Results of Proficiency Test
Phosphorus Flame Retardants, total
in Polymers
February 2021

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Organophosphate esters (OPs) are widely used as flame retardants in various consumer and industrial products, such as plastics, electronic equipment, furniture, textiles and building materials. However, production and use has been in decline since the 1980s, when Tris(2-chloro-ethyl) phosphate (TCEP) has been progressively replaced by other flame retardants. TCEP was comprehensively evaluated under the EU existing substances regulation (EEC) 793/93 in 2009. TCEP is classified under Regulation (EC) No 1272/2008 as a carcinogenic, mutagenic and toxic substance. Furthermore, the limits have been set under Regulation 2014/79/EU for TCEP, TCPP and TDCP (5 mg/kg).

Since 2014 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of total Phosphorus Flame Retardants in Polymers every year. During the annual proficiency testing program 2020/2021 it was decided to continue the proficiency test of Phosphorus Flame Retardants, total in Polymers.
In this interlaboratory study 39 laboratories in 18 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 this 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 two polymer samples both positive on Phosphorus Flame retardants of 3 grams each and labelled #21500 and #21501 respectively.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

For the first sample a batch of red PVC blocks which was made positive for Tris(2-chloroethyl) Phosphate (TCEP, CAS No. 115-96-8), Tris(1-chloro-2-propyl) Phosphate (TCPP, CAS No. 13674-84-5) and Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP, CAS No. 13674-87-8) was selected. After homogenization 60 plastic bags were filled with approximately 3 grams each and labelled #21500.
The batch for sample #21500 was used in a previous proficiency test on Phosphorus Flame Retardants in Polymers (as sample #17500 in iis17P01). Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of pink PVC rings which was made positive for Triisobutyl Phosphate (TiBP, CAS No. 126-71-6), Tricresyl Phosphate (TCP, CAS No. 1330-78-5) and Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP, CAS No. 13674-87-8) was selected. After homogenization 60 plastic bags were filled with approximately 3 grams each and labelled #21501.
The homogeneity of the subsamples was checked by determination of TiBP, TCP and TDCPP by an in-house test method on 10 stratified randomly selected subsamples.

	TiBP in mg/kg	TCP in mg/kg	TDCPP in mg/kg
Sample #21501-1	418	252	712
Sample #21501-2	399	226	677
Sample #21501-3	408	242	695
Sample #21501-4	415	246	683
Sample #21501-5	421	250	702
Sample #21501-6	416	251	705
Sample #21501-7	395	239	661
Sample #21501-8	407	249	721
Sample #21501-9	401	237	683
Sample #21501-10	393	233	663

Table 1: homogeneity test results of subsamples #21501

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

	TiBP in mg/kg	TCP in mg/kg	TDCPP in mg/kg
r (observed)	28	24	57
reference method	iis memo 2102	iis memo 2102	iis memo 2102
0.3 x R (reference method)	51	31	87

Table 2: evaluation of the repeatabilities of subsamples #21501

The calculated repeatabilities were in agreement with 0.3 times the corresponding reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample labelled #21500 and one sample labelled #21501 were sent on January 13, 2021.

2.5 ANALYZES

The participants were requested to determine:
TBEP – Tris(2-butoxyethyl) Phosphate, CAS No. 78-51-3
TBP – Tributyl Phosphate, CAS No. 126-73-8
TiBP – Triisobutyl Phosphate, CAS No. 126-71-6
TCP – Tricresyl Phosphate, CAS No. 1330-78-5
TCEP – Tris(2-chloroethyl) Phosphate, CAS No. 115-96-8
TCPP – Tris(1-chloro-2-propyl) Phosphate, CAS No. 13674-84-5
TDCPP – Tris(1,3-dichloro-2-propyl) Phosphate, CAS No. 13674-87-8
TPP – Triphenyl Phosphate, CAS No. 115-86-6
IPTPP – Isopropylated triphenyl Phosphate, CAS No. 68937-41-7

It was also requested to report if the laboratory was accredited for the requested components and to report some analytical details.
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 test results, but report as much significant figures as possible. It was also requested not to report ‘less than’ test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 and 2 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results (no reanalyzes). Additional or corrected test results are used for data analysis and the original test 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 was the one as described for proficiency testing in the report ‘iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of June 2018 (iis-protocol, version 3.5).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as ‘<…’ or ‘>…’ were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

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

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve (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, e.g. ISO reproducibilities, 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 literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were 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. Therefore, the usual interpretation of z-scores is as follows:

	|z|	< 1	good
1 <	|z|	< 2	satisfactory
2 <	|z|	< 3	questionable
3 <	|z|		unsatisfactory

4 EVALUATION

During the execution of this proficiency test some problems occurred with the dispatch of the samples due to the COVID-10 pandemic. Therefore, the reporting time on the data entry portal was extended with another week. Three participants did not report any test results and four other participants reported the test results after the extended final reporting date. Not all laboratories were able to report all components requested. In total 36 laboratories reported 174 numerical test results. Observed were 16 outlying test results, which is 9.2%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

Not all 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 SAMPLE AND PER COMPONENT

In this section the reported test results are discussed per sample and 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.

Unfortunately, no standard test method is available for the determination of Phosphorus Flame Retardants (e.g. TCEP, TDCPP, TCPP, TPP) in polymers. Most participating laboratories reported to use an in-house method. This consists of a preparation/extraction step and an analytical step. Some participants reported to have used ISO17881-2, which is a method for textiles.
Method EN71-11 describes the analytical determination of TCEP after migration/extraction. Regretfully in EN71-11:05 only the standard deviation for the repeatability of TCEP is mentioned and no reproducibility requirements of (other) Phosphorus Flame Retardants. Until now the precision statement for TCEP mentioned in EN71-11 was used for other Phosphorus Flame Retardants as well, but the requirements were never met.
The PT for the determination of Phosphorus Flame Retardants in polymers is organized by iis for several years now, which means that the group results can be compared. It appears that the estimated reproducibility from EN71-11 may be (too) strict. Therefore, it was decided to use the iis PT data gathered since 2014 to estimate a more realistic target reproducibility. This estimated target reproducibility was calculated from the relative standard deviation of 15% (lit. 19, iis memo 2102) multiplied by 2.8. This was used for the evaluation of the test results in this PT.

Sample #21500

TCEP: This determination was not problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility as derived from iis memo 2102.

TCPP: This determination was problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the target reproducibility as derived from iis memo 2102.

TDCPP: This determination was problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the target reproducibility as derived from iis memo 2102.

Other components: The majority of the participants agreed on a content near or below the quantification limit of all other requested Phosphorus Flame Retardants. Therefore, no z-scores are calculated. The test results are given in appendix 2.

Sample #21501

TiBP: This determination may be problematic for a number of laboratories. No statistical outliers were observed. The calculated reproducibility is in agreement with the target reproducibility as derived from iis memo 2102. See for more discussion paragraph 5.

TCP: This determination was problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the target reproducibility as derived from iis memo 2102. See for more discussion paragraph 5.

TDCPP: This determination may be problematic for a number of laboratories. Six statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility as derived from iis memo 2102.

Other components: The majority of the participants agreed on a content near or below the quantification limit of all other requested Phosphorus Flame Retardants. Therefore, no z-scores are calculated. The test results are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the target reproducibility as derived from iis memo 2102 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 as derived from iis memo 2102 are presented in the next tables.

Component	unit	n	average	2.8 * sd	R(target)
TCEP	mg/kg	32	177	55	74
TCPP	mg/kg	35	139	72	58
TDCPP	mg/kg	33	114	55	48

Table 3: reproducibilities of components in sample #21500

Component	unit	n	average	2.8 * sd	R(target)
TiBP	mg/kg	9	362	115	152
TCP	mg/kg	19	241	145	101
TDCPP	mg/kg	30	522	187	219

Table 4: reproducibilities of components in sample #21501

Without further statistical calculations, it can be concluded that for the observed Phosphorus Flame Retardants the group of participating laboratories have problems with the analysis of in polymers at these concentration levels. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2021 AGAINST PREVIOUS PTS

	February 2021	February 2020	February 2019	February 2018	February 2017
Number of reporting laboratories	36	35	29	44	40
Number of test results	174	169	92	158	239
Number of statistical outliers	16	16	6	18	18
Percentage of statistical outliers	9.2%	9.5%	6.5%	11.4%	7.5%

Table 5: comparison with previous proficiency tests

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

The performance of the determinations of the proficiency test was compared, expressed as relative standard deviation (RSD) of the PTs, see below table.

Component	February 2021	February 2020	February 2019	February 2018	2017 -2014	iis memo 2102
TBP	n.e.	11%	n.e.	n.e.	n.e.	15%
TiBP	11%	n.e.	n.e.	n.e.	n.e.	15%
TCP	21%	16%	12%	n.e.	n.e.	15%
TCEP	11%	11%	15%	17%	9-23%	15%
TCPP	18%	18%	n.e.	19%	13-15%	15%
TDCPP	13-17%	11%	19%	10%	13-15%	15%
TPP	n.e.	n.e.	17%	14%	n.e.	15%

Table 6: development of the uncertainties over the years

The uncertainties observed in this PT are in general comparable to the uncertainties observed in previous PTs. The uncertainty of TCP is large in comparison with the target reproducibility as derived from iis memo 2102.

Sample #21500 was used before in Proficiency Test iis17P01 as sample #17500. It is observed that the average concentrations of sample #21500 is in line with the previous PT, see next table.

Component	unit	#21500			#17500		
		n	average	R(calc)	n	average	R(calc)
TCEP	mg/kg	32	177	55	35	187	69
TCPP	mg/kg	35	139	72	37	158	68
TDCPP	mg/kg	33	114	55	36	124	51

Table 7: comparison of sample #21500 with sample #17500

4.4 EVALUATION ANALYTICAL DETAILS

The reported analytical details from the participants are listed in appendix 3.
About 75% of the reporting participants mentioned to be accredited for determination of Phosphorus Flame Retardants in polymer.
Prior to analysis the samples were further cut or grinded by about 80% of the reporting participants, about 20% used the samples as received. The amount of sample intake varied between 0.2 and 1 grams, about 80% used 0.5 to 1 grams.
All reporting laboratories reported to have used ultrasonic as technique to release/extract the analytes. About 30% used Toluene (mixture) as release solvent, about 25% used a combination of Hexane with Ethyl Acetate and about 20% used Acrylonitrile, THF or a combination of Acrylonitrile with THF.
A vast majority (about 90%) of the reporting laboratories used an extraction time of 60 minutes. The extraction temperature differs between room temperature and 70 °C. About 55% used an extraction temperature between 40 and 50 °C, about 40% used an extraction temperature between 60 and 70 °C.
When the analytical details where investigated separately, it appeared that the effect of the determination of Phosphorus Flame Retardants is negligible.

5 DISCUSSION

Sample #21501 was made positive for Tri-p-Cresyl Phosphate (TpCP). This is the para-isomer of Tricresyl Phosphate (TCP). TCP is in the list of reported components with CAS No. 1330-78-5 for the mixture of isomers.
Some participants reported (in the comments) of sample #21501 test results of Tri-o-Cresyl Phosphate (ToCP) with CAS No. 78-30-8. These test results were not taken into account for the evaluation of TCP as sample #21501 was not made positive for this isomer.

For the first time a sample positive on TiBP was used in the Phosphorus Flame Retardants PT. Only a third of the participants reported a numeric value as test result for TiBP, other participants reported a content near or below the quantification limit or didn’t detect this component at all.

The material of both samples in this PT (sample #21500 and sample #21501) was PVC. To extract the requested components (components mentioned in paragraph 2.5) from a polymer the extraction solvent, the extraction conditions and the extraction surface area are important. However, this effect is less demonstrated in this PT.

6 CONCLUSION

In the PT of 2021 most of the laboratories identified all added Phosphorus Flame Retardants correctly: sample #21500 contained TCEP, TCPP and TDCPP and sample #21501 contained TiBP, TCP and TDCPP.

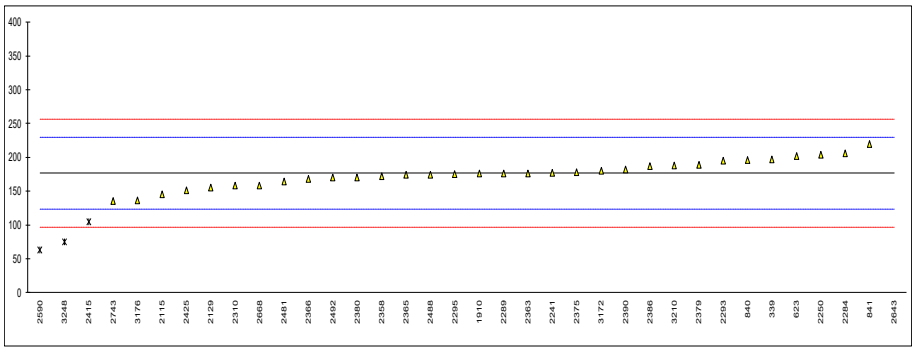
However, each laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

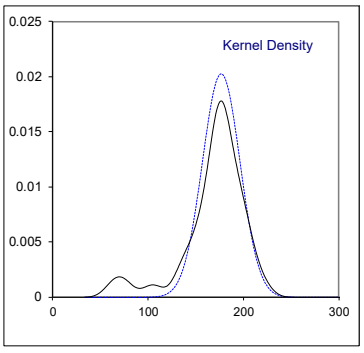
APPENDIX 1

Determination of Tris(2-chloroethyl) Phosphate (TCEP) CAS no.115-96-8 in sample #21500; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	IEC62321-6Mod.	197.09		0.77	
623	In house	201.96		0.96	
840	In house	196		0.73	
841	In house	219.7		1.63	
1910	In house	176.2510	C	-0.01	first reported 101.7314
2115	In house	145.4		-1.18	
2129	ISO17881-2	155.6		-0.79	
2241	In house	177.79		0.04	
2250	In house	204.5		1.05	
2284	ISO17881-2	206.29		1.12	
2289	ISO17881-2	177		0.01	
2293	ISO17881-2	195.48		0.71	
2295	ISO17881-2	176		-0.02	
2310	ISO17881-2	158.3		-0.69	
2320		-----		-----	
2358	In house	172.54		-0.15	
2363	In house	177		0.01	
2365	In house	174.8		-0.07	
2366	In house	169		-0.29	
2372		-----		-----	
2375	ISO17881-2	178		0.05	
2379	EPA3550B	189.8648		0.50	
2380	In house	170.95		-0.21	
2386	In house	187.3		0.40	
2390	In house	182.43	C	0.22	first reported 240.60
2415	ISO17881-2	104.71	R(0.05)	-2.71	
2425	In house	152.1		-0.93	
2481	In house	165		-0.44	
2488	EN71-11	175		-0.06	
2492	In house	170.41		-0.23	
2590	ISO17881-2	63.878	C,R(0.01)	-4.26	first reported 86.324
2643	In house	569	C,R(0.01)	14.81	first reported 258
2668	In house	159.09		-0.66	
2743	ISO17881-2	135.378321		-1.56	
3163		-----		-----	
3172	ISO17881-2	180.45	C	0.15	first reported <5
3176	ISO17881-2	136.48		-1.51	
3210	In house	188.29		0.44	
3248		75.5	C,R(0.01)	-3.82	first reported 22.5

normality	OK	
n	32	
outliers	4	
mean (n)	176.608	
st.dev. (n)	19.7102	RSD = 11%
R(calc.)	55.189	
st.dev.(iis memo 2102)	26.4911	
R(iis memo 2102)	74.175	
compare		
R(EN71-11:05)	38.571	

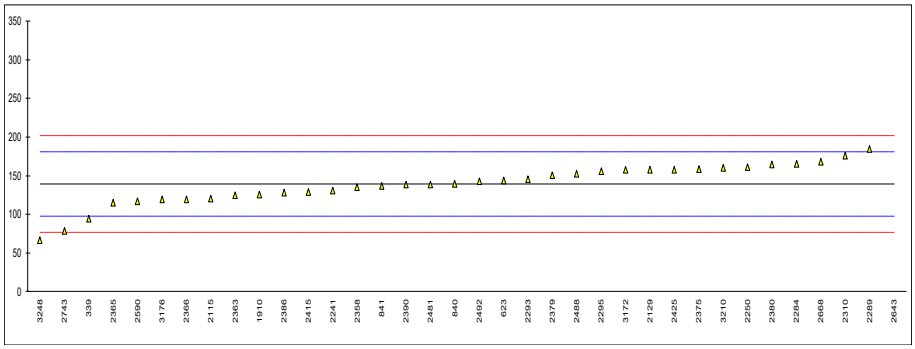


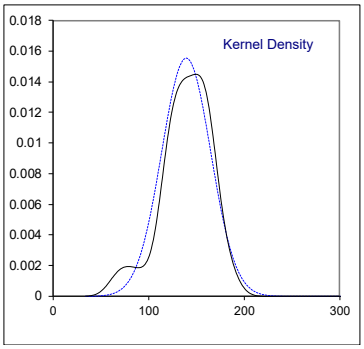


Determination of Tris(1-chloro-2-propyl) Phosphate (TCPP) CAS no. 13674-84-5 in sample #21500; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	IEC62321-6Mod.	94.46		-2.14	
623	In house	143.97		0.23	
840	In house	140		0.04	
841	In house	137.5		-0.08	
1910	In house	125.6608	C	-0.65	first reported 82.5245
2115	In house	120.7		-0.89	
2129	ISO17881-2	158.0		0.90	
2241	In house	131.35		-0.38	
2250	In house	161		1.04	
2284	ISO17881-2	166.10		1.29	
2289	ISO17881-2	185		2.19	
2293	ISO17881-2	145.98		0.32	
2295	ISO17881-2	156		0.80	
2310	ISO17881-2	176		1.76	
2320		-----		-----	
2358	In house	135.70		-0.17	
2363	In house	125		-0.68	
2365	In house	115.6		-1.13	
2366	In house	120		-0.92	
2372		-----		-----	
2375	ISO17881-2	159		0.95	
2379	EPA3550B	151.1129		0.57	
2380	In house	165.11		1.24	
2386	In house	128.7		-0.50	
2390	In house	138.5	C	-0.03	first reported 204.60
2415	ISO17881-2	129.36		-0.47	
2425	In house	158.2		0.91	
2481	In house	139		-0.01	
2488	EN71-11	152.7		0.65	
2492	In house	143.27		0.19	
2590	ISO17881-2	117.373		-1.05	
2643	In house	541	C,R(0.01)	19.24	first reported 234
2668	In house	168.38		1.40	
2743	ISO17881-2	79.301640		-2.87	
3163		-----		-----	
3172	ISO17881-2	157.50	C	0.88	first reported <5
3176	ISO17881-2	119.42		-0.95	
3210	In house	160.78		1.03	
3248		67.0	C	-3.46	first reported 19

	normality	suspect
	n	35
	outliers	1
	mean (n)	139.221
	st.dev. (n)	25.6561 RSD = 18%
	R(calc.)	71.837
	st.dev.(iis memo 2102)	20.8831
	R(iis memo 2102)	58.473
	compare	
	R(EN71-11:05)	30.406

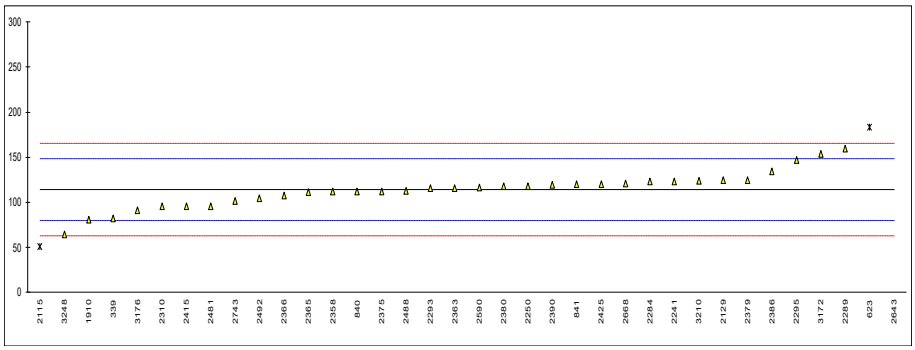


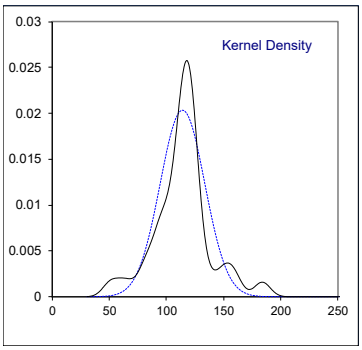


Determination of Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP) CAS no.13674-87-8 in sample #21500; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	IEC62321-6Mod.	82.41		-1.85	
623	In house	183.96	C,R(0.05)	4.08	first reported 167.97
840	In house	112		-0.12	
841	In house	120.5		0.37	
1910	In house	81.2530	C	-1.92	first reported 54.902
2115	In house	51.42	R(0.05)	-3.66	
2129	ISO17881-2	124.8		0.62	
2241	In house	123.37		0.54	
2250	In house	118.5		0.26	
2284	ISO17881-2	123.32		0.54	
2289	ISO17881-2	160		2.68	
2293	ISO17881-2	115.91		0.11	
2295	ISO17881-2	147		1.92	
2310	ISO17881-2	95.78		-1.07	
2320		-----		-----	
2358	In house	111.93		-0.13	
2363	In house	116		0.11	
2365	In house	111.8		-0.13	
2366	In house	108		-0.36	
2372		-----		-----	
2375	ISO17881-2	112		-0.12	
2379	EPA3550B	124.8363		0.63	
2380	In house	117.91		0.22	
2386	In house	134.7		1.20	
2390	In house	120	C	0.34	first reported 324.90
2415	ISO17881-2	95.83		-1.07	
2425	In house	120.5		0.37	
2481	In house	96		-1.06	
2488	EN71-11	113		-0.06	
2492	In house	104.70		-0.55	
2590	ISO17881-2	116.744	C	0.15	first reported 188.770
2643	In house	402	C,R(0.01)	16.82	first reported 168
2668	In house	121.13		0.41	
2743	ISO17881-2	101.562304		-0.73	
3163		-----		-----	
3172	ISO17881-2	154.08	C	2.34	first reported 583.04
3176	ISO17881-2	91.50		-1.32	
3210	In house	123.83		0.57	
3248		64.6	C	-2.89	first reported 8

normality	suspect	
n	33	
outliers	3	
mean (n)	114.106	
st.dev. (n)	19.5778	RSD = 17%
R(calc.)	54.818	
st.dev.(iis memo 2102)	17.1159	
R(iis memo 2102)	47.924	
compare		
R(EN71-11:05)	24.921	



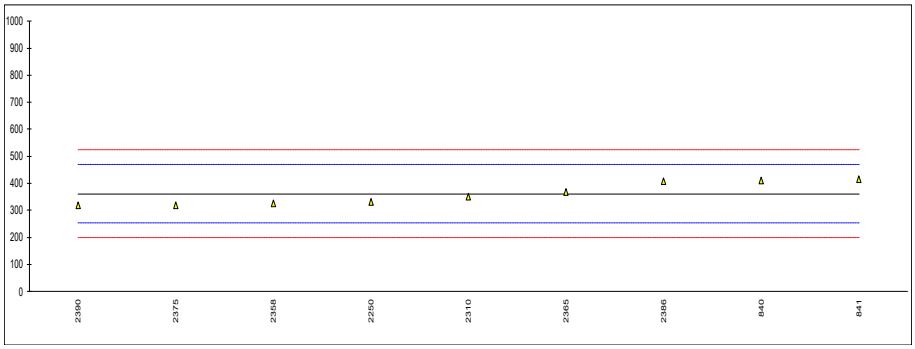


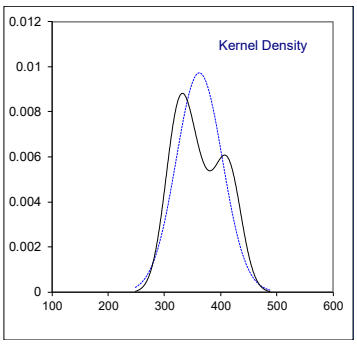
Determination of Triisobutyl Phosphate (TiBP) CAS no. 126-71-6 in sample #21501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	not detected		-----	possibly a false negative test result?
840	In house	412		0.93	
841	In house	415.8		1.00	
1910		-----		-----	
2115		-----		-----	
2129	ISO17881-2	n.d.		-----	
2241	In house	<5		<-6.57	possibly a false negative test result?
2250	In house	332.06		-0.55	
2284	ISO17881-2	NA		-----	
2289	ISO17881-2	<5		<-6.57	possibly a false negative test result?
2293	In house	Not Analyzed		-----	
2295		-----		-----	
2310	ISO17881-2	351.6		-0.19	
2320		-----		-----	
2358	In house	326.51		-0.65	
2363	In house	NA		-----	
2365	In house	369.1		0.14	
2366	In house	out capability		-----	
2372		-----		-----	
2375	ISO17881-2	320		-0.77	
2379	EPA3550B	Not tested		-----	
2380		-----		-----	
2386	In house	408.6		0.87	
2390	In house	319.25	C	-0.78	first reported 418.50
2415	ISO17881-2	not detected		-----	possibly a false negative test result?
2425		-----		-----	
2481		-----		-----	
2488		-----		-----	
2492		-----		-----	
2590		-----		-----	
2643		-----		-----	
2668	In house	Not Detected		-----	possibly a false negative test result?
2743		-----		-----	
3163		-----		-----	
3172		-----		-----	
3176		-----		-----	
3210		-----		-----	
3248		-----		-----	

normality	OK
n	9
outliers	0
mean (n)	361.658
st.dev. (n)	41.0351
R(calc.)	114.898
st.dev.(iis memo 2102)	54.2487
R(iis memo 2102)	151.896
compare	
R(EN71-11:05)	78.986

RSD = 11%

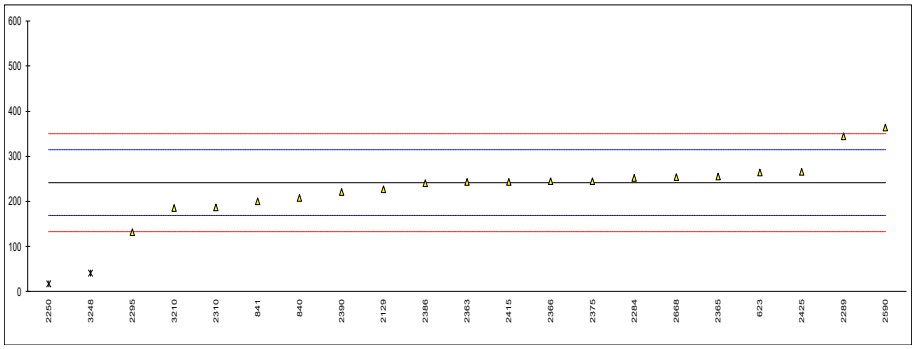


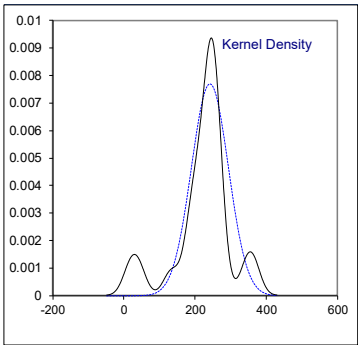


Determination of Tricresyl Phosphate (TCP) CAS no.1330-78-5 in sample #21501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	264.58	C	0.64	first reported not detected
840	In house	208		-0.92	
841	In house	201.2		-1.11	
1910		-----		-----	
2115		-----		-----	mentioned in comments ToCP = 96.42 mg/kg
2129	ISO17881-2	228.3		-0.36	
2241	In house	<5		<-6.53	possibly a false negative test result?
2250	In house	17.6	C,R(0.05)	-6.18	first reported 19.93
2284	ISO17881-2	253.20		0.32	
2289	ISO17881-2	345		2.86	
2293	In house	Not Analyzed		-----	
2295	ISO17881-2	133		-2.99	
2310	ISO17881-2	188		-1.48	
2320		-----		-----	
2358	In house	N/A		-----	
2363	In house	244		0.07	
2365	In house	255.1		0.38	
2366	In house	245		0.10	
2372		-----		-----	
2375	ISO17881-2	245		0.10	
2379	EPA3550B	Not tested		-----	
2380		-----		-----	
2386	In house	240.5		-0.03	
2390	In house	221.7		-0.54	
2415	ISO17881-2	244.60		0.09	
2425	In house	266.1		0.68	
2481		-----		-----	
2488		-----		-----	
2492		-----		-----	mentioned in comments ToCP CAS no. 78-30-8 = 88 mg/kg
2590		363.971		3.38	
2643		-----		-----	
2668	In house	253.66		0.34	
2743		-----		-----	
3163		-----		-----	
3172		-----	C	-----	fr<5; reported ToCP = ToCP CAS no. 78-30-8 = 137.75 mg/kg
3176		-----		-----	
3210	In house	186.39		-1.52	
3248		42	C,R(0.05)	-5.51	first reported 22.5

normality	suspect	
n	19	
outliers	2	
mean (n)	241.437	
st.dev. (n)	51.8247	RSD = 21%
R(calc.)	145.109	
st.dev.(iis memo 2102)	36.2155	
R(iis memo 2102)	101.404	
compare		
R(EN71-11:05)	52.730	

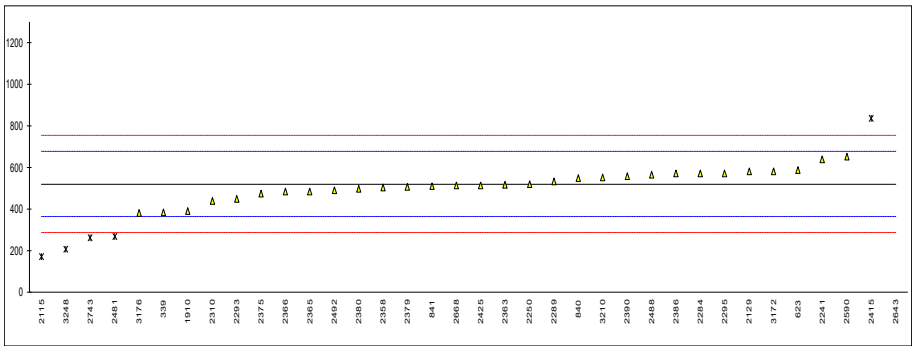


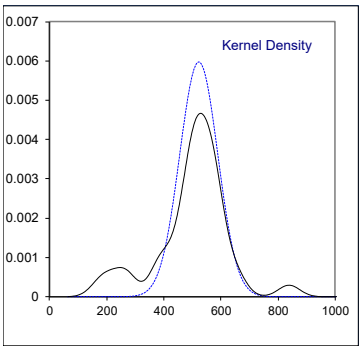


Determination of Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP) CAS no.13674-87-8 in sample #21501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	IEC62321-6Mod.	387.25		-1.72	
623	In house	589.06		0.86	
840	In house	550		0.36	
841	In house	513.550		-0.10	
1910	In house	393.420		-1.64	
2115	In house	175.4	R(0.05)	-4.42	
2129	ISO17881-2	581.8		0.77	
2241	In house	641.5		1.53	
2250	In house	522.5		0.01	
2284	ISO17881-2	573.51		0.66	
2289	ISO17881-2	536		0.18	
2293	In house	451.69		-0.89	
2295	ISO17881-2	575		0.68	
2310	ISO17881-2	443		-1.00	
2320		-----		-----	
2358	In house	505.56		-0.20	
2363	In house	520		-0.02	
2365	In house	487.7		-0.43	
2366	In house	485		-0.47	
2372		-----		-----	
2375	ISO17881-2	478		-0.56	
2379	EPA3550B	507.8833		-0.17	
2380	In house	500.16		-0.27	
2386	In house	573.4		0.66	
2390	In house	560.3	C	0.50	first reported 1123.95
2415	ISO17881-2	838.08	R(0.05)	4.05	
2425	In house	515.0		-0.08	
2481		269	R(0.05)	-3.23	
2488	EN71-11	567.7	C	0.59	first reported 927
2492	In house	494.55		-0.35	
2590		655.529		1.71	
2643	In house	1814	C,R(0.01)	16.52	first reported 789
2668	In house	514.80		-0.09	
2743	ISO17881-2	262.657576	R(0.05)	-3.31	
3163		-----		-----	
3172		583.04	C	0.79	first reported 154.08
3176	In house	383.70		-1.76	
3210	In house	555.68		0.44	
3248		209	C,R(0.05)	-4.00	first reported 107

normality	OK
n	30
outliers	6
mean (n)	521.543
st.dev. (n)	66.7049 RSD = 13%
R(calc.)	186.774
st.dev.(iis memo 2102)	78.2314
R(iis memo 2102)	219.048
compare	
R(EN71-11:05)	113.905





APPENDIX 2 Determination of other Phosphorus Flame Retardants; results in mg/kg

TBEP = Tris(2-butoxyethyl) Phosphate, CAS No. 78-51-3
TBP = Tributyl Phosphate, CAS No. 126-73-8
TiBP = Triisobutyl Phosphate, CAS No. 126-71-6
TCP = Tricresyl Phosphate, CAS No. 1330-78-5
TCEP = Tris(2-chloroethyl) Phosphate, CAS No. 115-96-8
TCPP = Tris(1-chloro-2-propyl) Phosphate, CAS No. 13674-84-5
TDCPP = Tris(1,3-dichloro-2-propyl) Phosphate, CAS No. 13674-87-8
TPP = Triphenyl Phosphate, CAS No. 115-86-6
IPTPP = Isopropylated triphenyl Phosphate, CAS No. 68937-41-7

Sample #21500

lab	TBEP	TBP	TiBP	TCP	TPP	IPTPP
339	-----	-----	-----	-----	4.34	-----
623	not detected	not detected	not detected	not detected	3.80	not detected
840	not detected	not detected	not detected	not detected	not detected	-----
841	<5	<5	<5	<5	<5	<5
1910	-----	-----	-----	-----	-----	-----
2115	-----	-----	-----	-----	-----	-----
2129	n.d.	n.d.	n.d.	<5	<5	n.d.
2241	<5	<5	<5	<5	<5	<5
2250	-----	-----	5.97	-----	-----	-----
2284	NA	NA	NA	ND<5	ND<5	NA
2289	<5	<5	<5	<5	<5	<5
2293	Not Analyzed	Not Analyzed	Not Analyzed	Not Analyzed	Not detected	Not Analyzed
2295	-----	-----	-----	-----	-----	-----
2310	Not Detected	Not Detected	4.0	Not Detected	Not Detected	Not Detected
2320	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	N/A	n.d.	N/A
2363	<5	<5	NA	<5	<5	<1
2365	<5	<5	<5	<5	<5	<5
2366	out capability	out capability	out capability	<5	<5	out capability
2372	-----	-----	-----	-----	-----	-----
2375	-----	-----	-----	-----	-----	-----
2379	Not tested	Not tested	Not tested	Not tested	Not detected	Not tested
2380	-----	-----	-----	-----	<10	-----
2386	<5	<5	3.3	<5	<5	-----
2390	-----	-----	-----	-----	-----	-----
2415	not detected	not detected	not detected	not detected	not detected	not detected
2425	-----	-----	-----	-----	-----	-----
2481	-----	-----	-----	-----	-----	-----
2488	-----	-----	-----	-----	-----	-----
2492	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----
2668	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2743	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----
3172	< 5	<5 C	-----	<5 C	-----	< 5
3176	-----	-----	-----	-----	-----	-----
3210	not detected	-----	-----	not detected	not detected	-----
3248	-----	-----	-----	-----	-----	-----

Lab 3172: first reported 124.17 and 137.75 (as ToCP) respectively

Determination of other Phosphorus Flame Retardants; results in mg/kg (continued)

Sample #21501

lab	TBEP	TBP	TCEP	TCPP	TPP	IPTPP
339	-----	-----	1.8	<1	1.2	-----
623	not detected	not detected	1.80	1.80	2.40	not detected
840	not detected	not detected	not detected	not detected	not detected	-----
841	<5	<5	<5	<5	<5	<5
1910	-----	-----	not detected	not detected	-----	-----
2115	-----	-----	-----	0.34	-----	-----
2129	n.d.	n.d.	<5	<5	<5	n.d.
2241	<5	<5	<5	<5	<5	<5
2250	-----	-----	-----	-----	-----	-----
2284	NA	NA	ND<5	ND<5	ND<5	NA
2289	<5	<5	<5	<5	<5	<5
2293	Not Analyzed	Not Analyzed	Not detected	Not detected	Not detected	Not Analyzed
2295	-----	122	-----	-----	-----	-----
2310	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2320	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	N/A
2363	<5	<5	<5	<5	<5	<1
2365	<5	<5	<5	<5	<5	<5
2366	out capability	out capability	<5	<5	<5	out capability
2372	-----	-----	-----	-----	-----	-----
2375	-----	-----	-----	-----	-----	-----
2379	Not tested	Not tested	Not detected	Not detected	Not detected	Not tested
2380	-----	-----	<5	<10	<10	-----
2386	<5	<5	<5	<5	<5	-----
2390	-----	-----	-----	----- C	-----	-----
2415	not detected	not detected	not detected	not detected	not detected	not detected
2425	-----	-----	-----	-----	-----	-----
2481	-----	-----	not detected	not detected	-----	-----
2488	-----	-----	-----	-----	-----	-----
2492	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----
2668	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2743	-----	-----	-----	0.193730	-----	-----
3163	-----	-----	-----	-----	-----	-----
3172	< 5	124.17 C	<5 C	<5 C	-----	< 5
3176	-----	-----	-----	-----	-----	-----
3210	not detected	-----	not detected	not detected	not detected	-----
3248	-----	-----	-----	-----	-----	-----

Lab 2390: first reported 257.07
Lab 3172: first reported <5, 180.45 and 157.50 respectively

APPENDIX 3 Analytical details

lab	ISO17025 accredited	sample grinded or cut	intake (g)	release/extract technique	release solvent	extraction time (min)	extraction temp (°C)
339	No	Used as received	1	Ultrasonic	Toluene	60	60
623	Yes	Further cut	0.5	Ultrasonic	Ethyl acetate : n Hexane (1:1)	60	50
840	Yes	Further cut	0.5	Ultrasonic	ethyl acetate : n-hexane (1:1)	60	50
841	Yes	Further cut	1	Ultrasonic	ethylacetate + n-hexane	60	60
1910	No	Further cut	0,5	Ultrasonic	acetonitrile	60	40
2115	No	Used as received	0.3	Ultrasonic	Acetone	60	40
2129	Yes	Used as received	0.5	Ultrasonic	Toluene	60	60
2241	Yes	Further cut	0.5	Ultrasonic	dichloromethane	60	room temp.
2250	Yes	Further cut	0,2	Ultrasonic	Aceton and THF/Methanol	30	40
2284	Yes	Further cut	0.5	Ultrasonic	THT extraction and ACN precipititation	60	40
2289	Yes	Further cut	1	Ultrasonic	acetone	1h	40
2293	Yes	Further cut	0.2	Ultrasonic	Tetrahydrofuran, Acetonitrile and Water	30	70
2295	No	Further cut	1	Ultrasonic	40 ml acetone	60	40
2310	Yes	Further cut	1	Ultrasonic	Ethyl acetate and Hexane (1:1)	60	50
2320	---	---		---			
2358	Yes	Further cut	0.5	Ultrasonic	Ethyl acetate: Hexane (1:1)	60	50
2363	No	Further cut	0.5	Ultrasonic	toluene	60	60
2365	Yes	Further cut	0.3	Ultrasonic	Toluene	60	60
2366	No	Further cut	0.3	Ultrasonic	toluene	60	60
2372	---	---		---			
2375	Yes	Further cut	0,5	Ultrasonic	Toluene	60	60
2379	No	Further cut	0.5	Ultrasonic	EA : Hexane (1 : 1)	60	50
2380	Yes	Further cut	0.3	Ultrasonic	Toluene	60	60
2386	Yes	Further cut	1	Ultrasonic	Ethylacete / n-Hexan 1:1	60	50
2390	Yes	Further cut	1	Ultrasonic	ethyl acetate and n-hexane (1:1)	60	50
2415	Yes	Further cut	0.5	Ultrasonic	Acetone / Acetonitrile	60	40
2425	Yes	Further cut	0.5	Ultrasonic	THF : ACN	1 hour	70
2481	No	Further grinded	0.25	Ultrasonic	toluene	60-70 min	60
2488	Yes	---		---			
2492	Yes	Used as received	0.5	Ultrasonic	acetone	40+20 min	40
2590	Yes	Used as received	0.5	Ultrasonic	Acetone and toluene	40+20 min	40
2643	Yes	Further cut	0.5	Ultrasonic	Toluene	60	40
2668	Yes	Further cut	0.5	Ultrasonic	THF : ACN	60	70
2743	Yes	Used as received	0.77	Ultrasonic	Acetone	60min total (40+20min)	40
3163	---	---		---			
3172	---	---		---			
3176	Yes	Further cut	0,5	Ultrasonic	#21500: Aceton #21501: Methanol	60	40
3210	No	Further cut	0.5	Ultrasonic	Toluene	60	60
3248	Yes	Further cut	0.5	Ultrasonic	methanol	30	room temp.

APPENDIX 4

Number of participants per country

2 labs in BANGLADESH
3 labs in FRANCE
3 labs in GERMANY
1 lab in GUATEMALA
3 labs in HONG KONG
2 labs in INDIA
1 lab in INDONESIA
4 labs in ITALY
6 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in POLAND
1 lab in SOUTH KOREA
1 lab in SRI LANKA
1 lab in TAIWAN
1 lab in THAILAND
1 lab in THE NETHERLANDS
4 labs in TURKEY
3 labs in VIETNAM

APPENDIX 5

Abbreviations

C	= final test result after checking of first reported suspect test result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported

Literature

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
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