Results of Proficiency Test
OPP & other preservatives
in leather
April 2018

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Corrector: ing. C.M. Nijssen-Wester & ing. G.A. Oosterlaken-Buijs

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1 INTRODUCTION

Since the 1990's, many countries have adopted environmental standards and requirements restricting the use of harmful chemicals in the production of textiles and clothing. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for textiles, some Eco-labelling schemes are imposing environmental requirements for leather products on a voluntary basis, e.g. Öko-Tex Standard 100 (Switzerland).

The Institute for Interlaboratory Studies organizes since 2004 a scheme of proficiency test for Orthophenylphenol (OPP), Pentachlorophenol (PCP) and Tetrachlorophenols (TeCP) in textile. On request of a number of participants, the Institute for Interlaboratory Studies (iis) decided to organize in 2018 a new proficiency tests for determination of Orthophenylphenol (OPP) and other preservatives in leather.
In this interlaboratory study 55 laboratories in 20 different countries registered for participation. See appendix 3 for the number of participants per country. In this report, the results of the 2018 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 organiser of the proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. Due to limited availability of samples positive on OPP and/or other preservatives on leather, it was decided to send one leather sample which was positive on OPP and 4-Chloro-3-methylphenol (PCMC). 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/IEC 17043:2010. 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 a 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 March 2017 (iis-protocol, version 3.4). 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 brown leather positive on OPP and PCMC was obtained from a third party. The bulk was cut into pieces. Out of this batch, after mixing well, 75 subsamples of 3 grams each, were packed and labelled #18551.
The homogeneity of the subsamples #18551 was checked by the determination of OPP on six 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 #18551-1	445.1
Sample #18551-2	452.9
Sample #18551-3	458.2
Sample #18551-4	480.1
Sample #18551-5	449.5
Sample #18551-6	486.9

Table 1: homogeneity test results of subsamples #18551

From the above test results of the homogeneity test, the repeatability was calculated and compared with 0.3 times the target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	OPP in mg/kg
r (observed)	48.3
Target	iis-memo (lit.18)
0.3 x R (Target)	56.5

Table 2: evaluation of the repeatability of subsamples #18551.

As target reproducibility, the reproducibility of OPP and PCP on textile (lit. 18) was taken, as it was concluded that the determination of OPP in leather is quite similar to OPP and PCP in textile.

The calculated repeatability of Orthophenylphenol (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 approx. 3 grams, labelled #18551 was sent on April 4, 2018.

2.5 ANALYSES

The participants were asked to determine the concentration of Orthophenylphenol (OPP), 2-(Thiocyanomethylthio)-benzothiazole (TCMTB), 4-Chloro-3-methylphenol (PCMC) and 2-Octylisothiazol-3(2H)-one (OIT) on sample #18551 applying the analysis procedure that is routinely used in the laboratory. Also, some method details were requested to be reported

It was explicitly requested to treat the samples as if they were routine samples and 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. 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 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 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 sample and 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 organisation 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 March 2017 (iis-protocol, version 3.4).

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 ISO 5725 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 the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs's test and by R(0.01) for the Rosner's. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1 was met for all evaluated tests, therefore, the 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 visualise 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 standard. 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 result tables of 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 serious problems occurred, although one participant reported the test results after the final reporting date and five participants did not report any test results at all. In total 55 laboratories reported 75 numerical test results. Observed were 2 statistical outlying test results, which is 2.7%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

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. It was therefore decided to calculate the target reproducibility with the formula as declared in a recent study (lit. 18).

4.1 EVALUATION PER DETERMINATION

OPP: 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 estimated reproducibility calculated from the iis memo (lit. 18). When the 25 ISO13365 test results were evaluated separately, the calculated reproducibility was in full agreement with the target reproducibility.

PCMC: The determination of this component was not problematic. No statistical outliers were observed. The calculated reproducibility is in full agreement with the estimated reproducibility calculated from the iis memo (lit. 18).

TCMTB and OIT: Sample #18551 did contain very little of the other two requested components, which concentrations were near or below the detection limit. Therefore, no significant conclusions were drawn.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibilities (see § 4.1) 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:

	unit	*n*	*average*	*2.8 x sd*	*R (target)*
OPP	mg/kg	48	558	363	221
PCMC	mg/kg	25	227	96	103

Table 3: reproducibility of phenols on sample #18551

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

4.3 OVERVIEW OF THE PROFICIENCY TEST OF APRIL 2018

	April 2018
Number of reporting labs	55
Number of results reported	75
Number of statistical outliers	2
Percentage outliers	2.7%

Table 4: Overview of the 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 table below.

	April 2018	RSD (iis) see lit 18
OPP	23%	14%
PCMC	15%	16%

Table 5: Comparison of observed uncertainties with targets

4.4 EVALUATION ANALYTICAL DETAILS

For this Proficiency Test some analytical details were requested (see appendix 2).
Based on the answers given by the participants the following can be summarized:
Thirty-two of the participants answered to be ISO/IEC17025 accredited for the determination of Orthophenylphenol in leather (=58%).
Twenty-five participants tested the leather samples according to the test method ISO13365, nine participants used ISO17070 and eleven participants reported to have used an in house method.
Almost all reporting laboratories did use a test portion between 0.5 - 1.0 grams. One mentioned to have use less material (0.2 gram) and two others used more testing material for intake (1.5 - 2 gram).
Thirty-six participants reported to have used ultrasonic extraction to release OPP and other preservatives from the leather. Eight reported to have used a different release technique (Soxhlet (2), Steam distillation (3), other (3)). The majority of the group used Acetonitrile as extraction solvent. A few used Hexane or another solvent.

5 DISCUSSION

In this proficiency test for the determination of preservatives in leather, not all laboratories followed the same procedure for extracting OPP and PCMC from the leather matrix. The majority of laboratories performed ISO13365, the others used ISO17070 or used an in house method or did not report any details.

Test method ISO13365 describes an Ultrasonic Extraction pathway to extract OPP and PCMC and quantify with Liquid Chromatography. Also test method ISO17070 can be used to determine and quantify OPP and PCMC by means of gas chromatography/mass spectroscopy (GC/MS) (see scope of ISO13365). However, ISO 17070 mentions two different methods to release/extract the preservatives by means of Steam distillation and Liquid-liquid extraction. It is not clear if there is a bias between the two extraction methods.

For the OPP determination, twenty-five laboratories, reported to have used test method ISO13365 and used ultrasonic as extraction with Acetonitril as extraction solvent.
When these ISO13365 test results were evaluated separately, the calculated reproducibility was in full agreement with the target reproducibility.
The large variation in all reported test results may therefore be explained by the variety of test methods used.

In table 6 the limits mentioned in standard 100 by OEKO-TEX are mentioned. 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
Orthophenylphenol (OPP)	<250	<750	<750	<750
4-Chloro-3methylphenol (PCMC)	<150	<300	<300	<300

Table 6: Ecolabelling Standard and Requirements Oko-tex for Leathers in EU

For the determination of OPP, seven participants would reject the sample for all categories (>750 mg/kg), all other laboratories would accept the sample for all classes except for baby clothes (>250 mg/kg, but <750 mg/kg).
For the determination of PCMC, one participant would accept the sample for all categories (<150 mg/kg), all other laboratories would accept the sample for all classes except for baby clothes. (>150 mg/kg, but <300 mg/kg).

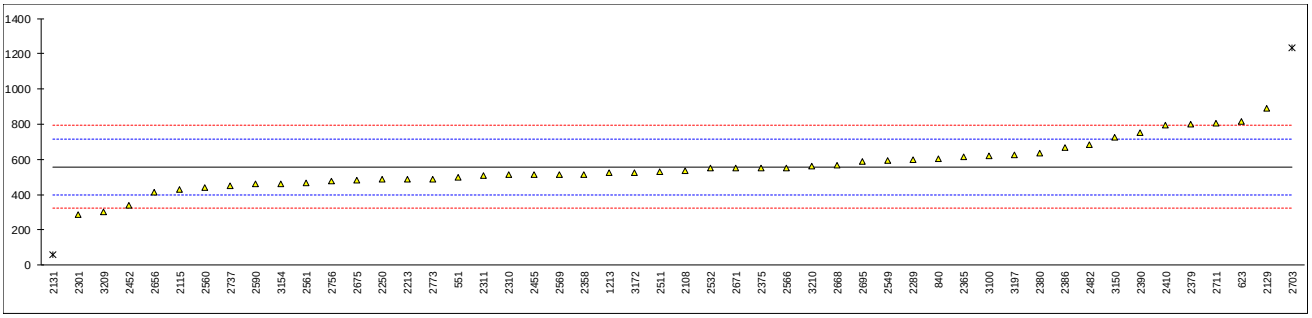
6 CONCLUSION

Although, it can be concluded that the majority of the participants has some problems with the determination of OPP in the sample of 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 Orthophenylphenol (OPP) on sample #18551; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	In house	499.4007		-0.75	
623	In house	816.99		3.27	
840	ISO13365	601.8		0.55	
841		-----		-----	
1213	ISO13365	524.34		-0.43	
2108	ISO13365	537		-0.27	
2115	ISO13365	429.405		-1.63	
2129	ISO17070	890		4.20	
2131	In house	59.995	R(0.05)	-6.31	
2213	ISO17070	490		-0.87	
2250	ISO17070	490		-0.87	
2289	ISO17070	600.5		0.53	
2301	In house	287.05		-3.43	
2310	In house	513		-0.57	
2311	ISO17070	510.96		-0.60	
2350		-----		-----	
2358	ISO13365	516.3		-0.53	
2365	ISO13365	613.2		0.69	
2375	ISO13365	552		-0.08	
2379	ISO17070	798.793		3.04	
2380	In house	633.16		0.95	
2386	In house	665.53		1.36	
2390	In house	751.750		2.45	
2410	ISO17070	793		2.97	
2452		338.0658		-2.79	
2455		514.0		-0.56	
2482	ISO13365	684.4		1.60	
2492		-----		-----	
2511	ISO17070	530.899		-0.35	
2532	ISO13365	550.23		-0.10	
2549	ISO13365	595.4		0.47	
2560		440.501		-1.49	
2561	ISO13365	466.97		-1.16	
2566	In house	552.4		-0.08	
2569	ISO13365	515		-0.55	
2590	ISO13365	459.95		-1.25	
2656	ISO13365	411.4		-1.86	
2668	ISO13365	564.81		0.08	
2671		550.6		-0.10	
2675	ISO13365	484.74		-0.93	
2695	ISO13365	586.27		0.35	
2703	In house	1235.2	R(0.01)	8.57	
2711		807.01		3.15	
2737	ISO13365	451.19		-1.36	
2756	ISO13365	478.8		-1.01	
2773	ISO17070	490		-0.87	
3100	ISO13365	618.28		0.76	
3146		-----		-----	
3150	ISO13365	725.0	C	2.11	First reported 1747
3154	ISO13365	461.23		-1.23	
3163		-----		-----	
3172	ISO13365	526.735		-0.40	
3197	ISO13365	622.7		0.81	
3209	In house	301.442		-3.25	
3210	ISO13365	559.07		0.01	
					Only ISO13365
	normality	OK			OK
	n	48			25
	outliers	2			0
	mean (n)	558.36			541.45
	st.dev. (n)	129.504			78.162
	R(calc.)	362.61			218.85
	st.dev.(iis, see lit 18)	79.001			76.963
	R(iis, see lit 18)	221.20			215.50
Compare					
	R(Horwitz)	96.55			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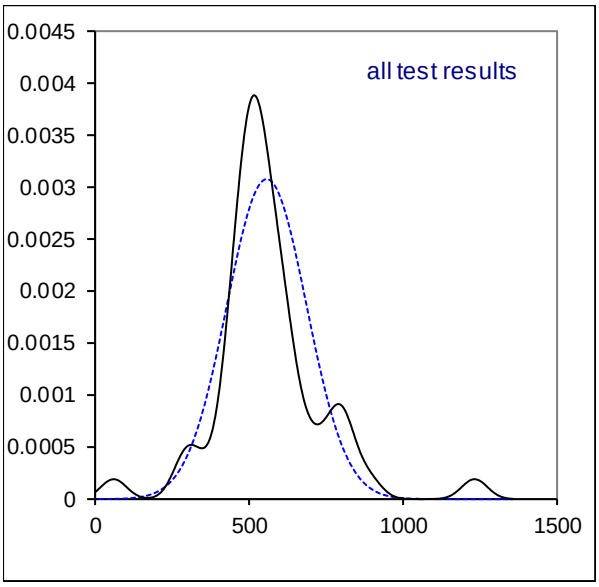
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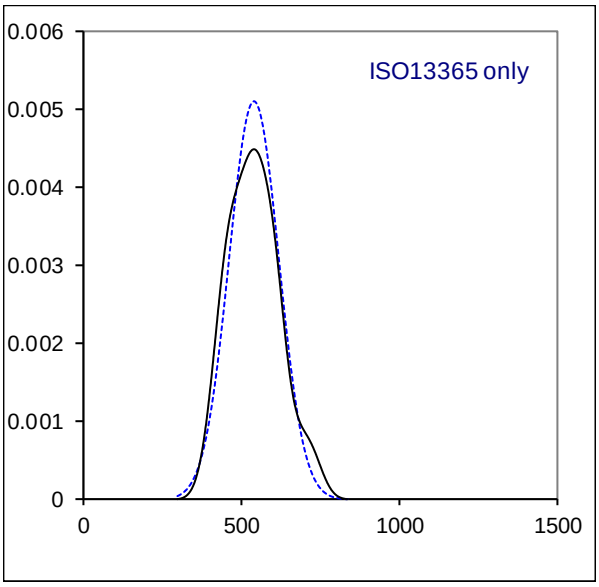
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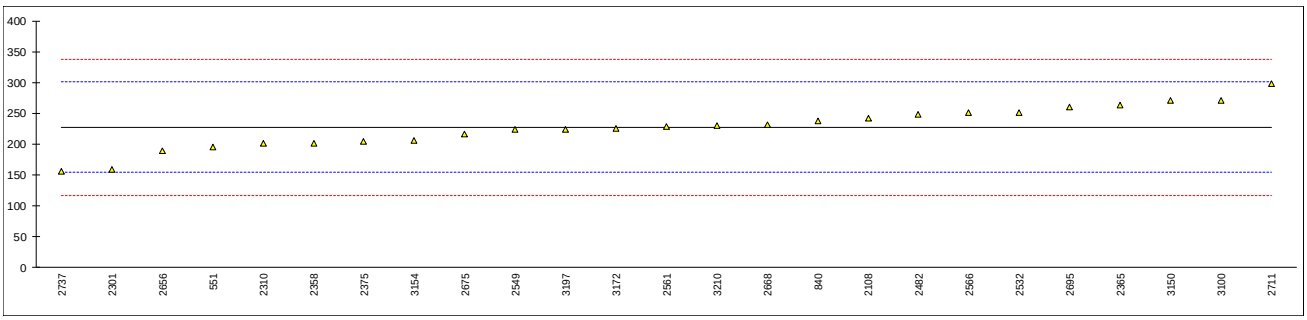
500
1000
1500

Determination of 4-chloro-3-methylphenol (PCMC) on sample #18551; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	In house	194.7663		-0.89	
623		-----		-----	
840	ISO13365	238.2		0.29	
841		-----		-----	
1213	ISO13365	NA		-----	
2108	ISO13365	242		0.39	
2115		-----		-----	
2129		-----		-----	
2131		-----		-----	
2213	ISO17070	<10		<-5.91	False negative test result?
2250		-----		-----	
2289		-----		-----	
2301	In house	158.24		-1.88	
2310	In house	201		-0.72	
2311		-----		-----	
2350		-----		-----	
2358	ISO13365	201.6		-0.70	
2365	ISO13365	263.9		0.99	
2375	ISO13365	205		-0.61	
2379		-----		-----	
2380		-----		-----	
2386		-----		-----	
2390		-----		-----	
2410		-----		-----	
2452		-----		-----	
2455		-----		-----	
2482	ISO13365	248.3		0.56	
2492		-----		-----	
2511		-----		-----	
2532	ISO13365	251.37		0.65	
2549	ISO13365	223.2		-0.12	
2560		-----		-----	
2561	ISO13365	228.27		0.02	
2566	In house	251		0.64	
2569		-----		-----	
2590		-----		-----	
2656	ISO13365	189.4		-1.03	
2668	ISO13365	231.27		0.10	
2671		-----		-----	
2675	ISO13365	216.54		-0.30	
2695	ISO13365	260.82		0.90	
2703		-----		-----	
2711		298.68		1.93	
2737	ISO13365	155.87		-1.94	
2756		-----		-----	
2773		-----		-----	
3100	ISO13365	271.53		1.20	
3146		-----		-----	
3150	ISO13365	271.2	C	1.19	First reported 563.7
3154	ISO13365	205.35		-0.60	
3163		-----		-----	
3172	ISO13365	224.730		-0.08	
3197	ISO13365	224.4		-0.08	
3209		-----		-----	
3210	ISO13365	230.7		0.09	

	normality	OK
	n	25
	outliers	0
	mean (n)	227.49
	st.dev. (n)	34.297
	R(calc.)	96.03
	st.dev.(iis, see lit 18)	36.828
	R(iis, see lit 18)	103.12
Compare		
	R(Horwitz)	45.03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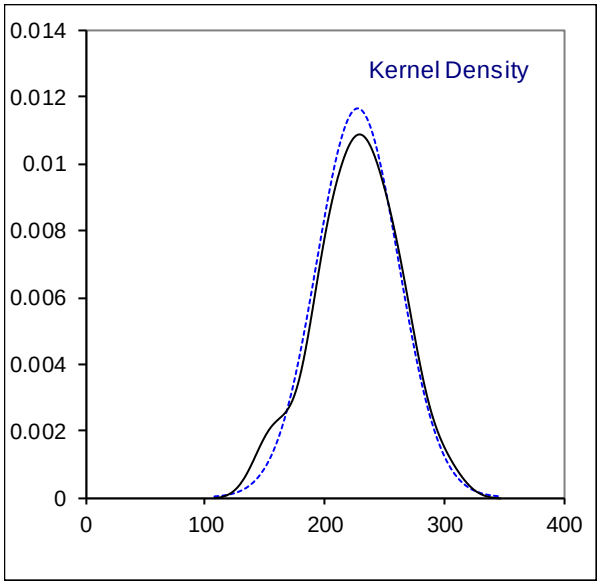
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200
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Determination of 2-(thiocyanomethylthio)-benzothiazole (TCMTB) and 2-octylisothiazol-3(2H)-one (OIT) on sample #18551; results in mg/kg

lab	method	TCMTB	OIT	remarks
551		-----	-----	
623		-----	-----	
840	ISO13365	not detected	not detected	
841		-----	-----	
1213	ISO13365	NA	NA	
2108		-----	-----	
2115		-----	-----	
2129		-----	-----	
2131		-----	-----	
2213	ISO17070	<10	<10	
2250		-----	-----	
2289		-----	-----	
2301		-----	-----	
2310	In house	Not Detected	Not Detected	
2311		-----	-----	
2350		-----	-----	
2358	ISO13365	<10	<10	
2365	ISO13365	<1.0	<1.0	
2375		-----	-----	
2379		-----	-----	
2380		-----	-----	
2386		-----	-----	
2390		-----	-----	
2410		-----	-----	
2452		-----	-----	
2455		-----	-----	
2482		-----	-----	
2492		-----	-----	
2511		-----	-----	
2532	ISO13365	Not Detected	Not Detected	
2549	ISO13365	ND	ND	
2560		-----	-----	
2561	ISO13365	<2.0	<2.0	
2566		-----	-----	
2569		-----	-----	
2590		-----	-----	
2656	ISO13365	<1	<1	
2668	ISO13365	Not Detected	Not Detected	
2671		-----	-----	
2675	ISO13365	0	0	
2695	ISO13365	< 10	< 10	
2703		-----	-----	
2711		0	0	
2737		-----	-----	
2756		-----	-----	
2773		-----	-----	
3100	ISO13365	less than 10	less than 10	
3146		-----	-----	
3150	ISO13365	422.5	422.5	
3154		-----	-----	
3163		-----	-----	
3172		-----	-----	
3197	ISO13365	ND	ND	
3209		-----	-----	
3210	ISO13365	<40	<40	

APPENDIX 2 Details of the test methods used by the participants

lab	testmethod	ISO17025 accr.?	Sample intake (g)	Release technique used	Solvent used to release analyte?	Extraction time (min)	Extraction temperature (°C)	Technique for quantification
551	In house	---		---				
623	In house	Yes	1	Ultrasonic extraction	KOH	60 min ultrasonic extraction + 15h oven	room temperature + 90°C (oven)	GC-MS
840	ISO13365	Yes	1	Ultrasonic extraction	ACN	60	Room temperature	HPLC-DAD
841		---		---				
1213	ISO13365	Yes	1.5	Ultrasonic extraction	Acetonitrile	60	< 35 oC	LCUV - Hitachi
2108	ISO13365	Yes	ca. 1	Ultrasonic extraction	Acetonitrile	60	Room Temperature	HPLC-DAD
2115	ISO13365	No	0.5	Ultrasonic extraction	Acetonitrile	60	25 °C	HPLC-UV
2129	ISO17070	Yes	1	Soxhlet / AES extraction	Aceton /acetic acid	6	100	
2131	In house	---		---				
2213	ISO17070	Yes	0.5	Other	Hexane	60n	room temperature	GC-ECD/ GC-MS
2250	ISO17070	Yes	0,5	Ultrasonic extraction	n-hexane	30	40	GC-MS
2289	ISO17070	Yes	1.0	Steam distillation	water	60		GC-MS
2301	In house	Yes	1	Ultrasonic extraction	Acetone		40	GCMS
2310	In house	No	1	Ultrasonic extraction	Acetonitrile	1 hr	30°C	LC-MS.
2311	ISO17070	Yes	1	Incubation in Oven	1M KOH	900 min	90 °C	GC-MS
2350		---		---				
2358	ISO13365	No	1.0	Ultrasonic extraction	ACN	60	Room Temp.	LC/DAD
2365	ISO13365	Yes	0.5	Ultrasonic extraction	Acetonitrile	60	At room temperature	LC-MS
2375	ISO13365	No	1	Ultrasonic extraction	Acetonitrile	60	25 C	LC-MS
2379	ISO17070	No	0.5	Ultrasonic extraction	KOH		70 DEGREE	GC/MS
2380	In house	Yes	0.5054	Ultrasonic extraction	n-Hexan	60	Room Temperature	
2386	In house	Yes	0,2	Ultrasonic extraction	KOH	60 min ultrasonic extraction + 15h oven	room temperature + 90°C (oven)	GC-MS
2390	In house	Yes	0.5	Ultrasonic extraction	ACN	60	60 C	LCMS
2410	ISO17070	Yes		Steam distillation	Hexane	15.	NA	Internal calibration
2452		No	0.95	Ultrasonic extraction	Hexane	120	ambiant	GC/MS
2455		---		---				
2482	ISO13365	Yes	0,5	Ultrasonic extraction	CH3CN	60	room temperature	HPLC DAD
2492		---		---				
2511	ISO17070	Yes		---				
2532	ISO13365	No	1	Ultrasonic extraction	Acetonitrile	1hour	Room Temperature	HPLC
2549	ISO13365	Yes	0.5	Ultrasonic extraction	Acetonitrile	60	30	UPLC
2560		Yes	0.950	KOH extraction	1M KOH Solution	15 hours	90	GC-MS
2561	ISO13365	Yes	1.04	Ultrasonic extraction	Acetronitrile	60	20	HPLC
2566	In house	Yes	0.5092	Ultrasonic extraction	ACETONE	30	40	GCMS
2569	ISO13365	Yes	1	Ultrasonic extraction	ACN	1 Hr	Room Temperature	HPLC
2590	ISO13365	No	0.5	Ultrasonic extraction	acetonitrile	60	35°C	LCMS
2656	ISO13365	No	1	Ultrasonic extraction	Acetonitrile	60	From 25°C (start) to 40°C (end of extraction)	HPLC-DAD
2668	ISO13365	Yes	0.5	Ultrasonic extraction	Acetonitrile	60	30°C	UPLC DAD
2671		No		Ultrasonic extraction	Acetone	30	40	GC MS
2675	ISO13365	Yes	1,0017	Ultrasonic extraction	Acetonitrile	60	at the beginning 22 °C, five minutes later 35 °C until the end	LC-PDA
2695	ISO13365	No	1	Ultrasonic extraction	Acetonitrile	1 hour	ambient temperature	HPLC-MS
2703	In house	Yes	1.01	---				

lab	testmethod	ISO17025 accr.?	Sample intake (g)	Release technique used	Solvent used to release analyte?	Extraction time (min)	Extraction temperature (°C)	Technique for quantification
2711		No	1.968	Reflux	Methanol	60	65	HPLC/DAD
2737	ISO13365	Yes	0.5	Ultrasonic extraction	acetonitrile	60	room temp	HPLC-DAD
2756	ISO13365	No	1	Ultrasonic extraction	ACETONITRILE	60	Room temperature	HPLC
2773	ISO17070	Yes		Steam distillation				
3100	ISO13365	Yes	1	Ultrasonic extraction	acetonitrile	60	Room temperature	HPLC-DAD
3146		---		---				
3150	ISO13365	No	0,5	Ultrasonic extraction	acetonitrile	60	room temperature	
3154	ISO13365	Yes		Ultrasonic extraction				
3163		---		---				
3172	ISO13365	Yes	0.5	Ultrasonic extraction	ACN	60	25	LC-DAD
3197	ISO13365	Yes	1	Ultrasonic extraction	ACN	60	Room temperature	HPLC-DAD
3209	In house	---		---				
3210	ISO13365	Yes	0.5	Ultrasonic extraction	Acetonitrile	60	room temperature	UPLC/DAD

APPENDIX 3

Number of participants per country

2 labs in BANGLADESH

1 lab in BRAZIL

5 labs in CHINA, P.R. of

1 lab in ETHIOPIA

2 labs in FRANCE

9 labs in GERMANY

2 labs in HONG KONG

10 labs in INDIA

2 labs in INDONESIA

5 labs in ITALY

1 lab in NETHERLANDS

1 lab in PAKISTAN

2 labs in SOUTH KOREA

1 lab in SWITZERLAND

1 lab in THAILAND

2 labs in TUNISIA

2 labs in TURKEY

1 lab in U.S.A.

2 labs in UNITED KINGDOM

3 labs 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) = utlier 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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