Results of Proficiency Test
Caustic Soda
September 2016

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis16C06

October 2016

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1 INTRODUCTION

On request of several laboratories, the Institute for Interlaboratory Studies decided to organise again a proficiency test for the analysis of Caustic Soda (aqueous Sodium Hydroxide solution) during the annual proficiency testing program 2016/2017.
This resulted in this international Interlaboratory study, in which 33 laboratories from 20 different countries have registered for participation, see appendix 2 for the number of participants per country. In this report the results of the 2016 proficiency test on Caustic Soda are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17043 accredited laboratory. Depending of the production process a number of Caustic Soda grades are available on the market. To fulfil the scope, in this proficiency test two different samples were prepared: one with a low concentration Chloride (low salt) and one with a relatively high concentration Chloride (high salt).
Sample #16165 was an original low NaCl Caustic Soda. Sample #16166 was the same Caustic spiked with Sodium Chloride, Sodium Chlorate and Sodium Sulfate. All materials used for spiking were >99% pure. The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for the statistical evaluations.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043:2010 (R007). 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 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). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

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 30 litre bulk material was provided by a third party. From this batch, after homogenizing, 44 HDPE bottles of 0.5 litre (labelled #16165) were filled.

The homogeneity of the subsamples #16165 was checked by determination of Density at 20°C in accordance with ASTM D4052 and Total Alkalinity as NaOH in accordance with ASTM E291 on 4 stratified randomly selected samples.

	Density at 20°C in kg/L	*Total Alkalinity as NaOH in %M/M*
sample #16165-1	1.52309	49.93
sample #16165-2	1.52308	49.94
sample #16165-3	1.52308	49.88
sample #16165-4	1.52308	49.87

Table 1: homogeneity test results of subsamples #16165

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

	Density at 20°C in kg/L	*Total Alkalinity as NaOH in %M/M*
r (observed)	0.00001	0.098
reference test method	ISO12185:96	ASTM E291:09
0.3 x R (ref. test method)	0.00015	0.210

Table 2: evaluation of repeatabilities of the subsamples #16165

The remaining bulk material of 6.5 L (10 kg) was spiked with the components listed in table 3:

Component	*Amount*
Sodium Chloride	90 g
Sodium Chlorate	10 g
Sodium Sulfate	2.5 g

Table 3: components that were added to bulk material for sample #16166

After homogenisation this batch was divided over 69 HDPE bottles of 100mL and labelled #16166. The homogeneity of the subsamples #16166 was checked by determination of Sodium Chloride as NaCl in accordance with ASTM E291 on 4 stratified randomly selected samples.

	Sodium Chloride as NaCl in mg/kg
sample #16166-1	8667
sample #16166-2	8664
sample #16166-3	8703
sample #16166-4	8685

Table 4: homogeneity test results of subsamples #16166

From the above test results the repeatability was calculated and compared with 0.3 times the corresponding reproducibility of the reference test method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Sodium Chloride as NaCl in mg/kg
r (observed)	51
reference test method	ASTM E291:09
0.3 x R (ref. test method)	240

Table 5: evaluation of the repeatability of the subsamples #16166

The calculated repeatabilities were in agreement with 0.3 times the corresponding reproducibilities of the reference test methods. Therefore, homogeneity of the subsamples #16165 and #16166 were assumed.

To the participants a sample of 1x0.5L, labelled #16165 and a sample of 1x100 mL, labelled #16166 were sent on August 17, 2016.

2.5 STABILITY OF THE SAMPLES

The stability of Caustic Soda, packed in the HDPE bottles, was checked. The material was found sufficiently stable for the period of the proficiency test.

2.6 ANALYSES

The participants were requested to determine Alkalinity as NaOH, Appearance, Density at 20°C, Iron as Fe, Sodium Chloride as NaCl, Sodium Chlorate as $NaClO_3$ and Sodium Sulphate as Na_2SO_4 on the low salt sample #16165. On the high salt sample #16166 was requested to determine Sodium Chloride as NaCl, Sodium Chlorate as $NaClO_3$ and Sodium Sulphate as Na_2SO_4.

To get comparable results a detailed report form, on which the units were prescribed as well as the required reference test method and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis/. The laboratories were also requested to confirm the sample receipt on the same data entry portal together with some details of the test methods used. A SDS was added to the samples.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis/. The reported test results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.
Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test 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 reported test results (no reanalysis). Additional or corrected test results are used for data analysis and original test results are placed under 'Remarks' in the test result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization 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).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test 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 test results should be used with due care.

According to ISO 5725 the original test results per determination were submitted to Dixon’s, 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. 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 them with a factor of 2.8.

3.2 GRAPHICS

In order to visualize 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 test 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 reference test method. 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. 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 variation 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.
The z-scores were calculated according to:

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

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

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 interlaboratory study, problems with sample dispatch were encountered due to custom clearance for the participants in Brazil. Three participants did not report any result at all. All other participants reported the test results in time before the final reporting date. Not all participants were able to report all requested parameters. Finally, 30 participants did report 175 numerical results. Observed were 17 outlying test results, which is 9.7% of the total of numerical test results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER SAMPLE AND PER TEST

In this section, the reported test 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 test results. The abbreviations, used in these tables, are listed in appendix 3. In this section, the results are discussed per test.

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.

Sample #16165

Alkalinity: This determination was not problematic. No statistical outliers were observed. The observed reproducibility is in good agreement with the requirements of ASTM E291:09.

Appearance: All labs agreed about the appearance of the sample #16165, which was Pass (bright, clear and free from suspended matter).

Density at 20°C: This determination was problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of ISO12185:96.
The current version of test method ASTM D4052:15 is applicable only for the density range 0.71 to 0.88 g/ml, being valid for gasolines, distillates, base stocks and lubricating oils. Therefore this 2015 version may be not applicable for Caustic Soda.

Iron: This determination was problematic. Five statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is not in agreement with the requirements of ASTM E291:09.

Sodium Chloride: This determination was problematic for a number of laboratories at the low level 42.4 mg/kg. Three statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in agreement with the requirements of ASTM E291:09.

Sodium Chlorate: This determination was not problematic at the low level 4.0 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of ASTM E1787:16.

Sodium Sulphate: This determination was not problematic at the low level 13.3 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of ASTM E1787:16.

Sample #16166

Sodium Chloride: This determination was problematic at the high level of 0.85%M/M. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the requirements of ASTM E291:09. This sample was spiked with Sodium Chloride. The recovery of 94% is good (($0.8545_{(avg.)} - 0.0042_{(avg. of blank)}$) / $0.9053_{(added amount)}$ * 100%).

Sodium Chlorate: This determination was not problematic at the high level of 0.097%M/M. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility estimated from the Horwitz equation.
This sample was spiked with Sodium Chlorate. The recovery of 96% is good (($0.0968_{(avg.)} - 0.0004_{(avg. of blank)}$) / $0.1003_{(added amount)}$ * 100%).

Sodium Sulphate: This determination was problematic at the high level of 0.0137%M/M. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the requirements of ASTM E291:09. This sample was spiked with Sodium Sulphate. The recovery of 43% is marginal (($0.0137_{(avg.)} - 0.0013_{(avg. of blank)}$) / $0.0290_{(added amount)}$ * 100%).

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant reference test method 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)*
Alkalinity as NaOH	%M/M	29	49.79	0.38	0.70
Appearance	---	23	Pass	n.a.	n.a.
Density at 20°C	kg/L	25	1.5231	0.0007	0.0005
Iron as Fe	mg/kg	19	1.33	0.43	0.39
Sodium Chloride as NaCl	mg/kg	20	42.4	15.3	15.0
Sodium Chlorate as $NaClO_3$	mg/kg	10	4.0	2.8	5.6
Sodium Sulphate as Na_2SO_4	mg/kg	10	13.3	24.4	30.8

Table 6: Reproducibilities for sample #16165

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (lit)*
Sodium Chloride as NaCl	%M/M	20	0.855	0.093	0.080
Sodium Chlorate as $NaClO_3$	%M/M	11	0.097	0.015	0.015
Sodium Sulphate as Na_2SO_4	%M/M	14	0.014	0.017	0.012

Table 7: Reproducibilities for sample #16166

Without further statistical calculations, it can be concluded that for several 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 SEPTEMBER 2016 WITH PREVIOUS PT

	September 2016	*September 2014*	*September 2012*
Number of reporting labs	30	26	25
Number of results reported	175	150	145
Statistical outliers	17	10	13
Percentage outliers	9.7%	6.7%	9.0%

Table 8: 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 reference test methods. The conclusions are given the following table:

	September 2016	*September 2014*	*September 2012*
Low Salt Caustic Soda:			
Alkalinity as NaOH	++	+	+
Density at 20°C	-	-	-
Iron as Fe	-	+/-	-
Sodium Chloride as NaCl	+/-	--	-
Sodium Chlorate as $NaClO_3$	++	(--)	(--)
Sodium Sulphate as Na_2SO_4	+	(--)	-
High Salt Caustic Soda:			
Sodium Chloride as NaCl	-	-	+
Sodium Chlorate as $NaClO_3$	+/-	+	--
Sodium Sulphate as Na_2SO_4	-	(-)	+

Table 9: comparison determinations against the standard

() the average was below the application range of the reference method

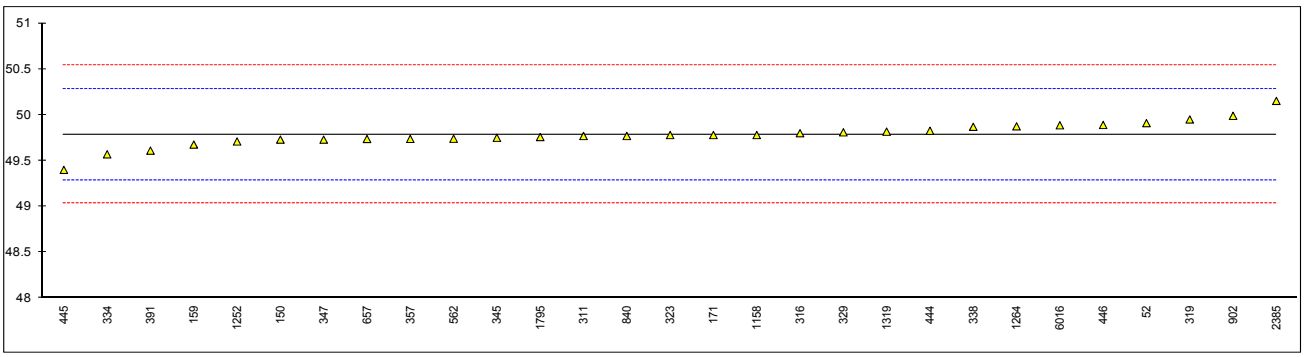
The performance of the determinations against the requirements of the respective standards is listed in the above table. The following performance categories were used:

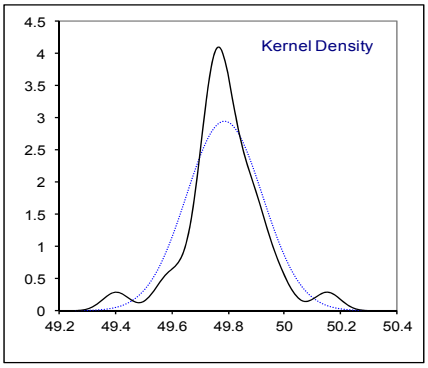
++: group performed much better than the reference test method
+ : group performed better than the reference test method
+/-: group performance equals the reference test method
- : group performed worse than the reference test method
-- : group performed much worse than the reference test method
n.e.: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

APPENDIX 1

Determination of Alkalinity as NaOH on sample #16165; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	E291	49.91		0.49	
150	E291	49.73		-0.23	
159	E291	49.676		-0.44	
169		-----		-----	
171	E291	49.78		-0.03	
311	E291	49.77		-0.07	
316	INH-041	49.8		0.05	
319	INH-726	49.95		0.65	
323	E291	49.78	C	-0.03	First reported 46.78
329	E291	49.81		0.09	
334	E291	49.57		-0.87	
338	E291	49.87		0.33	
345	E291	49.75		-0.15	
347	D501	49.73		-0.23	
357	E291	49.738		-0.19	
391	E291	49.61		-0.71	
444	E291	49.827		0.16	
445	E291	49.4		-1.55	
446	E291	49.89		0.41	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562	INH 480	49.74	C	-0.19	First reported 49.07
657	E291	49.737		-0.20	
840	E291	49.770		-0.07	
902	E291	49.99		0.81	
1158	E291	49.78		-0.03	
1252	E291	49.71		-0.31	
1264	In house	49.875		0.35	
1319	E291	49.817		0.12	
1795	INH-3068	49.758		-0.11	
2385	E291	50.153		1.47	
6016	UOP209	49.8865		0.40	
	normality	not OK			
	n	29			
	outliers	0			
	mean (n)	49.786			
	st.dev. (n)	0.1360			
	R(calc.)	0.381			
	R(E291:09)	0.700			





Determination of Appearance on sample #16165;

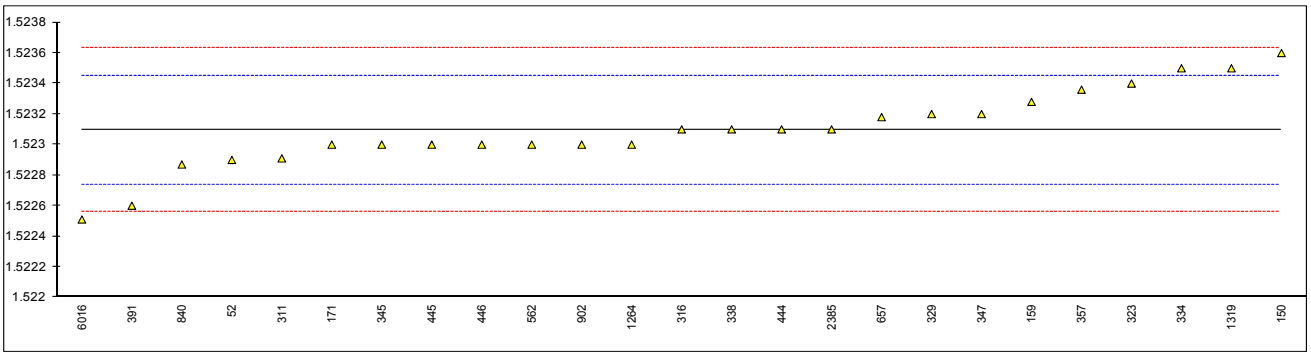
lab	method	value	mark	z(targ)	remarks
52	D4176	Pass		-----	
150	E2680	Pass		-----	
159	D4176	clear		-----	
169		-----		-----	
171	E2680	Pass		-----	
311	E2680	pass		-----	
316		-----		-----	
319		-----		-----	
323	E2680	clear & bright		-----	
329	E2680	PASS		-----	
334		-----		-----	
338	Visual	Clear and Bright		-----	
345	Visual	pass		-----	
347	E2680	Pass		-----	
357	E2680	Pass		-----	
391	E2680	Pass		-----	
444	E2680	Pass		-----	
445	E2680	Pass		-----	
446	E2680	Pass		-----	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562	E2680	PASS		-----	
657	E2680	PASS		-----	
840	E2680	Pass		-----	
902	E2680	PASS		-----	
1158		-----		-----	
1252	Visual	CLEAR		-----	
1264	Visual	Clear & Bright		-----	
1319	Visual	Clear liquid		-----	
1795		-----		-----	
2385	E2680	Clear&bright, colorless		-----	
6016		-----		-----	

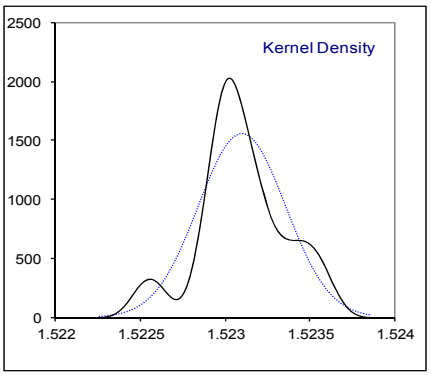
normality	unknown
n	23
outliers	n.a.
mean (n)	Pass
st.dev. (n)	n.a.
R(calc.)	n.a.
R(E2680:09e1)	n.a.

Determination of Density at 20°C on sample #16165; results in kg/L

lab	method	value	mark	z(targ)	remarks
52	D4052	1.5229		-1.10	
150	D4052	1.5236	C	2.82	First reported 1.5239
159	D4052	1.52328		1.03	
169		-----		-----	
171	D4052	1.523		-0.54	
311	D4052	1.52291	C	-1.04	First reported 1.52991
316	INH-009	1.5231		0.02	
319		-----		-----	
323	D4052	1.5234		1.70	
329	D4052	1.5232		0.58	
334	ISO12185	1.5235		2.26	
338	ISO12185	1.5231		0.02	
345	D4052	1.5230		-0.54	
347	D4052	1.5232		0.58	
357	D4052	1.52336		1.48	
391	ISO12185	1.5226		-2.78	
444	D4052	1.5231		0.02	
445	ISO12185	1.5230	C	-0.54	First reported 1.532
446	D4052	1.523		-0.54	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562	D4052	1.523		-0.54	
657	D4052	1.52318		0.47	
840	D4052	1.52287		-1.27	
902	D4052	1.5230		-0.54	
1158		-----		-----	
1252		-----		-----	
1264	D4052	1.5230		-0.54	
1319	ISO12185	1.5235		2.26	
1795		-----		-----	
2385	ISO12185	1.5231		0.02	
6016	D4052	1.52251		-3.28	

normality	OK
n	25
outliers	0
mean (n)	1.52310
st.dev. (n)	0.000257
R(calc.)	0.00072
R(ISO12185:96)	0.00050

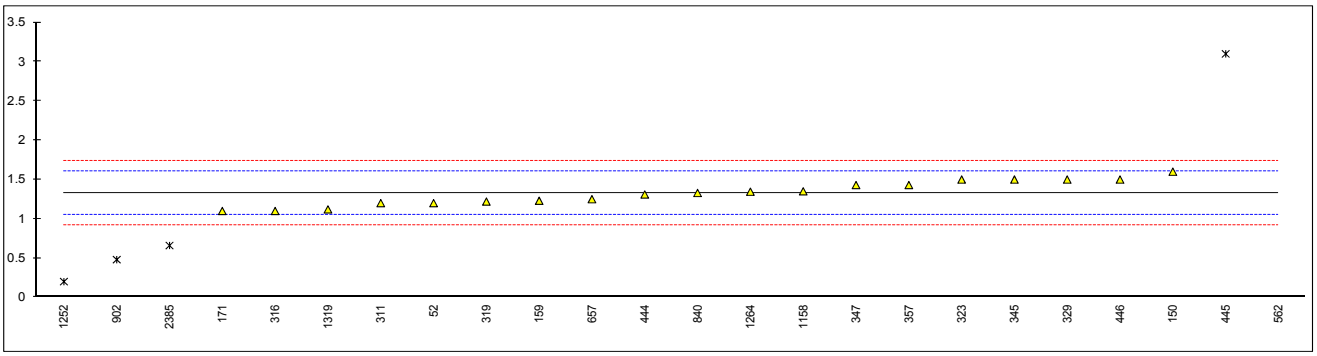


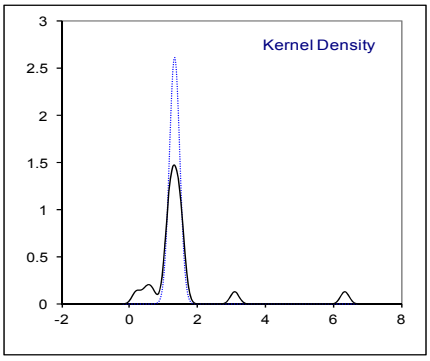


Determination of Iron as Fe on sample #16165; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	E291	1.2		-0.92	
150	E291	1.6		1.99	
159	E291	1.23		-0.71	
169		-----		-----	
171	E291	1.1		-1.65	
311	E291	1.2		-0.92	
316	INH-043	1.1		-1.65	
319	INH-104	1.22		-0.78	
323	E291	1.5		1.26	
329	E291	1.5		1.26	
334		-----		-----	
338		-----		-----	
345	E291	1.5		1.26	
347	E291	1.43		0.75	
357	E291	1.43		0.75	
391		-----		-----	
444	E291	1.31		-0.12	
445	E291	3.1	R(0.01)	12.90	
446	E291	1.5		1.26	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562	E291	6.347	C,R(0.01)	36.52	First reported 3.995
657	E291	1.25		-0.56	
840	E291	1.329		0.01	
902	E291	0.48	R(0.01)	-6.16	
1158	INH-3068	1.35		0.17	
1252	E291	0.20	R(0.01)	-8.20	
1264	E291	1.345		0.13	
1319	E291	1.12		-1.51	
1795		-----		-----	
2385	ICP	0.66	R(0.01)	-4.85	
6016		-----		-----	

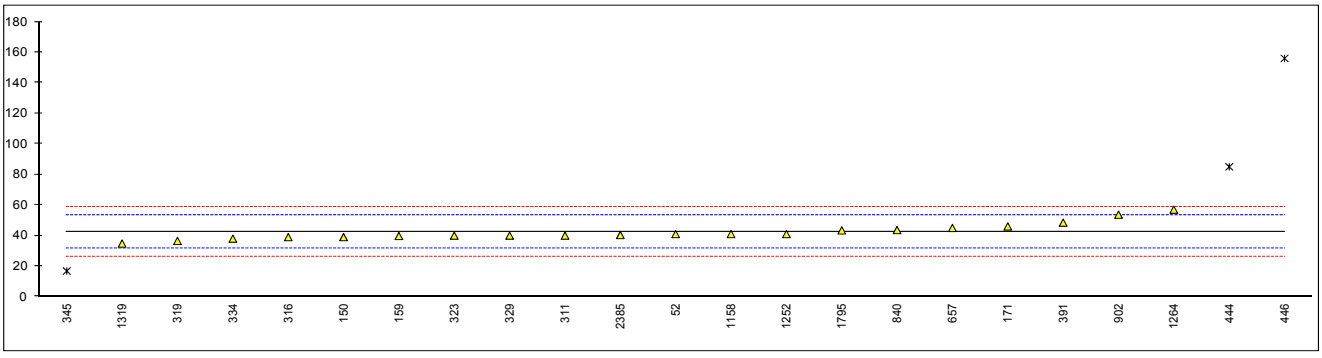
normality	OK
n	19
outliers	5
mean (n)	1.327
st.dev. (n)	0.1530
R(calc.)	0.429
R(E291:09)	0.385

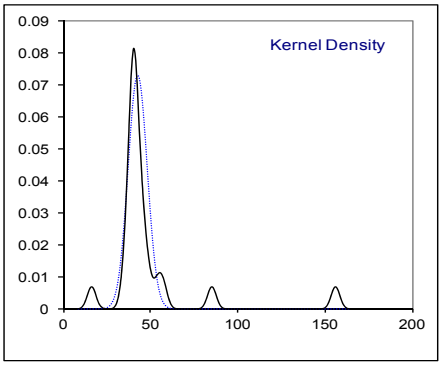




Determination of Sodium Chloride as NaCl on sample #16165; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	In house	41		-0.26	
150	E1787	39		-0.63	
159	In house	39.74		-0.49	
169		-----		-----	
171	E291	46		0.67	
311	INH-554	40		-0.45	
316	INH-044	39		-0.63	
319	INH-269	36.5		-1.10	
323	E291	40		-0.45	
329	E291	40		-0.45	
334	E1787	38		-0.82	
338		-----		-----	
345	E291	16.8	R(0.01)	-4.78	
347		-----		-----	
357	E291	<100		-----	
391	E291	48.5		1.14	
444	E291	85	C,R(0.01)	7.95	First reported 22
445		-----		-----	
446	E291	156	R(0.01)	21.21	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562		-----		-----	
657	E291	45	C	0.49	First reported15.94
840	E291	43.65		0.24	
902	In house	53.7		2.11	
1158	E291	41		-0.26	
1252	E291	41		-0.26	
1264	E291	57		2.73	
1319	INH-1200	34.8		-1.42	
1795	E291	43.41		0.19	
2385	E291	40.39		-0.37	
6016		-----		-----	
	normality	not OK			
	n	20			
	outliers	3			
	mean (n)	42.384			
	st.dev. (n)	5.4757			
	R(calc.)	15.332			
	R(E291:09)	15.000			Compare R(E1787:16) = 12.900



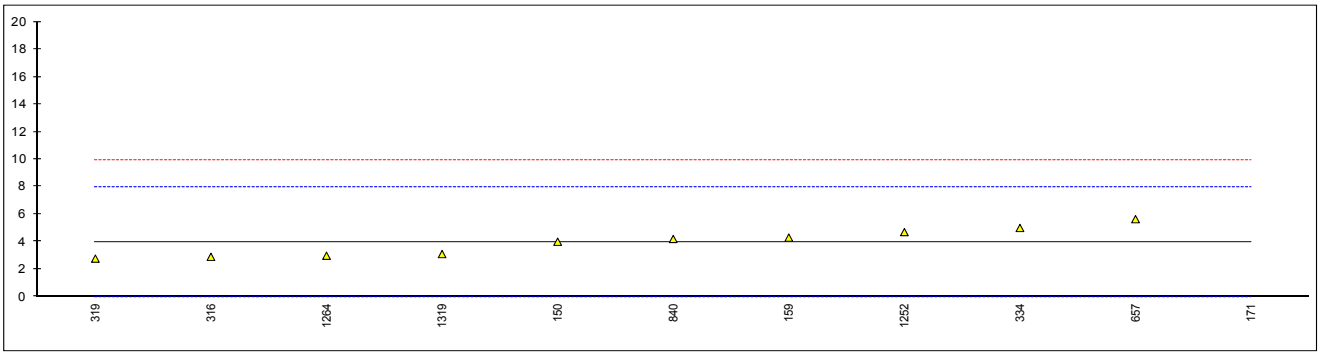


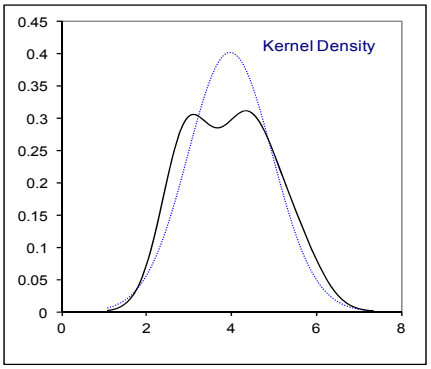
Determination of Sodium Chlorate as $NaClO_3$ on sample #16165; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	In house	<10	C	-----	First reported 18
150	E1787	4.0		0.02	
159	D2022	4.3		0.17	
169		-----		-----	
171	INH-1112	800	G(0.01)	398.02	
311		-----		-----	
316	INH-075	2.9		-0.53	
319	INH-888	2.77		-0.59	
323	In house	<10		-----	
329		-----		-----	
334	E1787	5		0.52	
338		-----		-----	
345		-----		-----	
347		-----		-----	
357		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562		-----		-----	
657	INH-1112	5.64		0.84	
840	INH-1112	4.2		0.12	
902		-----		-----	
1158		-----		-----	
1252	In house	4.7		0.37	
1264	In house	2.98		-0.49	
1319	In house	3.1		-0.43	
1795		-----		-----	
2385	EN896	<100		-----	
6016		-----		-----	

	normality	OK
	n	10
	outliers	1
	mean (n)	3.959
	st.dev. (n)	0.9925
	R(calc.)	2.779
	R(E1787:16)	5.600

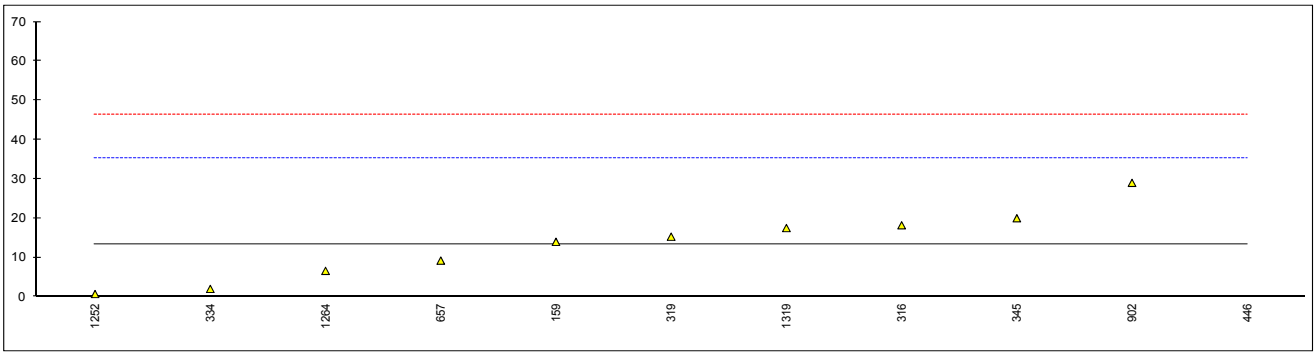
Compare R(Horwitz) = 1.442

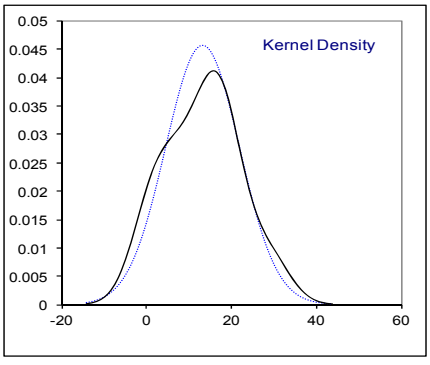




Determination of Sodium Sulphate as Na_2SO_4 on sample #16165; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	In house	<20		-----	
150		-----		-----	
159	E291	14		0.07	
169		-----		-----	
171		-----		-----	
311	E291	<40		-----	
316	INH-066	18.2		0.45	
319	INH-862	15.3		0.19	
323	E291	<10		-----	
329		-----		-----	
334	E1787	2		-1.02	
338		-----		-----	
345	E291	20	C	0.61	Reported 0.002 mg/kg, probably unit error?
347		-----		-----	
357		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446	E291	675	G(0.01)	60.16	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562		-----		-----	
657	E291	9.21		-0.37	
840	E291	<20		-----	
902	In house	29.0		1.43	
1158		-----		-----	
1252	E291	0.70		-1.14	
1264	E291	6.6		-0.60	
1319	INH-1200	17.5		0.39	
1795		-----		-----	
2385	E291	<20		-----	
6016		-----		-----	
	normality	OK			
	n	10			
	outliers	1			
	mean (n)	13.251			
	st.dev. (n)	8.7278			
	R(calc.)	24.438			
	R(E1787:16)	30.800			Compare R(E291:09) = 9.451



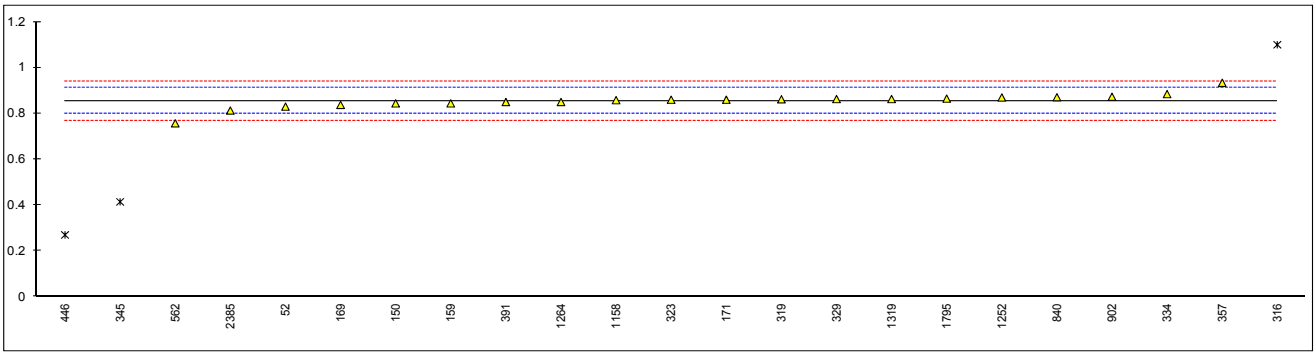


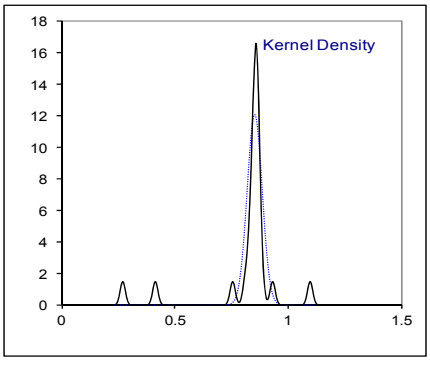
Determination of Sodium Chloride as NaCl on sample #16166; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	In house	0.83		-0.86	
150	E1787	0.844		-0.37	
159	In house	0.84406		-0.36	
169	E291	0.8375		-0.59	
171	E291	0.86		0.19	
311	INH-554	>0.02		-----	
316	INH-044	1.1	R(0.01)	8.59	
319	INH-269	0.862		0.26	
323	E291	0.86		0.19	
329	E291	0.8629		0.30	
334	E1787	0.8846		1.06	
338		-----		-----	
345	E291	0.41429	C,R(0.01)	-15.41	Reported 4142.9 %M/M, probably unit error?
347		-----		-----	
357	E291	0.934		2.78	
391	E291	0.85		-0.16	
444		-----		-----	
445		-----		-----	
446	E291	0.27	R(0.01)	-20.46	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562	E291	0.757		-3.41	
657		-----		-----	
840	E291	0.871		0.58	
902	E1787	0.873		0.65	
1158	E291	0.8581		0.13	
1252	E291	0.87		0.54	
1264	E291	0.85		-0.16	
1319	INH-1200	0.863		0.30	
1795	E291	0.8649		0.37	
2385	E291	0.813		-1.45	
6016		-----		-----	

	normality	not OK
	n	20
	outliers	3
	mean (n)	0.8545
	st.dev. (n)	0.03312
	R(calc.)	0.0927
	R(E291:09)	0.0800

Spike: 0.9053

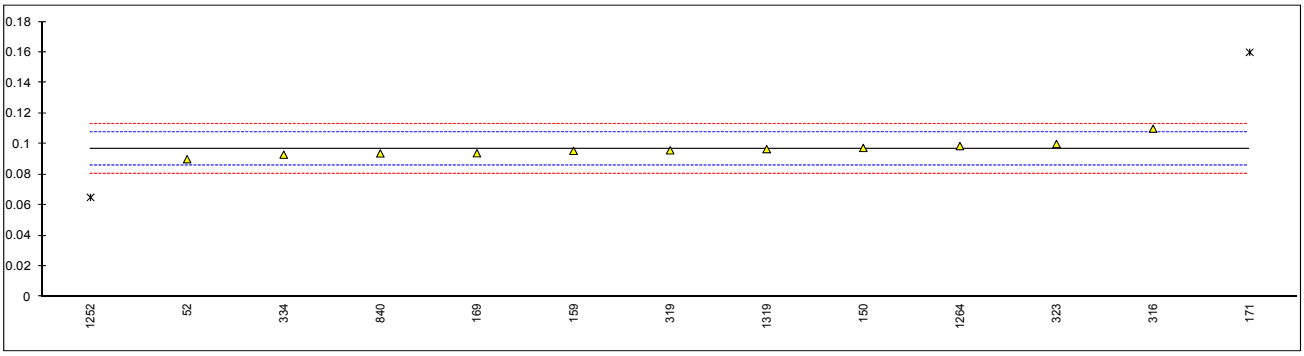


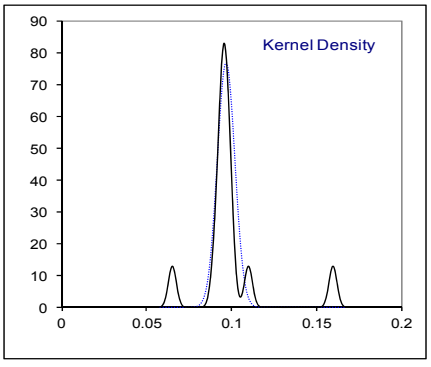


Determination of Sodium Chlorate as $NaClO_3$ on sample #16166; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	In house	0.090		-1.23	
150	E1787	0.0974		0.11	
159	D2022	0.0955		-0.23	
169	In house	0.0939		-0.52	
171	INH-1112	0.16	G(0.01)	11.49	
311		-----		-----	
316	INH-075	0.11		2.40	
319	INH-888	0.09582		-0.17	
323	In house	0.10		0.58	
329		-----		-----	
334	E1787	0.0930	C	-0.69	First reported 994
338		-----		-----	
345		-----		-----	
347		-----		-----	
357		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562		-----		-----	
657		-----		-----	
840	In house	0.09379		-0.54	
902		-----		-----	
1158		-----		-----	
1252	In house	0.065	G(0.01)	-5.78	
1264	In house	0.0986	C	0.33	First reported 986
1319	In house	0.0966		-0.03	
1795		-----		-----	
2385	EN896	<0.01		<-15.77	False negative test result?
6016		-----		-----	

	normality	not OK
	n	11
	outliers	2
	mean (n)	0.0968
	st.dev. (n)	0.00519
	R(calc.)	0.0145
	R(Horwitz)	0.0154



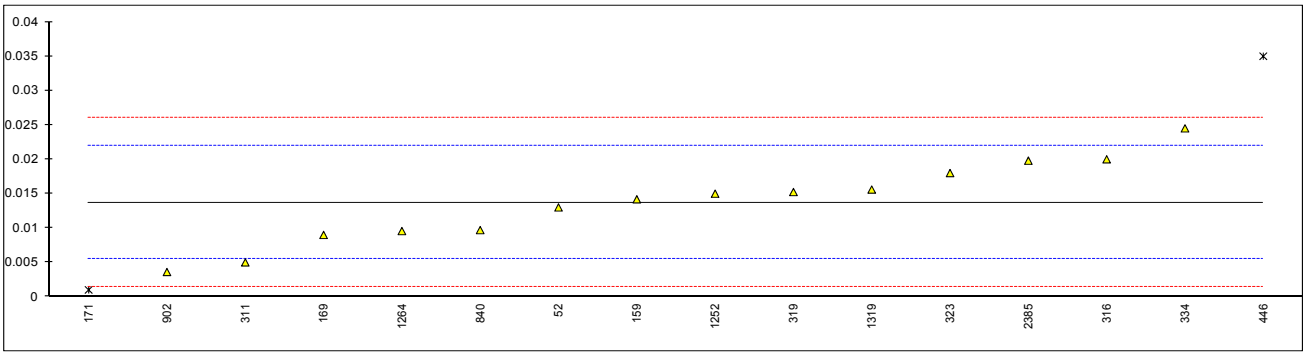


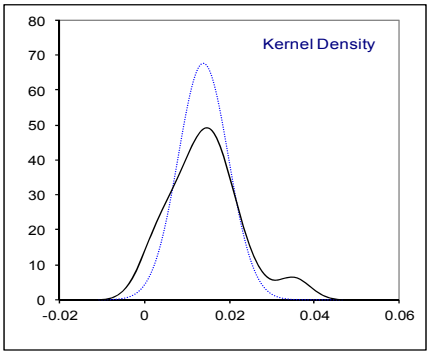
Determination of Sodium Sulphate as Na_2SO_4 on sample #16166; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	E291	0.013		-0.18	
150		-----		-----	
159	E291	0.01418		0.11	
169	E291	0.0090		-1.15	
171	E291	0.001	G(0.05)	-3.09	
311	E291	0.0050		-2.12	
316	INH-066	0.02		1.52	
319	INH-862	0.01524		0.37	
323	E291	0.018		1.04	
329		-----		-----	
334	E1787	0.0245	C	2.62	First reported 215
338		-----		-----	
345		-----		-----	
347		-----		-----	
357		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446	E291	0.035	G(0.05)	5.17	
551		-----		-----	
554		-----		-----	
557		-----		-----	
562		-----		-----	
657		-----		-----	
840	E291	0.0097		-0.98	
902	E1787	0.0036		-2.46	
1158		-----		-----	
1252	E291	0.0150		0.31	
1264	E291	0.00956	C	-1.01	First reported 95.6
1319	INH-1200	0.0156		0.45	
1795		-----		-----	
2385	E291	0.0198		1.47	
6016		-----		-----	

	normality	OK
	n	14
	outliers	2
	mean (n)	0.0137
	st.dev. (n)	0.00591
	R(calc.)	0.0165
	R(E291:09)	0.0115

<u>Spike:</u>
0.0290





APPENDIX 2

Number of participants per country

2 labs in BELGIUM
3 labs in BRAZIL
1 lab in CANADA
1 lab in CHILE
1 lab in FINLAND
2 labs in FRANCE
1 lab in GERMANY
1 lab in ITALY
1 lab in JAPAN
1 lab in KAZAKHSTAN
3 labs in NETHERLANDS
2 labs in ROMANIA
1 lab in SAUDI ARABIA
1 lab in SINGAPORE
2 labs in SPAIN
1 lab in TURKEY
1 lab in UNITED ARAB EMIRATES
3 labs in UNITED KINGDOM
4 labs in UNITED STATES OF AMERICA
1 lab in VIETNAM

APPENDIX 3

Abbreviations:

C = final test result after checking of first reported suspect test 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 = probably an error in calculations
U = test result probably reported in a different unit
W = test result withdrawn on request of participant
ex = test result excluded from calculations
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected
fr. = first reported
SDS = Safety Data Sheet

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
2 ASTM E178:02
3 ASTM E1301:95 (2003)
4 ISO 5725:86
5 ISO 5725, parts 1-6:94
6 ISO 13528:05
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 367:96
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 ASTM E346:03e1
14 Analytical Methods Committee Technical brief, No 4 January 2001.
15 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry 2002, Analyst 2002, 127, 1359-1364
16 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, *Technometrics*, 25(2), 165-172, (1983)