Institute for
Interlaboratory Studies

Results of Proficiency Test
Biodiesel B100 (100% FAME)
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Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since 2008 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the analysis of Fatty Acid Methyl Esters (FAME) used as Biodiesel B100 in accordance with the latest version of ASTM D6751 and EN14214+A2 twice a year. During the annual proficiency testing program of 2024 it was decided to continue the round robin for the analysis of Biodiesel B100.

In this interlaboratory study registered for participation:
- 60 laboratories in 25 countries for regular analyses iis24G03
- 29 laboratories in 17 countries on the determination of Metals iis24G03M
- 38 laboratories in 19 countries on the determination of Total Contamination iis24G03TC
- 24 laboratories in 13 countries on the Cold Soak Test iis24G03CST

In total 69 laboratories in 27 countries registered for participation in one or more proficiency tests, see appendix 2 for the number of participants per country. In this report the results of the Biodiesel B100 proficiency tests are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to a laboratory that has performed the tests in accordance with for ISO/IEC17043 relevant requirements of ISO/IEC17025.
In this proficiency test the participants received, depending on the registration, from one up to four different samples of Biodiesel B100, see table below.

Sample ID	PT ID	Quantity	Purpose
#24060	iis24G03	1x 1 L + 1x 0.5 L	Regular analysis
#24061	iis24G03M	1x 0.1 L	Metal analyzes
#24062	iis24G03TC	1x 1 L	Total Contamination
#24063	iis24G03CST	1x 0.5 L	Cold Soak Test

Table 1: samples used in Biodiesel B100 iis24G03

Participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 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 organization 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 June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

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

For the preparation of the sample for the regular analysis in Biodiesel B100 a batch of approximately 200 liters of Rapeseed Methyl Ester (RME) was obtained from a local supplier. After homogenization 75 amber glass bottles of 1 L and 75 amber glass bottles of 0.5 L were filled for the regular round and labelled #24060.
The homogeneity of the subsamples was checked by the determination of Density at 15 °C in accordance with ISO12185 on 8 stratified randomly selected subsamples.

	Density at 15 °C in kg/m^3
sample #24060-1	883.58
sample #24060-2	883.53
sample #24060-3	883.58
sample #24060-4	883.58
sample #24060-5	883.56
sample #24060-6	883.57
sample #24060-7	883.56
sample #24060-8	883.53

Table 2: homogeneity test results of subsamples #24060

From the above test results the repeatability was calculated and compared with 0.3 times the reproducibility of the reference test method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Density at 15 °C in kg/m^3
r (observed)	0.06
reference test method	ISO12185:96
0.3 x R (reference test method)	0.15

Table 3: evaluation of the repeatability of subsamples #24060

The calculated repeatability is in agreement with 0.3 times the reproducibility of the reference test method. Therefore, homogeneity of the subsamples was assumed.

For the preparation of the sample for the analyzes of Metals in Biodiesel B100 a batch of approximately 5 L biodiesel was selected and spiked with Calcium, Phosphorus, Potassium and Sodium. After homogenization 50 PE bottles of 100 mL were filled and labelled #24061. The homogeneity of the subsamples was checked by the determination of Phosphorus according EN14107 and Sodium in accordance with EN14538 on 8 stratified randomly selected subsamples.

	Phosphorus in mg/kg	Sodium in mg/kg
sample #24061-1	7.0	10.08
sample #24061-2	6.8	9.92
sample #24061-3	7.1	10.16
sample #24061-4	6.9	10.06
sample #24061-5	6.9	9.78
sample #24061-6	7.0	9.98
sample #24061-7	6.9	9.53
sample #24061-8	6.9	9.66

Table 4: homogeneity test results of subsamples #24061

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibility of the reference test method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Phosphorus in mg/kg	Sodium in mg/kg
r (observed)	0.26	0.62
reference test method	EN14107:03	EN14108:03
0.3 x R (reference test method)	0.41	1.19

Table 5: evaluation of the repeatabilities of subsamples #24061

The calculated repeatabilities are in agreement with 0.3 times the corresponding reproducibility of the reference test methods. Therefore, the homogeneity of the subsamples was assumed.

For the preparation of the sample for the determination of Total Contamination in Biodiesel B100 a batch of approximately 50 liters of Biodiesel B100 was obtained by a local supplier. A defined volume of freshly prepared and well shaken dust suspension of Arizona Dust material in a lubricating oil was added to empty amber glass bottle of 1 L by means of a calibrated pipette. The addition was checked by weighing the bottle before and after the addition. In total 42 bottles were prepared and subsequently filled up with 1 L Biodiesel B100 and homogenized. The subsamples were labelled #24062. A random subsample and a blank B100 sample from the batch were taken to check the Total Contamination.

For the preparation of the sample for the Cold Soak Test in Biodiesel B100 a batch of approximately 25 liters of Rapeseed Methyl Ester (RME) was obtained from a local supplier. After homogenization 45 amber glass bottles of 0.5 L were filled and labelled #24063.
The homogeneity of the subsamples was checked by the determination of Density at 15 °C in accordance with ISO12185 on 8 stratified randomly selected subsamples.

	Density at 15 °C in kg/m^3
sample #24063-1	883.69
sample #24063-2	883.69
sample #24063-3	883.69
sample #24063-4	883.69
sample#24063- 5	883.69
sample #24063-6	883.70
sample #24063-7	883.69
sample #24063-8	883.69

Table 6: homogeneity test results of subsamples #24063

From the above test results the repeatability was calculated and compared with 0.3 times the reproducibility of the reference test method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Density at 15 °C in kg/m^3
r (observed)	0.01
reference test method	ISO12185:96
0.3 x R (reference test method)	0.15

Table 7: evaluation of the repeatability of subsamples #24063

The calculated repeatability is in agreement with 0.3 times the reproducibility of the reference test method. Therefore, homogeneity of the subsamples was assumed.

Depending on the registration of the participant the appropriate set of PT samples was sent on April 10, 2024. An SDS was added to the sample package.

2.5 STABILITY OF THE SAMPLES

The stability of the Biodiesel B100 packed in amber glass bottles and PE bottles was checked. The material was found sufficiently stable for the period of the proficiency test.

2.6 ANALYZES

The requested analyzes for the Biodiesel B100 samples are in accordance with the requirements of EN14214:12+A2:19 and/or ASTM D6751:24.

Parameter	EN14214:12+A2:19	Parameter	ASTM D6751:24
Acid Value	EN14104	Acid Number	ASTM D664
Calorific Value	DIN51900		
		Carb. Res. 100% FAME	ASTM D4530
CFPP	EN116		
Cloud Point	EN23015	Cloud Point	ASTM D2500
Copper Strip Corrosion	ISO2160	Copper Strip Corrosion	ASTM D130
Density at 15 °C	ISO12185		
		Distillation	ASTM D1160
Flash Point (Recc)	ISO3679		
Flash Point (PMcc)	ISO2719	Flash Point	ASTM D93
Iodine Value	EN14111		
Kin. Viscosity at 40 °C	ISO3104	Kin. Viscosity at 40 °C	ASTM D445
Oxidation Stability	EN14112	Oxidation Stability	EN15751
Sulfated Ash	ISO3987	Sulfated Ash	ASTM D874
Sulfur	ISO20846	Sulfur	ASTM D5453
Water	ISO12937	Water and Sediment	ASTM D2709
Cetane Number	EN5165	Cetane Number	ASTM D613
		Derived Cetane Number	ASTM D7668
Calcium + Magnesium	EN14538	Calcium + Magnesium	EN14538
Phosphorus	EN14107	Phosphorus	ASTM D4951
Potassium + Sodium	EN14108/14109	Potassium + Sodium	EN14538
Polyunsaturated esters	EN15779		
Methanol	EN14110	Methanol	EN14110
mono-, di-, tri-Glycerides	EN14105	Monoglyceride content	ASTM D6584
Free + Total Glycerol	EN14105	Free + Total Glycerol	ASTM D6584
Total ester content	EN14103		
Linolenic Acid	EN14103		
Total Contamination	EN12662		
Cold Soak Filterability			ASTM D7501

Table 8: requirements and test methods acc. to specifications EN14214:12+A2:19 and/or ASTM D6751:24.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test results but report as much significant figures as possible. It was also requested not to report ‘less than’ test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

To get comparable test results, a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis/. The participating laboratories are also requested to confirm the

sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis/. The reported test results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test 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 reported test results (no reanalyzes). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization 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 June 2018 (iis-protocol, version 3.5).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test 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. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's 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 averages and 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. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

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

3.2 GRAPHICS

In order to visualize 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 test results are plotted. The corresponding laboratory numbers are on 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 reference test method. 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. Also, a normal Gauss curve (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

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 (derived from e.g. ISO or ASTM test methods), the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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 according to:

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

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

Absolute values for z<2 are very common and absolute values for z>3 are very rare.
The usual interpretation of z-scores is as follows:

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

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