Results of Proficiency Test
Cetane Number of Diesel Fuel
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Organised by: Institute for Interlaboratory Studies
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1 INTRODUCTION

Since 2000, the Institute for Interlaboratory Studies organized every year a proficiency test for the determination of Cetane Number (CN) on diesel fuel. As part of the annual proficiency test program of 2010/2011 the institute decided to continue this proficiency test and with the determination of Derived Cetane Number (DCN).
In this international interlaboratory study, 44 laboratories from 27 different countries have participated. See appendix 3 for the number of participants per country. In this report, the results of the "Cetane number and DCN" proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies (i.i.s.) in Spijkenisse, The Netherlands, was the organiser of this proficiency test. Sample analyses for fit-for-use and homogeneity testing were subcontracted. In this Interlaboratory study, it was decided to send four 1 L bottles of sample #1063. On sample #1063, it was requested to determine Cetane Number according ASTM D613 (CFR F-5 engine) or/and to determine Derived Cetane Number according D6890 or/and D7170 (both combustion analyzers). Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluations.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in accordance with ISO guide 43 and ILAC-G13:2007, (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This ensures 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

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

2.4 SAMPLES

The necessary bulk material was purchased from the local market. The approx. 200 litre gasoil was homogenised in a pre-cleaned metal drum. After homogenisation, the bulk sample was divided over 190 brown glass bottles of one litre (labelled #1063). The homogeneity of the subsamples was checked by determination of Density in accordance with ASTM D4052:09 on 8 stratified randomly selected samples.

	Density @ 15°C in kg/L
Sample #1063-1	0.83652
Sample #1063-2	0.83655
Sample #1063-3	0.83651
Sample #1063-4	0.83652
Sample #1063-5	0.83651
Sample #1063-6	0.83651
Sample #1063-7	0.83651
Sample #1063-8	0.83656

table 1: homogeneity test of subsample #1063

From the above results, the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities in agreement with the procedure of ISO13528, Annex B2 in the next table:

	Density @ 15°C in kg/L
r (observed)	0.00006
reference method	D 4052:09
0.3 x R (ref. method)	0.00015

table 2: homogeneity of subsample #1063

The calculated repeatability was less than 3 times the reproducibility of the reference method. Therefore, homogeneity of all subsamples was assumed.

Four identical samples of gasoil (4*1 L of sample #1063) were sent to each of the participating laboratories on September 15, 2010.

2.5 STABILITY OF THE SAMPLES

The stability of the material, packed in the brown glass bottles, was checked. The materials were found sufficiently stable for the period of the proficiency test.

2.6 ANALYSIS

The participants were asked to determine the Cetane number in accordance with ASTM D613 (or the equivalent IP 41 or ISO 5165) or/and DCN in accordance with ASTM D6890 or/and ASTM D7170 methods.

To get comparable results, a detailed report form on which the units and the standard methods were printed, was sent together with each set of samples. Also, a letter of instructions and a SDS were added to the package.

3 RESULTS

During four weeks after sample dispatch, the results of the individual laboratories were gathered. The original data are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to 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 ‘i.i.s. 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.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plot was made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported 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, a Kernel Density Graph was 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 4; nr.14 and 15)

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.

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:

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

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:

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

4 EVALUATION

In this interlaboratory study, only one problem was encountered during the dispatch of the samples. However, several laboratories reported that the engine was into maintenance and therefore they were not able to report any results.
In total 9 participants did not report test results and 6 participants reported test results after the final reporting date. In total 32 participants reported 40 numerical results. Observed were 5 outlying results, which is 12.5%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

CN - D613: This determination was not problematic. Three statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in good agreement with the requirements of ASTM D613:10. The participants were requested to report the used primary and secondary reference fuel, which

are listed in appendix 2. No correlation between reported results and details was observed.

DCN - D6890: Four laboratories reported results. Three results are in good agreement with the D613 results.

DCN - D7170: Only two laboratories reported results. Both results are not in agreement with the D613 results.

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 that participated. The average result of the evaluated parameter, calculated reproducibility and reproducibility, derived from literature standards (ASTM D 613:08 and ASTM D6890:09) is compared in the next table.

Parameters	n	Average	2.8 * sd	R (lit)	Test method
Cetane Number	25	58.06	2.96	5.05	D613:10
DCN	3	57.85	0.69	3.60	D6890:09
ID	3	3.49	0.04	0.21	D6890:09

Table 3: summary of test results on diesel fuel sample #1063

5 COMPARISON WITH PREVIOUS PROFICIENCY TESTS

	October 2010	*October 2009*	*October 2008*	*October 2007*
Number of reporting labs	32	31	33	31
Statistical outliers	5	0	1	0
Percentage outliers	12.5%	0%	2.2%	0%

table 4: comparison of statistical parameters with previous proficiency tests

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency test was compared against the requirements of the respective standard. The conclusions are given the following table:

Determination	*October 2010*	*October 2009*	*October 2008*	*October 2007*
Cetane Number	+	+/-	++	+
Derived Cetane Number	++	++	++	+
Ignition Delay	++	--	++	n.e.

table 5: comparison determinations against the standard requirements

The following performance categories were used in the above table:

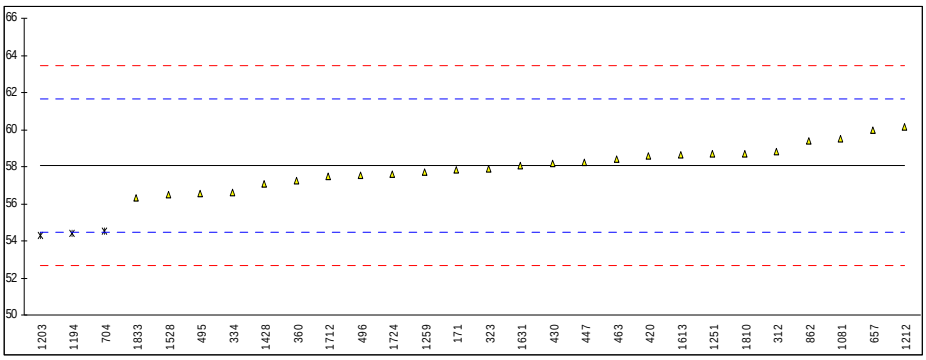
++: group performed much better than the standard
+ : group performed better than the standard
+/-: group performance equals the standard
- : group performed worse than the standard
-- : group performed much worse than the standard
n.e.: not evaluated

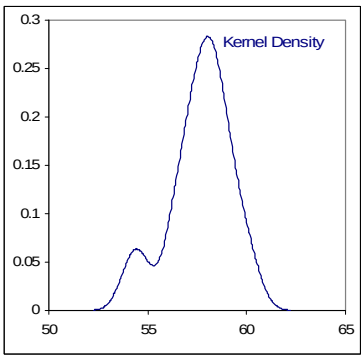
APPENDIX 1

Determination of Cetane Number (ASTM D613) of sample #1063

lab	method	value	mark	Z(targ)	remarks
171	D613	57.8		-0.15	
312	D613	58.8		0.41	
323	D613	57.9		-0.09	
334	D613	56.6		-0.81	
360	D613	57.27		-0.44	
420	D613	58.58		0.29	
430	D613	58.2		0.08	
445		-----		-----	
447	D613	58.22		0.09	
463	D613	58.4		0.19	
495	D613	56.53		-0.85	
496	D613	57.53		-0.30	
657	D613	60.0		1.07	
704	D613	54.50	DG(0.05)	-1.98	
862	D613	59.40		0.74	
962		-----		-----	
1080		-----		-----	
1081	D613	59.5		0.80	
1161		-----		-----	
1194	D613	54.4	DG(0.05)	-2.03	
1203	ISO5165	54.3	G(0.05)	-2.09	
1212	D613	60.15		1.16	
1218		-----		-----	
1251	D613	58.7		0.35	
1259	D613	57.69		-0.21	
1345		-----		-----	
1409		-----		-----	
1419		-----		-----	
1428	D613	57.1		-0.53	
1433		-----		-----	
1528	D613	56.50		-0.87	
1613	D613	58.66		0.33	
1631	D613	58.03		-0.02	
1634		-----		-----	
1636		-----		-----	
1650		-----		-----	
1712	D613	57.45	C	-0.34	First reported 61.85
1724	D613	57.6		-0.26	
1807		-----		-----	
1810	D613	58.71		0.36	
1833	D613	56.29		-0.98	
1936		-----		-----	
1937		-----		-----	
1938		-----		-----	

normality	OK
n	25
outliers	3
mean (n)	58.06
st.dev. (n)	1.058
R(calc.)	2.96
R(D613:10)	5.05





Determination of Derived Cetane Number (D6890) of sample #1063

lab	method	value	mark	z(targ)	Ignition delay	mark	z(targ)	Air Temp.	Remarks
171		-----		-----	-----		-----	-----	
312		-----		-----	-----		-----	-----	
323		-----		-----	-----		-----	-----	
334		-----		-----	-----		-----	-----	
360		-----		-----	-----		-----	-----	
420		-----		-----	-----		-----	-----	
430	D6890	58.0		0.11	3.485		-0.13	537	
445	IP498	60.63	G(0.01)	2.16	3.322	G(0.01)	-2.28	547	
447		-----		-----	-----		-----	-----	
463		-----		-----	-----		-----	-----	
495		-----		-----	-----		-----	-----	
496		-----		-----	-----		-----	-----	
657		-----		-----	-----		-----	-----	
704		-----		-----	-----		-----	-----	
862		-----		-----	-----		-----	-----	
962		-----		-----	-----		-----	-----	
1080	D6890	57.57		-0.22	3.513		0.24	586.1	
1081		-----		-----	-----		-----	-----	
1161		-----		-----	-----		-----	-----	
1194		-----		-----	-----		-----	-----	
1203		-----		-----	-----		-----	-----	
1212		-----		-----	-----		-----	-----	
1218		-----		-----	-----		-----	-----	
1251		-----		-----	-----		-----	-----	
1259		-----		-----	-----		-----	-----	
1345		-----		-----	-----		-----	-----	
1409		-----		-----	-----		-----	-----	
1419		-----		-----	-----		-----	-----	
1428		-----		-----	-----		-----	-----	
1433		-----		-----	-----		-----	-----	
1528		-----		-----	-----		-----	-----	
1613		-----		-----	-----		-----	-----	
1631		-----		-----	-----		-----	-----	
1634		-----		-----	-----		-----	-----	
1636		-----		-----	-----		-----	-----	
1650		-----		-----	-----		-----	-----	
1712		-----		-----	-----		-----	-----	
1724		-----		-----	-----		-----	-----	
1807	D6890	57.99		0.11	3.486		-0.11	592.6	
1810		-----		-----	-----		-----	-----	
1833		-----		-----	-----		-----	-----	
1936		-----		-----	-----		-----	-----	
1937		-----		-----	-----		-----	-----	
1938		-----		-----	-----		-----	-----	
	normality	n.a.			n.a.			n.a.	
	n	3			3			n.a.	
	outliers	1			1			n.a.	
	mean (n)	57.85			3.495			n.a.	
	st.dev. (n)	0.245			0.0159			n.a.	
	R(calc.)	0.69			0.045			n.a.	
	R(D6890:09)	3.60			0.212			n.a.	

Determination of Derived Cetane Number (D7170) of sample #1063

lab	method	value	mark	z(targ)	Ignition delay	mark	z(targ)	Air Temp.	Remarks
171	D7170	63.98		-----	2.67		-----	579.4	
312		-----		-----	-----		-----	-----	
323		-----		-----	-----		-----	-----	
334		-----		-----	-----		-----	-----	
360		-----		-----	-----		-----	-----	
420		-----		-----	-----		-----	-----	
430		-----		-----	-----		-----	-----	
445		-----		-----	-----		-----	-----	
447		-----		-----	-----		-----	-----	
463		-----		-----	-----		-----	-----	
495		-----		-----	-----		-----	-----	
496		-----		-----	-----		-----	-----	
657		-----		-----	-----		-----	-----	
704		-----		-----	-----		-----	-----	
862		-----		-----	-----		-----	-----	
962		-----		-----	-----		-----	-----	
1080		-----		-----	-----		-----	-----	
1081		-----		-----	-----		-----	-----	
1161		-----		-----	-----		-----	-----	
1194		-----		-----	-----		-----	-----	
1203		-----		-----	-----		-----	-----	
1212		-----		-----	-----		-----	-----	
1218		-----		-----	-----		-----	-----	
1251		-----		-----	-----		-----	-----	
1259		-----		-----	-----		-----	-----	
1345		-----		-----	-----		-----	-----	
1409		-----		-----	-----		-----	-----	
1419	D7170	47.89		-----	3.63		-----	552	
1428		-----		-----	-----		-----	-----	
1433		-----		-----	-----		-----	-----	
1528		-----		-----	-----		-----	-----	
1613		-----		-----	-----		-----	-----	
1631		-----		-----	-----		-----	-----	
1634		-----		-----	-----		-----	-----	
1636		-----		-----	-----		-----	-----	
1650		-----		-----	-----		-----	-----	
1712		-----		-----	-----		-----	-----	
1724		-----		-----	-----		-----	-----	
1807		-----		-----	-----		-----	-----	
1810		-----		-----	-----		-----	-----	
1833		-----		-----	-----		-----	-----	
1936		-----		-----	-----		-----	-----	
1937		-----		-----	-----		-----	-----	
1938		-----		-----	-----		-----	-----	
	normality	n.a.			n.a.			n.a.	
	n	2			2			2	
	outliers	0			0			0	
	mean (n)	n.a.			n.a.			n.a.	
	st.dev. (n)	n.a.			n.a.			n.a.	
	R(calc.)	n.a.			n.a.			n.a.	
	R(lit)	unknown			unknown			unknown	

APPENDIX 2

Test details as reported by participants

lab	method	Filtered	Primary Reference Fuel	Secondary Reference Fuel
171	D613	NO	T-25/ 54.7	U-18/ 59.6
312	D613	NO		T 24 / U 17
323	D613	NO	High Cetane check fuel (52.45 cet nr)	T25 / U18
334	D613	NO	U18	T25
360	D613	NO		T25 / U18
420	D613	NO	None	U16 / T23 (Chevron Philips Chemicals Co.)
430	D613	YES	T24	U17
445		YES		
447	D613	NO	U17 / T24	53.0 High Check
463	D613	NO		T24 / U17
495	D613	YES	n-Cetane / Isohexadecane	n-Cetane / Isohexadecane
496	D613	NO	Isohexadecane	n-Cetane
657	D613	NO		T25 / U18
704	D613	NO	n-Cetane / alpha-methylnaphthalene	
862	D613	NO		T24 / U17
962		-----		
1080		-----		
1081	D613	-----		
1161		-----		
1194	D613	NO		
1203	D613	NO		T25 / U17
1212	D613	NO	60.3	54.8
1218		-----		
1251	D613	NO		T25 / U18 / HCCF
1259	D613	YES		U17 / T24
1345		-----		
1409		-----		
1419		-----		
1428	D613	NO	55.8	59.1
1433		-----		
1528	D613	NO		U17 / T24
1613	D613	NO		T-24 / U-17
1631	D613	NO	54.8	58.7
1634		-----		
1636		-----		
1650		-----		
1712	D613	YES		
1724	D613	NO	high check fuel and low check fuel	T24 / U17
1807		-----		
1810	D613	YES	T24 / U17	
1833	D613	YES	not used	T24 / U18
1936		-----		
1937		-----		
1938		-----		

APPENDIX 3

Number of participants per country

1 laboratory in	AUSTRIA
2 laboratories in	BELGIUM
1 laboratory in	BULGARIA
1 laboratory in	CROATIA
1 laboratory in	CYPRUS
2 laboratories in	CZECH REPUBLIC
1 laboratory in	FRANCE
1 laboratory in	GEORGIA
2 laboratories in	GERMANY
2 laboratories in	HUNGARY
1 laboratory in	IRELAND
1 laboratory in	JORDAN
1 laboratory in	P.R. of CHINA
2 laboratories in	POLAND
1 laboratory in	PORTUGAL
2 laboratories in	REPUBLIC OF MACEDONIA
1 laboratory in	ROMANIA
1 laboratory in	SAUDI ARABIA
1 laboratory in	SINGAPORE
1 laboratory in	SLOVAKIA
1 laboratory in	SPAIN
2 laboratories in	SWEDEN
3 laboratories in	THE NETHERLANDS
8 laboratories in	TURKEY
1 laboratory in	U.S.A.
1 laboratory in	UKRAINE
2 laboratories in	UNITED KINGDOM

APPENDIX 4

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 wrong unit
ex	= excluded from calculations
n.a.	= not applicable
n.d.	= not detected

Literature:

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