

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 2009/2010 the institute decided to continue this proficiency test and with the determination of Derived Cetane Number (DCN).

In this international interlaboratory study 36 laboratories from 23 different countries have participated. See appendix 2 for a list of participants in alphabetical country order. 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 was decided to send a 4\*1 L (labelled #0966). On this sample 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% 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 November 2008 (iis-protocol, version 3.1).

### **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 of 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 sample was homogenised in a pre-cleaned metal drum. After homogenisation, the bulk sample was divided over 184 brown glass bottles of one litre (labelled #0966). The homogeneity of the subsamples was checked by determination of Density in accordance with ASTM D4052:02e1 of 8 stratified randomly selected samples.

	Density @ 15°C in kg/L
Sample #0966-1	0.83601
Sample #0966-2	0.83599
Sample #0966-3	0.83599
Sample #0966-4	0.83598
Sample #0966-5	0.83598
Sample #0966-6	0.83599
Sample #0966-7	0.83599
Sample #0966-8	0.83599

table 1: homogeneity test of subsample #0966

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)	0.00003
reference method	D 4052:02e1
0.3 x R (ref. method)	0.00015

table 2: homogeneity of subsample #0966

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 #0966) were sent to each of the participating laboratories on September 16, 2009.

## 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 November 2008 (iis-protocol, version 3.1).

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

## 4 EVALUATION

In this interlaboratory study no problems were encountered during the execution. Several laboratories reported that the engine was into maintenance and therefore they were not able to report any results.

In total 5 participants did not report results and 4 participants reported the results after the final reporting date. In total 31 participants reported 37 numerical results. Observed were no outlying results. In proficiency studies outlier percentages of 3 % - 7.5 % are quite normal.

**CN - D613:** This determination is not problematic. No statistical outliers were observed. The calculated reproducibility is almost in agreement with the requirements of ASTM D613:08. 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: Only three laboratories reported D6890 results. The three results are in good agreement with the D613 results.

DCN - D7170: Only two laboratories reported D7170 results. The two results are in good 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	27	54.95	4.49	4.30	D613:08
DCN	5	55.44	2.39	4.36	D6890:09
ID	5	3.44	0.85	0.21	D6890:09

Table 3: summary of test results on diesel fuel sample #0966

## 5 COMPARISON WITH PREVIOUS PROFICIENCY TESTS

	October 2009	October 2008	October 2007	October 2006
Number of reporting labs	31	33	31	26
Statistical outliers	0	1	0	0
Percentage outliers	0%	2.2%	0%	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 2009	October 2008	October 2007	October 2006
Cetane Number	+/-	++	+	+
Derived Cetane Number	++	++	+	n.e.
Ignition Delay	--	++	n.e.	n.e.

table 5: comparison determinations against the standard requirements

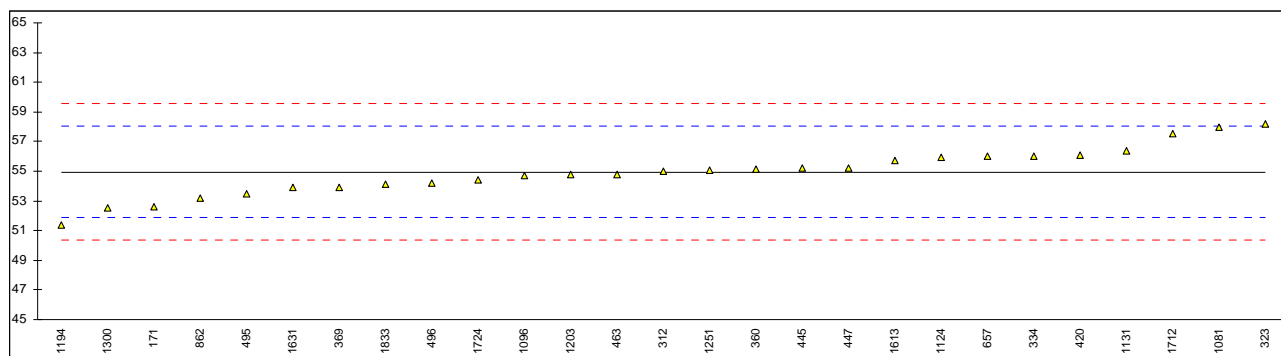
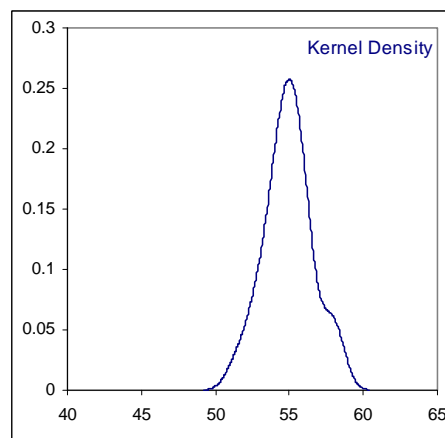
The following performance categories were used in the above table:

- ++: 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 #0966**

lab	method	value	mark	z(targ)	remarks
171	D613	52.6		-1.53	
312	D613	55.0		0.03	
323	D613	58.2		2.12	
334	D613	56.0		0.68	
360	D613	55.15		0.13	
369	D613	53.91		-0.68	
420	D613	56.064		0.73	
445	D613	55.2		0.16	
447	D613	55.25		0.20	
463	D613	54.8		-0.10	
495	D613	53.5		-0.94	
496	D613	54.20		-0.49	
657	D613	56.0		0.68	
840		----		----	
862	D613	53.19		-1.15	
1080		----		----	
1081	D613	58.0		1.99	
1096	D613	54.73		-0.14	
1124	D613	55.93		0.64	
1131	ISO5165	56.4		0.94	
1194	in house	51.4		-2.31	
1203	D613	54.8		-0.10	
1218		----		----	
1251	D613	55.1		0.10	
1300	D613	52.53		-1.58	
1318		----		----	
1613	D613	55.70		0.49	
1631	D613	53.9		-0.68	
1712	ISO5163	57.55		1.69	
1724	D613	54.4		-0.36	
1728		----		----	
1810		----		----	
1833	D613	54.15		-0.52	
1936		----		----	
1937		----		----	
1938		----		----	
normality	OK				
n	27				
outliers	0				
mean (n)	54.95				
st.dev. (n)	1.604				
R(calc.)	4.49				
R(D613:08)	4.30				



Determination of Derived Cetane Number of sample #0966

lab	method	value	mark	z(targ)	Ignition delay	mark	z(targ)	Air Temp.	Remarks
171		----		----	----			----	
312		----		----	----			----	
323		----		----	----			----	
334		----		----	----			----	
360		----		----	----			----	
369		----		----	----			----	
420		----		----	----			----	
445		----		----	----			----	
447		----		----	----			----	
463		----		----	----			----	
495		----		----	----			----	
496		----		----	----			----	
657		----		----	----			----	
840		----		----	----			----	
862		----		----	----			----	
1080	D6890	55.06		----	3.688			----	
1081		----		----	----			----	
1096		----		----	----			----	
1124		----		----	----			----	
1131	D6890	56.55		----	3.582			589.6	
1194		----		----	----			----	
1203		----		----	----			----	
1218		----		----	----			----	
1251		----		----	----			----	
1300		----		----	----			----	
1318	D7170	54.75		----	3.18			521.83	
1613		----		----	----			----	
1631		----		----	----			----	
1712		----		----	----			----	
1724		----		----	----			----	
1728	D7170	56.15		----	3.05			559.8	
1810	D6890	54.7		----	3.702			579	
1833		----		----	----			----	
1936		----		----	----			----	
1937		----		----	----			----	
1938		----		----	----			----	
	normality	OK			OK				
	n	5			5				
	outliers	0			0				
	mean (n)	55.44			3.44				
	st.dev. (n)	0.852			0.304				
	R(calc.)	2.39			0.85				
	R(D6890)	4.36			0.21				
		<u>Only</u>	<u>Only</u>		<u>Only</u>	<u>Only</u>			
		<u>D7170:</u>	<u>D6890:</u>		<u>D7170:</u>	<u>D6890:</u>			
	normality	n.a.	n.a.		n.a.	n.a.			
	n	2	3		2	3			
	outliers	0	0		0	0			
	mean (n)	55.44	55.44		3.12	3.66			
	st.dev. (n)	n.a.	n.a.		n.a.	n.a.			
	R(calc.)	n.a.	n.a.		n.a.	n.a.			
	R(lit)	n.a.	n.a.		n.a.	n.a.			

**APPENDIX 2****Test details as reported by participants**

lab	method	Filtered	Primary Reference Fuel	Secondary Reference Fuel
171	D613	No	T24	U17
312	D613	No	--	T24 / U17
323	D613	No	Diesel Cetane CK Fuel high (52.4)	T24 / U17
334	D613	No	U17	T24
360	D613	No	--	T24 / U17
369	D613	No	--	T23 / U16
420	D613	--	53.9	59.0
445	D613	No	T24	U17
447	D613	No	T24 / U13	53.0 High Check Reference
463	D613	No	U17	T24
495	D613	Yes	n-Cetane	Isohexadecan
496	D613	No	--	--
657	D613	No	--	T24 / U17
840	--	--	--	--
862	D613	No	n-Cetane	T23 / U16
1080	--	--	--	--
1081	D613	--	--	--
1096	D613	No	--	T23 / U16
1124	D613	No	--	T24 / U17
1131	ISO5165	No	--	--
1194	in house	No	1	1
1203	D613	No	--	--
1218	--	--	--	--
1251	D613	No	--	Hydrocarbon mixture tank T and tank U
1300	D613	No	--	--
1318	--	--	--	--
1613	D613	No	--	--
1631	D613	--	--	--
1712	ISO5163	No	--	--
1724	D613	No	High and low check fuel	T24 / U17
1728	--	--	--	--
1810	--	--	--	--
1833	D613	Yes	Primary reference is not used	T24 / U17
1936	--	--	--	--
1937	--	--	--	--
1938	--	--	--	--

## APPENDIX 3

### Number of participants per country

- 1 laboratory in BELGIUM
- 1 laboratory in BULGARIA
- 1 laboratory in CYPRUS
- 2 laboratories in CZECH REPUBLIC
- 1 laboratory in ESTONIA
- 1 laboratory in FRANCE
- 2 laboratories in GERMANY
- 2 laboratories in HUNGARY
- 1 laboratory in IRELAND
- 1 laboratory in JORDAN
- 2 laboratories in LATVIA
- 1 laboratory in LITHUANIA
- 1 laboratory in NORWAY
- 1 laboratory in P.R. of CHINA
- 2 laboratories in POLAND
- 1 laboratory in ROMANIA
- 1 laboratory in SINGAPORE
- 1 laboratory in SWEDEN
- 3 laboratories in THE NETHERLANDS
- 6 laboratories in TURKEY
- 1 laboratory in U.S.A.
- 2 laboratories in UNITED KINGDOM
- 1 laboratory in VIETNAM

## 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:

- 1 i.i.s. Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, November 2008
- 2 ASTM E178-02
- 3 ASTM E1301-03
- 4 ISO 5725-86
- 5 ISO 5725, parts 1-6, 1994
- 6 ISO13528:05
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- 9 IP 367/84
- 10 DIN 38402 T41/42
- 11 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
- 12 J.N. Miller, Analyst, 118, 455, (1993)
- 13 IMPCA Methanol Reference Specifications, IMPCA, Brussels, April 1999.
- 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/>).