# Results of Proficiency Test
# Dissolved Gas Analysis
# November 2010


Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Appendices:

# 1 INTRODUCTION

Since 2001, the Institute for Interlaboratory Studies organized a proficiency test for Transformer Oil every year. Since then several requests were received from laboratories to organize also a proficiency test for Dissolved Gas Analysis. The analytical test results of this DGA test are very important to evaluate the condition of a transformer oil. The first proficiency study for DGA was organized by iis in December 2007.
During the annual proficiency testing program 2010/2011, it was decided to continue the PT for Dissolved Gas Analysis.
In this international Interlaboratory study, 24 laboratories from 14 different countries have participated. See appendix 2 for a list of participants in alphabetical country order. In this report the results of the DGA proficiency test are presented and discussed.

# 2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, The Netherlands, was the organizer of this proficiency test.
In total one batch of 26 syringes (of 50 mL) was prepared (lot BG46) on September 8, 2010. Each syringe was uniquely numbered was provided by Morgan Schaffer, Quebec, Canada (True North). Each syringe was uniquely numbered and one syringe was sent to each participating laboratory. Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

## 2.1 QUALITY SYSTEM

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

## 2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

## 2.3 CONFIDENTIALITY STATEMENT

All data present in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

## 2.4 SAMPLES

In this proficiency test only one sample was used. The 50 mL gas tight syringes with sample material were prepared by Morgan Schaffer (Quebec, Canada) in accordance with principles outlined in ASTM Method D3612-01, Annex A2 (2001) and IEC 60567, clause 6.2 (1992). In total one batch of 26 syringes was prepared (lot BG46) on September 8, 2010. Each syringe was uniquely numbered and a certificate of analysis was provided by Morgan Schaffer. These certificates were removed after receipt by iis prior to the forwarding of the samples to the participating laboratories. The values, given on the Morgan Schaffer certificates are listed in below table:

| | Syringe S/N | Ethane in µl/L | Ethylene in µl/L | $CO_2$ in µl/L | Oxygen in µl/L | Nitrogen in µl/L |
|---|---|---|---|---|---|---|
| sample #1088-1 | 4736 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-2 | 4754 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-3 | 4758 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-4 | 4768 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-5 | 4774 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-6 | 4779 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-7 | 4805 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-8 | 4816 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-9 | 4817 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-10 | 4829 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-11 | 5169 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-12 | 5234 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-13 | 5317 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-14 | 5601 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-15 | 5674 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-16 | 5712 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-17 | 5805 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-18 | 5887 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-19 | 5989 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-20 | 6047 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-21 | 6087 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-22 | 6273 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-23 | 6419 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-24 | 6769 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-25 | 6769 | 2.8 | 6.7 | 1500 | 23300 | 60700 |
| sample #1088-26 | 6769 | 2.8 | 6.7 | 1500 | 23300 | 60700 |

Table 1: homogeneity test of sub samples #1088

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

To each of the participating laboratories one syringe of 50 mL (labelled #1088) was sent on October 20, 2010.

### 2.5 STABILITY OF THE SAMPLES

Morgan Schaffer declare that bulk storage prior to shipping has a shelf life of at least 6 months. This was assumed to be sufficient for the proficiency testing purposes.

### 2.6 ANALYSES

The participants were asked to determine on sample #1088: Hydrogen, Oxygen, Nitrogen, Carbon Monoxide, Carbon Dioxide, Methane, Ethane, Ethene, Ethyn, Propane and Propene. Also some method details were requested to be reported.

To get comparable results a detailed report form, on which the units were prescribed, was sent together with each set of samples. Also a letter of instructions and a SDS were added to the package as well as the Morgan Shaffer procedure how to deal with small gas bubbles in the syringe that may be present after transport.

## 3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered. The original results are tabulated per determination in the appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are put under 'Remarks' in the result tables in appendix 1. Results that came in after deadline were not taken into account in the screening for suspect data and thus these participants were not requested for checks.

### 3.1 STATISTICS

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…' were not used in the statistical evaluation.

First the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers this check was repeated. In case a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

In accordance with ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test and by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test and by G(0.05) or DG(0.05) for the Grubbs test. Both outliers and stragglers were not included in the calculations of the averages and the standard deviations.

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

### 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; nr.13 and 14).

### 3.3 Z-SCORES

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

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

In ISO13528 is stated that if $u_x \geq 0.3$ * standard deviation for proficiency testing, the uncertainly of the assigned value is not negligible and need to be included in the interpretation of the results of the proficiency test. Therefore in these cases (Hydrogen and Ethane) z'-scores were calculated in stead of the usual z-scores.

The z-scores were calculated in accordance with:

z(target) = (result - average of PT) / target standard deviation

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

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

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

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

## 4 EVALUATION

In this proficiency test no problems were encountered during execution. All participants did report one or more test results. In total 24 participating laboratories reported 218 numerical results. Observed were 10 outlying results, which is 4.6% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

### 4.1 EVALUATION PER TEST

In this section the results are discussed per component. The methods, which are used by the various laboratories, are taken into account for explaining the observed differences when possible and applicable. These methods are also in the tables together with the original data. The abbreviations, used in these tables, are listed in appendix 3.
All original data sets proved to have a normal distribution.
All eight test results reported by laboratory 398 were very low. Three of the eight test results appeared to be statistical outliers and at least two false negative test results were reported. As the eight test results are not independent, it was decided not to use any of the eight test results for the statistical evaluation.

Hydrogen: The determination of this component was problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, not at all in agreement with the requirements of IEC 60657:2005.

Oxygen: The determination of this component was problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, not in agreement with the requirements of IEC 60657:2005.

Nitrogen: The determination of this component was problematic. No statistical outlier was observed. However, the calculated reproducibility is not in agreement with the requirements of IEC 60657:2005.

Carbon monoxide: The determination of this component was problematic. Two statistical outliers were observed. Also, the calculated reproducibility is, after rejection of the statistical outliers, not in agreement with the requirements of IEC 60657:2005.

Carbon dioxide: The determination of this component was problematic. Two statistical outliers were observed. Also, the calculated reproducibility is, after rejection of the statistical outliers, not in agreement with the requirements of IEC 60657:2005.

Methane: The determination of this component was problematic. No statistical outlier was observed. However, the calculated reproducibility is not in agreement with the requirements of IEC 60657:2005.

Ethane: The determination of this component was problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, not in agreement with the requirements of IEC 60657:2005.

Ethene: The determination of this component was problematic. Two statistical outliers were observed. Also, the calculated reproducibility is, after rejection of the statistical outliers, not in agreement with the requirements of IEC 60657:2005.

Ethyn: The determination of this component was problematic. Only one statistical outlier was observed. However, the calculated reproducibility is, after rejection of the statistical outlier, not in agreement with the requirements of IEC 60657:2005.

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

### 4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard and the reproducibility as found for the group of participating laboratories. The average results per component, calculated reproducibilities and reproducibilities, derived from literature standards (in casu IEC 60657:2005) are compared in the next table.

| Parameter | unit | n | average | 2.8 * sd | R(lit) |
|---|---|---|---|---|---|
| Hydrogen $H_2$ | µl/L | 22 | 20.8 | 16.1 | 4.2 |
| Oxygen $O_2$ | mg/L | 19 | 23.1 | 13.6 | 4.6 |
| Nitrogen $N_2$ | mg/L | 20 | 61.0 | 34.7 | 12.2 |
| Carbon Monoxide CO | µl/L | 22 | 185.7 | 85.5 | 37.1 |
| Carbon Dioxide $CO_2$ | µl/L | 22 | 1467 | 469.6 | 293.5 |
| Methane $CH_4$ | µl/L | 23 | 9.8 | 4.9 | 2.0 |
| Ethane $C_2H_6$ | µl/L | 22 | 2.5 | 1.8 | 0.5 |
| Ethene $C_2H_4$ | µl/L | 21 | 6.6 | 3.4 | 1.3 |
| Ethyn $C_2H_2$ | µl/L | 22 | 2.7 | 1.7 | 0.5 |
| Propane $C_3H_8$ | µl/L | 4 | n/a | n/a | n/a |
| Propene $C_3H_6$ | µl/L | 5 | n/a | n/a | n/a |
| Sum of Propane $C_3H_8$ and Propene $C_3H_6$ | µl/L | 6 | 4.6 | 4.6 | n/a |

Table 2: Performance of the group on sample #1088

Without further statistical calculations it can be concluded from the overview given in table 2 that there is not a compliance of the performance of the group of participating laboratories with the relevant standard IEC 60657:2010.
The problematic components have been discussed in paragraph 4.1.

### 4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2010 WITH PREVIOUS PTS

| | *November 2010* | *November 2009* | *January 2009* | *December 2007* |
|---|---|---|---|---|
| Number of reporting labs | 24 | 18 | 14 | 13 |
| Number of results reported | 218 | 182 | 140 | 129 |
| Statistical outliers | 10 | 9 | 8 | 7 |
| Percentage outliers | 4.6% | 5.0% | 5.7% | 5.4% |

Table 3: Comparison of statistical summary parameters with previous proficiency tests

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

The performance of the determinations of the proficiency tests was compared against the requirements of the respective standards. The conclusions are given the following table:

| Determination | *November 2010* | *November 2009* | *January 2009* | *December 2007* |
|---|---|---|---|---|
| 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 | - | -- |
| Propene $C_3H_6$ | n.e. | n.e | - | -- |

Table 4: Comparison determinations against IEC 60657:2005

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

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

### 4.4 DISCUSSION

The consensus values as determined in this PT are compared with the average values from the homogeneity testing by Morgan Schaffer in the following table. From this comparison it is clear that all consensus values as determined in this PT are very well in line with the values as determined by Morgan Schaffer after the preparation of the syringes.

| Parameter | Average values by Morgan Schaffer in µL/L | Consensus values from participants results in µL/L | Absolute differences in µL/L |
|---|---|---|---|
| Hydrogen $H_2$ | 16 | 21 | +5 |
| Oxygen $O_2$ | 23300 | 23100 | -200 |
| Nitrogen $N_2$ | 60700 | 61000 | +300 |
| Carbon Monoxide CO | 207 | 186 | -21 |
| Carbon Dioxide $CO_2$ | 1500 | 1467 | -33 |
| Methane $CH_4$ | 9.9 | 9.8 | -0.1 |
| Ethane $C_2H_6$ | 2.8 | 2.5 | -0.3 |
| Ethene $C_2H_4$ | 6.7 | 6.6 | -0.1 |
| Ethyn $C_2H_2$ | 2.9 | 2.7 | -0.2 |

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* |
|---|---|---|---|
| 398 | unknown | 1516 | 16 November 2010 |
| 445 | unknown | 1529 | unknown |
| 614 | 11 November 2010 | 1660 | 19 November 2010 |
| 963 | 13 – 14 November 2010 | 1702 | 9 November 2010 |
| 1072 | 15 November 2010 | 1719 | 10 November 2010 |
| 1152 | 10 November 2010 | 1801 | 9 November 2010 |
| 1178 | 12 November 2010 | 1923 | 9 November 2010 |
| 1304 | 18 November 2010 | 1924 | 5 November 2010 |
| 1374 | 10 November 2010 | 1925 | 8 November 2010 |
| 1430 | 16 November 2010 | 1943 | 9 November 2010 |
| 1435 | 4 November 2010 | 2125 | 4 November 2010 |
| 1513 | 9 November 2010 | 7003 | 14 November 2010 |

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, 1513, 1516 and 1702) used the Toepler method (IEC 60567 clause 7.2), eleven laboratories (398, 963, 1152, 1374, 1430, 1435, 1529, 1660, 1943, 2125 and 7003) used the head-space method (IEC 60567 clause 7.5), three laboratories (1923, 1924 and 1925) used the Kelman method, two laboratories used partial extraction (1304 and 1801) one laboratory (614) used the ToGas method, one laboratory (1719) used the ASTM D3612-B stripper column extraction and one laboratory (445) did not report the extraction method that was used.

It is remarkable to note that the headspace results are the lowest observed for all components except for Ethane and Ethene. The spread of the headspace results is larger than the spread of the results of the other test methods for all components except for Hydrogen, Ethene and Ethyn.

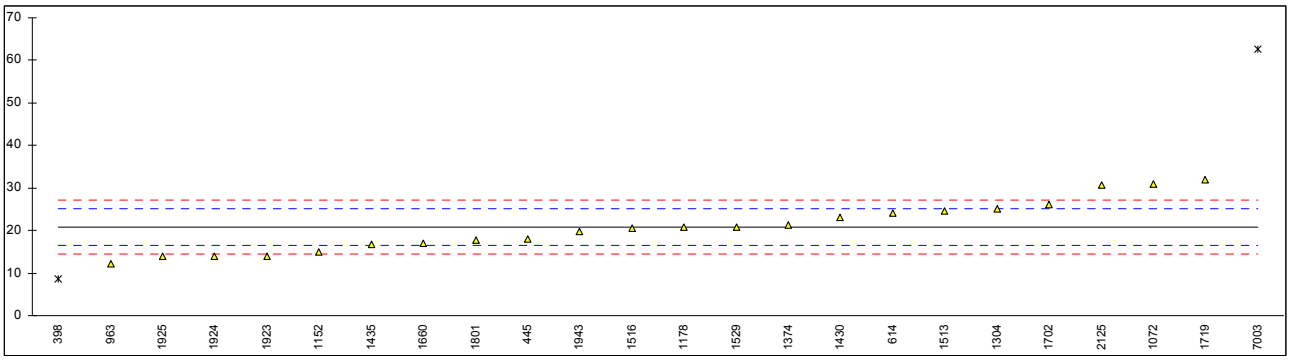
The target reproducibilities as required by IEC 60567 obviously appear to be very hard to meet, although the observed reproducibilities are decreasing during the subsequent annual PTs. Still, it is clear that the reproducibility requirements of IEC 60567 are quite strict as they are all smaller than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

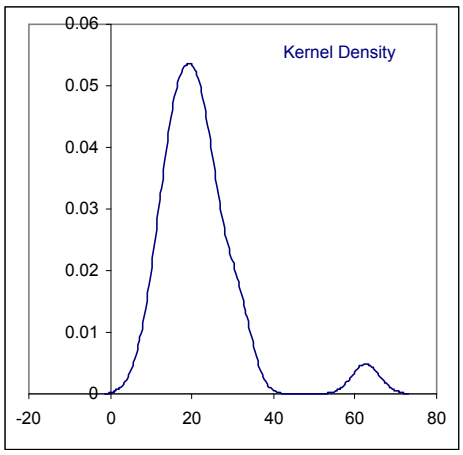
## APPENDIX 1

Determination of Hydrogen on sample #1088; results in µl/L

| lab | method | value | mark | z'(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 8.7 | ex | -5.71 | |
| 445 | IEC60567 | 17.9 | | -1.37 | |
| 614 | IEC60567 | 24.114 | | 1.56 | |
| 963 | D3612C | 12.281 | | -4.02 | |
| 1072 | IEC60567 | 31 | | 4.81 | |
| 1152 | D3612 | 14.8387 | | -2.82 | |
| 1178 | IEC60567 | 20.79 | | -0.01 | |
| 1304 | in house | 25 | | 1.98 | |
| 1374 | D3612 (mod) | 21.2 | | 0.18 | |
| 1430 | | 23 | | 1.03 | |
| 1435 | IEC60567 | 16.7 | | -1.94 | |
| 1513 | IEC60567 | 24.6 | | 1.79 | |
| 1516 | IEC60567 | 20.6 | | -0.10 | |
| 1529 | IEC60567 | 20.9 | | 0.04 | |
| 1660 | IEC60567 | 16.9 | | -1.84 | |
| 1702 | IEC60567 | 26 | | 2.45 | |
| 1719 | D3612B | 32 | | 5.28 | |
| 1801 | IEC60567 | 17.7 | C | -1.47 | First reported 202.9 |
| 1923 | IEC60567 | 14 | | -3.21 | |
| 1924 | in house | 14 | | -3.21 | |
| 1925 | IEC60567 | 14 | | -3.21 | |
| 1943 | D3612 | 19.693 | | -0.53 | |
| 2125 | IEC60567 | 30.58 | | 4.61 | |
| 7003 | D3612 | 62.61 | C,G(0.01) | 19.71 | First reported 42.03 |

| | | Only head space results: | All other results: |
|---|---|---|---|
| normality | OK | OK | OK |
| n | 22 | 9 | 13 |
| outliers | 1 | 1 | 0 |
| mean (n) | 20.809 | 19.566 | 21.670 |
| st.dev. (n) | 5.7668 | 5.3421 | 6.1001 |
| R(calc.) | 16.147 | 14.958 | 17.080 |
| R(IEC60567) | 4.162 | 3.913 | 4.334 |
| U(mean) | 1.512 | | |
| R'(IEC60567) | 5.937 | Compare R(Horwitz) = 5.904 | |

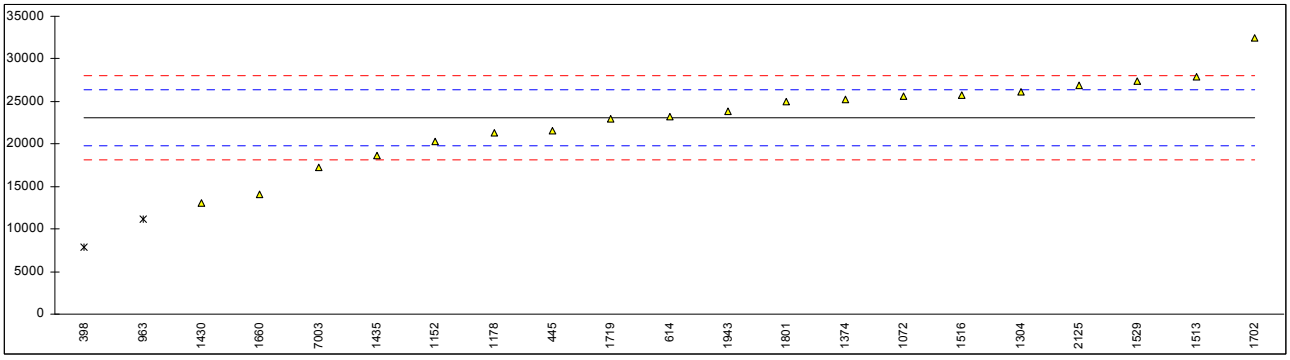


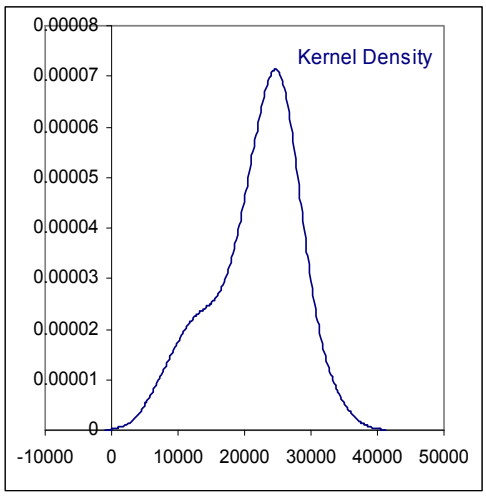



## Determination of Oxygen on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | Remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 7825 | ex | -9.25 | |
| 445 | IEC60567 | 21533.5 | | -0.94 | |
| 614 | IEC60567 | 23215.722 | | 0.08 | |
| 963 | D3612C | 11168.26 | G(0.05) | -7.23 | |
| 1072 | IEC60567 | 25568 | | 1.51 | |
| 1152 | D3612 | 20276.6625 | | -1.70 | |
| 1178 | IEC60567 | 21362.72 | | -1.04 | |
| 1304 | in house | 26158 | | 1.86 | |
| 1374 | D3612 (mod) | 25280.4 | | 1.33 | |
| 1430 | | 13120 | | -6.04 | |
| 1435 | IEC60567 | 18661 | | -2.68 | |
| 1513 | IEC60567 | 27900 | | 2.92 | |
| 1516 | IEC60567 | 25680.0 | | 1.57 | |
| 1529 | IEC60567 | 27400 | | 2.62 | |
| 1660 | IEC60567 | 14061 | | -5.47 | |
| 1702 | IEC60567 | 32500 | | 5.71 | |
| 1719 | D3612B | 22926 | | -0.10 | |
| 1801 | IEC60567 | 24983.2 | C | 1.15 | First reported 28707.9 |
| 1923 | | ----- | | ----- | |
| 1924 | | ----- | | ----- | |
| 1925 | | ----- | | ----- | |
| 1943 | D3612 | 23822.175 | | 0.45 | |
| 2125 | IEC60567 | 26932 | | 2.33 | |
| 7003 | D3612 | 17247.66 | | -3.54 | |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 19 | 9 | 10 |
| | outliers | 1 | 1 | 0 |
| | mean (n) | 23085.69 | 20755.66 | 25182.72 |
| | st.dev. (n) | 4854.761 | 5387.672 | 3319.705 |
| | R(calc.) | 13593.33 | 15085.48 | 9295.17 |
| | R(IEC60567) | 4617.14 | 4151.13 | 5036.54 |
| | U(mean) | 1369.92 | | |
| | R'(IEC60567) | n/a | Compare R(Horwitz) = 2279.67 | |

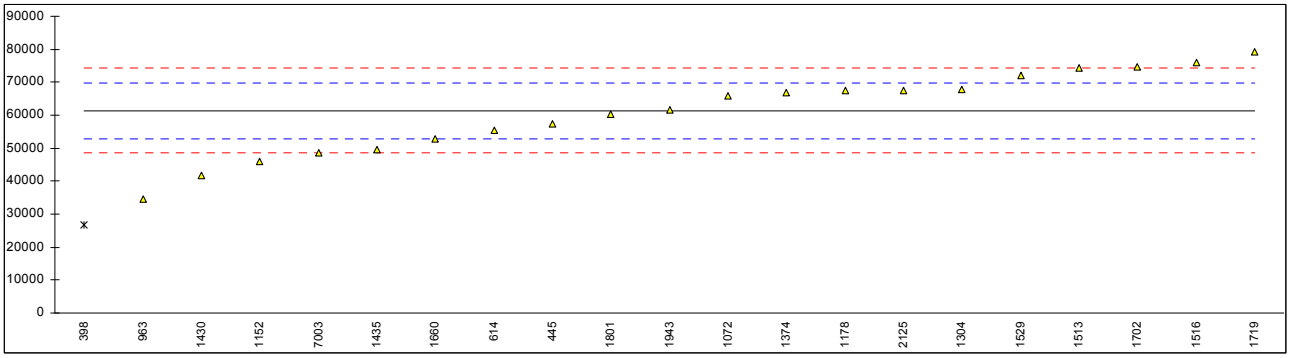


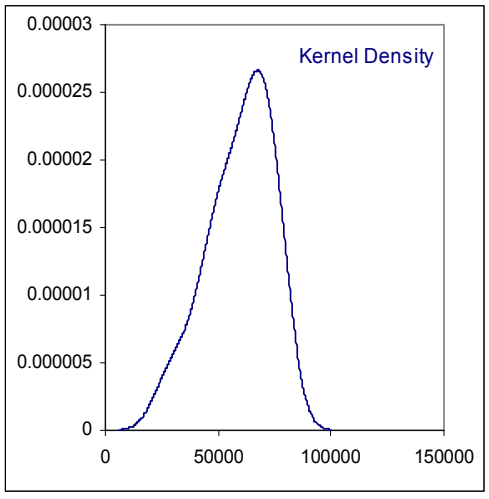



## Determination of Nitrogen on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | Remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 26875 | ex | -7.83 | |
| 445 | IEC60567 | 57510.5 | | -0.81 | |
| 614 | IEC60567 | 55484.202 | | -1.27 | |
| 963 | D3612C | 34652.06 | | -6.05 | |
| 1072 | IEC60567 | 65873 | | 1.11 | |
| 1152 | D3612 | 46007.9889 | | -3.44 | |
| 1178 | IEC60567 | 67377.71 | | 1.46 | |
| 1304 | in house | 67917 | | 1.58 | |
| 1374 | D3612 (mod) | 66818.1 | | 1.33 | |
| 1430 | | 41838 | | -4.40 | |
| 1435 | IEC60567 | 49717 | | -2.59 | |
| 1513 | IEC60567 | 74400 | | 3.07 | |
| 1516 | IEC60567 | 76040.0 | | 3.45 | |
| 1529 | IEC60567 | 72000 | | 2.52 | |
| 1660 | IEC60567 | 52797 | | -1.89 | |
| 1702 | IEC60567 | 74614 | | 3.12 | |
| 1719 | D3612B | 79271 | | 4.19 | |
| 1801 | IEC60567 | 60374.4 | C | -0.15 | First reported 695873.5 |
| 1923 | | ----- | | ----- | |
| 1924 | | ----- | | ----- | |
| 1925 | | ----- | | ----- | |
| 1943 | D3612 | 61555.975 | | 0.12 | |
| 2125 | IEC60567 | 67526 | | 1.49 | |
| 7003 | D3612 | 48647.53 | | -2.84 | |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 20 | 10 | 10 |
| | outliers | 0 | 0 | 0 |
| | mean (n) | 61021.07 | 54155.96 | 67886.18 |
| | st.dev. (n) | 12378.388 | 12304.812 | 8205.657 |
| | R(calc.) | 34659.49 | 34453.47 | 22975.84 |
| | R(IEC60567) | 12204.21 | 10831.19 | 13577.24 |
| | U(mean) | 3404.51 | | |
| | R'(IEC60567) | n/a | Compare R(Horwitz) = 5205.61 | |

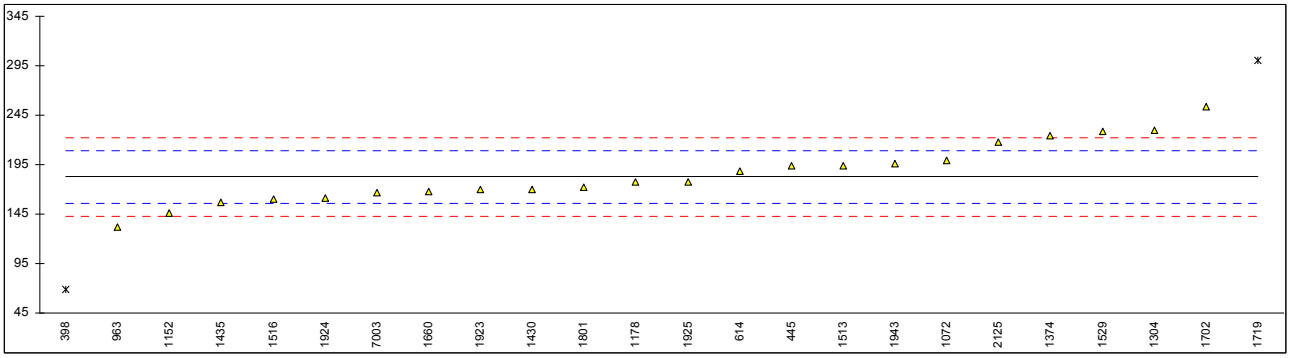


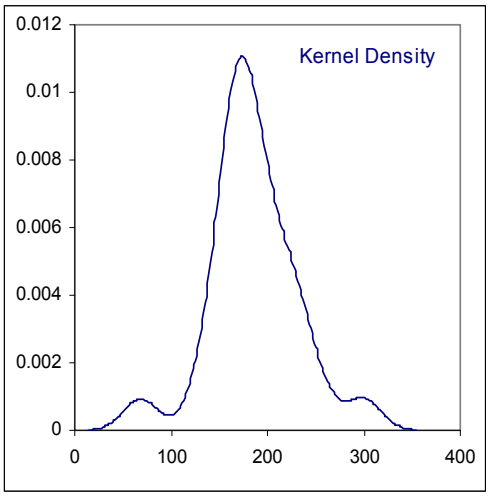



## Determination of Carbon monoxide on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 68.4 | D(0.05) | -8.84 | |
| 445 | IEC60567 | 193.7 | | 0.60 | |
| 614 | IEC60567 | 188.999 | | 0.25 | |
| 963 | D3612C | 132 | C | -4.05 | First reported 122.9795 |
| 1072 | IEC60567 | 199 | | 1.00 | |
| 1152 | D3612 | 145.8844 | | -3.00 | |
| 1178 | IEC60567 | 177.51 | | -0.62 | |
| 1304 | in house | 230 | | 3.34 | |
| 1374 | D3612 (mod) | 224.7 | | 2.94 | |
| 1430 | | 170 | | -1.19 | |
| 1435 | IEC60567 | 157 | | -2.17 | |
| 1513 | IEC60567 | 194.4 | | 0.65 | |
| 1516 | IEC60567 | 160.0 | | -1.94 | |
| 1529 | IEC60567 | 229 | | 3.26 | |
| 1660 | IEC60567 | 167.7 | | -1.36 | |
| 1702 | IEC60567 | 254 | | 5.15 | |
| 1719 | D3612B | 300 | D(0.05) | 8.61 | |
| 1801 | IEC60567 | 171.8 | C | -1.05 | First reported 99.4 |
| 1923 | IEC60567 | 170 | | -1.19 | |
| 1924 | in house | 161 | | -1.86 | |
| 1925 | IEC60567 | 178 | | -0.58 | |
| 1943 | D3612 | 196.303 | | 0.80 | |
| 2125 | IEC60567 | 218.1 | | 2.44 | |
| 7003 | D3612 | 167.01 | | -1.41 | |

| | | Only head space results: | All other test results: |
|---|---|---|---|
| normality | OK | OK | OK |
| n | 22 | 10 | 12 |
| outliers | 2 | 1 | 1 |
| mean (n) | 185.732 | 180.770 | 189.867 |
| st.dev. (n) | 30.5209 | 34.2011 | 27.9335 |
| R(calc.) | 85.458 | 95.763 | 78.214 |
| R(IEC60567) | 37.146 | 36.154 | 37.973 |
| U(mean) | 8.003 | | |
| R'(IEC60567) | n/a | Compare R(Horwitz) = 37.902 | |

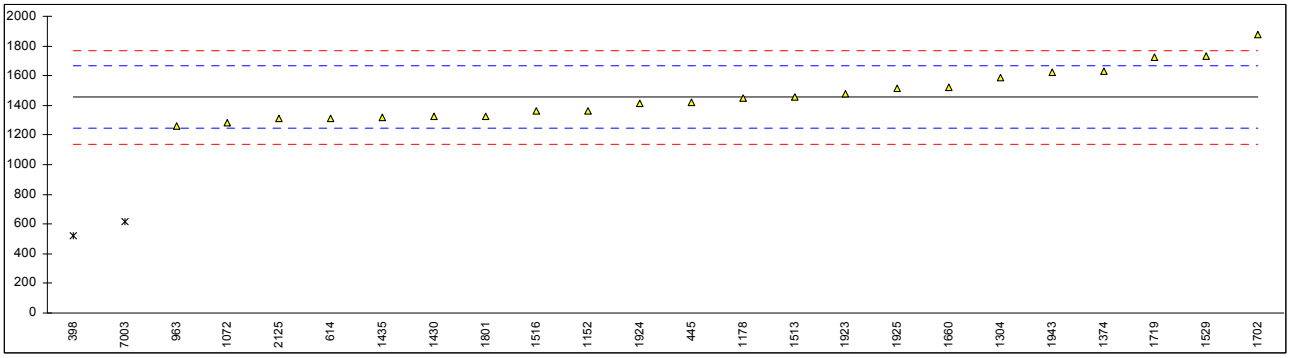


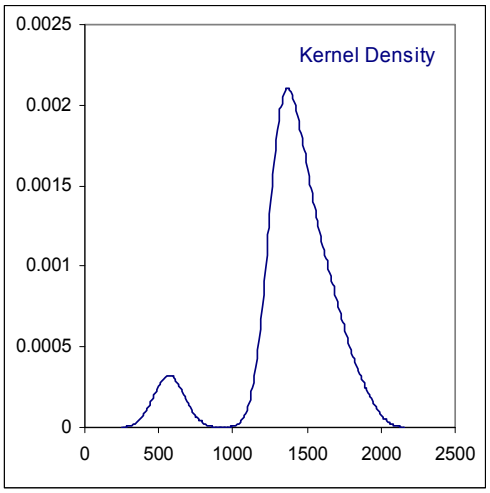



## Determination of Carbon dioxide on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 525 | G(0.05) | -8.99 | |
| 445 | IEC60567 | 1417.7 | | -0.47 | |
| 614 | IEC60567 | 1310.284 | | -1.50 | |
| 963 | D3612C | 1261.783 | | -1.96 | |
| 1072 | IEC60567 | 1283 | | -1.76 | |
| 1152 | D3612 | 1360.0235 | | -1.02 | |
| 1178 | IEC60567 | 1450.27 | | -0.16 | |
| 1304 | in house | 1584 | | 1.11 | |
| 1374 | D3612 (mod) | 1628.3 | | 1.54 | |
| 1430 | | 1325 | | -1.36 | |
| 1435 | IEC60567 | 1319 | | -1.42 | |
| 1513 | IEC60567 | 1460 | | -0.07 | |
| 1516 | IEC60567 | 1359.2 | | -1.03 | |
| 1529 | IEC60567 | 1730 | | 2.51 | |
| 1660 | IEC60567 | 1525 | | 0.55 | |
| 1702 | IEC60567 | 1878 | | 3.92 | |
| 1719 | D3612B | 1724 | | 2.45 | |
| 1801 | IEC60567 | 1328.4 | C | -1.33 | First reported 1974.8 |
| 1923 | IEC60567 | 1478 | | 0.10 | |
| 1924 | in house | 1412 | | -0.53 | |
| 1925 | IEC60567 | 1512 | | 0.43 | |
| 1943 | D3612 | 1626.573 | | 1.52 | |
| 2125 | IEC60567 | 1308.5 | | -1.52 | |
| 7003 | D3612 | 614.76 | C,G(0.01) | -8.13 | First reported 809.01 |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 22 | 9 | 13 |
| | outliers | 2 | 2 | 0 |
| | mean (n) | 1467.318 | 1453.7977 | 1476.681 |
| | st.dev. (n) | 167.7010 | 174.3537 | 169.4643 |
| | R(calc.) | 469.563 | 488.190 | 474.500 |
| | R(IEC60567) | 293.464 | 290.760 | 295.336 |
| | U(mean) | 43.977 | | |
| | R'(IEC60567) | n/a | Compare R(Horwitz) = 219.378 | |

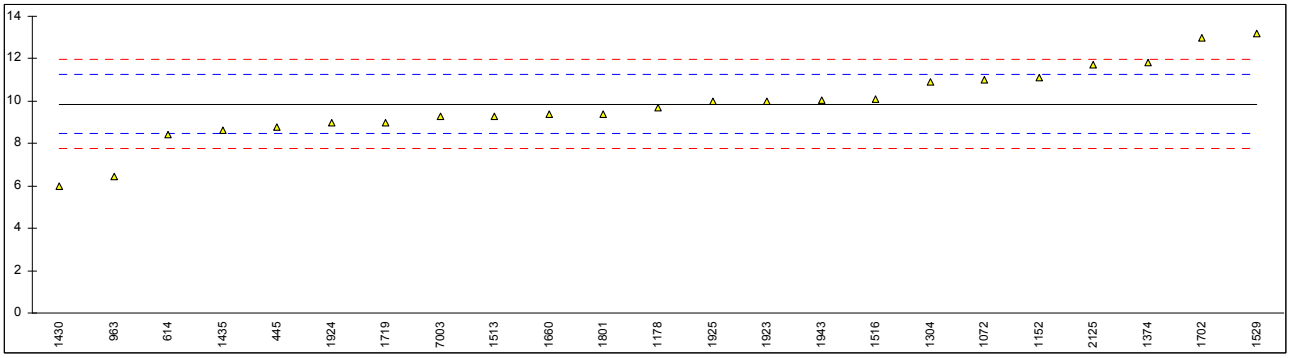


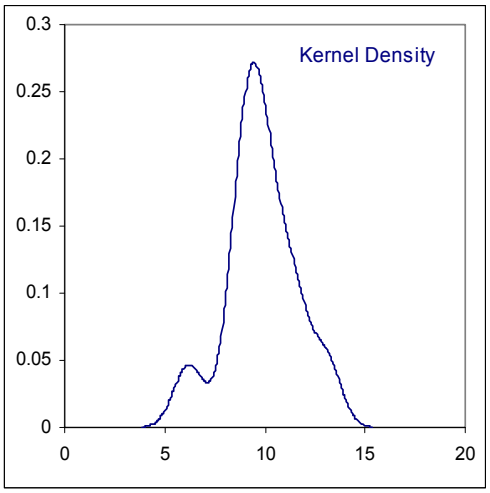



## Determination of Methane on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | <1 | | < -12.58 | False negative? |
| 445 | IEC60567 | 8.8 | | -1.48 | |
| 614 | IEC60567 | 8.444 | | -1.98 | |
| 963 | D3612C | 6.4225 | | -4.86 | |
| 1072 | IEC60567 | 11 | | 1.66 | |
| 1152 | D3612 | 11.1206 | | 1.83 | |
| 1178 | IEC60567 | 9.70 | | -0.19 | |
| 1304 | in house | 10.9 | | 1.51 | |
| 1374 | D3612 (mod) | 11.8 | | 2.79 | |
| 1430 | | 6 | | -5.46 | |
| 1435 | IEC60567 | 8.6 | | -1.76 | |
| 1513 | IEC60567 | 9.3 | | -0.76 | |
| 1516 | IEC60567 | 10.1 | | 0.37 | |
| 1529 | IEC60567 | 13.2 | | 4.79 | |
| 1660 | IEC60567 | 9.4 | | -0.62 | |
| 1702 | IEC60567 | 13 | | 4.50 | |
| 1719 | D3612B | 9 | | -1.19 | |
| 1801 | IEC60567 | 9.4 | C | -0.62 | First reported 14661.7 |
| 1923 | IEC60567 | 10 | | 0.23 | |
| 1924 | in house | 9 | | -1.19 | |
| 1925 | IEC60567 | 10 | | 0.23 | |
| 1943 | D3612 | 10.053 | | 0.31 | |
| 2125 | IEC60567 | 11.73 | | 2.69 | |
| 7003 | D3612 | 9.28 | | -0.79 | |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 23 | 10 | 13 |
| | outliers | 0 | 0 | 0 |
| | mean (n) | 9.837 | 9.7606 | 9.896 |
| | st.dev. (n) | 1.7370 | 2.3285 | 1.2069 |
| | R(calc.) | 4.864 | 6.520 | 3.379 |
| | R(IEC60567) | 1.967 | 1.952 | 1.979 |
| | U(mean) | 0.4455 | | |
| | R'(IEC60567) | n/a | Compare R(Horwitz) = 3.124 | |

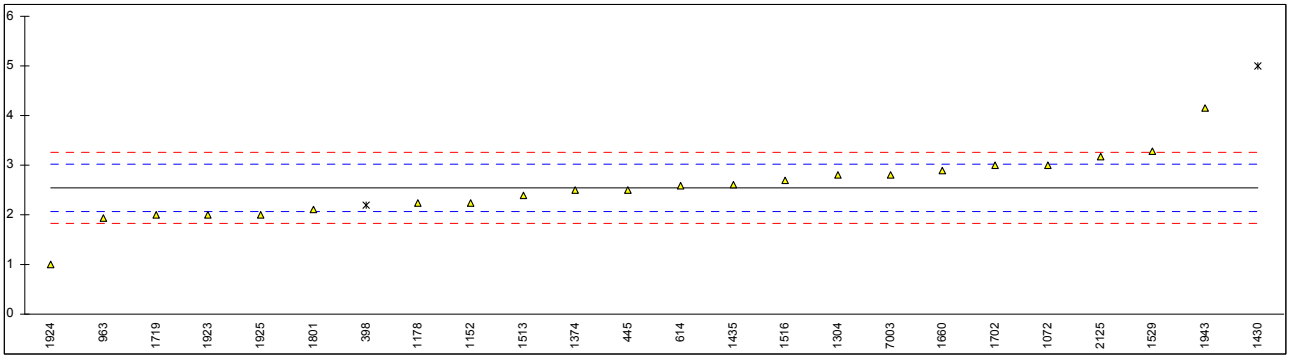


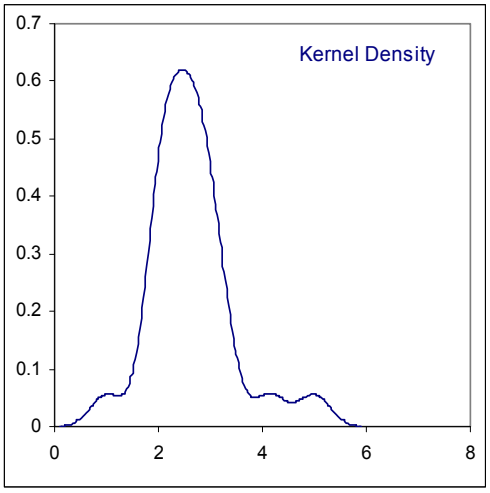



## Determination of Ethane on sample #1088; results in µl/L

| lab | method | value | mark | z'(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 2.2 | ex | -1.39 | |
| 445 | IEC60567 | 2.5 | | -0.17 | |
| 614 | IEC60567 | 2.593 | | 0.21 | |
| 963 | D3612C | 1.9315 | | -2.49 | |
| 1072 | IEC60567 | 3 | | 1.87 | |
| 1152 | D3612 | 2.2446 | | -1.21 | |
| 1178 | IEC60567 | 2.23 | | -1.27 | |
| 1304 | in house | 2.8 | | 1.05 | |
| 1374 | D3612 (mod) | 2.5 | | -0.17 | |
| 1430 | | 5 | G(0.05) | 10.02 | |
| 1435 | IEC60567 | 2.6 | | 0.24 | |
| 1513 | IEC60567 | 2.4 | | -0.58 | |
| 1516 | IEC60567 | 2.7 | | 0.65 | |
| 1529 | IEC60567 | 3.28 | | 3.01 | |
| 1660 | IEC60567 | 2.9 | | 1.46 | |
| 1702 | IEC60567 | 3 | | 1.87 | |
| 1719 | D3612B | 2 | | -2.21 | |
| 1801 | IEC60567 | 2.1 | C | -1.80 | First reported 58.0 |
| 1923 | IEC60567 | 2 | | -1.39 | |
| 1924 | in house | 1 | | -0.17 | |
| 1925 | IEC60567 | 2 | | 0.21 | |
| 1943 | D3612 | 4.155 | | -2.49 | |
| 2125 | IEC60567 | 3.18 | C | 1.87 | First reported 3.41 |
| 7003 | D3612 | 2.80 | | -1.21 | |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 22 | 9 | 13 |
| | outliers | 1 | 1 | 0 |
| | mean (n) | 2.542 | 2.843 | 2.333 |
| | st.dev. (n) | 0.6287 | 0.6516 | 0.5414 |
| | R(calc.) | 1.760 | 1.824 | 1.516 |
| | R(IEC60567) | 0.508 | 0.569 | 0.467 |
| | U(mean) | 0.165 | | |
| | R'(IEC60567) | 0.687 | Compare R(Horwitz) = 0.989 | |

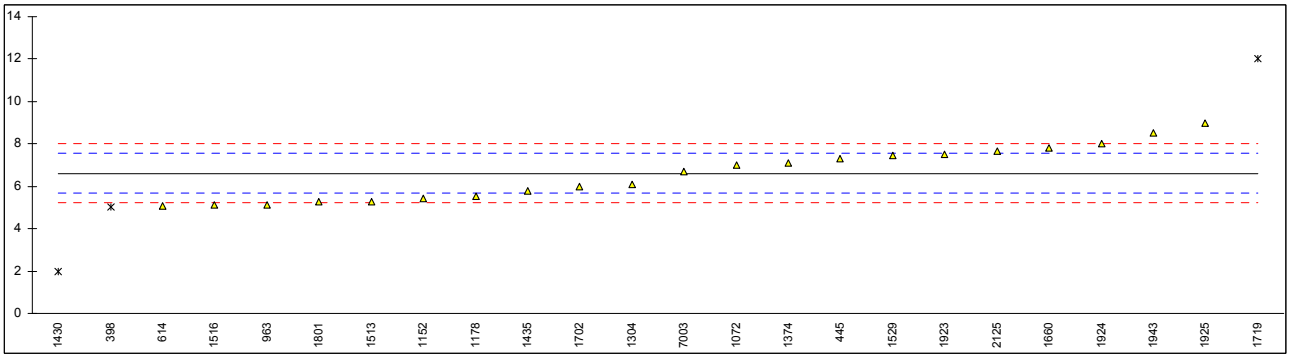


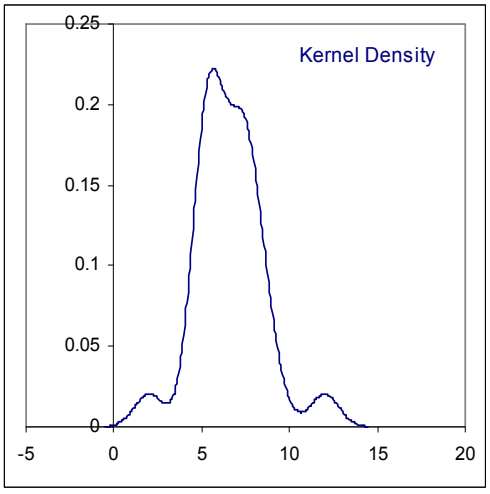



## Determination of Ethene (ethylene) on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 5.0 | ex | -3.41 | |
| 445 | IEC60567 | 7.3 | | 1.46 | |
| 614 | IEC60567 | 5.083 | | -3.24 | |
| 963 | D3612C | 5.1065 | | -3.19 | |
| 1072 | IEC60567 | 7 | | 0.82 | |
| 1152 | D3612 | 5.4444 | | -2.47 | |
| 1178 | IEC60567 | 5.55 | | -2.25 | |
| 1304 | in house | 6.1 | | -1.08 | |
| 1374 | D3612 (mod) | 7.1 | | 1.04 | |
| 1430 | | 2 | G(0.05) | -9.76 | |
| 1435 | IEC60567 | 5.8 | | -1.72 | |
| 1513 | IEC60567 | 5.3 | | -2.78 | |
| 1516 | IEC60567 | 5.1 | | -3.20 | |
| 1529 | IEC60567 | 7.48 | | 1.84 | |
| 1660 | IEC60567 | 7.8 | | 2.52 | |
| 1702 | IEC60567 | 6 | | -1.29 | |
| 1719 | D3612B | 12 | G(0.05) | 11.41 | |
| 1801 | IEC60567 | 5.3 | C | -2.78 | First reported 22.8 |
| 1923 | IEC60567 | 7.5 | | 1.88 | |
| 1924 | in house | 8 | | 2.94 | |
| 1925 | IEC60567 | 9 | | 5.06 | |
| 1943 | D3612 | 8.528 | | 4.06 | |
| 2125 | IEC60567 | 7.66 | | 2.22 | |
| 7003 | D3612 | 6.68 | | 0.15 | |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 21 | 9 | 12 |
| | outliers | 2 | 1 | 1 |
| | mean (n) | 6.611 | 6.844 | 6.436 |
| | st.dev. (n) | 1.2316 | 1.1716 | 1.2969 |
| | R(calc.) | 3.449 | 3.2803 | 3.631 |
| | R(IEC60567) | 1.322 | 1.369 | 1.287 |
| | U(mean) | 0.331 | | |
| | R'(IEC60567) | n/a | Compare R(Horwitz) = 2.229 | |

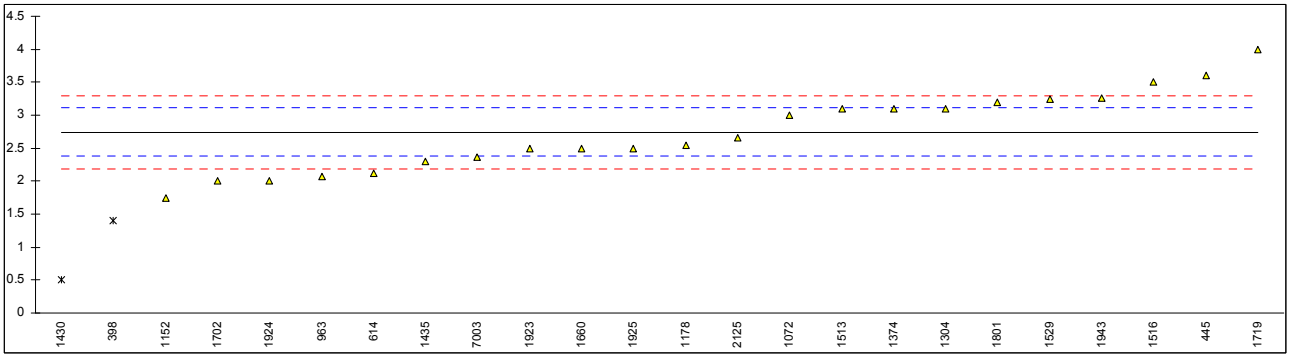


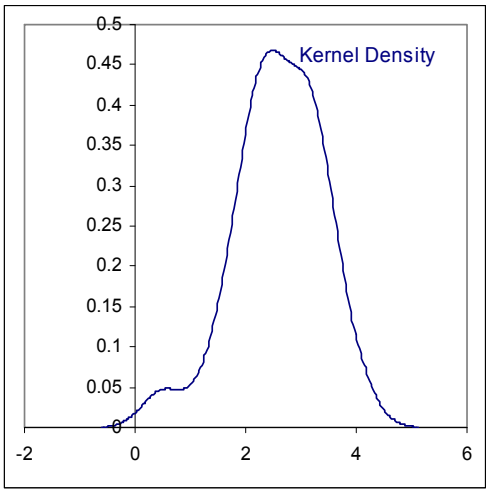



## Determination of Ethyn (acetylene) on sample #1088; results in µl/L

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | 1.4 | ex | -6.86 | |
| 445 | IEC60567 | 3.6 | | 4.36 | |
| 614 | IEC60567 | 2.114 | | -3.22 | |
| 963 | D3612C | 2.073 | | -3.43 | |
| 1072 | IEC60567 | 3 | | 1.30 | |
| 1152 | D3612 | 1.7374 | | -5.14 | |
| 1178 | IEC60567 | 2.54 | | -1.05 | |
| 1304 | in house | 3.1 | | 1.81 | |
| 1374 | D3612 (mod) | 3.1 | | 1.81 | |
| 1430 | | 0.5 | G(0.05) | -11.45 | |
| 1435 | IEC60567 | 2.3 | | -2.27 | |
| 1513 | IEC60567 | 3.1 | | 1.81 | |
| 1516 | IEC60567 | 3.5 | | 3.85 | |
| 1529 | IEC60567 | 3.25 | | 2.57 | |
| 1660 | IEC60567 | 2.5 | | -1.25 | |
| 1702 | IEC60567 | 2 | C | -3.80 | First reported 1 |
| 1719 | D3612B | 4 | | 6.40 | |
| 1801 | IEC60567 | 3.2 | C | 2.32 | First reported 35.2 |
| 1923 | IEC60567 | 2.5 | | -1.25 | |
| 1924 | in house | 2.0 | | -3.80 | |
| 1925 | IEC60567 | 2.5 | | -1.25 | |
| 1943 | D3612 | 3.263 | | 2.64 | |
| 2125 | IEC60567 | 2.65 | | -0.49 | |
| 7003 | D3612 | 2.37 | | -1.91 | |

| | | | Only head space results: | All other test results: |
|---|---|---|---|---|
| | normality | OK | OK | OK |
| | n | 22 | 9 | 13 |
| | outliers | 1 | 1 | 0 |
| | mean (n) | 2.745 | 2.583 | 2.858 |
| | st.dev. (n) | 0.6014 | 0.5346 | 0.6393 |
| | R(calc.) | 1.684 | 1.4970 | 1.790 |
| | R(IEC60567) | 0.549 | 0.517 | 0.572 |
| | U(mean) | 0.158 | | |
| | R'(IEC60567) | n/a | Compare R(Horwitz) = 1.056 | |



Determination of Propane and Propene on sample #1088; results in µl/L

| lab | method | Propane | Propene | Sum of Propane& Propene | remarks |
|---|---|---|---|---|---|
| 398 | IEC60567 | <1 | <1 | <1 | False negative? |
| 445 | | ----- | ----- | ----- | |
| 614 | | ----- | ----- | ----- | |
| 963 | D3612C | 0 | 4.769 | 4.769 | |
| 1072 | | ----- | ----- | ----- | |
| 1152 | | ----- | ----- | ----- | |
| 1178 | IEC60567 | 3.42 | ----- | 3.42 | |
| 1304 | | ----- | ----- | ----- | |
| 1374 | | ----- | ----- | ----- | |
| 1430 | | ----- | ----- | ----- | |
| 1435 | | ----- | ----- | ----- | |
| 1513 | | ----- | ----- | ----- | |
| 1516 | IEC60567 | 1.9 | 3.9 | 5.8 | |
| 1529 | IEC60567 | <0.1 | 5.2 | 5.2 | |
| 1660 | IEC60567 | 1.9 | 0 | 1.9 | |
| 1702 | | ----- | ----- | ----- | |
| 1719 | | ----- | ----- | ----- | |
| 1801 | | ----- | ----- | ----- | |
| 1923 | | ----- | ----- | ----- | |
| 1924 | | ----- | ----- | ----- | |
| 1925 | | ----- | ----- | ----- | |
| 1943 | D3612 | ----- | 6.398 | 6.398 | |
| 2125 | | ----- | ----- | ----- | |
| 7003 | | ----- | ----- | ----- | |
| | normality | n.a. | n.a. | OK | |
| | n | 4 | 5 | 6 | |
| | outliers | 0 | 0 | 0 | |
| | mean (n) | n.a. | n.a. | 4.58 | |
| | st.dev. (n) | n.a. | n.a. | 1.658 | |
| | R(calc.) | n.a. | n.a. | 4.64 | |
| | R(IEC60567) | n.a. | n.a. | 0.92 | |

## APPENDIX 2

### Number of participants per country

3 labs in AUSTRALIA
2 labs in BELGIUM
3 labs in BULGARIA
1 lab in CROATIA
1 lab in IRAN
2 labs in ITALY
1 lab in LATVIA
2 labs in MALAYSIA
1 lab in NEW ZEALAND
2 labs in PORTUGAL
1 lab in SAUDI ARABIA
3 labs in SPAIN
1 lab in THE NETHERLANDS
1 lab in UNITED KINGDOM

**APPENDIX 3**

**Abbreviations**:

| | |
|---|---|
| C | = final result after checking of first reported suspect result |
| D(0.01) | = outlier in Dixon's outlier test |
| D(0.05) | = straggler in Dixon's outlier test |
| G(0.01) | = outlier in Grubbs' outlier test |
| G(0.05) | = straggler in Grubbs' outlier test |
| DG(0.01) | = outlier in Double Grubbs' outlier test |
| DG(0.05) | = straggler in Double Grubbs' outlier test |
| ex | = excluded from calculations |
| n/a | = not applicable |
| 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 E178-89
4 ASTM E1301-89
5 ISO 5725-86
6 ISO 5725, parts 1-6, 1994
7 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
8 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
9 IP 367/84
10 DIN 38402 T41/42
11 P.L. Davies, First reported Z. Anal. Chem, 331, 513, (1988)
12 J.N. Miller, Analyst, 118, 455, (1993)
13 Analytical Methods Committee Technical Brief, No4 January 2001
14 The Royal Society of Chemistry 2002, Analyst 2002, 127 page1359-1364, P.J. Lowthian and M. Thompson. (see http://www.rsc.org/suppdata/an/b2/b205600n/)