Institute for
Interlaboratory Studies

Results of Proficiency Test
OPP and other Preservatives
in Textile
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Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Many countries have adopted environmental standards and requirements restricting the use of harmful chemicals in the production of textiles and clothing. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for textiles, some Eco-labelling schemes are imposing environmental requirements for textile products on a voluntary basis, e.g. Milieukeur (Netherlands), Bluesign® (Switzerland) and OEKO-TEX® Standard 100 (Switzerland).

Since 2004 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Ortho-Phenylphenol (OPP) in Textile every year, since 2019 this scheme is extended for other preservatives. During the annual proficiency testing program of 2023 it was decided to continue the proficiency test for the determination of OPP and other Preservatives in Textile.

In this interlaboratory study 29 laboratories in 14 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the OPP and other Preservatives 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 a laboratory that has performed the tests in accordance with for ISO/IEC17043 relevant requirements of ISO/IEC17025.
It was decided to send one textile sample of approximately 3 grams and labelled #23795. 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.

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 black ribbon pieces with a detectable level of OPP prepared by a third party was selected. After homogenization 35 small plastics bags were filled with approximately 3 grams each and labelled #23795.
The batch for sample #23795 was used in a previous proficiency test on OPP and other Preservatives in Textile as sample #19650 in iis19A15. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one textile sample labelled #23795 was sent on November 15, 2023.

2.5 ANALYZES

The participants were requested to determine Ortho-Phenylphenol (OPP), 2-(Thiocyanomethylthio)-Benzothiazole (TCMTB), 4-Chloro-3-Methylphenol (PCMC), 2-Octylisothiazol-3(2H)-one (OIT), Triclosan (TCS) and eventually other Preservatives detected.
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 components 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 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-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 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 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:

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

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:

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

4 EVALUATION

In this proficiency test no problems were encountered with the dispatch of the samples. One participant reported test results after the final reporting date and two other participants did not report any test results. Not all participants were able to report all tests requested. In total 27 laboratories reported 25 numerical test results. No statistical outliers were observed. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

The data set proved to have a normal Gaussian distribution.

4.1 EVALUATION PER COMPONENT

In this section the 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. These test methods are also in the tables together with the original data in appendix 1. The abbreviations, used in these tables, are explained in appendix 5.

Since 2019 test method EN17134 is available for the determination of OPP and Triclosan in textile. A new method EN17134-1 is under preparation. The test method EN17134:19 describes an extraction with Acetonitrile using ultrasonic. Unfortunately, no precision data is mentioned in this method. Therefore, in this PT the test results will be evaluated against the target reproducibility as given in memo 1601 (lit. 13). In iis memo 1601 an estimated iis target reproducibility based on iis PT data of OPP proficiency tests from 2004 until 2014 is determined.

Ortho-Phenylphenol (OPP): The group of participants met the target requirements. No statistical outliers were observed. The calculated reproducibility is in agreement with the estimated reproducibility from iis memo 1601.

The participants agreed on a concentration near or below the limit of detection for all other components mentioned in paragraph 2.5. Therefore, no z-scores are calculated for these components. The reported test results are given in appendix 2.

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(target)
Ortho-Phenylphenol (OPP)	mg/kg	25	12.6	5.3	8.8

Table 1: reproducibility of tests on sample #23795

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

4.3 COMPARISON OF THE PROFICIENCY TEST OF DECEMBER 2023 WITH PREVIOUS PTS

	December 2023	December 2022	December 2021	December 2020	December 2019
Number of reporting laboratories	27	26	25	27	28
Number of test results	25	26	24	25	28
Number of statistical outliers	0	0	2	2	0
Percentage of statistical outliers	0%	0%	8.3%	8.0%	0%

Table 2: comparison with previous proficiency tests

iis PTs with OPP were combined with PCP determination before 2019

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

The performance of the determinations of the proficiency test was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTS, see next table.

Component	December 2023	December 2022	December 2021	December 2020	December 2019	December 2004-2018
Ortho-Phenylphenol (OPP)	15%	25-52%	35-36%	16-29%	21%	16-66%

Table 3: development of the uncertainties over the years

The uncertainty observed in this PT is comparable to the uncertainties observed in previous PTs.

Sample #23795 was used in a previous PT as sample #19650 in iis19A15. The average found in both PTs are similar. The calculated reproducibility of Ortho-Phenylphenol (OPP) is smaller in this PT compared to the 2019 PT.

		sample #23795			sample #19650		
Component	unit	n	average	R(calc)	n	average	R(calc)
OPP	mg/kg	25	12.6	5.3	28	14.2	8.5

Table 4: comparison of sample #23795 with #19650

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT some analytical details were requested which are listed in appendix 3. Based on the answers given by the participants the following can be summarized:

- Twenty-four participants mentioned that they are ISO/IEC17025 accredited to determine the reported component(s).
- Prior to analysis the sample was further cut or grind by sixteen participants, nine participants used the sample as received.
- The sample intake varied from 0.5 grams to 3 grams. Eight participants used a sample intake of 0.5 grams and fifteen used 1 gram.
- Ultrasonic extraction was the most often reported technique to extract the components.
- Nineteen participants used Acetonitrile (mixture) and six participants used KOH or KOH followed by n-Hexane as extraction solvent.

The calculated reproducibility for Ortho-Phenylphenol (OPP) is in agreement with the requirements of the target reproducibility, therefore no further separate statistical analysis has been performed.

5 DISCUSSION

Of the participants who reported a numeric value almost all participants would have rejected the sample for class 1 of OEKO-TEX® Standard 100, five participants would have accepted the sample. For classes 2, 3 and 4 all participants who reported a numeric value would have accepted the sample.

Ecolabel	Class 1 Baby clothes in mg/kg	Class 2 Clothes direct skin contact in mg/kg	Class 3 Clothes, no direct contact in mg/kg	Class 4 Decoration material in mg/kg
Ortho-Phenylphenol (OPP)	10	25	25	25

Table 5: OEKO-TEX® Standard 100

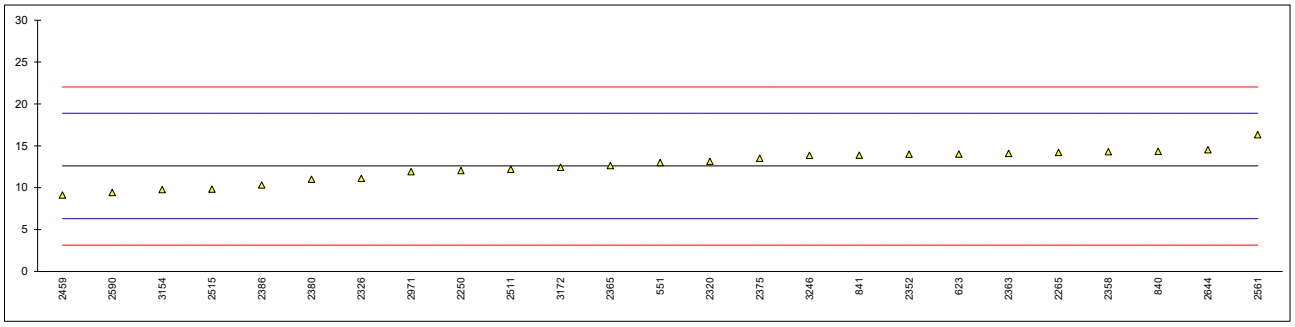
6 CONCLUSION

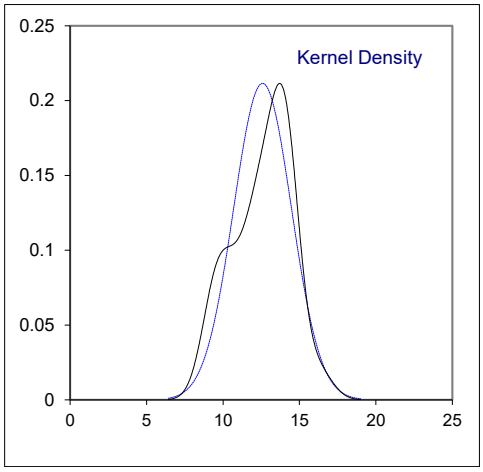
Although it can be concluded that the participants have no problem with the determination on Ortho-Phenylphenol (OPP) in this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular 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 Ortho-Phenylphenol (OPP) on sample #23795; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	EN17134	13.00248139		0.13	
623	EN17134	14.01		0.45	
840	In house	14.34		0.55	
841	In house	13.87		0.40	
2121		-----		-----	
2250	In house	12.03		-0.18	
2265	ISO17070Mod.	14.196		0.51	
2320	DIN50009	13.12		0.17	
2326	EN17134	11.111		-0.47	
2352	EN17134	14.0		0.45	
2358	In house	14.3		0.54	
2363	EN17134	14.08		0.47	
2365	EN17134	12.64		0.01	
2375	EN17134	13.5		0.29	
2380	ISO13365	11.0		-0.51	
2386	In house	10.311		-0.73	
2459	EN17134	9.11	C	-1.11	first reported 19.11
2511	EN17134	12.202		-0.13	
2515	EN17134	9.83		-0.88	
2538		-----		-----	
2561	ISO13365-1	16.32		1.18	
2590	EN17134	9.434		-1.00	
2644	EN17134	14.52		0.61	
2678		-----		-----	
2971	EN17134	11.92		-0.21	
3154	ISO13365/GB/T20386	9.776		-0.90	
3172	EN17134	12.418		-0.06	
3210	In house	<40		-----	
3246	In house	13.845		0.40	
	normality	OK			
	n	25			
	outliers	0			
	mean (n)	12.595			
	st.dev. (n)	1.8862	RSD = 15%		
	R(calc.)	5.281			
	st.dev.(iis-memo 1601)	3.1473			
	R(iis-memo 1601)	8.812			





APPENDIX 2 Other reported test results

TCMTB = 2-(Thiocyanomethylthio)-Benzothiazole
PCMC = 4-Chloro-3-Methylphenol
OIT = 2-Octylisothiazol-3(2H)-one
TCS = Triclosan

Determination individual and other Preservatives on sample #23795; in mg/kg

lab	TCMTB	PCMC	OIT	TCS	Other Preservatives
551	-----	not detected	-----	-----	-----
623	not detected	not detected	not detected	not detected	not detected
840	not detected	not detected	not detected	not detected	-----
841	-----	-----	-----	-----	-----
2121	-----	-----	-----	-----	-----
2250	<0,5	<0,5	<0,5	<0,5	-----
2265	not analized	not analized	not analized	not analized	not analized
2320	-----	-----	-----	-----	-----
2326	ND	ND	ND	ND	-----
2352	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not detected
2363	not detected	not detected	not detected	not detected	not detected
2365	<1.0	<1.0	<1.0	<1.0	-----
2375	-----	-----	-----	-----	-----
2380	<0.5	<0.5	<0.5	<0.5	-----
2386	< 5	< 5	< 5	< 10	< 5
2459	ND	ND	ND	ND	ND
2511	-----	-----	-----	-----	-----
2515	-----	-----	-----	-----	-----
2538	-----	-----	-----	< LOD (3 mg/kg)	-----
2561	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----
2644	not analyzed	not analyzed	not analyzed	not detected	not analyzed
2678	-----	-----	-----	-----	-----
2971	<1	<1	<1	<5	-----
3154	-----	-----	-----	-----	-----
3172	< 5	< 5	< 5	< 0.05	-----
3210	<40	<40	<40	-----	-----
3246	not detected	not detected	not detected	not detected	not analyzed

APPENDIX 3 Analytical details

lab	ISO17025 accredited	Sample preparation	Sample intake (grams)	Extraction technique	Extraction solvent
551	---	---	---	---	---
623	Yes	Further cut	1	Ultrasonic	Acetonitrile
840	Yes	Used as received	1	Ultrasonic	ACN:Water (1:1)
841	Yes	Used as received	0.5 g	Ultrasonic	Acetonitrile
2121	---	---	---	---	---
2250	Yes	Further cut	0,5 g	Ultrasonic	Acetonitrile
2265	Yes	Further cut	0,5	Mechanical Shaking	KOH followed by n-Hexane
2320	Yes	Further cut	1g	Mechanical Shaking	KOH followed by n-Hexane
2326	Yes	Further cut	1 gm	Ultrasonic	Acetonitrile
2352	Yes	Further cut	1g	Ultrasonic	Acetonitrile
2358	Yes	Used as received	1g	Ultrasonic	Acetonitrile
2363	Yes	Further cut	3g	Ultrasonic	Acetonitrile
2365	Yes	Further cut	1g	Ultrasonic	Acetonitrile
2375	Yes	Further cut	0.5 g	Ultrasonic	Acetonitrile
2380	Yes	Further cut	1.0 g	Ultrasonic	Acetonitrile
2386	Yes	Further cut	0,5 g	Ultrasonic	KOH
2459	Yes	Further cut	1.0 gram for a single run	Ultrasonic	KOH followed by n-Hexane
2511	No	Further grinded	---	Ultrasonic	Acetonitrile
2515	Yes	Used as received	1 gram	Ultrasonic	Acetonitrile
2538	Yes	Used as received	1 g	Ultrasonic	Acetonitrile
2561	Yes	Used as received	1g	Ultrasonic	Acetonitrile
2590	Yes	Used as received	1g	Thermal Desorption	Acetonitrile
2644	Yes	Used as received	0.5	Mechanical Shaking	KOH followed by n-Hexane
2678	---	---	---	---	---
2971	Yes	Further cut	1g	Ultrasonic	Acetonitrile
3154	Yes	Further cut	0,5	Ultrasonic	Acetonitrile
3172	Yes	---	---	---	---
3210	No	Further cut	0.5g	Ultrasonic	Acetonitrile
3246	Yes	Used as received	1g	Ultrasonic	KOH followed by n-Hexane

APPENDIX 4

Number of participants per country

1 lab in	BANGLADESH
1 lab in	BRAZIL
2 labs in	FRANCE
5 labs in	GERMANY
1 lab in	HONG KONG
1 lab in	INDONESIA
3 labs in	ITALY
3 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	SRI LANKA
2 labs in	TUNISIA
1 lab in	TURKEY
1 lab in	UNITED KINGDOM
5 labs in	VIETNAM

APPENDIX 5

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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