

Results of Proficiency Test
Phosphorus Flame retardants
in Polymers
February 2018

Organised by: Institute for Interlaboratory Studies (iis)
Spijkenisse, the Netherlands

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Report: iis18P01

April 2018

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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-chloroethyl)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.

In March 2012, the European Union decided to lower the limit of TCEP in toys (5 mg/kg) .

A proficiency testing scheme (laboratory-evaluating interlaboratory study) for the determination of Phosphorus Flame retardants in polymers was started by the Institute for Interlaboratory Studies in 2014. During the annual proficiency testing program 2017/2018, it was decided to continue the PT for the analysis of Phosphorus Flame retardants. In this interlaboratory study, 46 laboratories from 19 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 was the organizer of this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO17025 accredited laboratory. It was decided to send approximately 3 grams of two different polymer samples, both positive on Phosphorus Flame retardants, and labelled #18500 and #18501 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 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

Two different polymer samples, #18500 (red Polypropylene granulate) artificially fortified to be positive on TCEP and #18501 (white/grey PVC rings) artificially fortified on Tris(1-chloro-2-propyl)phosphate (TCPP), Tris(1,3-dichloro-2-propyl)phosphate (TDCPP), Triphenylphosphate (TPP) were selected. The batch of each sample were divided over 70 plastic bags, approximately 3 grams for each subsample.

The batch for sample #18500 was used in a previous proficiency test on Phosphorus Flame retardants (iis15P01). The relative standard deviation (%RSD) of the homogeneity data was calculated and compared with 0.3 times the relative standard deviation of the proficiency test iis15P01.

	<i>TCEP in %</i>
%RSD (homogeneity)	3.3
Reference	iis15P01
0.3 x %RSD (reference)	3.6

Table 1: relative standard deviation of TCEP content of subsamples #18500

The observed RSD of the homogeneity data is lower than 0.3 times the RSD of the group performance observed in PT iis15P01. Therefore, homogeneity of the subsamples #18500 was assumed.

The batch of material for sample #18501 was obtained from a third party laboratory, positive on TCPP, TDCPP and TPP. Eight stratified randomly selected samples were tested using an inhouse test method to check the homogeneity of the batch.

	<i>TCPP in mg/kg</i>
Sample #18501-1	568
Sample #18501-2	582
Sample #18501-3	584
Sample #18501-4	580
Sample #18501-5	582
Sample #18501-6	581
Sample #18501-7	593
Sample #18501-8	588

Table 2: homogeneity test results of subsamples #18501

From the test results of table 2, the repeatability was calculated and compared with 0.3 times the corresponding estimated target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	<i>TCPP in mg/kg</i>
r (observed)	20
reference test method	EN71-11:05
0.3 x R (reference test method)	38

Table 3: evaluation of the repeatability of subsamples #18501

The calculated repeatability of the test results was in agreement with 0.3 times the estimated reproducibility mentioned in the reference method EN71-11. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories 1 sample labelled #18500 and 1 sample labelled #18501 sent on January 17, 2018.

2.5 ANALYSES

The participants were requested to determine the following components:

- 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)
- Tris(2-butoxyethyl)phosphate (TBEP) (CAS No. 78-51-3)
- Tributylphosphate (TBP) (CAS No. 126-73-8)
- Tricresylphosphate (TCP) (CAS No. 1330-78-5)
- 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 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 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 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 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. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

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 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:

$$z_{(\text{target})} = (\text{test result} - \text{average of PT}) / \text{target standard deviation}$$

The $z_{(\text{target})}$ 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 serious problems occurred. Three participants reported the test results after the final reporting date and two other participants did not report any test result at all. Not all laboratories were able to report all analyses requested. In total 44 laboratories reported 158 numerical test results. Observed were 18 outlying test results, which is 11.4%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

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 inhouse method. This will consist of a preparation/extraction step and an analytical step. 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 for the other components: TDCPP, TCPP and TPP.

Regrettably 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.

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.

Sample #18500

TCEP: The determination of this component was very problematic at the measured level of 142 mg/kg. Nine statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers 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, TCP, TCPP, TDCPP, TPP and IPTPP.

Sample #18501

TCPP: The determination of this component was problematic at the measured level of 480 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers was not at all in agreement with the estimated target reproducibility of EN71-11:2005.

TDCPP: The determination of this component was problematic at the measured level of 940 mg/kg. Four 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 problematic at the measured level of 493 mg/kg. Two 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.

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

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 (standard deviation*2.8) and the target reproducibilities (EN71-11) are compared in the next tables.

Parameter	unit	n	average	2.8 * sd	R (target)
TCEP	mg/kg	32	141.7	67.2	31.0

Table 4: reproducibility of TCEP found in sample #18500

Parameter	unit	n	average	2.8 * sd	R (target)
TCPP	mg/kg	37	480	251	105
TDCPP	mg/kg	39	940	275	205
TPP	mg/kg	32	493	187	108

Table 5: reproducibilities of components found in sample #18501

Without further statistical calculations, it can be concluded that the group of participating laboratories have problems with the analysis of TCEP, TDCPP, TCPP 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 2018 AGAINST PREVIOUS PTs

	February 2018	February 2017	February 2016	February 2015	February 2014
Number of reporting labs	44	40	31	33	23
Number of results reported	158	239	61	32	23
Number of statistical outliers	18	18	9	2	1
Percentage outliers	11.4%	7.5%	14.8%	6.3%	4.3%

Table 6: Comparison with previous proficiency test

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

The uncertainty in the test results of TCEP and TCPP in the iis18P01 PT did not improve compared to the previous PTs. However, the uncertainty of the test results of TDCPP in iis18P01 PT did improve. TPP in the iis18P01 was determined for the first time. It is noticeable that the uncertainty was similar to the uncertainty of TCEP, TCPP and/or TDCPP.

Parameter	February 2018	February 2017	February 2016	February 2015	February 2014	Est. EN71-11:05
TCEP	17%	13%	9%	12%	23%	7.8%
TCPP	19%	13-15%	n.e.	n.e.	n.e.	7.8%
TDCPP	10%	13-14%	15%	n.e.	n.e.	7.8%
TPP	14%	n.e.	n.e.	n.e.	n.e.	7.8%

Table 7: Development of relative uncertainties over the years

4.4 EVALUATION ANALYTICAL DETAILS

For this PT, some analytical details were requested (see appendix 2). Questions like: Is your laboratory accredited in accordance with ISO/IEC17025 and some specific questions with regards to the analytical details of the test method used.

Based on the answers given by the participants the following can be summarized:

Twenty-five of the forty-four reporting participants mentioned that they are accredited for determination of P-flame retardants in polymer.

Thirty-four participants mentioned that they have cut/grinded the samples before use, fifteen other participants used the samples as received.

All, except four, participants reported to have used ultrasonic as technique to release/extract the analytes. One participant used Thermal Desorption as technique.

Ten participants used Toluene as extraction solvent, eleven used THF and/or ACN as extraction solvent. Sixteen participants used another solvent mixture, for instant hexane, methanol, ethylacetate 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 a Polypropylene granulate and PVC rings. To extract the requested components (see chapter 2.5) 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 the most important variables. This was mainly caused by the matrix of the samples used in these proficiency tests. In PT iis14P01 a foam block was used as sample and in PT iis15P01 a high density plastic was used as sample.

In the PTs of 2016 and 2017, PVC samples and a Polyester sample positive on TCEP and TDCPP were used. The observed large variation could not be explained from the reported analytical details. It was noticeable that the uncertainties of the TCEP, TCPP and TDCPP were similar.

In the PT of 2018 most of the group identified all added Phosphorus Flame retardants correctly: sample #18500 contained only TCEP and sample #18501 contained TCPP, TDCPP and TPP.

Sample #18500 was also used in a previous PT; labelled as sample #15007 in iis15P01.

		Sample #18500			Sample #15007		
Parameter	unit	n	average	2.8 * sd	n	average	2.8 * sd
TCEP	mg/kg	32	141.7	67.2	12	149.6	52.0

Table 8: comparison sample #18500 vs #15007

During the PT iis15P01 the evaluation of TCEP in sample #15007 was problematic.

Eighteen test results were excluded from the statistical evaluation to get a reliable estimate of the consensus value. In the 2018 proficiency test nine test results were excluded.

Probably the type of polymer (polypropylene) may be the main cause of the large variation observed.

For sample #18501, the average of the homogeneity test results is not in line with the average (consensus value) from the PT results. There is a feasible explanation for this. Most important point to make, is that the goal of the homogeneity testing is different from the goal of the evaluation of the reported test results. To prove the homogeneity of the PT samples, a test method is selected with a high precision (smallest variation). The accuracy (trueness) of the selected test method is less relevant.

Then, the homogeneity testing is done by one single laboratory. The test results of this (ISO/IEC 17025 accredited) laboratory will have a bias (systematic deviation) by definition. Also, each test result reported by one of the PT participants will have a bias. However, some will have a positive bias and others a negative bias. These different biases compensate each other in the PT average (consensus value). Therefore, the PT consensus value may deviate from the homogeneity test results. At the same time, the accuracy of the PT consensus value is more reliable than the accuracy of the results of the homogeneity test.

6 CONCLUSION

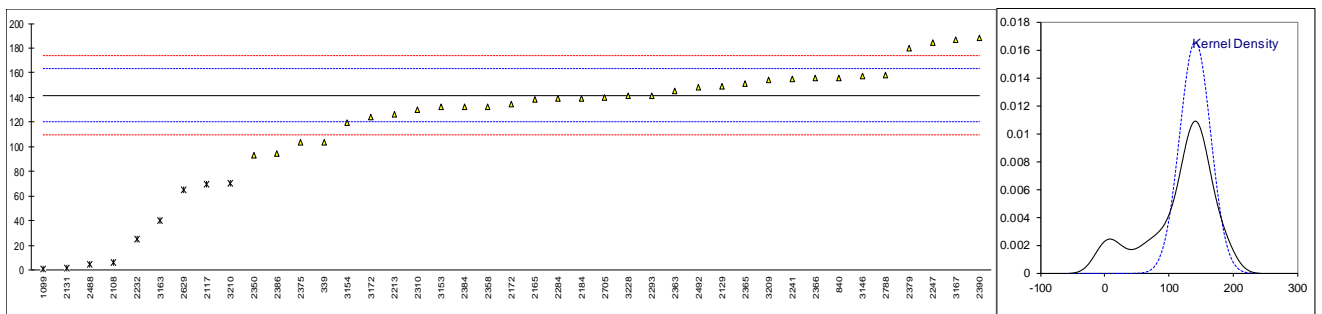
In this proficiency test the TCEP, TDCPP, TCPP and TPP in polymers were identified. The large variations observed in this interlaboratory study can be caused by the preparation or the conditioning of the sample and/or by the performance of the analysis by the participating laboratory. Consequently, the 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 #18500; results in mg/kg

lab	method	value	mark	z(target)	Remarks
339	IEC62321-6Mod.	104		-3.41	
840	In house	156.1		1.30	
841		-----		-----	
1099	EN71-11	1.047	R(0.01)	-12.73	
2108	ISO17881-2	6.127	R(0.01)	-12.27	
2115		-----		-----	
2117	In house	69.66	R(0.01)	-6.52	
2129	ISO17881-2	149.1		0.67	
2131	In house	1.99325	R(0.01)	-12.64	
2165	In house	138.2		-0.32	
2172	In house	134.42		-0.66	
2184	In house	139.5		-0.20	
2212	In house	<100		<-3.77	False negative test result?
2213	EN71-11	126.4		-1.39	
2232	In house	25.2	C,R(0.01)	-10.54	First reported 15.2
2241	EN71-11	155.2	C	1.22	First reported 5.8
2247	In house/ISO17881-2	184.28		3.85	
2284	EPA3550C/EPA8321B	139.4		-0.21	
2293	ISO17881-2	141.70	C	0.00	First reported 222.66
2310	In house	130.14		-1.05	
2350	In house	93.37		-4.37	
2358	In house	132.72		-0.82	
2363	In house	145		0.30	
2365	In house	150.9		0.83	
2366	In house	155.7		1.26	
2375	In house	103.3		-3.48	
2379	In house	179.68		3.43	
2384	In house	132.36		-0.85	
2386	In house	94.4		-4.28	
2389		-----		-----	
2390	In house	188.380		4.22	
2488		4.94	R(0.01)	-12.37	
2492	In house	148		0.57	
2629	ISO17881-2	65.4	R(0.01)	-6.90	
2705	In house	140		-0.16	
2737		-----		-----	
2788	In house	158.24		1.49	
3146	In house	157.4		1.42	
3153	In house	132		-0.88	
3154	In house	119.6		-2.00	
3163	In house	40	R(0.01)	-9.20	
3167	In house	186.57		4.06	
3172	EN71-11	123.997		-1.60	
3209	In house	154.21		1.13	
3210	In house	70.25	R(0.01)	-6.47	
3228	In house	141.2		-0.05	

	OK		Only Toluene	Only ACN/THF	Other solvents
normality	OK		OK	OK	OK
n	32		7	14	14
outliers	9		1	3	2
mean (n)	141.733		137.252	157.879	137.899
st.dev. (n)	24.0154	RSD = 17%	17.4868	20.6425	29.0391
R(calc.)	67.243		48.963	57.799	81.309
st.dev.(EN71-11:05)	11.0551		10.7057	12.3146	10.7561
R(EN71-11:05)	30.955		29.976	34.481	30.117



Determination of other Phosphorus Flame Retardants in sample #18500; results in mg/kg

Lab	TBEP	TBP	TCP	TCPP	TDCPP	TPP	IPTPP
339	----	----	----	<1	<1	<1	----
840	not detected	not detected	not detected	not detected	not detected	not detected	NA
841	----	----	----	----	----	----	----
1099	n.a	n.a	n.a	n.a	<1.0	n.a	n.a
2108	----	----	----	----	----	----	----
2115	----	----	----	Nd	25.90	----	----
2117	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2129	na	na	<5	<5	<5	<5	na
2131	n/a	n/a	n/d	n/d	n/d	n/d	n/a
2165	----	----	----	n.d.	n.d.	n.d.	----
2172	----	----	----	----	----	----	----
2184	----	----	----	n.d.	n.d.	n.d.	----
2212	N/A	N/A	N/A	<100	<100	N/A	N/A
2213	<10 mg/kg	<10 mg/kg	<10 mg/kg	<10 mg/kg	<10 mg/kg	<10 mg/kg	<10 mg/kg
2232	----	----	----	----	12.1	12.8	----
2241	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
2247	not analysed	not analysed	not analysed	Nd	Nd	Nd	not analysed
2284	----	----	----	----	----	----	----
2293	----	----	----	12.467	----	----	----
2310	----	----	Not Detected	Not Detected	Not Detected	Not Detected	----
2350	----	----	----	----	----	----	----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	ND	ND	NA
2365	<5	<5	<5	<5	<5	<5	<5
2366	out of capability	out of capability	out of capability	<5	<5	out of capability	out of capability
2375	----	----	----	----	----	----	----
2379	Not tested	Not tested	Not tested	Not detected	Not detected	Not detected	Not tested
2384	<5	<5	----	<5	<5	<5	----
2386	<5	<5	<5	<5	<5	<5	----
2389	----	----	120.5	----	----	----	----
2390	----	ND	ND	ND	ND	ND	ND
2488	----	----	----	----	----	----	----
2492	----	----	----	----	----	----	----
2629	----	----	----	----	----	ND	----
2705	1.1	0.9	----	0	0.4	0.1	----
2737	----	----	----	----	----	----	----
2788	----	----	----	----	----	----	----
3146	<10	<10	n.a.	<10	<10	<10	n.a.
3153	----	----	----	----	----	----	----
3154	----	----	----	----	----	----	----
3163	----	----	----	----	----	----	----
3167	----	----	----	----	----	----	----
3172	----	----	----	----	----	----	----
3209	----	----	----	----	----	----	----
3210	< 5	----	<5	----	<5	<5	----
3228	----	----	----	N.D.	N.D.	N.D.	----

TBEP = Tris(2-butoxyethyl)phosphate CAS no.78-51-3

TBP = Tributylphosphate CAS no.126-73-8

TCP = Tricresylphosphate CAS no.1330-78-5

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

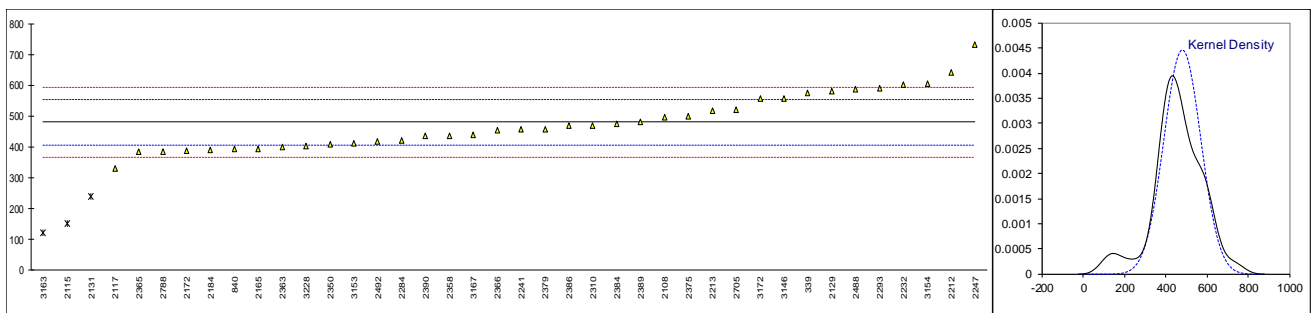
TPP = Triphenylphosphate CAS no.115-86-6

IPTPP = Isopropylated Triphenylphosphate CAS no.68937-41-7

Determination of Tris(1-chloro-2-propyl)phosphate (TCPP) CAS no.13674-84-5 in sample #18501; results in mg/kg

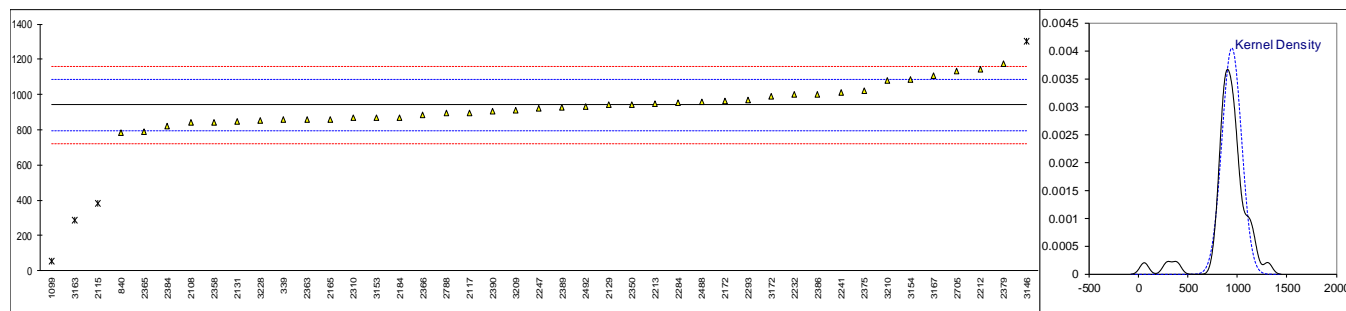
lab	method	value	mark	z(target)	remarks
339	IEC62321-6Mod.	576		2.56	
840	In house	392.7		-2.33	
841		-----		-----	
1099	EN71-11	n.a		-----	
2108	ISO17881-2	496.2		0.43	
2115	EN71	150.85	R(0.01)	-8.79	
2117	In house	329.00	C	-4.03	First reported 156.66
2129	ISO17881-2	581.2		2.70	
2131	In house	238.60605	R(0.01)	-6.45	
2165	In house	394.7		-2.28	
2172	In house	388.52		-2.45	
2184	In house	390		-2.41	
2212	In house	641.2		4.30	
2213	EN71-11	518		1.01	
2232	In house	601.5		3.24	
2241	EN71-11	457.3		-0.61	
2247	In house/ISO17881-2	733.26		6.76	
2284	EPA3550C/EPA8321B	421.9		-1.55	
2293	ISO17881-2	589.600	C	2.92	First reported 1093.875
2310	In house	470.34		-0.26	
2350	In house	408.29		-1.92	
2358	In house	437.08		-1.15	
2363	In house	400		-2.14	
2365	In house	383.4		-2.58	
2366	In house	453.1		-0.72	
2375	In house	499.2		0.51	
2379	In house	457.70		-0.60	
2384	In house	475.38		-0.13	
2386	In house	468		-0.32	
2389	In house	481.93		0.05	
2390	In house	436.450		-1.17	
2488		588.4		2.89	
2492	In house	419		-1.63	
2629		-----		-----	
2705	In house	521		1.09	
2737		-----		-----	
2788	In house	385.86		-2.52	
3146	In house	557.1		2.06	
3153	In house	412		-1.82	
3154	In house	604.4		3.32	
3163	In house	120	R(0.01)	-9.62	
3167	In house	437.51		-1.14	
3172	EN71-11	555.205		2.01	
3209		-----		-----	
3210		-----		-----	
3228	In house	401.3		-2.10	

normality OK
n 37
outliers 3
mean (n) 480.101
st.dev. (n) 89.4893 RSD = 19%
R(calc.) 250.570
st.dev.(EN71-11:05) 37.4479
R(EN71-11:05) 104.854



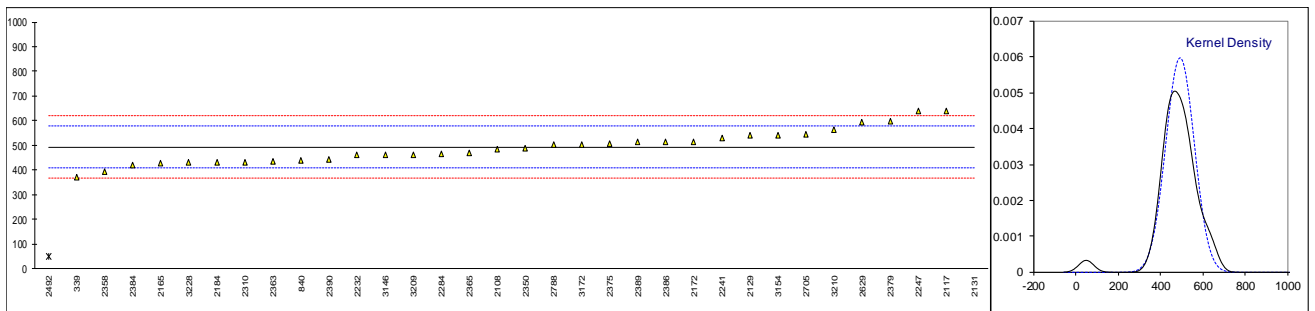
Determination of Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) CAS no.13674-87-8 in sample #18501; results in mg/kg

lab	method	value	mark	z(target)	remarks
339	IEC62321-6Mod.	857		-1.13	
840	In house	781.6		-2.16	
841		-----		-----	
1099	EN71-11	54.941	R(0.01)	-12.07	
2108	ISO17881-2	841.5		-1.34	
2115	EN71	384.37	R(0.01)	-7.58	
2117	In house	895.66	C	-0.60	First reported 620.00
2129	ISO17881-2	944.4		0.06	
2131	In house	848.5487		-1.25	
2165	In house	859.8		-1.09	
2172	In house	961.72		0.30	
2184	In house	870		-0.95	
2212	In house	1144		2.78	
2213	EN71-11	948		0.11	
2232	In house	998.4		0.80	
2241	EN71-11	1008.8		0.94	
2247	In house/ISO17881-2	922.15		-0.24	
2284	EPA3550C/EPA8321B	954.4		0.20	
2293	ISO17881-2	969.20	C	0.40	First reported 1501.80
2310	In house	867.14		-0.99	
2350	In house	945.05		0.07	
2358	In house	843.59		-1.31	
2363	In house	858		-1.12	
2365	In house	791.1		-2.03	
2366	In house	886.3		-0.73	
2375	In house	1023.8		1.14	
2379	In house	1175.76		3.22	
2384	In house	819.21		-1.65	
2386	In house	999		0.81	
2389	In house	927.33		-0.17	
2390	In house	907.820		-0.44	
2488		957.8		0.24	
2492	In house	930		-0.13	
2629		-----		-----	
2705	In house	1133		2.63	
2737		-----		-----	
2788	In house	894.04		-0.63	
3146	In house	1303.8	R(0.05)	4.96	
3153	In house	868		-0.98	
3154	In house	1083.3		1.96	
3163	In house	285	R(0.01)	-8.93	
3167	In house	1107.3		2.28	
3172	EN71-11	989.746		0.68	
3209	In house	909.22		-0.42	
3210	In house	1078.6		1.89	
3228	In house	854.8		-1.16	
normality		OK			
n		39			
outliers		4			
mean (n)		939.874			
st.dev. (n)		98.2336	RSD = 10%		
R(calc.)		275.054			
st.dev.(EN71-11:05)		73.3102			
R(EN71-11:05)		205.269			



Determination of Triphenylphosphate (TPP) CAS no.115-86-6 in sample #18501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	IEC62321-6Mod.	372		-3.14	
840	In house	437.7		-1.43	
841		----		----	
1099	EN71-11	n.a		----	
2108	ISO17881-2	485.1		-0.19	
2115		----		----	
2117	In house	640.66	C	3.85	First reported 266.66
2129	ISO17881-2	540.7		1.25	
2131	In house	2588.48515	R(0.01)	54.55	
2165	In house	428.2		-1.68	
2172	In house	515.79		0.60	
2184	In house	430		-1.63	
2212	In house	N/A		----	
2213	EN71-11	<10		<-12.56	False negative test result?
2232	In house	461.2		-0.82	
2241	EN71-11	529.3		0.96	
2247	In house/ISO17881-2	638.14		3.79	
2284	EPA3550C/EPA8321B	466.2		-0.69	
2293		----		----	
2310	In house	430.22		-1.62	
2350	In house	488.92		-0.10	
2358	In house	393.57		-2.58	
2363	In house	436		-1.47	
2365	In house	469.1		-0.61	
2366		----		----	
2375	In house	507.4		0.39	
2379	In house	596.51		2.71	
2384	In house	420.57		-1.87	
2386	In house	515		0.58	
2389	In house	513.79		0.55	
2390	In house	443.930		-1.27	
2488		----		----	
2492	In house	49	R(0.01)	-11.55	
2629	ISO17881-2	592.54		2.60	
2705	In house	546		1.39	
2737		----		----	
2788	In house	502.02		0.25	
3146	In house	461.5		-0.81	
3153		----		----	
3154	In house	542.2		1.29	
3163		----		----	
3167		----		----	
3172	EN71-11	502.454		0.26	
3209	In house	462.32		-0.79	
3210	In house	563.8		1.85	
3228	In house	429.7		-1.64	
	normality	OK			
	n	32			
	outliers	2			
	mean (n)	492.579			
	st.dev. (n)	66.7332	RSD = 14%		
	R(calc.)	186.853			
	st.dev.(EN71-11:05)	38.4212			
	R(EN71-11:05)	107.579			



Determination of other Phosphorus Flame Retardants in sample #18501; results in mg/kg

Lab	TBEP	TBP	TCP	TCEP	IPTPP
339	----	----	----	<10	----
840	not detected	not detected	not detected	not detected	NA
841	----	----	----	----	----
1099	n.a	n.a	n.a	< 1.0	n.a
2108	----	----	----	----	----
2115	----	----	----	----	----
2117	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2129	na	na	<5	<5	na
2131	n/a	n/a	n/d	1.5944	n/a
2165	----	----	----	n.d.	----
2172	----	----	----	----	----
2184	----	----	----	n.d.	----
2212	N/A	N/A	N/A	<100	N/A
2213	<10 mg/kg	<10 mg/kg	<10 mg/kg	<10 mg/kg	<10 mg/kg
2232	----	----	----	----	----
2241	<5.0	<5.0	<5.0	<5.0	<5.0
2247	not analysed	not analysed	not analysed	traces	not analysed
2284	----	----	----	----	----
2293	----	----	----	0.890	----
2310	----	----	Not Detected	Not Detected	----
2350	----	----	----	----	----
2358	n.d.	n.d.	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	NA
2365	<5	<5	<5	<5	<5
2366	out of capability	out of capability	out of capability	<5	out of capability
2375	----	----	----	----	----
2379	Not tested	Not tested	Not tested	Not detected	Not tested
2384	<5	<5	----	Not detected[<5]	----
2386	<5	<5	<5	<5	----
2389	----	----	----	----	----
2390	----	ND	ND	ND	ND
2488	----	----	----	2.08	----
2492	----	----	----	----	----
2629	----	----	----	ND	----
2705	0	0.8	----	0.5	----
2737	----	----	----	----	----
2788	----	----	----	----	----
3146	<10	<10	n.a.	<10	n.a.
3153	----	----	----	----	----
3154	----	----	----	----	----
3163	----	----	----	0	----
3167	----	----	----	----	----
3172	----	----	----	----	----
3209	----	----	374.62	----	----
3210	<5	----	<5	<5	----
3228	----	----	----	N.D.	----

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

IPTPP = Isopropylated Triphenylphosphate CAS no.68937-41-7

APPENDIX 2
Analytical details

Lab	Laboratory ISO/IEC17025 accredited?	Was the sample grinded prior to analysis?	What was the final estimated particle size before analysis?	Which technique was used to extract the analyte(s)?	What solvent (mixture) was used to release the analyte(s)?	What was the extraction time (minutes) and temperature (°C)?
339	No	Used as received	#18500: 1-2mm	Ultrasonic	Toluene	60min/60°C
840	Yes	Cut	#18501 : 2mm	Ultrasonic	hexan: ethyl acetate (1:1)	50 °C for 60 minutes
841	---	----		---	---	---
1099	Yes	Used as received	n/a	Ultrasonic	ACN/toluene	60 minutes at 40 deg.
2108	Yes	Used as received	as received	Ultrasonic	Acetone	1. 40 min at 40°C; 2. 20 min at 40°C
2115	Yes	Used as received		Ultrasonic	Acetonitrile	60 min, 40°C
2117	Yes	Cut	3mm	--	Toluol	2h 90 °C
2129	Yes	#18500,as received	#18501 cut to the same particle size as #18500	Ultrasonic	toluene	60 min / 60 °C
2131	No	Used as received		Ultrasonic	Aceton	40 min @ 40 °C
2165	Yes	Used as received	3mm*3mm	Ultrasonic	Hexane:Acetone:MTBE(1:1:1)	3 hrs, 60 deg C
2172	Yes	Grinded	less 1 mm	Ultrasonic	toluene	70°C 120min
2184	Yes	Used as received	3mm x 3mm	Ultrasonic	Hexane:Acetone:MTBE (1:1:1)	3 hrs, 60 deg C
2212	Yes	Cut	2mm	Mechanical Shaking	Tetrahydrofuran	60mins, room temperature
2213	Yes	Further Cut		--		
2232	Yes	Used as received	5mm*5mm*5mm	Ultrasonic	THF:ACN (1:2)	30minutes; 40°C
2241	Yes	Cut	2mm*2mm	Ultrasonic	acetonitrile	60min and 40 °C
2247	Yes	Cut	2X 2 mm approx	Ultrasonic	THF : Acetonitrile : water (1:2:3)	60 min at 70°C
2284	---	----		---	---	---
2293	Yes	Cut	0.2 +/- 0.01 grams	Ultrasonic	THF, ACN and water	60 minutes and 70 °C
2310	No	Used as received		Ultrasonic	Ethyl acetate:hexane(1:1)	1 hr & 50°C
2350	No	Used as received		Ultrasonic	Ethyl acetate and n-Hexane(1:1)	50°C for 1hour
2358	No	Cut	2mm x 2mm	Ultrasonic	Hexane/Ethylacetate(1:1)	60 mins & 50 degree C
2363	No	Cut	1mm*1mm*1mm	Ultrasonic	Toluene	60mins,60°C
2365	Yes	Cut	1mm*1mm	Ultrasonic	Toluene	60°C,60min
2366	Yes	Cut	2mm*2mm*2mm	Soxhlet	ethyl acetate: Hexane= 1:1(v/v)	50°C, 60min
2375	No	Cut	2mmx2mm	Ultrasonic	Ethyl acetate: Hexane (1:1)	60 min, 50°C
2379	No	Cut	2x2 mm	Ultrasonic	Ethy acetate : n-hexane (1:1)	60 min and 50 C
2384	Yes	Grinded	1-2mm	Soxhlet	toluene	reflux for 18hours
2386	Yes	---		Ultrasonic	Ethylacetat/n-Hexan	60 min at 50°C
2389	---	----		---	---	---
2390	Yes	Cut	2 mm X 2mm	Ultrasonic	n-Hexane & Ethyl Acetate	60 min at 50 C
2488	---	----		---	---	---
2492	Yes	Used as received	0.5 cm	Ultrasonic	THF	60 min & 60°C
2629	---	----		---	---	---
2705	No	Used as received		Soxhlet	Acetone/Hexane 10/90	120 min, 56 °C
2737	---	---	---	---	---	---
2788	No	Cut	3 X 3 mm	Ultrasonic	Toluene	3 hours / 60C
3146	No	Cut	#18500: used as received #18501: cut 2x2mm	Ultrasonic	Tetrahydrofurane / Acetonitrile 1/2	2x30 min, 70°C
3153	No	Cut	2mm X 2mm	Ultrasonic	THF / ACN	30 mins and 70 °C

Lab	Laboratory ISO/IEC17025 accredited?	Was the sample grinded prior to analysis?	What was the final estimated particle size before analysis?	Which technique was used to extract the analyte(s)?	What solvent (mixture) was used to release the analyte(s)?	What was the extraction time (minutes) and temperature (°C)?
3154	---	---		---	---	---
3163	No	Cut	0.5mg	Thermal Desorption	none	none
3167	Yes	Grinded	sifting	Ultrasonic	acetone/Tetrahydrofuran	10/40
3172	Yes	Grinded	< 1 mm	Ultrasonic	Toluene	60 min and 40°C
3209	Yes	Used as received		Ultrasonic	toluene:acetone=1:2	30 minutes
3210	No	Cut	1-2 mm	Ultrasonic	THF / ACN	60 min at 60°C
3228	Yes	Used as received	3mm*3mm	Ultrasonic	Hexane:Acetone:MTBE=1:1:1	3 hrs, 60deg C

APPENDIX 3

Number of participants per country

2 labs in FRANCE
6 labs in GERMANY
1 lab in GUATEMALA
5 labs in HONG KONG
3 labs in INDIA
2 labs in ITALY
1 lab in KOREA
1 lab in LUXEMBOURG
1 lab in MALAYSIA
11 labs in P.R. of CHINA
2 labs in PAKISTAN
1 lab in POLAND
1 lab in SINGAPORE
1 lab in SWITZERLAND
1 lab in THAILAND
1 lab in THE NETHERLANDS
2 labs in TURKEY
1 lab in U.S.A.
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)	= 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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