

Results of Proficiency Test
Acetic Acid
March 2010

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since 2003, the Institute for Interlaboratory Studies organizes a proficiency test for Acetic Acid. During the annual proficiency test program of 2009/2010, it was decided to continue the round robin for the analysis of Acetic Acid. In this international interlaboratory study 26 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 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) spiked with Iron (III) Chloride and Sodium Sulphate. 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 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO guide 43 and ILAC-G13:2007, (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). 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 Acetic Acid was obtained from a chemical producer. The approximately 25 litres of Acetic Acid was spiked with 281.1 mg Iron(III)Chloride.6H₂O and 195.7 mg Sodium Sulphate. After homogenisation, this material was divided over 50 brown glass bottles of 0.5 L and labelled #1015.

The homogeneity of the subsamples #1015 was checked by determination of Iron in accordance with ASTM E394:09 and by determination of Chloride as Cl in accordance with an in-house test method on 8 stratified random selected samples.

	<i>Iron in mg/kg</i>	<i>Chloride in mg/kg</i>
sample #1015-1	2.76	4.2
sample #1015-2	3.06	4.2
sample #1015-3	2.92	4.2
sample #1015-4	2.89	4.2
sample #1015-5	2.71	4.2
sample #1015-6	2.73	4.3
sample #1015-7	2.68	4.2
sample #1015-8	2.68	4.2

table 1: homogeneity test results of subsamples #1015

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;

	<i>Iron in mg/kg</i>	<i>Chloride in mg/kg</i>
r (sample #1015)	0.39	0.10
target	E394:04	Horwitz
0.3*R (target)	0.40	0.46

table 2: repeatabilities of subsamples #1015

The calculated repeatabilities were in agreement with 0.3 times the corresponding target reproducibility. Therefore, homogeneity of the samples was assumed.

To each of the participating laboratories 1* 0.5 litre (labelled #1015) was sent on February 24, 2010.

2.5 STABILITY OF THE SAMPLES

The stability of Acetic Acid, packed in an amber glass bottle, was checked. The material was found sufficiently stable for the period of the proficiency test.

2.6 ANALYSES

The participants were asked to determine Acetaldehyde, Chloride as Cl, Colour Pt/Co, Density @ 20 °C, Formic Acid, Freezing Point, Iron as Fe, Nonvolatile Matter, Purity (estimated from Freezing Point), Purity (titration) Sulphate as SO₄ and Water. 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' (i.i.s.-protocol, version 3.2) of January 2010.

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:

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

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. Four participants reported after the final reporting date, two of them received the samples near the reporting date. In total 193 numerical results were reported by 26 participants. Observed were 8 outlying results, which is 4.2% 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 results are discussed per test.

For comparison of the results of this interlaboratory study, the requirements from the specification ASTM D3620:09 "Standard Specification for Glacial Acetic Acid" were used. Unfortunately, for many determinations this specification is referring to ASTM E302 "Standard Test Methods for Monobasic Organic Acids", which was withdrawn in 2001 with no replacement.

For the determination of the Purity by Titration, the method used for comparison is ASTM E301:94, which was also withdrawn, with no replacement, in 2001. However, no other useful standardised method is published yet.

The target reproducibility used for the determination of the Purity by Freezing Point is calculated from the values in table 1 and the target reproducibility both from ASTM E302. For the other determinations without any stated reproducibilities the observed spreads were compared with the strict spreads estimated from the Horwitz equation.

A not-normal distribution was found for Acetaldehyde, Colour Pt/Co, Density @ 20°C, Freezing Point and Purity (estimated from Freezing Point). In these cases the statistical evaluations should be used with due care.

Acetaldehyde: This determination was problematic for one laboratory. One statistical outlier was observed. The calculated reproducibility, after rejection of the statistical outlier, is in good agreement with the requirements of ASTM D2191:06.

Appearance: No analytical problems were observed. All labs agreed about the appearance of sample #1015, 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').

Chloride: This determination was problematic for two laboratories. Two false negative test results were observed. The calculated reproducibility is in good agreement with the estimated reproducibility limit, calculated using

the Horwitz equation. The Chloride content before spiking is not known. However, based on the assumption of zero content before spiking, the average recovery was estimated to be max 95%.

Colour: This determination was problematic for one laboratory. No statistical outliers were observed, but only one false negative result was reported. The calculated reproducibility is in agreement with the requirements of ASTM D1209:05e1.

Density @ 20 °C: This determination was problematic for one laboratory. Only one statistical outlier was observed. The calculated reproducibility, after rejection of the statistical outlier, is in good agreement with the requirements of ASTM D4052:02e1.

Formic Acid: This determination was not problematic. Two statistical outliers were observed. The calculated reproducibility, after rejection of the statistical outliers, is in good agreement with ASTM D3546:05.

Freezing Point: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the obsolete method ASTM E302:95.

Iron as Fe: This determination was problematic. Two statistical outliers were observed and the calculated reproducibility, after rejection of the statistical outliers, is not in agreement with the requirements of ASTM E394:04. The Iron content before spiking is not known. However, based on the assumption of zero content before spiking, the average recovery was estimated to be max 111%.

Nonvolatile Matter: This determination may be problematic for two laboratories. However, one statistical outlier was observed and one false negative result was reported. The calculated reproducibility, after rejection of the statistical outlier, is in agreement with the requirements of ASTM D1353:03.

Purity (from FP): Regretfully, no suitable reference method with precision data exists for this determination. Therefore, a target reproducibility was calculated out of table 1 of the obsolete ASTM E302:95 and the reproducibility data of the obsolete ASTM E302:95.
No analytical problems were observed. No statistical outliers were observed. The calculated reproducibility is in good agreement with the estimated reproducibility limits.

Purity (titration): This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in good agreement with the requirements of the obsolete method ASTM E301:94.

Sulphate as SO₄: This determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of the estimated reproducibility limits using the Horwitz equation. The Sulphate content before spiking is not known. However, based on the assumption of zero content before spiking, the average recovery was estimated to be max 114%..

Water: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the requirements of the obsolete method ASTM E302:95.

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) are compared in the next tables.

<i>Parameter</i>	<i>unit</i>	<i>n</i>	<i>average</i>	<i>2.8 * sd</i>	<i>R (lit)</i>
Acetaldehyde	mg/kg	7	11.7	28.4	80.0
Chloride	mg/kg	8	4.00	0.50	1.40
Colour	Pt/Co	21	15.0	5.7	7.0
Density @ 20°C	kg/L	22	1.04934	0.00022	0.00050
Formic Acid	mg/kg	13	44.4	45.4	360.0
Freezing Point	°C	23	16.40	0.15	0.25
Iron as Fe	mg/kg	17	2.44	0.66	0.47
Nonvolatile Matter	mg/100 mL	15	2.06	1.43	2.40
Purity (Freezing Point)	%M/M	23	99.883	0.075	0.130
Purity (Titration)	%M/M	10	99.878	0.211	0.540
Sulphate as SO ₄	mg/kg	5	5.7	4.1	2.0
Water	%M/M	24	0.0789	0.0148	0.0500

table 3: Reproducibilities for sample #1015

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

4.3 COMPARISON OF THE PROFICIENCY TEST OF MARCH 2010 WITH PREVIOUS PTS

	<i>March 2010</i>	<i>February 2008</i>	<i>March 2007</i>	<i>March 2006</i>
Number of rep. participants	26	28	25	18
Number of results reported	193	197	181	146
Statistical outliers	8	7	17	4
Percentage outliers	4.2%	3.6%	9.4%	2.7%

table 4: comparison 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:

<i>Determination</i>	<i>March 2010</i>	<i>February 2008</i>	<i>March 2007</i>	<i>March 2006</i>
Aldehydes	++	++	++	++
Chloride	++	++	++	+
Colour	++	++	++	++
Density @ 20 °C	++	++	++	++
Formic Acid	++	++	++	++
Freezing Point	++	++	++	++
Iron as Fe	--	-	++	--
Nonvolatile matter	++	+	++	++
Purity (Freezing point)	++	++	++	++
Purity (Titration)	++	++	++	++
Sulphate as SO ₄	--	n.e.	n.e.	n.e.
Water	++	++	++	++

table 5: comparison determinations against the standard

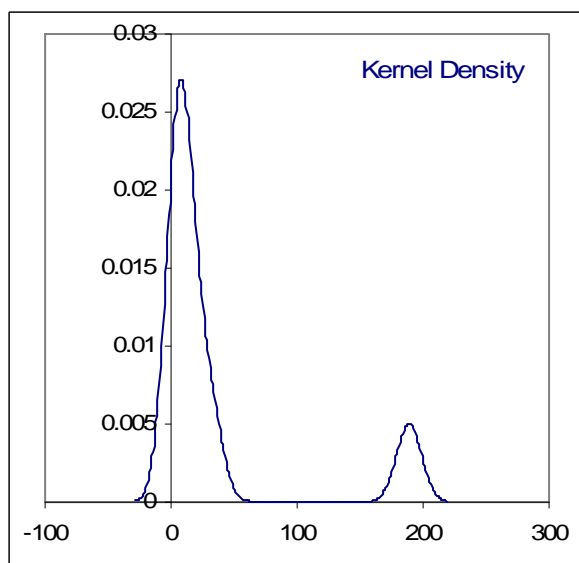
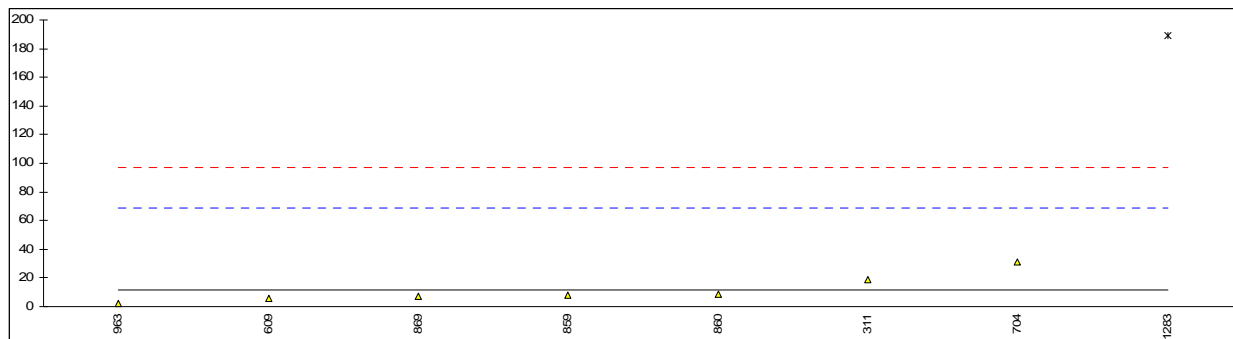
The performance of the determinations against the requirements of the respective standards is listed in the above table. The following performance categories were used:

- ++: 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.e.: not evaluated

APPENDIX 1

Determination of Acetaldehyde on sample #1015; results in mg/kg

lab	method	value	mark	z(targ)	remarks
169		----		----	
171		----		----	
174		----		----	
311	D2191	19		0.26	
315		----		----	
323	D2191	<10		<-0.06	
342		----		----	
347		----		----	
357	Inh-052	<50		<1.34	
359	Inh-052	<50		<1.34	
395		----		----	
396		----		----	
609	D2191	5.53		-0.22	
663		----		----	
704	D2191	31.4		0.69	
786	Inh-005	<10		<-0.06	
823		----		----	
859	D2191	8		-0.13	
860	D2191	9		-0.09	
869	D2191	7.0		-0.16	
913		----		----	
963	D2191	2		-0.34	
1283	Inh-695	189	G(0.01)	6.21	
1429	Client method	<100		<3.09	
1649		----		----	
normality		not OK			
n		7			
outliers		1			
mean (n)		11.7			
st.dev. (n)		10.14			
R(calc.)		28.4			
R(D2191:06)		80.0			

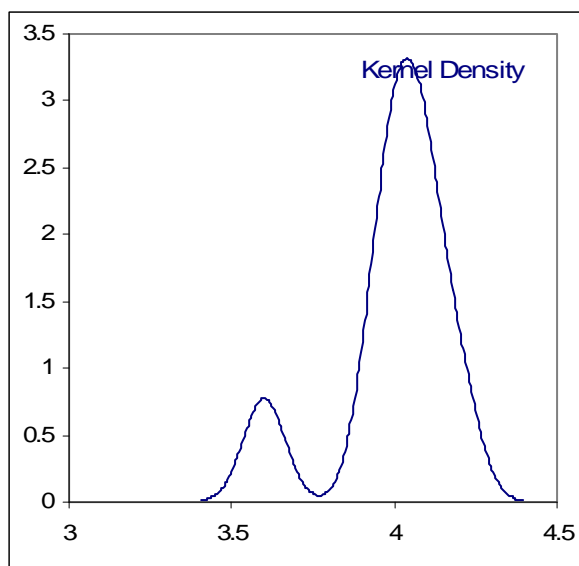
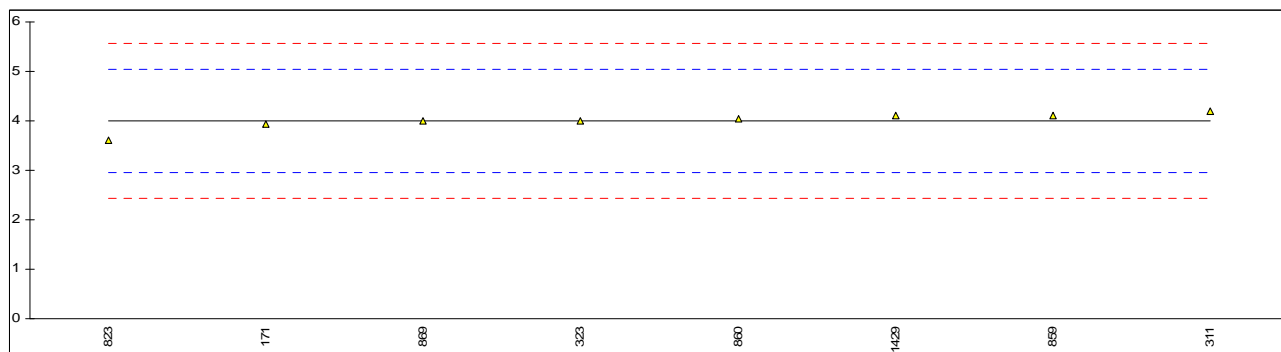


Determination of Appearance on sample #1015;

lab	method	value	mark	z(targ)	remarks
169	E2680	Pass		----	
171	E2680	C&F		----	
174	E2680	C&F		----	
311	E2680	Pass		----	
315	Inh-402	Pass		----	
323	E2680	Pass		----	
342		----		----	
347	E2680	Pass		----	
357	E2680	Pass		----	
359	E2680	Pass		----	
395	E2680	Pass		----	
396		----		----	
609	E2680	Pass		----	
663	E2680	Pass		----	
704	E2680	Pass		----	
786	E2680	Pass		----	
823	E2680	Pass		----	
859	E2680	Pass		----	
860	E2680	Pass		----	
869	E2680	Pass		----	
913	E2680	CFSM		----	
963	VISUAL	CFSM		----	
1283	Inh-001	Clear		----	
1429	D120	C&B		----	
1649		----		----	
	normality	n.a.			
	n	n.a.			
	outliers	n.a.			
	mean (n)	n.a.			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(lit)	unknown			

Determination of Chloride as Cl on sample #1015; results in mg/kg

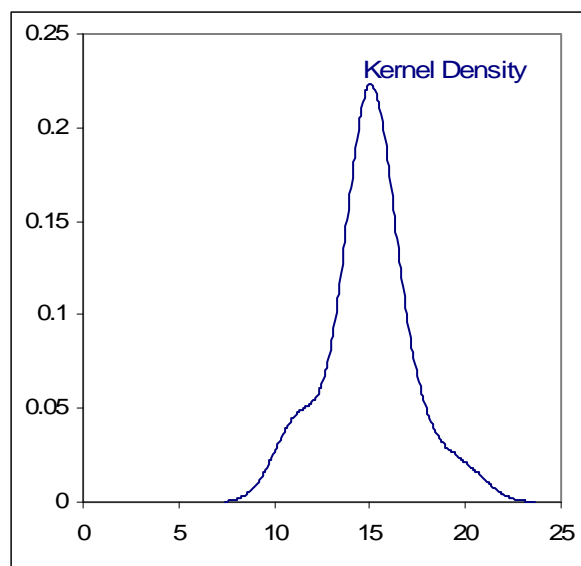
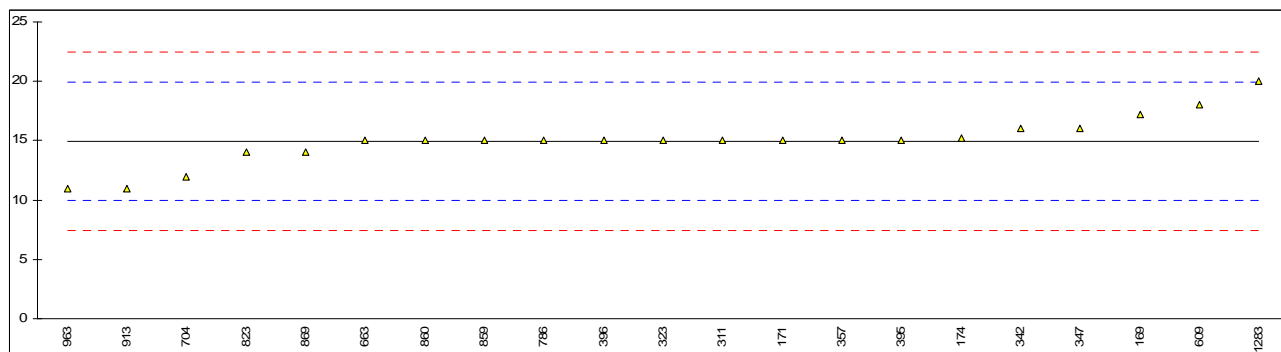
lab	method	value	mark	z(targ)	remarks
169		----		----	
171	E291	3.94		-0.11	
174		----		----	
311	Inh-158	4.2		0.39	
315		----		----	
323	Inh-008	4.0		0.00	
342		----		----	
347		----		----	
357	VISUAL	<1		<-5.79	False negative?
359	VISUAL	<1		<-5.79	False negative?
395		----		----	
396		----		----	
609		----		----	
663		----		----	
704	Inh-19814	<4		----	
786	Inh-19814	<4		----	
823	Inh-279	3.6		-0.77	
859	Inh-001	4.1		0.19	
860	IMPCA002	4.05		0.10	
869	Inh-001	4		0.00	
913		----		----	
963		----		----	
1283	Inh695	>1		----	
1429	Client method	4.1		0.19	
1649		----		----	
normality		OK			
n		8			
outliers		0	<u>Spike:</u>		
mean (n)		4.00	4.21		<95% recovered
st.dev. (n)		0.180			
R(calc.)		0.50			
R(Horwitz)		1.45			



Determination of Colour Pt/Co on sample #1015

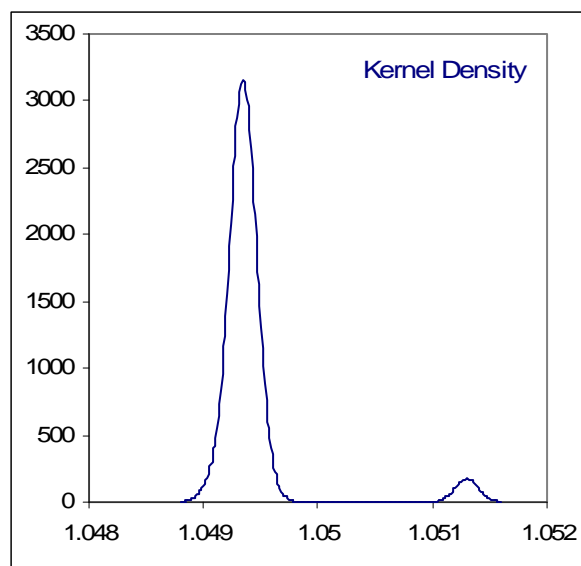
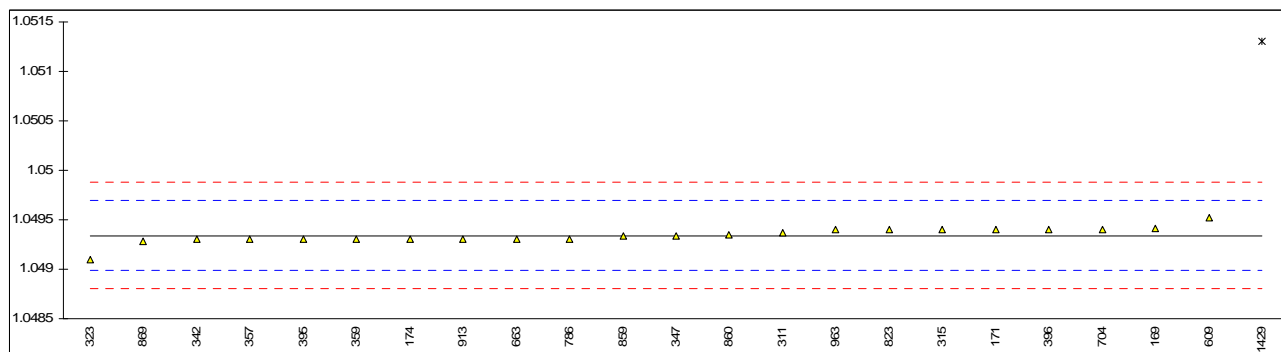
lab	method	value	mark	z(targ)	remarks
169	D5386	17.2		0.89	
171	E302	15		0.01	
174	E302	15.2		0.09	
311	E302	15		0.01	
315		----		----	
323	D1209	15		0.01	
342	D1209	16		0.41	
347	D1209	16		0.41	
357	D1209	15		0.01	
359		----		----	
395	D1209	15		0.01	
396	D1209	15		0.01	
609	D1209	18		1.21	
663	D1209	15		0.01	
704	D1209	12		-1.19	
786	D1209	15		0.01	
823	E302	14		-0.39	
859	D1209	15		0.01	
860	D1209	15		0.01	
869	E302	14		-0.39	
913	E302	11.0		-1.59	
963	D1209	11		-1.59	
1283	Inh-8768	20		2.01	
1429	D1209	<5		<-4.00	False negative
1649		----		----	

normality not OK
n 21
outliers 0
mean (n) 15.0
st.dev. (n) 2.05
R(calc.) 5.7
R(D1209:05e1) 7.0



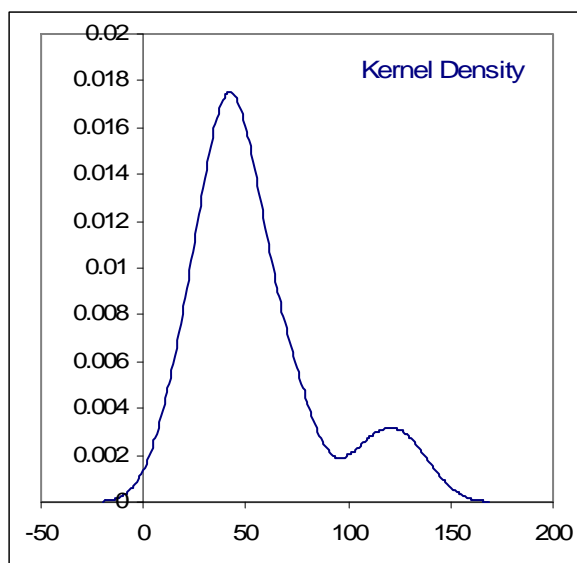
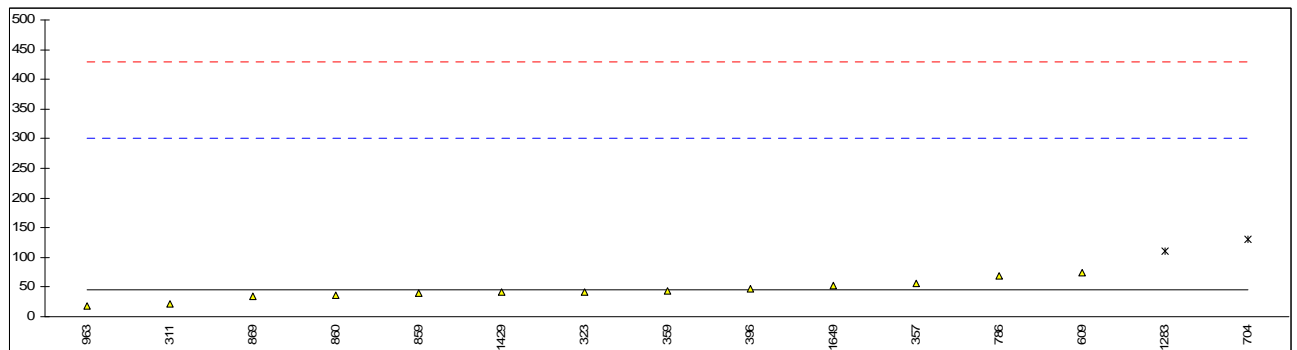
Determination of Density @ 20 °C on sample #1015; results in kg/L

lab	method	value	mark	z(targ)	remarks
169	D4052	1.04941		0.38	
171	D4052	1.0494		0.33	
174	D4052	1.0493		-0.23	
311	D4052	1.04937		0.16	
315	D4052	1.0494		0.33	
323	D4052	1.0491		-1.35	
342	D4052	1.0493		-0.23	
347	D4052	1.04934		-0.01	
357	D4052	1.0493		-0.23	
359	D4052	1.0493		-0.23	
395	D4052	1.0493		-0.23	
396	D4052	1.0494		0.33	
609	D4052	1.04952		1.00	
663	D4052	1.0493		-0.23	
704	D4052	1.0494		0.33	
786	D4052	1.0493		-0.23	
823	D4052	1.0494		0.33	
859	D4052	1.04934		-0.01	
860	D4052	1.04935		0.05	
869	D4052	1.04928		-0.34	
913	D4052	1.0493		-0.23	
963	D4052	1.0494		0.33	
1283		-----		-----	
1429	D4052	1.0513	G(0.01)	10.97	Measured at a different temperature?
1649		-----		-----	
normality	not OK				
n	22				
outliers	1				
mean (n)	1.04934				
st.dev. (n)	0.000080				
R(calc.)	0.00022				
R(D4052:02e1)	0.00050				



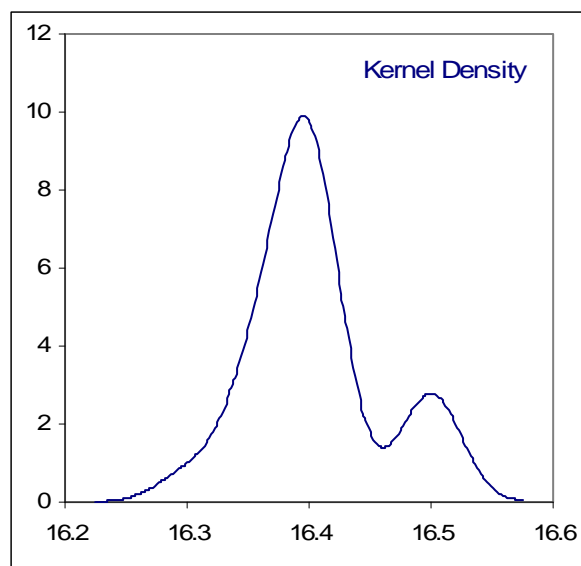
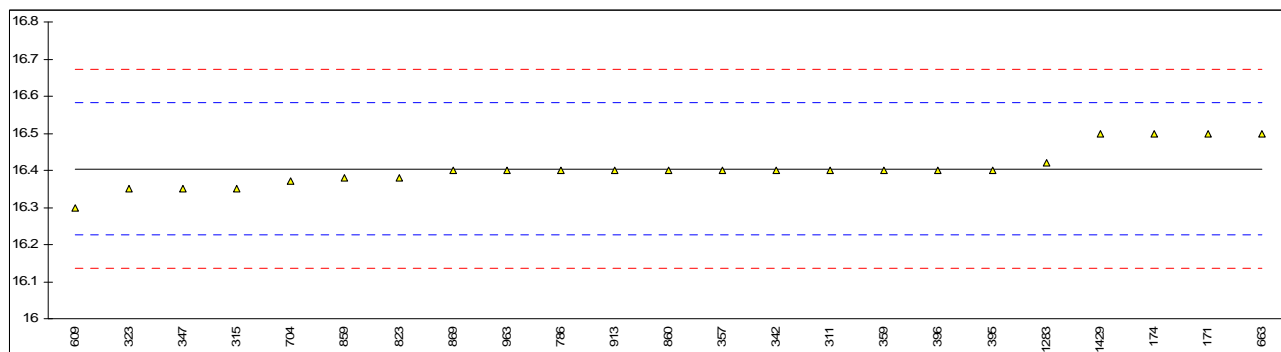
Determination of Formic Acid on sample #1015; results in mg/kg

lab	method	value	mark	z(targ)	remarks
169		----		----	
171		----		----	
174		----		----	
311	D3546	21		-0.18	
315		----		----	
323	D3546	42		-0.02	
342		----		----	
347		----		----	
357	D3546	57		0.10	
359	D3546	44		0.00	
395		----		----	
396	Inh-81	48		0.03	
609	D3546	74.85		0.24	
663		----		----	
704	Inh-19814	130	DG(0.01)	0.67	
786	Inh-19814	68.7		0.19	
823		----		----	
859	D3546	39		-0.04	
860	D3546	36		-0.07	
869	D3546	34		-0.08	
913		----		----	
963	D3546	19		-0.20	
1283	Inh-695	111	DG(0.01)	0.52	
1429	Client method	42		-0.02	
1649	GC	52		0.06	
normality		OK			
n		13			
outliers		2			
mean (n)		44.4			
st.dev. (n)		16.23			
R(calc.)		45.4			
R(D3546:05)		360.0			



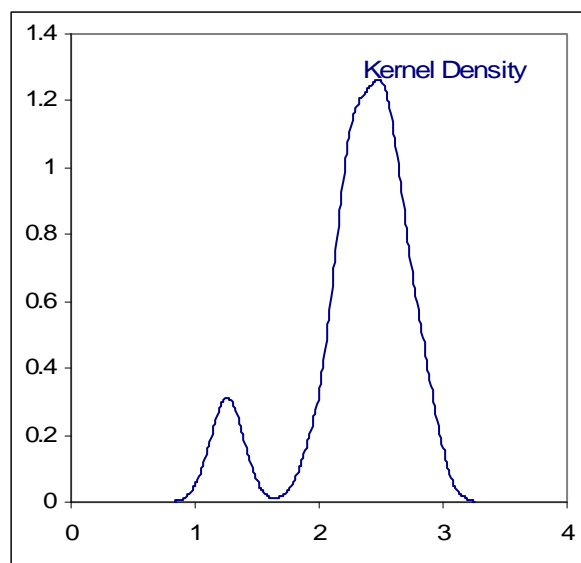
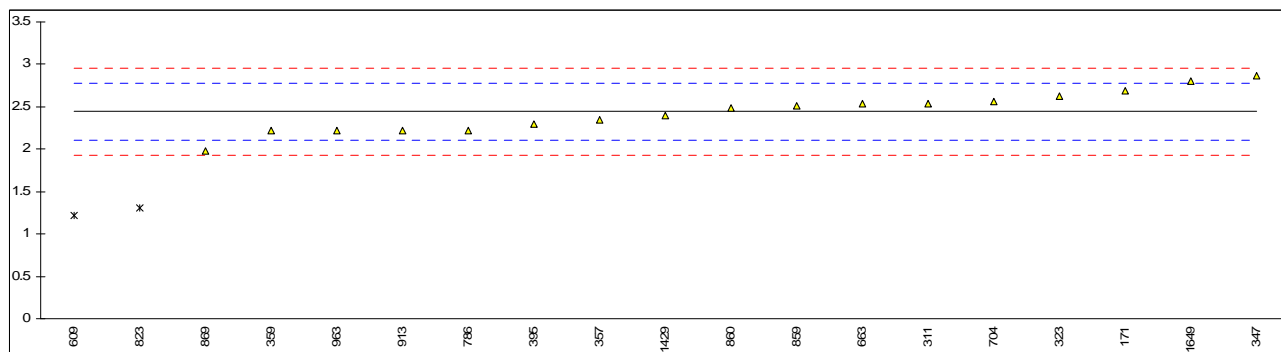
Determination of Freezing Point on sample #1015; results in °C

lab	method	value	mark	z(targ)	remarks
169		----		----	
171	E302	16.50		1.07	
174	E302	16.5		1.07	
311	E302	16.40		-0.05	
315	D1493	16.35		-0.61	
323	D1493	16.35		-0.61	
342	D1493	16.40		-0.05	
347	E302	16.35		-0.61	
357	E302	16.40		-0.05	
359	E302	16.4		-0.05	
395	Inh-124	16.4		-0.05	
396	D1493	16.4		-0.05	
609	Inh-70013	16.30		-1.17	
663	D6875	16.50		1.07	
704	Inh-61	16.37		-0.38	
786	E302	16.40		-0.05	
823	E302	16.38		-0.27	
859	E302	16.38		-0.27	
860	E302	16.40		-0.05	
869	E302	16.40		-0.05	
913	E302	16.4		-0.05	
963	E302	16.40		-0.05	
1283	Inh-695	16.42		0.18	
1429	Client method	16.50		1.07	
1649		----		----	
normality		not OK			
n		23			
outliers		0			
mean (n)		16.404			
st.dev. (n)		0.0519			
R(calc.)		0.145			
R(E302:95)		0.250			



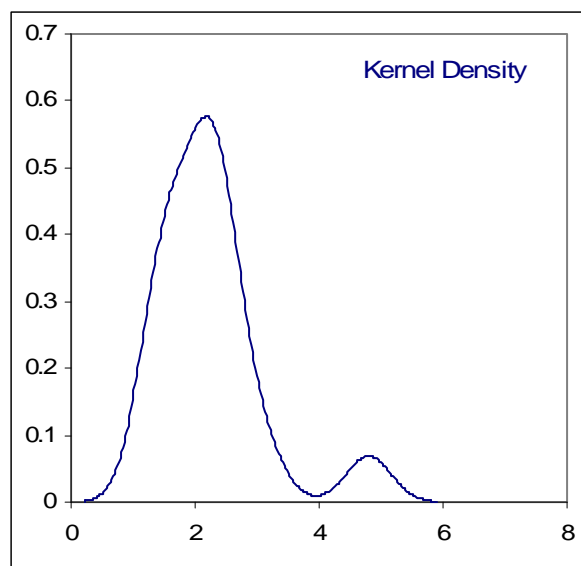
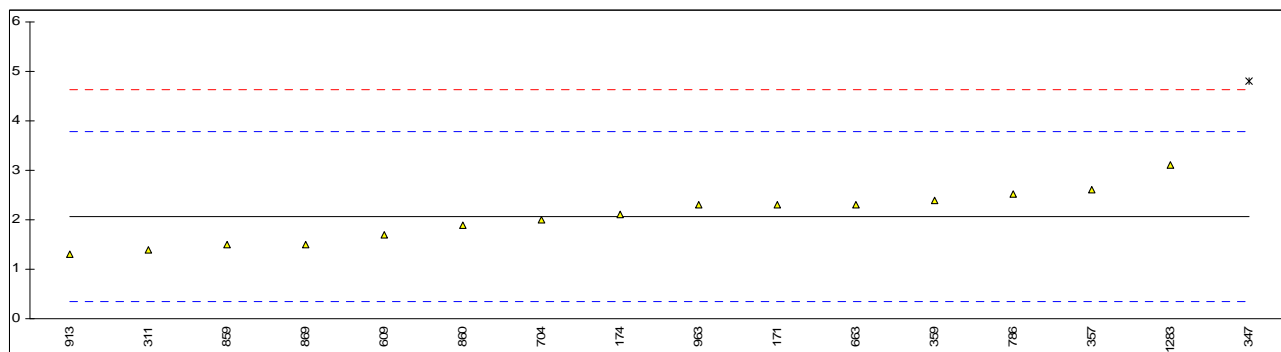
Determination of Iron as Fe on sample #1015; results in mg/kg

lab	method	value	mark	z(targ)	remarks
169		----		----	
171	E394	2.69		1.47	
174		----		----	
311	E394	2.53		0.52	
315		----		----	
323	E394	2.63		1.11	
342		----		----	
347	E394	2.87		2.53	
357	D3620	2.35		-0.54	
359	E394	2.22		-1.31	
395	E394	2.289		-0.90	
396		----		----	
609	E394	1.22	DG(0.01)	-7.22	
663	E394	2.53		0.52	
704	E394	2.565		0.73	
786	E394	2.223		-1.29	
823	E394	1.3	CDG(0.01)	-6.74	First reported 3.8
859	E394	2.51		0.40	
860	E394	2.48		0.23	
869	E394	1.978		-2.74	
913	E394	2.22		-1.31	
963	E394	2.22		-1.31	
1283	Inh-695	>1		----	
1429	E394	2.4		-0.25	
1649	Phot.	2.8		2.12	
normality		OK			
n		17			
outliers		2	<u>Spike</u>		
mean (n)		2.441	2.208		<111% recovered
st.dev. (n)		0.2358			
R(calc.)		0.660			
R(E394:04)		0.474			



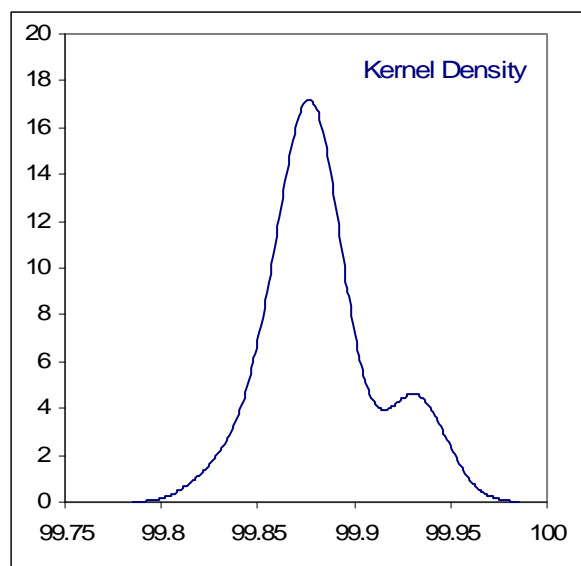
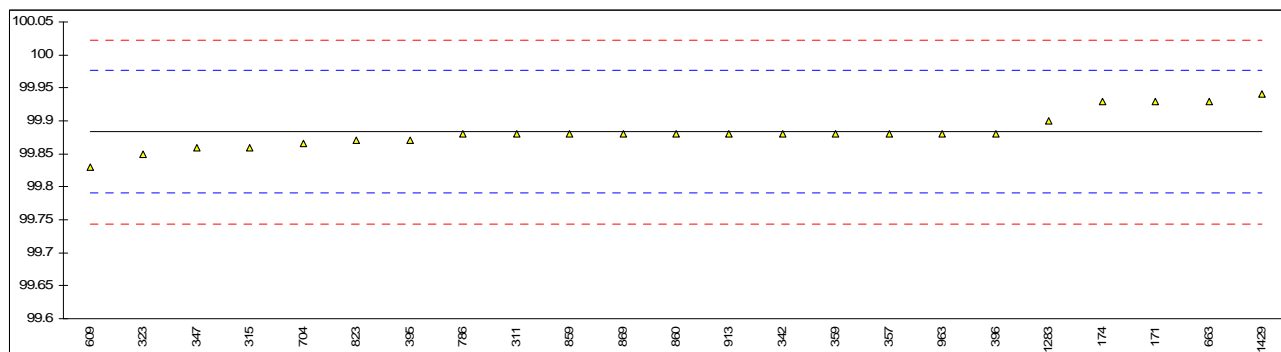
Determination of Nonvolatile Matter on sample #1015; results in mg/100 mL

lab	method	value	mark	z(targ)	remarks
169		----		----	
171	D1353	2.3		0.28	
174	D1353	2.1		0.05	
311	D1353	1.4		-0.77	
315		----		----	
323		----		----	
342		----		----	
347	D1353	4.8	G(0.01)	3.20	
357	D1353	2.6		0.63	
359	D1353	2.4		0.40	
395		----		----	
396		----		----	
609	D1353	1.7		-0.42	
663	D1353	2.3		0.28	
704	D1353	2.0		-0.07	
786	D1353	2.52		0.54	
823		----		----	
859	D1353	1.5		-0.65	
860	D1353	1.9		-0.19	
869	D1353	1.5		-0.65	
913	D1353	1.3		-0.89	
963	D1353	2.3		0.28	
1283	Inh-322	3.10		1.21	
1429	D1353	<0.001		----	False negative result, probably different unit?
1649		----		----	
normality	OK				
n	15				
outliers	1				
mean (n)	2.06				
st.dev. (n)	0.512				
R(calc.)	1.43				
R(D1353:03)	2.40				



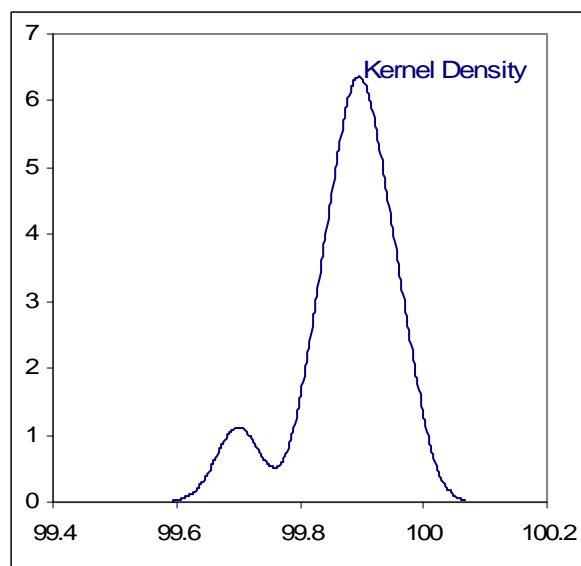
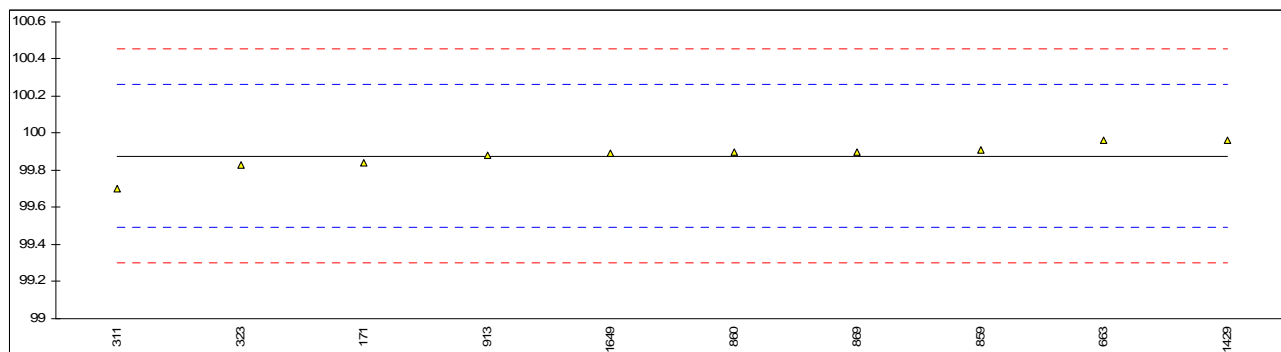
Determination of Purity (estimated from the Freezing Point) on sample #1015; results in % M/M

lab	method	value	mark	z(targ)	remarks
169		----		----	
171	E302	99.930		1.01	
174	E302	99.93		1.01	
311	E302	99.88		-0.07	
315	E302	99.86		-0.50	
323	E302	99.85		-0.72	
342	E302	99.88		-0.07	
347	E302	99.86		-0.50	
357	E302	99.88		-0.07	
359	E302	99.88		-0.07	
395	Inh-124	99.87		-0.29	
396	Inh-73	99.88		-0.07	
609	Inh-70014	99.83		-1.15	
663	E302	99.93		1.01	
704	E302	99.865		-0.39	
786	E302	99.88		-0.07	
823	E302	99.87		-0.29	
859	E302	99.88		-0.07	
860	E302	99.88		-0.07	
869	E302	99.88		-0.07	
913	E302	99.88		-0.07	
963	E302	99.88		-0.07	
1283	Inh576	99.9		0.36	
1429	Client method	99.94		1.22	
1649		----		----	
normality		not OK			
n		23			
outliers		0			
mean (n)		99.883			
st.dev. (n)		0.0269			
R(calc.)		0.075			
R(from E302:95)		0.130			



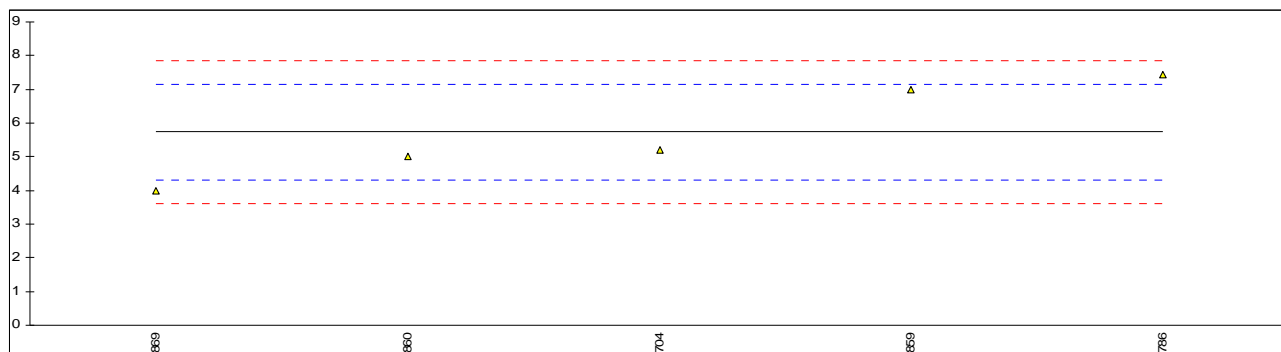
Determination of Purity (by titration) on sample #1015; results in %M/M

lab	method	value	mark	z(targ)	remarks
169		----		----	
171	E301	99.843		-0.18	
174		----		----	
311	E301	99.70		-0.92	
315		----		----	
323	E301	99.83		-0.25	
342		----		----	
347		----		----	
357		----		----	
359		----		----	
395		----		----	
396		----		----	
609		----		----	
663	Inh-576	99.96		0.43	
704		----		----	
786		----		----	
823		----		----	
859	E301	99.912		0.18	
860	E301	99.90		0.12	
869	E301	99.901		0.12	
913	E301	99.88		0.01	
963		----		----	
1283		----		----	
1429	Client method	99.96		0.43	
1649	GC	99.89		0.06	
normality		OK			
n		10			
outliers		0			
mean (n)		99.878			
st.dev. (n)		0.0753			
R(calc.)		0.211			
R(E301:94)		0.540			



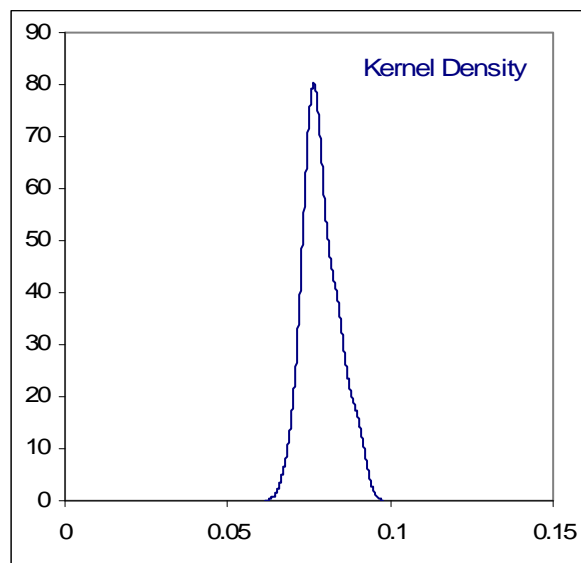
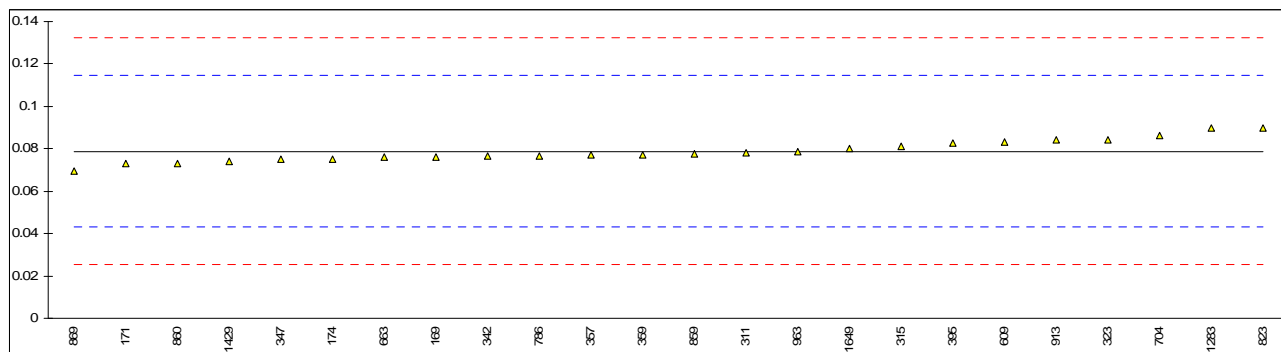
Determination of Sulphate as SO₄ on sample #1015, results in mg/kg

lab	method	value	mark	z(targ)	remarks
169		----		----	
171		----		----	
174		----		----	
311		----		----	
315		----		----	
323		----		----	
342		----		----	
347		----		----	
357		----		----	
359		----		----	
395		----		----	
396		----		----	
609		----		----	
663		----		----	
704	Inh-19814	5.2		-0.75	
786	Inh-19814	7.45		2.44	
823		----		----	
859	Inh-70021	7		1.80	
860	Inh-676	5		-1.04	
869	Inh-70021	4		-2.45	
913		----		----	
963	Inh-3.14	<10		----	
1283	Inh-695	>1		----	
1429	Client method	<1		<-6.58	False negative?
1649		----		----	
	normality	OK			
	n	5			
	outliers	0	<u>Spike</u>		
	mean (n)	5.7	5.0		<114% recovered
	st.dev. (n)	1.45			
	R(calc.)	4.1			
	R(Horwitz)	2.0			



Determination of Water on sample #1015, results in %M/M

lab	method	value	mark	z(targ)	remarks
169	E1064	0.0761		-0.15	
171	E302	0.0728		-0.34	
174	E302	0.0750		-0.22	
311	E302	0.078		-0.05	
315	E302	0.0810		0.12	
323	E203	0.084		0.29	
342	E1064	0.0764		-0.14	
347	E1064	0.0750		-0.22	
357	E1064	0.077		-0.10	
359	E302	0.077		-0.10	
395	E1064	0.0828		0.22	
396		-----		-----	
609	D1364	0.083		0.23	
663	E1064	0.076		-0.16	
704	E302	0.086		0.40	
786	E1064	0.0766		-0.13	
823	E302	0.090		0.62	
859	E203	0.0774		-0.08	
860	E302	0.073		-0.33	
869	E302	0.0693		-0.54	
913	E302	0.084		0.29	
963	E302	0.07849		-0.02	
1283	Inh-2362	0.0898		0.61	
1429	D1364	0.074	C	-0.27	First reported 740
1649	KF TITR	0.08		0.06	
normality		OK			
n		24			
outliers		0			
mean (n)		0.0789			
st.dev. (n)		0.00527			
R(calc.)		0.0148			
R(E302:95)		0.0500			



APPENDIX 2

List of participants

- 1 laboratory in AUSTRIA
- 1 laboratory in BELGIUM
- 2 laboratories in FINLAND
- 2 laboratories in INDIA
- 2 laboratories in ITALY
- 1 laboratory in KOREA
- 1 laboratory in MALAYSIA
- 3 laboratories in P.R. of CHINA
- 1 laboratory in RUSSIA
- 1 laboratory in SAUDI ARABIA
- 2 laboratories in SPAIN
- 1 laboratory in THAILAND
- 2 laboratories in THE NETHERLANDS
- 3 laboratories in U.S.A.
- 1 laboratory in UKRAINE
- 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
U	= error in reporting unit
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/>)