Institute for
Interlaboratory Studies

Results of Proficiency Test
Dimethyl Fumarate (DMFu) in Textile
April 2022

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 favour 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 this first interlaboratory study 79 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 a textile sample positive on Dimethyl Fumarate of approximately 3 grams and labelled #22570.
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 purple polyester was selected which was made positive on Dimethyl Fumarate (DMFu). The batch was cut into small pieces. After homogenization about 90 plastic bags were filled with approximately 3 grams of textile each and labelled #22570.
The homogeneity of the subsamples was checked by determination of DMFu using ISO16186 on 8 stratified randomly selected subsamples.

	DMFu in mg/kg
sample #22570-1	13.355
sample #22570-2	11.824
sample #22570-3	12.052
sample #22570-4	12.128
sample #22570-5	12.041
sample #22570-6	12.155
sample #22570-7	12.408
sample #22570-8	12.429

Table 1: homogeneity test results of subsamples #22570

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)	1.316
reference test method	ISO16186:2021
0.3 x R (reference test method)	2.678

Table 2: evaluation of the repeatability of subsamples #22570

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 #22570 was sent on March 16, 2022.

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 grams of the sample per determination. It was also requested to report if the laboratory was accredited to determine the reported 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 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 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 appropriate 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. Ten participants reported test results after the final reporting date and one other participant did not report any test results. In total 78 laboratories reported 78 numerical test results. Observed were 3 outlying test results, which is 3.8%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

The original data set given in appendix 1 proved to have a normal Gaussion distribution.

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 these tables, 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/TS 16186 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 proficiency test 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. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers 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	75	8.54	3.59	6.24

Table 3: reproducibility on sample #22570

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

4.3 OVERVIEW OF PROFICIENCY TEST OF APRIL 2022

The uncertainty of the determination in this proficiency test was expressed as relative standard deviation (RSD) of the PT, see next table.

	April 2022	Target
Dimethyl Fumarate (DMFu)	15%	26%

Table 4: uncertainty of DMFu

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT also some analytical details were requested. They 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 55% of the participants used the samples as received and about 45% further cut the samples prior to analysis.
- About 40% of the participants used 0.5 grams and about 55% 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 DMFu in sample #22570.

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 #22570 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 5: Ecolabelling Standards and Requirements for Textiles in EU

6 CONCLUSION

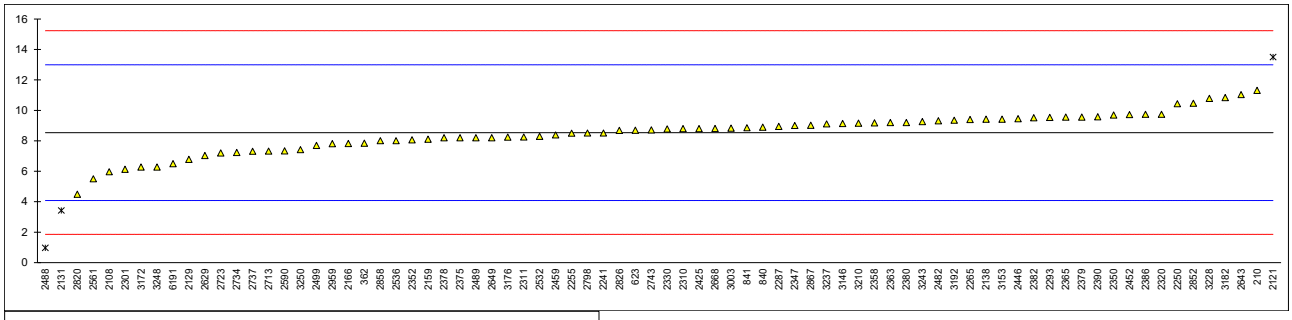
Although, it can be concluded that the majority of the participants has no problem with the determination of the Dimethyl Fumarate in the textile sample of this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. 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.

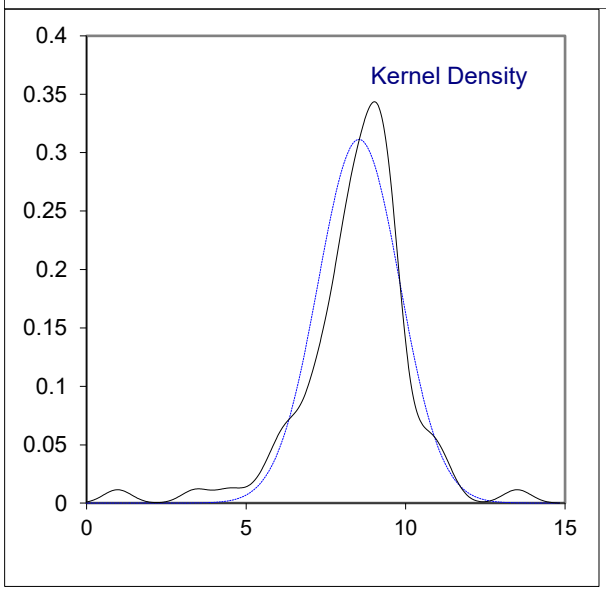
APPENDIX 1

Determination of Dimethyl Fumarate (DMFu), CAS No. 624-49-7 on sample #22570; results in mg/kg

Lab	method	value	mark	z(targ)	remarks
210	In house	11.31		1.24	
362	In house	7.840		-0.31	
623	In house	8.690		0.07	
840	ISO16186	8.90		0.16	
841	ISO16186	8.856		0.14	
2108	EN17130	5.97		-1.15	
2121	In house	13.5	C,R(0.05)	2.23	First reported 1.89
2129	ISO16186	6.778		-0.79	
2131	In house	3.42	R(0.05)	-2.30	
2138	ISO16186	9.414		0.39	
2159	ISO16186	8.1		-0.20	
2166	In house	7.827		-0.32	
2241	GB/T28190	8.512		-0.01	
2250	ISO16186	10.43		0.85	
2255	ISO16186	8.5		-0.02	
2265	EN17130	9.40		0.39	
2287	ISO16186	8.94		0.18	
2293	ISO16186	9.534		0.45	
2301	ISO16186	6.13		-1.08	
2310	ISO16186	8.80		0.12	
2311	EN17130	8.245		-0.13	
2320	ISO16186	9.734		0.54	
2330	ISO/TS16186	8.783		0.11	
2347	ISO16186	9.0		0.21	
2350	ISO16186	9.688		0.52	
2352	ISO16186	8.06		-0.22	
2358	EN17130	9.18		0.29	
2363	ISO16186	9.2		0.30	
2365	ISO16186	9.550		0.45	
2375	ISO16186	8.2		-0.15	
2378	ISO16186	8.2		-0.15	
2379	ISO16186	9.5558		0.46	
2380	ISO16186	9.2		0.30	
2382	EN17130	9.52		0.44	
2386	ISO16186	9.733		0.54	
2390	ISO16186	9.57		0.46	
2425	In house	8.80		0.12	
2446	EN17130	9.45		0.41	
2452	EN17130	9.715		0.53	
2459	EN17130	8.384		-0.07	
2482	ISO16186	9.31		0.35	
2488	ISO16186	0.969	R(0.01)	-3.40	
2489	ISO16186	8.2		-0.15	
2499	ISO16186	7.697		-0.38	
2522		-----		-----	
2532	EN17130	8.3		-0.11	
2536	EN17130	8.0063		-0.24	
2561	EN17130	5.49800676	C	-1.36	First reported 5.021359223
2590	ISO16186	7.341		-0.54	
2629	ISO16186	7.034	C	-0.68	First reported 17.034
2643	ISO16186	11.03		1.12	
2649	In house	8.2		-0.15	
2668	ISO16186	8.809		0.12	
2713	ISO16186	7.321		-0.55	
2723	ISO16186	7.2		-0.60	
2734	ISO16186	7.231		-0.59	
2737	ISO16186	7.3075		-0.55	
2743	ISO16186	8.7104		0.08	
2798	EN17130	8.51		-0.01	
2820	ISO16186	4.49		-1.82	
2826	ISO16186	8.6844		0.06	
2852	ISO16186	10.46		0.86	
2858	ISO16186	8.002		-0.24	
2867	ISO16186	9.024		0.22	
2959	ISO16186	7.81		-0.33	
3003	ISO16186	8.826		0.13	
3146	ISO16186	9.137		0.27	
3153	ISO16186	9.42		0.39	
3172	ISO16186	6.2763		-1.02	
3176	ISO16186	8.24		-0.13	
3182	ISO16186	10.8406	C	1.03	First reported 1.322
3192	ISO16186	9.3506		0.36	
3210	In house	9.16		0.28	

Lab	method	value	mark	z(targ)	remarks
3228	ISO16186	10.78		1.00	
3237	ISO16186	9.11		0.26	
3243	EN17130	9.26		0.32	
3248	In house	6.28		-1.01	
3250	ISO16186	7.42		-0.50	
6191	In house	6.497		-0.92	
	normality	OK			
	n	75			
	outliers	3			
	mean (n)	8.5396	RSD = 15%		
	st.dev. (n)	1.28161			
	R(calc.)	3.5885			
	st.dev.(ISO16186:2021)	2.22930			
	R(ISO16186:2021)	6.2421			





APPENDIX 2 Analytical details

lab	ISO/IEC 17025 accr.	Sample preparation	Sample intake used (grams)
210	No	Further cut	1g
362	Yes	Used as received	1g
623	Yes	Further cut	1
840	Yes	Used as received	1.0
841	Yes	Used as received	1 grams
2108	Yes	Further cut	0,5 g
2121	Yes	Used as received	m = 0.9981 g
2129	Yes	Used as received	0.5g
2131	Yes	Used as received	1
2138	Yes	Used as received	about 0.5g
2159	Yes	Further cut	0.5
2166	Yes	Used as received	1,0
2241	Yes	Used as received	0.5g
2250	Yes	Further cut	0,1 and 0,5
2255	Yes	Further cut	0.5
2265	No	Used as received	0,5g
2287	No	Further cut	0.5g
2293	No	Used as received	0.996grams
2301	No	Used as received	1.0023gram
2310	Yes	Further cut	1 gram
2311	No	Further cut	0.5
2320	Yes	Used as received	1g
2330	No	Further cut	0.50 g
2347	No	Used as received	0.5g
2350	Yes	Further cut	1g
2352	Yes	Further cut	0.5g
2358	Yes	Used as received	1 gram
2363	Yes	Used as received	2 g
2365	Yes	Used as received	1.0g
2375	Yes	Further cut	1.00gr
2378	Yes	Used as received	1G
2379	Yes	Further cut	1 gram
2380	Yes	Further cut	1.0 g
2382	Yes	Further cut	1.0 g
2386	Yes	Used as received	3 g
2390	Yes	Further cut	1 gram
2425	Yes	Used as received	0.5g
2446	Yes	Used as received	1 g
2452	No	Used as received	1
2459	---	Further cut	1.0 gm
2482	Yes	Used as received	0.5
2488	Yes	Further cut	0.5
2489	Yes	Further cut	0.5029 g
2499	No	Further cut	1 gram
2522	---	---	
2532	Yes	Further cut	0.5 grams
2536	Yes	Further cut	1.0063
2561	No	Used as received	1g

lab	ISO/IEC 17025 accr.	Sample preparation	Sample intake used (grams)
2590	Yes	Used as received	1g
2629	Yes	Further cut	1.0 gram
2643	Yes	Used as received	0.5 g
2649	Yes	Further cut	1 gram
2668	No	Further cut	0.5 gms
2713	Yes	Further cut	0,5 grams
2723	Yes	Used as received	1g
2734	No	Further cut	1.00
2737	Yes	Used as received	0.5g
2743	Yes	Used as received	1
2798	Yes	Used as received	1g
2820	Yes	Used as received	0,5
2826	Yes	Used as received	0.5g
2852	Yes	Used as received	1.5 g
2858	Yes	Further cut	1.0905
2867	Yes	Used as received	0.500g
2959	Yes	Used as received	1g
3003	No	Used as received	0.501 gm
3146	Yes	Other	0,5g
3153	Yes	Further cut	0.5 g
3172	Yes	---	
3176	Yes	Used as received	1
3182	No	Used as received	0.5 grams
3192	Yes	Further cut	1,00 g
3210	Yes	Used as received	1g
3228	Yes	Further cut	0.5
3237	Yes	Used as received	0,5
3243	Yes	Further cut	0,5
3248	Yes	Used as received	0.5g
3250	Yes	Used as received	1
6191	No	Further cut	1,0013 g

APPENDIX 3

Number of participants per country

7 labs in	BANGLADESH
1 lab in	BULGARIA
2 labs in	CAMBODIA
3 labs in	FRANCE
11 labs in	GERMANY
1 lab in	GUATEMALA
4 labs in	HONG KONG
5 labs in	INDIA
2 labs in	INDONESIA
6 labs in	ITALY
1 lab in	JAPAN
3 labs in	KOREA, Republic of
2 labs in	MOROCCO
13 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	SRI LANKA
2 labs in	SWITZERLAND
2 labs in	THAILAND
1 lab in	TUNISIA
6 labs in	TURKEY
1 lab in	UNITED KINGDOM
3 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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