



Institute for  
Interlaboratory Studies

**Results of Proficiency Test  
Naphtha P(IO)NA  
April 2024**

**Organized by:** Institute for Interlaboratory Studies  
Spijkenisse, the Netherlands

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**CONTENTS**

1 INTRODUCTION ..... 3

2 SET UP..... 3

2.1 ACCREDITATION..... 3

2.2 PROTOCOL ..... 3

2.3 CONFIDENTIALITY STATEMENT ..... 3

2.4 SAMPLES ..... 4

2.5 STABILITY OF THE SAMPLES ..... 4

2.6 ANALYZES ..... 5

3 RESULTS..... 5

3.1 STATISTICS ..... 5

3.2 GRAPHICS ..... 6

3.3 Z-SCORES..... 7

4 EVALUATION ..... 7

4.1 EVALUATION PER TEST ..... 8

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES ..... 12

4.3 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2024 WITH PREVIOUS PTS ..... 14

Appendices:

1. Data, statistical and graphical results..... 15

2. Number of participants per country ..... 66

3. Abbreviations and literature ..... 67

## 1 INTRODUCTION

Since 1994 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the analysis of Naphtha every year. During the annual proficiency testing program of 2024 it was decided to continue the round robin for the analysis of Naphtha P(IO)NA.

In this interlaboratory study 68 laboratories in 33 countries registered for participation, see appendix 2 for the number of participants per country. In this report the results of the Naphtha P(IO)NA proficiency test 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.

It was decided to send one sample of Naphtha in a 30 mL glass vial labelled #24044. 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 Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website [www.iisnl.com](http://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

A batch of approximately 3 liters of Naphtha was selected. This batch was especially prepared for the GC analyzes. After homogenization 80 glass vials of 30 mL were filled and labelled #24044.

The homogeneity of the subsamples was checked by determination of Ethanol in accordance with ASTM D7423 on 8 stratified randomly selected subsamples.

	Ethanol in mg/kg
sample #24044-1	9.9
sample #24044-2	9.8
sample #24044-3	9.6
sample #24044-4	9.3
sample #24044-5	9.3
sample #24044-6	9.3
sample #24044-7	9.4
sample #24044-8	8.9

Table 1: homogeneity test results of subsamples #24044

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.

	Ethanol in mg/kg
r (observed)	0.9
reference test method	D7423:23
0.3 x R (reference test method)	1.1

Table 2: evaluation of the repeatability of subsamples #24044

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

To each of the participating laboratories one 30 mL vial of Naphtha labelled #24044 was sent on March 13, 2024. An SDS was added to the sample package.

## 2.5 STABILITY OF THE SAMPLES

The stability of Naphtha packed in amber glass vial was checked. The material was found to be sufficiently stable for the period of the proficiency test.

## 2.6 ANALYZES

The participants were requested to determine: Acetone, DIPE, Ethyl Acetate, MEK, Methanol, Ethanol, MTBE, TAME, Total Oxygenates, PIONA GC Determination (Total Paraffins, n-Paraffins, i-Paraffins, Olefins, Aromatics, Naphthenes and C4 and lighter hydrocarbons) in %V/V and %M/M, PNA GC Determination (Total Paraffins, Total Naphthenes, Total Aromatics and C4 and lighter hydrocarbons) in %V/V and %M/M and Detail Hydrocarbon Analysis (DHA) (Pentane, Benzene, Cyclohexane, 2- and 3-Methylpentane, Heptane, Toluene and Octane).

It was explicitly requested to treat the sample as if it was a routine sample 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/](http://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](http://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/](http://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:

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

The  $Z_{(\text{target})}$  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:

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

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