Results of Proficiency Test Vinyl Acetate Monomer February 2015

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 2014/2015, it was decided to continue the round robin for the analysis of Vinyl Acetate Monomer. In this interlaboratory study 24 laboratories in 19 different countries have participated. See appendix 2 for the number of participants per country.
In this report, the results of the 2015 VAM proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test. It was decided to send one sample of VAM (0.5 litre bottle, labelled #15004) to the participants. Analyses for fit-for-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/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on a 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 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). The protocol can be downloaded from iis website http://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

The necessary amount of bulk material of Vinyl Acetate Monomer was obtained from a local supplier. The batch was spiked with Acetone (18.5 mg/kg) and Methyl Acetate (20.0 mg/kg). After homogenisation, 25 litre of the Vinyl Acetate Monomer was divided over 50 brown glass bottles of 500 mL and labelled #15004.

The homogeneity of the subsamples #15004 was checked by determination of density in accordance with ASTM D4052 and water in accordance with ASTM D1364 on 8 stratified randomly selected samples.

	Density @20°C in kg/L	Water in mg/kg
sample #15004-1	0.93215	70
sample #15004-2	0.93215	70
sample #15004-3	0.93215	80
sample #15004-4	0.93215	80
sample #15004-5	0.93214	70
sample #15004-6	0.93214	70
sample #15004-7	0.93214	80
sample #15004-8	0.93214	80

table 1: homogeneity test results of subsamples #15004

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities of the target methods in agreement with the procedure of ISO 13528, Annex B2 in table 2.

	Density @20°C in kg/L	Water in mg/kg
r (sample #15004)	0.00000	15.0
reference test	D4052:02e1	ASTM D1364:02(2012)
0.3*R (reference test)	0.00015	15.6

table 2: repeatabilities of subsamples #15004

The calculated repeatabilities for density and water are in agreement with 0.3 times the corresponding reproducibility of the target method. Therefore, homogeneity of the samples was assumed.

To each of the participating laboratories 1 bottle of 500 mL Vinyl Acetate Monomer, labelled #15004, was sent on January 21, 2015.

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 requested to determine according to the standard specification for VAM (ASTM D2190:07(2013)): Acetaldehyde, Acidity, Apparent Specific Gravity 20/20°C, Distillation (IBP, 50% recovery, Dry Point, Boiling Range), Inhibitor and Water, plus additionally Acidity with N_2 purging, Acetone, Color Pt-Co, Density at $20^{\circ}C$, Ethyl Acetate, Methyl Acetate and Purity.
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 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

The protocol followed in the organisation of this proficiency test is 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.

According to ISO 5725 the original results per determination were submitted to Dixon's and/or Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test (ref. 15). Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. 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 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 on 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; 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.

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 whether the reported test result is fit-for-use.

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, some problems were encountered with despatch of the samples. Participants in Brazil received the samples late. Of the 24 participants, no participants reported results after the final reporting date, while 4 participants did not report at all.

Not all participants were able to report results for all the requested tests. Finally, 20 participants reported in total 253 numerical results. Observed were 2 outlying test results, which is 0.8% of the total of numerical test 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, a suitable standard test method, providing the precision data, is not available for all determinations. For the tests, that have no available precision data, the spreads were compared against the spreads estimated from the Horwitz equation.
In the iis PT reports, ASTM methods are referred to with a number (e.g. D2086) and an added designation for the year that the method was adopted or revised (e.g. D2086-08). If applicable, a designation in parentheses is added to designate the year of reapproval (e.g. D2086-08 (2013)). In the results tables of Appendix 1 only the method number and year of adoption or revision will be used.

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, see also paragraph 3.1.

Acidity: This determination (with and without Nitrogen purging) was problematic. As can be expected, the acidity value determined with Nitrogen purging was somewhat lower, but not significantly. No statistical outliers were observed. Both calculated reproducibilities are not in agreement with the requirements of ASTM D2086:08(2012). Please note that the reproducibility of ASTM D2086:08(2012) was determined with only two laboratories (see note 5 in §13.2.2 of ASTM D2086:08(2012)). When compared to the spread found in the previous PT (iis14C01), the reproducibility value has not improved for both tests.

Apparent Specific Gravity 20/20°C: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the requirements of ASTM D4052:02e1.

Color Pt/Co: The determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the requirements of ASTM D1209:05(2012).

Density @ 20°C: This determination was 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 was not problematic. No statistical outliers were observed. The calculated reproducibilities are all in good agreement with the requirements of ASTM D1078:11 (Automated method).

Inhibitor: This determination was problematic. No statistical outliers were
(Hydroquinone)   observed. However the calculated reproducibility is not in agreement with the requirements of ASTM D2193:06(2012).

Purity: Regretfully, no reference method with precision data exists for this determination. One statistical outlier was observed. When compared to the spread found in the previous PT (iis14C01), the reproducibility value has improved.

Acetaldehyde: The determination of this impurity may be problematic. No statistical outliers were observed. However the reproducibility is not in agreement with the requirements estimated from the Horwitz equation.

Acetone: The determination of this impurity may be problematic. No outliers were observed. However, four laboratories reported a result of <10, which is not used for evaluation, but appear to be false negative test results. The reproducibility was not in agreement with the requirements estimated from the Horwitz equation.

The average recovery of Acetone (theoretical spike of 18.5 mg/kg) may just be satisfactory: "less than 80%". The actual concentration of Acetone before spiking is unknown.

Ethyl Acetate: The determination of this impurity may be problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the requirements estimated from the Horwitz equation.

Methyl Acetate: The determination of this impurity may be problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the requirements estimated from the Horwitz equation. The average recovery of Methyl Acetate (theoretical spike of 20.0 mg/kg) may be satisfactory: "less than 152%". The actual concentration of Methyl Acetate before spiking is unknown.

Water: This determination was not problematic. One statistical outliers was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of ASTM D1364:02(2012).

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 assigned values, calculated reproducibilities and reproducibilities, derived from literature standards (in casu ASTM, ISO, EN standards) are compared in the next table.

Parameter	unit	n	Mean	2.8 * sd	R (lit)
Acidity (without N_2 purging)	mg/kg	16	19.9	13.0	6.0
Acidity (with N_2 purging)	mg/kg	6	15.4	13.2	6.0
Apparent Specific Gravity 20/20°C		16	0.9339	0.0002	0.0005
Color Pt/Co		14	3	4	7
Density @ 20°C	kg/L	20	0.9322	0.0002	0.0005
Distillation, Initial Boiling Point	ºC	17	72.5	0.2	1.1
Distillation, 50% recovery	ºC	17	72.7	0.1	0.5
Distillation, Dry Point	ºC	17	72.8	0.2	0.8
Distillation, Boiling Range	ºC	17	0.3	0.3	0.7
Inhibitor	mg/kg	18	4.1	1.3	1.0
Purity	%M/M	16	99.978	0.013	unknown
Acetaldehyde	mg/kg	15	38.3	13.8	9.9
Acetone	mg/kg	11	14.7	8.3	4.4
Ethylacetate	mg/kg	17	114.0	30.5	25.0
Methyl Acetate	mg/kg	16	30.4	12.7	8.2
Water	mg/kg	18	66.4	32.6	48.9

table 3: performance evaluation sample #15004

4.3   EVALUATION OF THE PROFICIENCY TEST OF FEBRUARY 2015 WITH PREVIOUS PTS

	February 2015	February 2014	February 2013	February 2012
Number of rep. participants	20	23	24	24
Number of results reported	253	240	243	257
Number of statistical outliers	2	9	9	8
Percentage outliers	0.8%	3.8%	3.7%	3.1%

table 4: evaluation with previous proficiency tests.

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:

	February 2015	February 2014	February 2013	February 2012
Acidity (no purging)	--	-	--	--
Acidity (with purging)	--	-	--	+/-
Apparent Spec.Gravity	++	n.e.	n.e.	n.e.
Color Pt/Co	+	n.e.	n.e.	n.e.
Density @ 20°C	++	++	++	++
Distillation	++	++	++	++
Inhibitor	-	-	-	--
Purity	n.e.	n.e.	n.e.	n.e.
Acetaldehyde	-	++	++	++
Acetone	-	n.e.	n.e.	n.e.
Ethyl Acetate	-	++	+/-	+/-
Methyl Acetate	-	-	-	++
Water	+	+/-	+/-	-

table 5: comparison determinations against the reference standards

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

APPENDIX 1

Determination of Acidity (without N_2 purging) on sample #15004; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	INH-44	21		0.50	
174	D2086	22		0.96	
311	D2086	17	C	-1.37	First reported: 0.0017
315		-----		-----	
323	D2086	31		5.16	
337		-----		-----	
347	D2086	19		-0.44	
395	INH-44	21		0.50	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	D2086	16.5		-1.60	
663	D2086	24		1.90	
786		-----		-----	
823	D2086	19		-0.44	
859	D2086	12		-3.70	
861	D2086	12.8		-3.33	
902	D2086	17		-1.37	
913	D2086	22.25		1.08	
963	D2086	24.9		2.32	
974	D2086	18.5		-0.67	
1429	D1613	21	C	0.50	First reported: 0.0021
7006		-----		-----	

|		
normality	suspect	
n	16	
outliers	0	
mean (n)	19.93	
st.dev. (n)	4.643	
R(calc.)	13.00	
R(D2086:08)	6.00	Compare R(iis14C01) = 10.98
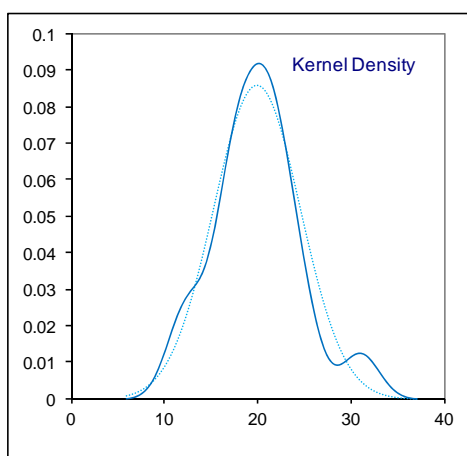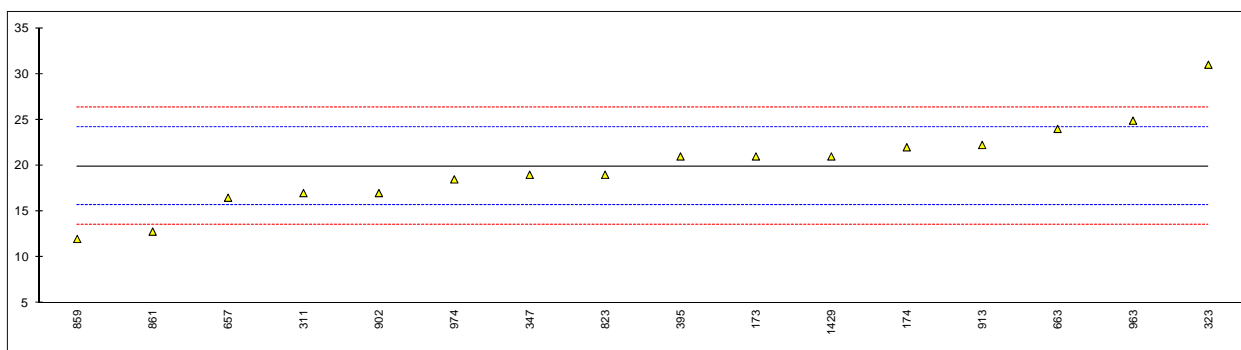
Determination of Acidity (with N$_2$ purging) on sample #15004; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173		-----		-----	
174		-----		-----	
311		-----		-----	
315		-----		-----	
323		-----		-----	
337		-----		-----	
347		-----		-----	
395		-----		-----	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	D2086	14.9		-0.24	
663		-----		-----	
786		-----		-----	
823		-----		-----	
859	D2086	10		-2.53	
861	D2086	10.2		-2.44	
902		-----		-----	
913	D2086	21.72		2.94	
963		-----		-----	
974	D2086	16.7		0.60	
1429	D1613	19	C	1.67	First reported: 0.0019
7006		-----		-----	

normality	unknown	
n	6	
outliers	0	
mean (n)	15.42	
st.dev. (n)	4.713	
R(calc.)	13.20	
R(D2086:08)	6.00	Compare R(iis14C01) = 11.09
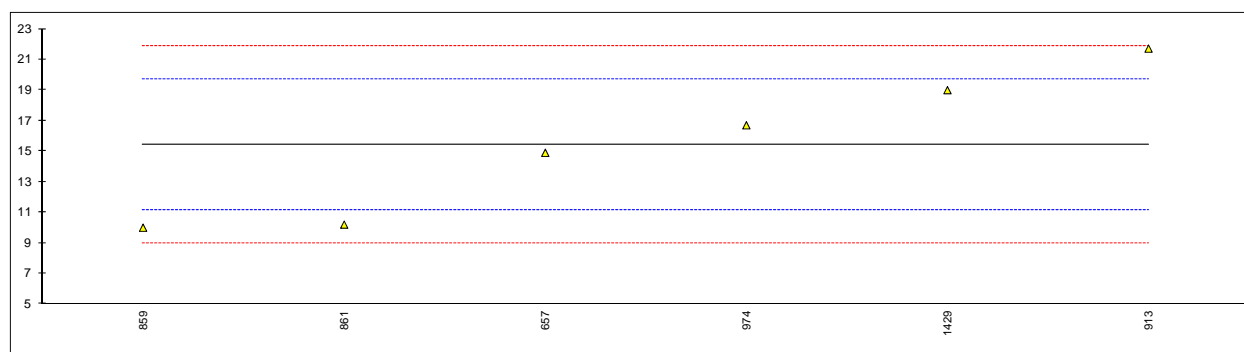
Determination of App. Specific Gravity 20/20 °C on sample #15004;

lab	method	value	mark	z(targ)	remarks
171	D4052	0.9339		0.27	
173	D4052	0.93389		0.22	
174	D4052	0.9339		0.27	
311	D4052	0.9339		0.27	
315		-----		-----	
323	D4052	0.9337		-0.85	
337		-----		-----	
347	D4052	0.9338		-0.29	
395	D4052	0.9338		-0.29	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	D4052	0.93374		-0.62	
663		-----		-----	
786		-----		-----	
823	D4052	0.93391		0.33	
859	D4052	0.9339		0.27	
861	D4052	0.93378		-0.40	
902	D4052	0.9339		0.27	
913	D4052	0.9339		0.27	
963	D4052	0.9339		0.27	
974	D4052	0.9338		-0.29	
1429	D4052	0.9339		0.27	
7006		-----		-----	

normality	OK
n	16
outliers	0
mean (n)	0.93385
st.dev. (n)	0.000069
R(calc.)	0.00019
R(D4052:02e1)	0.00050

Kernel Density
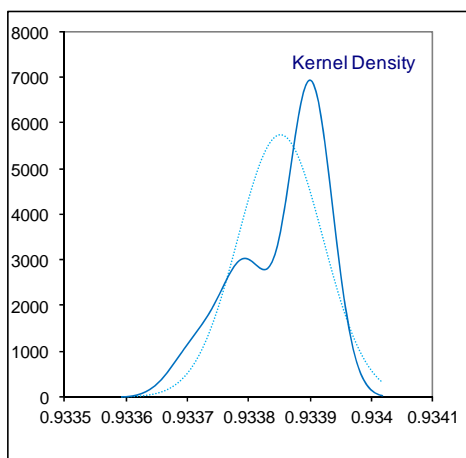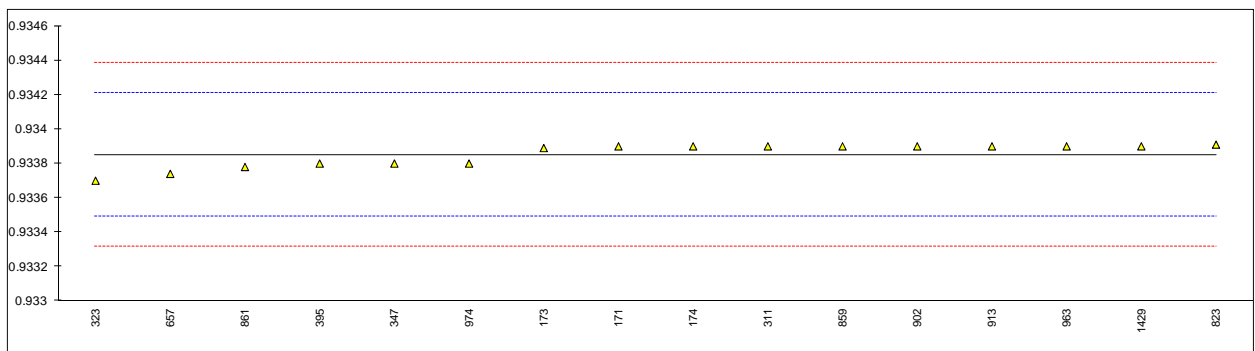
Determination of Color Pt-Co on sample #15004;

lab	method	value	mark	z(targ)	remarks
171	D5386	3		-0.11	
173	INH-46	<5		-----	
174	D1209	3		-0.11	
311	D1209	<5		-----	
315	D1209	5		0.69	
323	D1209	<5		-----	
337		-----		-----	
347	D5386	2		-0.51	
395	D1209	<5		-----	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	D1209	5		0.69	
663	D1209	4		0.29	
786	D1209	4		0.29	
823	D5386	4		0.29	
859	D1209	4		0.29	
861	D1209	3		-0.11	
902	D5386	2		-0.51	
913	D5386	4		0.29	
963	D1209	3		-0.11	
974	D5386	0		-1.31	
1429	D1209	<5		-----	
7006		-----		-----	

normality	suspect
n	14
outliers	0
mean (n)	3.3
st.dev. (n)	1.33
R(calc.)	3.7
R(D1209:05)	7.0

Kernel Density
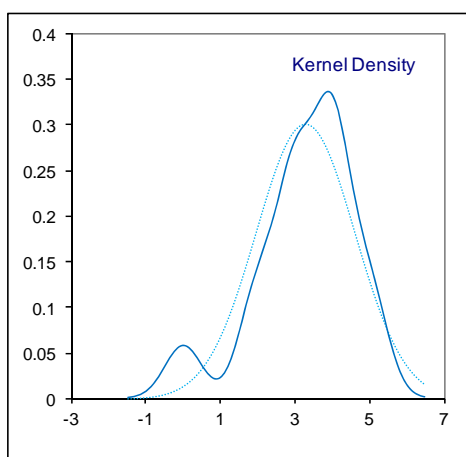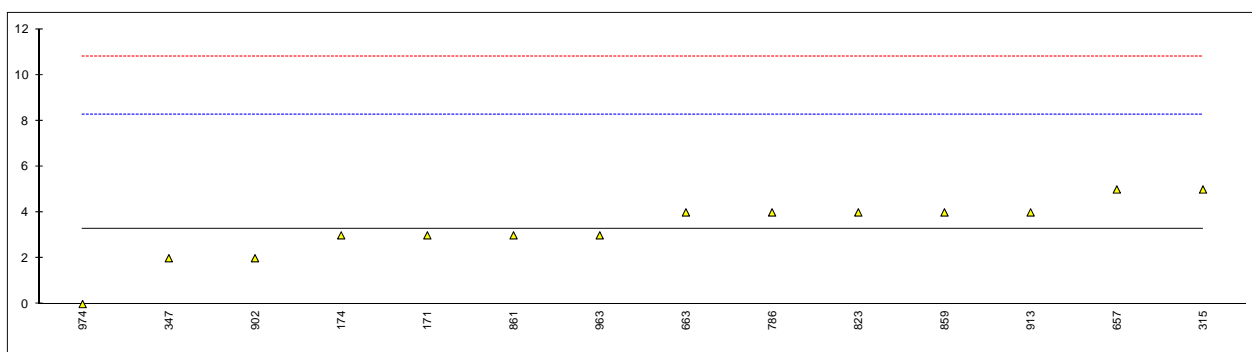
Determination of Density at 20 ^{o}C on sample #15004; results in kg/L

lab	method	value	mark	z(targ)	remarks
171	D4052	0.9322		0.11	
173	D4052	0.93221		0.17	
174	D4052	0.9323		0.67	
311	D4052	0.9322		0.11	
315	D4052	0.9322		0.11	
323	D4052	0.9322	C	0.11	First reported: 0.9922
337	D4052	0.9322		0.11	Reported: 932.2 kg/m^3
347	D4052	0.9321		-0.45	
395	D4052	0.9321		-0.45	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	D4052	0.93215		-0.17	
663	D4052	0.9321		-0.45	Reported: 932.1 kg/m^3
786	D4052	0.9320		-1.01	
823	D4052	0.93224		0.33	
859	D4052	0.9322		0.11	
861	D4052	0.93220		0.11	
902	D4052	0.9322		0.11	
913	D4052	0.9322		0.11	
963	D4052	0.9322		0.11	
974	D4052	0.9322		0.11	
1429	D4052	0.9322		0.11	
7006		-----		-----	

normality	not OK
n	20
outliers	0
mean (n)	0.93218
st.dev. (n)	0.000063
R(calc.)	0.00018
R(D4052:02e1)	0.00050
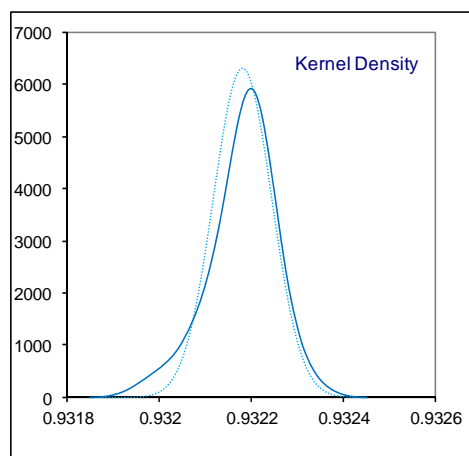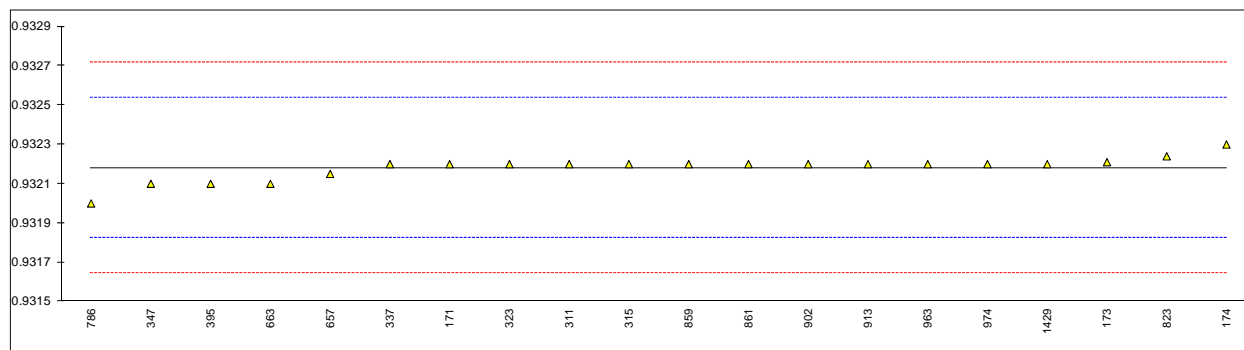
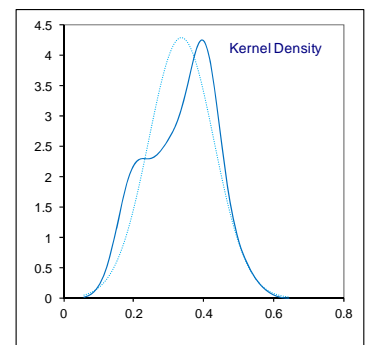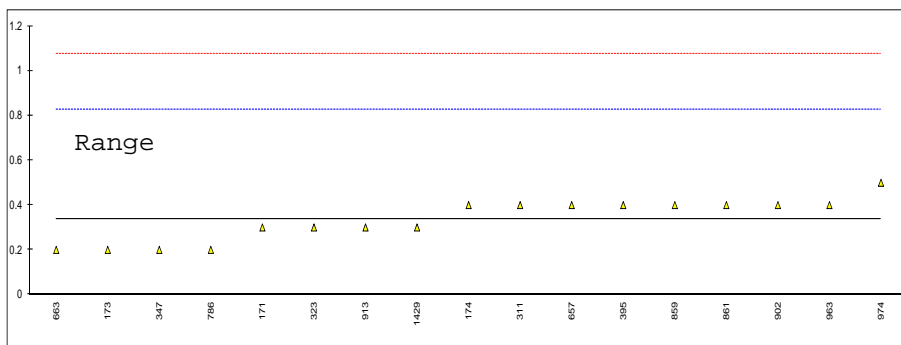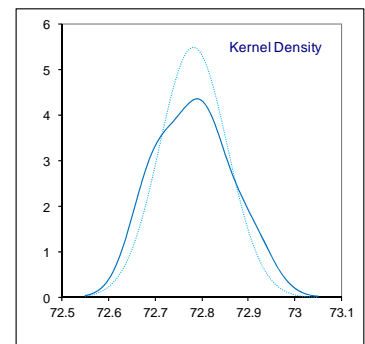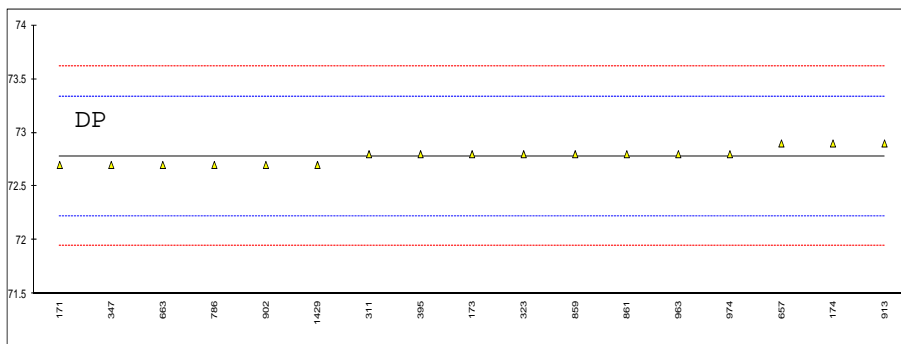Determination of Distillation on sample #15004; results in ºC

lab	method	IBP	mark	50% rec.	mark	DP	mark	range	mark
171	D1078	72.4	C	72.7	C	72.7	C	0.3	
173	D1078	72.6		72.7		72.8		0.2	
174	D1078	72.5		72.7		72.9		0.4	
311	D1078	72.4		72.7		72.8		0.4	
315		-----		-----		-----		-----	
323	D1078	72.5		72.7		72.8		0.3	
337		-----		-----		-----		-----	
347	D1078	72.5		72.7		72.7		0.2	
395	D1078	72.4		72.7		72.8		0.4	
522		-----		-----		-----		-----	
551		-----		-----		-----		-----	
557		-----		-----		-----		-----	
657	D1078	72.5		72.7		72.9		0.4	
663	D1078	72.5		72.7		72.7		0.2	
786	D1078	72.5		72.7		72.7		0.2	
823		-----		-----		-----		-----	
859	D1078	72.4		72.7		72.8		0.4	
861	D1078	72.4		72.7		72.8		0.4	
902	D1078	72.3		72.5		72.7		0.4	
913	D1078	72.6		72.7		72.9		0.3	
963	D1078	72.4		72.7		72.8		0.4	
974	D1078	72.3		72.7		72.8		0.5	
1429	D1078	72.4		72.7		72.7		0.3	
7006		-----		-----		-----		-----	
	normality	OK		not OK		OK		OK	
	n	17		17		17		17	
	outliers	0		0		0		0	
	mean (n)	72.45		72.69		72.78		0.34	
	st.dev. (n)	0.087		0.049		0.073		0.093	
	R(calc.)	0.24		0.14		0.20		0.26	
	R(D1078:11)	1.13		0.50		0.78		0.69	

Lab 171 first reported for IBP: 73.0, for 50% recovered: 73.3 and for DP: 73.3

z-scores of Distillation on sample #15004

lab	IBP	50% rec.	DP	range
171	-0.12	0.07	-0.30	-0.14
173	0.38	0.07	0.06	-0.55
174	0.13	0.07	0.42	0.26
311	-0.12	0.07	0.06	0.26
315	-----	-----	-----	-----
323	0.13	0.07	0.06	-0.14
337	-----	-----	-----	-----
347	0.13	0.07	-0.30	-0.55
395	-0.12	0.07	0.06	0.26
522	-----	-----	-----	-----
551	-----	-----	-----	-----
557	-----	-----	-----	-----
657	0.13	0.07	0.42	0.26
663	0.13	0.07	-0.30	-0.55
786	0.13	0.07	-0.30	-0.55
823	-----	-----	-----	-----
859	-0.12	0.07	0.06	0.26
861	-0.12	0.07	0.06	0.26
902	-0.36	-1.06	-0.30	0.26
913	0.38	0.07	0.42	-0.14
963	-0.12	0.07	0.06	0.26
974	-0.36	0.07	0.06	0.67
1429	-0.12	0.07	-0.30	-0.14
7006	-----	-----	-----	-----
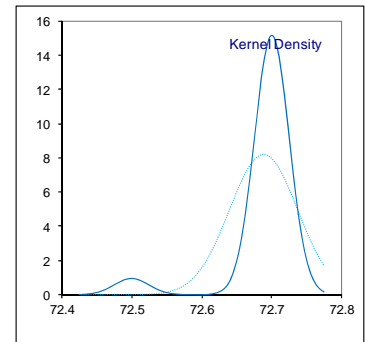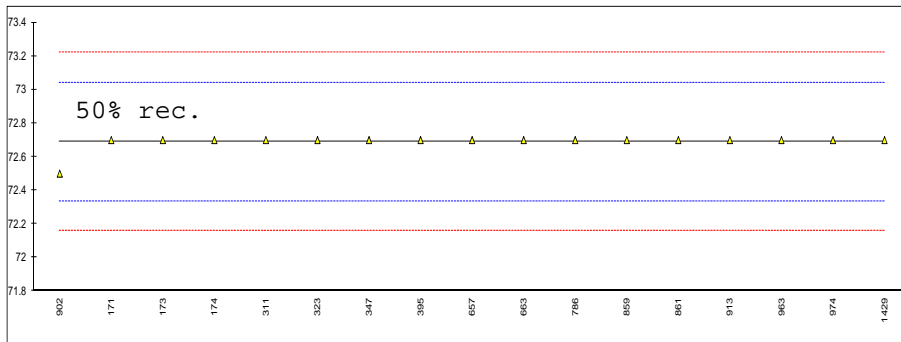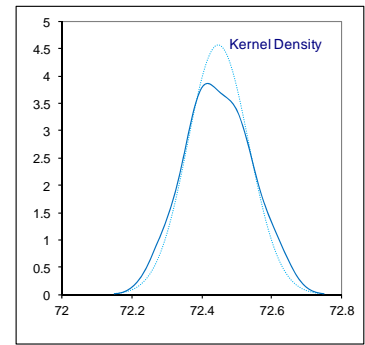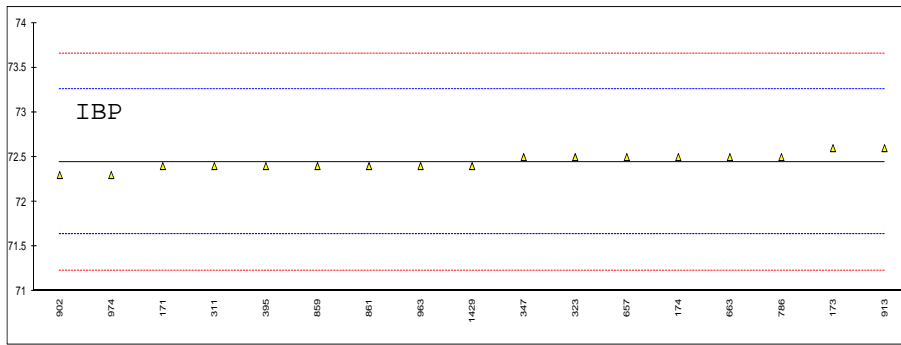
Determination of Inhibitor on sample #15004; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	in house	4.9		2.24	
173	INH-43	5.1		2.80	
174	D2193	3.5		-1.68	
311	D2193	3.7	C	-1.12	First reported: 5.7
315		-----		-----	
323	D2193	3.9		-0.56	
337		-----		-----	
347	D2193	3.6		-1.40	
395	INH-43	4.2		0.28	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	D2193	4.3		0.56	
663	D2193	3.67		-1.20	
786	D2193	4.3		0.56	
823	D2193	3.9		-0.56	
859	D2193	4.4		0.84	
861	D2193	4.64		1.51	
902	D2193	4.3		0.56	
913	D2193	3.6		-1.40	
963	D2193	4.0		-0.28	
974	D2193	3.51		-1.65	
1429	D2193	4.27		0.48	
7006		-----		-----	

normality	OK
n	18
outliers	0
mean (n)	4.10
st.dev. (n)	0.474
R(calc.)	1.33
R(D2193:06)	1.00
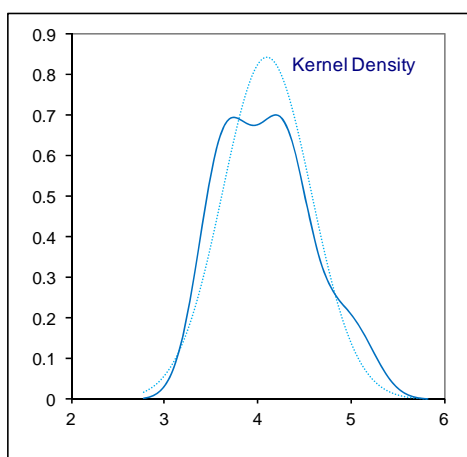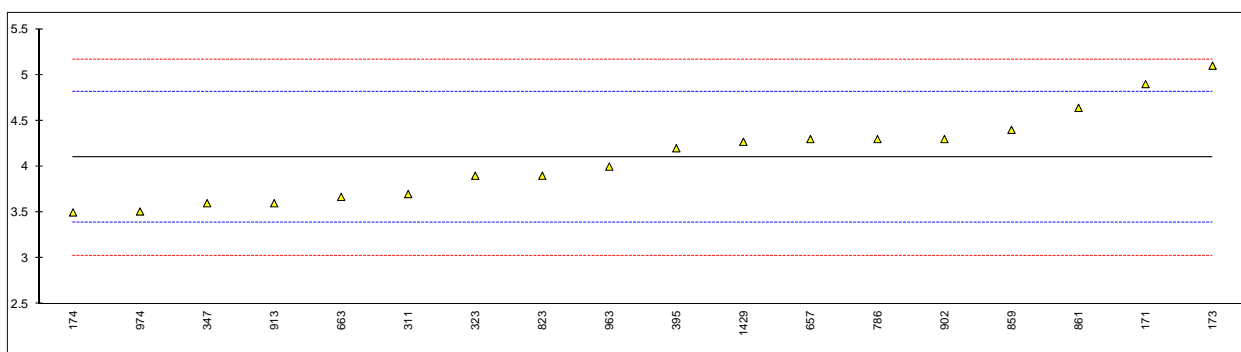
Determination of Purity on sample #15004; results in % M/M

lab	method	value	mark	z(targ)	remarks
171	in house	99.979		-----	
173	INH-257	99.9806		-----	
174	D3545	99.98		-----	
311	INH-122	99.98		-----	
315		-----		-----	
323	INH-067	99.97		-----	
337		-----		-----	
347	INH-096	99.98		-----	
395	INH-257	99.97		-----	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	INH-047	99.9732		-----	
663	INH-292	99.94	G(0.01)	-----	
786	INH-004	99.98		-----	
823	D3545	99.9697		-----	
859	SH/T1628.2	99.98		-----	
861	SH/T1628.2	99.982		-----	
902	INH-22	99.98		-----	
913	INH-12345	99.982		-----	
963	INH-009	99.979		-----	
974		-----		-----	
1429	in house	99.983		-----	
7006		-----		-----	

normality	OK	
n	16	
outliers	1	
mean (n)	99.9780	
st.dev. (n)	0.00454	
R(calc.)	0.0127	
R(lit.)	Unknown	Compare R(iis14C01) = 0.0196
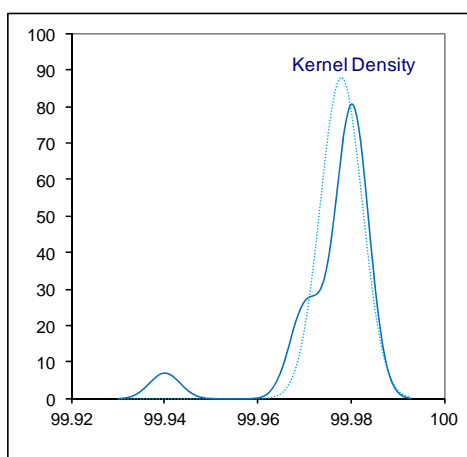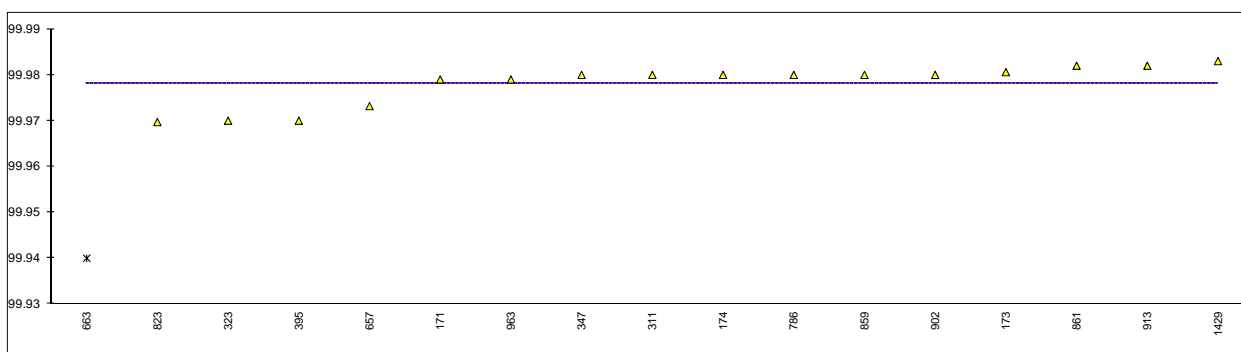
Determination of Acetaldehyde on sample #15004; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	in house	47.060		2.46	
173	INH-257	39.47		0.32	
174	D3545	39		0.18	
311	INH-122	30		-2.35	
315		-----		-----	
323	INH-067	40		0.47	
337		-----		-----	
347	INH-096	38		-0.10	
395	INH-257	33.34		-1.41	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657		-----		-----	
663	INH-292	40.2		0.52	
786	INH-004	32		-1.79	
823	D3545	42		1.03	
859	SH/T1628.2	37		-0.38	
861	SH/T1628.2	32		-1.79	
902	INH-22	38		-0.10	
913		-----		-----	
963	INH-009	41.1		0.78	
974		-----		-----	
1429	in house	46		2.16	
7006		-----		-----	

normality	OK
n	15
outliers	0
mean (n)	38.34
st.dev. (n)	4.933
R(calc.)	13.81
R(Horwitz)	9.92
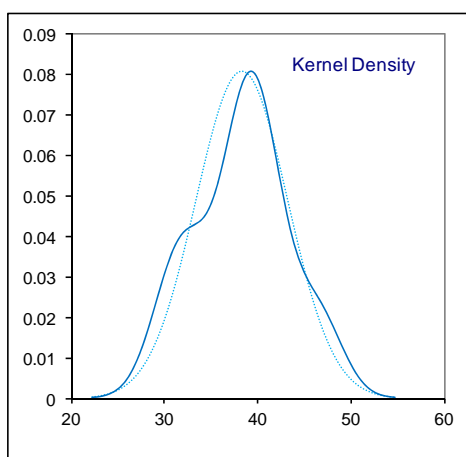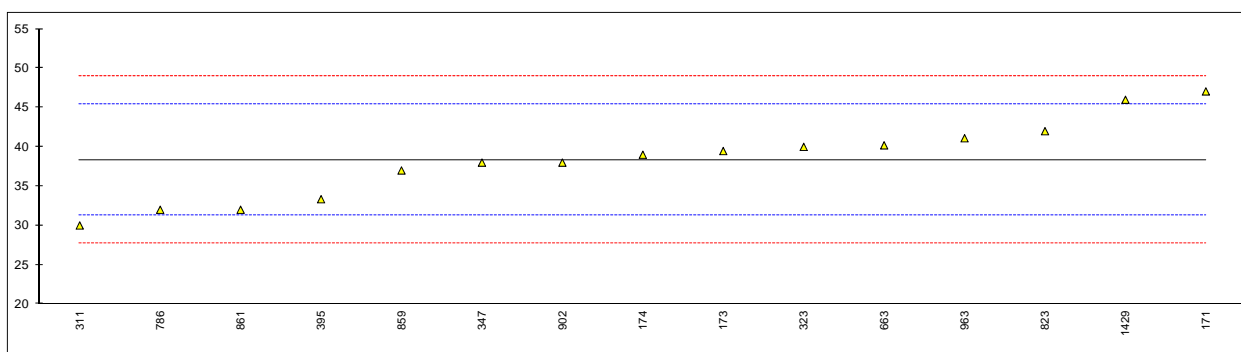
Determination of Acetone on sample #15004, results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	in house	12.8899		-1.18	
173	INH-257	12.8	C	-1.24	First reported: 2.8
174	D3545	<10		<-3.01	False negative?
311	INH-122	20		3.34	
315		-----		-----	
323	INH-067	12		-1.74	
337		-----		-----	
347	INH-096	<10		<-3.01	False negative?
395		-----		-----	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	INH-047	15		0.16	
663	INH-292	12.5		-1.43	
786	INH-004	11		-2.38	
823	D3545	16		0.80	
859	SH/T1628.2	14		-0.47	
861	SH/T1628.2	19		2.70	
902	INH-22	17		1.43	
913	INH-12345	<10		<-3.01	False negative?
963		-----		-----	
974		-----		-----	
1429	in house	<10		<-3.01	False negative?
7006		-----		-----	

normality	OK			
n	11			
outliers	0	Spike		
mean (n)	14.74	18.5		Recovery: <80%
st.dev. (n)	2.947			
R(calc.)	8.25			
R(Horwitz)	4.41			
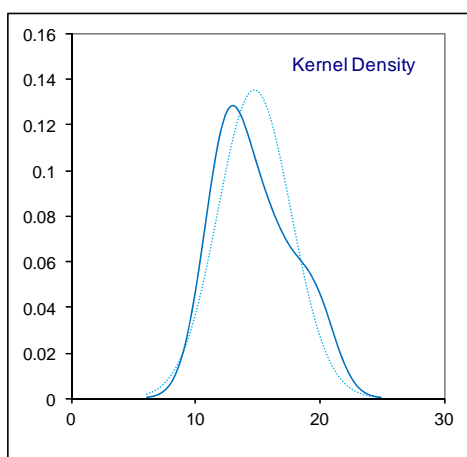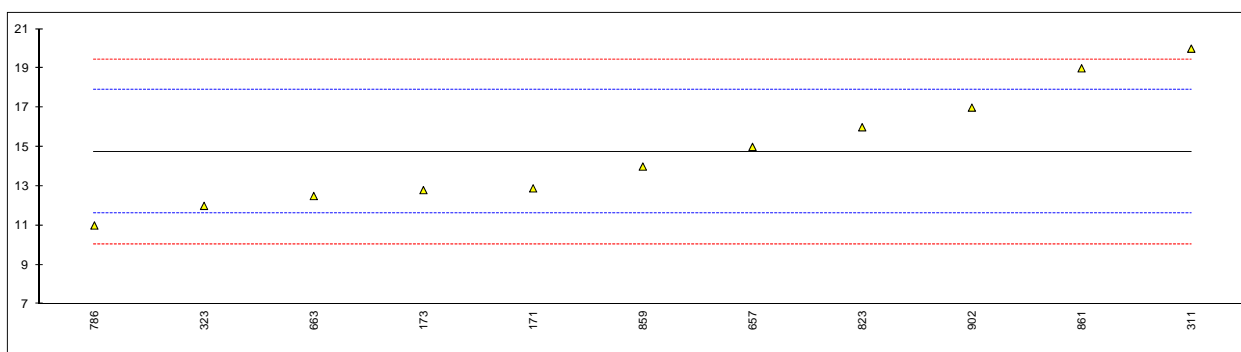
Determination of Ethyl Acetate on sample #15004, results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	in house	115.50		0.17	
173	INH-257	118.1		0.46	
174	D3545	120		0.67	
311	INH-122	130		1.79	
315		-----		-----	
323	INH-067	106		-0.89	
337		-----		-----	
347	INH-096	93		-2.35	
395	INH-257	112.23		-0.20	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	INH-047	120		0.67	
663	INH-292	109.9		-0.46	
786	INH-004	101		-1.45	
823	D3545	124		1.12	
859	SH/T1628.2	122		0.90	
861	SH/T1628.2	102		-1.34	
902	INH-22	118		0.45	
913	INH-12345	128		1.57	
963	INH-009	120.9		0.77	
974		-----		-----	
1429	in house	97		-1.90	
7006		-----		-----	

normality	OK
n	17
outliers	0
mean (n)	113.98
st.dev. (n)	10.890
R(calc.)	30.49
R(Horwitz)	25.03

Kernel Density
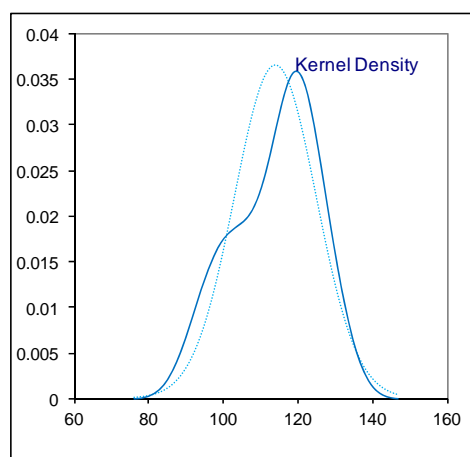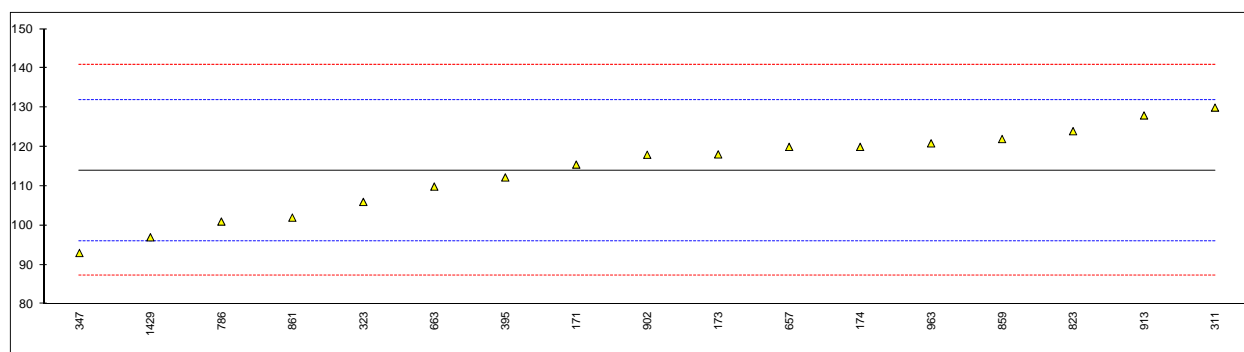
Determination of Methyl Acetate on sample #15004; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	in house	32.86		0.84	
173	INH-257	33.9		1.20	
174	D3545	33		0.89	
311	INH-122	30		-0.14	
315		-----		-----	
323	INH-067	26		-1.52	
337		-----		-----	
347	INH-096	21		-3.24	
395	INH-257	36.3		2.02	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	INH-047	35		1.57	
663	INH-292	30.3		-0.04	
786	INH-004	28		-0.83	
823	D3545	33		0.89	
859	SH/T1628.2	32		0.54	
861	SH/T1628.2	25		-1.86	
902	INH-22	34		1.23	
913		-----		-----	
963	INH-009	33.3		0.99	
974		-----		-----	
1429	in house	23		-2.55	
7006		-----		-----	

normality	OK		
n	16		
outliers	0	Spike	
mean (n)	30.42	20.0	Recovery: <152%
st.dev. (n)	4.541		
R(calc.)	12.71		
R(Horwitz)	8.15		
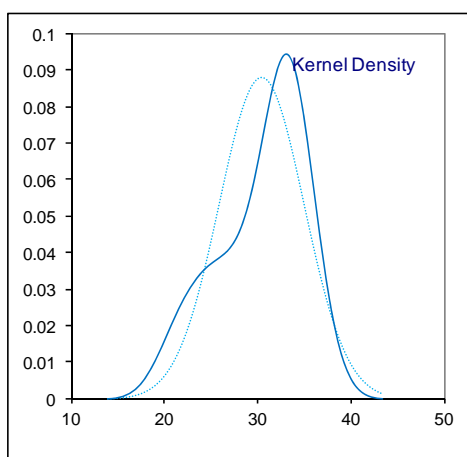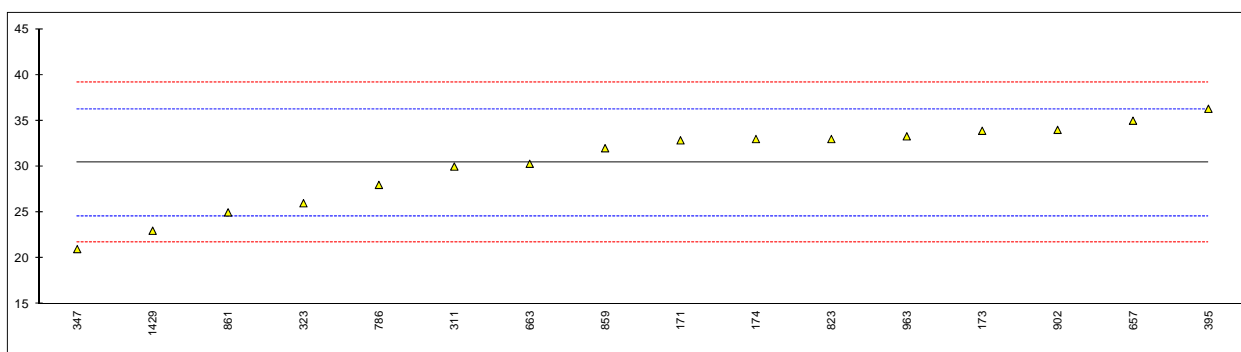
Determination of Water on sample #15004; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171	E203	82		0.89	
173	D1364	61		-0.31	
174	D1364	81		0.83	
311	D1364	60		-0.37	
315	D1364	60		-0.37	
323	D1364	82	C	0.89	First reported: 117
337		-----		-----	
347	D1364	62		-0.25	
395	D1364	40		-1.51	
522		-----		-----	
551		-----		-----	
557		-----		-----	
657	E1064	68.35		0.11	
663	E203	66		-0.02	
786	D1364	66		-0.02	
823	D1364	69		0.15	
859	D1364	72		0.32	
861	E1064	59		-0.43	
902	D1364	63		-0.20	
913	D1364	110	G(0.05)	2.50	
963	D1364	60		-0.37	
974	D1364	89		1.29	
1429	D1364	55.3		-0.64	
7006		-----		-----	

normality	OK
n	18
outliers	1
mean (n)	66.42
st.dev. (n)	11.659
R(calc.)	32.64
R(D1364:02)	48.90

Kernel Density
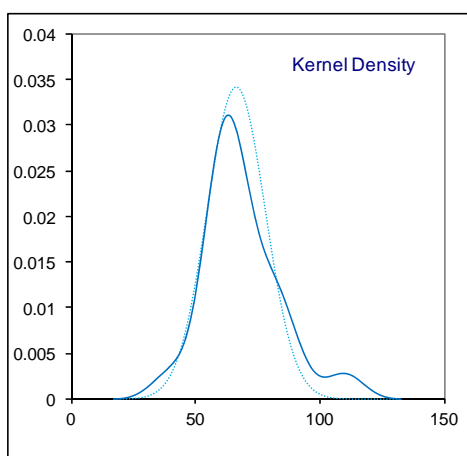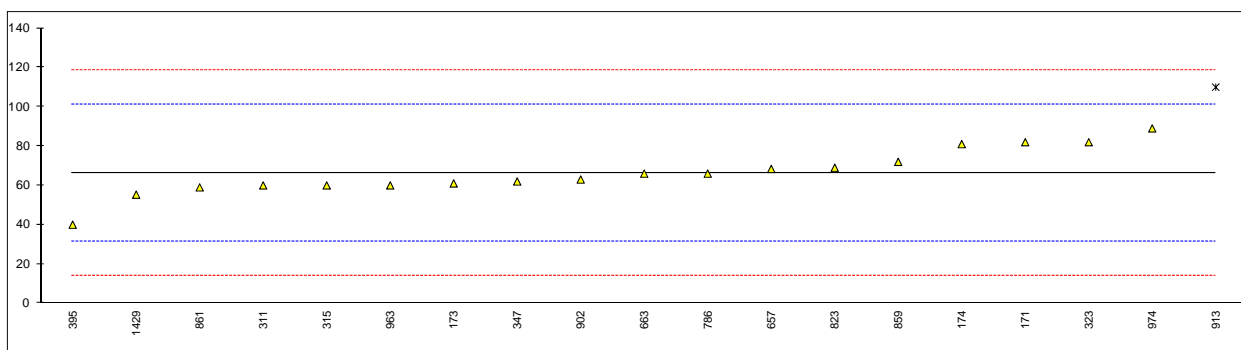
APPENDIX 2

Number of participants per country

1 lab in BELGIUM
2 labs in BRAZIL
2 labs in CHINA, People's Republic
1 lab in FRANCE
1 lab in INDIA
1 lab in IRAN, Islamic Republic of
1 lab in ITALY
1 lab in MEXICO
2 labs in NETHERLANDS
1 lab in RUSSIAN FEDERATION
1 lab in SAUDI ARABIA
1 lab in SINGAPORE
1 lab in SOUTH KOREA
1 lab in SPAIN
1 lab in THAILAND
1 lab in TURKEY
1 lab in UNITED ARAB EMIRATES
1 lab in UNITED KINGDOM
3 labs in UNITED STATES OF AMERICA

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
R(0.01)	= outlier in Rosner outlier test
R(0.05)	= straggler in Rosner outlier test
E	= error in calculations
ex	= excluded from calculations
n.e.	= not evaluated
wd	= withdrawn method

Literature:

1	i.i.s. Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
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/)
15	Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), pp. 165-172, (1983)