

Results of Proficiency Test
Caustic Soda
September 2014

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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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 2014/2015.

This resulted in this international Interlaboratory study, in which 30 laboratories from 18 different countries have participated. See appendix 2 for a list of participants in alphabetical country order. In this report the results of the 2014 proficiency test on Caustic Soda 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 in Spijkenisse, the Netherlands, was the organiser of this proficiency test. Sample analyses for fit-for-use and homogeneity testing were subcontracted. 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 very low concentration chloride (low salt) and one with a relatively high concentration chloride (high salt).

Sample #14163 was an original low NaCl Caustic Soda. Sample #14164 was the same Caustic spiked with Sodium Chloride (8999 mg/kg), Sodium Chlorate (1000 mg/kg) and Sodium Sulfate (11.1 mg/kg). All materials used for spiking were >99% pure. The participants were requested to report rounded and unrounded results. The unrounded 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. Also customer's satisfaction is measured on regular basis by the distribution of 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).

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 35 litre bulk material was provided by a third party. From this batch, after homogenizing, 50 HDPE bottles of 0.5 litre (labelled #14163) were filled.

The homogeneity of the subsamples #14163 was checked by determination of Density at 20°C in accordance with ASTM D4052 and Alkalinity in accordance with ASTM E291 on 4 stratified randomly selected samples.

	<i>Density at 20°C in kg/L</i>	<i>Alkalinity in %M/M</i>
sample #14163-1	1.52400	49.90
sample #14163-2	1.52401	49.87
sample #14163-3	1.52400	49.90
sample #14163-4	1.52402	49.91

Table 1: homogeneity test results of subsamples #14163

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

	<i>Density at 20°C in kg/L</i>	<i>Alkalinity in %M/M</i>
r (sample #14163)	0.00003	0.048
reference test	ASTM D4052:02e1	ASTM E291:09
0.3*R (reference test)	0.00015	0.210

Table 2: evaluation of repeatabilities of the subsamples #14163

The remaining bulk material (9.4 kg = approx. 7.4 litre) was spiked with the components listed in table 3:

<i>Component</i>	<i>Amount</i>
Sodium Chloride	100.4 g
Sodium Chlorate	11.18 g
Sodium Sulfate	0.125 g

Table 3: components that were added to bulk material for sample #14164

After homogenisation this batch was divided over 69 HDPE bottles of 100mL and labelled #14164.

The homogeneity of the subsamples #14164 was checked by determination of Density at 20°C in accordance with ASTM D4052 and Sodium Chloride in accordance with ASTM E291 on 4 stratified randomly selected samples.

	<i>Density at 20°C in kg/L</i>	<i>Sodium Chloride as NaCl in mg/kg</i>
sample #14164-1	1.50926	8205
sample #14164-2	1.50926	8245
sample #14164-3	1.50927	8215
sample #14164-4	1.50926	8235

Table 4: homogeneity tests results of subsamples #14164

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

	<i>Density at 20°C in kg/L</i>	<i>Sodium Chloride as NaCl in mg/kg</i>
r (sample #14164)	0.00001	51
reference test	ASTM D4052:02e	ASTM E291:09
0.3*R (reference test)	0.00015	240

Table 5: repeatabilities of the subsamples #14164

The calculated repeatabilities were less than 0.3 times the corresponding reproducibilities of the reference method. Therefore, homogeneity of the subsamples #14163 and #14164 was assumed.

To the participants, depending on the registration, 1*0.5L bottle, labelled #14163 and 1*100 mL bottle, labelled #14164 were sent on August 20, 2014.

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 NaClO₃ and Sodium Sulfate as SO₄ on the low salt sample #14163. On the high salt sample #14164 was requested to determine Sodium Chloride as NaCl, Sodium Chlorate as NaClO₃ and Sodium Sulfate as SO₄.

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 gathered. The original data are tabulated per determination in appendix 1 of this report. The laboratories are represented by their code numbers.

Directly after the deadline, a reminder fax was sent to the laboratories that had not reported 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 '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.16). 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.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them 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 is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3; no.14 and 15). Also a normal Gauss curve was projected over the Kernel Density Graph.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. ASTM reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study. The target standard deviation was calculated from the literature reproducibility by division with 2.8.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.

The z-scores were calculated in accordance with:

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

The $z_{(\text{target})}$ 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 maybe 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. Six participants reported after the deadline and 4 participants did not report any result at all. Not all participants were able to report all requested parameters. Finally, 26 participants did report 150 numerical results. Observed were 10 outlying results, which is 6.7% 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.

In the iis PT reports, ASTM methods are referred to with a number (e.g. D2086) and an added designation for the year that the method was adopted or revised (e.g. D2086-08). If applicable, a designation in parentheses is added to designate the year of reapproval (e.g. D2086-08 (2013)). In the results tables of Appendix 1 only the method number and year of adoption or revision will be used.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as "not OK" or "suspect". The statistical evaluation of these data sets should be used with due care.

Alkalinity: This determination was not problematic. One statistical outlier was observed. The observed reproducibility after rejection of the statistical outlier is in agreement with the requirements of ASTM E291:09.

Appearance: All labs, except one, agreed about the appearance of the sample #14163, which was bright, clear and free from suspended matter.

Density @ 20°C: This determination was problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of ASTM D4052:02e1. The current version of test method ASTM D4052:11 is applicable only for the density range 0.71 g/ml to 0.88 g/ml, being valid for gasoline's, distillates, base stocks and lubricating oils. Therefore this 2011 version is may be not applicable for Caustic Soda.

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

Sodium Chloride: For sample #14163, this determination was very problematic at the low level 48.3 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the requirements of ASTM E291:09. Sample #14164, was spiked with sodium chloride. 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. The recovery of 91% is good $((0.8111_{(avg.)} - 0.0048_{(avg. \text{ of blank})}) / 0.8999_{(added \text{ amount})} * 100\%)$.

Sodium Chlorate: For sample #14163, it is hard to draw conclusions, as the test results vary over a large range (2.1 -115). Therefore, no z-scores were calculated. Sample #14164 was spiked with sodium chlorate (NaClO₃). Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with requirements calculated using the Horwitz equation. The recovery of 86% is good $((0.0919_{(avg.)} - 0.0062_{(avg. \text{ of blank})}) / 0.100_{(added \text{ amount})} * 100\%)$.

Sodium Sulphate: For sample #14163 and #14164 it is hard to draw conclusions. The consensus value found for each sample was respectively 7.9 and 16 mg SO₄/kg. These are below the application range of ASTM E291:09 (chapter 67). Therefore, no z-scores were calculated for both samples. Regretfully, the amount Sulphate spiked on sample #14164 was too small to give significant differences. It is advised to use for Caustic Soda 50% membrane grade (maximum Na₂SO₄ of 30 mg/kg) an Ion chromatographic test method, as ASTM E291 is not suitable for this low concentration.

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>
Alkalinity as NaOH	%M/M	24	49.81	0.43	0.70
Appearance	---	21	pass	n.a.	n.a.
Density at 20 °C	kg/L	20	1.5237	0.0009	0.0005
Iron as Fe	mg/kg	20	6.75	2.05	1.96
Sodium Chloride as NaCl	mg/kg	21	48.3	30.0	15.0 *)
Sodium Chlorate as NaClO ₃	mg/kg	6	6.2	12.0	2.1
Sodium Sulphate as SO ₄	mg/kg	13	17.1	36.7	(14.4)

table 6: Reproducibilities for sample #14163

*) reproducibility from Ion selective electrode method ASTM E291:09, chapter 57

() The reproducibility should be used with care as the reported test results are below the limit of determination

<i>Parameter</i>	<i>unit</i>	<i>n</i>	<i>average</i>	<i>2.8 * sd</i>	<i>R (lit)</i>
Sodium Chloride as NaCl	%M/M	18	0.811	0.100	0.080 *)
Sodium Chlorate as NaClO ₃	%M/M	7	0.092	0.011	0.015
Sodium Sulphate as SO ₄	%M/M	11	0.001	0.001	(0.001)

table 7: Reproducibilities for sample #14164

*) reproducibility from Potentiometric titration method ASTM E291:09, chapter 48

() The reproducibility should be used with care as the reported test results are below the limit of determination

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 2014 WITH PREVIOUS PT

	<i>September 2014</i>	<i>September 2012</i>
Number of reporting labs	26	25
Number of results reported	150	145
Statistical outliers	10	13
Percentage outliers	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 standards. The conclusions are given the following table:

	<i>September 2014</i>	<i>September 2012</i>
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 SO ₄	(--)	-
High Salt Caustic Soda:		
-Sodium Chloride as NaCl	-	+
-Sodium Chlorate as NaClO ₃	+	--
-Sodium Sulphate as SO ₄	(-)	+

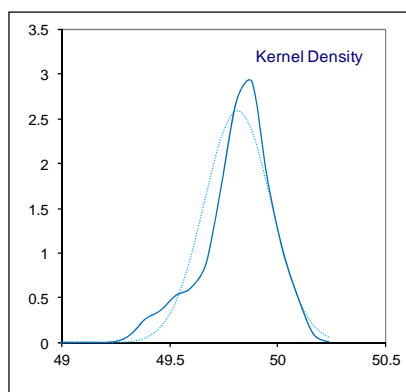
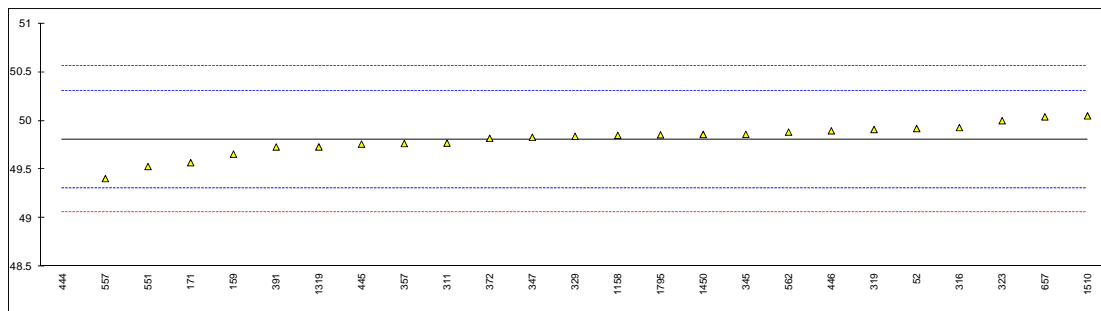
Table 9: comparison determinations against the standard

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

APPENDIX 1

Determination of Alkalinity as NaOH on sample #14163; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	E291	49.92		0.44	
159	E291	49.6569		-0.62	
171	E291	49.57		-0.96	
311	E291	49.77		-0.16	
316	INH-041	49.93		0.48	
319	INH-726	49.91		0.40	
323	E291	50.00		0.76	
329	E291	49.84		0.12	
338		----		----	
345	E291	49.86		0.20	
347	D501	49.83		0.08	
357	E291	49.766		-0.18	
372	E291	49.82		0.04	
391	E291	49.73		-0.32	
444	E291	32.32	C,R(0.01)	-69.96	First reported: 44.85
445	BS6075.1	49.76	C	-0.20	First reported: 50.4
446	E291	49.896		0.34	
551	E291	49.53		-1.12	
554		----		----	
557	E291	49.406		-1.62	
562	INH-480	49.883		0.29	
657	E291	50.04	C	0.92	First reported: 50.54
963		----		----	
1158	E291	49.85		0.16	
1181		----		----	
1264		----		----	
1319	INH-1200	49.731		-0.32	
1450	GB/T629	49.8592		0.19	
1510	E291	50.05		0.96	
1795	INH-3068	49.855		0.18	
normality		suspect			
n		24			
outliers		1			
mean (n)		49.811			
st.dev. (n)		0.1542			
R(calc.)		0.432			
R(E291:09)		0.700			

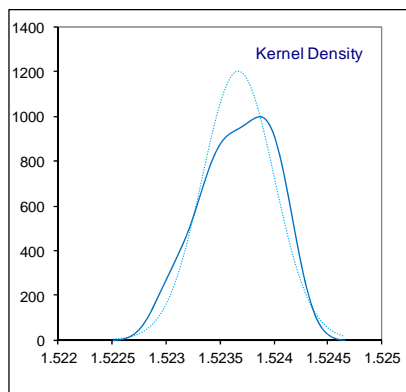
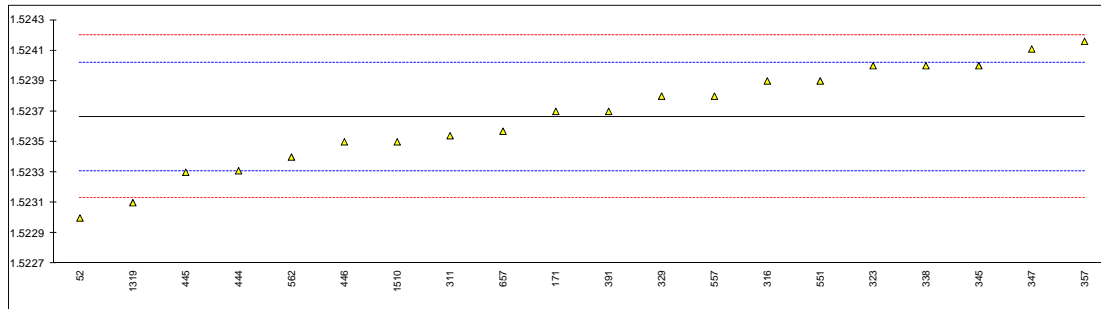


Determination of Appearance on sample #14163;

lab	method	value	mark	z(targ)	Remarks
52	E2680	Pass		----	
159	E2680	Pass		----	
171	E2680	Pass		----	
311	E2680	Pass		----	
316	Visual	Clear		----	
319		----		----	
323	E2680	Pass		----	
329	E2680	Pass		----	
338	Visual	C&B		----	
345	E2680	Pass		----	
347	E2680	Pass		----	
357	E2680	Pass		----	
372	E2680	Pass		----	
391	E2680	Pass		----	
444	E2680	Pass		----	
445	E2680	C&B		----	
446	E2680	Fail		----	
551	E2680	Pass		----	
554		----		----	
557	E2680	Pass		----	
562	E2680	Pass		----	
657	E2680	Pass		----	
963		----		----	
1158		----		----	
1181		----		----	
1264		----		----	
1319	E2680	Pass		----	
1450		----		----	
1510	E2680	Pass		----	
1795		----		----	
	normality	n.a.			
	n	21			
	outliers	1			1 participant reported Fail
	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 #14163; results in kg/L

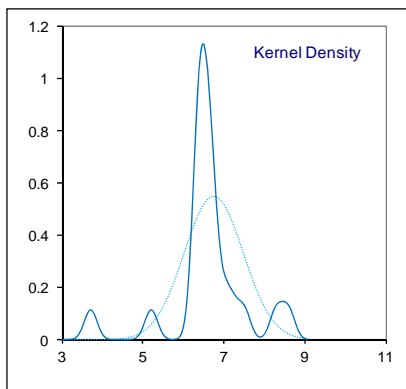
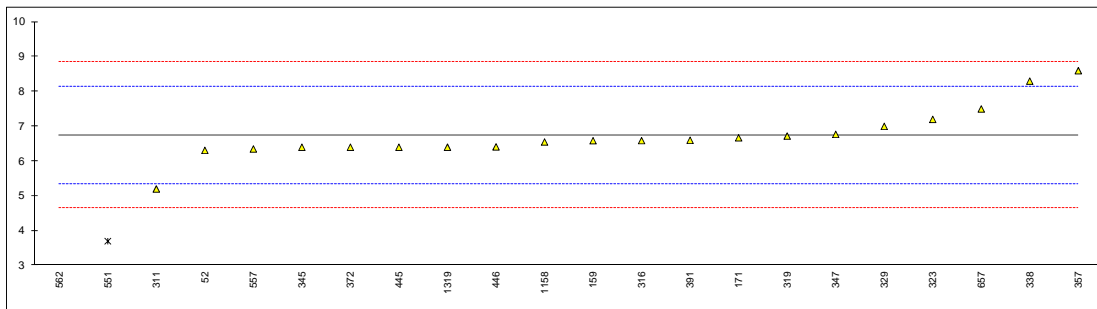
lab	method	value	mark	z(targ)	Remarks
52	D4052	1.523		-3.72	
159		----		----	
171	D4052	1.5237		0.20	
311	D4052	1.52354		-0.70	
316	INH-009	1.5239		1.32	
319		----		----	
323	D4052	1.5240		1.88	
329	D4052	1.5238		0.76	
338	D4052	1.5240		1.88	
345	D4052	1.5240		1.88	
347	D4052	1.52411		2.49	
357	D4052	1.52416		2.77	
372		----		----	
391	D4052	1.5237		0.20	
444	D4052	1.52331		-1.99	
445	D4052	1.5233	C	-2.04	First reported: 1.5275
446	D4052	1.5235		-0.92	
551	D4052	1.5239		1.32	
554		----		----	
557	D4052	1.5238		0.76	
562	D4052	1.5234		-1.48	
657	D4052	1.52357		-0.53	
963		----		----	
1158		----		----	
1181		----		----	
1264		----		----	
1319	D4052	1.5231	C	-3.16	First reported: 1.5228
1450		----		----	
1510	D4052	1.5235		-0.92	
1795		----		----	
normality		OK			
n		20			
outliers		0			
mean (n)		1.52366			
st.dev. (n)		0.000332			
R(calc.)		0.00093			
R(D4052:02e1)		0.00050			



Determination of Iron as Fe on sample #14163; results in mg/kg

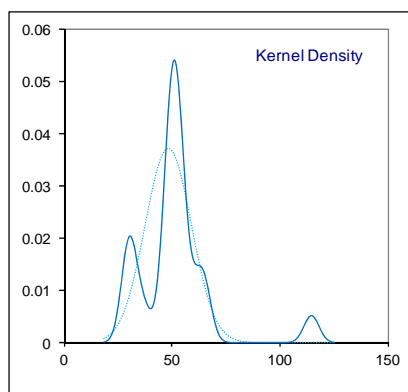
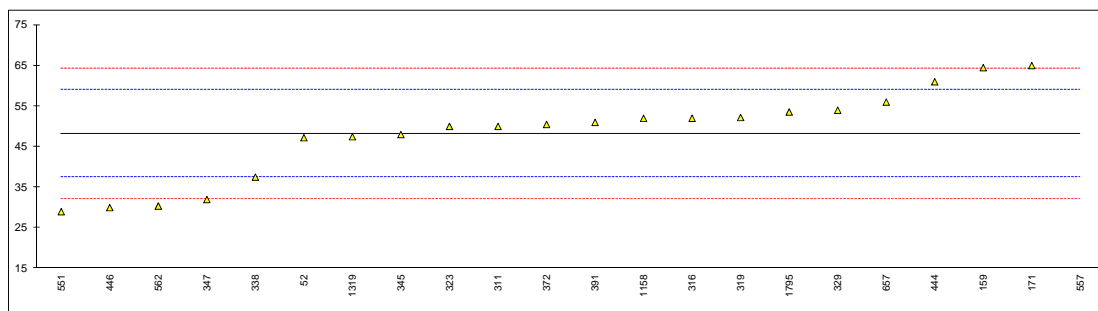
lab	method	Value	mark	z(targ)	remarks
52	E291	6.31		-0.63	
159	E291	6.5881		-0.23	
171	E291	6.67		-0.11	
311	E291	5.2	C	-2.21	First reported: 2.6
316	INH-043	6.59		-0.23	
319	INH-104	6.72		-0.04	
323	E291	7.2		0.65	
329	E291	7.0		0.36	
338	E291	8.3		2.22	
345	E291	6.4		-0.50	
347	E291	6.77		0.03	
357	E291	8.60		2.65	
372	E291	6.4		-0.50	
391	E291	6.6		-0.21	
444	E291	<0.1	C	<-9.06	First reported: 1.298, false negative test result?
445	BS6075.3	6.4		-0.50	
446	E291	6.41		-0.48	
551	E291	3.7	R(0.05)	-4.36	
554		----		----	
557	E291	6.35		-0.57	
562	E291	1.231	R(0.01)	-7.89	
657	E291	7.50	C	1.08	First reported: 1.50
963		----		----	
1158	INH-3068	6.55		-0.28	
1181		----		----	
1264		----		----	
1319	E291	6.40		-0.50	
1450		----		----	
1510		----		----	
1795		----		----	

normality not OK
n 20
outliers 2
mean (n) 6.748
st.dev. (n) 0.7304
R(calc.) 2.045
R(E291:09) 1.957



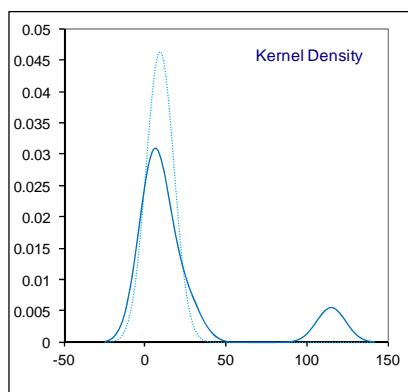
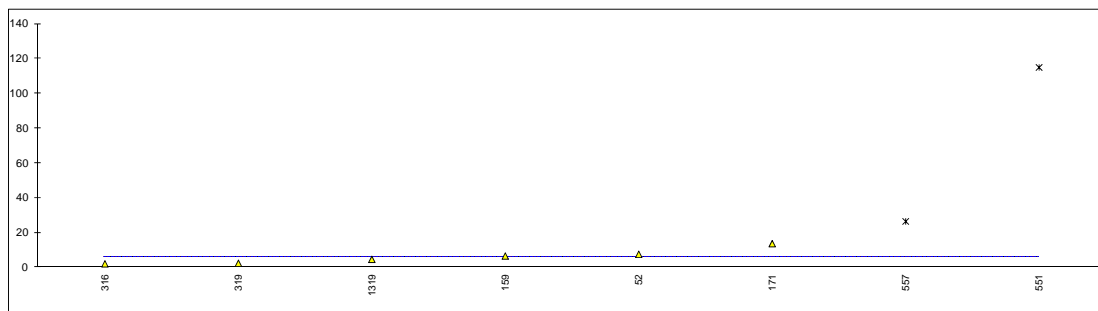
Determination of Sodium Chloride as NaCl on sample #14163; results in mg/kg

lab	method	value	mark	z(targ)	Remarks
52	E291	47.235		-0.19	
159	E291	64.49		3.03	
171	E291	65	C	3.13	First reported: 1.389
311	INH-554	50		0.33	
316	INH-044	52.0285		0.70	
319	INH-269	52.2		0.74	
323	E291	50		0.33	
329	E291	54		1.07	
338	E291	37.5		-2.01	
345	E291	48	C	-0.05	First reported: 0.0048
347	E291	32		-3.03	
357	E291	<100		-----	
372	E291	50.5		0.42	
391	E291	51		0.51	
444	E291	61	C	2.38	First reported: <10
445		-----		-----	
446	E291	30	C	-3.41	First reported: 0.003
551	E291	29		-3.59	
554		-----		-----	
557	E291	114.5	R(0.01)	12.37	
562	E291	30.39		-3.33	
657	E291	56.0		1.45	
963		-----		-----	
1158	E291	52		0.70	
1181		-----		-----	
1264		-----		-----	
1319	INH-1200	47.47		-0.15	
1450		-----		-----	
1510		-----		-----	
1795	E291	53.55		0.99	
normality		OK			
n		21			
outliers		1			
mean (n)		48.25			
st.dev. (n)		10.711			
R(calc.)		29.99			
R(E291:09)		15.00			



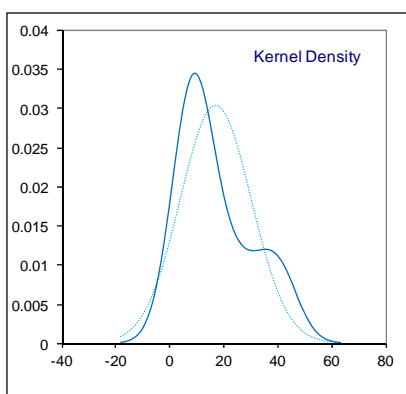
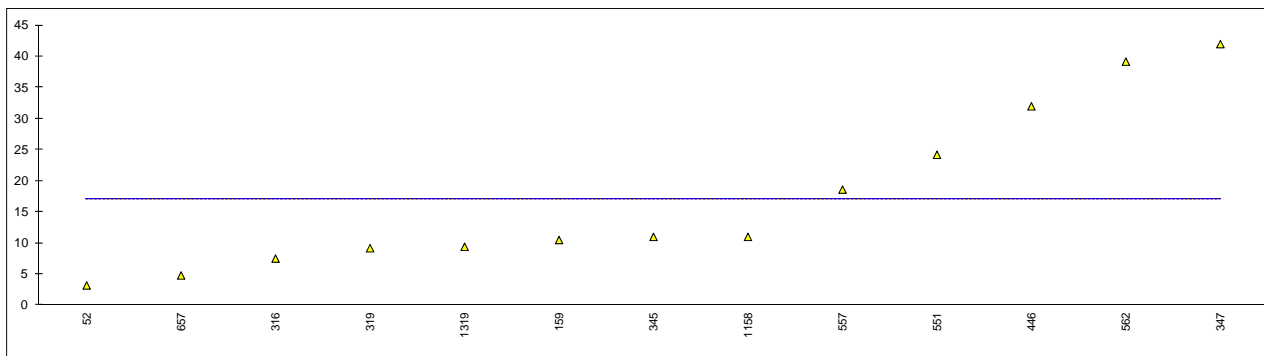
Determination of Sodium Chlorate as NaClO₃ on sample #14163; results in mg/kg

lab	method	value	mark	z(targ)	Remarks
52		7.6		----	
159		6.6		----	
171	D2022Mod.	13.7		----	
311		----		----	
316	INH-075	2.1		----	
319	INH-888	2.44		----	
323	INH-010	<10		----	
329		----		----	
338		----		----	
345		----		----	
347		----		----	
357		----		----	
372		----		----	
391		----		----	
444		----		----	
445		----		----	
446		----		----	
551	NBR9851	115	G(0.01)	----	
554		----		----	
557	NBR9851	26.5	G(0.05)	----	
562		----		----	
657		----		----	
963		----		----	
1158		----		----	
1181		----		----	
1264		----		----	
1319	INH-1200	4.66		----	
1450		----		----	
1510		----		----	
1795		----		----	
normality		unknown			
n		6			
outliers		2			
mean (n)		6.18			
st.dev. (n)		4.282			
R(calc.)		11.99			
R(Horwitz)		(2.11)			



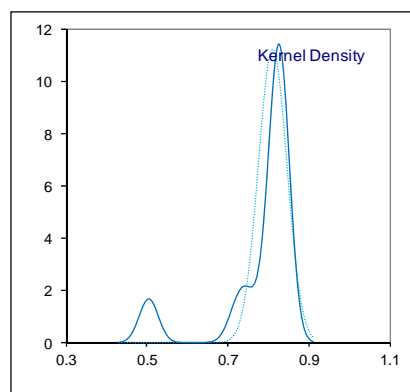
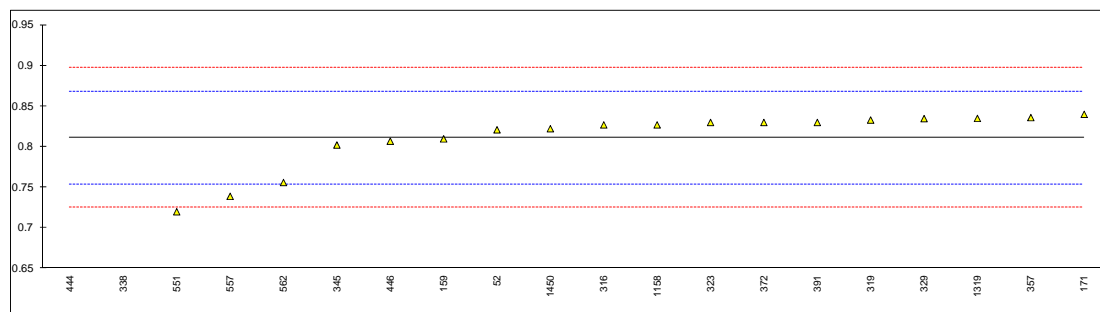
Determination of Sodium Sulfate as SO₄²⁻ on sample #14163; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	E291	3.2		----	
159	E291	10.5		----	
171		----		----	
311	E291	<40		----	
316	INH-073	7.520		----	
319	INH-862	9.18		----	
323	E291	<10		----	
329		----		----	
338		----		----	
345	E291	11		----	
347	E291	42		----	
357		----		----	
372	E291	<40		----	
391		----		----	
444		----		----	
445		----		----	
446	E291	32	C	----	First reported 0.0032
551	E291	24.2		----	
554		----		----	
557	in house	18.6		----	
562	E291	39.18		----	
657	E291	4.8		----	
963		----		----	
1158	INH-3068	11		----	
1181		----		----	
1264		----		----	
1319	INH-1200	9.41		----	
1450		----		----	
1510		----		----	
1795		----		----	
	normality	OK			
	n	13			
	outliers	0			
	mean (n)	17.12			
	st.dev. (n)	13.097			
	R(calc.)	36.67			
	R(E291:09)	(14.38)			



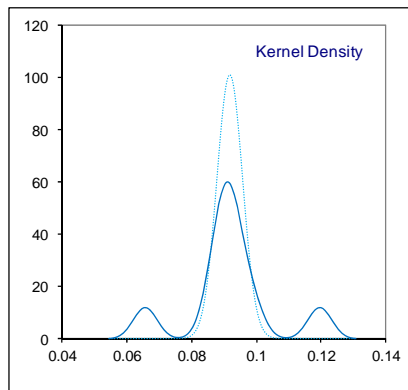
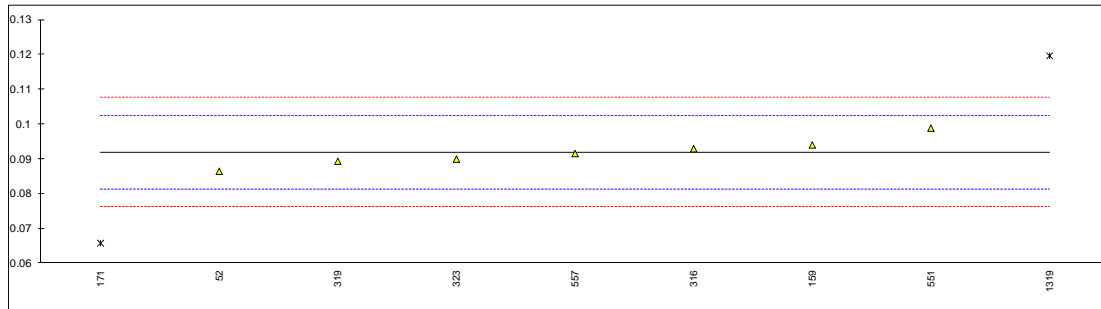
Determination of Sodium Chloride as NaCl on sample #14164; results in %M/M

lab	method	value	mark	z(targ)	Remarks
52	E291	0.821		0.35	
159	E291	0.8098		-0.05	
171	E291	0.84	C	1.01	First reported: 0.9547
311	INH-554	>0.02		----	
316	INH-044	0.8270		0.56	
319	INH-269	0.833		0.77	
323	E291	0.83		0.66	
329	E291	0.8348		0.83	
338	E291	0.5049	R(0.01)	-10.72	
345	E291	0.8022		-0.31	
347		----		----	
357	E291	0.836		0.87	
372	E291	0.83		0.66	
391	E291	0.83		0.66	
444	E291	0.5023	R(0.01)	-10.81	
445		----		----	
446	E291	0.807		-0.14	
551	E291	0.72		-3.19	
554		----		----	
557	E291	0.739		-2.52	
562	E291	0.7560		-1.93	
657		----		----	
963		----		----	
1158	E291	0.827		0.56	
1181		----		----	
1264		----		----	
1319	INH-1200	0.835		0.84	
1450	GB/T4348	0.8223		0.39	
1510		----		----	
1795		----		----	
normality		not OK			
n		18			
outliers		2	<u>Spike</u>		
mean (n)		0.8111	0.90		91% recovery
st.dev. (n)		0.03556			
R(calc.)		0.0996			
R(E291:09)		0.0800			



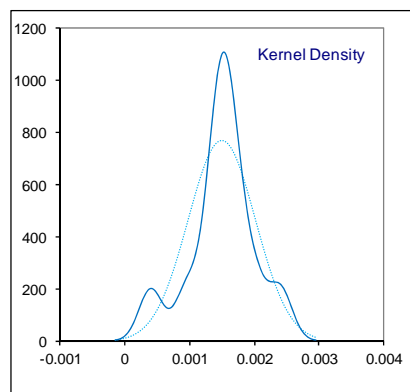
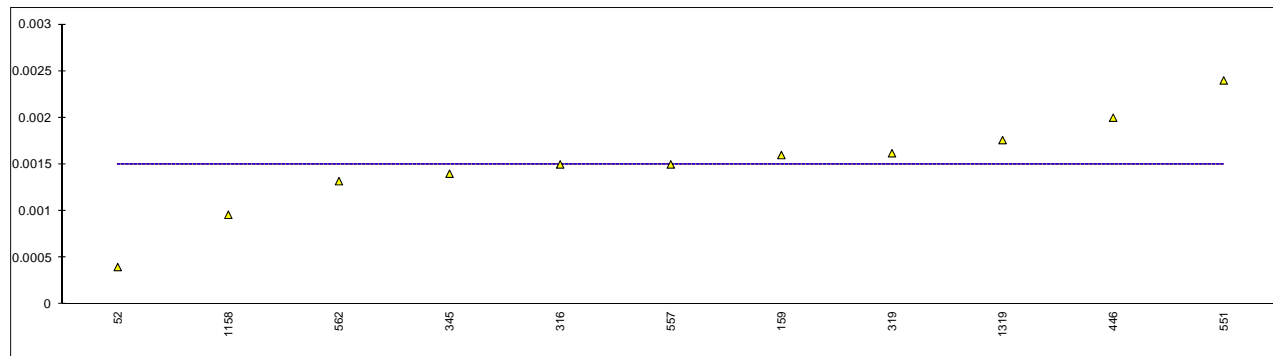
Determination of Sodium Chlorate as NaClO₃ on sample #14164; results in %M/M

lab	method	value	mark	z(targ)	Remarks
52		0.0865		-1.03	
159	D2022	0.09408		0.41	
171	D2202Mod.	0.065855	DG(0.05)	-4.95	
311		-----		-----	
316	INH-075	0.093		0.20	
319	INH-888	0.08939		-0.48	
323	INH-010	0.09	C	-0.37	First reported 0.19 on 100% NaOH base
329		-----		-----	
338		-----		-----	
345		-----		-----	
347		-----		-----	
357		-----		-----	
372		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
551	NBR9851	0.0989		1.32	
554		-----		-----	
557	NBR9851	0.0916		-0.06	
562		-----		-----	
657		-----		-----	
963		-----		-----	
1158		-----		-----	
1181		-----		-----	
1264		-----		-----	
1319	INH-1200	0.1197	DG(0.05)	5.27	
1450		-----		-----	
1510		-----		-----	
1795		-----		-----	
normality		OK			
n		7			
outliers		2	<u>Spike</u>		
mean (n)		0.0919	0.10		86% recovery
st.dev. (n)		0.00396			
R(calc.)		0.0111			
R(Horwitz)		0.0147			



Determination of Sodium Sulfate as SO₄²⁻ on sample #14164; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	E291	0.0004		----	
159	E291	0.0016		----	
171		----		----	
311	E291	<0.004		----	
316	INH-073	0.0015		----	
319	INH-862	0.00162		----	
323	E291	<0.0010	U	----	Reported <10, probably a unit error
329		----		----	
338		----		----	
345	E291	0.0014		----	
347		----		----	
357		----		----	
372		----		----	
391		----		----	
444		----		----	
445		----		----	
446	E291	0.002		----	
551	E291	0.0024		----	
554		----		----	
557	in house	0.0015		----	
562	E291	0.00132		----	
657		----		----	
963		----		----	
1158	INH-3068	0.00096		----	
1181		----		----	
1264		----		----	
1319	INH-1200	0.00176		----	
1450		----		----	
1510		----		----	
1795		----		----	
normality		suspect			
n		11			
outliers		0			
mean (n)		0.0015			
st.dev. (n)		0.00052			
R(calc.)		0.0015			
R(E291:09)		(0.0013)			



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 CHINA, People's Republic
1 lab in ESTONIA
1 lab in FINLAND
1 lab in FRANCE
1 lab in ITALY
1 lab in JAPAN
3 labs in NETHERLANDS
2 labs in ROMANIA
1 lab in SAUDI ARABIA
1 lab in SINGAPORE
2 labs in SPAIN
1 lab in UNITED ARAB EMIRATES
4 labs in UNITED KINGDOM
3 labs in UNITED STATES OF AMERICA

APPENDIX 3

Abbreviations:

C	= final result after checking of first reported suspect result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner outlier test
R(0.05)	= straggler in Rosner outlier test
E	= error in calculations
U	= reported in different unit
ex	= excluded from calculations
n.a.	= not applicable
W	= result withdrawn on request of participant

Literature:

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
- 2 ASTM E178-02
- 3 ASTM E1301-03
- 4 ISO 5725-86
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- 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, No4 January 2001.
- 15 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/>)
- 16 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, *Technometrics*, 25(2), pp. 165-172, (1983)