Results of Proficiency Test
Dissolved Gas Analysis
November 2014

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 2014/2015, it was decided to continue the PT for Dissolved Gas Analysis. In this international Interlaboratory study, 41 laboratories from 23 different countries have participated. See appendix 2 for the number of participants per country. In this report the results of the 2014 proficiency test are presented and discussed. This report is also electronically available through the iis web site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, The Netherlands, was the organizer of this proficiency test. In total one batch of 48 certified syringes (of 50 mL) was prepared (lot RN149). The syringes were provided by Morgan Schaffer Inc, Quebec, Canada (True North). Each syringe was uniquely numbered and one syringe was sent to each participating laboratory, without the certificate provided by Morgan Schaffer Inc. Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% 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 was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded from the iis website www.iisnl.com.

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 48 syringes was prepared (lot RN149). 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 #14226) was sent on November 5, 2014.

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 #14226: Hydrogen, Oxygen, Nitrogen, Carbon Monoxide, Carbon Dioxide, Methane, Ethane, Ethene, Ethyn, Propane and Propene.
Also some method details were requested to be reported.
To get comparable results a detailed report form, on which the units were prescribed as well as the required standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis/. The detailed report form was also 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 deadline, a reminder fax was sent to those laboratories that did not report results at that moment.
Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the raw data of these tests (no reanalysis). Additional or corrected results are used for data analysis and original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

Statistical calculations were performed as described in the report ‘iis Interlaboratory Studies-Protocol for the Organisation, Statistics and Evaluation’ of April 2014 (iis-protocol, version 3.3). For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as ‘<…’ or ‘>…’ were not used in the statistical evaluation. First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.
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, by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test (ref. 15). Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are 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 “x”. Accepted data are represented as a triangle. Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3; nos.13 and 14). Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

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

The z-scores were calculated in accordance with:

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

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate the fit-for-useness of the reported test result.

The $z_{(target)}$ scores are listed in the result tables in appendix 1.
Absolute values for $z<2$ are very common and absolute values for $z>3$ are very rare.

Therefore, the usual interpretation of z-scores is as follows:

$\lvert z \rvert < 1$	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. 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 40 participating laboratories reported 358 numerical results. Observed were 10 outlying results, which is 4.2% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER TEST

In this section the results are discussed per component.
Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care.
All test results reported by laboratory 1898 were deviating and many of the nine test results were reported as zero. As the nine test results are not independent, it was decided to reject all of the test results of this laboratory 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 strict requirements of IEC 60567:2011.

Oxygen: The determination of this component was very problematic. No statistical outliers were observed. One result was excluded. The calculated reproducibility after rejection of the excluded result is not at all in agreement with the requirements of IEC 60567:2011.

Nitrogen: The determination of this component was very problematic. Two statistical outliers were observed and one result was excluded. The calculated reproducibility after rejection of the suspect data 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. One statistical outlier was observed and one result was excluded. The calculated reproducibility after rejection of the suspect data 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 strict requirements of IEC 60567:2011.

Ethane: 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 strict requirements of IEC 60567:2011.

Ethene: The determination of this component was very problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the strict requirements of IEC 60567:2011.

Ethyn: The determination of this component was very problematic. No statistical outliers were observed. The calculated reproducibility is not at all in agreement with the strict requirements of IEC 60567:2011.

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

Propene: The determination of this component was very problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the strict requirements of IEC 60567:2011.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

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

Parameter	unit	n	average	2.8 * sd	R(lit)
Hydrogen H_2	µl/L	36	17.93	11.81	3.59
Oxygen O_2	µl/L	38	20823	10697	4165
Nitrogen N_2	µl/L	36	54496	20286	10899
Carbon Monoxide CO	µl/L	38	169.5	58.6	33.9
Carbon Dioxide CO_2	µl/L	37	1317	636	264
Methane CH_4	µl/L	38	8.19	4.14	1.64
Ethane C_2H_6	µl/L	32	2.57	1.70	0.51
Ethene C_2H_4	µl/L	37	5.68	4.55	1.14
Ethyn C_2H_2	µl/L	38	2.69	2.61	0.54
Propane C_3H_8	µl/L	10	<1	n.a	n.a
Propene C_3H_6	µl/L	7	4.98	2.85	1.00

Table 1: Performance of the group on sample #14226

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 2014 WITH PREVIOUS PTS

	November 2014	*November 2013*	*November 2012*	*November 2011*
Number of reporting labs	40	33	29	33
Number of results reported	358	293	265	299
Statistical outliers	10	10	15	18
Percentage outliers	2.8%	3.4%	6.0%	6.0%

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

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

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

Determination	*November 2014*	*November 2013*	*November 2012*	*November 2011*	*IEC60567:11*
Hydrogen H_2	24%	21%	20%	25%	7%
Oxygen O_2	18%	17%	16%	14%	7%
Nitrogen N_2	13%	19%	12%	12%	7%
Carbon Monoxide CO	12%	12%	15%	14%	7%
Carbon Dioxide CO_2	17%	15%	14%	14%	7%
Methane CH_4	18%	19%	18%	19%	7%
Ethane C_2H_6	24%	23%	18%	25%	7%
Ethene C_2H_4	29%	17%	21%	18%	7%
Ethyn C_2H_2	35%	19%	20%	24%	7%
Propane C_3H_8	n.e.	n.e	n.e	n.e	n.e
Propene C_3H_6	20%	n.e	n.e	n.e	n.e

Table 3: Comparison of the relative uncertainties on determinations

Comparing the results of the 2014 round robin to that of last year, the performance appears to be worse for almost all components, except for Nitrogen and Methane, which showed an improvement.

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	18	+3
Oxygen O_2	20600	20823	+223
Nitrogen N_2	52600	54496	+1896
Carbon Monoxide CO	176	170	-6
Carbon Dioxide CO_2	1330	1317	-13
Methane CH_4	8.9	8.2	-0.7
Ethane C_2H_6	2.6	2.7	+0.1
Ethene C_2H_4	6.1	5.7	-0.4
Ethyn C_2H_2	3.2	2.7	-0.5

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-six laboratories (360, 398, 445, 963, 1137, 1304, 1306, 1367, 1374, 1430, 1435, 1440, 1442, 1516, 1529, 1548, 1560, 1626, 1660 1687, 1743, 1777, 1888, 1890, 1891 and 1943) 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), one laboratory (614) used the ToGas method and three laboratories (179, 1458 and 1719) used the ASTM D3612-B stripper column extraction. Three laboratories (551, 1264, 16245) 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).

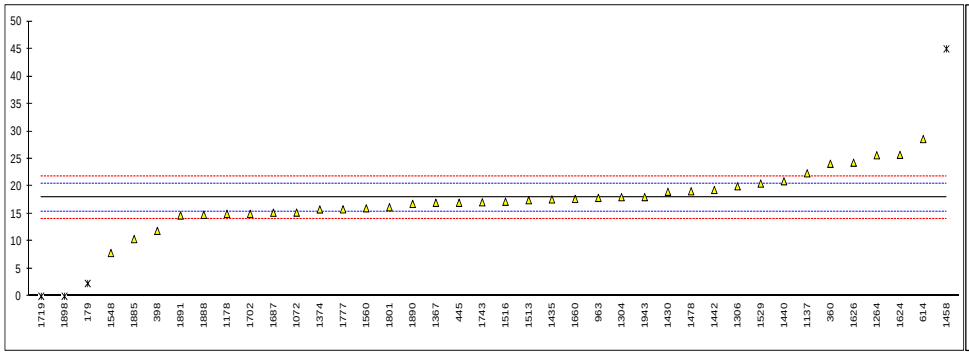
The target reproducibilities as required by IEC 60567 obviously appear to be very hard to meet, although the observed reproducibilities are decreasing during the subsequent annual PTs. Still, it is clear that the reproducibility requirements of IEC 60567 are quite strict as they are smaller than the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

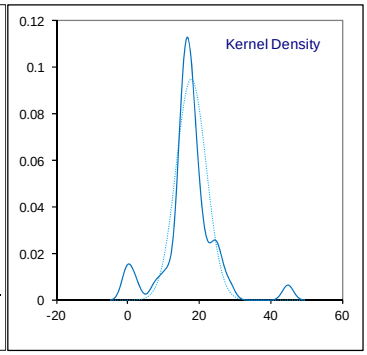
In order to evaluate whether the used test method has a significant influence on the test results, the headspace test results were evaluated separately, see appendix 2. From the evaluation is noted that for the majority of the components the consensus value for the headspace test results is slightly 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.

APPENDIX 1

Determination of Hydrogen on sample #14226; results in µl/L

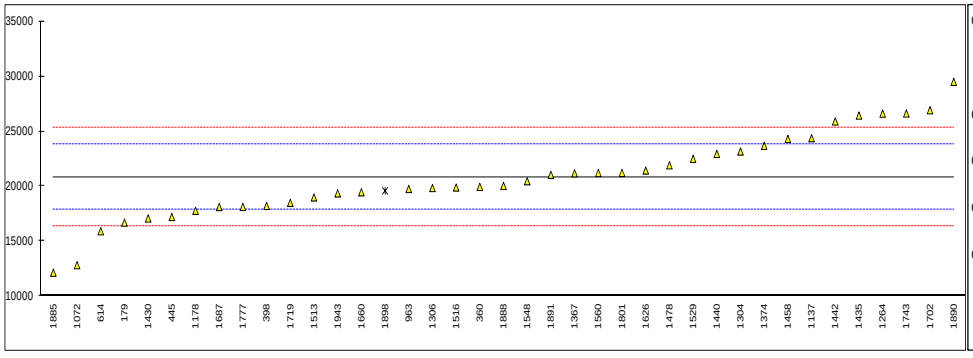
lab	method	value	mark	z(targ)	remarks
179	D3612	2.322	C,R(0.05)	-12.19	First reported 0
360	IEC60567	24.1		4.82	
398	IEC60567	11.9		-4.71	
445	IEC60567	17.0		-0.72	
511		-----		-----	
614	IEC60567	28.589		8.33	
963	D3612	17.9		-0.02	
1072	IEC60567	15.22		-2.11	
1137	D3612	22.3649		3.47	
1178	IEC60567	15.0		-2.29	
1264	D3612	25.65		6.03	
1304	INH-120	18.03		0.08	
1306	D3612	20		1.62	
1367	IEC60567	17		-0.72	
1374	D3612	15.8		-1.66	
1430	IEC60567	19		0.84	
1435	IEC60567	17.62		-0.24	
1440	IEC60567	20.92		2.34	
1442	IEC60567	19.33		1.10	
1458	D3612	45	R(0.01)	21.14	
1478	IEC60567	19.1		0.92	
1513	IEC60567	17.47		-0.36	
1516	IEC60567	17.2		-0.57	
1529	IEC60567	20.5		2.01	
1548	IEC60567	7.86881		-7.85	
1560	IEC60567	16		-1.50	
1624	IEC60567	25.7217		6.09	
1626	IEC60567	24.3		4.98	
1660	IEC60567	17.7		-0.18	
1687	IEC60567	15.2		-2.13	
1702	IEC60567	15		-2.29	
1719	D3612	0	ex	-14.00	Result excluded, zero is not a real result
1743	IEC60567	17.088		-0.66	
1777	IEC60567	15.82		-1.65	
1801	IEC60567	16.2		-1.35	
1885	D3612	10.4		-5.88	
1888	IEC60567	14.826		-2.42	
1890	IEC60567	16.81		-0.87	
1891	IEC60567	14.7		-2.52	
1898	in house	0	ex	-14.00	Result excluded, zero is not a real result
1943	D3612	18.042		0.09	
					Only headspace results
	normality	OK			suspect
	n	36			26
	outliers	2	(+2 excl)		0
	mean (n)	17.9270			17.5777
	st.dev. (n)	4.21962			3.46550
	R(calc.)	11.8149			9.7034
	R(IEC60567:11)	3.5854			3.5155 Compare R(Horwitz) = 5.1969

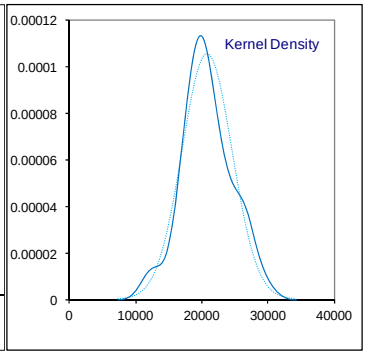




Determination of Oxygen on sample #14226; results in µl/L

lab	method	value	mark	z(targ)	remarks
179	D3612	16698		-2.77	
360	IEC60567	19947.2		-0.59	
398	IEC60567	18214		-1.75	
445	IEC60567	17207.3		-2.43	
511		-----		-----	
614	IEC60567	15913.329		-3.30	
963	D3612	19756.8		-0.72	
1072	IEC60567	12827.85		-5.38	
1137	D3612	24373.9	C	2.39	First reported 34373.9
1178	IEC60567	17771.2		-2.05	
1264	D3612	26609.5		3.89	
1304	INH-120	23164.59		1.57	
1306	D3612	19841		-0.66	
1367	IEC60567	21184		0.24	
1374	D3612	23682		1.92	
1430	IEC60567	17079		-2.52	
1435	IEC60567	26431.6		3.77	
1440	IEC60567	22945.23		1.43	
1442	IEC60567	25898		3.41	
1458	D3612	24308		2.34	
1478	IEC60567	21908.5		0.73	
1513	IEC60567	18990	C	-1.23	First reported 18.99
1516	IEC60567	19891.1		-0.63	
1529	IEC60567	22500		1.13	
1548	IEC60567	20459.3		-0.24	
1560	IEC60567	21214		0.26	
1624		-----		-----	
1626	IEC60567	21437		0.41	
1660	IEC60567	19459		-0.92	
1687	IEC60567	18114.6		-1.82	
1702	IEC60567	26918		4.10	
1719	D3612	18498		-1.56	
1743	IEC60567	26621.287		3.90	
1777	IEC60567	18125.3		-1.81	
1801	IEC60567	21219.9		0.27	
1885	D3612	12142.2		-5.84	
1888	IEC60567	20035		-0.53	
1890	IEC60567	29499		5.83	
1891	IEC60567	21043		0.15	
1898	in house	19584	ex	-0.83	Result excluded, see §4.1
1943	D3612	19356.900		-0.99	
					Only headspace results
	normality	OK			OK
	n	38			26
	outliers	0	(+1 excl)		0
	mean (n)	20823.28			21441.54
	st.dev. (n)	3820.281			3146.164
	R(calc.)	10696.79			8809.26
	R(IEC60567:11)	4164.66			4288.31 compare R(Horwitz) = 2088.43

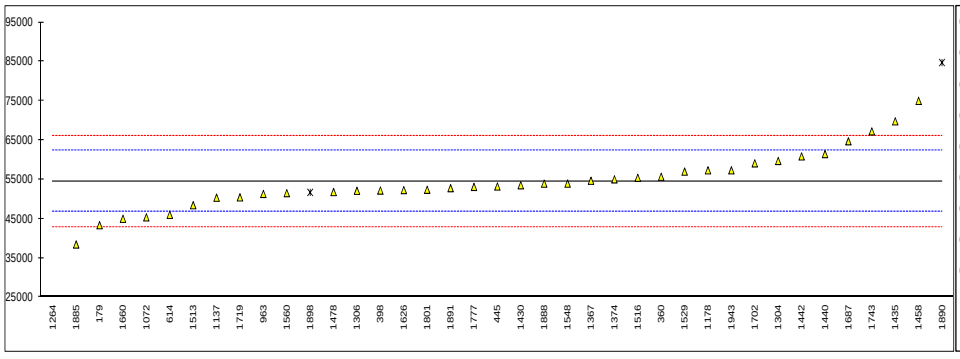


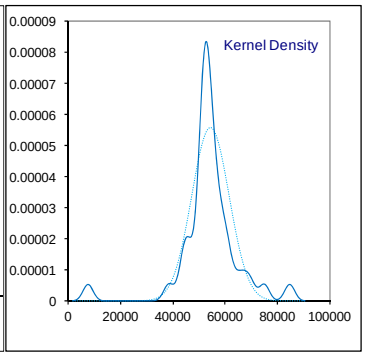


Determination of Nitrogen on sample #14226; results in µl/L

lab	method	value	mark	z(targ)	Remarks
179	D3612	43347		-2.86	
360	IEC60567	55691.1		0.31	
398	IEC60567	52176		-0.60	
445	IEC60567	53209.3		-0.33	
511		-----		-----	
614	IEC60567	46004.066		-2.18	
963	D3612	51314.3		-0.82	
1072	IEC60567	45342.03		-2.35	
1137	D3612	50355.8		-1.06	
1178	IEC60567	57318.6		0.73	
1264	D3612	7589.9	C,R(0.01)	-12.05	First reported 75899.2
1304	INH-120	59709.88		1.34	
1306	D3612	52119		-0.61	
1367	IEC60567	54670		0.04	
1374	D3612	55030		0.14	
1430	IEC60567	53524		-0.25	
1435	IEC60567	69792.6		3.93	
1440	IEC60567	61454.87		1.79	
1442	IEC60567	60864		1.64	
1458	D3612	75010		5.27	
1478	IEC60567	51793.6		-0.69	
1513	IEC60567	48450	C	-1.55	First reported 48.45
1516	IEC60567	55430.3		0.24	
1529	IEC60567	57000		0.64	
1548	IEC60567	53943.3		-0.14	
1560	IEC60567	51514		-0.77	
1624		-----		-----	
1626	IEC60567	52285		-0.57	
1660	IEC60567	44990		-2.44	
1687	IEC60567	64721.4		2.63	
1702	IEC60567	59105		1.18	
1719	D3612	50446		-1.04	
1743	IEC60567	67248.796		3.28	
1777	IEC60567	53113.2		-0.36	
1801	IEC60567	52378.8		-0.54	
1885	D3612	38449.2		-4.12	
1888	IEC60567	53935		-0.14	
1890	IEC60567	84750	R(0.01)	7.77	
1891	IEC60567	52783		-0.44	
1898	in house	51700	ex	-0.72	Result excluded, see §4.1
1943	D3612	57324.633		0.73	
					Only headspace results
	normality	suspect			suspect
	n	36			25
	outliers	2	(+1 excl)		1
	mean (n)	54495.66			55767.98
	st.dev. (n)	7245.139			5568.845
	R(calc.)	20286.39			15592.77
	R(IEC60567:11)	10899.13			11153.60

Compare R(Horwitz) = 4728.75

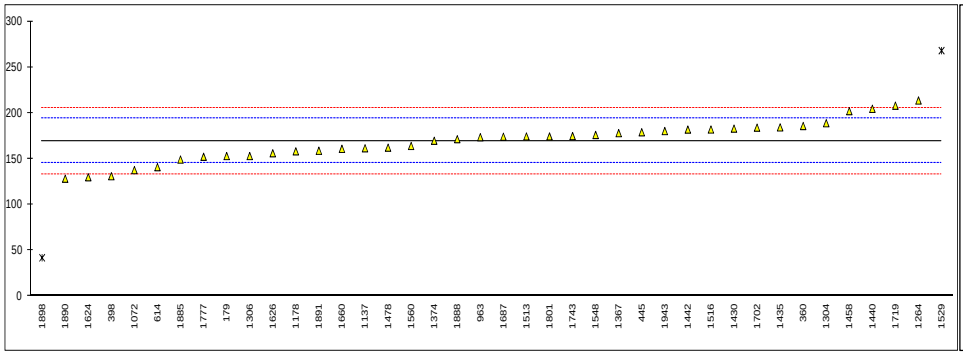


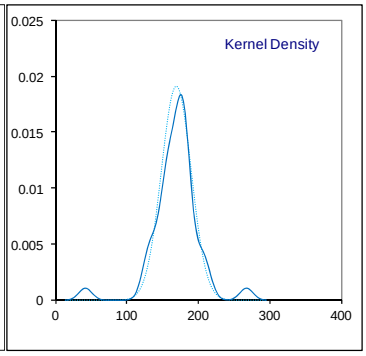


Determination of Carbon monoxide on sample #14226; results in µl/L

lab	method	value	mark	z(targ)	Remarks
179	D3612	153		-1.36	
360	IEC60567	185.8		1.35	
398	IEC60567	131	C	-3.18	First reported 241
445	IEC60567	179.0		0.78	
511		-----		-----	
614	IEC60567	140.924		-2.36	
963	D3612	173.6		0.34	
1072	IEC60567	137.71		-2.63	
1137	D3612	161.5343		-0.66	
1178	IEC60567	158.2		-0.93	
1264	D3612	213.64		3.65	
1304	INH-120	188.86		1.60	
1306	D3612	153		-1.36	
1367	IEC60567	178		0.70	
1374	D3612	169.7		0.02	
1430	IEC60567	183		1.12	
1435	IEC60567	184.32		1.22	
1440	IEC60567	204.57		2.90	
1442	IEC60567	181.9		1.02	
1458	D3612	202		2.68	
1478	IEC60567	162.2		-0.60	
1513	IEC60567	174.4		0.41	
1516	IEC60567	182.0		1.03	
1529	IEC60567	268	R(0.01)	8.14	
1548	IEC60567	176.03767		0.54	
1560	IEC60567	164		-0.45	
1624	IEC60567	129.8826		-3.27	
1626	IEC60567	156.1		-1.11	
1660	IEC60567	160.9		-0.71	
1687	IEC60567	174.1		0.38	
1702	IEC60567	184		1.20	
1719	D3612	208		3.18	
1743	IEC60567	174.8355		0.44	
1777	IEC60567	152.23		-1.43	
1801	IEC60567	174.4		0.41	
1885	D3612	149.2		-1.68	
1888	IEC60567	171.450		0.16	
1890	IEC60567	128.3		-3.40	
1891	IEC60567	158.8		-0.88	
1898	in house	42	R(0.01)	-10.53	
1943	D3612	180.268		0.89	
					Only headspace results
	normality	OK			suspect
	n	38			25
	outliers	2			1
	mean (n)	169.4964			170.1322
	st.dev. (n)	20.91994			17.29124
	R(calc.)	58.5758			48.4155
	R(IEC60567:11)	33.8993			34.0264

Compare R(Horwitz) = 35.0684

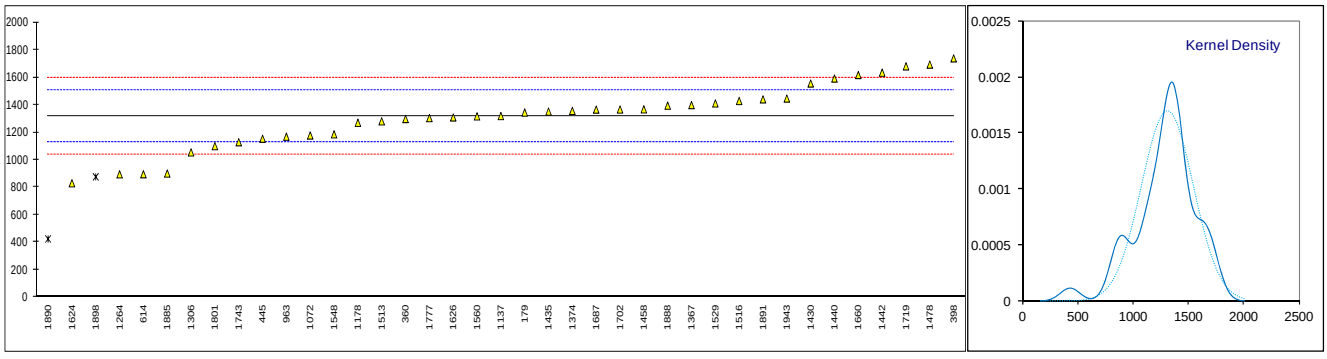




Determination of Carbon dioxide on sample #14226; results in µl/L

lab	method	value	mark	z(targ)	remarks
179	D3612	1344		0.28	
360	IEC60567	1296.9		-0.22	
398	IEC60567	1738		4.47	
445	IEC60567	1153.3		-1.75	
511		-----		-----	
614	IEC60567	895.128		-4.49	
963	D3612	1168.0		-1.59	
1072	IEC60567	1177.13		-1.49	
1137	D3612	1318.2484		0.01	
1178	IEC60567	1269.3		-0.51	
1264	D3612	894.41		-4.50	
1304		-----		-----	
1306	D3612	1054		-2.80	
1367	IEC60567	1398		0.85	
1374	D3612	1355.8		0.41	
1430	IEC60567	1555		2.52	
1435	IEC60567	1350.83		0.35	
1440	IEC60567	1591.22		2.91	
1442	IEC60567	1634		3.36	
1458	D3612	1367		0.53	
1478	IEC60567	1692.7		3.99	
1513	IEC60567	1280	C	-0.40	First reported 1.280
1516	IEC60567	1428.0		1.17	
1529	IEC60567	1410		0.98	
1548	IEC60567	1185.43451		-1.40	
1560	IEC60567	1316		-0.02	
1624	IEC60567	829.4463		-5.19	
1626	IEC60567	1308.3		-0.10	
1660	IEC60567	1617		3.18	
1687	IEC60567	1365.2		0.51	
1702	IEC60567	1366		0.51	
1719	D3612	1680		3.85	
1743	IEC60567	1128.134		-2.01	
1777	IEC60567	1303.37		-0.15	
1801	IEC60567	1099.4		-2.32	
1885	D3612	900.1		-4.44	
1888	IEC60567	1394.222		0.81	
1890	IEC60567	424.3	R(0.05)	-9.49	
1891	IEC60567	1440.0		1.30	
1898	in house	876	ex	-4.69	Result excluded, see §4.1
1943	D3612	1445.886		1.36	
					Only headspace results
	normality	OK			OK
	n	37			24
	outliers	1	(+1 excl)		15
	mean (n)	1317.553			1373.119
	st.dev. (n)	227.2274			170.1676
	R(calc.)	636.237			476.469
	R(IEC60567:11)	263.511			274.624

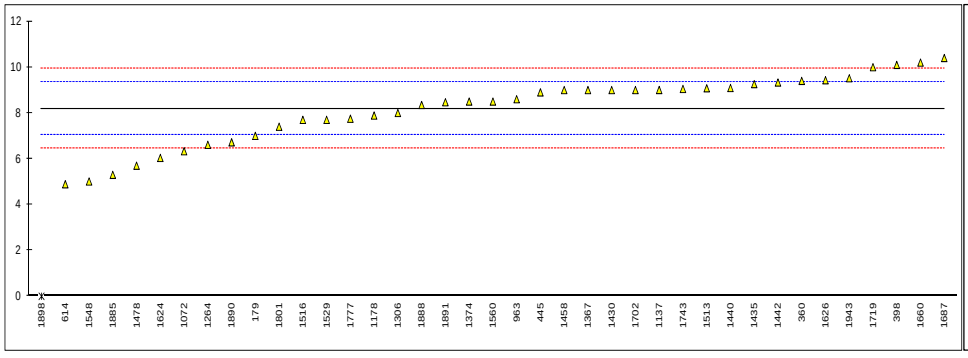
Compare R(Horwitz) = 198.0738

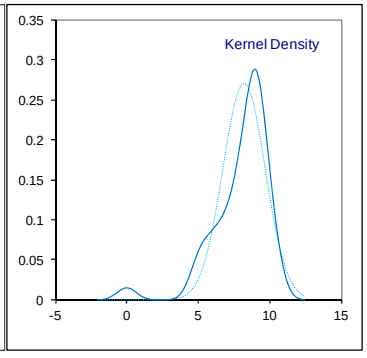


Determination of Methane on sample #14226; results in µl/L

lab	method	value	mark	z(targ)	remarks
179	D3612	7		-2.03	
360	IEC60567	9.4		2.07	
398	IEC60567	10.1		3.27	
445	IEC60567	8.9		1.21	
511		-----		-----	
614	IEC60567	4.8899		-5.64	
963	D3612	8.6		0.70	
1072	IEC60567	6.33		-3.18	
1137	D3612	9.0044		1.39	
1178	IEC60567	7.89		-0.51	
1264	D3612	6.61		-2.70	
1304		-----		-----	
1306	D3612	8		-0.32	
1367	IEC60567	9		1.38	
1374	D3612	8.5		0.53	
1430	IEC60567	9		1.38	
1435	IEC60567	9.26		1.83	
1440	IEC60567	9.09		1.54	
1442	IEC60567	9.33		1.95	
1458	D3612	9		1.38	
1478	IEC60567	5.7		-4.26	
1513	IEC60567	9.08		1.52	
1516	IEC60567	7.7		-0.84	
1529	IEC60567	7.7		-0.84	
1548	IEC60567	5.01123		-5.43	
1560	IEC60567	8.5		0.53	
1624	IEC60567	6.0370		-3.68	
1626	IEC60567	9.43		2.12	
1660	IEC60567	10.2		3.44	
1687	IEC60567	10.4		3.78	
1702	IEC60567	9		1.38	
1719	D3612	10		3.09	
1743	IEC60567	9.0482		1.47	
1777	IEC60567	7.75		-0.75	
1801	IEC60567	7.4		-1.35	
1885	D3612	5.3		-4.94	
1888	IEC60567	8.349		0.27	
1890	IEC60567	6.72		-2.51	
1891	IEC60567	8.47		0.48	
1898	in house	0	ex	-14.00	Result excluded, zero is not a real result
1943	D3612	9.518		2.27	
					Only headspace results
	normality	OK			not OK
	n	38			25
	outliers	0	(+1 excl)		0
	mean (n)	8.1899			8.6792
	st.dev. (n)	1.47769			1.14134
	R(calc.)	4.1375			3.1958
	R(IEC60567:11)	1.6380			1.7358

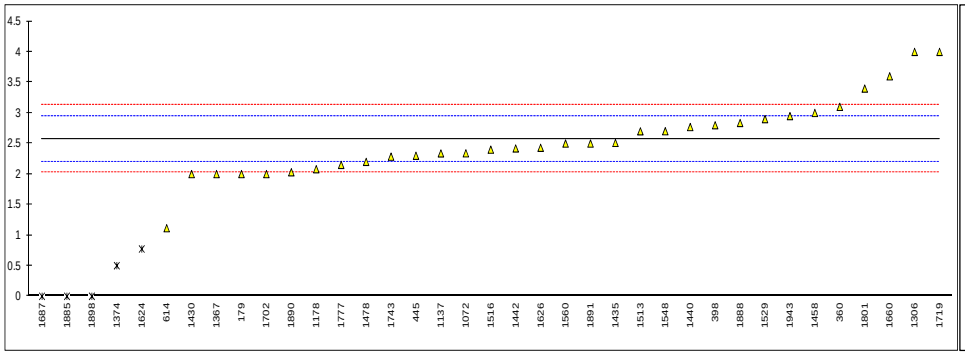
Compare R(Horwitz) = 2.6736

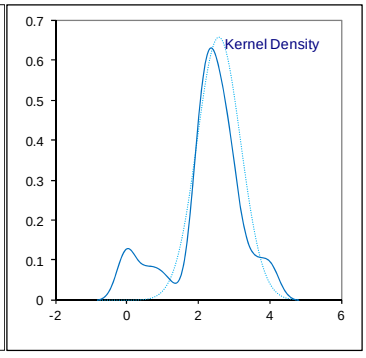




Determination of Ethane on sample #14226; results in µl/L

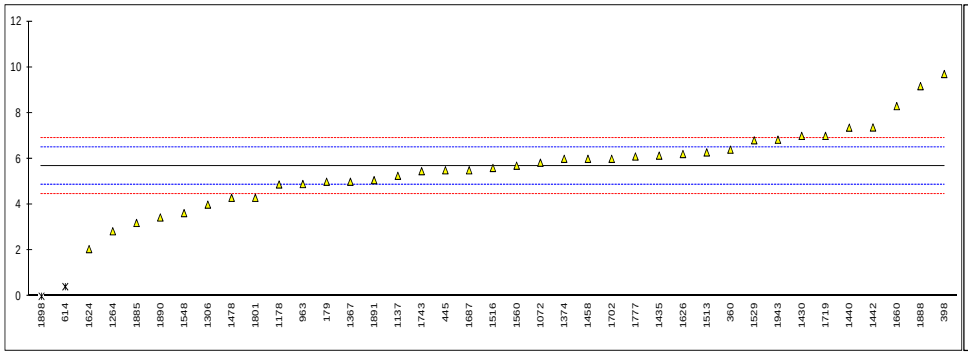
lab	method	value	mark	z(targ)	remarks
179	D3612	2		-3.12	
360	IEC60567	3.1		2.86	
398	IEC60567	2.8		1.23	
445	IEC60567	2.3		-1.49	
511		-----		-----	
614	IEC60567	1.1139		-7.94	
963		-----		-----	
1072	IEC60567	2.34		-1.27	
1137	D3612	2.3385		-1.28	
1178	IEC60567	2.08		-2.69	
1264	D3612	<1		<-8.56	False negative result?
1304		-----		-----	
1306	D3612	4		7.76	
1367	IEC60567	2		-3.12	
1374	D3612	0.5	D(0.05)	-11.28	
1430	IEC60567	2		-3.12	
1435	IEC60567	2.51		-0.35	
1440	IEC60567	2.77		1.07	
1442	IEC60567	2.42		-0.84	
1458	D3612	3		2.32	
1478	IEC60567	2.2		-2.03	
1513	IEC60567	2.70		0.69	
1516	IEC60567	2.4		-0.94	
1529	IEC60567	2.90		1.78	
1548	IEC60567	2.70190		0.70	
1560	IEC60567	2.5		-0.40	
1624	IEC60567	0.7732	D(0.05)	-9.79	
1626	IEC60567	2.43		-0.78	
1660	IEC60567	3.6		5.58	
1687	IEC60567	0.0	ex	-14.00	Result excluded, zero is not a real result
1702	IEC60567	2		-3.12	
1719	D3612	4		7.76	
1743	IEC60567	2.2854		-1.57	
1777	IEC60567	2.15		-2.30	
1801	IEC60567	3.4		4.50	
1885	D3612	0	ex	-14.00	Result excluded, zero is not a real result
1888	IEC60567	2.836		1.43	
1890	IEC60567	2.03		-2.96	
1891	IEC60567	2.50		-0.40	
1898	in house	0	ex	-14.00	Result excluded, zero is not a real result
1943	D3612	2.949		2.04	
					Only headspace results
	normality	suspect			not OK
	n	32			22
	outliers	2	(+ 3 excl)		1 (+ 1 excl)
	mean (n)	2.5736			2.6146
	st.dev. (n)	0.60549			0.49696
	R(calc.)	1.6954			1.3915
	R(IEC60567:11)	0.5147			0.5229 Compare r(Horwitz) = 1.0001

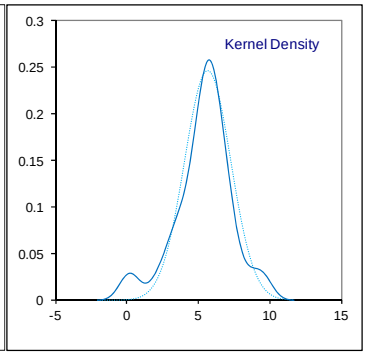




Determination of Ethene (ethylene) on sample #14226; results in µl/L

lab	method	value	mark	z(targ)	remarks
179	D3612	5		-1.68	
360	IEC60567	6.4		1.78	
398	IEC60567	9.7		9.91	
445	IEC60567	5.5		-0.44	
511		-----		-----	
614	IEC60567	0.4192	R(0.05)	-12.97	
963	D3612	4.9		-1.92	
1072	IEC60567	5.83		0.37	
1137	D3612	5.2583		-1.04	
1178	IEC60567	4.88		-1.97	
1264	D3612	2.84		-7.00	
1304		-----		-----	
1306	D3612	4		-4.14	
1367	IEC60567	5		-1.68	
1374	D3612	6.0		0.79	
1430	IEC60567	7		3.25	
1435	IEC60567	6.14		1.13	
1440	IEC60567	7.36		4.14	
1442	IEC60567	7.37		4.17	
1458	D3612	6		0.79	
1478	IEC60567	4.3		-3.40	
1513	IEC60567	6.28		1.48	
1516	IEC60567	5.6		-0.20	
1529	IEC60567	6.81		2.79	
1548	IEC60567	3.63143		-5.05	
1560	IEC60567	5.7		0.05	
1624	IEC60567	2.0601		-8.92	
1626	IEC60567	6.21		1.31	
1660	IEC60567	8.3		6.46	
1687	IEC60567	5.5		-0.44	
1702	IEC60567	6		0.79	
1719	D3612	7		3.25	
1743	IEC60567	5.46044		-0.54	
1777	IEC60567	6.1		1.04	
1801	IEC60567	4.3		-3.40	
1885	D3612	3.2		-6.11	
1888	IEC60567	9.172		8.61	
1890	IEC60567	3.44		-5.52	
1891	IEC60567	5.07		-1.50	
1898	in house	0	ex	-14.00	Result excluded, zero is not a real result
1943	D3612	6.834		2.85	
					Only headspace results
	normality	OK			OK
	n	37			25
	outliers	1	(+1 excl)		0
	mean (n)	5.6796			6.0982
	st.dev. (n)	1.62340			1.52673
	R(calc.)	4.5455			4.2749
	R(IEC60567:11)	1.1359			1.2196 Compare R(Horwitz) = 1.9591

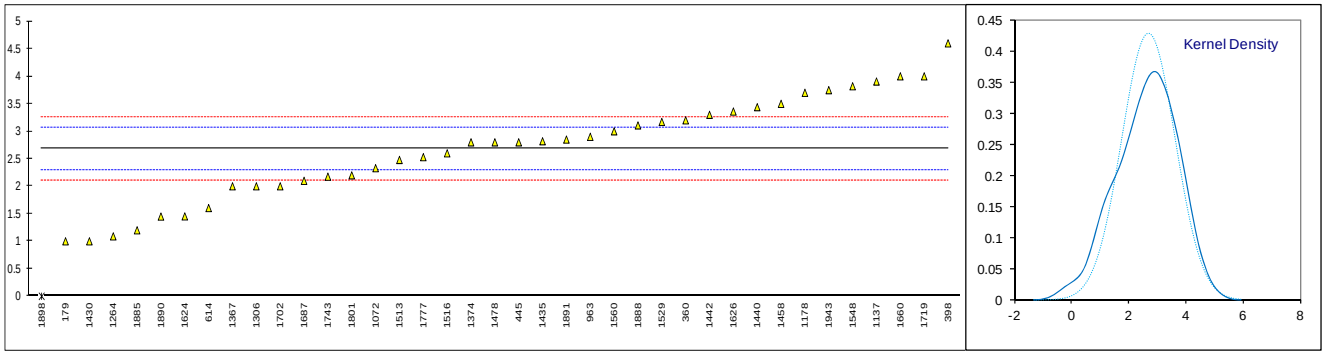




Determination of Ethyn (acetylene) on sample #14226; results in µl/L

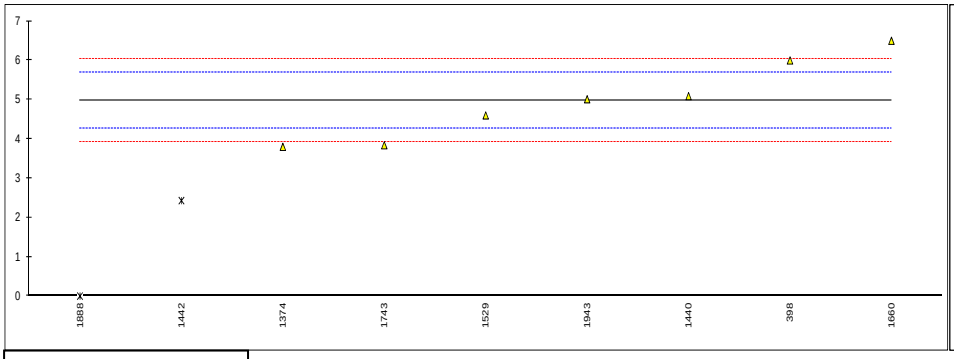
lab	method	value	mark	z(targ)	remarks
179	D3612	1		-8.79	
360	IEC60567	3.2		2.68	
398	IEC60567	4.6		9.98	
445	IEC60567	2.8		0.60	
511		-----		-----	
614	IEC60567	1.6040		-5.64	
963	D3612	2.9		1.12	
1072	IEC60567	2.33		-1.85	
1137	D3612	3.9058		6.36	
1178	IEC60567	3.70		5.29	
1264	D3612	1.09		-8.32	
1304		-----		-----	
1306	D3612	2		-3.57	
1367	IEC60567	2		-3.57	
1374	D3612	2.8		0.60	
1430	IEC60567	1		-8.79	
1435	IEC60567	2.82		0.70	
1440	IEC60567	3.44		3.94	
1442	IEC60567	3.30		3.21	
1458	D3612	3.5		4.25	
1478	IEC60567	2.8		0.60	
1513	IEC60567	2.48		-1.07	
1516	IEC60567	2.6		-0.44	
1529	IEC60567	3.17		2.53	
1548	IEC60567	3.81909		5.91	
1560	IEC60567	3.0		1.64	
1624	IEC60567	1.4528		-6.43	
1626	IEC60567	3.36		3.52	
1660	IEC60567	4.0		6.86	
1687	IEC60567	2.1		-3.05	
1702	IEC60567	2		-3.57	
1719	D3612	4		6.86	
1743	IEC60567	2.175031		-2.66	
1777	IEC60567	2.53		-0.81	
1801	IEC60567	2.2		-2.53	
1885	D3612	1.2		-7.74	
1888	IEC60567	3.108		2.20	
1890	IEC60567	1.45		-6.44	
1891	IEC60567	2.85		0.86	
1898	in house	0	ex	-14.00	Result excluded, zero is not a real result
1943	D3612	3.749		5.55	
					Only headspace results
	normality	OK			OK
	n	38			25
	outliers	0	(+1 excl)		0
	mean (n)	2.6851			2.9071
	st.dev. (n)	0.93182			0.82435
	R(calc.)	2.6091			2.3082
	R(IEC60567:11)	0.5370			0.5801

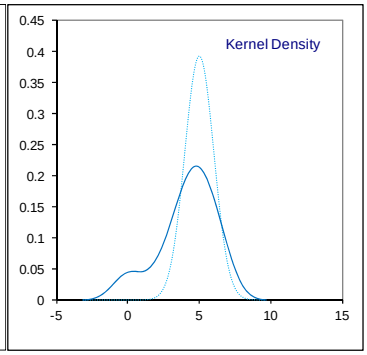
Compare R(Horwitz) = 1.0367



Determination of Propane and Propene on sample #14226; results in µl/L

lab	method	Propane	mark	z(targ)	Propene	mark	z(targ)	remarks
179		-----		-----	-----		-----	
360		-----		-----	-----		-----	
398	IEC60567	<1		-----	6.0		2.88	
445		-----		-----	-----		-----	
511		-----		-----	-----		-----	
614		-----		-----	-----		-----	
963		-----		-----	-----		-----	
1072		-----		-----	-----		-----	
1137		-----		-----	-----		-----	
1178		-----		-----	-----		-----	
1264		-----		-----	-----		-----	
1304		-----		-----	-----		-----	
1306		-----		-----	-----		-----	
1367		-----		-----	-----		-----	
1374	D3612	0		-----	3.8		-3.31	
1430		-----		-----	-----		-----	
1435		-----		-----	-----		-----	
1440	IEC60567	<ld		-----	5.09		0.32	
1442	IEC60567	0		-----	2.43	G(0.05)	-7.17	
1458		-----		-----	-----		-----	
1478		-----		-----	-----		-----	
1513		-----		-----	-----		-----	
1516		-----		-----	-----		-----	
1529	IEC60567	< 0.1		-----	4.6		-1.06	
1548		-----		-----	-----		-----	
1560		-----		-----	-----		-----	
1624	IEC60567	0.3453		-----	<1		<-11.19	False negative?
1626		-----		-----	-----		-----	
1660	IEC60567	0		-----	6.5		4.28	
1687		-----		-----	-----		-----	
1702		-----		-----	-----		-----	
1719		-----		-----	-----		-----	
1743	IEC60567	0		-----	3.8401		-3.20	
1777		-----		-----	-----		-----	
1801		-----		-----	-----		-----	
1885		-----		-----	-----		-----	
1888	IEC60567	0		-----	0	ex	-14.00	
1890		-----		-----	-----		-----	
1891		-----		-----	-----		-----	
1898		-----		-----	-----		-----	
1943	D3612	0		-----	5.012		0.10	
	normality	n.a.			OK			
	n	10			7			
	outliers	0			1	(+1 excl)		
	mean (n)	<1			4.9774			
	st.dev. (n)	n.a.			1.01653			
	R(calc.)	n.a.			2.8463			
	R(IEC60567:11)	n.a.			0.9955			





Propene

APPENDIX 2

Extraction method used

lab	Extraction method	remarks
179	Stripper Column (D3612B)	
360	Headspace	
398	Headspace	
445	Headspace	
511		
614	ToPas	
963	Headspace	
1072	Toepler	
1137	Headspace	
1178	Toepler	
1264		
1304	Headspace	
1306	Headspace	
1367	Headspace	
1374	Headspace	
1430	Headspace	
1435	Headspace	
1440	Headspace	
1442	Headspace	
1458	Stripper Column (D3612B)	
1478	Toepler	
1513	Toepler	
1516	Headspace	
1529	Headspace	
1548	Headspace	
1560	Headspace	
1624		
1626	Headspace	
1660	Headspace	
1687	Headspace	
1702	Toepler	
1719	Stripper Column (D3612B)	
1743	Headspace	
1777	Headspace	
1801	partial desgassing	
1885	Vacuum extraction	
1888	Headspace	
1890	Headspace	
1891	Headspace	
1898	Shake method	
1943	Headspace	

APPENDIX 3

Number of participants per country

6 labs in AUSTRALIA
2 labs in BELGIUM
1 lab in BULGARIA
1 lab in CROATIA
2 labs in FRANCE
2 labs in GERMANY
2 labs in ITALY
1 lab in LATVIA
1 lab in MALAYSIA
2 labs in NETHERLANDS
1 lab in NEW ZEALAND
1 lab in PERU
2 labs in PORTUGAL
1 lab in SAUDI ARABIA
1 lab in SERBIA
1 lab in SLOVENIA
2 labs in SOUTH AFRICA
3 labs in SPAIN
1 lab in SWEDEN
2 labs in TURKEY
2 labs in UNITED ARAB EMIRATES
2 labs in UNITED KINGDOM
1 lab in UNITED STATES OF AMERICA

APPENDIX 4

Abbreviations:

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

Literature:

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