**Institute for
Interlaboratory Studies**

Results of Proficiency Test
Liquefied Propane and
Sulfur (total) in LPG
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Organized by: **Institute for Interlaboratory Studies
Spijkenisse, the Netherlands**

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1   INTRODUCTION

Since 2009 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the analysis of Liquefied Propane every year. From 2017 onwards a proficiency scheme for the analysis of Total Sulfur in LPG is also organized every year. During the annual proficiency testing program of 2024, it was decided to continue the round robin for both the analysis of Liquefied Propane and the analysis of Total Sulfur in LPG.

Because iis has limited gas-handling facilities in place to prepare gas samples, a co-operation with EffecTech (Uttoxeter, United Kingdom) was set up for the Liquefied Propane PT (iis24S04P) and a co-operation with Nippon Gases (Belgium) was set up for the Total Sulfur in LPG PT (iis24S04PS). Both EffecTech and Nippon Gases are fully equipped and have experience in the preparation of gas mixtures.

In the interlaboratory studies for Liquefied Propane 82 laboratories in 34 countries and for Total Sulfur in LPG 49 laboratories in 26 countries registered for participation, see appendix 2 for the number of participants per country. In this report the results of the Liquefied Propane and Total Sulfur in LPG 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). In this proficiency test the participants received, depending on the registration, one or two different samples of Liquefied Propane, see table below.

Sample ID	PT ID	Quantity	Purpose
#24200	iis24S04P	1 L cylinder	Composition and Physical properties
#24201	iis24S04S	5 L cylinder	Total Sulfur

Table 1: Gas samples used in PTs Liquefied Propane and Sulfur (total) in LPG

To optimize the costs for the participating laboratories it was decided to prepare one Liquified Propane Gas mixture per PT. For the Liquefied Propane PT, the mixture was divided over a batch of 75 cost-effective one-liter cylinders with dip tube device. For the Total Sulfur PT, the mixture was divided over a batch of 51 cost-effective five-liter cylinders with dip tube device. Each of the cylinders was uniquely numbered. The limited cylinder size is chosen to optimize transport and handling costs.
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.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043:2010. 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.
EffecTech is accredited in conformance ISO17025:2017 by UKAS (no. 0590).
Nippon Gases is accredited in conformance with ISO 9001:2015.

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.

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 PT on Liquefied Propane a batch of 75 uniquely coded one-liter cylinders with an artificial Liquefied Propane mixture was prepared and tested for homogeneity by EffecTech (Uttoxeter, United Kingdom) in conformance with ISO guide 35 and ISO/IEC17025 (job 24/0986). Each cylinder (with dip tube device) was filled with approximately 200 grams of Liquefied Propane mixture and labelled #24200. Every cylinder in the batch was analyzed using replicate measurements. The within bottle and between bottle variations were assessed in accordance with ISO Guide 35. This evaluation showed that all between bottle variations were small compared to the uncertainties on the reference values on each component.

The calculated repeatabilities were calculated per component 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.

	r (observed) in %mol/mol	0.3 x R (D2163:23) in %mol/mol
Ethane	0.0025	0.0543
Propane	0.0338	1.2441
Propene	0.0028	0.0670
iso-Butane	0.0071	0.0613

	r (observed) in %mol/mol	0.3 x R (D2163:23) in %mol/mol
n-Butane	0.0125	0.0632
1-Butene	0.0018	0.0237
iso-Butene	0.0033	0.0350
n-Pentane	0.0071	0.0276

Table 2: homogeneity test results of subsamples #24200

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.

For the PT on Total Sulfur in LPG a batch of 51 uniquely coded five-liter cylinders (with dip tube device) was prepared and tested for homogeneity by Nippon Gases (Belgium) (order/ref. nr. 467,654,001). Each cylinder was filled with approximately 1500 grams of LPG, spiked with Dimethyl Sulfide (DMS) and labelled #24201. Every cylinder in the batch was analyzed using replicate measurements. The within bottle and between bottle variations were assessed in accordance with ISO Guide 35. This evaluation showed that all between bottle variations were small compared to the uncertainties on the reference values on each component.

The repeatability of the determination of Total Sulfur 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.

	Total Sulfur in mg/kg
r (observed)	2.8
reference test method	ASTM D6667:21 LP gases
0.3 x R (reference test method)	14.5

Table 3: evaluation of the repeatability of subsamples #24201

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 October 18th, 2024. An SDS was added to the sample package.

2.5 STABILITY OF THE SAMPLES

EffecTech (Uttoxeter, United Kingdom) and Nippon Gases (Belgium) declare that the prepared gas cylinders have a shelf life of at least 6 months. This is sufficient for the proficiency testing purposes.

2.6 ANALYZES

The participants were requested to determine on sample #24200: Ethane, Propane, Propene, iso-Butane, n-Butane, 1-Butene, iso-Butene, n-Pentane, iso-Pentane, Molar Mass, Relative Density at 60/60 °F, Absolute and Relative Vapor Pressure at 100 °F, Absolute and Relative Vapor Pressure at 40 °C, Motor Octane Number (MON), Ideal Gross Heating Value and Ideal Net Heating Value at 14.696 psia and 60 °F.
On sample #24201 it was requested to determine Total Sulfur.

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

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

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:

$$
\begin{array}{ll}
|z| < 1 & \text{good} \\
1 < |z| < 2 & \text{satisfactory} \\
2 < |z| < 3 & \text{questionable} \\
3 < |z| & \text{unsatisfactory}
\end{array}
$$

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