Results of Proficiency Test OPP & Other Preservatives in Leather/Footwear May 2021

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

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 (iis) organizes a proficiency test for the determination of Ortho-Phenylphenol (OPP) and other preservatives in Leather/Footwear every year. During the annual proficiency testing program 2020/2021 it was decided to continue the proficiency test for the analysis of OPP and other preservatives in Leather/Footwear.

In this interlaboratory study 35 laboratories in 16 different countries registered for participation. See appendix 4 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 labelled #21590.
The participants were asked 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 black leather positive on OPP was obtained from a third party. After cutting and homogenization 70 small bags were filled with approximately 3 grams each and labelled #21590.
The homogeneity of the subsamples was checked by determination of OPP in accordance with ISO17070 on eight stratified randomly selected subsamples.

	OPP in mg/kg
Sample #21590-1	64.03
Sample #21590-2	72.54
Sample #21590-3	74.59
Sample #21590-4	78.35
Sample #21590-5	74.63
Sample #21590-6	77.12
Sample #21590-7	77.72
Sample #21590-8	75.95

Table 1: homogeneity test results of subsamples #21590

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)	12.85
reference method	iis memo 1601
0.3 x R (reference method)	11.96

Table 2: evaluation of the repeatability of subsamples #21590

For the target reproducibility the reproducibility of iis memo 1601 “Precision data of Orthophenyl Phenol and Pentachlorophenol in textile” (lit. 16) was taken. It was concluded that the determination of OPP in leather is quite comparable to OPP and PCP in textile.
The calculated repeatability is in agreement with 0.3 times the reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample labelled #21590 was sent on April 14, 2021.

2.5 ANALYZES

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

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 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 (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, 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, 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. 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

In this interlaboratory study no problems were encountered with the dispatch of the samples. One participant reported test results after the final reporting date and one other participant did not report any test results at all. Not all participants were able to report all components requested.
In total 34 participants reported 102 numerical test results. Observed were 5 outlying test results, which is 4.9%. 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 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. These test methods are also in the tables together with the original data. The abbreviations, used in these tables, are explained in appendix 5.

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. 16).

OPP: The determination of this component was not problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

TCMTB: The determination of this component was problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

PCMC: 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.

OIT: The determination of this component was problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

The majority of the participants agreed on a concentration near or below the limit of detection for all other Preservatives mentioned in paragraph 2.5. Therefore, no z-scores were calculated for these Preservatives. The reported results can be found in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibility based on former iis proficiency tests 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 based on previous proficiency tests are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
OPP	mg/kg	31	110.5	43.5	55.8
TCMTB	mg/kg	26	14.6	12.2	10.0
PCMC	mg/kg	14	4.6	2.0	3.8
OIT	mg/kg	26	26.0	18.4	16.3

Table 3: reproducibilities of preservatives on sample #21590

Without further statistical calculations, it can be concluded that for OPP, PCMC, TCMTB and OIT the participating laboratories have a good compliance with the reference method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2021 WITH PREVIOUS PTS

	May 2021	May 2020	May 2019	April 2018
Number of reporting laboratories	34	32	38	55
Number of test results	102	59	89	75
Number of statistical outliers	5	0	5	2
Percentage of statistical outliers	4.9%	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 2021	May 2019	May 2019	April 2018	Target 600-15 mg/kg
OPP	14%	15%	21%	23%	14-24%
TCMTB	30%	n.e.	n.e.	n.e.	14-24%
PCMC	16%	26%	16%	15%	14-24%
OIT	25%	n.e.	39%	n.e.	14-24%

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.
Of the thirthy-two participants that reported a test method, twenty-five participants (=78%) tested the leather samples according to the test method ISO13365, and four participants (=13%) reported to have used an in-house method. Only one participant reported ISO17070.

For this proficiency test some analytical details were requested, see appendix 3 for the reported answers. Based on the answers given by the participants the following can be summarized:

- About 80% of the reporting participants mentioned that they are accredited for the determination of the reported components.
- About 25% of the reporting participants used the sample as received and about 75% of the reporting participants did further cut the sample.
- About 90% of the reporting participants did use a test portion between 0.5 and 1 grams. Two others used more material: 2 – 3 grams.
- About 90% of the reporting participants used Ultrasonic as technique to release the Preservatives. Others reported to have used Soxhlet or AES.
- About 75% of the reporting participants used Acetonitrile as extraction solvent. About 20% reported to have used a different extraction solvent (eg. Hexane, Methanol, KOH).
- About 90% of the reporting participants used an extraction time of 60 minutes or longer at room temperature. Others reported to have used a shorter or longer extraction time and about 20% reported have used a higher temperature (between 35 – 70°C).
- About 80% of the reporting participants used Liquid Chromatography (eg. LC, HPLC) for quantification of the Preservatives and about 10% used Gas Chromatography.

Since the majority of the laboratories used the same method (ISO13665) to extract and determine the preservatives, no major differences are found in the measuring procedures. Therefore, the differences cannot be used to prove an effect on the determination on Preservatives in Leather/Footwear and therefore are negligible.

5 DISCUSSION

In the next table the limits of the OEKO-TEX® Leather standard are given.

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 and other Preservatives, all participants would accept the sample for all classes of the Oekotex® standard for Leather.

Bluesign has two lists. A Bluesign® Systems Substances List (BSSL) and the Bluesign® Restricted List (RSL). The BSSL contains all chemicals that are restricted or suspected to restricted and are therefore monitored. The RSL is an extract of the BSSL and contains the restricted chemicals with consumer safety limits.

Preservatives (mg/kg)	Class A Next to skin and Baby	Class B Occasional skin contact	Class C No skin contact
OPP	50	100	200

Table 7: Product classes specific limit values, Bluesign® RSL list

Preservatives (mg/kg)	Class A Next to skin and Baby	Class B Occasional skin contact	Class C No skin contact
TCMTB	Monitoring	Monitoring	Monitoring
PCMC	Monitoring	Monitoring	Monitoring
OIT	10	10	10

Table 8: Product classes specific limit values, Bluesign® BSSL list

For the determination of OPP and other Preservatives, all participants would reject the sample for Class A of the RSL list of the Bluesign®, except for one participant.

6 CONCLUSION

It can be concluded that the majority of the participants had no major problems with the determination of OPP and other Preservatives in the sample in this PT.

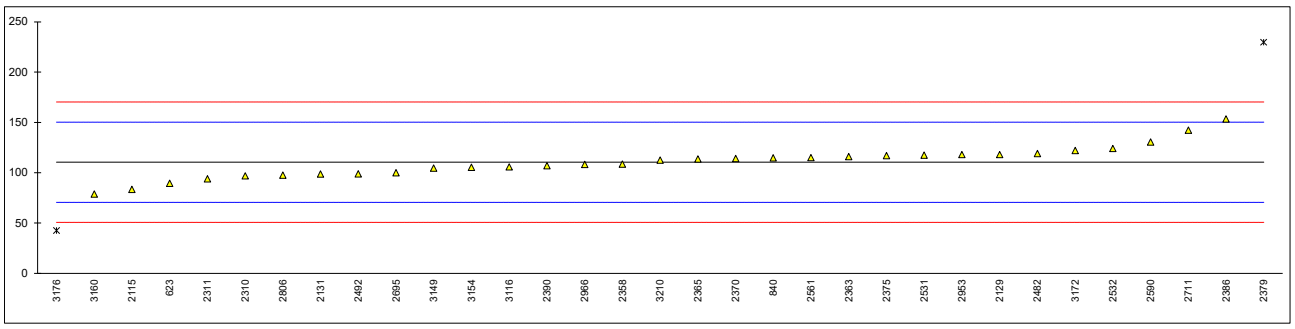
Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

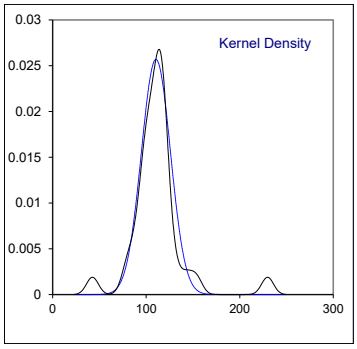
APPENDIX 1

Determination of Ortho-Phenylphenol (OPP) on sample #21590; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	ISO13365:2011	89.500		-1.05	
840		114.6		0.21	
2115	ISO13365:2011	83.36		-1.36	
2129	ISO13365:2011	118		0.38	
2131	OEKO-TEX ML-29	98.7		-0.59	
2265		-----		-----	
2310	ISO13365-1:2020	96.9		-0.68	
2311	ISO13365-1:2020	93.9335		-0.83	
2358	ISO13365:2011	108.458		-0.10	
2363	ISO13365-1:2020	116.1		0.28	
2365	ISO13365:2011	113.58		0.16	
2370	ISO13365-1:2020	114		0.18	
2375	ISO13365-1:2020	117		0.33	
2379	§64 LFGB B82.02.8	229.7162	C,R(0.01)	5.98	first reported: 192.6311
2386	In house	153.43		2.16	
2390	ISO17070	107	C	-0.17	first reported: 40.13
2410		-----		-----	
2482	ISO13365-1:2020	119		0.43	
2492	In house	98.8		-0.59	
2531	ISO13365-1:2020	117.41		0.35	
2532	ISO13365-1:2020	124		0.68	
2561	ISO13365-1:2020	115		0.23	
2590	ISO13365:2011	130.604		1.01	
2695	ISO13365:2011	100		-0.53	
2711	In house	142.3		1.60	
2806	ISO13365-1:2020	97.6		-0.65	
2953	ISO13365-1:2020	117.96		0.38	
2966	ISO13365-1:2020	108.214		-0.11	
3116	ISO13365:2011	105.8		-0.23	
3149	In house	104.6		-0.29	
3154	ISO13365-1:2020	105.25		-0.26	
3160	ISO13365:2011	78.91		-1.58	
3172	ISO13365-1:2020	122.0333		0.58	
3176	In house	42.6	C,R(0.01)	-3.41	first reported: 46.306
3210		112.62		0.11	

normality	suspect	
n	31	
outliers	2	
mean (n)	110.4730	
st.dev. (n)	15.53089	RSD = 14%
R(calc.)	43.4865	
st.dev.(iis memo 1601)	19.93084	
R(iis memo 1601)	55.8063	

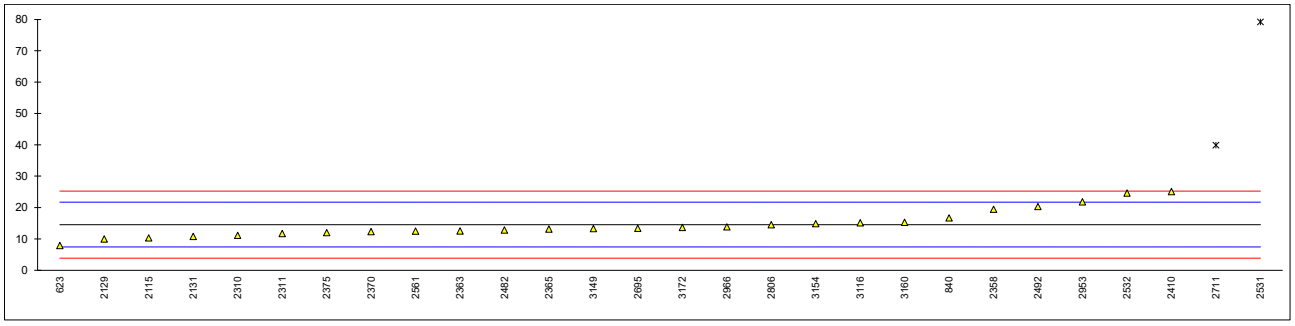


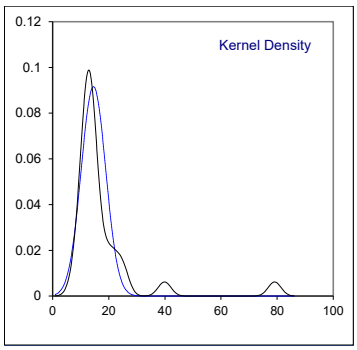


Determination of 2-(Thiocyanomethylthio)-Benzothiazole (TCMTB) on sample #21590; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	ISO13365:2011	7.860		-1.88	
840		16.7		0.60	
2115	ISO13365:2011	10.29		-1.20	
2129	ISO13365:2011	9.96		-1.29	
2131	OEKO-TEX ML-29	10.8		-1.06	
2265		-----		-----	
2310	ISO13365-1:2020	11.1		-0.97	
2311	ISO13365-1:2020	11.7130		-0.80	
2358	ISO13365:2011	19.448		1.37	
2363	ISO13365-1:2020	12.5		-0.58	
2365	ISO13365:2011	13.14		-0.40	
2370	ISO13365-1:2020	12.3		-0.64	
2375	ISO13365-1:2020	12		-0.72	
2379	§64 LFGB B82.02.8	Not tested		-----	
2386		-----		-----	
2390		-----		-----	
2410	ISO13365-1:2020	25.1		2.96	
2482	ISO13365-1:2020	12.8		-0.50	
2492	In house	20.3		1.61	
2531	ISO13365-1:2020	79.13	R(0.01)	18.13	
2532	ISO13365-1:2020	24.6		2.82	
2561	ISO13365-1:2020	12.465		-0.59	
2590		-----		-----	
2695	ISO13365:2011	13.4		-0.33	
2711	In house	39.9	R(0.01)	7.11	
2806	ISO13365-1:2020	14.5		-0.02	
2953	ISO13365-1:2020	21.78		2.02	
2966	ISO13365-1:2020	13.834		-0.21	
3116	ISO13365:2011	15.15		0.16	
3149	ISO13365-1:2020	13.3		-0.36	
3154	ISO13365-1:2020	14.84		0.08	
3160	ISO13365:2011	15.25		0.19	
3172	ISO13365-1:2020	13.6533		-0.26	
3176		-----		-----	
3210		-----		-----	

normality	suspect	
n	26	
outliers	2	
mean (n)	14.5686	
st.dev. (n)	4.35676	RSD = 30%
R(calc.)	12.1989	
st.dev.(iis memo 1601)	3.56174	
R(iis memo 1601)	9.9729	

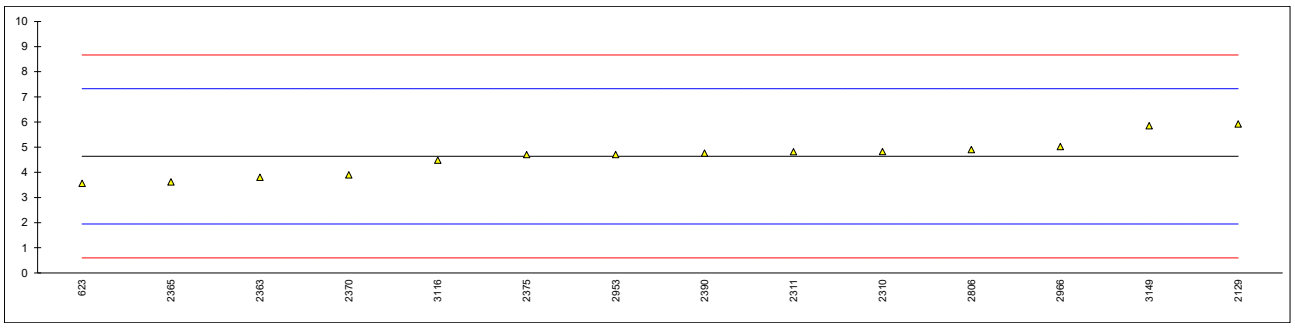


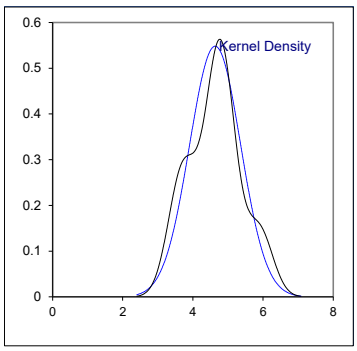


Determination of 4-Chloro-3-Methylphenol (PCMC) on sample #21590; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	ISO13365:2011	3.560		-0.80	
840		not detected		-----	
2115		-----		-----	
2129	ISO13365:2011	5.92		0.96	
2131	OEKO-TEX ML-29	not detected		-----	
2265		-----		-----	
2310	ISO13365-1:2020	4.82		0.14	
2311	ISO13365-1:2020	4.8170		0.14	
2358	ISO13365:2011	n.d.		-----	
2363	ISO13365-1:2020	3.8		-0.62	
2365	ISO13365:2011	3.62		-0.75	
2370	ISO13365-1:2020	3.90		-0.55	
2375	ISO13365-1:2020	4.7		0.05	
2379	§64 LFGB B82.02.8	Not tested		-----	
2386		-----		-----	
2390	ISO17070	4.76		0.09	
2410		-----		-----	
2482	ISO13365-1:2020	<1		-----	
2492		-----		-----	
2531	ISO13365-1:2020	Not detected		-----	
2532	ISO13365-1:2020	Not Detected		-----	
2561	ISO13365-1:2020	<2		-----	
2590		-----		-----	
2695	ISO13365:2011	not detected		-----	
2711	In house	not detected		-----	
2806	ISO13365-1:2020	4.9		0.20	
2953	ISO13365-1:2020	4.71		0.06	
2966	ISO13365-1:2020	5.0238		0.29	
3116	ISO13365:2011	4.485		-0.11	
3149	In house	5.85		0.90	
3154	ISO13365-1:2020	n.d.		-----	
3160	ISO13365:2011	not detected		-----	
3172	ISO13365-1:2020	< 5		-----	
3176		-----		-----	
3210		-----		-----	

normality	OK	
n	14	
outliers	0	
mean (n)	4.6333	
st.dev. (n)	0.72787	RSD = 16%
R(calc.)	2.0380	
st.dev.(iis memo 1601)	1.34512	
R(iis memo 1601)	3.7663	



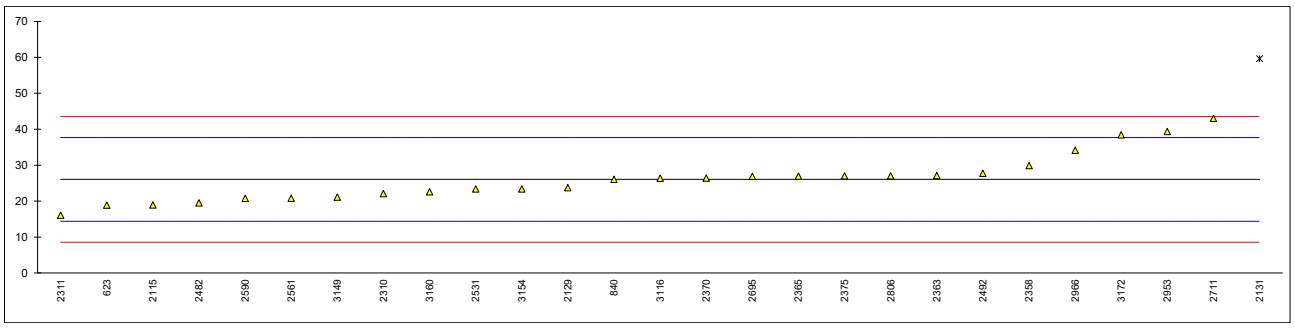


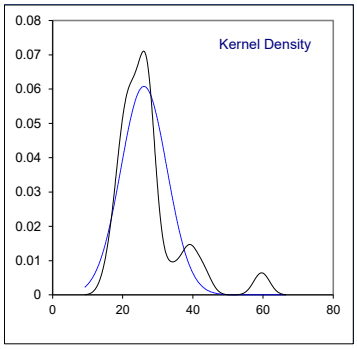
Determination of 2-Octylisothiazol-3(2H)-one (OIT) on sample #21590; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	ISO13365:2011	18.880		-1.23	
840		26.0		-0.01	
2115	ISO13365:2011	18.91		-1.22	
2129	ISO13365:2011	23.75		-0.39	
2131	OEKO-TEX ML-29	59.6	R(0.01)	5.75	
2265		-----		-----	
2310	ISO13365-1:2020	22.1		-0.68	
2311	ISO13365-1:2020	16.0903		-1.71	
2358	ISO13365:2011	29.858		0.65	
2363	ISO13365-1:2020	27.1		0.18	
2365	ISO13365:2011	26.89		0.15	
2370	ISO13365-1:2020	26.4		0.06	
2375	ISO13365-1:2020	27		0.16	
2379	§64 LFGB B82.02.8	Not tested		-----	
2386		-----		-----	
2390		-----		-----	
2410		-----		-----	
2482	ISO13365-1:2020	19.5		-1.12	
2492	In house	27.7		0.28	
2531	ISO13365-1:2020	23.33		-0.46	
2532	ISO13365-1:2020	Not Detected		-----	
2561	ISO13365-1:2020	20.76		-0.91	
2590	ISO13365:2011	20.713		-0.91	
2695	ISO13365:2011	26.85		0.14	
2711	In house	43.0		2.91	
2806	ISO13365-1:2020	27.0		0.16	
2953	ISO13365-1:2020	39.33		2.28	
2966	ISO13365-1:2020	34.1465		1.39	
3116	ISO13365:2011	26.36		0.05	
3149	ISO13365-1:2020	21.1		-0.85	
3154	ISO13365-1:2020	23.35		-0.46	
3160	ISO13365:2011	22.55		-0.60	
3172	ISO13365-1:2020	38.4045		2.12	
3176		-----		-----	
3210		<40		-----	

	normality	not OK
	n	26
	outliers	1
	mean (n)	26.0412
	st.dev. (n)	6.56302
	R(calc.)	18.3765
	st.dev.(iis memo 1601)	5.83540
	R(iis memo 1601)	16.3391

RSD = 25%





APPENDIX 2 Other reported Preservatives

lab	Triclosan	Other	Remarks
623	not detected	not detected	
840	not detected	not detected	
2115	-----	-----	
2129	<10	-----	
2131	not analyzed	22.4	Methylisothiazolinone (MIT) CAS 2682-20-4
2265	-----	-----	
2310	Not detected	Not detected	
2311	Not Detected	-----	
2358	n.d.	n.d.	
2363	<1.0	-----	
2365	＜1.0	-----	
2370	<2	<2	
2375	-----	-----	
2379	Not tested	Not tested	
2386	-----	-----	
2390	-----	-----	
2410	-----	-----	
2482	<1	-----	
2492	-----	-----	
2531	69.15	not analyzed	
2532	Not Detected	-----	
2561	<2	-----	
2590	-----	-----	
2695	not analyzed	not analyzed	
2711	-----	-----	
2806	-----	-----	
2953	0.82	-----	
2966	-----	-----	
3116	-----	-----	
3149	-----	-----	
3154	n.d.	-----	
3160	not detected	-----	
3172	-----	-----	
3176	-----	-----	
3210	Not detected	-----	

APPENDIX 3 Analytical Details

lab	ISO 17025 accr.	sample preparation	sample intake (g)	release technique	release solvent	extraction time (min)	extraction temp. (°C)	technique for quantification
623	Yes	Further cut	1	Ultrasonic	Acetonitrile	60	20-35	LC-MS
840	Yes	Further cut	0.5	Ultrasonic	Acetonitrile	60	room temp.	HPLC-DAD
2115	No	Used as received	1	Ultrasonic	Acetonitrile	60	20	LC-UV
2129	Yes	Further cut	0.5	Ultrasonic	Acetonitrile	60	room temp.	LC-DAD and LC-MSD
2131	Yes	Used as received	1	Ultrasonic	Acetonitrile	60	Room temp.	External standard
2265	---	---	---	---	---	---	---	---
2310	Yes	Further cut	1	---	Acetonitrile	one hour	Room temp.	Solvent Extr. by LCMS
2311	Yes	Further cut	0.5	Ultrasonic	Acetonitrile	60	25	LCMS
2358	Yes	Used as received	1	Ultrasonic	Acetonitrile	60	Room temp.	LC-DAD
2363	Yes	Further cut	1	Ultrasonic	Acetonitrile	60	room temp.	
2365	Yes	Further cut	1.0	Ultrasonic	Acetonitrile	60	Room temp.	HPLC-MS
2370	Yes	Further cut	1	Ultrasonic	Acetonitrile	1 h	33-35	LC/MS
2375	Yes	Further cut	0.5	Ultrasonic	Acetonitrile	60	room temp.	LCMS
2379	No	Further cut	0.5	Ultrasonic	KOH then n-Hex.	90	70	GC-MS
2386	Yes	Further cut	0,5	Ultrasonic	KOH then n-Hex.	60	Room temp.	GC-MS
2390	Yes	Further cut	0.5009	Ultrasonic	KOH then n-Hex.	60	Room temp.	GCMS
2410	Yes	Used as received	0.5	Ultrasonic	Acetonitrile	60	60	HPLC
2482	Yes	Further cut	0.5	Ultrasonic	Acetonitrile	60	room temp.	HPLC-DAD [1]
2492	Yes	Used as received	0.5	Ultrasonic	Acetonitrile	60	25 degree	HPLC-DAD
2531	Yes	Further cut	3	Ultrasonic	Acetonitrile	60	35	HPLC-DAD
2532	Yes	Further cut	1	Ultrasonic	Acetonitrile	60	Room temp.	HPLC-DAD
2561	Yes	Used as received	1	Ultrasonic	Acetonitrile	60	room temp.	hplc-dad
2590	Yes	Used as received	1	ASE	KOH then n-Hex.	60	35	LCMS
2695	Yes	Further cut	1,0027	Ultrasonic	Acetonitrile	60	20	[2]
2711	No	Further cut	1.918	Soxhlet	Methanol	60	65	HPLC-DAD
2806	Yes	---	---	---	---	---	---	---
2953	No	Further cut	1	Ultrasonic	Acetonitrile	60	27	LC-MSMS
2966	No	Further cut	1	Ultrasonic	Acetonitrile	60	25-38	HPLC-DAD
3116	No	Used as received	1	Ultrasonic	Acetonitrile	60	40	LC/MS
3149	Yes	Further cut	1	[3]	[4]	[5]	---	[6]
3154	---	---	---	---	---	---	---	---
3160	No	Further cut	1	Ultrasonic	Acetonitrile	60	Room temp.	HPLC-DAD
3172	---	---	---	---	---	---	---	---
3176	Yes	Further cut	1	Ultrasonic	n-Hexane only	30	40	GC-MS
3210	Yes	Further cut	1	Ultrasonic	Acetonitrile	60	ambient	LC-DAD

[1] and HPLC-QQQ (TCMTB)
[2] TCMTB (LC-DAD) OIT, OPP, PCMC (LC-MS)
[3] TCMTB/OIT: Ultrasonic, OPP/PCMC: Methanol/acetone
[4] TCMBT/OIT: Acetonitrile, OPP/PCMC: Soxhlet
[5] TCMBT/OIT: 60 min, OPP/PCMC: 5 h
[6] TCMBT/OIT: HPLC-DAD, OPP/PCMC: GC-ECD

APPENDIX 4

Number of participants per country

1 lab in FRANCE
6 labs in GERMANY
3 labs in HONG KONG
3 labs in INDIA
1 lab in INDONESIA
9 labs in ITALY
2 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in SOUTH KOREA
1 lab in SPAIN
1 lab in SWITZERLAND
1 lab in TAIWAN
1 lab in THAILAND
2 labs in TURKEY
1 lab in UNITED KINGDOM
1 lab 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.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

Literature

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