Institute for
Interlaboratory Studies

Results of Proficiency Test
Methanol
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Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

Appendices:

1 INTRODUCTION

Since 1999 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the analysis of Methanol based on the latest version of the IMPCA specification every year. During the annual proficiency testing program of 2024 it was decided to continue the round robin for the analysis of Methanol.

In this interlaboratory study registered for participation:
- 100 laboratories in 34 countries for regular analyzes in Methanol iis24C04
- 58 laboratories in 22 countries on the UV analyzes iis24C04UV

In total 101 laboratories in 34 countries registered for participation in one or both proficiency tests, see appendix 3 for the number of participants per country. In this report the results of the Methanol 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, two or three different samples of Methanol, see table below.

Sample ID	PT ID	Quantity	Purpose
#24160	iis24C04	1x 1 L	Regular analyzes
#24161	iis24C04	1x 250 mL	NVM
#24162	iis24C04UV	1x 100 mL	UV

Table 1: Methanol samples used in PTs iis24C04 and iis24C04UV

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.

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 Methanol a batch of approximately 130 liters of Methanol was obtained from a local supplier. The batch was spiked with Iron Chloride. After homogenization 120 amber glass bottles of 1 L were filled and labelled #24160.
The homogeneity of the subsamples was checked by the determination of Density at 20 °C in accordance with ASTM D4052 and Chlorides as Cl in accordance with IMPCA002 on 8 stratified randomly selected subsamples.

	Density at 20 °C in kg/L	Chlorides as Cl in mg/kg
sample #24160-1	0.79123	0.72
sample #24160-2	0.79125	0.72
sample #24160-3	0.79124	0.76
sample #24160-4	0.79124	0.76
sample #24160-5	0.79126	0.75
sample #24160-6	0.79124	0.75
sample #24160-7	0.79126	0.76
sample #24160-8	0.79127	0.74

Table 2: homogeneity test results of subsamples #24160

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 20 °C in kg/L	Chlorides as Cl in mg/kg
r (observed)	0.00004	0.05
reference test method	ISO12185:24	IMPCA002:98
0.3 x R (reference test method)	0.00015	0.09

Table 3: evaluation of the repeatabilities of subsamples #24160

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 preparation of the sample for the analyzes of NVM in Methanol a batch of approximately 30 liters of Methanol was obtained from a local supplier. This batch was spiked with Sodium Chloride. After homogenization 120 amber glass bottles of 250 mL were filled and labelled #24161.
The homogeneity of the subsamples was checked by the determination of Nonvolatile matter in accordance with EN15691 on 8 stratified randomly selected subsamples.

	Nonvolatile matter in mg/100 mL
sample #24161-1	19.8
sample #24161-2	19.9
sample #24161-3	19.5
sample #24161-4	19.3
sample #24161-5	19.8
sample #24161-6	19.7
sample #24161-7	19.4
sample #24161-8	19.7

Table 4: homogeneity test results of subsamples #24161

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.

	Nonvolatile matter in mg/100 mL
r (observed)	0.6
reference test method	D1353:13R21
0.3 x R (reference test method)	2.5

Table 5: evaluation of the repeatability of subsamples #24161

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 UV Absorbance in Methanol a batch of approximately 10 liters of Methanol was obtained from a local supplier. After homogenization 80 amber glass bottles of 100 mL were filled and labelled #24162.
The homogeneity of the subsamples was checked by the determination of UV Absorbance at at 268.5 nm using a 50 mm cuvette in accordance with IMPCA004 on 7 stratified randomly selected subsamples.

	UV Absorbance at 268.5 nm
sample #24162-1	0.022
sample #24162-2	0.025
sample #24162-3	0.023
sample #24162-4	0.025
sample #24162-5	0.021
sample #24162-6	0.022
sample #24162-7	0.021

Table 6: homogeneity test results of subsamples #24162

It appeared that the above test values are close to zero and the smooth UV scans were all identical so that seven times a pass evaluation of the subsamples has been obtained. Because of the smooth scans homogeneity of the subsamples was assumed.

Depending on the registration of the participant the appropriate set of PT samples was sent on August 21, 2024. An SDS was added to the sample package.

2.5 STABILITY OF THE SAMPLES

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

2.6 ANALYZES

The participants were requested to determine on sample #24160: Acidity as Acetic acid, Appearance, Carbonizables Pt/Co, Inorganic Chloride as Cl, Color Pt/Co, Density at 20 °C, Specific Gravity 20/20 °C, Distillation (IBP, 50% recovered, DP and Range), Iron as Fe, Water miscibility (Hydrocarbons), Permanganate Time Test at 15 °C, Purity by GC (as received and on dry basis), Acetone, Benzene, Ethanol, Toluene, Total Sulfur, Trimethylamine (TMA) and Water (Coulometric and Volumetric).
On sample #24161 it was requested to determine Nonvolatile matter only.
On sample #24162 it was requested to determine the UV Absorbance at 300, 268.5, 250, 240, 230 and 220 nm and an evaluation (Pass or Fail) of the UV scan.

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 appendices 1 and 2 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 appendices 1 and 2. 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 may be 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 result tables of 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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