Institute for
Interlaboratory Studies

Results of Proficiency Test
Crude Oil
November 2024

Preview

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since 1998 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the analysis of Crude Oil every year. During the annual proficiency testing program of 2024 it was decided to continue the round robin for the analysis of Crude Oil.

In this interlaboratory study registered for participation:
- 169 laboratories in 56 countries for regular analyzes in Crude Oil iis24R01
- 45 laboratories in 24 countries on the Mercury analysis in Crude Oil iis24R01Hg

In total 174 laboratories in 57 countries registered for participation in one or both proficiency tests, see appendix 2 for the number of participants per country. In this report the results of the Crude Oil 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, one or two different samples of Crude Oil, see table below. A 1 Liter wide-neck bottle is used to enable the use of a large size diameter high speed shear mixer for homogenization.

Sample ID	PT ID	Quantity	Purpose
#24210	iis24R01	1x 1 L	Regular analyzes
#24211	iis24R01Hg	1x 40 mL vial	Mercury

Table 1: Crude Oil samples used in PTs iis24R01 and iis24R01Hg

The 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 Organization, Statistics and Evaluation' of October 2024 (iis-protocol, version 4.0). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

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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 analyzes in Crude Oil a batch of approximately 190 liters of Crude Oil was obtained from a local refinery. After homogenization 180 wide-neck transparent colorless 1 L glass bottles were filled and labelled #24210. The bottles were put into red plastic bags to protect it from light.
The homogeneity of the subsamples was checked by determination of Density at 15 °C in accordance with ASTM D5002 and Water in accordance with ASTM D4377 on 8 stratified randomly selected subsamples.

	Density at 15 °C in kg/m^3	Water %V/V
sample #24210-1	855.39	0.0544
sample #24210-2	855.27	0.0644
sample #24210-3	855.31	0.0581
sample #24210-4	855.45	0.0613
sample #24210-5	855.27	0.0665
sample #24210-6	855.27	0.0607
sample #24210-7	855.27	0.0568
sample #24210-8	855.23	0.0622

Table 2: homogeneity test results of subsamples #24210

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.

	Density at 15 °C in kg/m^3	Water %V/V
r (observed)	0.21	0.0112
reference test method	ASTM D5002:22	D4377:00R17, W20
0.3 x R (reference test method)	1.06	0.0131

Table 3: evaluation of the repeatabilities of subsamples #24210

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

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For the preparation of the sample for the Mercury determination in Crude Oil a batch of approximately 12 liters of Crude Oil was obtained from a local refinery. The batch was spiked with organic and inorganic bounded Mercury. After homogenization 65 vials of 40 mL were filled and labelled #24211.
The homogeneity of the subsamples was checked by the determination of Mercury in accordance with ASTM D7623 on 8 stratified randomly selected subsamples.

	Mercury as Hg in µg/kg
sample #24211-1	23
sample #24211-2	23
sample #24211-3	24
sample #24211-4	23
sample #24211-5	23
sample #24211-6	23
sample #24211-7	23
sample #24211-8	24

Table 4: homogeneity test results of subsamples #24211

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

	Mercury as Hg in µg/kg
r (observed)	1
reference method	Horwitz
0.3 x R (reference method)	6

Table 5: evaluation of the repeatability of subsamples #24211

The calculated repeatability is in agreement with 0.3 times the estimated reproducibility calculated with the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

Depending on the registration of the participant the appropriate set of PT samples was sent on October 9, 2024. An SDS was added to the sample package.

2.5 STABILITY OF THE SAMPLES

The stability of Crude Oil packed in the transparent colorless glass bottles and put into red plastic bags to protect it from light and in amber glass vials was checked. The material has been found sufficiently stable for the period of the proficiency test.

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2.6 ANALYZES

The participants were requested to determine on sample #24210: Total Acid Number, API Gravity, BS&W, Density at 15 °C, Kinematic Viscosity at 40 °C, Light ends (Methane, Ethane, Propane, iso-Butane, n-Butane, iso-Pentane, n-Pentane, cyclo-Pentane, Total Hexanes and Total of all C1-C6), Average Molecular Mass, Pour Point Maximum, Salt as Chloride, Sediment (Extraction method and Membrane filtration), Total Sulfur, Water and Simulated Distillation. It was also requested to report some analytical details about Total Acid Number determination.
On sample #24211 it was requested to determine Total Mercury.

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 download 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 Organization, Statistics and Evaluation’ of October 2024 (iis-protocol, version 4.0).

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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

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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:

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

The $z_{(target)}$ scores are listed in the test 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:

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

End of preview of this report, requests to obtain the full report can be sent to nl.iis@sgs.com

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