Results of Proficiency Test OPP & Other Preservatives in Leather May 2020

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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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 leather there are some Ecolabelling schemes imposing environmental requirements for textile and leather products on a voluntary basis. Well-known Ecolabelling organizations are OekoTex® and Bluesign®.

Since 2018 the Institute for Interlaboratory Studies organizes a scheme of proficiency test for Ortho-Phenyl Phenol (OPP) and other preservatives in leather every year. During the annual proficiency testing program 2019/2020, it was decided to continue this proficiency test.

In this interlaboratory study 34 laboratories in 17 different countries registered for participation. See appendix 3 for the number of participants per country. In this report the results of this 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 the 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 leather sample of 3 grams, which was positive on some preservatives and labelled #20595. 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 organisation 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 leather positive on OPP and 4-Chloro-3-Methyl Phenol (PCMC) was obtained from a third party. After grinding and homogenization 100 small bags were filled with approximately 3 grams each and labelled #20595.The homogeneity of the subsamples was checked by the determination of OPP in accordance with an in-house test method for OPP on seven stratified randomly selected subsamples.

	OPP in mg/kg
Sample #20595-1	98.4
Sample #20595-2	105.3
Sample #20595-3	105.6
Sample #20595-4	109.3
Sample #20595-5	105.7
Sample #20595-6	102.9
Sample #20595-7	113.4

Table 1: homogeneity test results of subsamples #20595

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

	OPP in mg/kg
r (observed)	13.3
reference method	iis memo 1601
0.3 x R (reference method)	16.1

Table 2: evaluation of the repeatability of subsamples #20595

For the target reproducibility the reproducibility of iis memo 1601 “Precision data of Orthophenyl Phenol and Pentachlorophenol in textile” (lit. 18) was taken. It was concluded that the determination of OPP in leather is quite comparable to OPP and PCP in textile. The calculated repeatability of OPP was in agreement with 0.3 times the target reproducibility. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample labelled #20595 was sent on April 15, 2020.

2.5 ANALYZES

The participants were requested to determine on sample #20595 the concentrations of Ortho-Phenyl Phenol (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. It was also requested to report if the laboratory was accredited to determine the requested components and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample, but not to age nor to dry the sample nor to determine volatile matter. The amount of sample was not enough to allow aging and/or determine the volatile matter content.
It was also requested to report the test results using the indicated units on the report form and not to round the results, but report as much significant figures as possible and 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.kmpd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 of this report. The laboratories are presented by the 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 reanalyses). Additional or corrected test results are used for the data analysis and the original 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 wast 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 subsequently to Dixon's, Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for Dixon's test, by G(0.01) or DG(0.01) for Grubbs's test and by R(0.01) for Rosner's test. Stragglers are marked by D(0.05) for Dixon's test, by G(0.05) or DG(0.05) for Grubbs' test and by R(0.05) for 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 uncertainly 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 analysis 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. The Kernel Density Graph 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 in this interlaboratory study.

The target standard deviation was calculated from the target reproducibility by division with 2.8. In case no literature reproducibility was available, other target values are 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:

	$\lvert z\rvert < 1$	good
$1 <$	$\lvert z\rvert < 2$	satisfactory
$2 <$	$\lvert z\rvert < 3$	questionable
$3 <$	$\lvert z\rvert$	unsatisfactory

4 EVALUATION

During the execution of this proficiency test no problems occurred with the dispatch of the samples. One participant reported the test results after the final reporting date and two other participants did not report any test results at all. Not all laboratories were able to report all components requested.
In total 32 laboratories reported 59 numerical test results. No statistical outlying test results were observed. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER COMPONENT

In this section the 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. These test methods are also in the tables in appendix 1 together with the original data. The abbreviations used in these tables are explained in appendix 4.

For OPP and PCMC, the test method to be used is ISO13365 or ISO17070, see note in scope of test method ISO13365. Regretfully ISO13365 and ISO17070 do not provide any precision data for OPP or PCMC. Therefore, it was decided to calculate the target reproducibility with the formula based on iis PT data from OPP in textile, see iis memo 1601 (lit. 18).

Sample #20595

OPP: The determination of this component was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

TCMTB: The concentrations were near or below the detection limit. Therefore, no z-scores were calculated.

PCMC: The determination of this component may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

OIT: The concentrations were near or below the detection limit. Therefore, no z-scores were calculated.

TCS: The concentrations were near or below the detection limit. Therefore, no z-scores were calculated.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

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

Component	unit	n	average	2.8 * sd	R(target)
OPP	mg/kg	32	255.8	106.6	113.9
PCMC	mg/kg	27	43.2	31.0	25.1

Table 3: reproducibility of preservatives on sample #20595

Without further statistical calculations, it can be concluded that for OPP the group of participating laboratories have no difficulties with the analysis. However, for PCMC the group have some difficulties. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON OF PROFICIENCY TEST OF MAY 2020 WITH PREVIOUS PTS

	May 2020	May 2019	April 2018
Number of reporting laboratories	32	38	55
Number of test results	59	89	75
Number of statistical outliers	0	5	2
Percentage of statistical outliers	0%	5.6%	2.7%

Table 4: comparison with previous proficiency tests

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

The performance of the proficiency test was compared expressed as relative standard deviation of the PTs, see next table.

Component	May 2019	May 2019	April 2018	Target
OPP	15%	21%	23%	15%
PCMC	26%	16%	15%	17%
OIT	n.e.	39%	n.e.	25%

Table 5: comparison of observed uncertainties with targets

4.4 EVALUATION OF THE ANALYTICAL DETAILS

Test method ISO13365 describes an Ultrasonic Extraction pathway to extract the analytes and quantify with Liquid Chromatography. Test method ISO17070 can be used to determine and quantify OPP and PCMC by means of Gas Chromatography/Mass Spectroscopy. Twenty-one participants (=66%) tested the leather samples according to the test method ISO13365, four participants (=13%) used ISO17070 and six participants (=19%) reported to have used an in-house method.

For this proficiency test some analytical details were requested, see appendix 2 for the reported answers. Based on the answers given by the participantsthe following can be summarized:

- About 65% of the reporting participants mentioned that they are accredited for the determination of the reported components.
- About 65% of the reporting participants did use a test portion between 0.5 and 1 grams. Two others used less testing material for intake: <0.5 and one other participant used more material: 2.5 gram.
- About 70% of the reporting participants used Ultrasonic as technique to release the Preservatives and about 10% reported to have used Steam distillation or Soxhlet/AES.

- About 55% of the reporting participants used Acetonitrile as extraction solvent. About 20% reported to have used a different extraction solvent (eg. Hexane, Methanol, KOH, Acetone).
- About 70% of the reporting participants used an extraction time of 60 minutes or longer at room temperature. About 10% reported to have used a shorter extraction time and about 20% reported have used a higher temperature (between 35 – 70°C).
- About 60% of the reporting participants used Liquid Chromatography (eg. LC, HPLC) for quantification of the Preservatives and about 15% used Gas Chromatography.

When the analytical details were investigated separately, it appeared that the effect on the determination on OPP and PCMC in Leather is negligible.

5 DISCUSSION

In this PT, the average of the homogeneity test results is not in line with the average (consensus value) from the PT results. There are several reasons for this. First, the goal of the homogeneity testing is different from the goal of the evaluation of the reported PT results. In order to prove the homogeneity of the PT samples, a test method is selected with a high precision (smallest variation). The accuracy (trueness) of the test method is less relevant. Secondly, the homogeneity testing is done by one laboratory only. The test results of this ISO/IEC17025 accredited laboratory will have a bias (systematic deviation) depending on the test method used. The desire to detect small variations between the PT samples leads to the use of a sensitive test method with high precision, which may be a test method with significant bias.
Also, each test result reported by the laboratories that participate in the PT will have a bias. However, some will have a positive bias and others a negative bias. These different biases compensate each other in the PT average (consensus value). Therefore, the PT consensus value may deviate from the average of the homogeneity test. At the same time the accuracy of the PT consensus value is more reliable than the accuracy of the average of the homogeneity test.

In the next table the limits of standard 100 by OEKO-TEX® are given. It was noticed that not all participants would make identical decisions about the acceptability of the leather.

Preservatives (mg/kg)	Baby clothes	In direct skin contact	With no direct skin contact	Decoration material
OPP	<250	<750	<750	<750
TCMTB	<250	<500	<500	<500
PCMC	<150	<300	<300	<300
OIT	<50	<100	<100	<100

Table 6: OEKO-TEX Ecolabelling Standard and Requirements for leathers in EU

For the determination of OPP sixteen participants would have rejected the sample for baby clothes and sixteen participants would have accepted the leather. For all other categories the leather would have been accepted.
For the determination of PCMC all participants would have accepted the sample for all categories.

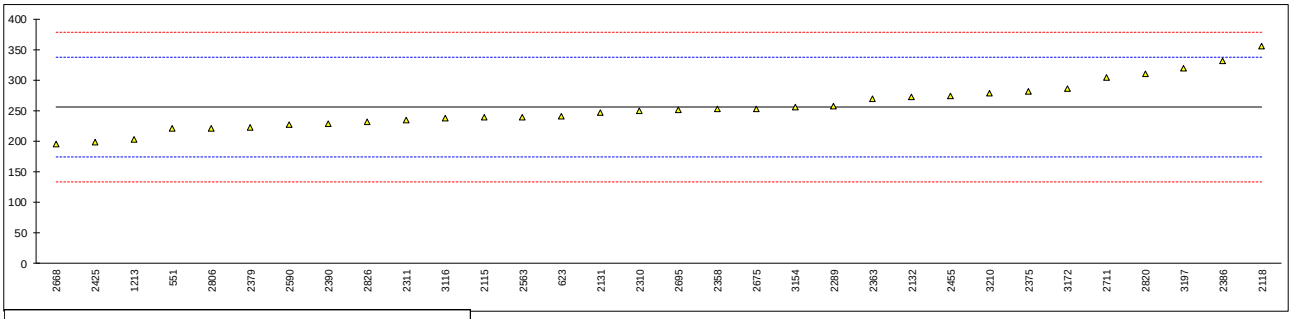
6 CONCLUSION

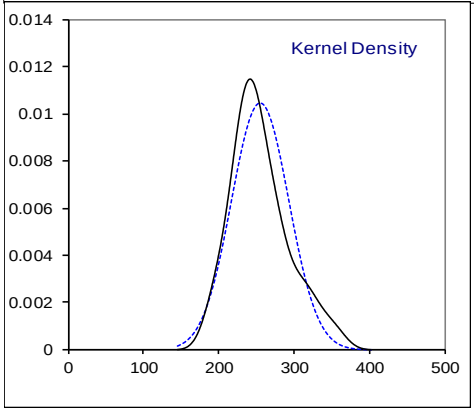
It can be concluded that the majority of the participants had no major problems with the determination of OPP and PCMC in the sample in this PT.
Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation 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-Phenyl Phenol (OPP) on sample #20595; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	In house	221.351		-0.85	
623	ISO13365	241.00		-0.36	
1213	ISO13365	203.214		-1.29	
2115	ISO13365	239.44		-0.40	
2118	ISO13365	354.899		2.43	
2131	In house	246.892		-0.22	
2132	In house	271.8		0.39	
2289	ISO17070	257.6		0.04	
2310	ISO13365	250		-0.14	
2311	ISO13365	235		-0.51	
2358	ISO13365	252.25		-0.09	
2363	ISO13365	268.8		0.32	
2375	ISO13365	282		0.64	
2379	§64 LFGB B82.02.8	222.7546		-0.81	
2386	In house	331.97	C	1.87	First reported 421.85
2390	ISO17070	228.28		-0.68	
2425	In house	198		-1.42	
2455	ISO13365	273.4		0.43	
2561		-----		-----	
2563	ISO17070	239.8		-0.39	
2590	ISO13365	226.845		-0.71	
2644		-----		-----	
2668	ISO13365	194.50		-1.51	
2675	ISO13365	252.72		-0.08	
2695	ISO13365	250.572		-0.13	
2711	In house	303.6		1.17	
2806	ISO13365	221.4		-0.85	
2820	ISO13365	309.6		1.32	
2826	ISO13365	232.11		-0.58	
3116	ISO13365	237.2		-0.46	
3154	ISO13365	255.1		-0.02	
3172	ISO17070	286		0.74	
3197	ISO13365	319.7		1.57	
3210	ISO13365	278.97		0.57	
	normality	OK			
	n	32			
	outliers	0			
	mean (n)	255.837			
	st.dev. (n)	38.0684	RSD = 15%		
	R(calc.)	106.592			
	st.dev.(iis memo 1601)	40.6936			
	R(iis memo 1601)	113.942			
Compare					
	R(Horwitz)	49.751			

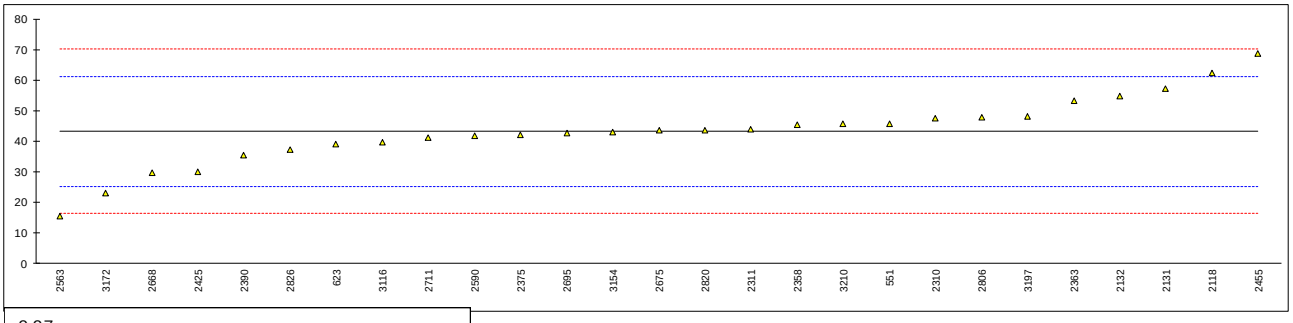


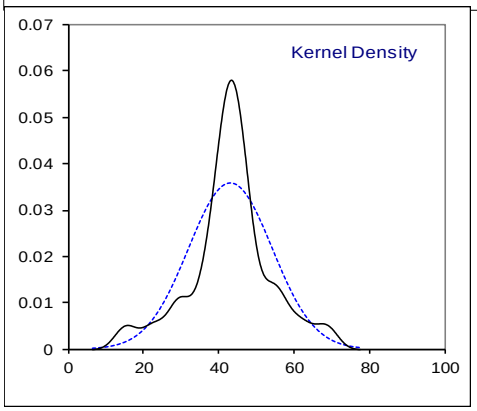


Determination of 4-Chloro-3-Methyl Phenol (PCMC) on sample #20595; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	In house	45.659		0.27	
623	ISO13365	39.13	C	-0.46	First reported 22.06
1213	ISO13365	-----		-----	
2115		-----		-----	
2118	ISO13365	62.229		2.12	
2131	In house	57.088		1.54	
2132	In house	54.9		1.30	
2289		-----		-----	
2310	ISO13365	47.6		0.49	
2311	ISO13365	43.9		0.07	
2358	ISO13365	45.53		0.26	
2363	ISO13365	53.2		1.11	
2375	ISO13365	42		-0.14	
2379		-----		-----	
2386		-----		-----	
2390	ISO17070	35.49		-0.86	
2425	In house	29.84		-1.49	
2455	ISO13365	68.7		2.84	
2561		-----		-----	
2563	ISO17070	15.6		-3.08	
2590	ISO13365	41.808		-0.16	
2644		-----		-----	
2668	ISO13365	29.53		-1.53	
2675	ISO13365	43.44		0.02	
2695	ISO13365	42.645		-0.07	
2711	In house	41.2		-0.23	
2806	ISO13365	47.7		0.50	
2820	ISO13365	43.5		0.03	
2826	ISO13365	37.245		-0.67	
3116	ISO13365	39.54		-0.41	
3154	ISO13365	43.12		-0.01	
3172	ISO17070	22.89		-2.27	
3197	ISO13365	48.2		0.55	
3210	ISO13365	45.59		0.26	

	normality	suspect
	n	27
	outliers	0
	mean (n)	43.232
	st.dev. (n)	11.0883 RSD = 26%
	R(calc.)	31.047
	st.dev.(iis memo 1601)	8.9783
	R(iis memo 1601)	25.139
Compare		
	R(Horwitz)	10.987





Determination of 2-(Thio Cyano Methyl Thio)-Benzothiazole (TCMTB), 2-Octyl-Iso-Thiazol-3(2H)-one (OIT), Triclosan (TCS) and Other Preservatives on sample #20595; results in mg/kg

lab	TCMTB	OIT	TCS		Other	remarks
551	-----	-----	-----		-----	
623	ND	1.06	ND		ND	
1213	n/a	n/a	n/a		n/a	
2115	-----	3.54	-----		-----	
2118	0	0	0		-----	
2131	-----	-----	-----		-----	
2132	<10	<10	<10		NA	
2289	<0.05	<0.05	<0.05		<0.05	
2310	Not detected	1.86	Not detected		Not detected	
2311	Not Detected	1.6	Not Detected		-----	
2358	n.d.	n.d.	n.d.		n.d.	
2363	ND	ND	ND		ND	
2375	-----	1.9	-----		-----	
2379	Not tested	Not tested	Not tested		Not tested	
2386	-----	-----	-----		-----	
2390	-----	-----	-----		-----	
2425	Not Detected	Not Detected	Not Detected		Not Detected	
2455	nd	nd	-----		-----	
2561	-----	-----	-----		-----	
2563	-----	-----	-----		-----	
2590	-----	-----	-----		-----	
2644	-----	-----	-----		-----	
2668	Not Detected	Not detected	Not detected		Not detected	
2675	0	1.65	7.55		344.68	o-Benzyl-p-chlorphenol
2695	-----	-----	-----		-----	
2711	<1	<1	Not determined		Not determined	
2806	-----	2.2	-----		-----	
2820	-----	2.2	-----		-----	
2826	<20	<20	<20		<20	
3116	-----	1.939	-----		-----	
3154	-----	-----	-----		45.82	2-Mercaptobenzothiazole
3172	n.d.	6.648	-----		-----	
3197	ND	ND	Not Detected	C	ND	
3210	<40	<40	-----		-----	

Lab 3197: first reported 195.6

APPENDIX 2 Analytical Details

lab	ISO17025 accredited	sample intake (g)	release technique	solvent to release analytes	extraction time (min)	extraction temp. (°C)	technique for quantification
551	Yes	1	---	---	---	---	---
623	Yes	1	Ultrasonic	Acetonitrile	60	25-30	LC-MS
1213	Yes	0.25	Ultrasonic	Acetonitrile	60	< 35	HPLC
2115	No	1	Ultrasonic	Acetonitrile	60	25	LC-UV
2118	No	0.75	Ultrasonic	Acetonitrile	60	Room	HPLC-DAD
2131	Yes	1.0	Ultrasonic	Methanol	60	60	UHPLC-DAD
2132	No	1	Ultrasonic	Acetonitrile	60	40	LC-DAD
2289	Yes	3mm	Steam	Hexane	30	Room	GCMS
2310	No	1	Ultrasonic	Acetonitrile	60	Room	LCMS
2311	---	---	---	---	---	---	---
2358	Yes	---	Ultrasonic	---	---	---	LC-MS
2363	Yes	2.5	Ultrasonic	Acetonitrile	60	Room	ESM
2375	No	0.5	Ultrasonic	Acetonitrile	60	Room	LC-MS
2379	No	0.5	Ultrasonic	KOH/Hexane	90	70	GC-MS
2386	Yes	0.334	Ultrasonic	KOH/Hexane	60	Room	GC/MS
2390	Yes	0.5	Ultrasonic	KOH	60	Room	GCMS
2425	---	---	---	---	---	---	---
2455	Yes	0.8817	Ultrasonic	Acetonitrile	~90	~24	---
2561	---	---	---	---	---	---	---
2563	Yes	---	Soxhlet / AES	Aceton/HAc	10	100	GC-MS
2590	Yes	1	Ultrasonic	Acetonitrile	60	40	LC-MS
2644	---	---	---	---	---	---	---
2668	---	---	---	---	---	---	---
2675	Yes	1.0077	Ultrasonic	Acetonitrile	60	from 22 - 35	LC-PAD
2695	Yes	1	Ultrasonic	Acetonitrile	60	from 20 -	HPLC-DAD/MS
2711	No	0.997	Soxhlet / AES	Methanol	60	65	HPLC-DAD
2806	Yes	---	---	---	---	---	---
2820	Yes	1	Ultrasonic	Acetonitrile	60	20	HPLC-DAD
2826	No	1	Ultrasonic	Acetonitrile	60	Room	LC-DAD
3116	Yes	1	Ultrasonic	Acetonitrile	60	35	LC MS
3154	Yes	0.5	Ultrasonic	Acetonitrile	60	Room	HPLC-DAD
3172	---	---	---	---	---	---	---
3197	Yes	1	Ultrasonic	Acetonitrile	60	Room	HPLC
3210	Yes	1	Ultrasonic	Acetonitrile	60	Room	HPLC/DAD

APPENDIX 3

Number of participants per country

1 lab in BANGLADESH
1 lab in BELGIUM
1 lab in BRAZIL
1 lab in FRANCE
4 labs in GERMANY
4 labs in HONG KONG
3 labs in INDIA
1 lab in INDONESIA
8 labs in ITALY
2 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in SWITZERLAND
1 lab in THAILAND
2 labs in TURKEY
1 lab in U.S.A.
1 lab in UNITED KINGDOM
1 lab 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
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
fr. = first reported result

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