Results of Proficiency Test
OPP & Other Preservatives
in Leather
May 2019

Organised 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 textiles, some Eco-labelling schemes are imposing environmental requirements for leather products on a voluntary basis, for example OEKO-TEX Standard 100 (Switzerland).

Since 2004 the Institute for Interlaboratory Studies organizes a scheme of proficiency test for Ortho-Phenyl Phenol (OPP), Penta-Chloro Phenol (PCP) and Tetra-Chloro Phenols (TeCP) in textile every year. On request of a number of participants, the Institute for Interlaboratory Studies (iis) decided to organize in 2018 a new proficiency test for determination of Ortho-Phenyl Phenol (OPP) and other preservatives in leather. During the annual proficiency testing program 2018/2019, it was decided to continue this proficiency test.

In this interlaboratory study 40 laboratories in 17 different countries registered for participation. See appendix 3 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 the 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 sample of 3 grams green grinded leather labelled #19542, which was positive on some preservatives. 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 green leather positive on OPP and 4-Chloro-3-Methyl Phenol (PCMC) was obtained from a third party. The bulk was grinded. Out of this batch, after mixing well, 108 subsamples of 3 grams each were packed and labelled #19542.
The homogeneity of the subsamples #19542 was checked by the determination of OPP on seven stratified randomly selected samples. The determination is performed in accordance with an in-house test method for OPP. See the following table for the test results.

	OPP in mg/kg
Sample #19542-1	404.76
Sample #19542-2	381.56
Sample #19542-3	398.23
Sample #19542-4	375.65
Sample #19542-5	392.86
Sample #19542-6	378.53
Sample #19542-7	366.33

Table 1: homogeneity test results of subsamples #19542

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

	OPP in mg/kg
r (observed)	38.2
reference method	iis memo 1601
0.3 x R (reference method)	48.4

Table 2: evaluation of the repeatability of subsamples #19542

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 participating laboratory one sample of approximately 3 grams, labelled #19542 was sent on April 17, 2019.

2.5 ANALYSES

The participants were requested to determine on sample #19542 the concentrations of Ortho-Phenyl Phenol (OPP), 2-(Thio Cyano Methyl Thio)-Benzothiazole (TCMTB), 4-Chloro-3-Methyl Phenol (PCMC) and 2-Octyl Iso Thiazol-3(2H)-one (OIT) 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 report as much significant figures as possible. It was also requested not to report ‘less than’ 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 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 38 laboratories reported 89 numerical test results. Observed were 5 statistical outlying test results, which is 5.6%. 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 listed 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).

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-seven participants (=71%) tested the leather samples according to the test method ISO13365, three participants (=8%) used ISO17070 and eight participants (=21%) reported to have used an in-house method.

Sample #19542

OPP: This determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated reproducibility calculated from iis memo 1601. When the ISO13365 test results were evaluated separately, the calculated reproducibility is lower but still not in agreement with the target reproducibility.

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

PCMC: This determination was not problematic. Three statistical outliers were observed. However, the calculated reproducibility is in full agreement with the estimated reproducibility calculated from iis memo 1601.
When the ISO13365 test results were evaluated separately, the calculated reproducibility is again in agreement with the target reproducibility.

OIT: This determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated reproducibility calculated from iis memo 1601.

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 test results, the calculated reproducibilities (standard deviation * 2.8) and the target reproducibilities are compared in the next table.

Component	unit	n	average	2.8 * sd	R (target)
OPP	mg/kg	37	280	161	123
TCMTB	mg/kg	12	<40	n.e.	n.e.
PCMC	mg/kg	25	138	61	67
OIT	mg/kg	16	11.7	12.8	8.3

Table 3: reproducibility of preservatives on sample #19542

Without further statistical calculations, it can be concluded that for OPP and OIT the total group of participating laboratories may have difficulties with the analysis. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON OF PROFICIENCY TEST OF MAY 2019 WITH PREVIOUS PT

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

Table 4: comparison with previous proficiency test

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

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

Component	May 2019	April 2018	target (iis memo 1601)
OPP	21%	23%	15%
PCMC	16%	15%	17%
OIT	39%	n.e.	25%

Table 5: Comparison of observed uncertainties with targets

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this proficiency test some analytical details were requested, see appendix 2 for the reported answers. Based on the answers the following can be summarized:
Twenty participants (=53%) answered to be ISO/IEC17025 accredited for the determination of the reported components in leather.
Almost all participants did use a test portion of either 0.5 or 1.0 grams, about equally divided. Two others used more testing material for intake: 1.5 to 2 grams.
Twenty-eight participants (74%) reported to have used Ultrasonic extraction to release the analytes from the leather. Four reported to have used a different release technique.
The majority of the group (about 67%) used Acetonitrile as extraction solvent and one-hour extraction time. A few used Hexane. Most participants extract at room temperature.
Majority used an LC method for quantification, six a GC method.

5 DISCUSSION

The effect of the reported analytical details (paragraph 4.4) were further investigated on OPP and PCMC, see tables 6 and 7 respectively.

Analytical Details	unit	n	average	RSD (%)
ISO/IEC 17025 accredited	mg/kg	20	284.3	19.7
Not ISO/IEC 17025 accredited	mg/kg	12	273.6	26.1
0.5g sample intake	mg/kg	15	290.0	22.3
1g sample intake	mg/kg	16	279.1	21.4
room temperature extraction	mg/kg	18	273.0	21.0
>30°C extraction	mg/kg	12	286.2	23.2

Table 6: effect of analytical details on OPP leather sample #19542

Analytical Details	unit	n	average	RSD (%)
ISO/IEC 17025 accredited	mg/kg	14	137.2	17.5
Not ISO/IEC 17025 accredited	mg/kg	6	136.7	17.3
0.5g sample intake	mg/kg	10	133.8	17.7
1g sample intake	mg/kg	10	139.8	16.9
room temperature extraction	mg/kg	14	130.7	15.0
>30°C extraction	mg/kg	6	151.0	17.6

Table 7: effect of analytical details on PCMC leather sample #19542

It is observed that extraction at higher temperatures than room temperature yields higher levels of preservatives although the observed effects is not statistically significant.

In table 8 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 8: OEKO-TEX Ecolabelling Standard and Requirements for leathers in EU

For the determination of OPP twenty-eight participants would reject the sample for baby clothes and ten laboratories would accept the sample.
For the determination of TCMTB all laboratories would accept the sample for all classes.
For the determination of PCMC six participants would reject the sample for baby clothes and twenty-two laboratories would accept the sample.
For the determination of OIT one participant would reject the sample for baby clothes and clothes in direct skin contact and twenty laboratories would accept the sample.

6 CONCLUSION

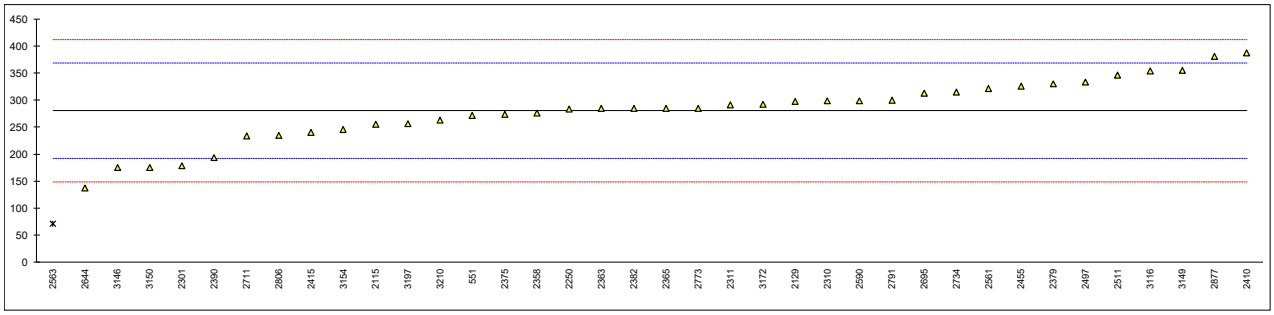
It can be concluded that the majority of the participants had no major problems with the determination of OPP, TCMTB and OIT in the sample in this PT.

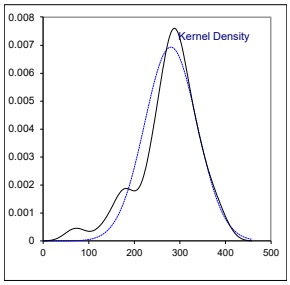
Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

APPENDIX 1

Determination of Ortho-Phenyl Phenol (OPP) on sample #19542; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	ISO17070	271.5203		-0.20	
2115	ISO13365	255.01		-0.57	
2129	ISO13365	297.83		0.40	
2250	ISO13365	283.11		0.06	
2301	In house	178.46		-2.32	
2310	ISO13365	299	C	0.43	first reported 513
2311	ISO13365	291.3487	C	0.25	first reported 509.2043
2358	ISO13365	276.299		-0.09	
2363	In house	284		0.08	
2365	ISO13365	284.04		0.09	
2375	ISO13365	274		-0.14	
2379	ISO17070	330.208	C	1.14	first reported 488.014
2382	In house	284		0.08	
2390	In house	193.59		-1.97	
2410	ISO13365	387.50		2.44	
2415	ISO13365	240.45		-0.91	
2455	ISO13365	326.043		1.04	
2497	ISO13365	333.29		1.21	
2511	In house	346.487		1.51	
2561	ISO13365	321.00		0.93	
2563	ISO17070	71.7	R(0.05)	-4.74	
2590	ISO13365	299.109		0.43	
2644	ISO13365	137		-3.26	
2656		-----		-----	
2695	ISO13365	312.36		0.73	
2711	In house	233.81		-1.06	
2734	ISO13365	315.250		0.80	
2756		-----		-----	
2773	ISO13365	285		0.11	
2791	ISO13365	299.27		0.43	
2806	ISO13365	234.7		-1.04	
2877	ISO13365	380.6625		2.28	
3116	ISO13365	353.83		1.67	
3146	In house	174.7		-2.40	
3149	In house	355.0	C	1.70	first reported 541.7
3150	ISO13365	175.33		-2.39	
3154	ISO13365	246.0		-0.78	
3172	ISO13365	292.0		0.27	
3197	ISO13365	256.0		-0.55	
3210	ISO13365	263.07		-0.39	
					ISO13365 only
	normality	OK			suspect
	n	37			27
	outliers	1			0
	mean (n)	280.28			285.87
	st.dev. (n)	57.540	RSD=21%		53.563 RSD=19%
	R(calc.)	161.11			149.98
	st.dev.(iis memo 1601)	43.975			44.720
	R(iis memo 1601)	123.13			125.22
Compare					
	R(Horwitz)	53.76			



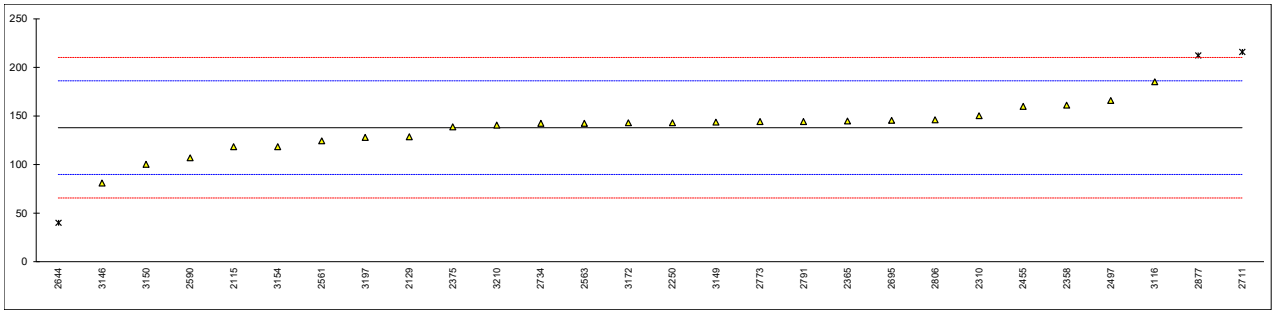


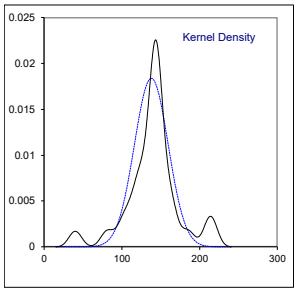
Determination of 2-(Thio Cyano Methyl Thio)-Benzothiazole (TCMTB) on sample #19542; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551		-----		-----	
2115		-----		-----	
2129	ISO13365	<10		-----	
2250	ISO13365	1.09		-----	
2301		-----		-----	
2310	ISO13365	Not detected		-----	
2311	ISO13365	Not Detected		-----	
2358	ISO13365	n.d.		-----	
2363		-----		-----	
2365	ISO13365	1.02		-----	
2375		-----		-----	
2379	ISO17070	Not tested		-----	
2382		-----		-----	
2390		-----		-----	
2410		-----		-----	
2415		-----		-----	
2455	ISO13365	< 5 n/d		-----	
2497	ISO13365	9.49		-----	
2511		-----		-----	
2561	ISO13365	<2.00		-----	
2563		-----		-----	
2590		-----		-----	
2644		-----		-----	
2656		-----		-----	
2695		-----		-----	
2711	In house	0		-----	
2734	ISO13365	nd		-----	
2756		-----		-----	
2773	ISO13365	ND		-----	
2791	ISO13365	<10		-----	
2806	ISO13365	1.2		-----	
2877		-----		-----	
3116	ISO13365	1.11		-----	
3146		-----		-----	
3149		-----		-----	
3150	ISO13365	<20		-----	
3154		-----		-----	
3172		-----		-----	
3197	ISO13365	Not detected	C	-----	first reported 127.8
3210	ISO13365	<40		-----	
	n	12			
	mean (n)	<40			

Determination of 4-Chloro-3-Methyl Phenol (PCMC) on sample #19542; results in mg/kg

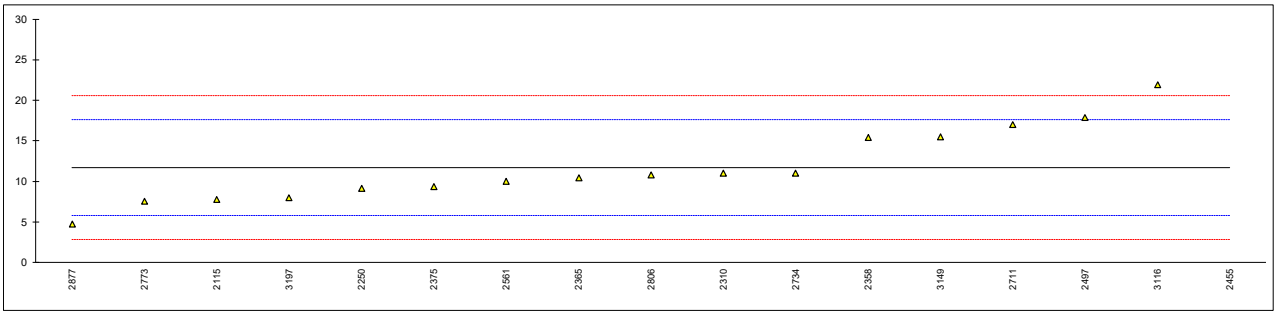
lab	method	value	mark	z(targ)	remarks
551		-----		-----	
2115	ISO13365	118.30		-0.82	
2129	ISO13365	128.67		-0.38	
2250	ISO13365	143.28		0.22	
2301		-----		-----	
2310	ISO13365	150	C	0.50	first reported 212
2311		-----		-----	
2358	ISO13365	161.295		0.97	
2363		-----		-----	
2365	ISO13365	144.61		0.28	
2375	ISO13365	139		0.04	
2379	ISO17070	Not tested		-----	
2382		-----		-----	
2390		-----		-----	
2410		-----		-----	
2415		-----		-----	
2455	ISO13365	160.086		0.92	
2497	ISO13365	166.18		1.17	
2511		-----		-----	
2561	ISO13365	124.15		-0.57	
2563	ISO17070	142.7		0.20	
2590	ISO13365	107.145		-1.28	
2644	ISO13365	40.2	G(0.05)	-4.06	
2656		-----		-----	
2695	ISO13365	145.22		0.30	
2711	In house	216	C,DG(0.05)	3.24	first reported 563.87
2734	ISO13365	142.405		0.19	
2756		-----		-----	
2773	ISO13365	144		0.25	
2791	ISO13365	144.45		0.27	
2806	ISO13365	146.2		0.34	
2877	ISO13365	212.0828	DG(0.05)	3.08	
3116	ISO13365	185.34		1.97	
3146	In house	81.2		-2.36	
3149	In house	143.8	C	0.24	first reported 236.7
3150	ISO13365	100.4		-1.56	
3154	ISO13365	118.5		-0.81	
3172	ISO13365	143.0		0.21	
3197	ISO13365	127.8	C	-0.42	first reported as TCMTB
3210	ISO13365	140.52		0.11	
					ISO13365 only
	normality	suspect			OK
	n	25			22
	outliers	3			2
	mean (n)	137.93			140.03
	st.dev. (n)	21.726	RSD=16%		19.465 RSD=14%
	R(calc.)	60.83			54.50
	st.dev.(iis memo 1601)	24.070			24.380
	R(iis memo 1601)	67.39			68.26
Compare					
	R(Horwitz)	29.44			

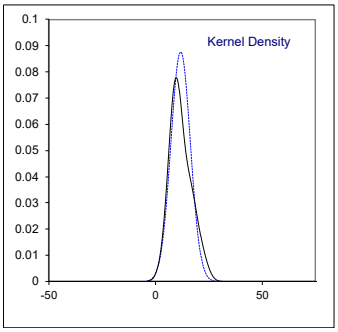




Determination of 2-Octyl Iso Thiazol-3(2H)-one (OIT) on sample #19542; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551		-----		-----	
2115	ISO13365	7.80		-1.33	
2129	ISO13365	<10		-----	
2250	ISO13365	9.13		-0.88	
2301		-----		-----	
2310	ISO13365	11	C	-0.25	first reported 29.2
2311		-----		-----	
2358	ISO13365	15.4625		1.26	
2363		-----		-----	
2365	ISO13365	10.43		-0.44	
2375	ISO13365	9.4		-0.79	
2379	ISO17070	Not tested		-----	
2382		-----		-----	
2390		-----		-----	
2410		-----		-----	
2415		-----		-----	
2455	ISO13365	103.0	C,G(0.01)	30.80	first reported <5/ n.d.
2497	ISO13365	17.88		2.07	
2511		-----		-----	
2561	ISO13365	10.05		-0.57	
2563		-----		-----	
2590		-----		-----	
2644		-----		-----	
2656		-----		-----	
2695		-----		-----	
2711	In house	17	C	1.78	first reported 37.81
2734	ISO13365	11.029		-0.24	
2756		-----		-----	
2773	ISO13365	7.6	C	-1.39	first reported n.d.
2791	ISO13365	<10		-----	
2806	ISO13365	10.8		-0.31	
2877	ISO13365	4.7515		-2.36	
3116	ISO13365	21.91		3.43	
3146		-----		-----	
3149	In house	15.49		1.27	
3150	ISO13365	<20		-----	
3154		-----		-----	
3172		-----		-----	
3197	ISO13365	8.0		-1.26	
3210	ISO13365	<40		-----	
	normality	OK			
	n	16			
	outliers	1			
	mean (n)	11.73			
	st.dev. (n)	4.553	RSD=39%		
	R(calc.)	12.75			
	st.dev.(iis memo 1601)	2.963			
	R(iis memo 1601)	8.30			





APPENDIX 2 Details of the test methods used by the participants

lab	ISO17025 accredited	sample intake (g)	release technique	solvent to release analytes	extraction time (min)	extraction temp. (°C)	technique for quantification
551	---	---	---	---	---	---	---
2115	No	1	Ultrasonic	Acetonitrile	60	25	LC-UV
2129	Yes	0.5	Ultrasonic	Acetontrile (10mL)	60	room temp.	LC-DAD
2250	Yes	0.5	Ultrasonic	Acetonitril	60	20	LC-MS
2301	Yes	1	Ultrasonic	Aceton	30	40	GC-MS
2310	No	1	Ultrasonic	Acetonitrile	60	room temp.	LC-MS
2311	Yes	1	Ultrasonic	Acetonitrile	60	room temp.	LC-MS
2358	---	---	---	---	---	---	---
2363	No	1	Ultrasonic	Acetonitrile	60	room temp.	GC-MS
2365	Yes	1	Ultrasonic	acetonitrile	60	room temp.	LC-MS
2375	No	0.5	Ultrasonic	Acetonitrile	60	room temp.	LC-MS
2379	No	0.5	Ultrasonic	KOH	60	70	GC-MS
2382	Yes	0.5	Other	N-hexane	900	90	Internal standard
2390	Yes	1.005	Ultrasonic	n-hexane	60	room temp.	GC-MS
2410	Yes	0.5	Ultrasonic	Acetonitrile	60	ambient	HPLC
2415	Yes	1	Ultrasonic	ACN	60	30	LC-DAD
2455	Yes	1.0	Ultrasonic	Acetonitrile only	80	30	HPLC
2497	No	0.5	Ultrasonic	methanol/acetone	60	60	LC-MS
2511	No	0.5	---	---	---	---	---
2561	Yes	1	Ultrasonic	Acetonitrile	60	room temp.	HPLC-DAD
2563	---	1.5	Soxhlet/AES	Aceton/acetic acid	3	100	GC-MS
2590	Yes	0.5	Ultrasonic	ACN	60	35	LC-MS
2644	No	0.5	Ultrasonic	ACN	60	25	LC-UV
2656	---	---	---	---	---	---	---
2695	Yes	1	Ultrasonic	ACETONITRILE	60	20	HPLC-DAD/MS
2711	No	1.95	Soxhlet/AES	Methanol	60	65	HPLC-DAD
2734	---	1	Ultrasonic	ACN	60	room temp.	HPLC-UV
2756	---	---	---	---	---	---	---
2773	Yes	0.5	Ultrasonic	ACN	60	room temp.	HPLC-DAD
2791	Yes	0.5	Ultrasonic	Acetonitrile	60	35	HPLC-DAD
2806	No	---	---	---	---	---	---
2877	No	1	Ultrasonic	Acetonitrile	60	39	HPLC
3116	Yes	1	Ultrasonic	Acetonitrile	60	35	
3146	Yes	0.5	Ultrasonic	OPP: KOH/Hexan	960/ 30	90/ room	GC-MS/ LC-MS
3149	Yes	0.5	Soxhlet	Acetonitrile	60/ 300		GC-MS
3150	No	1	Ultrasonic	acetonitrile	60	room temp.	HPLC-DAD
3154	---	---	---	---	---	---	---
3172	---	---	---	---	---	---	---
3197	Yes	1	Ultrasonic	ACN	60	room temp.	HPLC
3210	Yes	0.5	Ultrasonic	Acetonitrile	60	ambient	LC-DAD

APPENDIX 3

Number of participants per country

1 lab in BRAZIL
1 lab in ETHIOPIA
2 labs in FRANCE
7 labs in GERMANY
2 labs in HONG KONG
5 labs in INDIA
1 lab in INDONESIA
9 labs in ITALY
1 lab in KOREA
3 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in THAILAND
1 lab in TUNISIA
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

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 OEKO-TEX Standard 100; January 2017
3 Directive 94/783/EC
4 Impacts of Environmental Standards and requirements in EU Countries, August 1999
5 Horwitz, Journal of AOAC International, 79-3, (1996)
6 P.L. Davies, Fr. Z., Anal. Chem., 351, 513. (1988)
7 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons. NY, 302, (1971)
8 ISO 5725:86
9 ISO 5725 parts 1-6:94
10 ISO105 E4:94
11 ISO14184-1:94
12 ISO13528:05
13 M. Thompson and R. Wood, J. AOAC Int., 76, 926, (1993)
14 Analytical Methods Committee Technical brief, No 4, January 2001
15 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst 2002, 127, 1359-1364, (2002)
16 Official Journal of the European Communities, L133/29, May 2002
17 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
18 iis memo 1601: Precision data of OPP/PCP in textile, February 2016
19 ISO17070:15
20 ISO13365:17