Institute for
Interlaboratory Studies

Results of Proficiency Test
Total Phosphorus Flame Retardants
in Polymers
March 2022

CONTENTS

Appendices:

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 2021/2022 it was decided to continue the proficiency test for the determination of Total Phosphorus Flame Retardants in Polymers.

In this interlaboratory study 31 laboratories in 15 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the Total Phosphorus Flame Retardants in Polymers 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 different polymer samples both positive on Phosphorus Flame Retardants of 3 grams each and labelled #22525 and #22526 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 Polypropylene granulates artificially fortified with TCEP was selected. After homogenization 55 plastic bags were filled with approximately 3 grams each and labelled #22525.
The batch for sample #22525 was used in a previous proficiency test on Phosphorus Flame Retardants in Polymers as sample #18500 in iis18P01. Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of brown Polypropylene granulates, which are artificially fortified with some Phosphorus Flame Retardants, was selected. After homogenization 60 plastic bags were filled with approximately 3 grams each and labelled #22526.
The homogeneity of the subsamples was checked by determination of TCEP and TCPP by an in house test method on 8 stratified randomly selected subsamples.

	TCEP in mg/kg	TCPP in mg/kg
sample #22526-1	413	496
sample #22526-2	412	505
sample #22526-3	421	511
sample #22526-4	410	508
sample #22526-5	431	532
sample #22526-6	425	529
sample #22526-7	424	521
sample #22526-8	419	518

Table 1: homogeneity test results of subsamples #22526

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.

	TCEP in mg/kg	TCPP in mg/kg
r (observed)	20.5	34.4
reference method	iis memo 2102	iis memo 2102
0.3 x R (reference method)	52.8	64.9

Table 2: evaluation of the repeatabilities of subsamples #22526

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 polymer sample labelled #22525 and one polymer sample labelled #22526 were sent on February 16, 2022.

2.5   ANALYZES

The participants were requested to determine on sample #22525 and #22526:
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 determined 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 appendices 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 appendices 1 and 2. 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 (derived from e.g. ISO test methods) 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:

$z_{(target)}$ = (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

In this proficiency test no problems were encountered with the dispatch of the samples. Three participants reported test results after the final reporting date and four other participants were not able to report any test results. Not all laboratories were able to report all components requested. In total 27 laboratories reported 77 numerical test results. Observed were 5 outlying test results, which is 6.5%. 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 in appendix 1. 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. The majority of the 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.
It was decided in 2021 to use the iis PT data gathered from 2014 up to and including 2021 to estimate a more realistic target reproducibility. This estimated target reproducibility was calculated from the relative standard deviation of 15% (lit. 13, iis memo 2102) multiplied by 2.8. This was used for the evaluation of the test results in this PT.

sample #22525

TCEP: This determination was problematic. Five 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.

For all other requested Phosphorus Flame Retardants the group of participants agreed on a concentration near or below the limit of detection. Therefore, these components were not evaluated. See appendix 2 for the reported test results.

sample #22526

The polymer material for samples #22525 and #22526 is Polypropylene and both samples contain TCEP. Therefore, it was decided to exclude corresponding test results from participants in sample #22526 based on statistical outliers in sample #22525.

TCEP: This determination was problematic. No statistical outliers were observed but five test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the target reproducibility as derived from iis memo 2102.

TCPP: This determination was problematic. No statistical outliers were observed but four test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the target reproducibility as derived from iis memo 2102.

For all other requested Phosphorus Flame Retardants the group of participants agreed on a concentration near or below the limit of detection. Therefore, these components were not evaluated. See appendix 2 for the reported test results.

4.2   PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the reference method 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 the reference method are presented in the next tables.

Component	unit	n	average	2.8 * sd	R(target)
TCEP	mg/kg	22	119	68	50

Table 3: reproducibility of component in sample #22525

Component	unit	n	average	2.8 * sd	R(target)
TCEP	mg/kg	22	231	178	97
TCPP	mg/kg	19	388	297	163

Table 4: reproducibilities of components in sample #22526

Without further statistical calculations it can be concluded that for the Phosphorus Flame Retardants present in the samples there is not a good compliance of the group of participating laboratories with the target. See also the discussion in paragraphs 4.1 and 5.

4.3   COMPARISON OF THE PROFICIENCY TEST OF MARCH 2022 WITH PREVIOUS PTS

	March 2022	February 2021	February 2020	February 2019	February 2018
Number of reporting laboratories	27	36	35	29	44
Number of test results	77	174	169	92	158
Number of statistical outliers	5	16	16	6	18
Percentage of statistical outliers	6.5%	9.2%	9.5%	6.5%	11.4%

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	March 2022	February 2021	February 2020	February 2019	2018 -2014	Target
TBP	n.e.	n.e.	11%	n.e.	n.e.	15%
TiBP	n.e.	11%	n.e.	n.e.	n.e.	15%
TCP	n.e.	21%	16%	12%	n.e.	15%
TCEP	20-28%	11%	11%	15%	9-23%	15%
TCPP	27%	18%	18%	n.e.	13-19%	15%
TDCPP	n.e.	13-17%	11%	19%	13-15%	15%
TPP	n.e.	n.e.	n.e.	17%	14%	15%

Table 6: development of uncertainties over the years

The uncertainties observed in this PT are somewhat larger in comparison to former iis PTs.

Sample #22525 was used before in proficiency test iis18P01 as sample #18500. It is observed that the average concentrations of sample #22525 is in line with the previous PT, see next table.

Component	unit	#22525			#18500		
		n	average	2.8 * sd	n	average	2.8 * sd
TCEP	mg/kg	22	119	68	32	142	67

Table 7: comparison of sample #22525 with sample #18500

4.4 EVALUATION ANALYTICAL DETAILS

The reported analytical details from the participants are listed in appendix 3. Based on the answers given by the participants the following can be summarized:
- About 65% 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 40% of the reporting participants, about 60% used the samples as received.
- The amount of sample intake varied between 0.1 and 1 grams, about 70% used 0.5 to 1 grams.
- Almost all reporting laboratories reported to have used ultrasonic as technique to release/extract the analytes.
- About 35% used Toluene or a mixture with Toluene as release solvent, about 30% used a combination of Hexane with Ethyl Acetate and about 15% used THF or a THF mixture with Acrylonitrile or Methanol and about 20% used Acetone.
- A vast majority (about 85%) of the reporting laboratories used an extraction time of 60 minutes. The extraction temperature differs between room temperature and 70 °C. About 46% used an extraction temperature between 40 and 50 °C, about 45% used an extraction temperature between 60 and 70 °C.

When the analytical details were investigated separately it appeared that no profound conclusion could be drawn due to the limited number of test results. However, the use of Acetone appeared to have a negative effect on Polypropylene.

5 DISCUSSION

The matrix of the PT samples #22525 and #22526 was Polypropylene. To extract the requested Phosphorus Flame Retardants from a polymer matrix the extraction solvent, the extraction conditions and the extraction surface could be significant on the amount of Phosphorus Flame Retardants determined. It is noticed that participants who had reported test results which were statistical outliers in sample #22525 have used Acetone as solvent to release the Phosphorus Flame Retardants from the matrix. The test results in sample #22526 of corresponding participants were also lower than the rest of the group. Therefore, it was decided to exclude these test results in sample #22526.

In this PT the average of the homogeneity test results are not in line with the average (consensus value) from the PT results. There are several reasons for this. First, the goal of the homogeneity testing is very different from the goal of the evaluation of the reported PT results. In order to prove the homogeneity of the PT samples, a test method is selected with a high precision (smallest variation). The accuracy (trueness) of the test method is less relevant.
Secondly, the homogeneity testing is done by one laboratory only. The test results of this (ISO/IEC 17025 accredited) laboratory will have a bias (systematic deviation) depending on the test method used. The desire to detect small variations between the PT samples leads to the use of a sensitive test method with high precision, which may be a test method with significant bias.

Also each test result reported by the laboratories that participate in the PT 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 average of the homogeneity test.

At the same time the accuracy of the PT consensus value is more reliable than the accuracy of the average of the results of the homogeneity test.

6   CONCLUSION

In the PT of 2022 the majority of the participants identified all Phosphorus Flame Retardants correctly. In sample #22525 TCEP was determined and in sample #22526 TCEP and TCPP were determined.

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 #22525; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	105.52		-0.77	
623	In house	95.808		-1.31	
2115	ISO17881-2	2.65	R(0.05)	-6.52	
2232	ISO17881-2	10.4	C,R(0.05)	-6.09	first reported 9.05
2247	ISO17881-2	120.80		0.08	
2250	In house	150.4		1.74	
2265	ISO17881-1	22.2	R(0.05)	-5.43	
2297	ISO17881-2Mod.	108.1		-0.63	
2310	ISO17881-2	137		0.99	
2320	ISO17881-2	144.99		1.43	
2358	ISO17881-2	125.92		0.37	
2363	ISO17881-1/2	119.45		0.01	
2365	In house	119.73		0.02	
2366	In house	125.1		0.32	
2375	ISO17881-2	130		0.60	
2379	EPA3550B	130.6892		0.64	
2380	In house	135.58		0.91	
2386	In house	89.0		-1.69	
2390		-----		-----	
2459	ISO17881-2	147.035		1.55	
2481	In house	129		0.54	
2488	ISO17881-2	2.3688	R(0.05)	-6.53	
2532	ISO17881-2	136		0.93	
2590	ISO17881-2	77.364	C	-2.34	first reported 24.029
2826	ISO17881-2	50.78		-3.83	
2917	In house	105.774		-0.76	
3001		-----		-----	
3163		-----		-----	
3172	ISO17881-2	16.663	C,R(0.05)	-5.74	first reported 25.432
3197	ISO17881-2	140.8		1.20	
3228		-----		-----	

normality	suspect	
n	22	
outliers	5	
mean (n)	119.311	
st.dev. (n)	24.4521	RSD = 20%
R(calc.)	68.466	
st.dev.(iis memo 2102)	17.8966	
R(iis memo 2102)	50.111	
compare		
R(EN71-11:05)	26.058	
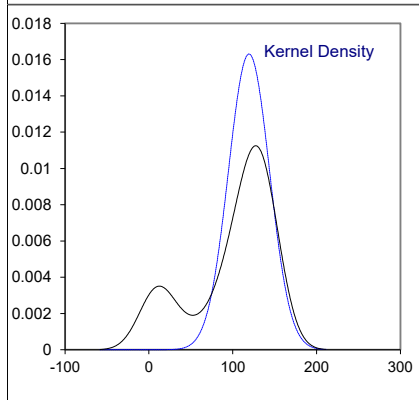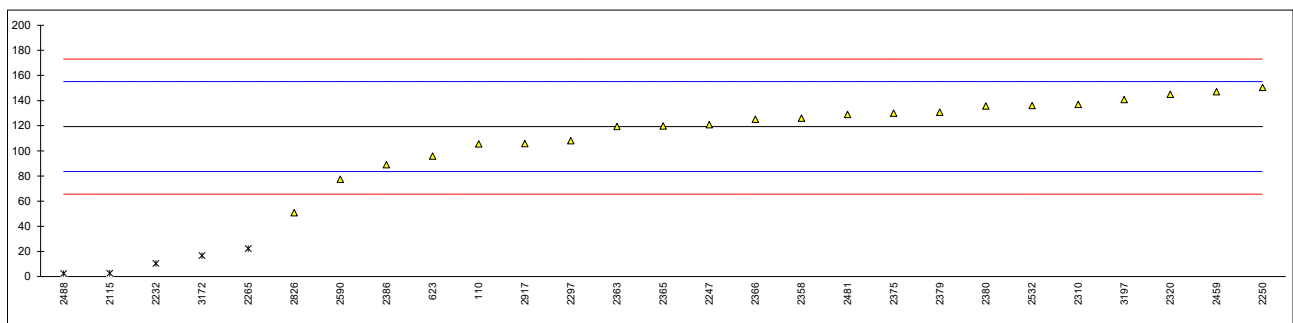
Determination of Tris(2-chloroethyl) Phosphate (TCEP) CAS no.115-96-8 in sample #22526; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	197.08		-0.97	
623	In house	194.650		-1.04	
2115	ISO17881-2	5.47	ex	-6.51	test result excluded, see § 4.1
2232	ISO17881-2	22.8	ex,C	-6.01	test result excluded, see § 4.1, first reported 19.8
2247	ISO17881-2	222.93		-0.23	
2250	In house	350.2		3.45	
2265	ISO17881-1	50.9	ex	-5.20	test result excluded, see § 4.1
2297	ISO17881-2Mod.	228.0		-0.08	
2310	ISO17881-2	250		0.55	
2320	ISO17881-2	348.07		3.39	
2358	ISO17881-2	240.27		0.27	
2363	ISO17881-1/2	225.33		-0.16	
2365	In house	240.16		0.27	
2366	In house	236.2		0.16	
2375	ISO17881-2	240		0.27	
2379	EPA3550B	235.6000		0.14	
2380	In house	260.24		0.85	
2386	In house	147.4		-2.41	
2390		-----		-----	
2459	ISO17881-2	303.548		2.10	
2481	In house	179		-1.50	
2488	ISO17881-2	4.5900	ex	-6.53	test result excluded, see § 4.1
2532	ISO17881-2	277.0		1.33	
2590	ISO17881-2	109.820	C	-3.49	first reported 48.858
2826	ISO17881-2	98.79		-3.81	
2917	In house	204.132		-0.77	
3001		-----		-----	
3163		-----		-----	
3172	ISO17881-2	33.955	ex,C	-5.69	test result excluded, see § 4.1, first reported 44,756
3197	ISO17881-2	289.1		1.68	
3228		-----		-----	

	normality	OK		
	n	22		
	outliers	0 + 5 ex		
	mean (n)	230.796		
	st.dev. (n)	63.7480	RSD = 28%	
	R(calc.)	178.494		
	st.dev.(iis memo 2102)	34.6194		
	R(iis memo 2102)	96.934		
	compare			
	R(EN71-11:05)	50.406		

Kernel Density
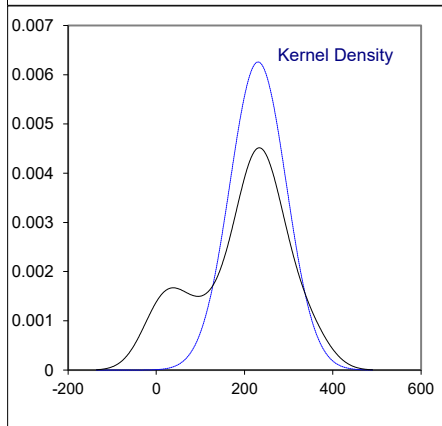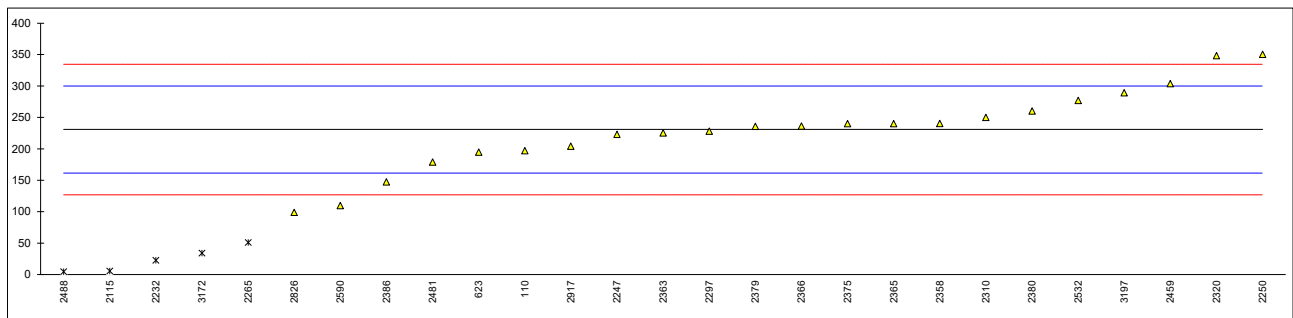
Determination of Tris(1-chloro-2-propyl) Phosphate (TCPP) CAS no. 126-71-6 in sample #22526; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	255.57		-2.28	
623	In house	224.596		-2.81	
2115	ISO17881-2	9.16	ex	-6.51	test result excluded, see § 4.1
2232	ISO17881-2	297	ex	-1.57	test result excluded, see § 4.1
2247	ISO17881-2	549.98		2.78	
2250	In house	503		1.97	
2265	ISO17881-1	70.0	ex	-5.46	test result excluded, see § 4.1
2297	ISO17881-2Mod.	373.6		-0.25	
2310	ISO17881-2	430		0.72	
2320		-----		-----	
2358	ISO17881-2	405.01		0.29	
2363	ISO17881-1/2	410.67		0.38	
2365	In house	406.59		0.31	
2366	In house	422.3		0.58	
2375	ISO17881-2	375		-0.23	
2379	EPA3550B	354.8204		-0.57	
2380	In house	417.38		0.50	
2386	In house	203.2		-3.18	
2390		-----		-----	
2459		-----		-----	
2481	In house	290		-1.69	
2488		-----		-----	
2532	ISO17881-2	512	C	2.12	first reported 632.5
2590	ISO17881-2	232.705		-2.67	
2826		-----		-----	
2917	In house	535.104		2.52	
3001		-----		-----	
3163		-----		-----	
3172	ISO17881-2	60.536	ex,C	-5.63	test result excluded, see § 4.1, first reported 94.874
3197	ISO17881-2	476.2	C	1.51	first reported 665.7
3228		-----		-----	

normality	OK	
n	19	
outliers	0 + 4 ex	
mean (n)	388.301	
st.dev. (n)	106.1434	RSD = 27%
R(calc.)	297.202	
st.dev.(iis memo 2102)	58.2452	
R(iis memo 2102)	163.087	
compare		
R(EN71-11:05)	84.805	
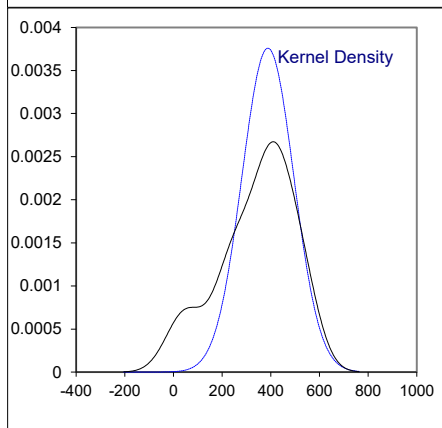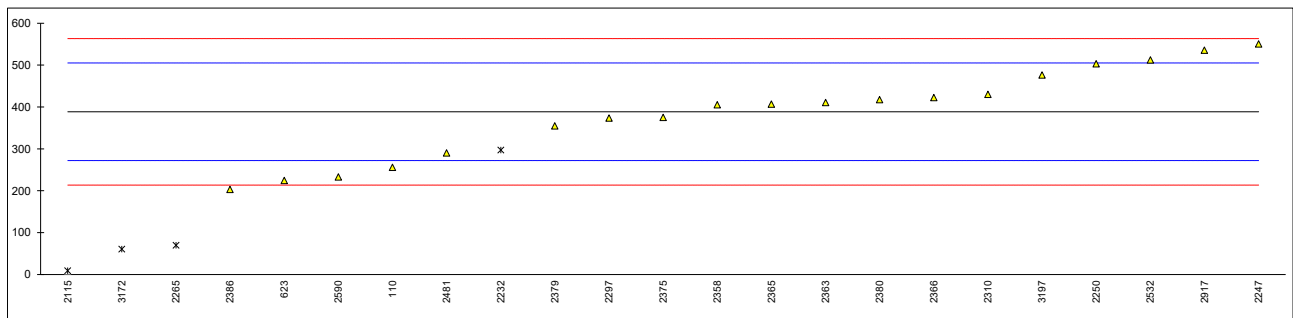
APPENDIX 2 Determination of other Phosphorus Flame Retardants; results in mg/kg

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
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 #22525

lab	TBEP	TBP	TiBP	TCP	TCPP	TDCPP	TPP	IPTPP
110	-----	-----	-----	-----	< 5 mg/kg	< 5 mg/kg	< 5 mg/kg	-----
623	not detected	not detected	not analyzed	not detected	not detected	not detected	not detected	not analyzed
2115	-----	-----	-----	-----	-----	-----	-----	-----
2232	-----	-----	-----	-----	-----	-----	-----	-----
2247	Not Detected	Not Detected	Not analyzed	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2250	-----	-----	-----	-----	-----	-----	-----	-----
2265	< 1	< 1	-----	-----	< 1	< 1	< 1	-----
2297	ND	ND	ND	ND	ND	ND	ND	ND
2310	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2320	-----	-----	-----	-----	-----	Not Detected	-----	-----
2358	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2363	<5	<5	<5	<5	<5	<5	<5	<5
2365	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
2366	<5	<5	<5	<5	<5	<5	<5	<5
2375	-----	-----	-----	-----	-----	-----	-----	-----
2379	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not detected	Not detected	Not detected	Not analyzed
2380	-----	-----	-----	-----	<5	<5	<5	-----
2386	<5	<5	<5	<5	<5	<5	<5	-----
2390	-----	-----	-----	-----	-----	-----	-----	-----
2459	-----	-----	-----	-----	-----	-----	-----	-----
2481	-----	-----	-----	-----	Not detected	Not detected	-----	-----
2488	-----	-----	-----	-----	-----	-----	-----	-----
2532	-----	-----	-----	-----	Not Detected	Not Detected	Not Detected	Not Detected
2590	-----	-----	-----	-----	-----	-----	-----	-----
2826	-----	-----	-----	-----	-----	-----	-----	-----
2917	not detected	not detected	not analyzed	not detected	not detected	not detected	not detected	not analyzed
3001	-----	-----	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----	-----	-----
3172	< 5	< 5	-----	-----	< 5	< 5	< 5	< 5
3197	-----	<10	-----	<10	<10	<10	<10	<10
3228	-----	-----	-----	-----	-----	-----	-----	-----

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

sample #22526

lab	TBEP	TBP	TiBP	TCP	TDCPP	TPP	IPTPP
110	-----	-----	-----	-----	< 5 mg/kg	< 5 mg/kg	-----
623	not detected	not detected	not analyzed	not detected	not detected	not detected	not analyzed
2115	-----	-----	-----	-----	-----	-----	-----
2232	-----	-----	-----	-----	-----	-----	-----
2247	Not Detected	Not Detected	Not analyzed	Not Detected	Not Detected	Not Detected	Not Detected
2250	-----	-----	-----	-----	-----	-----	-----
2265	< 1	< 1	-----	-----	< 1	< 1	-----
2297	ND	ND	ND	ND	ND	ND	ND
2310	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2320	-----	-----	-----	-----	Not Detected	-----	-----
2358	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2363	<5	<5	<5	<5	<5	<5	<5
2365	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
2366	<5	<5	<5	<5	<5	<5	<5
2375	-----	-----	-----	-----	-----	-----	-----
2379	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not detected	Not detected	Not detected
2380	-----	-----	-----	-----	<5	<5	-----
2386	<5	<5	<5	<5	<5	<5	-----
2390	-----	-----	-----	-----	-----	-----	-----
2459	-----	-----	-----	-----	-----	-----	-----
2481	-----	-----	-----	-----	Not detected	-----	-----
2488	-----	-----	-----	-----	-----	-----	-----
2532	-----	-----	-----	-----	Not Detected	Not Detected	Not Detected
2590	-----	-----	-----	-----	-----	-----	-----
2826	-----	-----	-----	-----	-----	-----	-----
2917	not detected	not detected	not analyzed	not detected	not detected	not detected	not analyzed
3001	-----	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----	-----
3172	< 5	< 5	-----	-----	< 5	< 5	< 5
3197	-----	<10	-----	<10	<10	<10	<10
3228	-----	-----	-----	-----	-----	-----	-----

APPENDIX 3 Analytical details

lab	ISO17025 accredited	sample preparation	intake (g)	release technique	release/extract solvent	extraction time (min)	extraction temp (°C)
110	Yes	Further grinded	0.2 g	Ultrasonic	Toluene	60 minutes	60°C
623	Yes	Further cut	1	Ultrasonic	ethylacetate : hexane	60	50
2115	No	Used as received	1 g	Ultrasonic	Acetone	60 min	40°C
2232	Yes	Used as received	1g	Ultrasonic	acetone	40	40°C
2247	---	---		---			
2250	Yes	Used as received	0,1 g	Ultrasonic	THF/MeOH	60 min	60°C
2265	No	Used as received	1g	Ultrasonic	Toluene	60min	60°C
2297	No	Used as received	0.2-1.0	Ultrasonic	toluene	1hr	60
2310	Yes	Further cut	1gram	Ultrasonic	Ethyl acetate:Hexane(1:1)	1 hour	50°C
2320	No	Further cut	0.5g	Ultrasonic	Ethyl acetate: n-hexane(1:1)	60min	50°C
2358	Yes	Used as received	0.5 gr	Ultrasonic	Ethyl acetate/Hexane (1:1)	60 minutes	50 °C
2363	Yes	Further grinded	0.5g	Ultrasonic	Toluene	60mins	60°C
2365	No	Used as received	about 0.3g	Ultrasonic	toluene	60min	60°C
2366	No	Further cut	0.3	Ultrasonic	ethyl acetate : Hexane 1:1(v/v)	60	50
2375	Yes	Further cut	0.5	Ultrasonic	Toluene	60 min	60°C
2379	No	Further cut	1 g	Ultrasonic	EA: Hexane 1 : 1	60 min	50 C
2380	Yes	Used as received	1.0 g	Ultrasonic	Ethyl acetate : n-hexane (1:1)	60 Minute	50 °C
2386	Yes	Used as received	1	Ultrasonic	Ethylacetat/n-Hexan	60	50
2390	---	---		---			
2459	No	Used as received	1.0g	Ultrasonic	Acetone	40 + 20 min	Room temp
2481	Yes	Used as received	0.5 g	Ultrasonic	Toluene	1h	60°C
2488	Yes	Used as received		Ultrasonic	Acetone		
2532	Yes	Further cut	0.2g	Ultrasonic	THF:ACN:Water	90 minutes	70 °C
2590	Yes	Used as received	0.5	Soxhlet	toluene:acetone	360	N/A
2826	Yes	Used as received	1 g	Ultrasonic	Acetone	60 mins	40
2917	No	Used as received	0.1 g	Ultrasonic	1. 3 mL THF 2. 2 mL ACN	1. 30 min THF 2. 30 min ACN	70°C
3001	---	---		---			
3163	---	---		---			
3172	Yes	Further cut		---	Toluene/Aceton 1:1		
3197	Yes	Further cut	0,2 g	Ultrasonic	THF/ACN	30 + 30 min	70 C
3228	---	---		---			

APPENDIX 4

Number of participants per country

1 lab in BANGLADESH

1 lab in FRANCE

4 labs in GERMANY

2 labs in HONG KONG

3 labs in INDIA

1 lab in INDONESIA

3 labs in ITALY

5 labs in P.R. of CHINA

2 labs in PAKISTAN

1 lab in SINGAPORE

1 lab in SRI LANKA

1 lab in THAILAND

1 lab in THE NETHERLANDS

4 labs in TURKEY

1 lab in U.S.A.

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
E	= calculation difference between reported test result and result calculated by iis
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

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4   ISO13528:05
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7   P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
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9   Analytical Methods Committee, Technical Brief, No 4, January 2001
10   P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
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