Results of Proficiency Test OPP & other Preservatives in Textile December 2019

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis19A15

March 2020

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1 INTRODUCTION

Since the 1990's, 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 Orthophenylphenol (OPP), Pentachlorophenol (PCP), Tetrachlorophenols (TeCPs) and Trichlorophenols (TriCPs) in Textile every year. During the annual proficiency test program 2019/2020 it was decided to separate the proficiency tests on the determination of Orthophenylphenol and Chlorinated Phenols and to continue this proficiency test as OPP & other Preservatives in Textile.

In this interlaboratory study 28 laboratories in 10 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the results of the 2019 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 analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send one textile sample of approximately 3 grams labelled #19650, which was positive on OPP. 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 black ribbed cotton fabric positive on OPP obtained from a third party was cut into pieces. From this batch, after mixing well, 40 subsamples of approximately 3 grams each were filled and labelled #19650. The homogeneity of 8 stratified randomly selected subsamples was checked by determination of OPP in accordance with an in-house test method. See the following table for the test results.

	OPP in mg/kg
Sample #19650-1	12.3
Sample #19650-2	12.1
Sample #19650-3	11.2
Sample #19650-4	12.8
Sample #19650-5	10.6
Sample #19650-6	10.9
Sample #19650-7	12.1
Sample #19650-8	11.9

Table 1: homogeneity test results of subsamples #19650

From the above test results the repeatability was calculated and compared with 0.3 times the estimated reproducibility of the reference method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	OPP in mg/kg
r (observed)	2.1
reference method	iis memo 1601 (see lit. 18)
0.3 x R (reference method)	2.5

Table 2: evaluation of the repeatability of subsamples #19650

The calculated repeatability of Ortho-Phenylphenol (OPP) was in agreement with 0.3 times the estimated reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each participating laboratory 1 sample labelled #19650 was sent on November 13, 2019.

2.5 ANALYZES

The participants were requested to determine on samples #19650 the concentrations of Ortho-Phenylphenol (OPP), 2-(Thio Cyano Methyl Thio)-Benzothiazole (TCMTB), 4-Chloro-3-Methyl Phenol (PCMC), 2-Octyl Iso Thiazol-3(2H)-one (OIT), Triclosan (TCS) and other Preservatives applying the analysis procedure that is routinely used in the laboratory. It was also requested to report if the laboratory was accredited to determine the requested components and to report some analytical details of the test method used.

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 to 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 appropriate 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 appendix 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 reanalysis). Additional or corrected test results are used for data analysis and the original test results are placed under ‘Remarks’ in the test 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.

According to ISO5725 the original test results per determination were submitted to Dixon’s, Grubbs’ and/or Rosner’s outlier tests. 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 was projected over the Kernel Density Graph for reference.

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, 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. In some cases, a reproducibility based on former iis proficiency tests could be used.
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.
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

During the execution of this proficiency test no problems occurred with the dispatch of the samples. All participants reported test results and all but one reported before the final reporting date. Not all laboratories were able to report all components requested. In total 28 laboratories reported 28 numerical test results. No statistical outliers were observed. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

The original 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 in appendix 1 together with the reported test results. The abbreviations used in these tables are explained in appendix 5.

Due to the lack of relevant reference test methods and/or precision data for the determination of OPP in Textile the calculated reproducibility was compared with an estimated target reproducibility based on iis PT data of OPP/PCP proficiency tests from 2004 until 2014, iis memo 1601 (see lit.18). As it was assumed that the variation in the PT test results will be dependent on the concentration, this resulted in a Horwitz-like equation to estimate the target reproducibilities for the evaluation of the PT test results by iis from 2015 onwards.

Sample #19650

OPP: This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the estimated reproducibility calculated from iis memo 1601.

Other Preservatives: The reported concentrations of all other components were near or below the detection limit, see appendix 2. Therefore, no z-scores were calculated.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibility and the reproducibility as found for the group of participating laboratories.
The number of significant test results, the average test result, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility are compared in the next table.

Component	unit	n	average	2.8 * sd	R(target)
Ortho-Phenylphenol (OPP)	mg/kg	28	14.2	8.5	9.8

Table 3: performance evaluation sample #19650

Without further statistical calculations it can be concluded that the total group of participating laboratories have no difficulties with the analysis of OPP at a level of 14 mg/kg. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON OF THE PROFICIENCY TEST OF DECEMBER 2019 WITH PREVIOUS PTS

In this PT, the observed variation expressed as the relative standard deviation RSD of the test results is similar in comparison with the uncertainties observed in previous PTs, see the table below.

Component	December 2019	December 2018	December 2017	December 2016	November 2015	iis memo 1601
Ortho-Phenylphenol (OPP)	21%	16-58%	39-54%	38%	24%	24%

Table 4: comparison of uncertainties in iis proficiency tests over the years

Sample #19650 was used before in Proficiency Test iis15A07 as sample #15243. It is observed that the PT findings of the subsamples of textile containing OPP give a good correlation on the OPP averages and the calculated reproducibilities.

	unit	#19650			#15243		
		n	average	R(calc)	n	average	R(calc)
Ortho-Phenylphenol (OPP)	mg/kg	28	14.2	8.5	70	14.9	10.1

Table 5: comparison of sample #19650 with sample #15243

4.4 EVALUATION OF ANALYTICAL DETAILS

The reported analytical details from the participants are listed in appendix 3. From the 28 participants in total the following analytical details were reported:

- to determine the reported component(s) in textile 17 participants (61%) were accredited in accordance with ISO/IEC17025 and 10 participants were not accredited (36%)
- 8 participants (29%) used a sample intake of around 0.5 gram and 16 participants (57%) used around 1 gram. Only two participants (7%) used around 1.5 gram
- prior to analysis the samples were further cut by 20 participants (71%) while 5 participants (18%) used the sample as received
- to extract the components the most often used technique was Ultrasonic extraction by 17 participants (61%). Other techniques like Soxhlet/AES, Oven or Steam Distillation was used by 8 participants (29%)
- 11 participants (39%) used KOH as extraction solvent and 9 participants (32%) used ACN. Three participants (11%) used other solvents.

The effect of the reported analytical details on the determination of OPP in sample #19650 was further investigated on those analytical details where it was possible to distinguish two or more meaningful subgroups.

Analytical Details	unit	n	average	RSD(%)
ISO/IEC17025 accredited	mg/kg	17	14.2	24.3
Not ISO/IEC17025 accredited	mg/kg	10	14.4	17.2
0.5 g sample intake	mg/kg	8	14.5	17.1
1 g sample intake	mg/kg	16	14.3	22.5
KOH extraction solvent	mg/kg	11	14.1	29.4
ACN extraction solvent	mg/kg	9	14.9	8.2

Table 6: effect of analytical details on OPP in textile sample #19650

It is observed that the use of ACN extraction solvent gives much less variation between the laboratories compared to KOH extraction solvent. Please note that the observed effects are not statistically significant given the sample sizes in this PT.

5 DISCUSSION

When the test results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (see table 6) it could be noticed that all of the participants were able to detect OPP in sample #19650.
All reported test results for OPP were <50.0 mg/kg for sample #19650. Based on this the textile material would have been accepted for all four classes mentioned in table 6 by all reporting laboratories.

Ecolabel	Class 1 Baby clothes (mg/kg)	Class 2 Clothes direct skin contact (mg/kg)	Class 3 Clothes, no direct skin contact (mg/kg)	Class 4 Decoration material (mg/kg)
Ortho-Phenylphenol (OPP)	50.0	100.0	100.0	100.0

Table 7: Ecolabelling Standards and Requirements for Textiles in EU

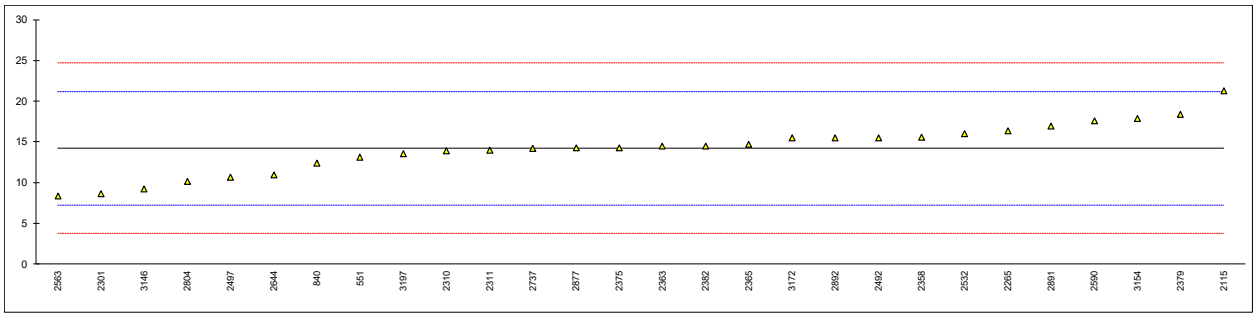
6 CONCLUSION

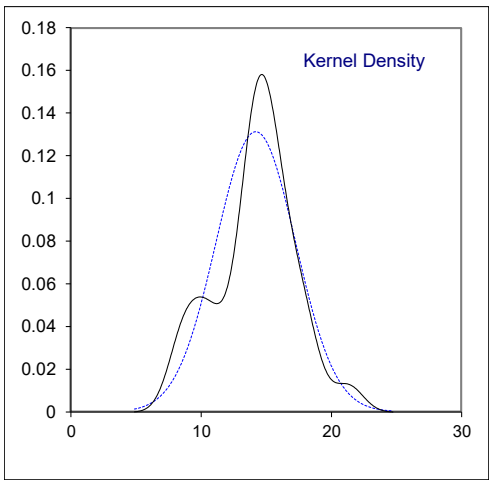
In this proficiency test OPP and other Preservatives in Textile were determined. The participating laboratories had no problems in determining the Ortho-Phenylphenol (OPP) content at a level of 14 mg/kg. Other Preservatives in the sample were not detected or were close or underneath the detection limit.
Each laboratory should evaluate its performance in this study and make decisions about possible corrective actions. 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 #19650; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	In house	13.0999		-0.32	
840	In house	12.4		-0.52	
2115	In house	21.3		2.03	
2265	In house	16.375		0.62	
2301	LFGB B82.02.8	8.67		-1.59	
2310	ISO13365	13.92		-0.09	
2311	ISO13365	14.017		-0.06	
2358	In house	15.55		0.38	
2363	ISO13365	14.5		0.08	
2365	ISO13365	14.72		0.14	
2375	ISO13365	14.3		0.02	
2379	LFGB B82.02.8	18.413		1.20	
2382	ISO13365	14.52		0.08	
2492	In house	15.530		0.37	
2497	ISO17070	10.677		-1.02	
2532	ISO13365	16.0		0.51	
2563	ISO17070	8.36		-1.68	
2590		17.6		0.97	
2644		10.96		-0.94	
2737		14.214		0.00	
2804	In house	10.2		-1.15	
2877	In house	14.2815		0.02	
2891	LFGB B82.02.8	16.97		0.79	
2892	ISO13365	15.510		0.37	
3146	In house	9.22		-1.43	
3154	In house	17.89		1.05	
3172		15.47		0.36	
3197	In house	13.59		-0.18	
	normality	OK			
	n	28			
	outliers	0			
	mean (n)	14.223			
	st.dev. (n)	3.0410	RSD=21%		
	R(calc.)	8.515			
	st.dev.(iis-memo 1601)	3.4899			
	R(iis-memo 1601)	9.772			
Compare					
	R(Horwitz)	4.273			





APPENDIX 2 Other reported test results

Determination of 2-(Thio Cyano Methyl Thio)-Benzothiazole (TCMTB), 4-Chloro-3-Methyl Phenol (PCMC), 2-Octyl Iso Thiazol-3(2H)-one (OIT), Triclosan (TCS) and Other Preservatives on sample #19650; in mg/kg

lab	TCMTB	PCMC	OIT	TCS	Other Preservatives
551	-----	N.D.	-----	-----	-----
840	n.d.	n.d.	n.d.	n.d.	n.d.
2115	-----	-----	-----	-----	-----
2265	-----	-----	-----	-----	-----
2301	-----	-----	-----	-----	-----
2310	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
2311	Not Detected	-----	-----	Not Detected	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	NA
2365	<1.00	<1.00	<1.00	<1.00	-----
2375	-----	-----	-----	-----	-----
2379	-----	Not detected	-----	-----	-----
2382	-----	-----	-----	-----	-----
2492	-----	-----	-----	-----	36.9
2497	-----	-----	0.0236	-----	0.246
2532	Not Detected	Not Detected	Not Detected	Not Detected	-----
2563	-----	< 0.1	-----	-----	-----
2590	-----	-----	-----	-----	-----
2644	-----	-----	-----	-----	-----
2737	-----	-----	-----	-----	-----
2804	-----	-----	-----	-----	-----
2877	-----	-----	-----	-----	-----
2891	-----	-----	-----	-----	-----
2892	-----	4.560	-----	-----	-----
3146	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----
3172	-----	-----	-----	-----	-----
3197	-----	-----	-----	-----	-----

APPENDIX 3 Analytical details

lab	ISO/IEC17025 accredited	Sample intake (grams)	Extraction technique	Extraction solvent	Sample preparation
551	Yes	1.0	Ultrasonic	KOH	Further cut
840	---	---	---	---	---
2115	Yes	1	Soxhlet/ AES	KOH	Further cut
2265	No	0.5	0.5g/10 ml KOH over night at 90°C	KOH	Further cut
2301	Yes	1	Oven	KOH	Further cut
2310	No	1	Ultrasonic	ACN	Further cut
2311	Yes	1	Ultrasonic	ACN	Further cut
2358	Yes	1	---	KOH	Further cut
2363	No	0.5	Ultrasonic	---	Further cut
2365	Yes	0.5	Ultrasonic	---	Further cut
2375	No	0.5	Ultrasonic	ACN	Further cut
2379	No	1	Ultrasonic	KOH	Further cut
2382	Yes	0.5	Ultrasonic	ACN	Further cut
2492	Yes	1.0	Soxhlet/ AES	---	Further cut
2497	No	1	Ultrasonic	MeOH	Further cut
2532	No	1.0017	Ultrasonic	ACN	Further cut
2563	Yes	1.5	Soxhlet/ AES	Acetone/HAc	Further cut
2590	Yes	1.5	Ultrasonic	ACN ISO13365	Further cut
2644	Yes	1	Ultrasonic	KOH	Further cut
2737	Yes	0.5	Ultrasonic	ACN ISO 13365:2011	Further cut
2804	No	1	Soxhlet/ AES	KOH	Used as received
2877	No	1	Ultrasonic	ACN	Used as received
2891	Yes	1.0075 & 1.077	Steam distillation	H2SO4 1M	Further cut
2892	No	1.0	Ultrasonic	ACN	---
3146	Yes	0.5	Ultrasonic	KOH	Used as received
3154	Yes	0.5	Oven, 16h 90°C drying	KOH	Used as received
3172	Yes	---	---	---	---
3197	Yes	1	Ultrasonic	KOH	Used as received

APPENDIX 4

Number of participants per country

2 labs in BRAZIL
4 labs in GERMANY
3 labs in HONG KONG
4 labs in INDIA
1 lab in INDONESIA
5 labs in ITALY
4 labs in P.R. of CHINA
1 lab in THAILAND
2 labs in TURKEY
2 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
n.a. = not applicable
n.d. = not detected
n.e. = not evaluated
W = test result withdrawn on request of participant
ex = test result excluded from the statistical evaluation

Literature:

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