Results of Proficiency Test
Acetic Acid
February 2015

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

1 INTRODUCTION

Since 2003, the Institute for Interlaboratory Studies organizes a proficiency test for Acetic Acid. During the annual proficiency test program of 2014/2015, it was decided to continue the proficiency test for the analysis of Acetic Acid. In this interlaboratory study 27 laboratories in 17 different countries have participated. See appendix 2 for the number of participants per country. In this report, the results of the 2015 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 bottle of 0.5L Acetic Acid (labelled #15005).The sample was spiked with Iron(III)Chloride and Sodium Sulphate. Analyses for fit-for-use and homogeneity were subcontracted.
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/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded from the iis website www.iisnl.com.

2.3 CONFIDENTIALITY STATEMENT

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

2.4 SAMPLES

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 244.4 mg Iron(III)Chloride.$6H_2O$ and 191.9 mg Sodium Sulphate. After homogenisation, this material was divided over 41 brown glass bottles of 0.5 L and labelled #15005.
The homogeneity of the subsamples #15005 was checked by determination of Chloride in accordance with an in-house test method and Density in accordance with ASTM D4052 on 8 stratified randomly selected samples.

	Chloride in mg/kg	*Density @20ºC in kg/l*
sample #15005-1	3.9	1.04929
sample #15005-2	3.9	1.04928
sample #15005-3	3.9	1.04929
sample #15005-4	3.9	1.04928
sample #15005-5	3.9	1.04929
sample #15005-6	3.9	1.04929
sample #15005-7	3.9	1.04929
sample #15005-8	3.9	1.04929

Table 1: homogeneity test results of subsamples #15005

From the above test results the repeatabilities were calculated and compared with 0.3 times the respective reproducibility of the standard test method and the estimated reproducibility calculated using the Horwitz equation in agreement with the procedure of ISO 13528, Annex B2 in the next table;

	Chloride in mg/kg	*Density @20ºC in kg/l*
r (sample #15005)	0.0	0.00001
Reference test method	Horwitz	ASTM D4052:02e1
0.3*R (reference)	0.4	0.00015

table 2: repeatabilities of subsamples #15005

The calculated repeatabilities were both 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 #15005) was sent on January 21, 2015.

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, Anorganic Chloride as Cl, Appearance, Colour Pt/Co, Density @ 20 ^{o}C, Formic Acid, Freezing Point, Iron as Fe, Nonvolatile Matter, Purity (estimated from Freezing Point), Purity (titration), Sulphate as SO_4 and Water.

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.
Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the (raw data of the) reported results.
Additional or corrected results have been used for data analysis and original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' (iis-protocol, April 2014 version 3.3). For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.
In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon, Grubbs and Rosner 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 and by R(0.01) for

the Rosner General ESD test (see appendix 3, no.15). Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of the averages and the 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.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for each 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 is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3; nos.13 and 14). Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. ASTM reproducibilities, the z-scores were calculated using a target standard deviation. This 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 the fit-for-useness of the reported test result.
The z-scor es were calculated according to:

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

The $z_{(target)}$ scores are listed in the result tables in appendix 1.

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

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

4 EVALUATION

In this interlaboratory study, problems with sample despatch were encountered due to several reasons. Five participants reported after the final reporting date and five laboratories did not report any results at all due to various reasons. Not all laboratories were able to perform all analyses requested.
In total 159 numerical results were reported by 22 participants. Observed were 6 outlying results, which is 3.8% 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 sample and per test. The specified test methods and requirements were taken into account for explaining the observed differences when possible and applicable. These methods are also in the tables together with the reported data. The abbreviations, used in these tables, are listed in appendix 3.

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. Regretfully, for many determinations this specification is referring to ASTM E302:95 “Standard Test Methods for Monobasic Organic Acids”, which was withdrawn already in 2001. As there was no replacement, this specification was used as reference method.

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 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.

In the iis PT reports, ASTM methods are referred to with a number (e.g. D1209) and an added designation for the year that the method was adopted or revised (e.g. D1209:05). If applicable, a designation in parentheses is added to designate the year of reapproval (e.g. D1209:05 (2011)). 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.

Acetaldehyde: Only three participants reported a numerical result. Therefore no significant conclusions were drawn. Please note that ASTM D2191 is meant for vinyl acetate.

Anorganic Chloride: This determination may not be problematic. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in good agreement with the estimated reproducibility limit, calculated using the Horwitz equation. The average recovery of Anorganic Chloride (theoretical increment of 3.84 mg/kg) may be good: “less than 94%”. The actual blank concentration for Anorganic Chloride is unknown.

Appearance: No analytical problems were observed. All labs agreed about the appearance, which is bright, clear and free of suspended matter.

Colour: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in agreement with the requirements of ASTM D1209:05(2011).

Density at 20 ^{o}C: This determination was not problematic. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in good agreement with the requirements of ASTM D4052:02e1.

Formic Acid: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in good agreement with the requirements of ASTM D3546:11.

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

Iron as Fe: This determination was problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of ASTM E394:09. The average recovery of Iron (theoretical increment of 2.02 mg/kg) may be good: “less than 93%”. The actual blank concentration for Iron is unknown.

Nonvolatile Matter: This determination was not problematic. No statistical outliers were observed and the calculated reproducibility is in agreement with the requirements of ASTM D1353:13.

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 withdrawn ASTM E302:95 and the reproducibility data of

the withdrawn ASTM E302:95. No analytical problems were observed. No statistical outliers were observed and the calculated reproducibility is in good agreement with the estimated reproducibility limits.

Purity (titration): This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in good agreement with the requirements of ASTM E301:94.

Sulphate as SO4: Only three participants reported a numerical result. Therefore no significant conclusions were drawn.

Water: This determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in good agreement with the requirements of the withdrawn 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.

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (lit)*
Acetaldehyde	mg/kg	10	<50	n.a.	n.a.
Anorganic Chloride	mg/kg	5	4.1	0.3	1.5
Appearance		21	Pass	n.a.	n.a.
Colour Pt/Co		18	11.5	4.7	7.0
Density at 20°C	kg/L	19	1.0493	0.0002	0.0005
Formic Acid	mg/kg	11	47.4	70.0	360.0
Freezing Point	°C	19	16.41	0.10	0.25
Iron as Fe	mg/kg	18	1.87	1.04	0.89
Nonvolatile Matter	mg/100 mL	12	2.2	2.2	2.1
Purity (Freezing Point)	%M/M	19	99.89	0.06	0.13
Purity (Titration)	%M/M	8	99.86	0.15	0.54
Sulphate as SO_4	mg/kg	3	4.5	n.a.	n.a.
Water	%M/M	18	0.075	0.019	0.050

Table 3: Reproducibilities for sample #15005

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 FEBRUARY 2015 WITH PREVIOUS PTS

	February 2015	*February 2013*	*February 2011*	*March 2010*
Number of rep. participants	22	23	28	26
Number of results reported	159	177	236	193
Statistical outliers	6	10	10	8
Percentage outliers	3.8%	5.7%	4.2%	4.2%

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:

Determination	*February 2015*	*February 2013*	*February 2011*	*March 2010*
Acetaldehyde	n.e.	++	++	++
Anorganic Chloride	++	++	++	++
Colour	+	++	++	++
Density @ 20 ^{o}C	++	++	++	++
Formic Acid	++	++	++	++
Freezing Point	++	++	++	++
Iron as Fe	-	++	++	--
Nonvolatile matter	+/-	--	++	++
Purity (Freezing point)	++	++	++	++
Purity (Titration)	++	+	++	++
Sulphate as SO_4	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

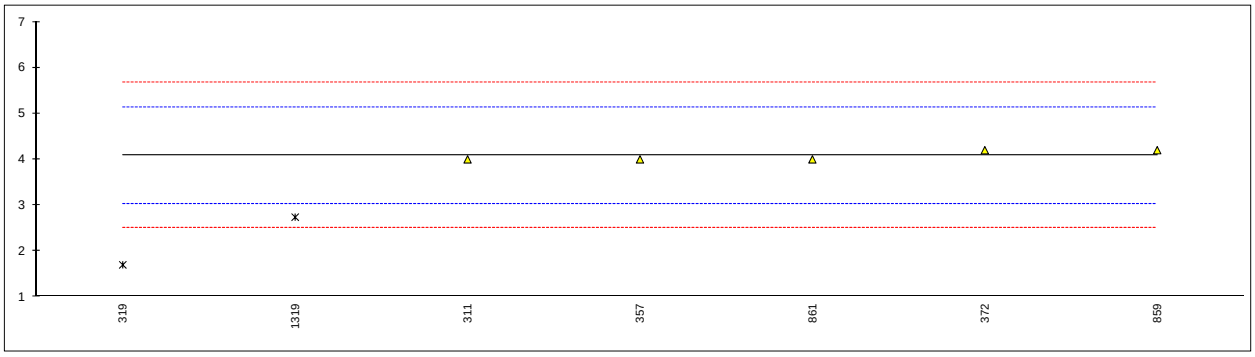
APPENDIX 1

Determination of Acetaldehyde on sample #15005; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	INH-245	<1		-----	
174		-----		-----	
311	D2191	<10		-----	
315		-----		-----	
319	INH-5033	<2		-----	
323	D2191	<10		-----	
347		-----		-----	
357	INH-052	<50		-----	
372	in house	<50		-----	
395		-----		-----	
551		-----		-----	
558		-----		-----	
609	D2191	3.77		-----	
663		-----		-----	
786		-----		-----	
823		-----		-----	
859	D2191	<10		-----	
861		-----		-----	
912		-----		-----	
913		-----		-----	
963	D2191	16		-----	
1319	D2191	10.8		-----	
7002		-----		-----	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	
	normality	n.a.			
	n	10			
	outliers	n.a.			
	mean (n)	<50			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(D2191:06)	n.a.			

Determination of Anorganic Chloride as Cl on sample #15005; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173		-----		-----	
174		-----		-----	
311	INH-158	4.0		-0.15	
315		-----		-----	
319	ISO753	1.7	DG(0.01)	-4.51	
323		-----		-----	
347		-----		-----	
357	INH-709	4.0		-0.15	
372	in house	4.2		0.23	
395		-----		-----	
551		-----		-----	
558		-----		-----	
609	INH-70020	<4		-----	
663		-----		-----	
786		-----		-----	
823		-----		-----	
859	INH-001	4.2		0.23	
861	INH-001	4		-0.15	
912		-----		-----	
913		-----		-----	
963	INH-1351	>2		-----	
1319	in house	2.74	DG(0.01)	-2.54	
7002		-----		-----	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	
	normality	unknown			
	n	5			
	outliers	2		Spike	
	mean (n)	4.08		3.84	Recovery < 94%
	st.dev. (n)	0.110			
	R(calc.)	0.31			
	R(Horwitz)	1.48			



Determination of Appearance on sample #15005;

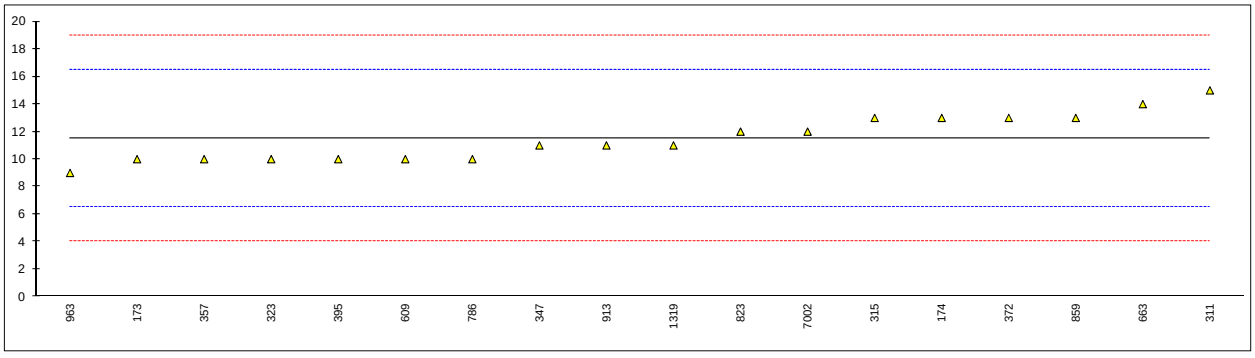
lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	E2680	Pass		-----	
174	E2680	Pass		-----	
311	E2680	Pass		-----	
315	INH-402	C&B		-----	
319		CCL		-----	
323	E2680	Pass, C&B		-----	
347	E2680	Pass		-----	
357	E2680	Pass		-----	
372	E2680	Pass		-----	
395	E2680	Pass		-----	
551		-----		-----	
558		-----		-----	
609	INH-111	Pass		-----	
663	Visual	Pass		-----	
786	E2680	Pass		-----	
823	E2680	Pass		-----	
859	Visual	C&B		-----	
861	E2680	C&B		-----	
912		-----		-----	
913	Visual	Pass		-----	
963	E2680	Pass		-----	
1319	Visual	Clear		-----	
7002		Pass		-----	
7006		-----		-----	
7015		-----		-----	
7016		Pass		-----	
	normality	n.a.			
	n	21			
	outliers	n.a.			
	mean (n)	Pass			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(Lit)	n.a.			

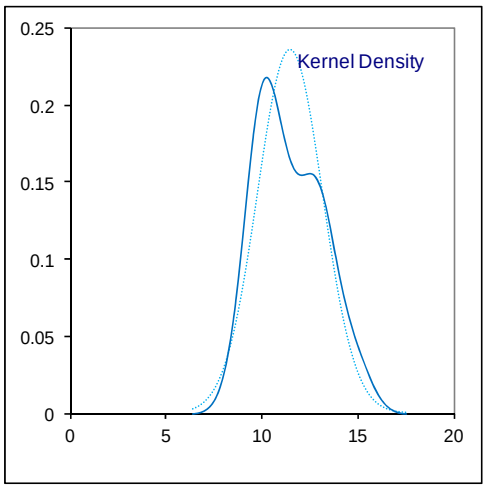
C&B = Clear and Bright
CCL = Clear and Colourless Liquid

Determination of Colour Pt/Co on sample #15005

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	D1209	10		-0.60	
174	D1209	13		0.60	
311	D1209	15		1.40	
315	D5386	13.0		0.60	
319		-----		-----	
323	D1209	10		-0.60	
347	D5386	11		-0.20	
357	D1209	10		-0.60	
372	D1209	13		0.60	
395	D1209	10		-0.60	
551		-----		-----	
558		-----		-----	
609	D1209	10		-0.60	
663	D1209	14		1.00	
786	D1209	10		-0.60	
823	D5386	12		0.20	
859	D1209	13		0.60	
861		-----		-----	reported test result: 10 -15
912		-----		-----	
913	D5386	11		-0.20	
963	D1209	9		-1.00	
1319	D1209	11		-0.20	
7002	D1209	12		0.20	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	

normality	OK
n	18
outliers	0
mean (n)	11.5
st.dev. (n)	1.69
R(calc.)	4.7
R(D1209:05)	7.0

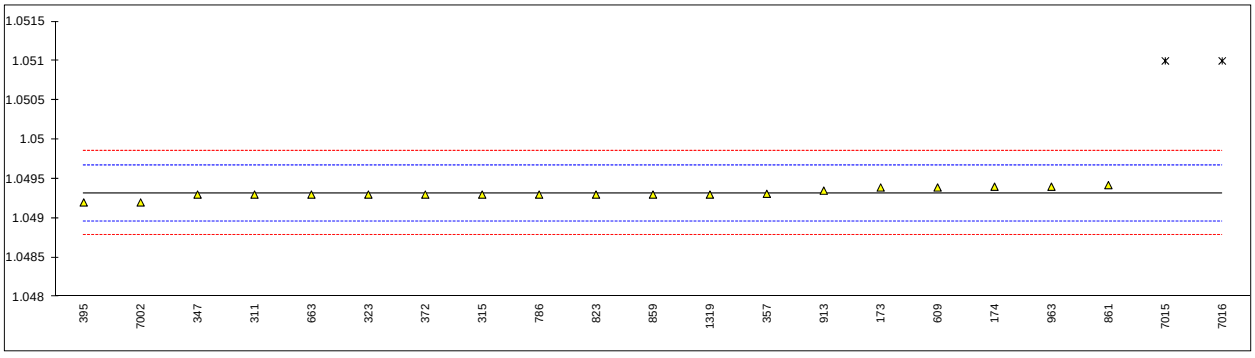


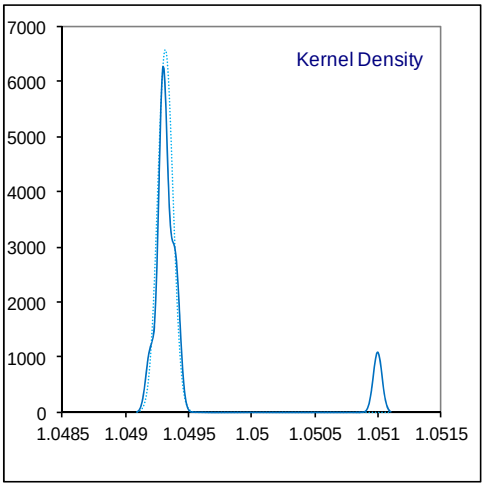


Determination of Density at 20°C on sample #15005; results in kg/L

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	D4052	1.04939		0.40	
174	D4052	1.0494		0.45	
311	D4052	1.0493		-0.11	
315	D4052	1.0493		-0.11	
319		-----		-----	
323	D4052	1.0493		-0.11	
347	D4052	1.0493		-0.11	
357	D4052	1.04931		-0.05	
372	D4052	1.0493		-0.11	
395	D4052	1.0492		-0.67	
551		-----		-----	
558		-----		-----	
609	D4052	1.04939		0.40	
663	D4052	1.0493		-0.11	
786	D4052	1.0493		-0.11	
823	D4052	1.0493		-0.11	
859	D4052	1.0493		-0.11	
861	D4052	1.04942		0.57	
912		-----		-----	
913	D4052	1.04935		0.17	
963	D4052	1.0494		0.45	
1319	D4052	1.0493		-0.11	
7002	in house	1.0492		-0.67	
7006		-----		-----	
7015	D891	1.051	R(0.01)	9.41	
7016	D4052	1.0510	C,R(0.01)	9.41	first reported: 1.510

normality	OK
n	19
outliers	2
mean (n)	1.04932
st.dev. (n)	0.000061
R(calc.)	0.00017
R(D4052:02e1)	0.00050

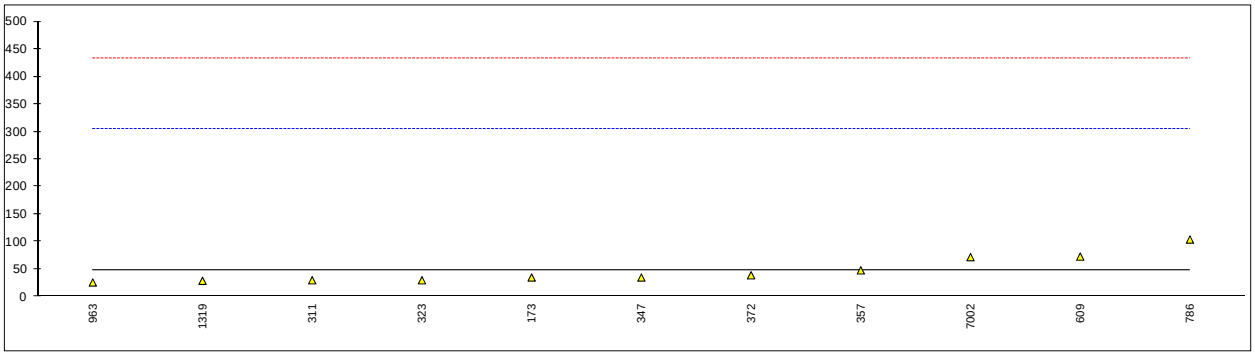


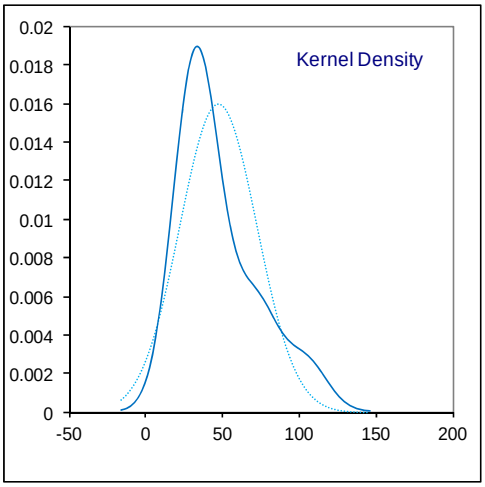


Determination of Formic Acid on sample #15005; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	D3546	35		-0.10	
174		-----		-----	
311	D3546	30		-0.14	
315		-----		-----	
319	INH-5032	<50		-----	
323	D3546	30		-0.14	
347	D3546	35		-0.10	
357	D3546	48		0.00	
372	D3546	39		-0.07	
395		-----		-----	
551		-----		-----	
558		-----		-----	
609	D3546	73		0.20	
663		-----		-----	
786	INH-19814	104		0.44	
823		-----		-----	
859		-----		-----	
861		-----		-----	
912		-----		-----	
913		-----		-----	
963	D3546	26		-0.17	
1319	in house	29		-0.14	
7002	D3546	72		0.19	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	

normality	not OK
n	11
outliers	0
mean (n)	47.4
st.dev. (n)	24.99
R(calc.)	70.0
R(D3546:11)	360.0

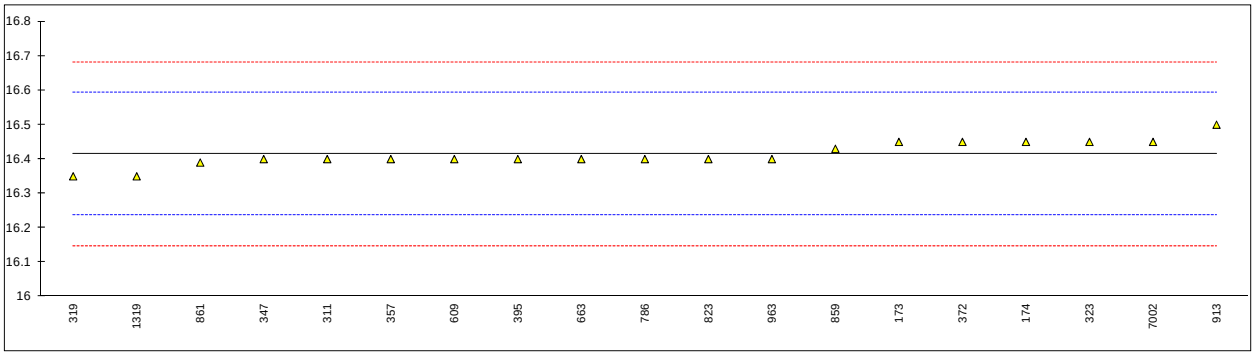


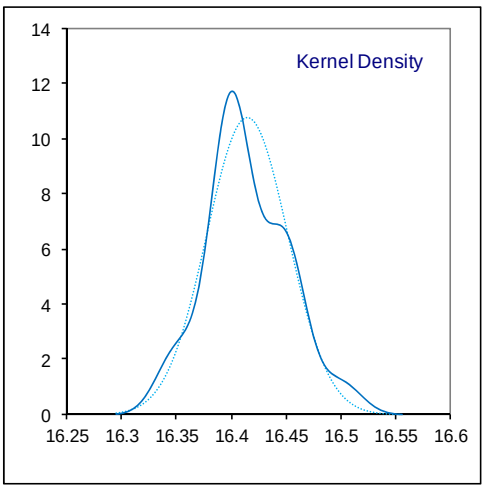


Determination of Freezing Point on sample #15005; results in °C

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	INH-124	16.45		0.40	
174	E302	16.45		0.40	
311	E302	16.40		-0.16	
315		-----		-----	
319	ISO1392	16.35		-0.72	
323	E302	16.45		0.40	
347	E302	16.40		-0.16	
357	E302	16.40		-0.16	
372	E302	16.45		0.40	
395	INH-124	16.40		-0.16	
551		-----		-----	
558		-----		-----	
609	INH-70013	16.40		-0.16	
663	E302	16.40		-0.16	
786	E302	16.4		-0.16	
823	E302	16.40		-0.16	
859	E302	16.43		0.18	
861	E302	16.39		-0.27	
912		-----		-----	
913	E302	16.5		0.96	
963	E302	16.4		-0.16	
1319	E302	16.35		-0.72	
7002	in house	16.45		0.40	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	

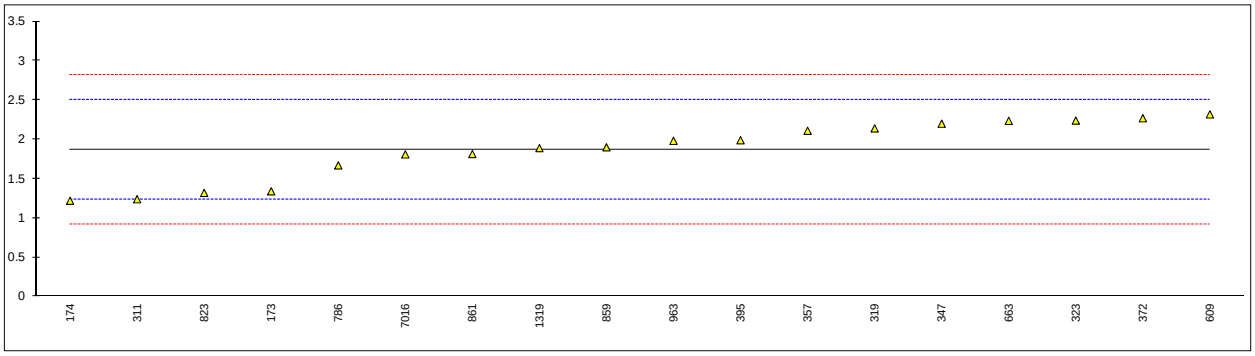
normality	OK
n	19
outliers	0
mean (n)	16.414
st.dev. (n)	0.0370
R(calc.)	0.104
R(E302:95)	0.250

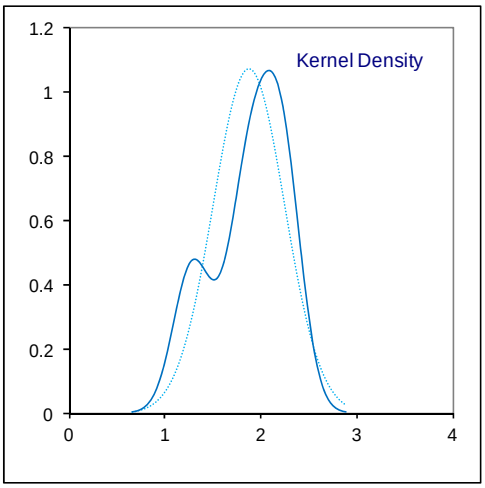




Determination of Iron as Fe on sample #15005; results in mg/kg

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	INH-290	1.34		-1.68	
174	E394	1.22		-2.06	
311	E394	1.24		-1.99	
315		-----		-----	
319	E394	2.14		0.85	
323	E394	2.24		1.16	
347	E394	2.20		1.04	
357	E394	2.11		0.75	
372	E394	2.27		1.26	
395	E394	1.99		0.37	
551		-----		-----	
558		-----		-----	
609	E394	2.319		1.41	
663	E394	2.237		1.15	
786	E394	1.67		-0.64	
823	E394	1.32		-1.74	
859	E394	1.90		0.09	
861	E394	1.815		-0.18	
912		-----		-----	
913		-----		-----	
963	E394	1.983		0.35	
1319	E394	1.89		0.06	
7002		-----		-----	
7006		-----		-----	
7015		-----		-----	
7016	E394	1.81		-0.20	
	normality	OK			
	n	18			
	outliers	0		Spike	
	mean (n)	1.872		2.02	Recovery < 93%
	st.dev. (n)	0.3718			
	R(calc.)	1.041			
	R(E394:09)	0.887			

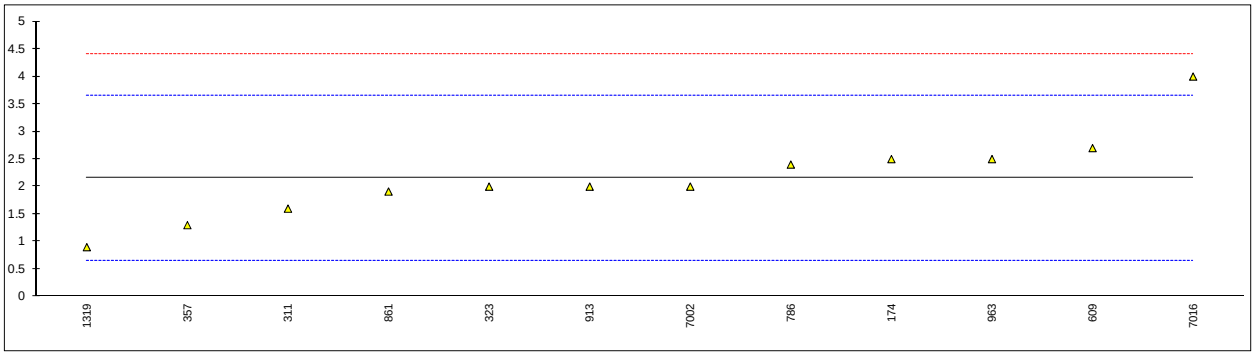


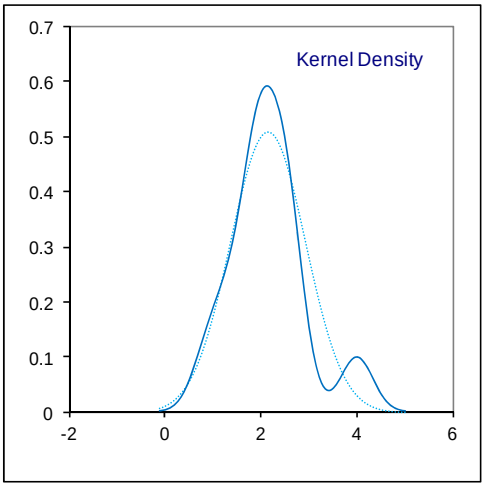


Determination of Nonvolatile Matter on sample #15005; results in mg/100 mL

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173		-----		-----	
174	D1353	2.5		0.46	
311	D1353	1.6		-0.73	
315		-----		-----	
319	D1353	<2		-----	
323	D1353	2		-0.20	
347		-----		-----	
357	D1353	1.3		-1.13	
372		-----		-----	
395		-----		-----	
551		-----		-----	
558		-----		-----	
609	D1353	2.7		0.73	
663		-----		-----	
786	D1353	2.40		0.33	
823		-----		-----	
859		-----		-----	
861	D1353	1.91		-0.32	
912		-----		-----	
913	D1353	2.0		-0.20	
963	D1353	2.5		0.46	
1319	D1353	0.9		-1.66	
7002	D1353	2.0		-0.20	
7006		-----		-----	
7015		-----		-----	
7016	D1353	4		2.45	

normality	not OK
n	12
outliers	0
mean (n)	2.15
st.dev. (n)	0.783
R(calc.)	2.19
R(D1353:13)	2.11

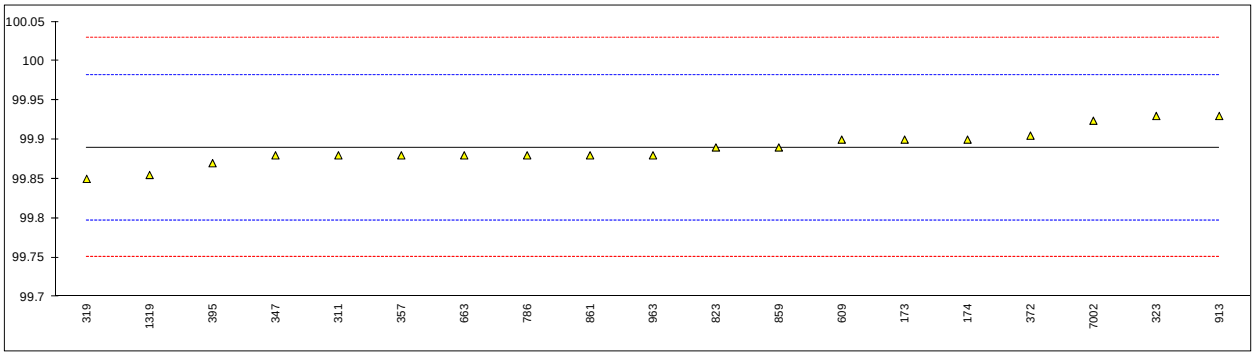


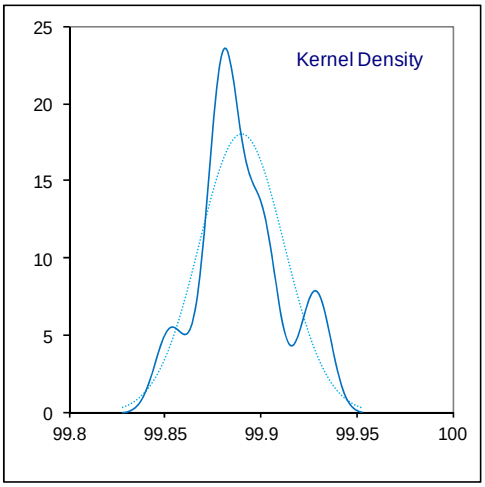


Determination of Purity (estimated from the Freezing Point) on sample #15005; results in %M/M

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	INH-124	99.90		0.22	
174	E302	99.90		0.22	
311		99.88		-0.21	
315		-----		-----	
319	ISO1392	99.85		-0.85	
323	E302	99.93		0.87	
347	E302	99.88		-0.21	
357	E302	99.88		-0.21	
372	E302	99.905		0.33	
395	INH-124	99.87		-0.42	
551		-----		-----	
558		-----		-----	
609	INH-70014	99.90		0.22	
663	E302	99.88		-0.21	
786	E302	99.88		-0.21	
823	E302	99.89		0.01	
859	E302	99.89		0.01	
861	E302	99.88		-0.21	
912		-----		-----	
913	E302	99.93		0.87	
963	E302	99.88		-0.21	
1319	E302	99.855		-0.75	
7002	in house	99.924		0.74	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	

normality	OK
n	19
outliers	0
mean (n)	99.890
st.dev. (n)	0.0221
R(calc.)	0.062
R(E302:95)	0.130

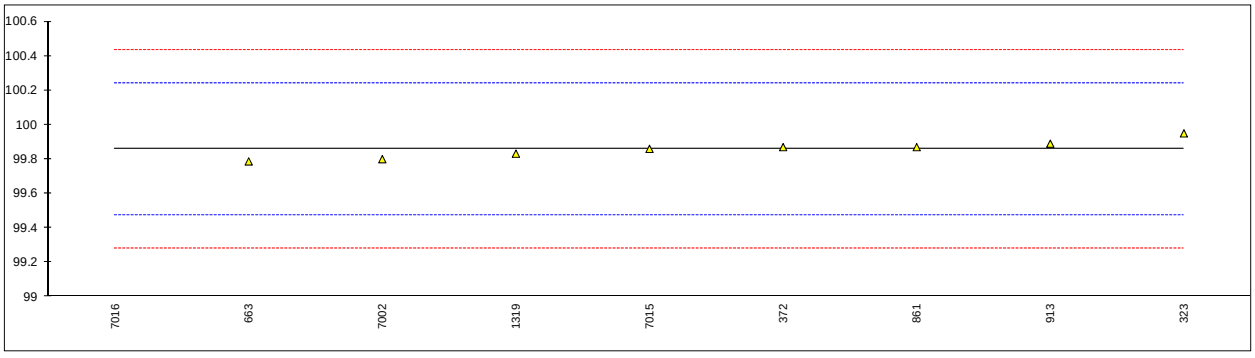


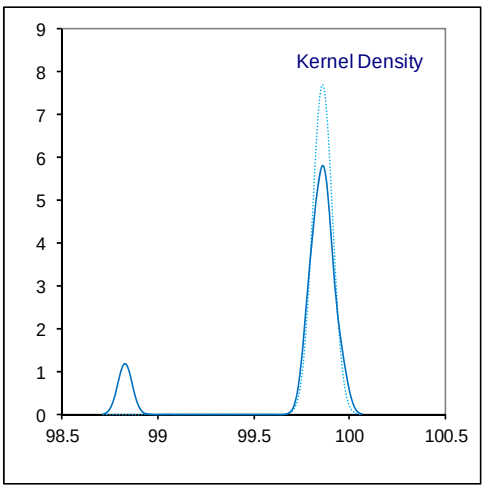


Determination of Purity (by titration) on sample #15005; results in %M/M

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173		-----		-----	
174		-----		-----	
311		-----		-----	
315		-----		-----	
319		-----		-----	
323	E301	99.95		0.48	
347		-----		-----	
357		-----		-----	
372	E301	99.87		0.07	
395		-----		-----	
551		-----		-----	
558		-----		-----	
609		-----		-----	
663	BS576-2	99.787		-0.36	
786		-----		-----	
823		-----		-----	
859		-----		-----	
861	E301	99.87		0.07	
912		-----		-----	
913	E301	99.89		0.17	
963		-----		-----	
1319	E301	99.832		-0.13	
7002	in house	99.80		-0.30	
7006		-----		-----	
7015	in house	99.86		0.01	
7016	E301	98.83	G(0.01)	-5.33	

normality	OK
n	8
outliers	1
mean (n)	99.857
st.dev. (n)	0.0519
R(calc.)	0.145
R(E301:94)	0.540





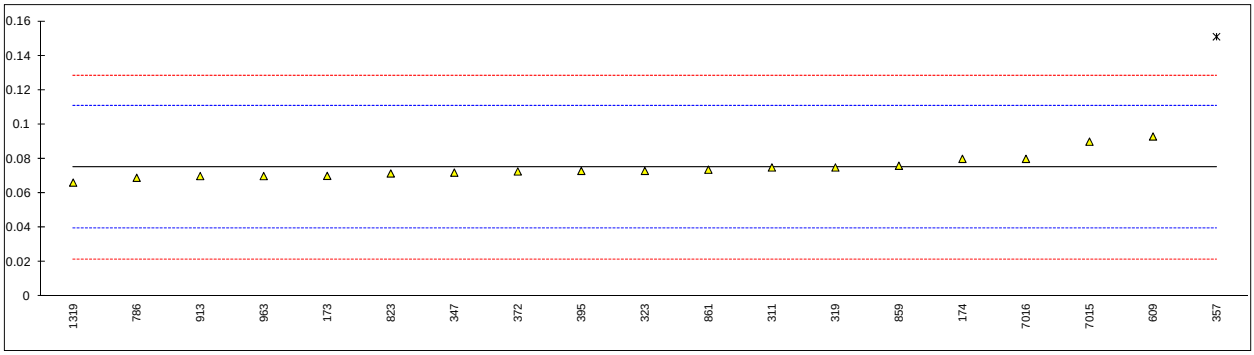
Determination of Sulphate as SO_4 on sample #15005, results in mg/kg

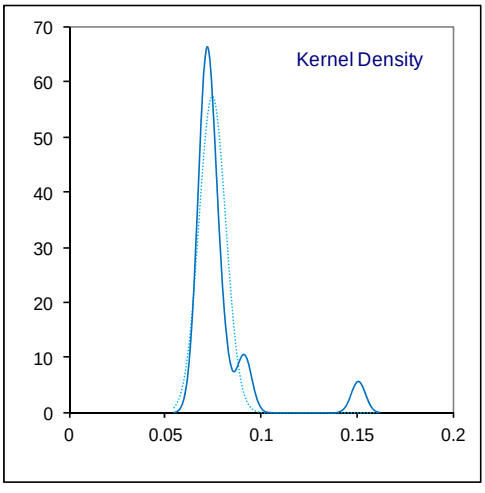
lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173		-----		-----	
174		-----		-----	
311		-----		-----	
315		-----		-----	
319	ISO753	3.4		-----	
323		-----		-----	
347		-----		-----	
357	EN15492	6.3		-----	
372		-----		-----	
395		-----		-----	
551		-----		-----	
558		-----		-----	
609		-----		-----	
663		-----		-----	
786		-----		-----	
823		-----		-----	
859		-----		-----	
861		-----		-----	
912		-----		-----	
913		-----		-----	
963	INH-1351	<10		-----	
1319	in house	3.84		-----	
7002		-----		-----	
7006		-----		-----	
7015		-----		-----	
7016		-----		-----	
	normality	n.a.			
	n	3			
	outliers	n.a.		Spike	
	mean (n)	4.51		5.19	Recovery <87%
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(Horwitz)	n.a.			

Determination of Water on sample #15005, results in %M/M

lab	method	value	mark	z(targ)	remarks
171		-----		-----	
173	E203	0.0701		-0.28	
174	E203	0.080		0.28	
311	E203	0.075		0.00	
315		-----		-----	
319	INH-5008	0.075		0.00	
323	E302	0.073		-0.11	
347	E1064	0.0720		-0.17	
357	E1064	0.151	G(0.01)	4.26	
372	E302	0.0727		-0.13	
395	E1064	0.0730		-0.11	
551		-----		-----	
558		-----		-----	
609	D1364	0.093		1.01	
663		-----		-----	
786	E1064	0.069		-0.34	
823	D1364	0.0715		-0.20	
859	E302	0.076		0.06	
861	E1064	0.0737		-0.07	
912		-----		-----	
913	E203	0.0700		-0.28	
963	E302	0.070		-0.28	
1319	E302	0.0662		-0.49	
7002		-----		-----	
7006		-----		-----	
7015	E302	0.09		0.84	
7016	E302	0.08		0.28	

normality	not OK
n	18
outliers	1
mean (n)	0.0750
st.dev. (n)	0.00696
R(calc.)	0.0195
R(E302:95)	0.0500





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	ESTONIA
1 lab in	FINLAND
2 labs in	INDIA
4 labs in	IRAN, Islamic Republic of
1 lab in	ITALY
1 lab in	JAPAN
1 lab in	MALAYSIA
3 labs in	NETHERLANDS
1 lab in	RUSSIAN FEDERATION
1 lab in	SAUDI ARABIA
1 lab in	SOUTH KOREA
1 lab in	SPAIN
1 lab in	THAILAND
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
U	= error in reporting unit
ex	= excluded from calculations
n.a.	= not applicable
wd	= withdrawn method

Literature:

1 iis 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)