Institute for
Interlaboratory Studies

Results of Proficiency Test
Dimethyl Fumarate (DMFu) in Textile
May 2023

Organized by: Institute for Interlaboratory Studies
Spijkenisse, The Netherlands

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1 INTRODUCTION

In January 2009 Member States of the European Union (EU) voted in favor to ban the anti-fungal/biocidal agent Dimethyl Fumarate (DMFu) in consumer products. In the EU the restriction on the usage of DMFu in products is governed by Commission Decision 2009/251/EC of 17 March 2009. From May 2009 a product or part of a product containing DMFu in a concentration more than 0.1 mg/kg is prohibited from being placed on the market.

On request of a number of participants the Institute for Interlaboratory Studies (iis) decided to organize a proficiency scheme for the determination of Dimethyl Fumarate (DMFu) in Textile in 2022 for the first time. During the annual proficiency testing program 2022/2023 it was decided to continue the proficiency test for the determination of Dimethyl Fumarate (DMFu) in Textile.

In this interlaboratory study 57 laboratories in 22 countries registered for participation, see appendix 3 for the number of participants per country. In this report the results of the Dimethyl Fumarate in Textile proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

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 an ISO/IEC17025 accredited laboratory.
It was decided to send one textile sample of 3 grams labelled #23575.
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 a 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

A batch of blue polyester which was made positive on Dimethyl Fumarate (DMFu) by a third party was selected. After homogenization about 85 small plastic bags were filled with approximately 3 grams each and labelled #23575.
The homogeneity of the subsamples was checked by determination of DMFu using ISO16186 on 8 stratified randomly selected subsamples.

	DMFu in mg/kg
sample #23575-1	22
sample #23575-2	23
sample #23575-3	25
sample #23575-4	23
sample #23575-5	22
sample #23575-6	21
sample #23575-7	23
sample #23575-8	26

Table 1: homogeneity test results of subsamples #23575

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.

	DMFu in mg/kg
r (observed)	4.6
reference test method	ISO16186:2021
0.3 x R (reference test method)	5.0

Table 2: evaluation of the repeatability of subsamples #23575

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 textile sample labelled #23575 was sent on April 5, 2023.

2.5 ANALYZES

The participants were requested to determine Dimethyl Fumarate (DMFu).
To ensure homogeneity it was requested not to use less than 0.5 gram per determination. It was also requested to report if the laboratory was accredited for the determined component and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample and to report the test result using the indicated unit on the report form and not to round the test result but report as much significant figures as possible. It was also requested not to report a ‘less than’ test result, which is above the detection limit, because such a test result 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 unit is given as well as the reference test method (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-cts. 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-cts/. 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 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 dataset 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 of 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:

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

4 EVALUATION

In this interlaboratory study no problems were encountered with the dispatch of the samples. Two participants reported test results after the final reporting date and two other participants did not report a test result. In total 55 laboratories reported 55 numerical test results. Observed was 1 outlying test result, which is 1.8%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

The original data set given in appendix 1 did not have a normal Gaussion distribution. This is referred to as “not OK” or “suspect”. The statistical evaluation of this data set should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER COMPONENT

In this section the reported test results are discussed per component. The test methods which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. The test methods are also in the table together with the original data in appendix 1. The abbreviations, used in this table, are explained in appendix 4.

For the determinaton of Dimethyl Fumarate in Textile two test methods are available, ISO16186 and EN17130. ISO/TS16186:2012 was adopted by EN17130 in 2019. In 2021 ISO/TS16186 was superseded by a new version of ISO16186. In this new method some changes were made which are also partly mentioned in EN17130. The presicion data mentioned in ISO/TS16186:12 and EN17130:19 was not changed in ISO16186:21 and is used in this proficiency test for reference. Both precision data sets mentioned in ISO16186:21 for textile have been combined to a linear expression dependent on the concentration of DMFu.

DMFu: This determination was not problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of ISO16186:21.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the reference test method and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility derived from the reference method are presented in the next table.

Component	unit	n	average	2.8 * sd	R(lit)
DMFu	mg/kg	54	42.08	20.65	30.19

Table 3: reproducibility on sample #23575

Without further statistical calculations it can be concluded that for DMFu there is a good compliance of the group of participating laboratories with the reference test method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2023 WITH THE PREVIOUS PT

	May 2023	April 2022
Number of reporting laboratories	55	78
Number of test results	55	78
Number of statistical outliers	1	3
Percentage of statistical outliers	1.8%	3.8%

Table 4: comparison with previous proficiency test

In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

The performance of the determination of the proficiency test, expressed as relative standard deviation (RSD) of the PT, was compared to the previous PT, see next table.

	May 2023	April 2022	Target
Dimethyl Fumarate (DMFu)	18%	15%	26%

Table 5: development of the uncertainties over the years

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT also some analytical details were requested, which are listed in appendix 2. Based on the answers given by the participants the following can be summarized:

- About 80% of the participants mentioned that they are accredited for the determination of Dimethyl Fumarate in Textile.
- About 40% of the participants used the samples as received and about 60% further cut the samples prior to analysis.
- About 35% of the participants used 0.5 grams and 56% used 1 gram as sample intake. It is remarkable that a large group used 0.5 grams for intake as 1 gram was mentioned in test method ISO16186:21.

No further analysis is performed because the reproducibility of the reported test results is in line with the reference test method.

5 DISCUSSION

All reporting participants were able to detect Dimethy Fumarate (DMFu) in sample #23575.

The test results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (see table below). It was noticed that all participants would have made identical decisions about the acceptability of the textile for the presence of DMFu. All reporting laboratories would have rejected sample #23575 for all categories

Ecolabel	baby clothes	in direct skin contact	no direct skin contact
Bluesign® BSSL	<0.1 mg/kg	<0.1 mg/kg	<0.1 mg/kg
OEKO-TEX® 100	<0.1 mg/kg	<0.1 mg/kg	<0.1 mg/kg

Table 6: Ecolabelling Standards and Requirements for Textiles in EU

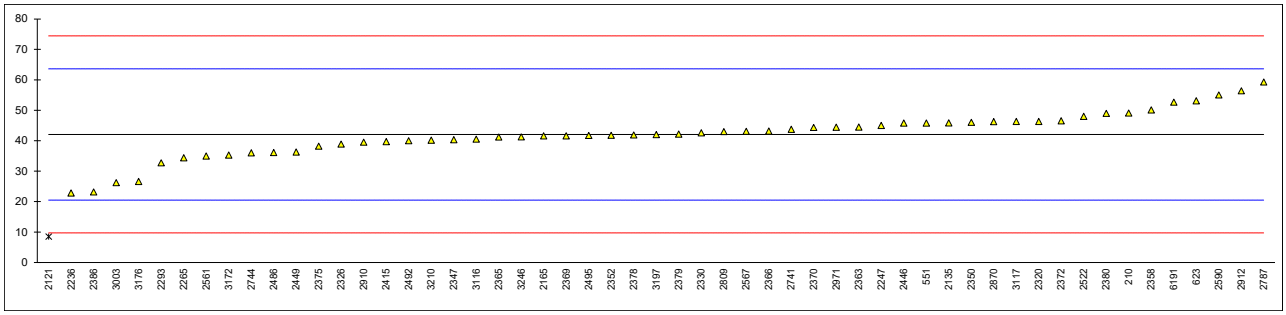
6 CONCLUSION

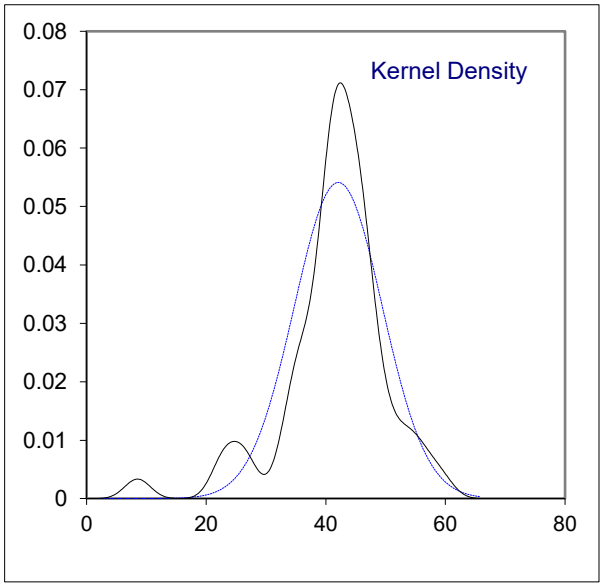
Although, it can be concluded that the majority of the participants has no problem with the determination of the Dimethyl Fumarate in the textile sample of this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

APPENDIX 1

Determination of Dimethyl Fumarate (DMFu), CAS No. 624-49-7 on sample #23575; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	In house	49.07		0.65	
339		-----		-----	
551	ISO16186	45.78		0.34	
623	ISO16186	53.108		1.02	
2121	EN17130	8.49	C,R(0.01)	-3.12	First reported 12.73
2135	ISO16186	45.858		0.35	
2165	ISO16186	41.6		-0.04	
2236	ISO16186	22.799		-1.79	
2247	EN17130	45.03		0.27	
2265	EN17130	34.38	C	-0.71	First reported 34375.8
2293	ISO16186	32.73		-0.87	
2320	ISO16186	46.34		0.40	
2326	EN17130	38.86		-0.30	
2330	ISO/TS16186	42.591		0.05	
2347	ISO16186	40.32		-0.16	
2350	ISO16186	46.028		0.37	
2352	EN17130	41.765		-0.03	
2358	ISO16186	50.10		0.74	
2363	ISO16186	44.5		0.22	
2365	ISO16186	41.19		-0.08	
2366	ISO16186	43.17		0.10	
2369	GB/T28190	41.6		-0.04	
2370	EN17130	44.36		0.21	
2372	CNS15331	46.5001		0.41	
2375	ISO16186	38.2		-0.36	
2378	ISO16186	41.892		-0.02	
2379	ISO16186	42.157		0.01	
2380	ISO16186	49.0		0.64	
2386	EN17130	23.175		-1.75	
2415	ISO16186	39.7		-0.22	
2446	EN17130	45.775		0.34	
2449	ISO16186	36.24		-0.54	
2486	In house	36.14		-0.55	
2492	ISO16186	40		-0.19	
2495	ISO16186	41.74		-0.03	
2522	ISO16186	48.0		0.55	
2561	ISO16186	34.9520		-0.66	
2567	ISO16186	43.1	C	0.09	First reported 92.8
2590	ISO16186	55.013		1.20	
2671		-----		-----	
2741	ISO16186	43.740		0.15	
2744	ISO16186	36		-0.56	
2787	ISO16186	59.29		1.60	
2809	EN17130	43		0.09	
2870	In house	46.29		0.39	
2910	ISO16186	39.5		-0.24	
2912	ISO16186	56.377		1.33	
2971	ISO16186	44.41		0.22	
3003	ISO16186	26.2		-1.47	
3116	ISO16186	40.5		-0.15	
3117	ISO16186	46.3		0.39	
3172	ISO16186	35.297		-0.63	
3176	In house	26.61		-1.43	
3197	EN17130	42.0		-0.01	
3210	ISO16186	40.16		-0.18	
3246	ISO16186	41.2286		-0.08	
6191	ISO16186	52.652		0.98	
	normality	suspect			
	n	54			
	outliers	1			
	mean (n)	42.0800			
	st.dev. (n)	7.37560	RSD = 18%		
	R(calc.)	20.6517			
	st.dev.(ISO16186:21)	10.78209			
	R(ISO16186:21)	30.1898			


80
70
60
50
40
30
20
10
0
2121 2236 2386 3003 3176 2293 2265 2561 3172 2744 2486 2449 2375 2326 2910 2415 2492 3210 2347 3116 2365 3246 2165 2369 2495 2352 2378 3197 2379 2330 2809 2567 2366 2741 2370 2971 2363 2247 2446 551 2135 2350 2870 3117 2320 2372 2522 2380 210 2358 6191 623 2590 2912 2787


Kernel Density
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
20
40
60
80

APPENDIX 2 Analytical details

lab	ISO/IEC 17025 accr.	Sample preparation	Sample intake used (grams)
210	Yes	Further cut	1g
339	---	---	
551	No	Further cut	1g
623	Yes	Further cut	1
2121	No	Used as received	1g
2135	Yes	Used as received	0,5
2165	Yes	Used as received	1.5g
2236	Yes	Used as received	1.00 g / 0.5 g
2247	Yes	Further cut	0.5 g
2265	No	Used as received	0,5
2293	Yes	Further cut	1.000 g
2320	Yes	Further cut	1.0g
2326	Yes	Further cut	1.0036 g
2330	No	Further cut	0.5 g
2347	Yes	Further cut	0.5g
2350	Yes	Further grinded	1g
2352	Yes	Further cut	0.5g
2358	Yes	Used as received	0.5
2363	Yes	Further cut	3g
2365	Yes	Used as received	0.5g
2366	No	Further cut	
2369	No	---	
2370	Yes	Further cut	0.5g
2372	No	Further cut	1g
2375	Yes	Further cut	1 g
2378	Yes	Further cut	1g
2379	Yes	Further cut	0.5 g
2380	Yes	Further cut	1.0 g
2386	Yes	Used as received	1.0 g
2415	Yes	Further cut	0.5 g
2446	Yes	Used as received	1 g
2449	No	Further cut	1.0 g
2486	Yes	Further cut	1.0007 g
2492	Yes	Used as received	1g
2495	Yes	Used as received	0.5g
2522	Yes	Further cut	1g
2561	Yes	Used as received	1g
2567	Yes	Further cut	0.2 g
2590	Yes	Used as received	1g
2671	---	---	
2741	Yes	Further cut	0.5
2744	Yes	Used as received	0,5
2787	No	Used as received	1 g in 10 ml of acetone
2809	Yes	Further cut	0.5 g
2870	No	Further cut	2.0 g
2910	Yes	Further cut	2g
2912	Yes	Used as received	1 g
2971	Yes	Further cut	0.5g
3003	Yes	Further cut	1 g
3116	Yes	Used as received	1
3117	Yes	Used as received	1.0017g
3172	Yes	---	
3176	Yes	Used as received	0,5
3197	Yes	Further cut	0,5 g
3210	Yes	Further cut	1g
3246	Yes	Used as received	1g
6191	No	Used as received	1,0060 g

APPENDIX 3

Number of participants per country

3 labs in	BANGLADESH
1 lab in	BRAZIL
2 labs in	CAMBODIA
4 labs in	FRANCE
4 labs in	GERMANY
1 lab in	GUATEMALA
3 labs in	HONG KONG
3 labs in	INDIA
1 lab in	INDONESIA
4 labs in	ITALY
1 lab in	KOREA, Republic of
1 lab in	MOROCCO
11 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	SERBIA
1 lab in	SRI LANKA
2 labs in	TAIWAN
1 lab in	THAILAND
4 labs in	TURKEY
1 lab in	U.S.A.
1 lab in	UNITED KINGDOM
5 labs in	VIETNAM

APPENDIX 4

Abbreviations

C	= final test result after checking of first reported suspect test result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
E	= calculation difference between reported test result and result calculated by iis
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

Literature

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