Results of Proficiency Test
Caustic Soda
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Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

1 INTRODUCTION

During the last years, with increasing frequency, requests were received by iis from laboratories that participated in the iis PT program, to organize also a proficiency test for the analysis of Caustic Soda (aqueous Sodium Hydroxide solution).
This resulted in this international Interlaboratory study, in which 32 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 proficiency test on Caustic Soda are presented and discussed.

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 at least two different grades of Caustic Soda are available on the market. To full fill 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 #12092 was an original low NaCl Caustic Soda. Sample #12093 was the same Caustic spiked with Sodium Chloride (7176 mg/kg), Sodium Chlorate (718 mg/kg) and Sodium Sulfate (8.0 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 guide 43, ILAC-G13:2007 and ISO/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Also, customer's satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

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 25 litre bulk material was provided by a third party. After homogenisation 46 of 0.5 litre HDPE bottles were filled with approx. 350 ml each.

The homogeneity of the subsamples #12092 was checked by determination of Density in accordance with ASTM D4052:02E1and Alkalinity in accordance with ASTM E291:09 on 4 stratified randomly selected samples.

	Density at 20ºC in kg/L	*Alkalinity in %M/M*
sample #12092-1	1.52381	49.79
sample #12092-2	1.52381	49.82
sample #12092-3	1.52387	49.82
sample #12092-4	1.52387	49.82

Table 1: homogeneity test results of subsamples #12092

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:

	Density at 20ºC in kg/L	*Alkalinity in %M/M*
r (sample #12092)	0.00010	0.042
reference test	ASTM D4052:02e1	ASTM E291:09
0.3*R (reference test)	0.00015	0.075

Table 2: evaluation of repeatabilities of the subsamples #12092

The remaining bulk material (9.4 kg = approx. 6.2 litre) was spiked with the components listed in table 1:

Component	*Amount*
Sodium Chloride	67458 mg
Sodium Chlorate	6752 mg
Sodium Sulfate	75.5 mg

Table 3: components that were added to bulk material for sample #12093

After homogenisation this batch was divided over 46 HDPE bottles of 100mL and labelled #12093.
The homogeneity of the subsamples #12093 was checked by determination of Density in accordance with ASTM D4052:02E1and Sodium Chloride in accordance with ASTM E291:09 on 4 stratified randomly selected samples.

	Density at 20ºC in kg/L	*Sodium Chloride as NaCl in %M/M*
sample #12093-1	1.51554	6907
sample #12093-2	1.51561	6911
sample #12093-3	1.51562	6902
sample #12093-4	1.51564	6909

Table 4: homogeneity tests results of subsamples #12093

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:

	Density at 20ºC in kg/L	*Sodium Chloride as NaCl in %M/M*
r (sample #12093)	0.00012	11
reference test	ASTM D4052:11	ASTM E291:09
0.3*R (reference test)	0.00015	58

Table 5: repeatabilities of the subsamples #12093

Each calculated repeatability was equal or less than 0.3 times the corresponding reproducibility of the reference method. Therefore, homogeneity of the subsamples #12092 and #12093 was assumed.

To the participants, depending on the registration, 1*0.5L bottle labelled #12092 and 1*100 mL bottle, labelled #12093 were sent on August 22, 2012.

2.5 STABILITY OF THE SAMPLES

The stability of Caustic Soda, packed in the plastic 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^{o}C, Iron as Fe, Sodium Chloride as NaCl, Sodium Chlorate as $NaClO_3$ and Sodium Sulfate as SO_4 on the low salt sample #12092. On the high salt sample #12093 was requested to determine Sodium Chloride as NaCl, Sodium Chlorate as $NaClO_3$ and Sodium Sulfate as SO_4.

To get comparable results a detailed report form, on which the units were prescribed as well as some of the required standards and a letter of instructions were prepared and made available for download on the iis website.
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’ of January 2010 (iis-protocol, version 3.2).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers, this check was repeated. In case a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.
In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test and by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test and by G(0.05) or DG(0.05) for the Grubbs test. Both outliers and stragglers were not included in the calculations of the averages and the standard deviations.

Finally, the reproducibilities were calculated from the standard deviations by multiplying these with a factor of 2.8. 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 significant 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 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).

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, 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 target reproducibility (preferably taken from a standardized test method) by division with 2.8.
The z-scores were calculated in accordance with:

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

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

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.

To evaluate the performance of the participating laboratories the z-scores were calculated. 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:

	$\lvert z \rvert < 1$	good
$1 <$	$\lvert z \rvert < 2$	satisfactory
$2 <$	$\lvert z \rvert < 3$	questionable
	$\lvert z \rvert > 3$	unsatisfactory

4 EVALUATION

In this proficiency test, some major problems were encountered with despatch of the samples to the laboratories in Brazil, Saudi Arabia and U.S.A. Five participants received the samples late. In total, 5 participants reported after the deadline and 7 participants did not report any result at all. Not all participants were able to report all requested parameters. Finally, 25 participants did report 145 numerical results. Observed were 13 outlying results, which is 9.0% 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.

Alkalinity: This determination was problematic for two laboratories. Two statistical outliers were observed. However, the observed reproducibility after rejection of the statistical outliers is in good agreement with the requirements of ASTM E291:09.

Appearance: No analytical problems were observed. All labs agreed about the appearance of the sample #12092, which was bright, clear and free from suspended matter.

Density @ 20°C: This determination was problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers 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 gasolines, distillates, basestocks and lubricating oils. Therefore this 2011 version is not applicable for Caustic Soda.

Iron: This determination was very problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the requirements of ASTM E291:09.

Sodium Chloride: For sample #12092, this determination was very problematic at the low level 58.7 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the requirements of ASTM E291:09.
For sample #12093 serious analytical problems have been observed. The samples were spiked with sodium chloride (NaCl). Therefore the minimum NaCl concentration to be found was known (added amount = 0.7176%M/M). The laboratories should be able to find at least 0.6376%M/M [$0.7176\%M/M_{(\text{added amount})} - 0.0800\%M/M_{(R\ E291)}$].
No less than 6 of 18 laboratories reported lower concentrations than 0.637%M/M. And therefore these test results were rejected prior to data analysis. The calculated reproducibility after rejection of the suspect data is in

good agreement with the requirements of ASTM E291:09. The recovery of 97% ((0.7047 – 0.0059) / 0.7176) is good.

Sodium Chlorate: For sample #12092, it is hard to draw conclusions, as the sodium chlorate content is below or near the detection limit. Therefore, no z-scores were calculated.
For sample #12093 serious analytical problems have been observed. The samples were spiked with sodium chlorate ($NaClO_3$). Therefore the minimal $NaClO_3$ concentration to be found was known (added amount = 0.0718%M/M). The laboratories should be able to find at least 0.0599%M/M [$0.0718\%M/M_{(added\ amount)} - 0.0119\%M/M_{(R\ Horwitz)}$].
No less than 3 of 9 laboratories reported lower amounts than 0.0599%M/M. And therefore these test results were rejected prior to data analysis. The calculated reproducibility after rejection of the suspicious data is not in agreement with the estimated requirements calculated using the Horwitz equation. The recovery of 99% ((0.0713 – 0.0020) / 0.0718) is good.

Sodium Sulphate: The results of laboratory 1481 were excluded for statistical calculations as the test result reported for sample #12092 was larger the test results report for sample #12093. This is impossible as sample #12093 was spiked with sodium sulphate (see §2.4).
This determination seems problematic for sample #12092. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the requirements of ASTM E291:09.
This determination seems not problematic for Sample #12093. As the samples were spiked with sodium sulphate (Na_2SO_4) the minimal Na_2SO_4 concentration to be found was known (added amount = 0.0008%M/M). The laboratories should be able to find at least 0.0001%M/M [$0.0008\%M/M_{(added\ amount)} - 0.0007\%M/M_{(R\ E291)}$]. None of the reporting laboratories reported a test result below 0.0001%M/M. Probably the positive blank value of the sample has contributed.
The calculated reproducibility is in full agreement with the requirements of ASTM E291:09. However, the recovery of 56% ((0.00146 – 0.00101) / 0.00080) is unsatisfactory.

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)*
Alkalinity as NaOH	%M/M	24	49.84	0.46	0.70
Appearance	---	20	pass	n.a.	n.a.
Density at 20 ^{o}C	kg/L	20	1.5238	0.0006	0.0005
Iron as Fe	mg/kg	20	1.62	0.66	0.47
Sodium Chloride as NaCl	mg/kg	18	58.7	25.3	15.0 *)
Sodium Chlorate as $NaClO_3$	mg/kg	5	1.7	2.1	(0.7)
Sodium Sulfate as SO_4	mg/kg	10	10.1	11.2	8.5

table 6: Reproducibilities for sample #12092

Reproducibility values between brackets are for concentrations near of below the detection limit

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

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (lit)*
Sodium Chloride as NaCl	%M/M	12	0.705	0.048	0.080 *)
Sodium Chlorate as $NaClO_3$	%M/M	6	0.071	0.023	0.012
Sodium Sulfate as SO_4	%M/M	6	0.0015	0.0011	0.0012

table 7: Reproducibilities for sample #12093

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

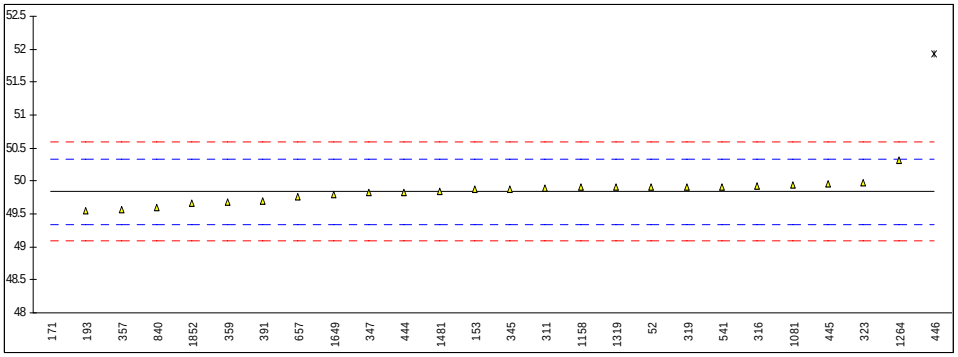
Without further statistical calculations, it can be concluded that for several tests there is a good compliance of the group of participating laboratories with the relevant standards. The tests that are problematic have been discussed in paragraph 4.1.

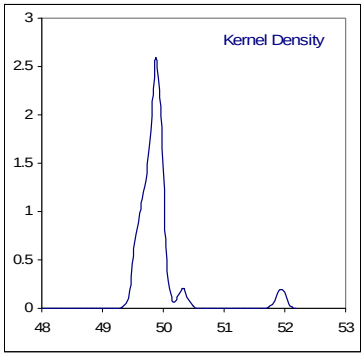
APPENDIX 1

Determination of Alkalinity as NaOH on sample #12092; results in %M/M

lab	method	value	mark	z(targ)	Remarks
52	E291	49.91		0.29	
153	E291	49.87		0.13	
169		-----		-----	
171	E291	38.48	G(0.01)	-45.43	Reported a deviating unit?
193	E291	49.54819	C	-1.15	First reported 49.1158
311	E291	49.89		0.21	
316	INH-041	49.93		0.37	
319	INH-726	49.91		0.29	
323	E291	49.98		0.57	
345	E291	49.88		0.17	
347	E291	49.82		-0.07	
357	E291	49.560		-1.11	
359	E291	49.675		-0.65	
391	E291	49.69		-0.59	
444	E291	49.83		-0.03	
445	INH-6075	49.963		0.51	Note: not corrected for Carbonate content
446	E291	51.936	G(0.01)	8.40	
541	E291	49.91		0.29	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	E291	49.76		-0.31	
840	E291	49.598		-0.95	
1081	in house	49.94		0.41	
1158	E291	49.900		0.25	
1252		-----		-----	
1264	E291	50.32	C	1.93	First reported 49.1
1319	INH-1200	49.900		0.25	
1343		-----		-----	
1481	E291	49.84		0.01	
1649	in house	49.79		-0.19	
1852	UOP209	49.664		-0.69	

normality	OK
n	24
outliers	2
mean (n)	49.837
st.dev. (n)	0.1645
R(calc.)	0.460
R(E291:09)	0.700





Determination of Appearance on sample #12092;

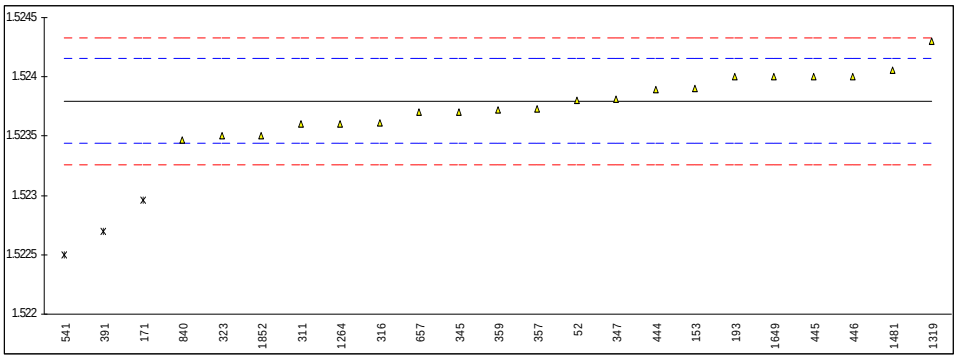
lab	method	value	mark	z(targ)	remarks
52	visual	pass		-----	
153		-----		-----	
169		-----		-----	
171	E2680	pass		-----	
193	E2680	Clear		-----	
311	INH-402	B&C		-----	
316	visual	Clear		-----	
319		-----		-----	
323	E2680	pass		-----	
345	E291	pass		-----	
347	E2680	pass		-----	
357	E2680	pass		-----	
359	E2680	pass		-----	
391	E2680	pass		-----	
444	E2680	pass		-----	
445	E2680	pass		-----	
446	E2680	pass		-----	
541	E2680	pass		-----	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	E2680	pass		-----	
840	E2680	pass		-----	
1081		-----		-----	
1158		-----		-----	
1252		-----		-----	
1264	E2680	pass		-----	
1319	E2680	B&C		-----	
1343		-----		-----	
1481	E2680	pass		-----	
1649		-----		-----	
1852		-----		-----	

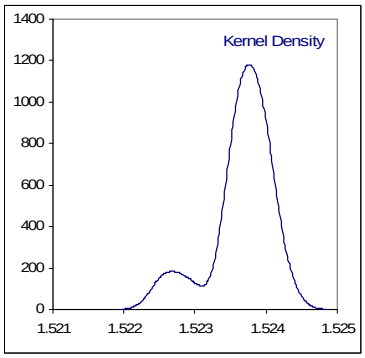
normality	n.a.
n	20
outliers	0
mean (n)	Pass
st.dev. (n)	n.a.
R(calc.)	n.a.
R(E2680:09)	unknown

Determination of Density at 20°C on sample #12092; results in kg/L

lab	method	value	mark	z(targ)	remarks
52	D4052	1.5238		0.03	
153	D4052	1.5239		0.59	
169		-----		-----	
171	D4052	1.52296	G(0.05)	-4.67	
193	D4052	1.5240		1.15	
311	D4052	1.5236		-1.09	
316	INH-009	1.52361		-1.03	
319		-----		-----	
323	D4052	1.5235		-1.65	
345	D4052	1.5237		-0.53	
347	D4052	1.52381		0.09	
357	D4052	1.52373		-0.36	
359	D4052	1.52372		-0.42	
391	D4052	1.5227	DG(0.01)	-6.13	
444	D4052	1.52389		0.54	
445	D4052	1.5240		1.15	
446	D4052	1.524		1.15	
541	D4052	1.5225	DG(0.01)	-7.25	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	D4052	1.5237		-0.53	
840	D4052	1.52347		-1.82	
1081		-----		-----	
1158		-----		-----	
1252		-----		-----	
1264	D4052	1.5236		-1.09	
1319	D4052	1.5243		2.83	
1343		-----		-----	
1481	D4052	1.52406		1.49	
1649	in house	1.524		1.15	
1852	ISO12185	1.5235		-1.65	

normality	OK
n	20
outliers	3
mean (n)	1.52379
st.dev. (n)	0.000221
R(calc.)	0.00062
R(D4052:02e1)	0.00050

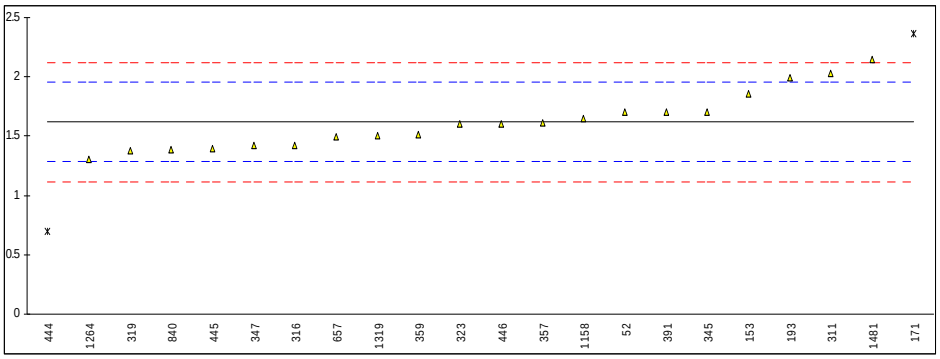


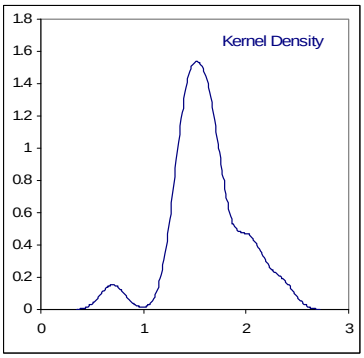


Determination of Iron as Fe on sample #12092; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	E291	1.7		0.47	
153	E291	1.86		1.43	
169		-----		-----	
171	E291	2.36	G(0.05)	4.41	
193	E291	1.996		2.24	
311	E291	2.03		2.44	
316	INH-043	1.42		-1.19	
319	INH-104	1.38		-1.43	
323	E291	1.6		-0.12	
345	E291	1.7		0.47	
347	E291	1.42		-1.19	
357	E291	1.61		-0.06	
359	E291	1.51		-0.66	
391	E291	1.7		0.47	
444	E291	0.7	D(0.05)	-5.48	
445	INH-6075	1.398		-1.33	
446	E291	1.6		-0.12	
541		-----		-----	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	E291	1.497		-0.74	
840	E291	1.39		-1.37	
1081		-----		-----	
1158	INH-3068	1.65		0.18	
1252		-----		-----	
1264	E291	1.3	C	-1.91	First reported 1.0
1319	INH-1200	1.50	C	-0.72	First reported 0.314
1343		-----		-----	
1481	E291	2.15		3.15	
1649		-----		-----	
1852		-----		-----	

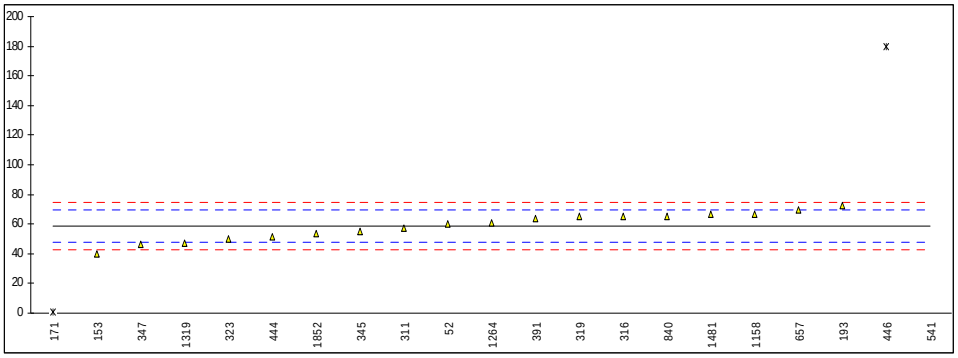
normality	OK
n	20
outliers	2
mean (n)	1.621
st.dev. (n)	0.2354
R(calc.)	0.659
R(E291:09)	0.470

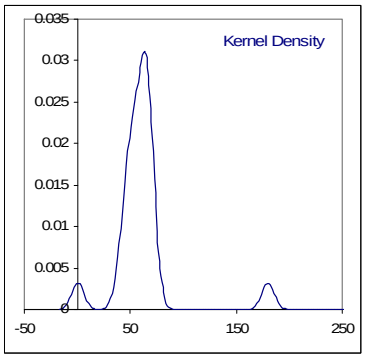




Determination of Sodium Chloride as NaCl on sample #12092; results in mg/kg

lab	method	value	mark	z(targ)	remarks
52	E291	60		0.25	
153	INH-003	40.20		-3.44	
169		-----		-----	
171	E291	0.66	G(0.01)	-10.83	Unit error?
193	E291	72.189		2.53	
311	INH-554	57		-0.31	
316	INH-044	65.0167		1.19	
319	INH-269	64.9		1.17	
323	E291	50		-1.62	
345	E291	55		-0.68	
347	E291	46.5	C	-2.27	First reported 28.2
357	E291	<3000		-----	
359	E291	<3000		-----	
391	E291	64		1.00	
444	E291	51.2		-1.39	
445		-----		-----	
446	E291	180	G(0.01)	22.65	
541	E291	670	G(0.01)	114.12	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	E291	69.7		2.06	
840	ISO6227	65.3		1.24	
1081		-----		-----	
1158	E291	66.9		1.54	
1252		-----		-----	
1264	E291	61	C	0.44	First reported 36.5
1319	INH-1200	47.0		-2.18	
1343		-----		-----	
1481	E291	66.47		1.46	
1649		-----		-----	
1852	DIN38405	53.4		-0.98	
	normality	OK			
	n	18			
	outliers	3			
	mean (n)	58.65			
	st.dev. (n)	9.049			
	R(calc.)	25.34			
	R(E291:09)	15.00			

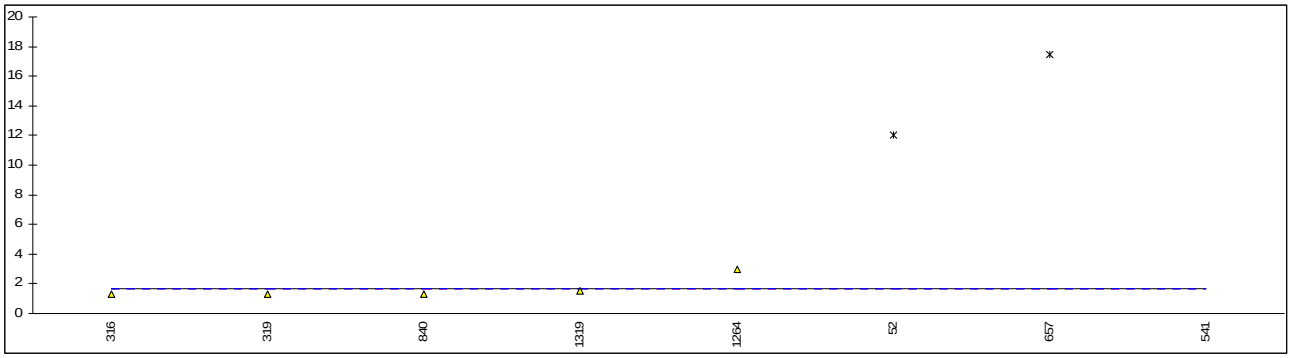




Determination of Sodium Chlorate as $NaClO_3$ on sample #12092; results in mg/kg

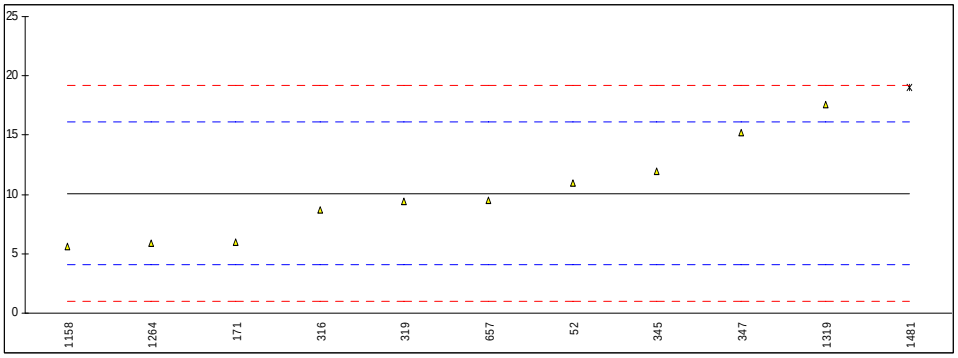
lab	method	value	mark	z(targ)	remarks
52	INH-0.16	12	DG(0.01)	-----	
153		-----		-----	
169		-----		-----	
171		-----		-----	
193		-----		-----	
311	INH-225	<2		-----	
316	INH-075	1.28		-----	
319	INH-888	1.3		-----	
323		-----		-----	
345		-----		-----	
347		-----		-----	
357		-----		-----	
359		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
541	E291	1230	G(0.01)	-----	Unit error?
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	INH134	17.5	DG(0.01)	-----	
840	INH-11200	1.3		-----	
1081		-----		-----	
1158		-----		-----	
1252		-----		-----	
1264		3	C	-----	First reported 51.0
1319	in house	1.5		-----	
1343		-----		-----	
1481		<1		-----	
1649		-----		-----	
1852		-----		-----	

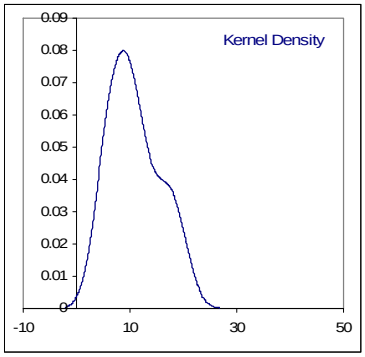
normality	not OK
n	5
outliers	3
mean (n)	1.68
st.dev. (n)	0.746
R(calc.)	2.09
R(Horwitz)	(0.69)



Determination of Sodium Sulfate as SO_4^{2-} on sample #12092; results in mg/kg

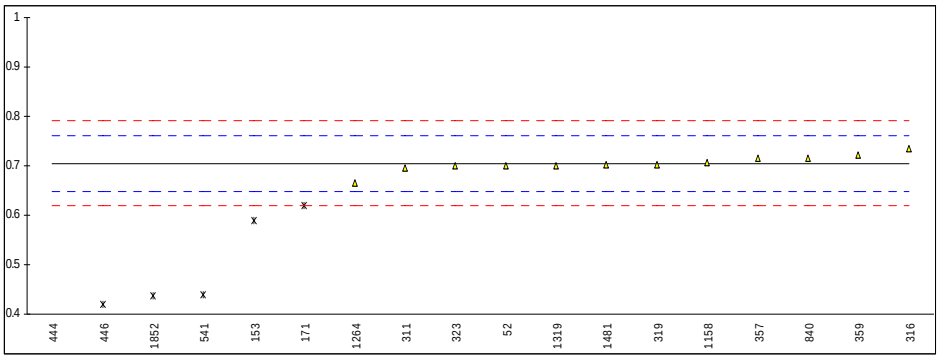
lab	method	value	mark	z(targ)	remarks
52	E291	11		0.30	
153		-----		-----	
169		-----		-----	
171	E291	6	C	-1.35	First reported 0.0006
193		-----		-----	
311	E291	<40		-----	
316	INH-073	8.724		-0.45	
319	INH-862	9.40		-0.23	
323	E291	<10		-----	
345	E291	12		0.63	
347	E291	15.2		1.69	
357		-----		-----	
359		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
541		-----		-----	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657	E291	9.5		-0.20	
840	E291	<20		-----	
1081		-----		-----	
1158	INH-3068	5.6		-1.48	
1252		-----		-----	
1264	E291	5.9		-1.38	
1319	INH-1200	17.6		2.48	
1343		-----		-----	
1481	E291	19	ex	2.94	Result excluded as reported result sample #12092 > sample #12093
1649		-----		-----	
1852		-----		-----	
	normality	OK			
	n	10			
	outliers	0			1 result excluded
	mean (n)	10.09			
	st.dev. (n)	4.002			
	R(calc.)	11.20			
	R(E291:09)	8.48			

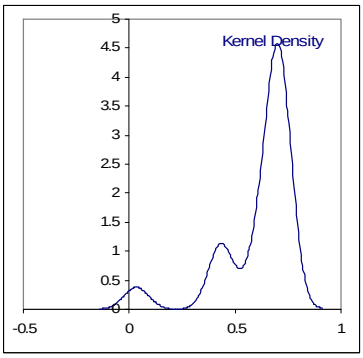




Determination of Sodium Chloride as NaCl on sample #12093; results in %M/M

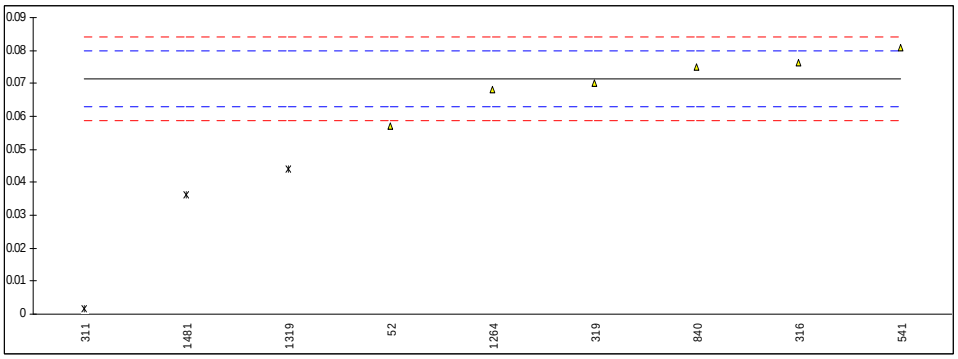
lab	method	value	mark	z(targ)	remarks
52	E291	0.70		-0.16	
153	E291	0.59	ex	-4.01	Result excluded, see §4.1
169		-----		-----	
171	E291	0.6194	ex	-2.99	Result excluded, see §4.1
193		-----		-----	
311	INH-554	0.6947		-0.35	
316	INH-044	0.7344		1.04	
319	INH-269	0.702		-0.09	
323	E291	0.70		-0.16	
345		-----		-----	
347		-----		-----	
357	E291	0.715		0.36	
359	E291	0.722		0.61	
391		-----		-----	
444	E291	0.0328	ex	-23.52	Result excluded, see §4.1
445		-----		-----	
446	E291	0.420	ex	-9.96	Result excluded, see §4.1
541	E291	0.440	C,ex	-9.26	First reported 440. Result excluded, see §4.1
551		-----		-----	
554		-----		-----	
562		-----		-----	
657		-----		-----	
840	E291	0.716		0.40	
1081		-----		-----	
1158	E291	0.7055		0.03	
1252		-----		-----	
1264	E291	0.665	C	-1.39	First reported 3963
1319	E291	0.700		-0.16	
1343		-----		-----	
1481	E291	0.7018		-0.10	
1649		-----		-----	
1852	DIN38405	0.4380	ex	-9.33	Result excluded, see §4.1
	normality	OK			
	n	12			
	outliers	0	Spike:		6 results excluded
	mean (n)	0.7047	0.7176		97% recovered
	st.dev. (n)	0.01699			
	R(calc.)	0.0476			
	R(E291:09)	0.0800			

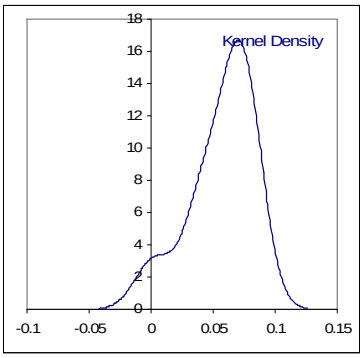




Determination of Sodium Chlorate as $NaClO_3$ on sample #12093; results in %M/M

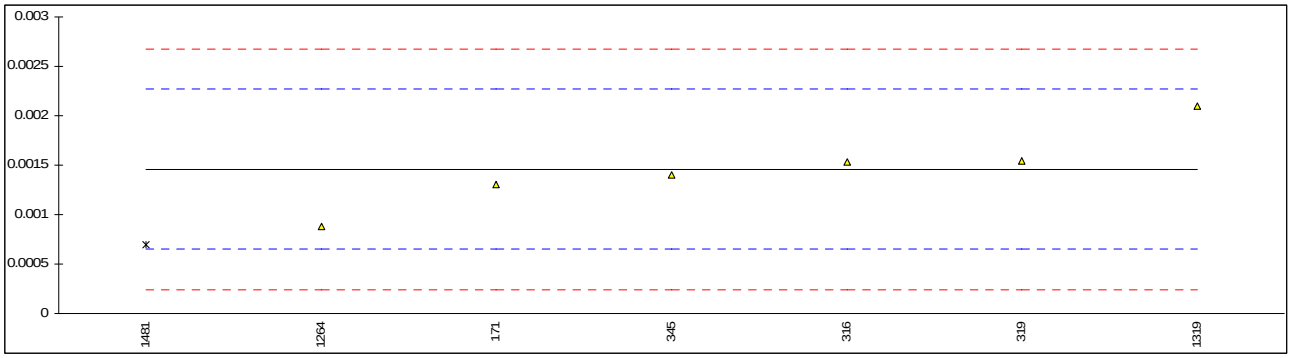
lab	method	value	mark	z(targ)	remarks
52	INH-016	0.057		-3.37	
153		-----		-----	
169		-----		-----	
171		-----		-----	
193		-----		-----	
311	INH-225	0.0017	ex	-16.40	Result excluded, see §4.1
316	INH-075	0.0764		1.20	
319	INH-888	0.07026		-0.25	
323		-----		-----	
345		-----		-----	
347		-----		-----	
357		-----		-----	
359		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
541	E291	0.0810	C	2.28	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657		-----		-----	
840	INH-11200	0.0751		0.89	
1081		-----		-----	
1158		-----		-----	
1252		-----		-----	
1264		0.0681	C	-0.76	
1319	in house	0.044	ex	-6.43	Result excluded, see §4.1
1343		-----		-----	
1481		0.0363	ex	-8.25	Result excluded, see §4.1
1649		-----		-----	
1852		-----		-----	
	normality	OK			
	n	6			3 results excluded
	outliers	0	Spike:		
	mean (n)	0.0713	0.0718		99% recovered
	st.dev. (n)	0.00837			
	R(calc.)	0.0234			
	R(Horwitz)	0.0119			





Determination of Sodium Sulfate as SO_4 on sample #12093; results in %M/M

lab	method	value	mark	z(targ)	remarks
52	E291	<0.001		-----	
153		-----		-----	
169		-----		-----	
171	E291	0.0013		-0.36	
193		-----		-----	
311	E291	<0.0040		-----	
316	INH-073	0.00153		0.16	
319	INH-862	0.001547		0.20	
323	E291	<0.001		-----	
345	E291	0.0014	C	-0.14	First reported 14
347		-----		-----	
357		-----		-----	
359		-----		-----	
391		-----		-----	
444		-----		-----	
445		-----		-----	
446		-----		-----	
541		-----		-----	
551		-----		-----	
554		-----		-----	
562		-----		-----	
657		-----		-----	
840	E291	<0.002		-----	
1081		-----		-----	
1158		-----		-----	
1252		-----		-----	
1264	E291	0.00088	C	-1.32	First reported 5.1
1319	in house	0.0021		1.46	
1343		-----		-----	
1481	E291	0.0007	ex	-1.73	Result excluded as reported result sample #12092 > sample #12093
1649		-----		-----	
1852		-----		-----	
	normality	OK			
	n	6			1 excluded result
	outliers	0	Spike:		
	mean (n)	0.00146	0.0008		
	st.dev. (n)	0.000397			
	R(calc.)	0.00111			
	R(E291:09)	0.00123			



APPENDIX 2

Number of participants per country

1 lab in	ARGENTINA
1 lab in	AUSTRIA
1 lab in	BELGIUM
2 labs in	BRAZIL
1 lab in	CANADA
1 lab in	CHILE
2 labs in	FINLAND
1 lab in	GERMANY
1 lab in	ITALY
1 lab in	JAPAN
1 lab in	ROMANIA
2 labs in	SAUDI ARABIA
1 lab in	SINGAPORE
2 labs in	SPAIN
5 labs in	THE NETHERLANDS
5 labs in	U.S.A.
3 labs in	UNITED KINGDOM
1 lab in	VIETNAM

APPENDIX 3

Abbreviations:

C	= final result after checking of first reported suspect result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
E	= error in calculations
U	= 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, January 2010
2 ASTM E178-02
3 ASTM E1301-03
4 ISO 5725-86
5 ISO 5725, parts 1-6, 1994
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/).