

**Results of Proficiency Test
Cetane Number of Diesel Fuel
October 2003**

**Organised by: Institute for Interlaboratory Studies
Dordrecht, the Netherlands**

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1 INTRODUCTION

On request of several participants it was decided to organize again a proficiency test for the analysis of Cetane Number on diesel fuel, as part of the annual proficiency test program of 2003/2004. In this international interlaboratory study 27 laboratories from 14 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 on diesel fuel' proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies (i.i.s.) in Dordrecht, The Netherlands, was the organiser of this proficiency test. Participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Dordrecht, the Netherlands, is accredited in agreement with ISO guide 43 and ILAC-G13:2000, (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie).

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of November 2003 (i.i.s.-protocol, version 3.0).

The participants were asked to report the analytical results using the indicated units on the report form.

2.3 SAMPLES

The -not doped- bulk material was purchased from the local market. The approx. 150 litre sample was homogenised in a pre-cleaned metal drum. After homogenisation, 30 subsamples were transferred to 5 litre metal cans and labelled 0362. The homogeneity of the subsamples was checked by determination of density in accordance with ASTM D4052:02 of 5 stratified random selected samples.

	<i>density @ 15 °C (kg/L)</i>
Sample 0362-1	0.8288
Sample 0362-2	0.8288
Sample 0362-3	0.8288
Sample 0362-4	0.8288
Sample 0362-5	0.8288

table 1: homogeneity test of subsample 0362

From table 1 the repeatabilities of the results were calculated by multiplication of the standard deviation by 2.8:

	<i>density @ 15 °C (kg/L)</i>
r (sample 0362)	0.0000
Reference test	D4052:02
r (reference test)	0.0001

table 2: repeatability of subsample 0362

The repeatability of the results for density was in agreement with the repeatability as required by ASTM D4052:02. Therefore, homogeneity of the samples 0362 was assumed.

One 5 litre sample was sent to each of the participating laboratories on September 24, 2003.

2.4 STABILITY OF THE SAMPLES

In order to be sure that the material, which was used in this proficiency test, was stable for the valid period, the stability of the material, packed in the metal can, was checked prior to use.

2.5 ANALYSIS

The participants were asked to determine the cetane number.

To get comparable results a detailed report form, on which the units were prescribed as well as some of the required standards, was sent together with each set of samples. Also a letter of instructions and a MSDS were added to the 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 the appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after deadline, a reminder fax was sent to those laboratories that had not yet reported.

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 (raw data of the) reported results. Additional or corrected results have been used for data analysis and the 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 August 1998 (iis98protocol, version 2.0).

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. Not all data sets proved to have a normal distribution, in which cases the conclusions of statistical evaluation should be used with due care.

In accordance with 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, by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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 results are plotted. The corresponding laboratory numbers are under the X-axis. A straight line presents the average of the reported data. Two striped lines present the reproducibility limits of the relevant standard, calculated as mean \pm target reproducibility, parallel to the average line. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

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. The z-scores were calculated according to:

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

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 is as follows:

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

4 EVALUATION

In this interlaboratory study some problems with sample despatch were encountered during the execution. Not all 27 participants reported their result in this proficiency test. Five participants could not report their result, because their apparatus was in repair. No outlying results were observed.

The determination of Cetane Number of diesel fuel was not at all problematic for this group of participants. No results were outside the reproducibility limits and no outliers were observed. The calculated reproducibility was in good agreement with the requirements of ASTM D613:03.

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 results of the evaluated parameter, calculated reproducibility and reproducibility, derived from literature standard (in casu ASTM D613:03) is compared in the next tables.

<i>Parameters</i>	<i>unit</i>	<i>n</i>	<i>Average</i>	<i>2.8 * sd</i>	<i>R (lit)</i>
Cetane Number		22	53.893	3.217	4.537

Table 3: summary of testresults of diesel fuel sample 0362

Without further statistical calculations it can be concluded that for this test there is a good compliance of the group of participating laboratories with the relevant standard.

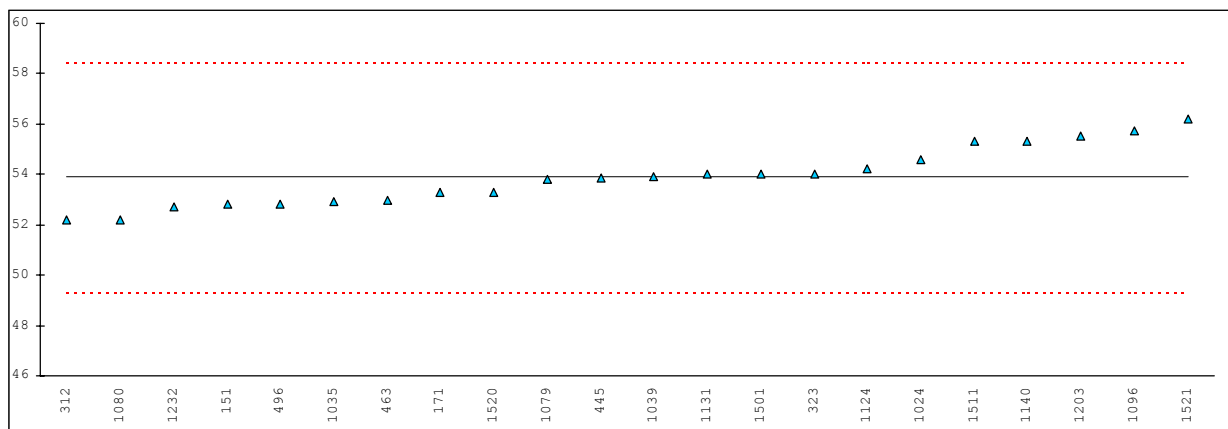
5 COMPARISON WITH THE PREVIOUS PROFICIENCY TEST OF OCTOBER 2002

Since the last round of this proficiency test in October 2002 the number of participants has increased from 23 to 27. Like in the previous round no statistical outliers were found. The performance of the group in 2002 was compared with the performance of the group in the last round (2003) and a small improvement was noticed. (RSD(2003)=6.0% vs RSD(2002)=6.2%)

Determination of Cetane Number of sample 0362

lab	Method	value	mark	Z(targ)	Remarks
151	D613	52.8		-0.67	
171	D613	53.3		-0.37	
238		-----		-----	
312	D613	52.2		-1.05	
323	D613	54.0		0.07	
445	D613	53.86		-0.02	
447		-----		-----	
463	D613	53.0		-0.55	
496	D613	52.83		-0.66	
1024	DIN51773	54.6		0.44	
1033		-----		-----	
1035	D613	52.9		-0.61	
1039	D613	53.9		0.00	
1079	D613	53.8		-0.06	
1080	D6890	52.2		-1.05	
1096	D613	55.71		1.12	
1124	D613	54.22		0.20	
1131	D613	54.0		0.07	
1140	D613	55.3		0.87	
1203	D613	55.5		0.99	
1218		-----		-----	
1232	D613	52.72		-0.72	
1501	D613	54.0		0.07	
1511	D613	55.30	C	0.87	First reported 57.3
1520	D613	53.31		-0.36	
1521	In house	56.2	C	1.42	First reported 58.1
2130		-----		-----	

normality OK
n 22
outliers 0
mean (n) 53.893
st.dev. (n) 1.1490
R(calc.) 3.217
R(D163:03) 4.537



APPENDIX 2**List of number of participants per country**

Number	Country
1 lab in	AUSTRIA
2 labs in	BELGIUM
2 labs in	ESTONIA
2 labs in	GERMANY
2 labs in	HUNGARY
1 lab in	IRELAND
1 lab in	LATVIA
2 labs in	LITHUANIA
1 lab in	NIGERIA
2 labs in	POLAND
1 lab in	SWEDEN
3 labs in	THE NETHERLANDS
2 labs in	U.S.A.
5 labs in	UNITED KINGDOM

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
ex	= excluded from calculations
E	= error in calculations
n.a.	= not applicable

Literature:

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, August 1998
- 2 ASTM E178-89
- 3 ASTM E1301-89
- 4 ISO 5725-86
- 5 ISO 5725, parts 1-6, 1994
- 6 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
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- 8 IP 367/84
- 9 DIN 38402 T41/42
- 10 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
- 11 J.N. Miller, Analyst, 118, 455, (1993)