# Results of Proficiency Test
## Vinyl Acetate Monomer
## March 2010

**CONTENTS**

Appendices:

## 1    INTRODUCTION

Since 2007, the Institute for Interlaboratory Studies organizes a proficiency test for the analysis of Vinyl Acetate Monomer (VAM). During the annual proficiency testing program 2009/2010, it was decided to continue the round robin for the analysis of Vinyl Acetate Monomer. In this international interlaboratory study 21 laboratories in 16 different countries have participated. See appendix 2 for a list of participants in alphabetical country order. In this report, the results of the Vinyl Acetate Monomer proficiency test are presented and discussed. This report is also electronically available through the i.i.s. internet site www.iisnl.com.

## 2    SET UP

The Institute for Interlaboratory studies (i.i.s.) in Spijkenisse, The Netherlands, was the organiser of this proficiency test. It was decided to send one sample (500 mL). Analyses for fit-four-use and homogeneity were subcontracted to an accredited laboratory. Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluations.

### 2.1   QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO guide 43 and ILAC-G13:2007. This ensures 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out 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 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (i.i.s.-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**

The necessary amount of bulk material of Vinyl Acetate Monomer Acid was obtained from a chemical producer. The approximately 25 litre of Vinyl Acetate Monomer was after homogenisation divided over 46 brown glass bottles of 500 mL and labelled #1016. The homogeneity of the subsamples #1016 was checked by determination of Density in accordance with ASTM D4052:02e1, Water in accordance with ASTM D1364:07 and by determination of Total impurities in accordance with an in-house method on 5 stratified random selected samples.

|  | Density in kg/L | Water in mg/kg | Total Impurities In mg/kg |
|---|---|---|---|
| sample #1016-1 | 0.93219 | 68 | 160 |
| sample #1016-2 | 0.93222 | 82 | 170 |
| sample #1016-3 | 0.93220 | 63 | 170 |
| sample #1016-4 | 0.93220 | 77 | 164 |
| sample #1016-5 | 0.93220 | 65 | 170 |

table 1: homogeneity test results of subsamples #1016

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities of the target methods or with the reproducibility calculate using the Horwitz equation in agreement with the procedure of ISO 13528, Annex B2 in the next table

|  | Density in kg/L | Water in mg/kg | Total Impurities In mg/kg |
|---|---|---|---|
| r (sample #1016) | 0.00001 | 22.8 | 12.9 |
| reference test | D4052:02e1 | ASTM D1364:07 | Horwitz |
| 0.3*R (reference test) | 0.00015 | 15.2 | 18.0 |

table 2: repeatabilities of subsamples #1016

The calculated repeatabilities were in agreement with 0.3 times the corresponding reproducibility of the target method, except for Water. However, the calculated repeatability for Water is in agreement with the repeatability limits of ASTM D1364:07 ($r_{D1364}$= 25.3). Therefore, homogeneity of the samples was assumed.

To each of the participating laboratories 1 bottle of 500 mL Vinyl Acetate Monomer (sample #1016) was sent on February 24, 2010.

**2.5  STABILITY OF THE SAMPLES**

The stability of Vinyl Acetate Monomer, packed in the brown glass bottles was checked. The material has been found stable for the period of the proficiency test

### 2.6   ANALYSES

The participants were asked to analyse according standard specification for VAM (ASTM D2190:07) plus additional tests: Acetaldehyde, Acidity, Density @ 20 $^o$C, Distillation, Inhibitor, Water, Purity, Acetone, Ethyl Acetate and Methyl Acetate. To get comparable results, a detailed report form on which the units and the standard methods were printed, was sent together with each set of samples. Also a letter of instructions and a SDS were added to the package.

### 3   RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received. The original reported results are tabulated per determination in 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 had not yet reported any 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 results. 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 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' January 2010 (i.i.s.-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. Not all data sets proved to have a normal distribution, in which cases 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, 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. Both outliers and stragglers were not included in the calculations of averages and standard deviations. Finally, the reproducibilities were calculated from the standard deviations by multiplying these with a factor of 2.8.

### 3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are under the X-axis.
The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle. Furthermore, Kernel Density Graphs were made. This method is 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 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.
In case no literature reproducibility was available, other target values were used. In some cases literature repeatability is available; in other cases a reproducibility of a former iis proficiency test could be used and also the Horwitz equation can be used to estimate target reproducibility.

The z-scores were calculated according to:

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

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The usual interpretation of z-scores is as follows:

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

## 4    EVALUATION

In this proficiency test, no serious problems were encountered with despatch of the samples. The participants in Chile and India did receive the samples late due to customs clearance problems. Of the 21 participants, 3 participants reported results after the final reporting date. Not all participants were able to report results for all the requested tests. In total 201 numerical results were reported. Observed were 8 outlying results, which is 4.0 % of the total of numerical results. In proficiency studies, outlier percentages of 3 % - 7.5 % are quite normal.

### 4.1    EVALUATION PER TEST

In this section, the reported results are discussed per test.
Unfortunately, not for all determinations a suitable standard test method exists with precision data. For these determinations, the spreads were compared against the strict spreads estimated from the Horwitz equation.

A not-normal distribution was found for Density, Distillation (IBP, Mid Boiling Point, DP and Boiling Range) and Water. In this case the statistical evaluation should be used with due care.

Acidity:    This determination (with and without Nitrogen purging) was very problematic. In total four statistical outliers were observed. Both calculated reproducibilities, after rejection of the statistical outliers, are not in agreement with the requirements of ASTM D2086:08. One should keep in mind that the reproducibility of ASTM D2086 was determined with only two laboratories and therefore may not be very reliable (see note 5 in §13.2.2). Remarkably, the spread of the results with nitrogen purge was larger than the spread without nitrogen purge (110% vs 50%)

Appearance:    No analytical problems were observed. All labs agreed about the appearance of sample #1016, which is bright, clear and free of suspended matter. The uniformity of reporting can be improved. A new standardized method is available for Appearance since 2009, being ASTM E2680. According this method the appearance should be reported as 'pass' (or 'fail').

Density @ 20 $^{\circ}$C: This determination is not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the requirements of ASTM D4052:02e1.

Distillation:    This determination is not problematic. No statistical outliers were observed and the calculated reproducibilities are all in good agreement with the requirements of ASTM D1078:05.

Inhibitor:          This determination is problematic. One statistical outlier was observed. However, the calculated reproducibility, after rejection of the statistical outlier, is not at all in agreement with the requirements of ASTM D2193:06.

Water:              This determination is problematic. No statistical outliers were observed, but the calculated reproducibility is not in agreement with the requirements of ASTM D1364:07.

Purity:             Regretfully, no suitable reference method with precision data exists for this determination. One statistical outlier is observed and compared with the spread found in the previous PT (iis09C03), the calculated reproducibility, after rejection of the statistical outlier, is small.

Acetaldehyde:       This determination was problematic for two laboratories. Two statistical outliers were observed. The calculated reproducibility, after rejection of the statistical outliers, is in full agreement with the estimated reproducibility limits calculated using the Horwitz equation. Remarkably, almost all reporting laboratories decided to use an in-house method based on GC and not ASTM D2191. Therefore, Horwitz was chosen for evaluation instead of ASTM D2191, which is a titration method.

Acetone:            No numerical results were reported. Therefore no significant statistical conclusions were drawn.

Ethyl Acetate:      This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the estimated requirements, calculated using the Horwitz equation.

Methyl Acetate:     This determination seems to be not problematic. All reporting participants agreed on a result below or near the detection limit of the method. Therefore no significant statistical conclusions were drawn.

**4.2   PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES**

A comparison has been made between the reproducibility as declared by the relevant standard and the reproducibility as found for the group of participating laboratories. The average results per sample, calculated reproducibilities and reproducibilities derived from literature standards (in casu ASTM standards) or estimated using the Horwitz equation are compared in the next tables.

| Parameter | | unit | n | average | 2.8 * sd | R (lit) |
|---|---|---|---|---|---|---|
| Acidity as Acetic Acid without $N_2$ | | mg/kg | 15 | 13.23 | 7.52 | 6.00 |
| Acidity as Acetic Acid with $N_2$ | | mg/kg | 8 | 9.12 | 10.13 | 6.00 |
| Density @ 20$^o$C | | kg/L | 19 | 0.93219 | 0.00024 | 0.00050 |
| Distillation | IBP | °C | 16 | 72.50 | 0.26 | 1.13 |
| | MBP | °C | 16 | 72.72 | 0.11 | 0.50 |
| | DP | °C | 16 | 72.85 | 0.27 | 0.78 |
| | Range | °C | 16 | 0.34 | 0.20 | 0.69 |
| Inhibitor | | mg/kg | 18 | 2.66 | 1.37 | 2.00 |
| Water | | mg/kg | 20 | 63.98 | 61.06 | 47.99 |
| Purity | | %M/M | 16 | 99.980 | 0.006 | unknown |
| Acetaldehyde | | mg/kg | 12 | 26.02 | 6.53 | 7.14 |
| Acetone | | mg/kg | 0 | unknown | unknown | unknown |
| Ethyl Acetate | | mg/kg | 16 | 131.93 | 20.98 | 28.34 |
| Methyl Acetate | | mg/kg | 5 | 3.00 | 4.85 | unknown |

table 3: Reproducibilities for sample #1016

Without further statistical calculations, it can be concluded that for many tests there is a good compliance of the group of participating laboratories with the relevant standards. The problematic tests have been discussed in paragraph 4.1.

**4.3**   **EVALUTION OF THE PROFICIENCY TEST OF MARCH 2010 WITH PREVIOUS PT'S**

|  | *March 2010* | *March 2009* | *February 2008* |
|---|---|---|---|
| Number of rep. participants | 21 | 26 | 24 |
| Number of results reported | 201 | 239 | 205 |
| Statistical outliers | 8 | 10 | 10 |
| Percentage outliers | 4.0% | 4.2% | 4.9% |

table 4: evaluation of the proficiency test.

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

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

| *Determination* | *March 2010* | *March 2009* | *February 2008* |
|---|---|---|---|
| Acidity as Acetic Acid | -- | -- | n.e. |
| Density @ 20$^o$C | ++ | ++ | ++ |
| Distillation | ++ | ++ | ++ |
| Inhibitor | -- | -- | -- |
| Water | -- | ++ | ++ |
| Purity | n.a. | n.a. | n.a. |
| Acetaldehyde | ++ | ++ | n.e. |
| Acetone | n.a. | n.a. | n.a. |
| Ethyl Acetate | ++ | ++ | ++ |
| Methyl Acetate | n.a. | ++ | +/- |

table 5: comparison determinations against the standard

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.a.:    not applicable
- n.e.:    not evaluated

## APPENDIX 1

Determination of Acidity (without $N_2$ purging) on sample #1016; results in mg/kg

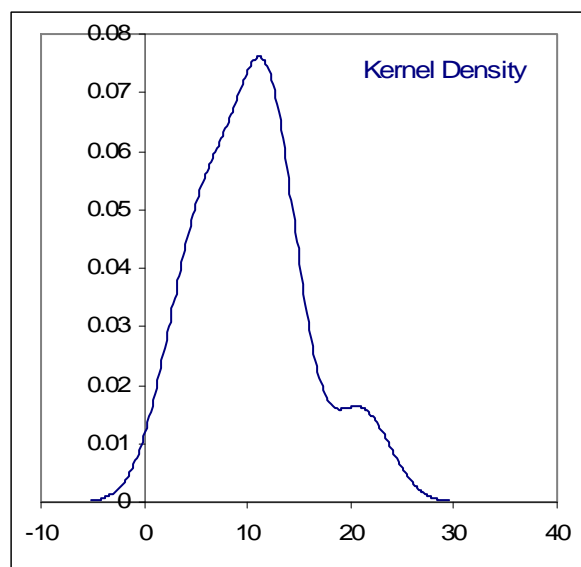| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D2086 | 14.1 | | 0.40 | |
| 174 | D2086 | 15.1 | | 0.87 | |
| 176 | D2086 | 14.1 | | 0.40 | |
| 311 | D2086 | 9 | | -1.98 | |
| 315 | | ----- | | ----- | |
| 323 | D2086 | 17 | | 1.76 | |
| 347 | D2086 | 11.9 | | -0.62 | |
| 357 | D2086 | 16 | | 1.29 | |
| 395 | INH44 | 14 | | 0.36 | |
| 522 | | ----- | | ----- | |
| 562 | D2086 | 16.6 | | 1.57 | |
| 613 | | ----- | | ----- | |
| 786 | D2086 | 14.2 | | 0.45 | |
| 823 | D2086 | 14 | | 0.36 | |
| 859 | D2086 | 8 | | -2.44 | |
| 861 | D2086 | 10.0 | | -1.51 | |
| 902 | D2086 | 11.5 | | -0.81 | |
| 913 | D2086 | 25.5 | DG(0.05) | 5.72 | |
| 963 | D2086 | 3.28 | G(0.05) | -4.64 | |
| 1283 | D2086 | 25.5 | DG(0.05) | 5.72 | |
| 1429 | D1613 | 13 | | -0.11 | |

| | | |
|---|---|---|
| normality | OK | |
| n | 15 | |
| outliers | 3 | |
| mean (n) | 13.23 | |
| st.dev. (n) | 2.684 | |
| R(calc.) | 7.52 | |
| R(D2086:08) | 6.00 | |
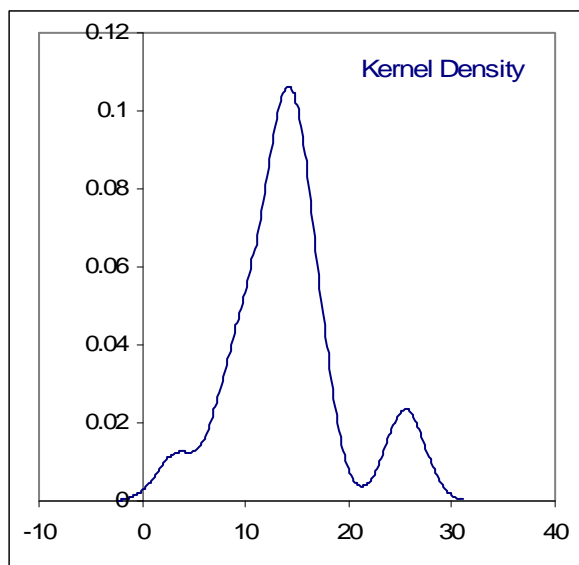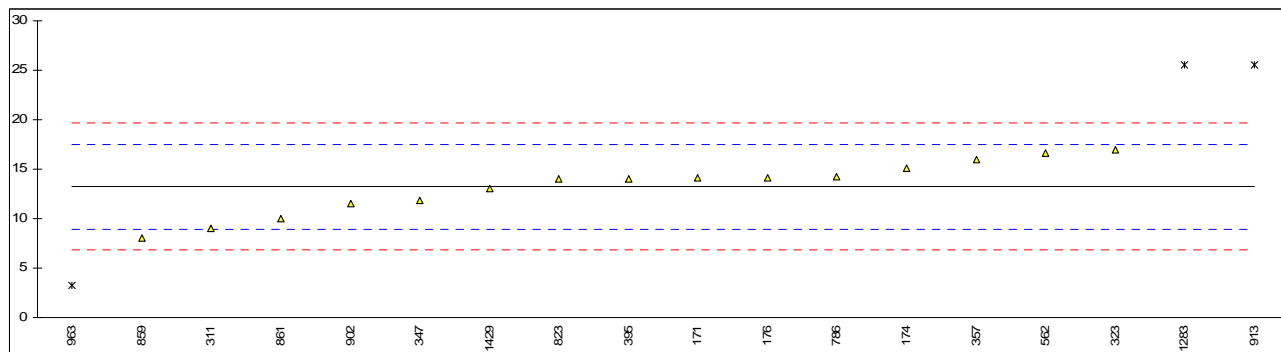
Determination of Acidity (with $N_2$ purging) on sample #1016; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D2086 | 11.6 | | 1.16 | |
| 174 | | ----- | | ----- | |
| 176 | D2086 | 12.8 | | 1.72 | |
| 311 | D2086 | 9 | | -0.06 | |
| 315 | | ----- | | ----- | |
| 323 | D2086 | 6 | | -1.46 | |
| 347 | | ----- | | ----- | |
| 357 | | ----- | | ----- | |
| 395 | | ----- | | ----- | |
| 522 | INH40-1 | 21 | G(0.05) | 5.54 | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | | ----- | | ----- | |
| 823 | | ----- | | ----- | |
| 859 | D2086 | 6 | | -1.46 | |
| 861 | | ----- | | ----- | |
| 902 | D2086 | 12.3 | | 1.48 | |
| 913 | | ----- | | ----- | |
| 963 | D2086 | 3.28 | | -2.73 | |
| 1283 | | ----- | | ----- | |
| 1429 | D1613 | 12 | | 1.34 | |

|  |  |
|--|--|
| normality | OK |
| n | 8 |
| outliers | 1 |
| mean (n) | 9.12 |
| st.dev. (n) | 3.619 |
| R(calc.) | 10.13 |
| R(D2086:08) | 6.00 |





Kernel Density
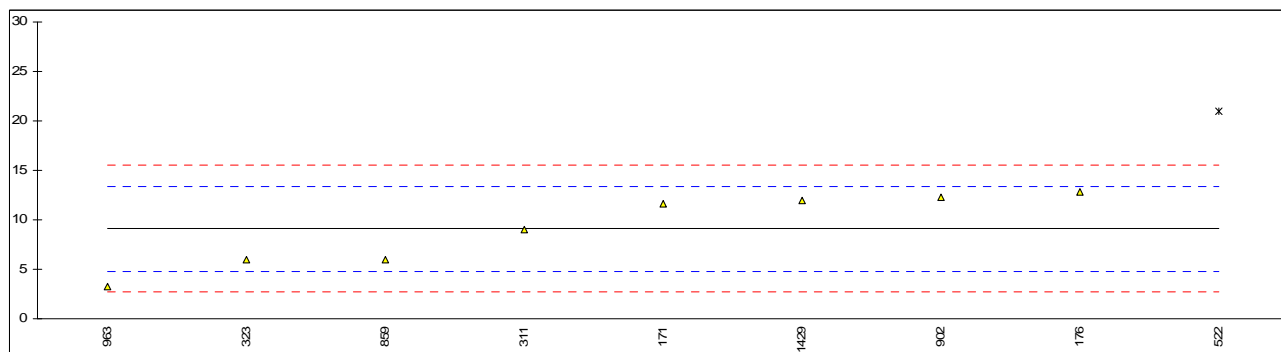
Determination of Appearance on sample #1016;

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | E2680 | C&F | | ----- | |
| 174 | E2680 | C&F | | ----- | |
| 176 | E2680 | PASS | | ----- | |
| 311 | E2680 | PASS | | ----- | |
| 315 | INH-402 | PASS | | ----- | |
| 323 | E2680 | PASS | | ----- | |
| 347 | E2680 | PASS | | ----- | |
| 357 | E2680 | PASS | | ----- | |
| 395 | E2680 | PASS | | ----- | |
| 522 | INH40-1 | CFSM | | ----- | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | E2680 | PASS | | ----- | |
| 823 | E2680 | PASS | | ----- | |
| 859 | E2680 | PASS | | ----- | |
| 861 | E2680 | B&C | | ----- | |
| 902 | E2680 | PASS | | ----- | |
| 913 | E2680 | CFSM | | ----- | |
| 963 | E2680 | PASS | | ----- | |
| 1283 | INH001 | CCL | | ----- | |
| 1429 | D120 | B&C | | ----- | |

C&F      = Clear and free
CFSM    = Clear and free from suspended matter
B&C      = Bright and clear
CCL      = Clear colorless liquid

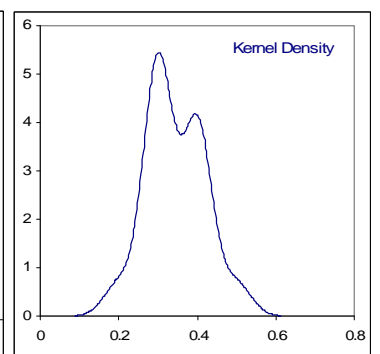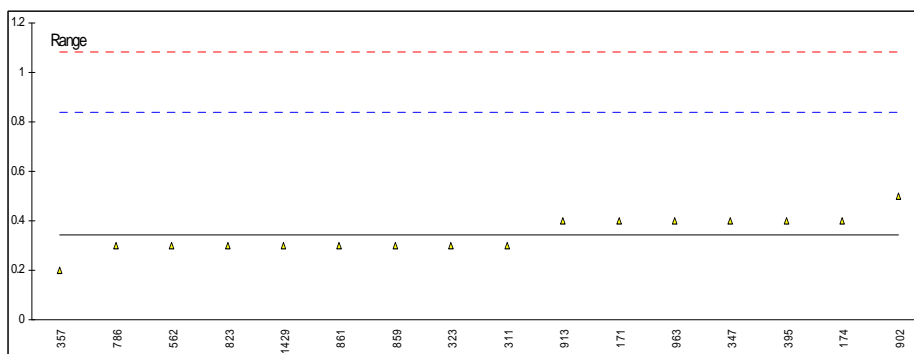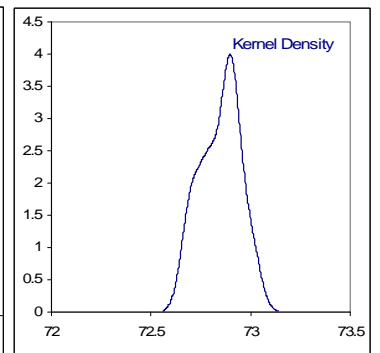Determination of Density @ 20 $^{\circ}$C on sample #1016; results in kg/L

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D4052 | 0.9321 | | -0.49 | |
| 174 | D4052 | 0.9322 | | 0.07 | |
| 176 | D4052 | 0.9320 | | -1.05 | |
| 311 | D4052 | 0.9322 | | 0.07 | |
| 315 | D4052 | 0.9322 | | 0.07 | |
| 323 | D4052 | 0.9323 | | 0.63 | |
| 347 | D4052 | 0.93217 | | -0.10 | |
| 357 | D4052 | 0.9322 | | 0.07 | |
| 395 | D4052 | 0.9321 | | -0.49 | |
| 522 | | ----- | | ----- | |
| 562 | D4052 | 0.9324 | | 1.19 | |
| 613 | D4052 | 0.93217 | | -0.10 | |
| 786 | D4052 | 0.9321 | | -0.49 | |
| 823 | D4052 | 0.9322 | | 0.07 | |
| 859 | D4052 | 0.93219 | | 0.01 | |
| 861 | D4052 | 0.93216 | | -0.16 | |
| 902 | D4052 | 0.93218 | | -0.04 | |
| 913 | D4052 | 0.9322 | | 0.07 | |
| 963 | D4052 | 0.9322 | | 0.07 | |
| 1283 | | ----- | | ----- | |
| 1429 | D4052 | 0.9323 | | 0.63 | |

|  |  |
|--|--|
| normality | not OK |
| n | 19 |
| outliers | 0 |
| mean (n) | 0.93219 |
| st.dev. (n) | 0.000085 |
| R(calc.) | 0.00024 |
| R(D4052:02e1) | 0.00050 |
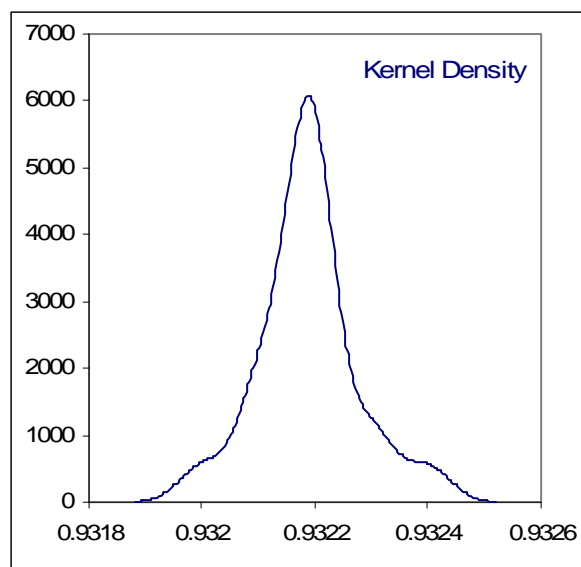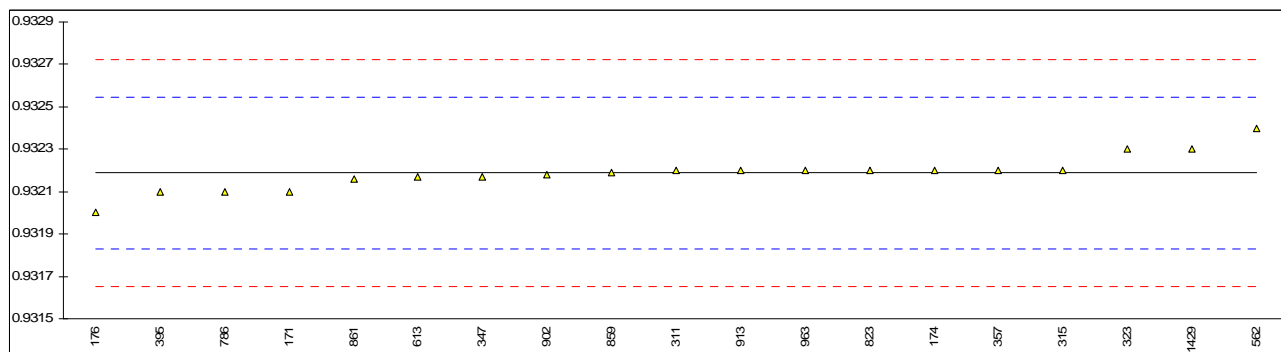
Determination of Distillation on sample #1016; results in ºC

| lab | method | IBP | mark | Mid BP | mark | DP | mark | range | mark |
|-----|--------|-----|------|--------|------|-----|------|-------|------|
| 171 | D1078 | 72.3 | | 72.7 | | 72.7 | | 0.4 | |
| 174 | D1078 | 72.5 | | 72.8 | | 72.9 | | 0.4 | |
| 176 | | ----- | | ----- | | ----- | | ----- | |
| 311 | D1078 | 72.5 | | 72.7 | | 72.8 | | 0.3 | |
| 315 | | ----- | | ----- | | ----- | | ----- | |
| 323 | D1078 | 72.6 | | 72.8 | | 72.9 | | 0.3 | |
| 347 | D1078 | 72.5 | | 72.7 | | 72.9 | | 0.4 | |
| 357 | D1078 | 72.6 | | 72.7 | | 72.8 | | 0.2 | |
| 395 | D1078 | 72.5 | | 72.7 | | 72.9 | | 0.4 | |
| 522 | | ----- | | ----- | | ----- | | ----- | |
| 562 | D1078 | 72.7 | | 72.7 | | 73 | | 0.3 | |
| 613 | | ----- | | ----- | | ----- | | ----- | |
| 786 | D1078 | 72.47 | | 72.70 | | 72.77 | | 0.3 | |
| 823 | D1078 | 72.6 | Fr 72.2 | 72.7 | Fr 72.4 | 72.9 | Fr 72.5 | 0.3 | |
| 859 | D1078 | 72.4 | | 72.7 | | 72.7 | | 0.3 | |
| 861 | D1078 | 72.5 | | 72.7 | | 72.8 | | 0.3 | |
| 902 | D1078 | 72.5 | | 72.8 | | 73.0 | | 0.5 | |
| 913 | D1078 | 72.5 | | 72.7 | | 72.9 | | 0.4 | |
| 963 | D1078 | 72.5 | | 72.7 | | 72.9 | | 0.4 | |
| 1283 | | ----- | | ----- | | ----- | | ----- | |
| 1429 | D1078 | 72.4 | | 72.7 | | 72.7 | | 0.3 | |
| | normality | not OK | | not OK | | not OK | | not OK | |
| | n | 16 | | 16 | | 16 | | 16 | |
| | outliers | 0 | | 0 | | 0 | | 0 | |
| | mean (n) | 72.50 | | 72.72 | | 72.85 | | 0.34 | |
| | st.dev. (n) | 0.093 | | 0.040 | | 0.098 | | 0.073 | |
| | R(calc.) | 0.26 | | 0.11 | | 0.27 | | 0.20 | |
| | R(D1078:05) | 1.13 | | 0.50 | | 0.78 | | 0.69 | |

| lab | method | Z(targ) | Z(targ) | Z(targ) | Z(targ) |
|-----|--------|---------|---------|---------|---------|
| 171 | | -0.51 | -0.11 | -0.53 | 0.23 |
| 174 | | -0.01 | 0.46 | 0.19 | 0.23 |
| 176 | | ----- | ----- | ----- | ----- |
| 311 | | -0.01 | -0.11 | -0.17 | -0.18 |
| 315 | | ----- | ----- | ----- | ----- |
| 323 | | 0.24 | 0.46 | 0.19 | -0.18 |
| 347 | | -0.01 | -0.11 | 0.19 | 0.23 |
| 357 | | 0.24 | -0.11 | -0.17 | -0.58 |
| 395 | | -0.01 | -0.11 | 0.19 | 0.23 |
| 522 | | ----- | ----- | ----- | ----- |
| 562 | | 0.48 | -0.11 | 0.55 | -0.18 |
| 613 | | ----- | ----- | ----- | ----- |
| 786 | | -0.09 | -0.11 | -0.28 | -0.18 |
| 823 | | 0.24 | -0.11 | 0.19 | -0.18 |
| 859 | | -0.26 | -0.11 | -0.53 | -0.18 |
| 861 | | -0.01 | -0.11 | -0.17 | -0.18 |
| 902 | | -0.01 | 0.46 | 0.55 | 0.63 |
| 913 | | -0.01 | -0.11 | 0.19 | 0.23 |
| 963 | | -0.01 | -0.11 | 0.19 | 0.23 |
| 1283 | | ----- | ----- | ----- | ----- |
| 1429 | | -0.26 | -0.11 | -0.53 | -0.18 |
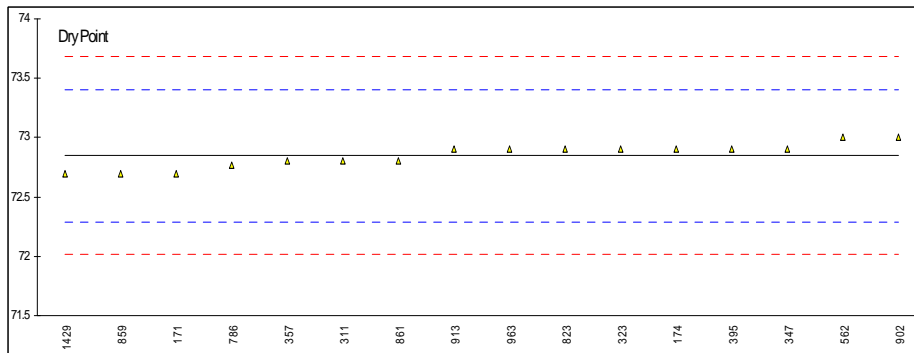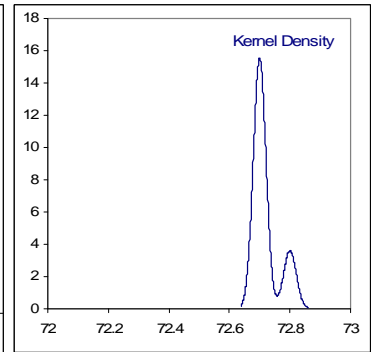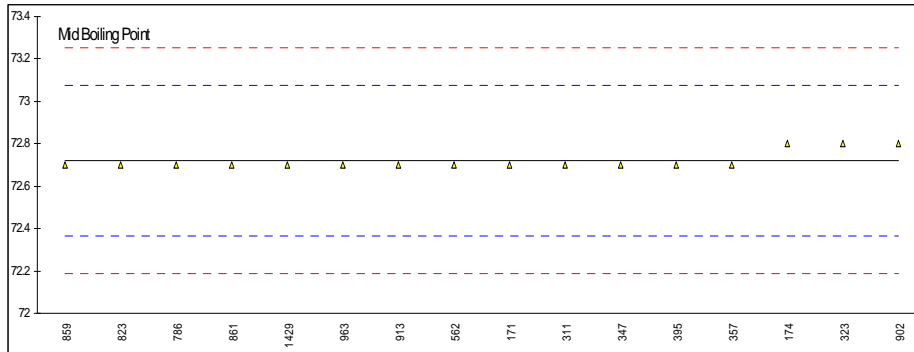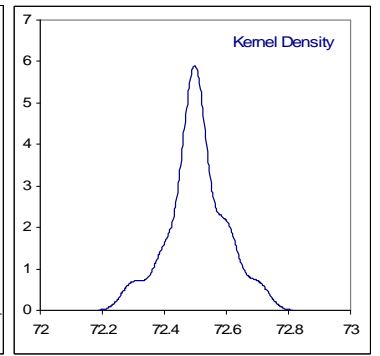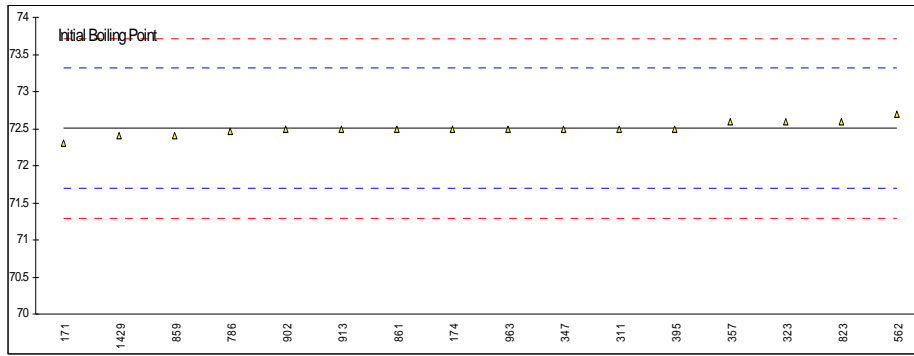
Determination of Inhibitor on sample #1016; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D2193 | 3.13 | | 1.33 | |
| 174 | D2193 | 3.2 | | 1.52 | |
| 176 | INH-43 | 2.8 | | 0.40 | |
| 311 | D2193 | 3.2 | | 1.52 | |
| 315 | | ----- | | ----- | |
| 323 | D2193 | 2.9 | | 0.68 | |
| 347 | D2193 | 3.5 | | 2.36 | |
| 357 | D2193 | 2.1 | | -1.56 | |
| 395 | INH43 | 2.38 | | -0.77 | |
| 522 | INH40-1 | 2 | | -1.84 | |
| 562 | D2193 | 1.97 | | -1.92 | |
| 613 | | ----- | | ----- | |
| 786 | D2193 | 2.64 | | -0.05 | |
| 823 | D2193 | 2.2 | | -1.28 | |
| 859 | D2193 | 2.70 | | 0.12 | |
| 861 | D2193 | 2.36 | | -0.83 | |
| 902 | D2193 | 3.2 | | 1.52 | |
| 913 | D2193 | 3.07 | | 1.16 | |
| 963 | D2193 | 2.07 | | -1.64 | |
| 1283 | D2193 | 2.3905 | | -0.74 | |
| 1429 | D2193 | 4 | G(0.05) | 3.76 | |

|  |  |
|--|--|
| normality | OK |
| n | 18 |
| outliers | 1 |
| mean (n) | 2.66 |
| st.dev. (n) | 0.490 |
| R(calc.) | 1.37 |
| R(D2193:06) | 1.00 |
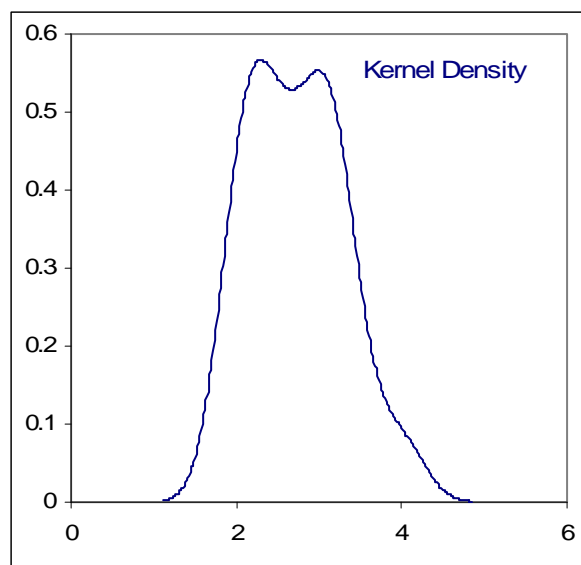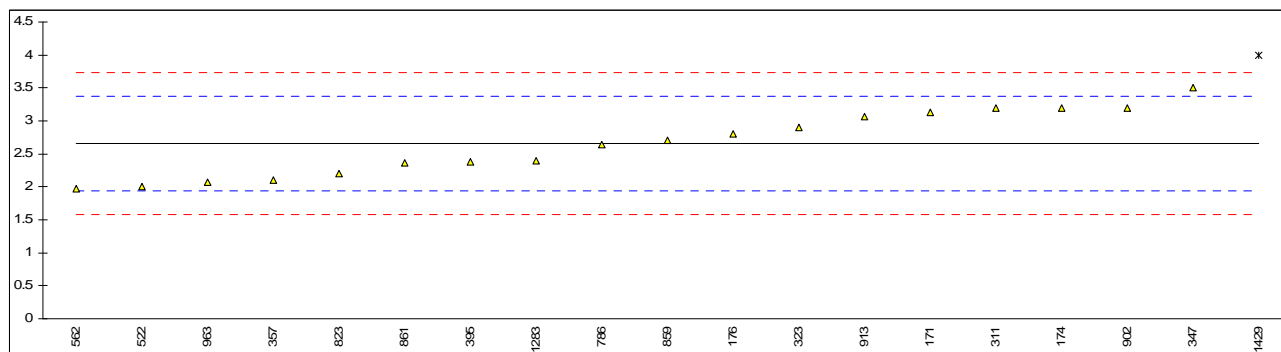
## Determination of Water on sample #1016; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D1364 | 46 | | -1.05 | |
| 174 | D1364 | 50 | | -0.82 | |
| 176 | E203 | 44.0 | | -1.17 | |
| 311 | D1364 | 64 | | 0.00 | |
| 315 | D1364 | 46.5 | | -1.02 | |
| 323 | D1364 | 69 | | 0.29 | |
| 347 | D1364 | 56 | | -0.47 | |
| 357 | D1364 | 90 | C | 1.52 | First reported 166 |
| 395 | D1364 | 48.25 | | -0.92 | |
| 522 | INH40-1 | 89 | | 1.46 | |
| 562 | D1364 | 104 | | 2.33 | |
| 613 | | ----- | | ----- | |
| 786 | D1364 | 54.3 | | -0.56 | |
| 823 | D1364 | 73 | | 0.53 | |
| 859 | D1364 | 38 | | -1.52 | |
| 861 | D1064 | 43 | | -1.22 | |
| 902 | D1364 | 41 | | -1.34 | |
| 913 | D1364 | 100 | | 2.10 | |
| 963 | D1364 | 48.6 | | -0.90 | |
| 1283 | INH2362 | 80 | | 0.93 | |
| 1429 | D1364 | 95 | | 1.81 | |

| | |
|---|---|
| normality | not OK |
| n | 20 |
| outliers | 0 |
| mean (n) | 63.98 |
| st.dev. (n) | 21.807 |
| R(calc.) | 61.06 |
| R(D1364:07) | 47.99 |





Kernel Density
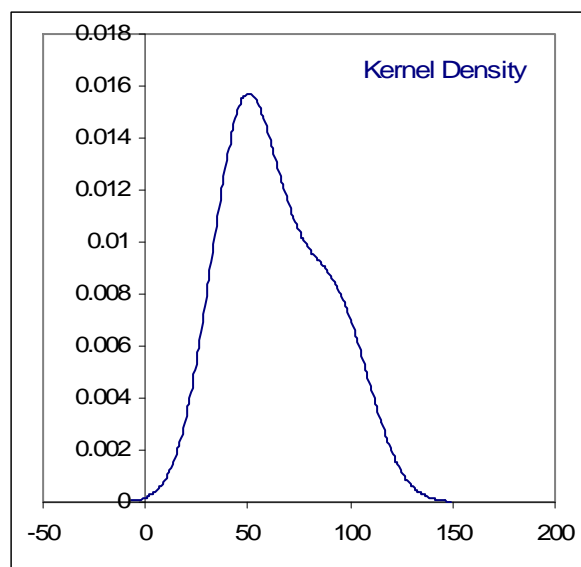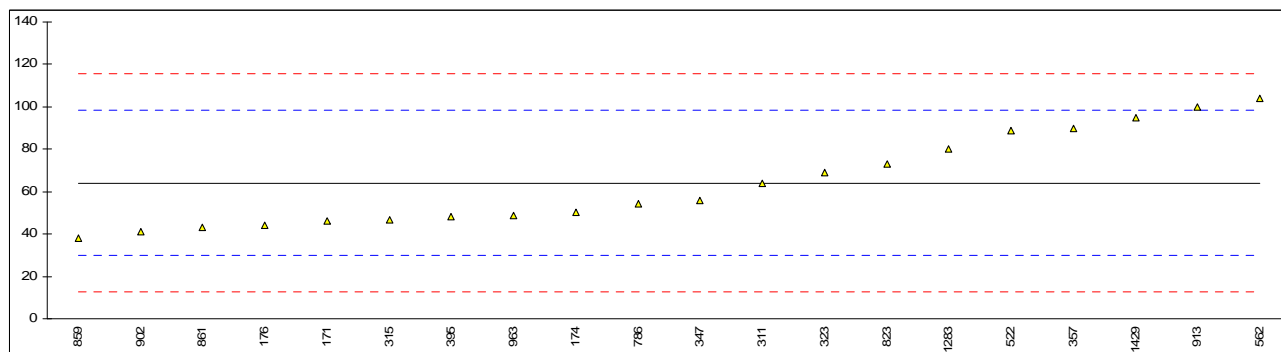
Determination of Purity on sample #1016; results in % M/M

| lab | method | Reported | mark | z(targ) | remarks |
|-----|--------|----------|------|---------|---------|
| 171 | D3545 | 99.978 | C | ----- | First reported 99.980 |
| 174 | D3545 | 99.98 | | ----- | |
| 176 | INH-256 | 99.981 | | ----- | |
| 311 | INH-122 | 99.984 | | ----- | |
| 315 | | ----- | | ----- | |
| 323 | INH-067 | 99.98 | | ----- | |
| 347 | INH-916 | 99.9817 | | ----- | |
| 357 | INH052 | 99.97 | G(0.01) | ----- | |
| 395 | INH-257 | 99.977 | | ----- | |
| 522 | INH40-1 | 99.98 | | ----- | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | INH-004 | 99.978 | | ----- | |
| 823 | inh-278 | 99.98 | | ----- | |
| 859 | inh-065 | 99.979 | | ----- | |
| 861 | INH-065 | 99.978 | | ----- | |
| 902 | | ----- | | ----- | |
| 913 | D3545 | 99.98 | | ----- | |
| 963 | INH-8124 | 99.979 | | ----- | |
| 1283 | INH-020 | 99.976 | | ----- | |
| 1429 | Client method | 99.9827 | | ----- | |

| | | |
|---|---|---|
| normality | OK | |
| n | 16 | |
| outliers | 1 | |
| mean (n) | 99.980 | |
| st.dev. (n) | 0.0021 | |
| R(calc.) | 0.006 | |
| R(lit) | unknown | Compare R(iis09C03) = 0.023 |
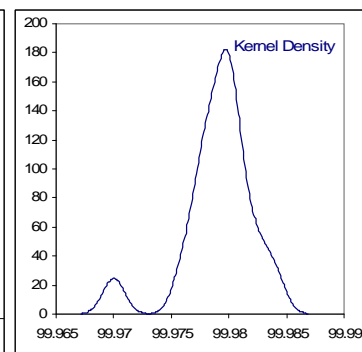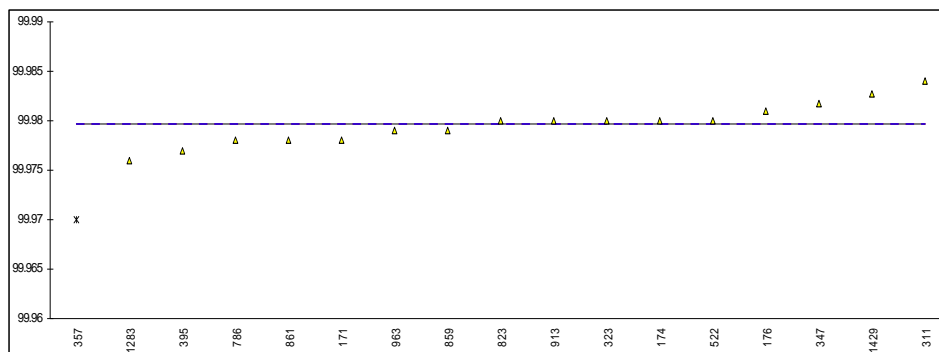
Determination of Acetaldehyde on sample #1016; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D3545 | 23.7 | | -0.91 | |
| 174 | | ----- | | ----- | |
| 176 | INH-256 | 23.4 | | -1.03 | |
| 311 | INH-122 | 28 | | 0.78 | |
| 315 | | ----- | | ----- | |
| 323 | | ----- | | ----- | |
| 347 | INH-916 | 26 | | -0.01 | |
| 357 | INH-052 | 42 | G(0.05) | 6.27 | |
| 395 | INH-47 | 28 | | 0.78 | |
| 522 | INH40-1 | 22 | | -1.58 | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | INH-004 | 26.2 | | 0.07 | |
| 823 | D2191 | 26 | | -0.01 | |
| 859 | D2191 | 29 | | 1.17 | |
| 861 | | ----- | | ----- | |
| 902 | INH-22 | 29.2 | | 1.25 | |
| 913 | | ----- | | ----- | |
| 963 | D2191 | 26.7 | | 0.27 | |
| 1283 | INH-020 | 24 | | -0.79 | |
| 1429 | Client Method | 36 | G(0.05) | 3.92 | |

| | | | |
|---|---|---|---|
| normality | OK | | |
| n | 12 | | |
| outliers | 2 | | |
| mean (n) | 26.02 | | |
| st.dev. (n) | 2.332 | | |
| R(calc.) | 6.53 | | |
| R(Horwitz) | 7.14 | Compare R(D2191:06) = 80.0 | |





Kernel Density
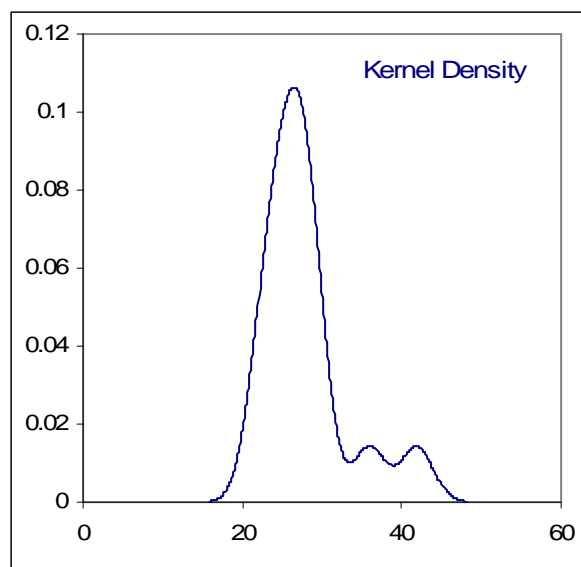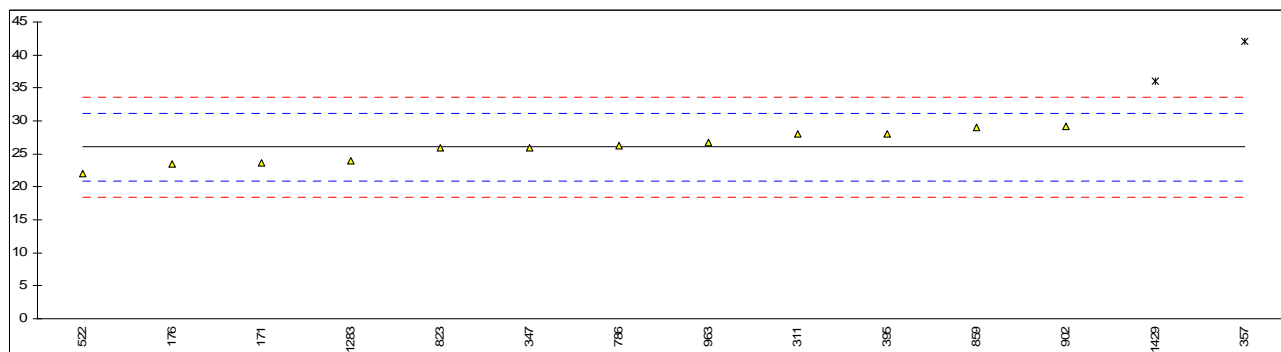
Determination of Acetone on sample #1016; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D3545 | <10 | | ----- | |
| 174 | D3545 | <1 | | ----- | |
| 176 | | ----- | | ----- | |
| 311 | INH-122 | <10 | | ----- | |
| 315 | | ----- | | ----- | |
| 323 | INH-067 | <10 | | ----- | |
| 347 | INH-916 | <10 | | ----- | |
| 357 | INH052 | <10 | | ----- | |
| 395 | | ----- | | ----- | |
| 522 | | ----- | | ----- | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | | ----- | | ----- | |
| 823 | inh-278 | <1 | | ----- | |
| 859 | inh-065 | <10 | | ----- | |
| 861 | INH-065 | <10 | | ----- | |
| 902 | INH-22 | <10 | | ----- | |
| 913 | | ----- | | ----- | |
| 963 | INH-8124 | <10 | | ----- | |
| 1283 | INH-020 | NIL | | ----- | |
| 1429 | Client method | <10 | | ----- | |

| | | |
|---|---|---|
| normality | n.a. | |
| n | 0 | |
| outliers | 0 | |
| mean (n) | n.a. | |
| st.dev. (n) | n.a. | |
| R(calc.) | n.a. | |
| R(lit) | n.a. | |

## Determination of Ethyl Acetate on sample #1016, results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D3545 | 136.4 | C | 0.44 | First reported 119.7 |
| 174 | D3545 | 122 | | -0.98 | |
| 176 | INH-256 | 121.4 | | -1.04 | |
| 311 | INH-122 | 128 | | -0.39 | |
| 315 | | ----- | | ----- | |
| 323 | INH-067 | 132 | | 0.01 | |
| 347 | INH-916 | 145 | | 1.29 | |
| 357 | INH052 | 120 | | -1.18 | |
| 395 | INH-47 | 134 | | 0.20 | |
| 522 | | ----- | | ----- | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | INH-004 | 143.8 | | 1.17 | |
| 823 | inh-278 | 129 | | -0.29 | |
| 859 | inh-065 | 137 | | 0.50 | |
| 861 | INH-065 | 133.2 | | 0.13 | |
| 902 | INH-22 | 139 | | 0.70 | |
| 913 | | ----- | | ----- | |
| 963 | INH-8124 | 126 | | -0.59 | |
| 1283 | INH-020 | 129 | | -0.29 | |
| 1429 | Client method | 135 | | 0.30 | |

| | |
|---|---|
| normality | OK |
| n | 16 |
| outliers | 0 |
| mean (n) | 131.93 |
| st.dev. (n) | 7.494 |
| R(calc.) | 20.98 |
| R(Horwitz) | 28.34 |
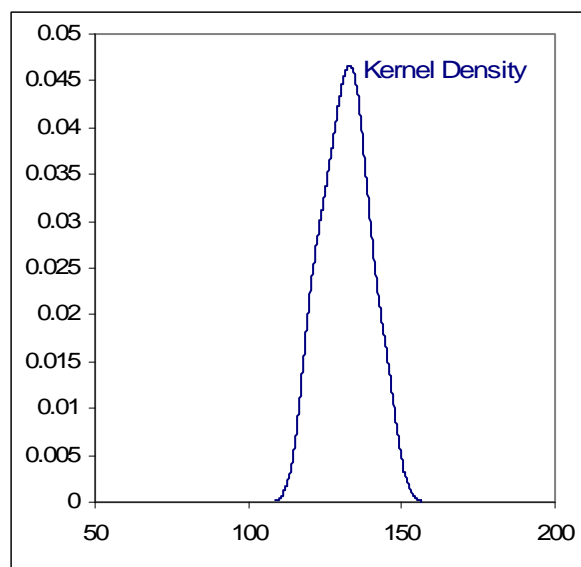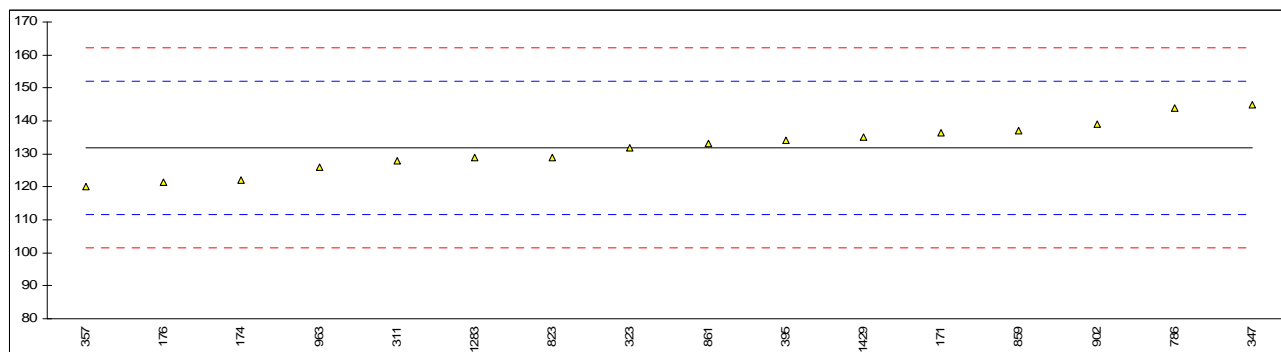
Determination of Methyl Acetate on sample #1016; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|-----|--------|-------|------|---------|---------|
| 171 | D3545 | <10 | | ----- | |
| 174 | D3545 | <1 | | ----- | |
| 176 | | ----- | | ----- | |
| 311 | INH-122 | 3 | | ----- | |
| 315 | | ----- | | ----- | |
| 323 | INH-067 | <10 | | ----- | |
| 347 | INH-916 | <10 | | ----- | |
| 357 | INH052 | <10 | | ----- | |
| 395 | | ----- | | ----- | |
| 522 | | ----- | | ----- | |
| 562 | | ----- | | ----- | |
| 613 | | ----- | | ----- | |
| 786 | | ----- | | ----- | |
| 823 | inh-278 | 2 | | ----- | |
| 859 | inh-065 | 2.0 | | ----- | |
| 861 | | ----- | | ----- | |
| 902 | INH-22 | <10 | | ----- | |
| 913 | | ----- | | ----- | |
| 963 | INH-8124 | <10 | | ----- | |
| 1283 | INH-020 | 6 | | ----- | |
| 1429 | Client method | 2 | | ----- | |

| | |
|---|---|
| normality | unknown |
| n | 5 |
| outliers | 0 |
| mean (n) | 3.00 |
| st.dev. (n) | 1.732 |
| R(calc.) | 4.85 |
| R(lit) | unknown |
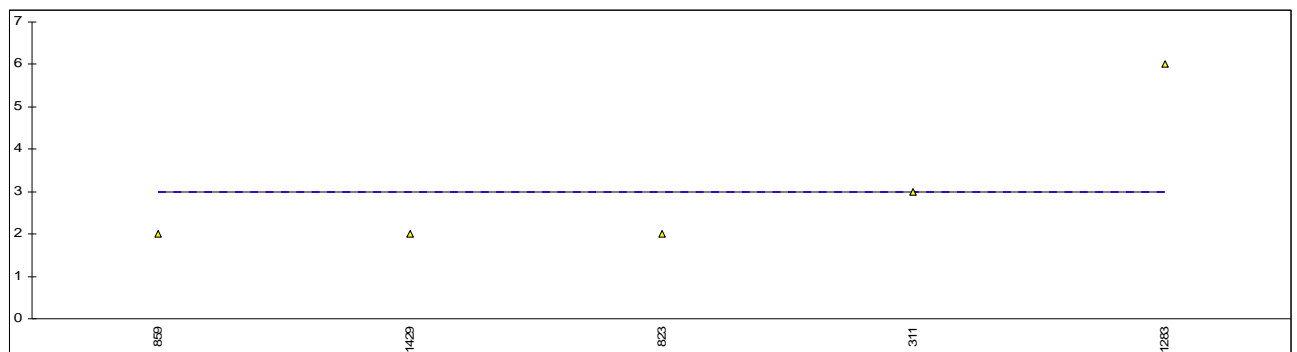
**APPENDIX 2**

**List of participants**

    1 laboratory in  AUSTRALIA

    1 laboratory in  BELGIUM

    1 laboratory in  CHILE

    1 laboratory in  FINLAND

  2 laboratories in  INDIA

    1 laboratory in  ITALY

    1 laboratory in  KOREA

    1 laboratory in  MEXICO

  2 laboratories in  P.R. of CHINA

    1 laboratory in  RUSSIA

    1 laboratory in  SAUDI ARABIA

    1 laboratory in  SPAIN

  2 laboratories in  THE NETHERLANDS

    1 laboratory in  TURKEY

  3 laboratories in  U.S.A.

    1 laboratory 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 |
| E | = error in calculations |
| ex | = excluded from calculations |
| n.a. | = not applicable |
| wd | = withdrawn method |

**Literature**:

1       i.i.s. Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, January 2010

2       ASTM E178:89

3       ASTM E1301:89

4       ISO 5725:86

5       ISO 5725, parts 1-6, 1994

6       ISO13528-05

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, Fr. 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 page 1359-1364, P.J. Lowthian and M. Thompson (see http://www.rsc.org/suppdata/an/b2/b205600n/)