Results of Proficiency Test Phosphorus Flame retardants in Polymers February 2019

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

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 from 21 December 2015).

Since 2014, the Institute for Interlaboratory Studies organizes a proficiency scheme for the determination of Phosphorus Flame Retardants in polymers every year. During the annual proficiency testing program 2018/2019, it was decided to continue the PT for the analysis of Phosphorus Flame retardants. In this interlaboratory study, 30 laboratories from 17 different countries registered for participation. See appendix 4 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 this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send two polymer samples (3 grams each), both positive on Phosphorus Flame retardants and labelled #19500 and #19501 respectively. 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/IEC 17043:2010 (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 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

The batch of green colored PVC squares for sample #19500 was obtained from a third party laboratory. This batch was positive on TCEP and TDCPP and were divided over 60 plastic bags, approximately 3 grams each. The homogeneity of subsamples #19500 was checked using an in-house method on eight stratified randomly selected samples.

	TDCPP in mg/kg
Sample #19500-1	301
Sample #19500-2	295
Sample #19500-3	293
Sample #19500-4	277
Sample #19500-5	290
Sample #19500-6	291
Sample #19500-7	290
Sample #19500-8	283

Table 1: homogeneity test results of subsamples #19500

From the above test results the repeatability was calculated and compared with the repeatability of the reference test method in agreement with the procedure of ISO 13528, Annex B2 in the next table.

	TDCPP in mg/kg
r (observed)	20.5
reference test method	EN71-11:05
r (ref. test method)	21.1

Table 2: evaluation of the repeatability of subsamples #19500

The calculated repeatability was in agreement with the estimated repeatability from the reference test method EN71-11. Therefore, homogeneity of the subsamples was assumed.

The batch of lilac colored PVC rings for sample #19501 was obtained from a third party laboratory. This batch was positive on TCP and TPP and were divided over 60 bags of approximately 3 grams each. The homogeneity of subsamples #19501 was checked using an in-house method on eight stratified randomly selected samples.

	TCP in mg/kg
Sample #19501-1	175
Sample #19501-2	167
Sample #19501-3	172
Sample #19501-4	171
Sample #19501-5	166
Sample #19501-6	167
Sample #19501-7	159
Sample #19501-8	166

Table 3: homogeneity test results of subsamples #19501

From the above test results, the repeatability was calculated and compared with the repeatability of the reference test method in agreement with the procedure of ISO 13528, Annex B2 in the next table.

	TCP in mg/kg
r (observed)	13.6
reference test method	EN71-11:05
r (ref. test method)	12.2

Table 4: evaluation of the repeatability of subsamples #19501

The calculated repeatability was in agreement with the estimated repeatability mentioned in the reference method EN71-11. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample labelled #19500 and one sample labelled #19501, 3 grams each, were sent on January 16, 2019.

2.5 ANALYSES

The participants were requested to determine the following components:

- Tris(2-butoxyethyl)phosphate (TBEP) (CAS No. 78-51-3)
- Tributylphosphate (TBP) (CAS No. 126-73-8)
- Tricresylphosphate (TCP) (CAS No. 1330-78-5)
- Tris(2-chloro-ethyl)phosphate (TCEP) (CAS No. 115-96-8)
- Tris(1-chloro-2-propyl)phosphate (TCPP) (CAS No. 13674-84-5)
- Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) (CAS No. 13674-87-8)
- Triphenylphosphate (TPP) (CAS No. 115-86-6)
- Isopropylated Triphenylphosphate (IPTPP) (CAS No. 68937-41-7)

Also, it was requested to report some method 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 to report as much significant figures as possible. It was also requested not 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 were 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.iisn.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 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 reanalysis). Additional or corrected test results are used for data analysis and original test results are placed under 'Remarks' in the test 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 Organization, 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 dataset 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 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' 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 these 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 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 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 of 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. 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. 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 no problems occurred with the dispatch of the samples. One participant did not report any test result and the other participants reported the test results before the final reporting date. Not all laboratories were able to report all components requested. In total 29 laboratories reported 92 numerical test results. Observed were 6 outlying test results, which is 6.5%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

All original data sets proved to have a normal gaussian distribution.

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 reported to use by the laboratories were taken into account for explaining the observed differences when possible and applicable. These methods are also in the table together with the original data. The abbreviations, used in these tables, are listed in appendix 4.

Unfortunately, no standard test method is available for the determination of Phosphorus Flame retardants (e.g. TCEP, TDCPP, TCPP, TPP) in polymer. Most participating laboratories reported to use an in-house method. This consist of a preparation/extraction step and an analytical step. Some participants performed ISO17881-2, which is method for textiles. Method EN71-11 describes the analytical determination of TCEP after migration/extraction and has a precision statement for TCEP. Therefore, EN71-11 is used as reference test method (for the analytical determination). It would also be possible to use the estimated reproducibility calculated with the Horwitz equation. However, it was decided

to use the precision statement for TCEP in EN71-11 also as reference test method for the other components: TDCPP, TCP and TPP.
Regretfully in EN71-11:2005, no reproducibility requirements for TCEP are mentioned, but only the standard deviation for the repeatability. The target reproducibility is estimated as follows: the standard deviation was multiplied with 2.8 to get the target repeatability. This was multiplied with 3 to get an estimate of the target reproducibility.

Sample #19500

TCEP: The determination of this component was very problematic at the measured level of 437 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier was not at all in agreement with the estimated target reproducibility of EN71-11:2005.

TDCPP: The determination of this component was very problematic at the measured level of 307 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier was not at all in agreement with the estimated target reproducibility of EN71-11:2005.

Other components: All participants agreed on a content close to or below the quantification limit of TBEP, TBP, TCP, TCPP, TPP and IPTPP.

Sample #19501

TCP: The determination of this component was problematic at the measured level of 228 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers was not in agreement with the estimated target reproducibility of EN71-11:2005.

TPP: The determination of this component was very problematic at the measured level of 845 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier was not at all in agreement with the estimated target reproducibility of EN71-11:2005.

Other components: Most of the participants agreed on a content close to or below the quantification limit of TBEP, TBP, TCEP, TCPP, TDCPP and IPTPP.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the calculated reproducibilities estimated from EN71-11:05 and the reproducibilities as found for the group of participating laboratories. The number of significant results, the average results, the calculated reproducibilities (2.8*standard deviation) and the target reproducibilities derived from literature reference test methods (in casu EN71-11) are presented in the next tables.

Component	unit	n	average	2.8 * sd	R (target)
TCEP	mg/kg	26	437	184	96
TDCPP	mg/kg	24	307	167	67

Table 5: reproducibilities of components in sample #19500

Component	unit	n	average	2.8 * sd	R (target)
TCP	mg/kg	12	228	80	50
TPP	mg/kg	24	845	400	185

Table 6: reproducibilities of components in sample #19501

Without further statistical calculations, it can be concluded that the group of participating laboratories have problems with the analysis of TCEP, TDCPP, TCP and TPP in polymer at these concentration levels. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2019 AGAINST PREVIOUS PTS

	February 2019	February 2018	February 2017	February 2016	February 2015
Number of reporting labs	29	44	40	31	33
Number of results reported	92	158	239	61	32
Number of statistical outliers	6	18	18	9	2
Percentage outliers	6.5%	11.4%	7.5%	14.8%	6.3%

Table 7: comparison with previous proficiency tests

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

The uncertainty in the test results of TDCPP and TPP in the iis19P01 PT did not improve compared to the previous PTs. However, the uncertainty of the test results of TCEP in iis19P01 PT did improve. TCP in the iis19P01 was determined for the first time. It is noticeable that the uncertainty was smaller than the uncertainty of TCEP, TDCPP and/or TPP.

Component	February 2019	February 2018	February 2017	February 2016	February 2015	February 2014	Est. EN71-11
TCP	12%	n.e.	n.e.	n.e.	n.e.	n.e.	8%
TCEP	15%	17%	13%	9%	12%	23%	8%
TCPP	n.e.	19%	13-15%	n.e.	n.e.	n.e.	8%
TDCPP	19%	10%	13-14%	15%	n.e.	n.e.	8%
TPP	17%	14%	n.e.	n.e.	n.e.	n.e.	8%

Table 8: development of relative uncertainties over the years

4.4 EVALUATION ANALYTICAL DETAILS

For this PT, some analytical details were requested (see appendix 3).
Of the reporting participants 54% mentioned that they are accredited for determination of P-flame retardants in polymer.
Twenty-one of the twenty-nine participants mentioned that they have cut/grinded the samples before use, seven other participants used the samples as received.
All participants, except two, reported to have used ultrasonic as technique to release/extract the analytes. One participant used Thermal Desorption as technique.
Eight participants used Toluene as extraction solvent, six used a combination of Acrylonitrile with THF and seven used a combination of Hexane with Ethyl Acetate. The other participants used solvent (mixtures) such as Hexane, MTBE and/or Acetone.
When evaluating the above differences in the execution of the test, no clear correlation was found between these test conditions and the reported test results.

5 DISCUSSION

The materials used in this PT were PVC squares and PVC rings. To extract the requested components from a polymer, the extraction solvent, the extraction conditions and the contact surface area could be important variables.
In previous proficiency tests on Phosphorus Flame retardants it appeared that the choice of the extraction solvent (see PT report iis14P01) and the grain size of the granulate (see PT report iis15P01) were important variables. This was mainly caused by the matrix of the samples used in these proficiency tests. In the PT of 2014 a foam block was used as sample and in PT of 2015 and 2018 a high density plastic was used as sample.
In the PTs of 2016, 2017 and 2018, PVC samples, a Polypropylene and a Polyester sample positive Phosphorus Flame Retardants were used. The observed large variation could unfortunately not be explained from the reported analytical details. It was noticeable that the uncertainties of the different Phosphorus Flame Retardants were similar.

In the PT of 2019 most of the laboratories identified all added Phosphorus Flame retardants correctly: sample #19500 contained TCEP and TDCPP and sample #19501 contained TCP and TPP.

Sample #19500 was also used in a previous PT; labelled as sample #16500 in iis16P01.

		Sample #19500			Sample #16500		
Component	unit	n	average	2.8 * sd	n	average	2.8 * sd
TCEP	mg/kg	26	437	184	26	479	117
TDCPP	mg/kg	24	307	167	26	325	139

Table 9: comparison sample #19500 vs #16500

During the PT iis16P01 the evaluation of TCEP and TDCPP in sample #16500 was problematic. Although the calculated reproducibility (2.8*standard deviation) was smaller than observed in this PT, the mean values were very comparable.

This PT has been organised for six years now, which means the group results can be compared. It appears that the estimated reproducibility from EN71-11 may be (too) strict when looking at the calculated reproducibilities of TCEP over the years, till 2015 (see table 8). The relative standard deviation varies from 9% to 17%, with an average of 13%, while the relative standard deviation from method EN71-11 is 8%. The second observation is that the other components tested show similar relative standard deviations, varying from 10% to 19%, with an average of 14%. From this, iis could decide to start using the calculated reproducibilities of the PTs over the years as target reproducibility rather than use the (more) strict EN71-11.

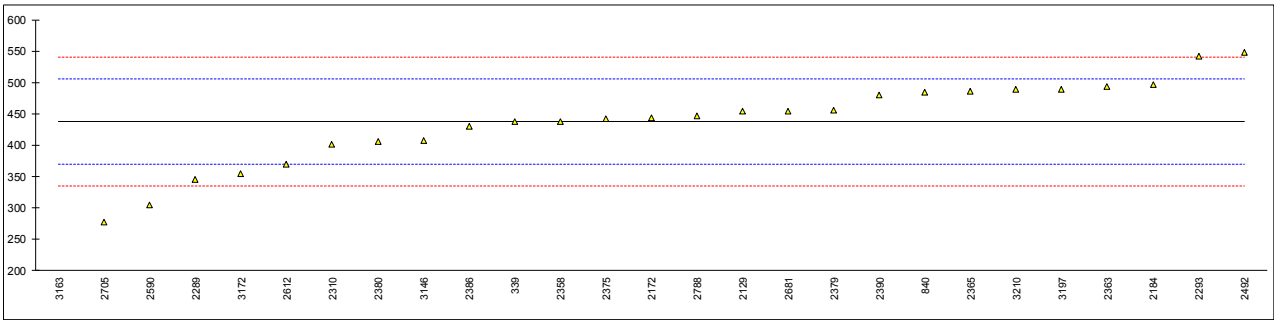
6 CONCLUSION

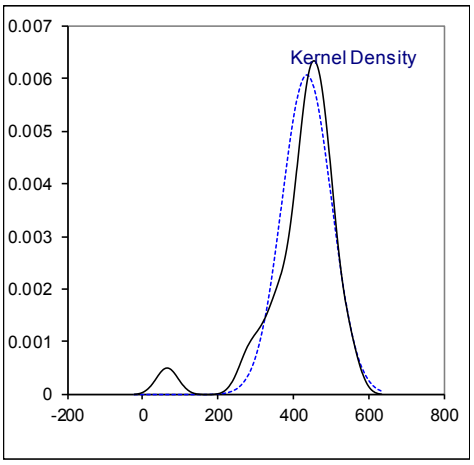
In this proficiency test the TCEP, TDCPP, TCP and TPP in polymers were identified correctly. The large variations observed in this interlaboratory study can be caused by the preparation or the conditioning of the sample and/or by the performance of the analysis by the participating laboratory. Consequently, the reproducibility cannot be improved by only one change in the analysis. Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. 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-chloro-ethyl)phosphate (TCEP) CAS no.115-96-8 in sample #19500; results in mg/kg

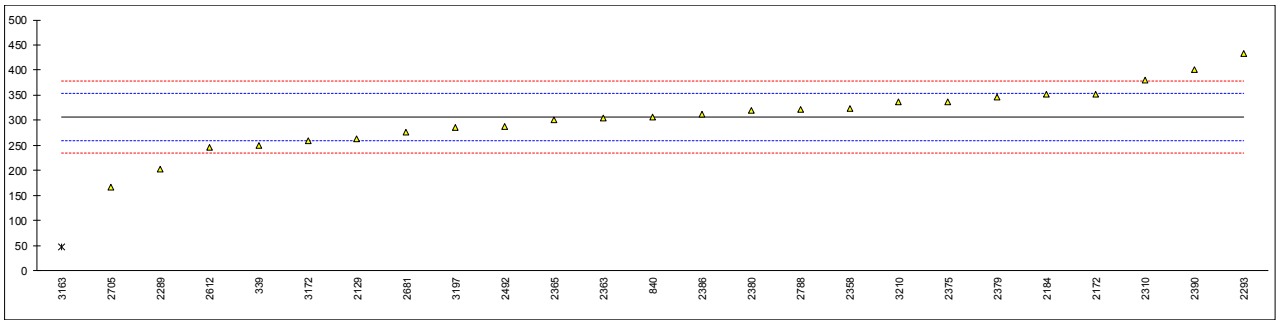
lab	method	value	mark	z(targ)	remarks
339	In house	437		-0.01	
840	In house	485		1.39	
1099		-----		-----	
2129	ISO17881-2	454		0.48	
2172	In house	443.24		0.17	
2184	In house	496.15		1.72	
2212	In house	<100		<-9.89	possible false negative test result
2289	ISO17881-2	346		-2.68	
2293	ISO17881-2	541.11		3.04	
2310	ISO17881-2	401.1		-1.07	
2330		-----		-----	
2358	In house	437.83		0.01	
2363	In house	494		1.66	
2365	In house	485.3		1.40	
2375	ISO17881-2	442		0.13	
2379	In house	455.4741		0.53	
2380	In house	405.87		-0.93	
2386	In house	429.998		-0.22	
2390	In house	480.42	C	1.26	first reported: 678.57
2492	In house	548.4		3.25	
2590	ISO17881-2	305.2	C	-3.88	first reported: 193.794
2612	In house	369.7		-1.99	
2681	EN71-11	454.37		0.50	
2705	In house	278.0	C	-4.67	first reported: 0.1
2788	In house	446		0.25	
3146	In house	406.9		-0.90	
3163	In house	66	R(0.01)	-10.89	
3172	In house	354		-2.45	
3197	ISO17881-2	489.2		1.52	
3210	In house	488.18		1.49	
	normality	OK			
	n	26			
	outliers	1			
	mean (n)	437.479			
	st.dev. (n)	65.8784	RSD = 15%		
	R(calc.)	184.460			
	st.dev.(EN71-11:05)	34.1233			Compare R(ISO17881-2:16) = 124.944
	R(EN71-11:05)	95.545			Compare R(Horwitz) = 78.475

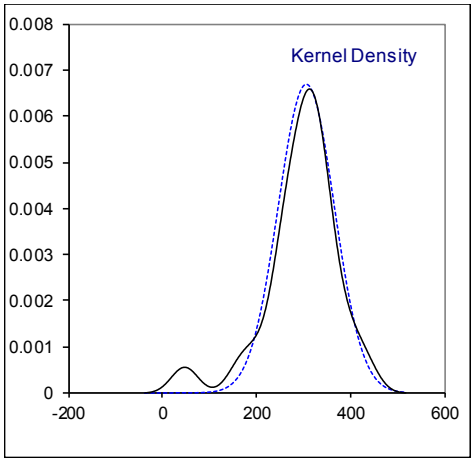




Determination of Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) CAS no.13674-87-8 in sample #19500; results in mg/kg

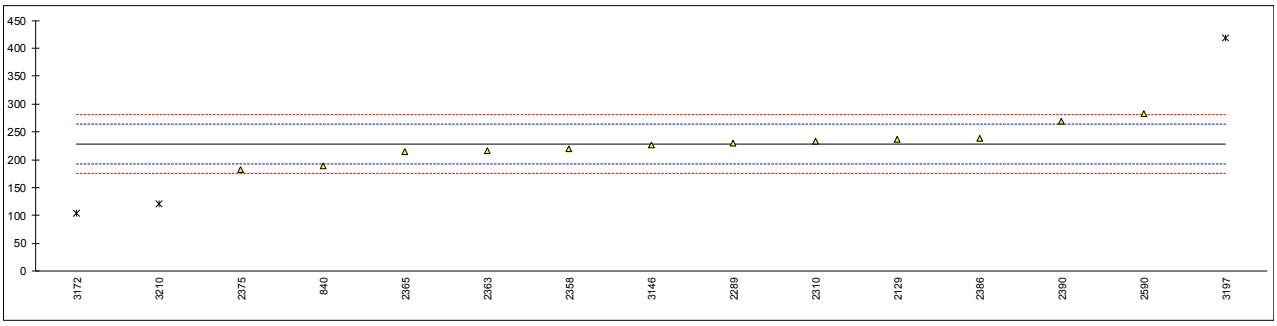
lab	method	value	mark	z(targ)	remarks
339	In house	250		-2.37	
840	In house	307		0.01	
1099		-----		-----	
2129	ISO17881-2	263		-1.83	
2172	In house	352.13		1.90	
2184	In house	351.92		1.89	
2212	In house	<100		<-8.64	possible false negative test result
2289	ISO17881-2	202		-4.38	
2293	ISO17881-2	433.41		5.30	
2310	ISO17881-2	380.2		3.07	
2330		-----		-----	
2358	In house	322.61		0.67	
2363	In house	304		-0.11	
2365	In house	301.1		-0.23	
2375	ISO17881-2	337		1.27	
2379	In house	346.6863		1.67	
2380	In house	318.72		0.50	
2386	In house	311.333		0.20	
2390	In house	400.79		3.94	
2492	In house	287.4		-0.81	
2590		-----		-----	
2612	In house	245.8		-2.54	
2681	EN71-11	275.68		-1.30	
2705	In house	166.3	C	-5.87	first reported: 0.1
2788	In house	321		0.60	
3146		-----		-----	
3163	In house	47	R(0.01)	-10.86	
3172	In house	259		-1.99	
3197	ISO17881-2	285.9		-0.87	
3210	In house	336.802		1.26	
	normality	OK			
	n	24			
	outliers	1			
	mean (n)	306.658			
	st.dev. (n)	59.7295	RSD = 19%		
	R(calc.)	167.243			
	st.dev.(EN71-11:05)	23.9193			Compare R(ISO17881-2:16) = 87.581
	R(EN71-11:05)	66.974			Compare R(Horwitz) = 58.030

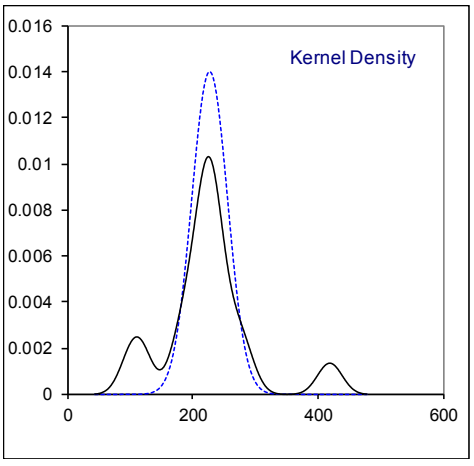




Determination of Tricresylphosphate (TCP) CAS no.1330-78-5 in sample #19501; results in mg/kg

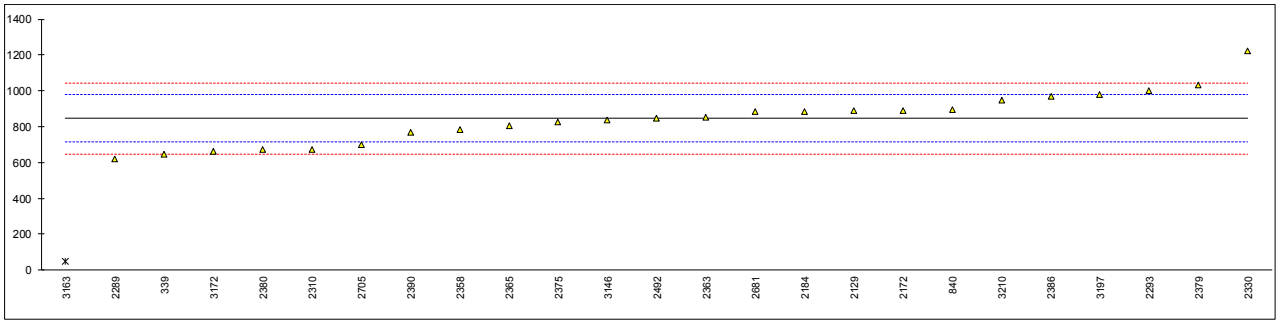
lab	method	value	mark	z(targ)	remarks
339		-----		-----	
840		189	C	-2.20	first reported: not detected
1099		-----		-----	
2129	ISO17881-2	237		0.50	
2172		-----		-----	
2184		-----	W	-----	first reported: n.d.
2212		-----		-----	
2289	ISO17881-2	229		0.05	
2293		-----		-----	
2310	ISO17881-2	234	C	0.33	first reported: not detected
2330		-----		-----	
2358	In house	219.286271	C	-0.50	first reported: n.d.
2363	In house	216		-0.68	
2365	In house	214.7		-0.75	
2375	ISO17881-2	182		-2.59	
2379		-----		-----	
2380		-----		-----	
2386	In house	239.192		0.62	
2390	In house	268.29		2.26	
2492		-----		-----	
2590	ISO17881-2	282.8	C	3.07	first reported: 513.024
2612	In house	< 5		<-12.54	possible false negative test result
2681		-----		-----	
2705		-----		-----	
2788		-----		-----	
3146	In house	226.3		-0.10	
3163		-----		-----	
3172	In house	104	C,DG(0.05)	-6.98	first reported: n.d.
3197	ISO17881-2	419.3	C,G(0.05)	10.74	first reported: 308.9
3210	In house	120.28	DG(0.05)	-6.06	
	normality	OK			
	n	12			
	outliers	3			
	mean (n)	228.131			
	st.dev. (n)	28.4543	RSD = 12%		
	R(calc.)	79.672			
	st.dev.(EN71-11:05)	17.7942			Compare R(ISO17881-2:16) = 65.154
	R(EN71-11:05)	49.824			Compare R(Horwitz) = 45.136

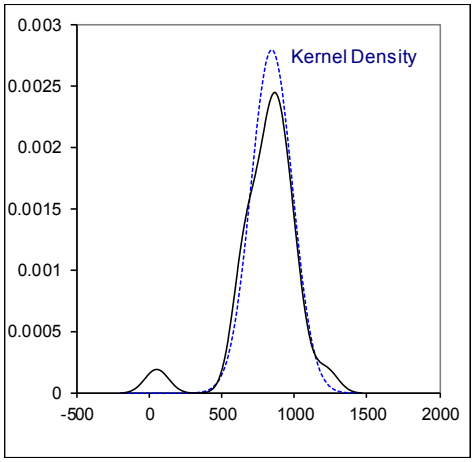




Determination of Triphenylphosphate (TPP) CAS no.115-86-6 in sample #19501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	646		-3.02	
840		895		0.76	
1099		-----		-----	
2129	ISO17881-2	887		0.63	
2172	In house	888.37		0.66	
2184	In house	886.36		0.63	
2212		-----		-----	
2289	ISO17881-2	622		-3.39	
2293	ISO17881-2	1000.875		2.36	
2310	ISO17881-2	674.2		-2.59	
2330	In house	1220.31		5.69	
2358	In house	782.47		-0.95	
2363	In house	850		0.07	
2365	In house	802.4		-0.65	
2375	ISO17881-2	824		-0.32	
2379	In house	1033.1053		2.85	
2380	In house	670.42		-2.65	
2386	In house	968.84		1.88	
2390	In house	767.43		-1.18	
2492	In house	849.2		0.06	
2590		-----		-----	
2612		-----		-----	
2681	EN71-11	885.92		0.62	
2705	In house	700.7	C	-2.19	first reported: 0.1
2788		-----		-----	
3146	In house	837.9		-0.11	
3163		50	G(0.01)	-12.06	
3172	In house	663		-2.76	
3197	ISO17881-2	981.4		2.07	
3210	In house	946.850		1.54	
	normality	OK			
	n	24			
	outliers	1			
	mean (n)	845.156			
	st.dev. (n)	142.8873	RSD = 17%		
	R(calc.)	400.084			
	st.dev.(EN71-11:05)	65.9222			Compare R(ISO17881-2:16) = 241.377
	R(EN71-11:05)	184.582			Compare R(Horwitz) = 137.299





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

Sample #19500

Lab	TBEP	TBP	TCP	TCPP	TPP	IPTPP
339	-----	-----	-----	<1	<1	-----
840	not detected	not detected	not detected	not detected	not detected	NA
1099	-----	-----	-----	-----	-----	-----
2129	-----	-----	<5	<5	<5	-----
2172	-----	-----	-----	-----	-----	-----
2184	n.d.	n.d.	----- W fr n.d.	n.d.	n.d.	n.d.
2212	-----	-----	-----	<100	-----	-----
2289	-----	<5	<5	<5	<5	-----
2293	-----	-----	-----	ND	< 10 ppm	-----
2310	-----	-----	NOT DETECTED	NOT DETECTED	NOT DETECTED	-----
2330	-----	-----	-----	-----	ND	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	ND	NA
2365	ND	ND	ND	ND	ND	ND
2375	-----	-----	-----	-----	-----	-----
2379	-----	-----	-----	Not detected	Not detected	-----
2380	-----	-----	-----	N.D.	N.D.	-----
2386	<5	<5	<5	<5	<5	-----
2390	-----	-----	-----	-----	-----	-----
2492	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2612	-----	-----	< 5	< 2	-----	-----
2681	-----	-----	-----	-----	-----	-----
2705	0.1	0.1 C fr 1.4	-----	0.2 C fr 0.1	0.1 C fr 700.7	-----
2788	-----	-----	-----	-----	-----	-----
3146	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----
3172	nd	nd	nd	nd	nd	nd
3197	NA	NA	<10	<10	<10	<10
3210	ND	-----	ND	-----	ND	-----

Sample #19501

Lab	TBEP	TBP	TCEP	TCPP	TDCPP	IPTPP
339	-----	-----	<0.1	<0.1	<0.1	-----
840	not detected	not detected	not detected	not detected	not detected	NA
1099	-----	-----	-----	-----	-----	-----
2129	-----	-----	<5	<5	<5	-----
2172	-----	-----	-----	-----	-----	-----
2184	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2212	-----	-----	<100	<100	<100	-----
2289	-----	<5	<5	<5	<5	-----
2293	-----	-----	ND	ND	ND	-----
2310	-----	-----	NOT DETECTED	NOT DETECTED	NOT DETECTED	-----
2330	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	ND	NA
2365	ND	ND	ND	ND	ND	ND
2375	-----	-----	-----	-----	-----	-----
2379	-----	-----	Not detected	Not detected	Not detected	-----
2380	-----	-----	N.D.	N.D.	N.D.	-----
2386	<5	<5	<5	<5	<5	-----
2390	-----	-----	-----	-----	-----	-----
2492	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2612	-----	-----	< 2	< 2	< 1	-----
2681	-----	-----	-----	-----	-----	-----
2705	0.1	1.4 C fr 0.1	0.1 C fr 278.0	0.1 C fr 0.2	0.1 C fr 166.3	-----
2788	-----	-----	0	-----	0	-----
3146	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----
3172	nd	nd	nd	nd	nd	nd
3197	NA	NA	<10	<10	<10	<10
3210	ND	-----	<5	-----	ND	-----

TBEP = Tris(2-butoxyethyl)phosphate CAS no.78-51-3
TBP = Tributylphosphate CAS no.126-73-8
TCP = Tricresylphosphate CAS no.1330-78-5
TCEP = Tris(2-chloro-ethyl)phosphate CAS no.115-96-8
TCPP = Tris(1-chloro-2-propyl)phosphate CAS no.13674-84-5
TPP = Triphenylphosphate CAS no.115-86-6
TDCPP = Tris(1,3-dichloro-2-propyl)phosphate CAS no.13674-87-8
IPTPP = Isopropylated Triphenylphosphate CAS no.68937-41-7

APPENDIX 3 Analytical details

Lab	ISO17025 accr.	Sample preparation	Final estimated particle size	Sample intake (in grams)
339	No	Used as received	#19500: 5x5mm, #19501: 3x15mm	1 g
840	-----	Further Cut	1X1mm	0.5g
1099	-----	-----	-----	
2129	Yes	Further Cut	3*3 mm	0,5 g
2172	Yes	Further Cut	less than 0.1mm*0.1mm	0.2g
2184	Yes	Used as received	-----	0.05 ~ 0.5
2212	No	Further Cut	2mm x 2mm	0.5 grams
2289	No	Further Grinded	<250um	1.0g
2293	Yes	Further Cut	2 mm x 2 mm	0.2 g
2310	No	Further Cut	-----	0.5 gram
2330	No	Further Cut	1mm x 1mm x 1mm	0.50g
2358	Yes	Used as received	5mm X 5mm	0.58 grams
2363	No	Further Cut	1mm*1mm	0.5g
2365	Yes	Further Cut	1mm*1mm	0.3g
2375	No	Further Cut	1mm x 1mm x 1mm	0,3 gr
2379	No	Further Cut	2x2 mm.	0.5 grams
2380	No	#19500 Used as received, #19501 Further cut.	2-3 mm x 2-3 mm	0.3
2386	Yes	Further Cut	2*2mm	0,5g
2390	No	Further Cut	The actual size is 2x2mm	#19500 0.5040g, #19501 0.5049g
2492	Yes	Used as received	-----	
2590	Yes	Further Cut	4mmx4mm	0.5g
2612	Yes	Further Cut	1 to 2 mm	0,5
2681	Yes	Further Cut	<3mm*3mm	0.5g
2705	No	Used as received		0.281
2788	No	Further Cut	3x3mm	.5
3146	No	Further Cut	2 * 2 mm	0,5
3163	No	Further Cut	0.0003g	0.0003g
3172	Yes	Further Cut	1mm	2
3197	Yes	Further Cut	2 mm x 2 mm	0.2
3210	No	Used as received	-----	0.25 gram

Lab	Technique to release/extract the analyte(s)	Solvent to release/extract the analyte(s)	Extraction time (min)	Extraction temp. (°C)
339	Ultrasonic	Toluene	60	60
840	Ultrasonic	hexan: ethylacetat(1:1)	1hour	50
1099	---	-----	-----	-----
2129	Ultrasonic	toluene	60 min	60 °C
2172	Ultrasonic	toluene	2 hours	70°C
2184	Ultrasonic	3 mix, Hexane:MTBE:Acetone = 1:1:1	180	60
2212	Ultrasonic	THF	30 mins	40 oC
2289	Ultrasonic	acetone	60	40
2293	Ultrasonic	THF and ACN	30 min. in THF 30 minutes in ACN	70°C
2310	Ultrasonic	Ethyl acetate & Hexane(1:1)	1 hr	50°C
2330	Ultrasonic	Toluene	60±5 min	60±2°C
2358	Ultrasonic	1:1 Ethyl acetate : n-hexane	60 minutes	50 degree C
2363	Ultrasonic	Tolune	60min	70
2365	Ultrasonic	Hexane£ºethyl acetate=1:1(v/v)	60min	50
2375	Ultrasonic	Toluene	60 mins	60 C
2379	Ultrasonic	Ethyl acetate : Hexane (1:1)	60 minutes	50 degree
2380	Ultrasonic	Toluene	60	60
2386	Ultrasonic	Ethylacetat/Hexan 1:1	60	50
2390	Ultrasonic	n-hexane+ Ethyl acetate	60 minute	50°C
2492	-----	-----	-----	-----
2590	Ultrasonic	Acetone	Double extraction 40 min + 20 min	40°C
2612	Ultrasonic	Acetonitrile	60 min	40 °C
2681	Ultrasonic	acetonitrile	60min	40
2705	ASE	Hexane/Aceton	15	160
2788	Ultrasonic	Toluene	180 mins	60
3146	Ultrasonic	Tetrahydrofurane : Acetonitrile 1:2	60	70
3163	Thermal Desorption	x	x	x
3172	Ultrasonic	Toluene	60	40
3197	Ultrasonic	THF/ACN	2 x 30 min	70
3210	Ultrasonic	THF/Acetonitrile	30 minutes	50 °C

APPENDIX 4

Number of participants per country

1 lab in BANGLADESH

1 lab in CAMBODIA

2 labs in FRANCE

4 labs in GERMANY

1 lab in GUATEMALA

4 labs in HONG KONG

1 lab in INDIA

2 labs in ITALY

1 lab in LUXEMBOURG

5 labs in P.R. of CHINA

1 lab in PAKISTAN

1 lab in POLAND

1 lab in THAILAND

1 lab in THE NETHERLANDS

2 labs in TURKEY

1 lab in U.S.A.

1 lab in VIETNAM

APPENDIX 5

Abbreviations:

C = final test result after checking of first reported suspect test result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner's outlier test
R(0.05) = straggler in Rosner's outlier test
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

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