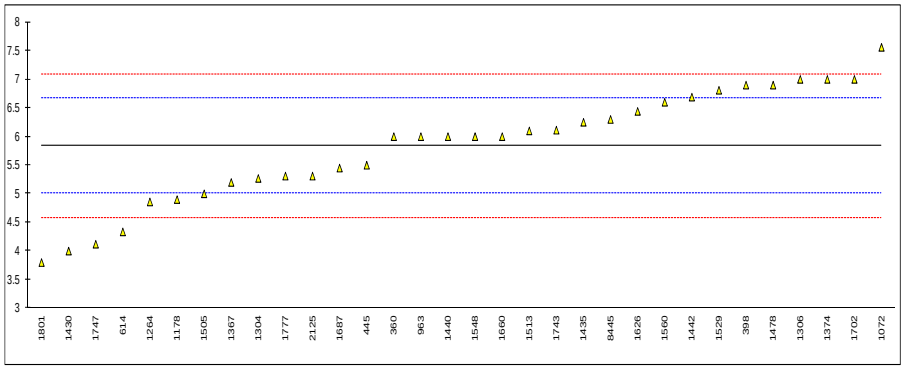


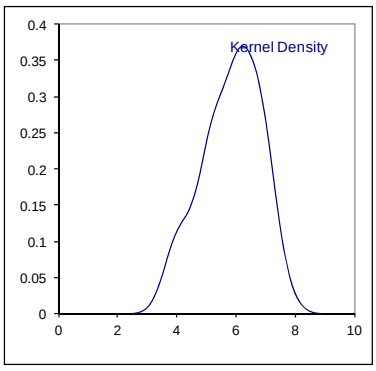


Determination of Ethene (ethylene) on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	6.0		0.40	
398	IEC60567	6.9		2.56	
445	IEC60567	5.5		-0.80	
614	IEC60567	4.336		-3.60	
963	D3612	6		0.40	
1072	IEC60567	7.56		4.14	
1178	IEC60567	4.90		-2.24	
1264	D3612	4.8593		-2.34	
1304	INH-120	5.27		-1.36	
1306	IEC60567	7		2.80	
1367	IEC60567	5.2		-1.52	
1374	D3612	7		2.80	
1430	IEC60567	4		-4.40	
1435	IEC60567	6.25		1.00	
1440	D3612	6.0		0.40	
1442	IEC60567	6.69		2.05	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	6.9		2.56	
1505	D3612	5		-2.00	
1513	IEC60567	6.1		0.64	
1529	IEC60567	6.81		2.34	
1548		6		0.40	
1560	IEC60567	6.6		1.84	
1626	IEC60567	6.44		1.45	
1660	IEC60567	6.0		0.40	
1687	IEC60567	5.45		-0.92	
1702	IEC60567	7		2.80	
1743	IEC60567	6.1123		0.67	
1747	IEC60567	4.12002		-4.11	
1777	D3612	5.31		-1.26	
1801	IEC60567	3.8		-4.88	
2125	IEC60567	5.31		-1.26	
8445	IEC60567	6.3		1.12	
					Only headspace results:
	normality	not OK			OK
	n	32			20
	outliers	0			0
	mean (n)	5.8349			5.9941
	st.dev. (n)	0.97343			0.66912
	R(calc.)	2.7256			1.8735
	R(IEC60567:11)	1.1670			1.1988

Compare R(Horwitz): 2.005

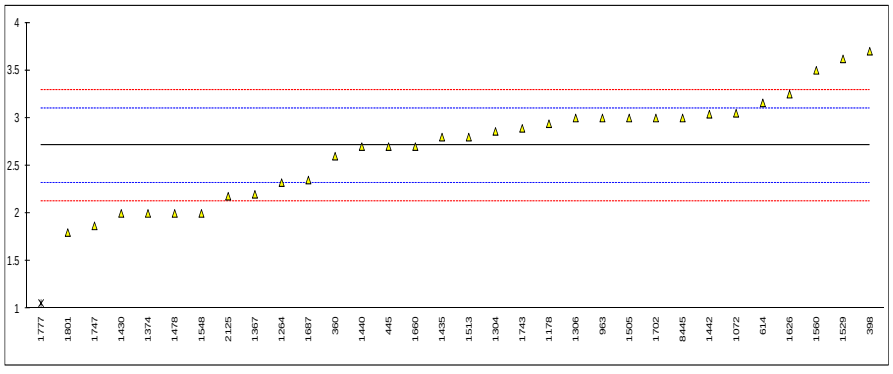


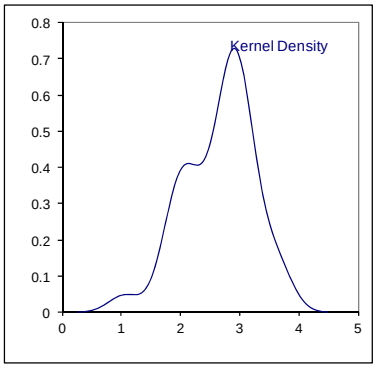


Determination of Ethyn (acetylene) on sample #13209; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	IEC60567	2.6		-0.57	
398	IEC60567	3.7		5.11	
445	IEC60567	2.7		-0.06	
614	IEC60567	3.159		2.32	
963	D3612	3		1.49	
1072	IEC60567	3.05		1.75	
1178	IEC60567	2.94		1.18	
1264	D3612	2.3228		-2.00	
1304	INH-120	2.86		0.77	
1306	IEC60567	3		1.49	
1367	IEC60567	2.2		-2.64	
1374	D3612	2		-3.67	
1430	IEC60567	2		-3.67	
1435	IEC60567	2.80		0.46	
1440	D3612	2.7		-0.06	
1442	IEC60567	3.04		1.70	
1458		-----		-----	
1473		-----		-----	
1478	IEC60567	2.0		-3.67	
1505	D3612	3		1.49	
1513	IEC60567	2.8		0.46	
1529	IEC60567	3.62		4.70	
1548		2		-3.67	
1560	IEC60567	3.5		4.08	
1626	IEC60567	3.25		2.78	
1660	IEC60567	2.7		-0.06	
1687	IEC60567	2.35		-1.86	
1702	IEC60567	3	C	1.49	First reported: 4
1743	IEC60567	2.8921		0.94	
1747	IEC60567	1.8695		-4.34	
1777	D3612	1.06	G(0.05)	-8.53	
1801	IEC60567	1.8		-4.70	
2125	IEC60567	2.18		-2.74	
8445	IEC60567	3.0		1.49	
					Only headspace results:
	normality	OK			OK
	n	31			19
	outliers	1			1
	mean (n)	2.7108			2.8218
	st.dev. (n)	0.51894			0.42317
	R(calc.)	1.4530			1.1849
	R(IEC60567:11)	0.5422			0.5644

Compare R(Horwitz): 1.045





Determination of Propane and Propene on sample #13209; results in µl/L

lab	method	Propane	mark	z(targ)	Propene	mark	z(targ)	remarks
360		-----		-----	-----		-----	
398	IEC60567	8.5		-----	<1		-----	
445		-----		-----	-----		-----	
614		-----		-----	-----		-----	
963		-----		-----	-----		-----	
1072		-----		-----	-----		-----	
1178		-----		-----	-----		-----	
1264		-----		-----	-----		-----	
1304		-----		-----	-----		-----	
1306		-----		-----	-----		-----	
1367		-----		-----	-----		-----	
1374		-----		-----	-----		-----	
1430		-----		-----	-----		-----	
1435		-----		-----	-----		-----	
1440	D3612	<5.4		-----	3.6		0.45	
1442		-----		-----	12.87	G(0.01)	37.67	
1458		-----		-----	-----		-----	
1473		-----		-----	-----		-----	
1478		-----		-----	-----		-----	
1505	D3612	<1		-----	2		-5.97	
1513		-----		-----	-----		-----	
1529	IEC60567	<0.1		-----	5.0		6.08	
1548		-----		-----	-----		-----	
1560		-----		-----	-----		-----	
1626		-----		-----	-----		-----	
1660	IEC60567	<0.1		-----	4.2		2.86	
1687	IEC60567	<1		-----	3.3		-0.75	
1702		-----		-----	-----		-----	
1743	IEC60567	0		-----	2.8214		-2.67	
1747		-----		-----	-----		-----	
1777		-----		-----	-----		-----	
1801		-----		-----	-----		-----	
2125		-----		-----	-----		-----	
8445		-----		-----	-----		-----	
	normality	n.a.			OK			
	n	n.a.			6			
	outliers	n.a.			1			
	mean (n)	n.a.			3.4869			
	st.dev. (n)	n.a.			1.04876			
	R(calc.)	n.a.			2.9365			
	R(IEC60567:11)	n.a.			0.6974			

APPENDIX 2

Number of participants per country

4 labs in AUSTRALIA
2 labs in BELGIUM
1 lab in BULGARIA
1 lab in CROATIA
2 labs in FRANCE
2 labs in GERMANY
1 lab in GREECE
2 labs in ITALY
1 lab in KINGDOM OF BAHRAIN
1 lab in MALAYSIA
1 lab in NETHERLANDS
1 lab in PORTUGAL
2 labs in SAUDI ARABIA
1 lab in SERBIA
1 lab in SINGAPORE
1 lab in SLOVENIA
1 lab in SOUTH AFRICA
3 labs in SPAIN
1 lab in SWEDEN
1 lab in TURKEY
1 lab in UNITED ARAB EMIRATES
2 labs 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:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation, January 2010 (version 3.2.).
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/)