Results of Proficiency Test
Dissolved Gas Analysis
November 2012

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Appendices:

1 INTRODUCTION

Since 2007, the Institute for Interlaboratory Studies organized a proficiency test for the analysis of Dissolved Gas Analysis (DGA) in Transformer Oil. During the annual proficiency testing program 2012/2013, it was decided to continue the PT for Dissolved Gas Analysis. In this international Interlaboratory study, 31 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 2012 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.
In total one batch of 37 certified syringes (of 50 mL) was prepared (lot RN26) on October 16, 2012. 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 certificate. 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 ILAC-G13:2007 and ISO/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Also customer's satisfaction is measured on regular basis by the distribution of 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 EN 60567, clause 6.2 (2011).
In total one batch of 37 syringes was prepared (lot RN26) on October 16, 2012. Each syringe was uniquely numbered and a certificate of analysis was provided by Morgan Schaffer Inc. These certificates were removed by iis after receipt prior to the forwarding of the samples to the participating laboratories.

The differences between the test results of each syringe are statistically not 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 #12148) was sent on October 24, 2012.

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 #12148: 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 EN 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(target) = (result - average of PT) / 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:

	| 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 two laboratories. These laboratories needed two more syringes to determine DGA.
All participants did report one or more test results. In total 29 participating laboratories reported 265 numerical results. Observed were 15 outlying results, which is 5.7% 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 determination: Methane. In this case the statistical evaluation should be used with due care.
Two laboratories were excluded from the evaluation. One laboratory reported very low results for all requested components. The other laboratory reported very high results for all requested components. 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. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the requirements of EN 60567:2011.

Oxygen: 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 EN 60567:2011.

Nitrogen: The determination of this component was problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the requirements of EN 60567:2011.

Carbon monoxide: 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 EN 60567:2011.

Carbon dioxide: 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 EN 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 EN 60567:2011.

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

Ethene: 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 EN 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 EN 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, derived from literature standards (in casu EN 60567:2011) are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
Hydrogen H_2	µl/L	25	20.05	11.31	4.01
Oxygen O_2	µl/L	25	20685	9144	4137
Nitrogen N_2	µl/L	24	55063	18215	11013
Carbon Monoxide CO	µl/L	26	154.1	64.5	30.8
Carbon Dioxide CO_2	µl/L	26	1289	497	258
Methane CH_4	µl/L	27	7.80	3.83	1.56
Ethane C_2H_6	µl/L	23	2.36	1.18	0.47
Ethene C_2H_4	µl/L	24	5.44	3.23	1.09
Ethyn C_2H_2	µl/L	25	2.79	1.60	0.56
Propane C_3H_8	µl/L	5	0.39	n.a	n.a
Propene C_3H_6	µl/L	5	3.70	n.a	n.a
Sum of Propane C_3H_8 and Propene C_3H_6	µl/L	8	4.09	n.a	n.a

Table 2: Performance of the group on sample #12148

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 EN 60567:2011.
The problematic components have been discussed in paragraph 4.1.

4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2012 WITH PREVIOUS PTS

	November 2012	*November 2011*	*November 2010*	*November 2009*
Number of reporting labs	29	33	24	18
Number of results reported	265	299	218	182
Statistical outliers	15	18	10	9
Percentage outliers	6.0%	6.0%	4.6%	5.0%

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 2012*	*November 2011*	*November 2010*	*November 2009*
Hydrogen H_2	--	--	--	--
Oxygen O_2	--	-	-	-
Nitrogen N_2	-	-	-	--
Carbon Monoxide CO	--	-	-	--
Carbon Dioxide CO_2	--	-	-	-
Methane CH_4	--	--	-	--
Ethane C_2H_6	--	--	--	--
Ethene C_2H_4	--	--	-	--
Ethyn C_2H_2	--	--	--	--
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 4: Comparison determinations against EN 60567:2011

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_2	15	20	+5
Oxygen O_2	21500	20685	-815
Nitrogen N_2	53400	55063	+1663
Carbon Monoxide CO	167	154	-13
Carbon Dioxide CO_2	1270	1289	+19
Methane CH_4	8.2	7.8	-0.4
Ethane C_2H_6	2.3	2.4	+0.1
Ethene C_2H_4	5.6	5.4	-0.2
Ethyn C_2H_2	2.8	2.8	0

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	*actual testing date*	laboratory	*actual testing date*
360	14 November 2012	1463	16 November 2012
398	12 November 2012	1473	7 November 2012
445	16 November 2012	1478	19 November 2012
614	8 November 2012	1513	14 November 2012
963	6 November 2012	1529	Unknown
1072	19 November 2012	1547	5 November 2012
1178	19 November 2012	1560	11 November 2012
1264	20 November 2012	1565	2 November 2012
1304	20 November 2012	1626	19 November 2012
1306	13 November 2012	1660	3 December 2012
1375	19 November 2012	1704	23 November 2012
1435	6 November 2012	1801	8 November 2012
1440	7 November 2012	2125	6 November 2012
1442	5 November 2012		
1453	12 November 2012		
1458	13 November 2012		

Table 6: Actual testing dates

However, a correlation could be found between the methods used by the laboratories and the reported results. Five laboratories (1072, 1178, 1478, 1513 and 1704) used the Toepler method (EN 60567 clause 7.2), seventeen laboratories (360, 398, 445, 963, 1304, 1306, 1375, 1435, 1440, 1442, 1453, 1473, 1560, 1565, 1626, 1660 and 2125) used the head-space method (EN 60567 clause 7.5), one laboratory used partial extraction (1801) two laboratories (614, 1458) used the ToGas method and one laboratory (1463) used the ASTM D3612-B

stripper column extraction and one laboratory (1529) did not report the extraction method that was used.

When the headspace method is evaluated separately it is noted that the consensus values for headspace are higher for Hydrogen, Oxygen, Methane, Ethane and Ethene. The consensus values for Nitrogen, Carbon monoxide, Carbon dioxide and Ethyn are lower for the headspace method than for all methods.
The spread of the headspace results is larger than the spread of the results of the other test methods, except for Hydrogen and Ethyn.

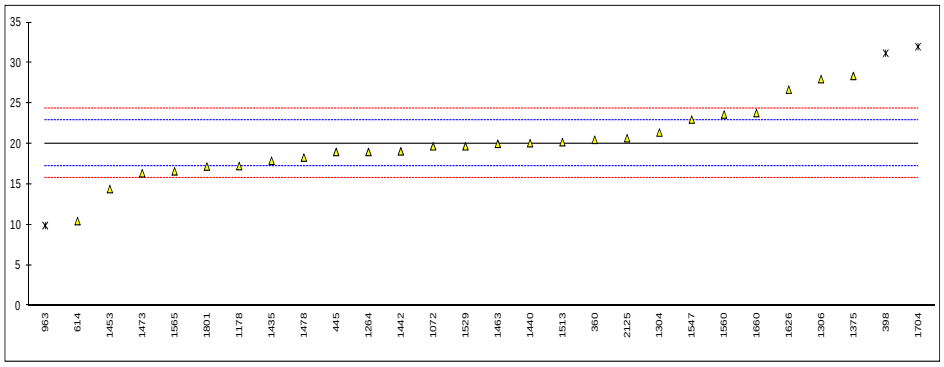
The target reproducibilities as required by EN 60567 obviously appear to be very hard to meet, although the observed reproducibilities are decreasing during the subsequent annual PTs. Still, it is clear that the reproducibility requirements of EN 60567 are quite strict as they are smaller than the reproducibilities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

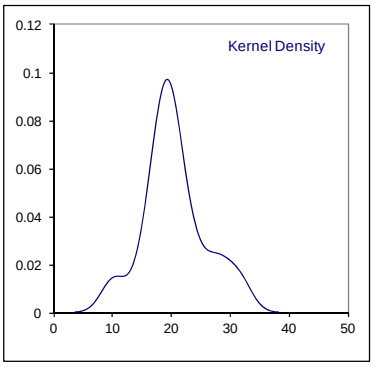
APPENDIX 1

Determination of Hydrogen on sample #12148; results in µl/L

lab	method	Value	mark	z(targ)	remarks
360	EN60567	20.5		0.31	
398	EN60567	31.2	G(0.05)	7.78	
445	EN60567	19		-0.74	
614	IEC60567	10.451		-6.70	
963	D3612C	9.9	ex	-7.09	See § 4.1
1072	EN60567	19.70		-0.25	
1178	EN60567	17.26		-1.95	
1264	D3612C	19		-0.74	
1304	INH-120	21.4		0.94	
1306	in house	28		5.55	
1375	IEC60567	28.39		5.82	
1430		-----		-----	
1435	IEC60567	17.91		-1.50	
1440	D3612C	20.08		0.02	
1442	IEC60567	19.07		-0.69	
1453	EN60567	14.40986		-3.94	
1458	D3612	<20		-----	
1463	D3612	20		-0.04	
1473	IEC60567	16.37		-2.57	
1478	IEC60567	18.3		-1.22	
1513	IEC60567	20.2		0.10	
1529	IEC60567	19.7		-0.25	
1547	EN60567	23		2.06	
1560	IEC60567	23.62		2.49	
1565	D3612C	16.6		-2.41	
1626	IEC60567	26.7		4.64	
1660	IEC60567	23.8		2.61	
1702		-----		-----	
1704	EN60567	32	G(0.05)	8.34	
1801	EN60567	17.2		-1.99	
2125	IEC60567	20.7		0.45	
					Only head space results:
	normality	OK			OK
	n	25			15
	outliers	2			2
	mean (n)	20.0544			21.1033
	st.dev. (n)	4.03794			4.25519
	R(calc.)	11.3062			11.9145
	R(IEC60567:11)	4.0109			4.2207

Compare R(Horwitz) = 5.721

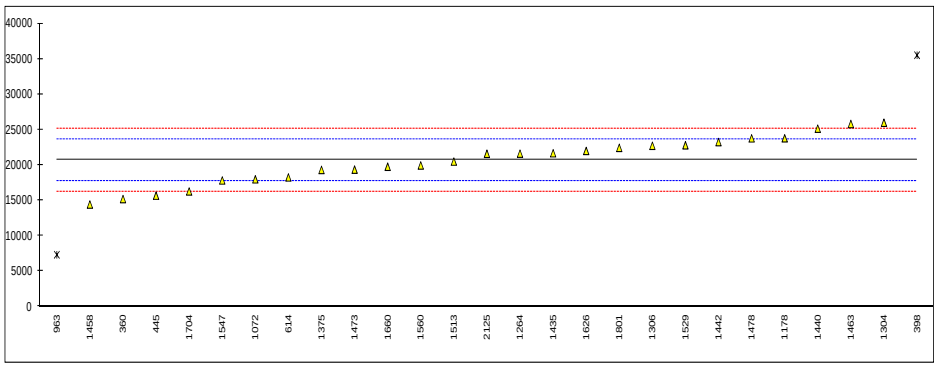


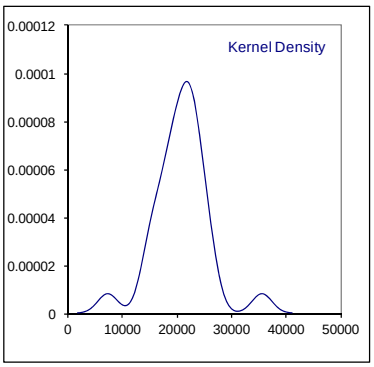


Determination of Oxygen on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	15193		-3.72	
398	EN60567	35516	G(0.05)	10.04	
445	EN60567	15681		-3.39	
614	IEC60567	18259.519		-1.64	
963	D3612C	7323	G(0.05)	-9.04	
1072	EN60567	17992.52		-1.82	
1178	EN60567	23781.3		2.10	
1264	D3612C	21613		0.63	
1304	INH-120	25977.4		3.58	
1306	in house	22722		1.38	
1375	IEC60567	19313		-0.93	
1430		-----		-----	
1435	IEC60567	21672.7		0.67	
1440	D3612C	25141.12		3.02	
1442	IEC60567	23251		1.74	
1453		-----		-----	
1458	D3612	14428		-4.23	
1463	D3612	25800		3.46	
1473	IEC60567	19362		-0.90	
1478	IEC60567	23781		2.10	
1513	IEC60567	20500		-0.13	
1529	IEC60567	22800		1.43	
1547	EN60567	17834		-1.93	
1560	IEC60567	19947.8		-0.50	
1565		-----		-----	
1626	IEC60567	21995.5		0.89	
1660	IEC60567	19768		-0.62	
1702		-----		-----	
1704	EN60567	16277		-2.98	
1801	EN60567	22438.1		1.19	
2125	IEC60567	21599		0.62	
					Only head space results:
	normality	OK			OK
	n	25			13
	outliers	2			2
	mean (n)	20685.12			20894.13
	st.dev. (n)	3265.771			3185.635
	R(calc.)	9144.16			8919.78
	R(IEC60567:11)	4137.02			4178.83

Compare R(Horwitz) = 2076.66

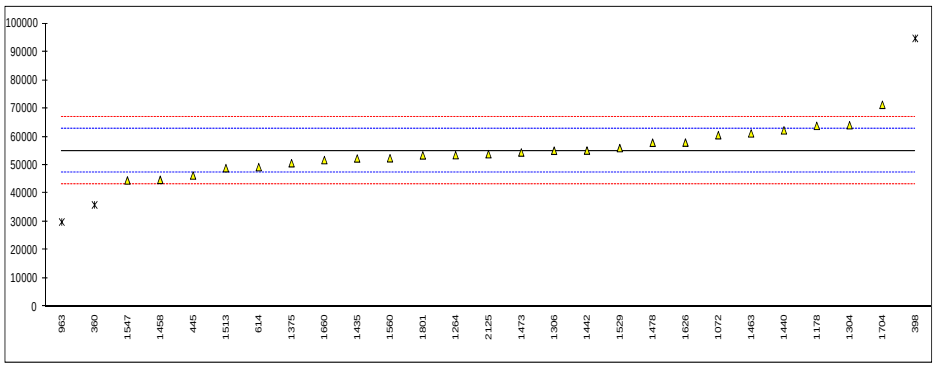


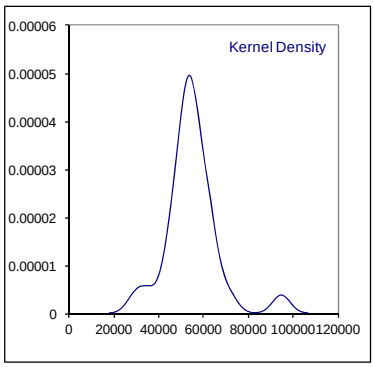


Determination of Nitrogen on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	35923	DG(0.05)	-4.87	
398	EN60567	94727	G(0.01)	10.08	
445	EN60567	46324		-2.22	
614	IEC60567	49278.397		-1.47	
963	D3612C	29889	DG(0.05)	-6.40	
1072	EN60567	60547.77		1.39	
1178	EN60567	63855.2		2.24	
1264	D3612C	53503		-0.40	
1304	INH-120	64076.7		2.29	
1306	in house	55076		0.00	
1375	IEC60567	50645		-1.12	
1430		-----		-----	
1435	IEC60567	52333.8		-0.69	
1440	D3612C	62261.67		1.83	
1442	IEC60567	55135		0.02	
1453		-----		-----	
1458	D3612	44779		-2.61	
1463	D3612	61200		1.56	
1473	IEC60567	54454		-0.15	
1478	IEC60567	57901		0.72	
1513	IEC60567	48900		-1.57	
1529	IEC60567	56000		0.24	
1547	EN60567	44588		-2.66	
1560	IEC60567	52397.4		-0.68	
1565		-----		-----	
1626	IEC60567	57934.5		0.73	
1660	IEC60567	51762		-0.84	
1702		-----		-----	
1704	EN60567	71274		4.12	
1801	EN60567	53433.2		-0.41	
2125	IEC60567	53842		-0.31	
					Only head space results:
	normality	OK			OK
	n	24			12
	outliers	3			3
	mean (n)	55062.57			54686.84
	st.dev. (n)	6505.239			4888.034
	R(calc.)	18214.67			13686.50
	R(IEC60567:11)	11012.51			10937.37

Compare R(Horwitz) = 4770.51

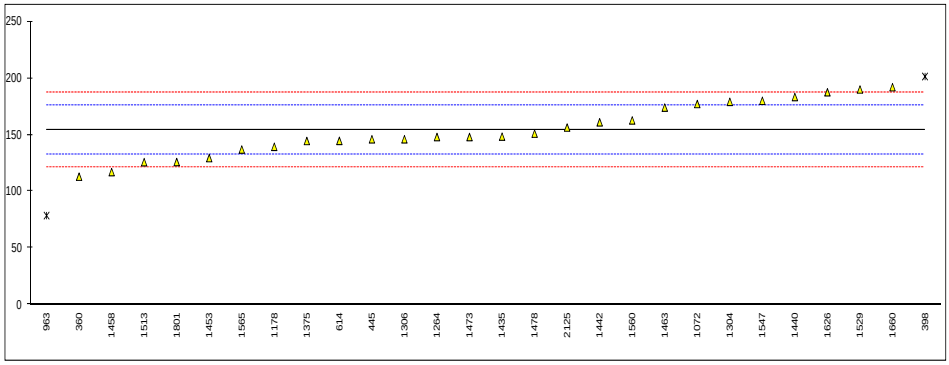


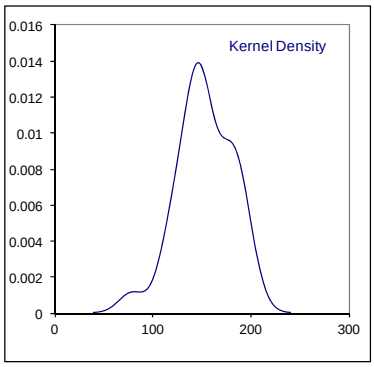


Determination of Carbon monoxide on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	113		-3.73	
398	EN60567	201.4	ex	4.30	See § 4.1
445	EN60567	146		-0.74	
614	IEC60567	144.589		-0.87	
963	D3612C	78.6	G(0.05)	-6.86	
1072	EN60567	177.16		2.09	
1178	EN60567	139.38		-1.34	
1264	D3612C	148		-0.56	
1304	INH-120	179.1		2.27	
1306	in house	146		-0.74	
1375	IEC60567	144.51		-0.87	
1430		-----		-----	
1435	IEC60567	148.36		-0.52	
1440	D3612C	183.34		2.65	
1442	IEC60567	160.95		0.62	
1453	EN60567	129.3743		-2.25	
1458	D3612	117		-3.37	
1463	D3612	174		1.81	
1473	IEC60567	148.0		-0.56	
1478	IEC60567	151		-0.28	
1513	IEC60567	125.8		-2.57	
1529	IEC60567	190		3.26	
1547	EN60567	180		2.35	
1560	IEC60567	162.64		0.77	
1565	D3612C	137		-1.55	
1626	IEC60567	187.5		3.03	
1660	IEC60567	192		3.44	
1702		-----		-----	
1704	EN60567	n.d.		-----	
1801	EN60567	125.9		-2.56	
2125	IEC60567	156.4		0.21	
					Only head space results:
	normality	OK			OK
	n	26			15
	outliers	1			1
	mean (n)	154.1155			155.6116
	st.dev. (n)	23.02807			22.37528
	R(calc.)	64.4786			62.6508
	R(IEC60567:11)	30.8231			31.1223

Compare R(Horwitz) = 32.346

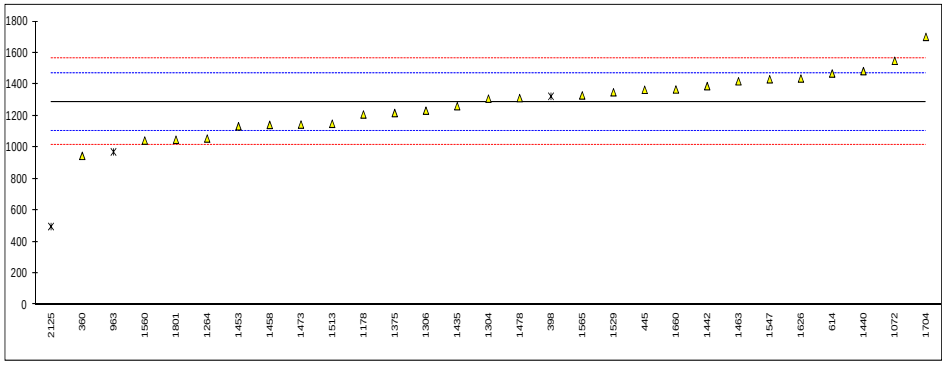


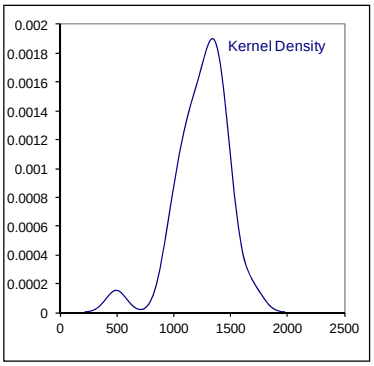


Determination of Carbon dioxide on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	946		-3.72	
398	EN60567	1324.3	ex	0.39	See § 4.1
445	EN60567	1366		0.84	
614	IEC60567	1469.211		1.96	
963	D3612C	971	ex	-3.45	See § 4.1
1072	EN60567	1550.12		2.84	
1178	EN60567	1208.66		-0.87	
1264	D3612C	1056		-2.53	
1304	INH-120	1309.4		0.22	
1306	in house	1233		-0.61	
1375	IEC60567	1218		-0.77	
1430		-----		-----	
1435	IEC60567	1261.86		-0.29	
1440	D3612C	1484.43		2.13	
1442	IEC60567	1389		1.09	
1453	EN60567	1133.901		-1.68	
1458	D3612	1143		-1.58	
1463	D3612	1420		1.43	
1473	IEC60567	1145		-1.56	
1478	IEC60567	1313		0.26	
1513	IEC60567	1150		-1.51	
1529	IEC60567	1350		0.66	
1547	EN60567	1433		1.57	
1560	IEC60567	1043.02		-2.67	
1565	D3612C	1330		0.45	
1626	IEC60567	1437.5		1.62	
1660	IEC60567	1368		0.86	
1702		-----		-----	
1704	EN60567	1702		4.49	
1801	EN60567	1048.3		-2.61	
2125	IEC60567	496.5	G(0.01)	-8.61	
					Only head space results
	normality	OK			OK
	n	26			14
	outliers	1			1
	mean (n)	1288.785			1261.794
	st.dev. (n)	177.6638			153.4250
	R(calc.)	497.459			429.590
	R(IEC60567:11)	257.757			252.359

Compare R(Horwitz) = 196.485

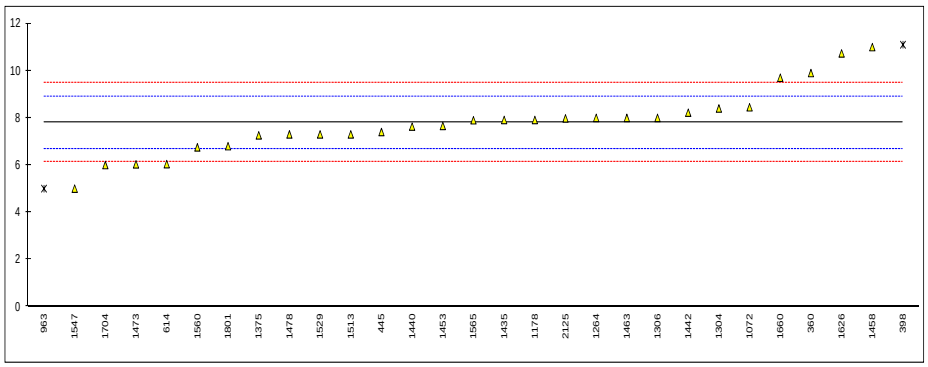


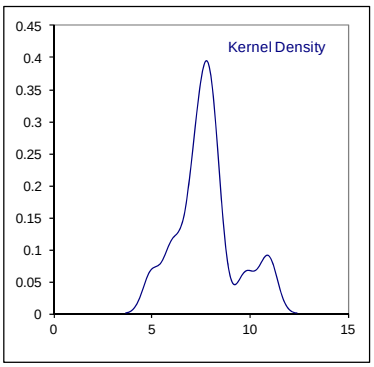


Determination of Methane on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	9.9		3.77	
398	EN60567	11.1	ex	5.93	See § 4.1
445	EN60567	7.4		-0.72	
614	IEC60567	6.038		-3.16	
963	D3612C	5	ex	-5.02	See § 4.1
1072	EN60567	8.45		1.17	
1178	EN60567	7.91		0.20	
1264	D3612C	8		0.36	
1304	INH-120	8.4		1.08	
1306	in house	8		0.36	
1375	IEC60567	7.26		-0.97	
1430		-----		-----	
1435	IEC60567	7.91		0.20	
1440	D3612C	7.63		-0.30	
1442	IEC60567	8.22		0.76	
1453	EN60567	7.661104		-0.25	
1458	D3612	11		5.75	
1463	D3612	8		0.36	
1473	IEC60567	6.03		-3.18	
1478	IEC60567	7.3		-0.90	
1513	IEC60567	7.3		-0.90	
1529	IEC60567	7.3		-0.90	
1547	EN60567	5		-5.02	
1560	IEC60567	6.75		-1.88	
1565	D3612C	7.9		0.18	
1626	IEC60567	10.73		5.26	
1660	IEC60567	9.7		3.41	
1702		-----		-----	
1704	EN60567	6		-3.23	
1801	EN60567	6.8		-1.79	
2125	IEC60567	7.98		0.33	
					Only head space results
	normality	not OK			OK
	n	27			15
	outliers	0			0
	mean (n)	7.7989			8.0981
	st.dev. (n)	1.36804			1.21415
	R(calc.)	3.8305			3.3996
	R(IEC60567:11)	1.5598			1.6196

Compare R(Horwitz) = 2.565

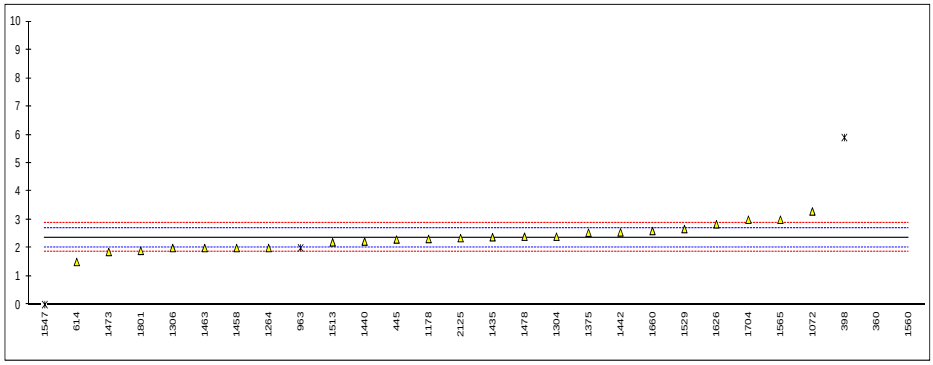


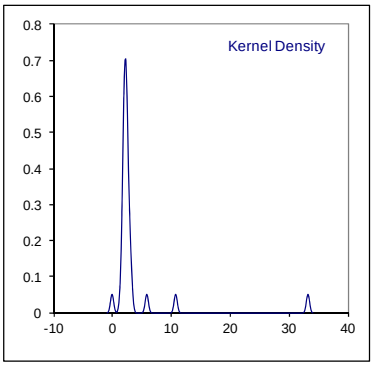


Determination of Ethane on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	10.8	G(0.01)	50.00	
398	EN60567	5.9	G(0.01)	20.96	
445	EN60567	2.3		-0.37	
614	IEC60567	1.508		-5.06	
963	D3612C	2	ex	-2.15	See § 4.1
1072	EN60567	3.29		5.50	
1178	EN60567	2.32		-0.25	
1264	D3612C	2		-2.15	
1304	INH-120	2.4		0.22	
1306	in house	2		-2.15	
1375	IEC60567	2.54		1.05	
1430		-----		-----	
1435	IEC60567	2.38		0.10	
1440	D3612C	2.23		-0.79	
1442	IEC60567	2.55		1.11	
1453		-----		-----	
1458	D3612	2		-2.15	
1463	D3612	2		-2.15	
1473	IEC60567	1.86		-2.98	
1478	IEC60567	2.4		0.22	
1513	IEC60567	2.2		-0.96	
1529	IEC60567	2.67		1.82	
1547	EN60567	0	ex	-14.00	Result excluded, zero is not a real result.
1560	IEC60567	33.26	G(0.01)	183.09	
1565	D3612C	3.0		3.78	
1626	IEC60567	2.84		2.83	
1660	IEC60567	2.6		1.41	
1702		-----		-----	
1704	EN60567	3		3.78	
1801	EN60567	1.9		-2.74	
2125	IEC60567	2.35		-0.07	
					Only head space results only:
	normality	OK			OK
	n	23			12
	outliers	4			3
	mean (n)	2.3625			2.4208
	st.dev. (n)	0.42071			0.31964
	R(calc.)	1.1780			0.8950
	R(IEC60567:11)	0.4725			0.4842

Compare R(Horwitz) = 0.930

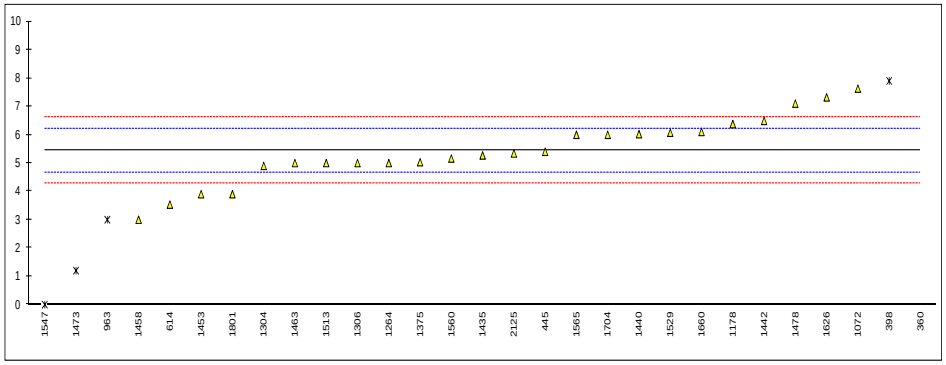


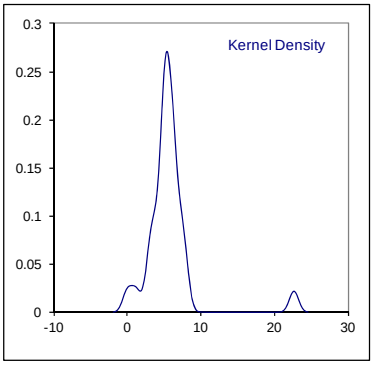


Determination of Ethene (ethylene) on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	22.6	G(0.01)	44.17	
398	EN60567	7.9	ex	6.33	See § 4.1
445	EN60567	5.4		-0.10	
614	IEC60567	3.533		-4.91	
963	D3612C	3	ex	-6.28	See § 4.1
1072	EN60567	7.63		5.64	
1178	EN60567	6.38		2.42	
1264	D3612C	5		-1.13	
1304	INH-120	4.9		-1.39	
1306	in house	5		-1.13	
1375	IEC60567	5.03		-1.05	
1430		-----		-----	
1435	IEC60567	5.27		-0.44	
1440	D3612C	6.02		1.49	
1442	IEC60567	6.49		2.70	
1453	EN60567	3.899852		-3.96	
1458	D3612	3		-6.28	
1463	D3612	5		-1.13	
1473	IEC60567	1.20	G(0.05)	-10.91	
1478	IEC60567	7.1		4.27	
1513	IEC60567	5.0		-1.13	
1529	IEC60567	6.07		1.62	
1547	EN60567	0	ex	-14.00	Result excluded, zero is not a real result.
1560	IEC60567	5.16		-0.72	
1565	D3612C	6.0		1.44	
1626	IEC60567	7.32		4.84	
1660	IEC60567	6.1		1.70	
1702		-----		-----	
1704	EN60567	6		1.44	
1801	EN60567	3.9		-3.96	
2125	IEC60567	5.34		-0.26	
					Only head space results:
	normality	OK			OK
	n	24			13
	outliers	2			2
	mean (n)	5.4393			5.5331
	st.dev. (n)	1.15260			0.85412
	R(calc.)	3.2273			2.3915
	R(IEC60567:11)	1.0879			1.1066

Compare R(Horwitz) = 1.888

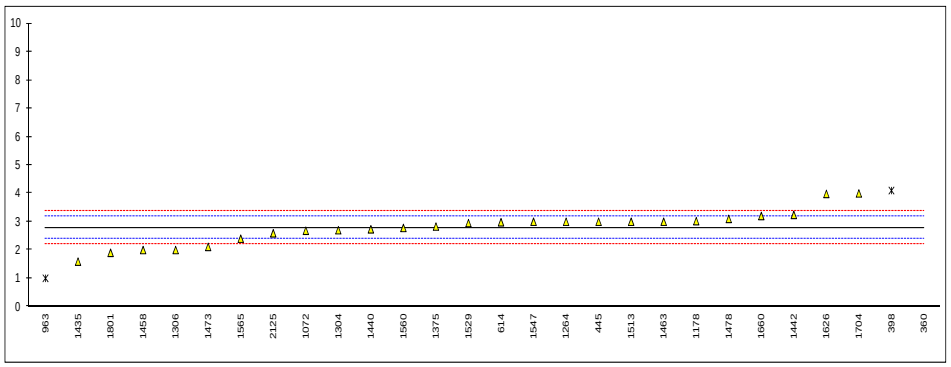


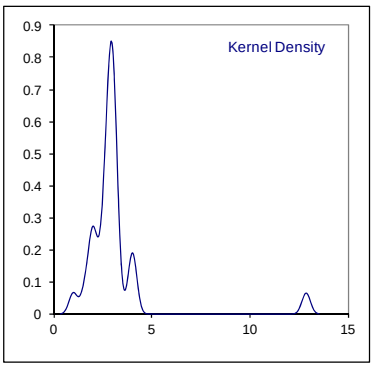


Determination of Ethyn (acetylene) on sample #12148; results in µl/L

lab	method	value	mark	z(targ)	remarks
360	EN60567	12.9	G(0.01)	50.70	
398	EN60567	4.1	ex	6.56	See § 4.1
445	EN60567	3.0		1.05	
614	IEC60567	2.98	C	0.95	First reported 1.324
963	D3612C	1	ex	-8.98	See § 4.1
1072	EN60567	2.68		-0.56	
1178	EN60567	3.02		1.15	
1264	D3612C	3		1.05	
1304	INH-120	2.7		-0.46	
1306	in house	2		-3.97	
1375	IEC60567	2.83		0.19	
1430		-----		-----	
1435	IEC60567	1.59		-6.02	
1440	D3612C	2.73		-0.31	
1442	IEC60567	3.24		2.25	
1453		-----		-----	
1458	D3612	2		-3.97	
1463	D3612	3		1.05	
1473	IEC60567	2.11		-3.42	
1478	IEC60567	3.1		1.55	
1513	IEC60567	3	C	1.05	First reported 4.2
1529	IEC60567	2.95		0.80	
1547	EN60567	3		1.05	
1560	IEC60567	2.78		-0.06	
1565	D3612C	2.4		-1.96	
1626	IEC60567	3.98		5.96	
1660	IEC60567	3.2		2.05	
1702		-----		-----	
1704	EN60567	4		6.06	
1801	EN60567	1.9		-4.47	
2125	IEC60567	2.59		-1.01	
					Only head space results:
	normality	OK			OK
	n	25			13
	outliers	1			1
	mean (n)	2.7912			2.7038
	st.dev. (n)	0.57163			0.61008
	R(calc.)	1.6006			1.7082
	R(IEC60567:11)	0.5582			0.5408

Compare R(Horwitz) = 1.071





Determination of Propane and Propene on sample #12148; results in µl/L

lab	method	Propane	mark	Propene	mark	Sum of Propane & and Propene	remarks
360		-----		-----		-----	
398	EN60567	<1		6.7	ex	6.7 (ex)	See § 4.1
445		-----		-----		-----	
614		-----		-----		-----	
963	D3612C	2.8	ex	<1		2.8 (ex)	See § 4.1
1072		-----		-----		-----	
1178		-----		-----		-----	
1264		-----		-----		-----	
1304		-----		-----		-----	
1306	in house	0		-----		0 (ex)	
1375	IEC60567	0.634		4.71		5.344	
1430		-----		-----		-----	
1435		-----		-----		-----	
1440	D3612C	0.00		3.42		3.42	
1442		-----		1.86		1.86	
1453		-----		-----		-----	
1458		-----		-----		-----	
1463		-----		-----		-----	
1473		-----		-----		-----	
1478		-----		-----		-----	
1513		-----		-----		-----	
1529	IEC60567	0.74		4.3		5.04	
1547		-----		-----		-----	
1560		-----		-----		-----	
1565		-----	W	-----		-----	
1626		-----		-----		-----	
1660	IEC60567	0.6		4.2		4.8	
1702		-----		-----		-----	
1704		-----		-----		-----	
1801		-----		-----		-----	
2125		-----		-----		-----	
	normality	OK		OK		n.a.	
	n	5		5		8	
	outliers	0		0		0	
	mean (n)	0.3948		3.6980		4.0928	
	st.dev. (n)	n.a.		n.a.		n.a.	
	R(calc.)	n.a.		n.a.		n.a.	
	R(IEC60567:11)	n.a.		n.a.		n.a.	

APPENDIX 2

Number of participants per country

3 labs in AUSTRALIA
2 labs in BELGIUM
2 labs in BULGARIA
1 lab in CANADA
1 lab in CROATIA
2 labs in FRANCE
1 lab in GERMANY
1 lab in INDIA
2 labs in ITALY
1 lab in KINGDOM OF BAHRAIN
1 lab in KOREA
1 lab in MALAYSIA
1 lab in PORTUGAL
2 labs in SAUDI ARABIA
1 lab in SLOVENIA
1 lab in SOUTH AFRICA
3 labs in SPAIN
1 lab in SWEDEN
1 lab in THE NETHERLANDS
1 lab in TURKEY
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:

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/)