



Institute for  
Interlaboratory Studies

# Results of Proficiency Test Total Phosphorus Flame Retardants in Polymers March 2023

**Organized by:** Institute for Interlaboratory Studies  
Spijkenisse, the Netherlands

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## 1 INTRODUCTION

Organophosphate esters (OPs) are widely used as flame retardants in various consumer and industrial products, such as plastics, electronic equipment, furniture, textiles and building materials. However, production and use has been in decline since the 1980s, when Tris(2-chloro-ethyl) phosphate (TCEP) has been progressively replaced by other flame retardants. There is evidence that TCEP is a carcinogenic, mutagenic and toxic substance for children and therefore banned in toys.

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 2022/2023 it was decided to continue the proficiency test for the determination of Total Phosphorus Flame Retardants in Polymers.

In this interlaboratory study 28 laboratories in 13 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](http://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 of 3 grams each labelled #23530 and #23531 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](http://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 black foam blocks positive on some Phosphorus Flame Retardants was selected. After homogenization 50 small plastic bags were filled with approximately 3 grams each and labelled #23530.

The homogeneity of the subsamples was checked by determination of TCEP using an in house test method on 8 stratified randomly selected subsamples.

	TCEP in mg/kg
sample #23530-1	1022
sample #23530-2	987
sample #23530-3	1020
sample #23530-4	941
sample #23530-5	1001
sample #23530-6	1028
sample #23530-7	1058
sample #23530-8	1052

Table 1: homogeneity test results of subsamples #23530

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

	TCEP in mg/kg
r (observed)	105
reference method	iis memo 2102
0.3 x R (reference method)	128

Table 2: evaluation of the repeatability of subsamples #23530

The calculated repeatability is in agreement with 0.3 times the reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of green PVC pieces, positive on TCEP and TDCPP, was selected. After homogenization 50 small plastic bags were filled with approximately 3 grams each and labelled #23531.

The batch for sample #23531 was used in a previous proficiency test on Phosphorus Flame Retardants in Polymers as sample #19500 in iis19P01. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one polymer sample labelled #23530 and one polymer sample labelled #23531 were sent on February 22, 2023.

## 2.5 ANALYZES

The participants were requested to determine on samples #23530 and #23531:

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

TDCPP – 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/](http://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](http://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/](http://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 or ASTM 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:

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

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

In this proficiency test no problems were encountered with the dispatch of the samples. One participant reported test results after the final reporting date and five other participants did not report any test results. Not all participants were able to report all components requested. In total 23 participants reported 130 numerical test results. Observed were 4 outlying test results, which is 3.1%. In proficiency tests 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. A few 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. In 2021 it was decided to use the iis PT data gathered from 2014 up to and including 2021 to estimate a more realistic target reproducibility and this investigation is described in iis memo 2102. The target reproducibility was calculated from the relative standard deviation of  $15\% * PT \text{ mean} * 2.8$  (iis memo 2102). This was used for the evaluation of the test results in this PT.

#### **sample #23530**

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

TCPP: This determination was problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the target reproducibility as derived from iis memo 2102.

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



**TPP:** This determination was problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the target reproducibility as derived from iis memo 2102.

The participants agreed on a concentration near or below the limit of detection for all other components mentioned in paragraph 2.5. Therefore, no z-scores are calculated for these components. The reported test results are given in appendix 2.

#### **sample #23531**

**TCEP:** This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the target reproducibility as derived from iis memo 2102.

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

The participants agreed on a concentration near or below the limit of detection for all other components mentioned in paragraph 2.5. Therefore, no z-scores are calculated for these components. The reported test results are given in appendix 2.

## **4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES**

A comparison has been made between the reproducibility as declared by the reference test method and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility ( $2.8 \cdot$  standard deviation) and the target reproducibility derived from the reference method are presented in the next table.

Component	unit	n	average	$2.8 \cdot$ sd	R(target)
TCEP	mg/kg	21	817	242	343
T CPP	mg/kg	22	221	110	93
TDCPP	mg/kg	22	9635	3208	4047
TPP	mg/kg	18	94	73	40

Table 3: reproducibilities of components on sample #23530

Component	unit	n	average	$2.8 \cdot$ sd	R(target)
TCEP	mg/kg	22	411	180	173
TDCPP	mg/kg	21	292	144	123

Table 4: reproducibilities of components on sample #23531

Without further statistical calculations it can be concluded that for some Phosphorus Flame Retardants present in the samples there is a good compliance of the group of participants with the target, see also the discussion in paragraphs 4.1 and 5.

#### 4.3 COMPARISON OF THE PROFICIENCY TEST OF MARCH 2023 WITH PREVIOUS PTS

	March 2023	March 2022	February 2021	February 2020	February 2019
Number of reporting laboratories	23	27	36	35	29
Number of test results	130	77	174	169	92
Number of statistical outliers	4	5	16	16	6
Percentage of statistical outliers	3.1%	6.5%	9.2%	9.5%	6.5%

Table 5: comparison with previous proficiency tests

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

The performance of the determinations of the proficiency test was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTs, see next table.

Component	March 2023	March 2022	February 2021	February 2020	2019 – 2014	Target iis memo 2021
TBP	---	---	---	11%	---	15%
TiBP	---	---	11%	---	---	15%
TCP	---	---	21%	16%	12%	15%
TCEP	11-16%	20-28%	11%	11%	9-23%	15%
T CPP	18%	27%	18%	18%	13-19%	15%
TDCPP	12-18%	---	13-17%	11%	13-19%	15%
TPP	28%	---	---	---	14-17%	15%

Table 6: development of the uncertainties over the years

The uncertainties observed in this PT are comparable to the uncertainties observed in previous iis PTs. The uncertainty for TPP is large in comparison with earlier iis PTs. Probably due to low amount present in the sample.

Sample #23531 was used in a previous PT as sample #19500 in iis19P01. The averages found in both PTs are comparable. The calculated reproducibility for TDCPP in this PT has been improved compared to the PT of 2019, see next table.

Component	unit	sample #23531			sample #19500		
		n	average	R(calc)	n	average	R(calc)
TCEP	mg/kg	22	411	180	26	437	184
TDCPP	mg/kg	21	292	144	24	307	167

Table 7: comparison of sample #23531 with sample #19500

#### 4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT some analytical details were requested which are given in appendix 3. Based on the answers given by the participants the following can be summarized:

- Eighteen participants mentioned to be accredited for the determination of Phosphorus Flame Retardants in polymers.
- Prior to analysis the samples were further cut or further grinded by eighteen participants, five participants used the samples as received.
- The amount of sample intake varied between 0.1 and 2 grams, thirteen participants used an intake between 0.5 to 1 gram and about ten participants used less than 0.5 grams.
- Almost all participants reported to have used ultrasonic as technique to release/extract the analytes.
- Nine participants used Toluene or a mixture with Toluene as release solvent, six participants used a combination of Hexane with Ethyl Acetate and four participants used THF or a THF mixture with Acetonitrile or Methanol and one participant used Acetone only.
- A vast majority (20 participants) used an extraction time of 60 minutes. The extraction temperature differs between room temperature and 100 °C. Ten participants used an extraction temperature between 40 and 50 °C while nine participants used an extraction temperature of 60 °C.

The influence of these analytical details could not be determined because the group of participants is too small for further sub analyzes.

## 5 DISCUSSION

With both PT samples the participants have no problem with the TCEP determination. TCEP has been under investigation for a long time. TCEP was comprehensively evaluated under the EU existing substances regulation (EEC) (EC) 1907/2006 REACH. It is classified under Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures as a carcinogenic, mutagenic and toxic substance. Furthermore, the limits have been set under Regulation 2014/79/EU amending Appendix C of Annex II to Directive 2009/48/EC and of the Council on the safety of toys, as regards TCEP, TCPP and TDCP (these should not be present with a detection limit of 5 mg/kg).

Furthermore, the EU released version 3 of a Screening report for TCEP, TCPP and TDCP in April 2018 and a Regulatory strategy for flame retardants from ECHA in March 2023. There is evidence that TCEP is hazardous for children and data is now gathered for adults. In the future it may also be banned for use in products for adults.

A general overview of TCEP, TCPP and TDCP requirements on articles in the EU and the USA is given in next table.

All participants would have rejected the samples based on the limit of 5 mg/kg for toys intended for children or intended to be put in the mouth but would have accepted it for all other applications. The exception is component TDCPP in sample #23530 which would be rejected by all participants.

Region	Scope	Reference	Limit
EU	All articles	REACH candidate list	TCEP: 0.1% by weight
	Toys intended for children under 36 months and in toys intended to be put in the mouth	Toy Directive 2009/48/EC	TCEP, TCPP and TDCP: 5 mg/kg (each)
USA	Children's product and residential upholstered furniture	Various US states law	TCEP, TCPP and TDCP: 0.1% by weight (each)

Table 8: Limits for Phosphorus Flame Retardants

## 6 CONCLUSION

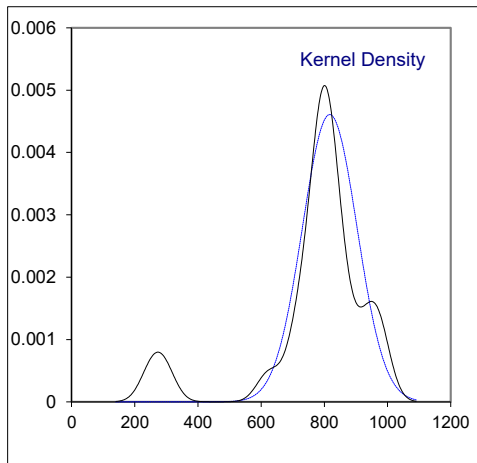
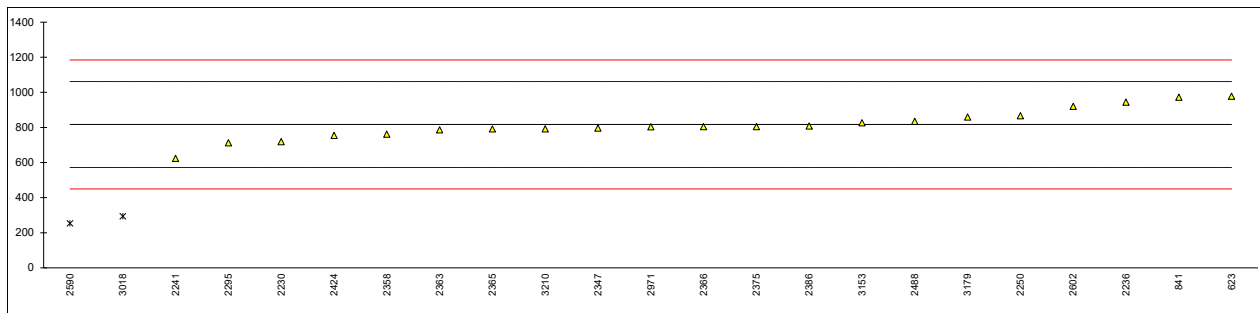
Each laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

**APPENDIX 1**

Determination of Tris(2-chloroethyl) Phosphate (TCEP) CAS no.115-96-8 in sample #23530; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	In house	977.654		1.31	
841	In house	971.85		1.26	
1099		----		----	
2115		----		----	
2230	ISO17881-2	718		-0.81	
2236	In house	944.39		1.04	
2241	In house	623.939	C	-1.58	first reported 300.222
2250	In house	866.3		0.40	
2265		----		----	
2295	In house	712		-0.86	
2347	In house	795.9		-0.17	
2358	ISO17881-2	761.71		-0.45	
2363	In house	786.0		-0.25	
2365	In house	791		-0.21	
2366	In house	805		-0.10	
2375	ISO17881-2	805		-0.10	
2386	In house	807.66		-0.08	
2424	In house	753.97		-0.51	
2426		----		----	
2488	In house	834.36		0.14	
2590	In house	252.8	C,R(0.01)	-4.60	first reported 501.584
2602	In house	921		0.85	
2971	In house	803.4		-0.11	
3018	In house	293.37	R(0.01)	-4.27	
3153	In house	826.3		0.08	
3163		----		----	
3179	ISO17881-2	859		0.34	
3210	In house	791.78		-0.21	

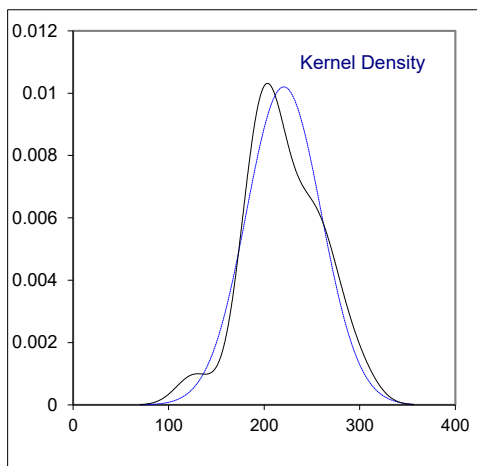
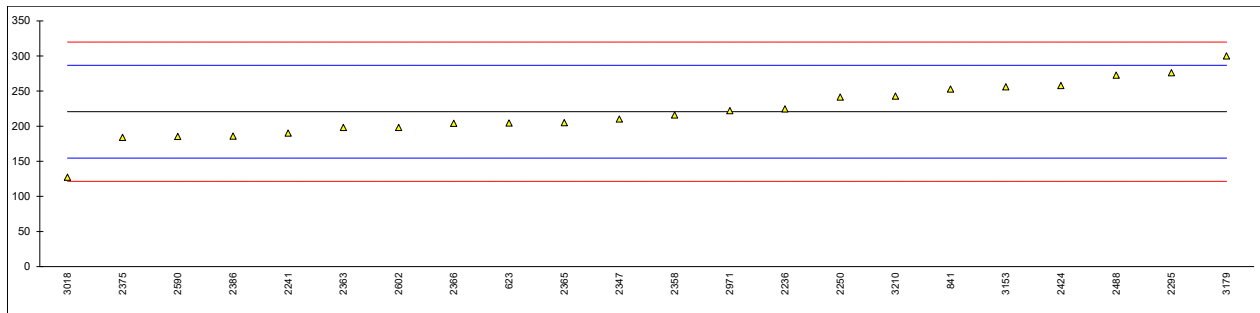
normality OK  
n 21  
outliers 2  
mean (n) 816.963  
st.dev. (n) 86.5510 RSD=11%  
R(calc.) 242.343  
st.dev.(iis memo 2102) 122.5444  
R(iis memo 2102) 343.124  
Compare:  
R(ISO17881-2:16) 233.324



Determination of Tris(1-chloro-2-propyl) Phosphate (TCPP) CAS no. 13674-84-5 in sample #23530; results in mg/kg

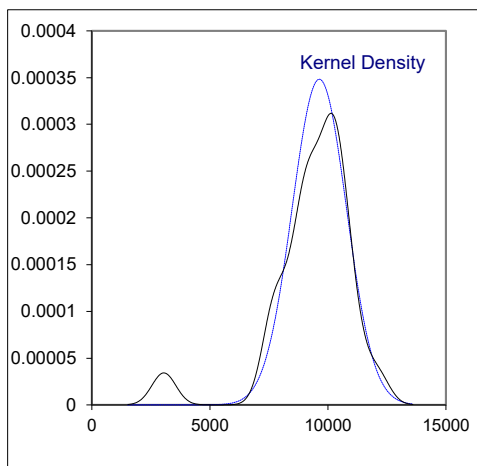
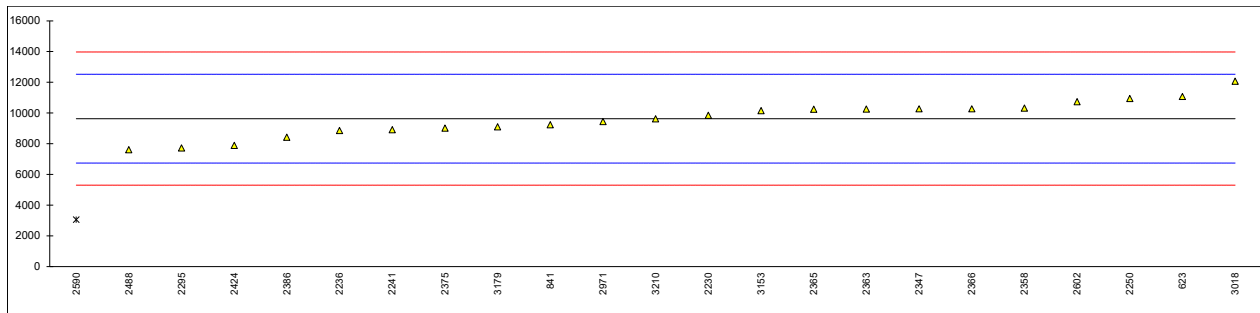
lab	method	value	mark	z(targ)	remarks
623	In house	204.509		-0.49	
841	In house	252.84		0.97	
1099		----		----	
2115		----		----	
2230		----		----	
2236	In house	224.39		0.11	
2241	In house	190.245		-0.92	
2250	In house	241.3		0.62	
2265		----		----	
2295	In house	276		1.67	
2347	In house	210.0		-0.32	
2358	ISO17881-2	216.02		-0.14	
2363	In house	197.9		-0.69	
2365	In house	205		-0.47	
2366	In house	204		-0.50	
2375	ISO17881-2	184		-1.11	
2386	In house	185.68		-1.06	
2424	In house	257.94		1.13	
2426		----		----	
2488	In house	272.77		1.58	
2590	In house	185.2	C	-1.07	first reported 94.777
2602	In house	198		-0.68	
2971	In house	222.1		0.04	
3018	In house	127.12		-2.83	
3153	In house	256.0		1.07	
3163		----		----	
3179	ISO17881-2	299.9		2.40	
3210	In house	242.93		0.67	

normality OK  
 n 22  
 outliers 0  
 mean (n) 220.629  
 st.dev. (n) 39.1087 RSD=18%  
 R(calc.) 109.504  
 st.dev.(iis memo 2102) 33.0944  
 R(iis memo 2102) 92.664  
 Compare:  
 R(ISO17881-2:16) 63.012



Determination of Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP) CAS No. 13674-87-8 in sample #23530; results in mg/kg

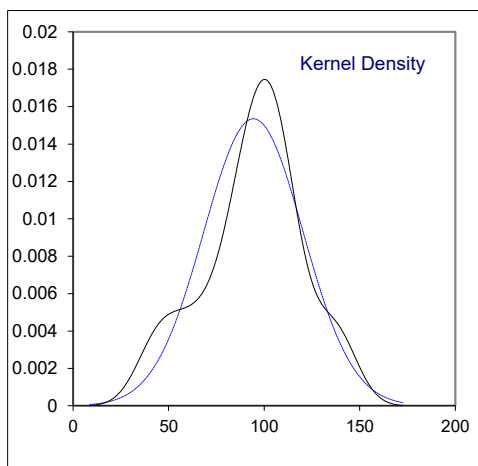
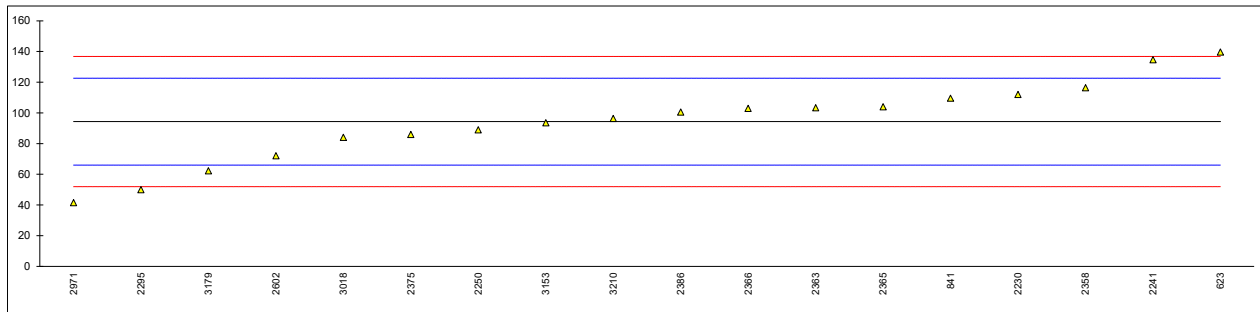
lab	method	value	mark	z(targ)	remarks
623	In house	11073.424		1.00	
841	In house	9235.57		-0.28	
1099		-----		-----	
2115		-----		-----	
2230	ISO17881-2	9840		0.14	
2236	In house	8858.53		-0.54	
2241	In house	8904.338	C	-0.51	first reported 14056.441
2250	In house	10945		0.91	
2265		-----		-----	
2295	In house	7717		-1.33	
2347	In house	10266.6		0.44	
2358	ISO17881-2	10317.38		0.47	
2363	In house	10250.0		0.43	
2365	In house	10237		0.42	
2366	In house	10274		0.44	
2375	ISO17881-2	9012		-0.43	
2386	In house	8424.49		-0.84	
2424	In house	7886.90		-1.21	
2426		-----		-----	
2488	In house	7610.53		-1.40	
2590	In house	3054.2	C,R(0.01)	-4.55	first reported 2299.043
2602	In house	10735		0.76	
2971	In house	9438.3		-0.14	
3018	In house	12071.0		1.69	
3153	In house	10150.0		0.36	
3163		-----		-----	
3179	ISO17881-2	9097.3		-0.37	
3210	In house	9620.27		-0.01	
normality		OK			
n		22			
outliers		1			
mean (n)		9634.755			
st.dev. (n)		1145.6104	RSD=12%		
R(calc.)		3207.709			
st.dev. (iis memo 2102)		1445.2132			
R(iis memo 2102)		4046.597			
Compare:					
R(ISO17881-2:16)		2751.686			



Determination of Triphenyl Phosphate (TPP) CAS No. 115-86-6 in sample #23530; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	In house	139.665		3.20	
841	In house	109.6		1.08	
1099		----		----	
2115		----		----	
2230	ISO17881-2	112		1.25	
2236	In house	Not Analyzed		----	
2241	In house	134.579		2.84	
2250	In house	89.0		-0.38	
2265		----		----	
2295	In house	50	C	-3.13	first reported 20
2347	In house	out of Capability		----	
2358	ISO17881-2	116.47		1.56	
2363	In house	103.4		0.64	
2365	In house	104		0.68	
2366	In house	103		0.61	
2375	ISO17881-2	86		-0.59	
2386	In house	100.59		0.44	
2424		----		----	
2426		----		----	
2488		----		----	
2590		----		----	
2602	In house	72		-1.58	
2971	In house	41.6		-3.73	
3018	In house	84.075		-0.73	
3153	In house	93.5		-0.06	
3163		----		----	
3179	ISO17881-2	62.3		-2.26	
3210	In house	96.44		0.15	

normality OK  
 n 18  
 outliers 0  
 mean (n) 94.345  
 st.dev. (n) 25.9855 RSD=28%  
 R(calc.) 72.759  
 st.dev. (iis memo 2102) 14.1518  
 R(iis memo 2102) 39.625  
 Compare:  
 R(ISO17881-2:16) 26.945

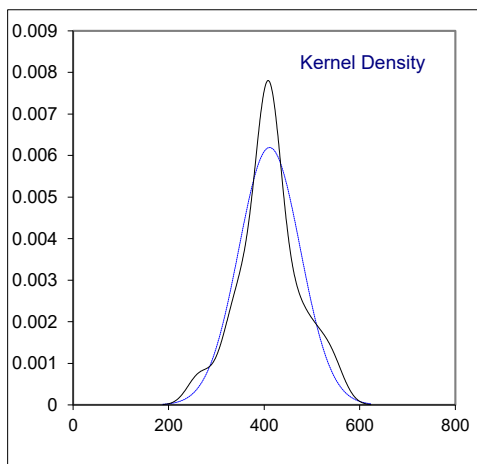
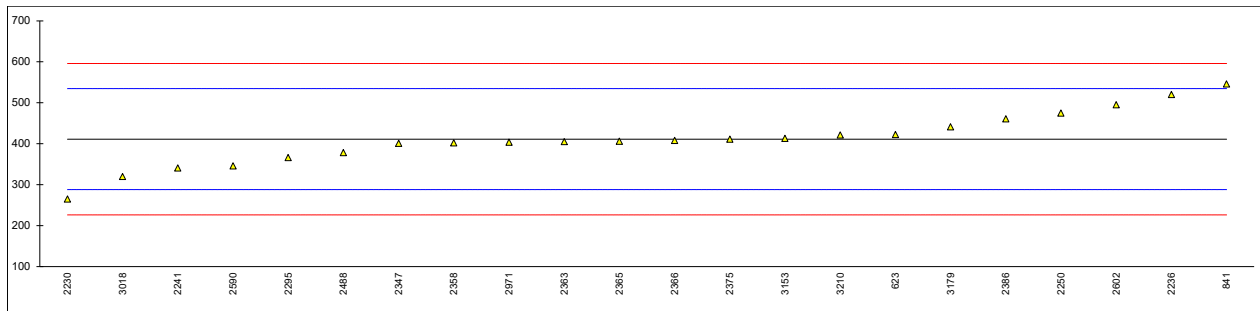




Determination of Tris(2-chloroethyl) Phosphate (TCEP) CAS no.115-96-8 in sample #23531; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	In house	422.397	C	0.18	first reported 572.823
841	In house	546.18		2.19	
1099		----		----	
2115		----		----	
2230	ISO17881-2	265		-2.37	
2236	In house	520		1.76	
2241	In house	340.892	C	-1.14	first reported 162.024
2250	In house	474.7		1.03	
2265		----		----	
2295	In house	366		-0.73	
2347	In house	401.0		-0.17	
2358	ISO17881-2	402.09		-0.15	
2363	In house	405.0		-0.10	
2365	In house	406		-0.08	
2366	In house	408		-0.05	
2375	ISO17881-2	411		0.00	
2386	In house	460.71		0.80	
2424		----		----	
2426		----		----	
2488	In house	378.00		-0.54	
2590	In house	346.000		-1.06	
2602	In house	495		1.36	
2971	In house	403.5		-0.13	
3018	In house	319.71		-1.48	
3153	In house	413.0		0.03	
3163		----		----	
3179	ISO17881-2	441.2		0.49	
3210	In house	421.39		0.16	

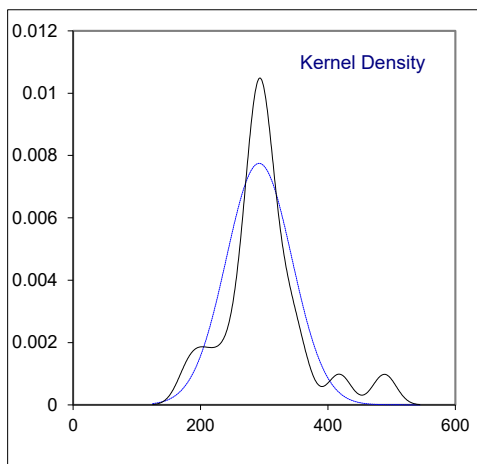
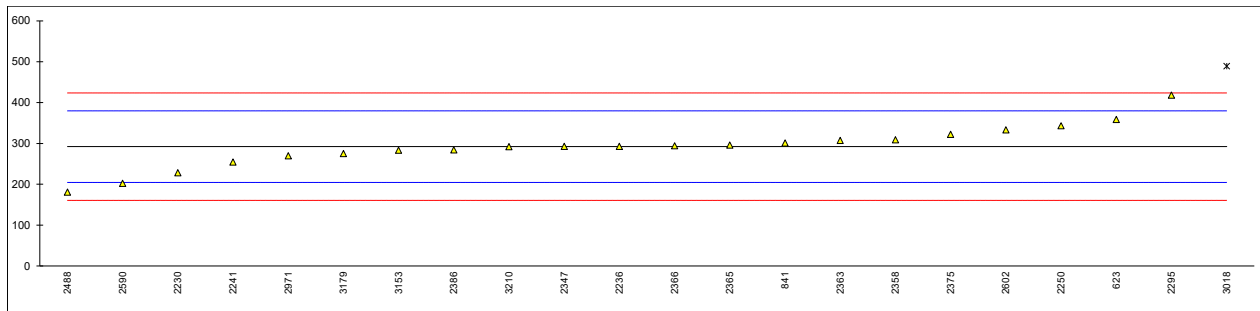
normality OK  
 n 22  
 outliers 0  
 mean (n) 411.217  
 st.dev. (n) 64.4027 RSD=16%  
 R(calc.) 180.328  
 st.dev.(iis memo 2102) 61.6825  
 R(iis memo 2102) 172.711  
 Compare:  
 R(ISO17881-2:16) 117.444



Determination of Tris(1,3-dichloro-2-propyl) Phosphate (TDCPP) CAS No. 13674-87-8 in sample #23531; results in mg/kg

lab	method	value	mark	z(targ)	remarks
623	In house	358.546	C	1.52	first reported 468.221
841	In house	300.97		0.20	
1099		----		----	
2115		----		----	
2230	ISO17881-2	228		-1.46	
2236	In house	292.72		0.01	
2241	In house	254.122	C	-0.87	first reported 438.682
2250	In house	343.0		1.16	
2265		----		----	
2295	In house	418	C	2.87	first reported 185
2347	In house	292.6		0.01	
2358	ISO17881-2	308.71		0.38	
2363	In house	307.0		0.34	
2365	In house	296		0.09	
2366	In house	294		0.04	
2375	ISO17881-2	322		0.68	
2386	In house	283.89		-0.19	
2424		----		----	
2426		----		----	
2488	In house	180.50		-2.55	
2590	In house	202.416		-2.05	
2602	In house	333		0.93	
2971	In house	269.3		-0.52	
3018	In house	488.83	R(0.05)	4.49	
3153	In house	283.2		-0.20	
3163		----		----	
3179	ISO17881-2	275.1		-0.39	
3210	In house	291.88		-0.01	

normality suspect  
 n 21  
 outliers 1  
 mean (n) 292.141  
 st.dev. (n) 51.4898 RSD=18%  
 R(calc.) 144.171  
 st.dev.(iis memo 2102) 43.8211  
 R(iis memo 2102) 122.699  
 Compare:  
 R(ISO17881-2:16) 83.435



**APPENDIX 2** Other reported Total 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
TPP	= Triphenyl Phosphate, CAS No. 115-86-6
IPTPP	= Isopropylated triphenyl Phosphate, CAS No. 68937-41-7

## sample #23530

lab	TBEP	TBP	TiBP	TCP	IPTPP
623	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
841	<5	<5	<5	no cap	no cap
1099	----	----	----	----	----
2115	----	----	----	----	----
2230	----	----	----	----	----
2236	Not Analyzed	Not Analyzed	Not Analyzed	Not Analyzed	Not Analyzed
2241	----	----	----	----	----
2250	< 5	< 5	< 5	< 5	----
2265	----	----	----	----	----
2295	----	----	----	----	----
2347	out of Capability	out of Capability	out of Capability	out of Capability	out of Capability
2358	not detected	not detected	not detected	not detected	not detected
2363	<5	<5	<5	<5	<5
2365	<5	<5	<5	<5	<5
2366	----	----	----	----	----
2375	----	----	----	----	----
2386	< 5	< 5	< 5	< 5	not analysed
2424	----	----	----	----	----
2426	----	----	----	----	----
2488	----	----	----	----	----
2590	----	----	----	----	----
2602	----	----	----	----	----
2971	----	----	----	----	----
3018	<4	<1	<4	<5	----
3153	Not detected	Not detected	Not detected	Not detected	Not detected
3163	----	----	----	----	----
3179	<5	<5	not tested	<5	<100
3210	Not detected	----	----	Not detected	----

## Other reported Total Phosphorus Flame Retardants; results in mg/kg (continued)

sample #23531

lab	TBEP	TBP	TiBP	TCP	TCPP	TPP	IPTPP
623	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
841	<5	<5	<5	no cap	<5	<5	no cap
1099	----	----	----	----	----	----	----
2115	----	----	----	----	----	----	----
2230	----	----	----	----	----	----	----
2236	Not Analyzed	Not Analyzed	Not Analyzed	Not Analyzed	Not detected	Not Analyzed	Not Analyzed
2241	----	----	----	----	<5.0	<5.0	----
2250	< 5	< 5	< 5	< 5	< 5	< 5	----
2265	----	----	----	----	----	----	----
2295	----	----	----	----	----	----	----
2347	out of Capability	out of Capability	out of Capability	out of Capability	<5	out of Capability	out of Capability
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	<5	<5	<5	<5	<5	<5
2366	----	----	----	----	----	----	----
2375	----	----	----	----	----	----	----
2386	< 5	< 5	< 5	< 5	< 5	< 5	not analysed
2424	----	----	----	----	----	----	----
2426	----	----	----	----	----	----	----
2488	----	----	----	----	----	----	----
2590	----	----	----	----	----	----	----
2602	----	----	----	----	not detected	not detected	----
2971	----	----	----	----	----	----	----
3018	<1	<1	<1	<5	<1	<1	----
3153	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
3163	----	----	----	----	----	----	----
3179	<5	<5	not tested	<5	<5	<5	<100
3210	Not detected	----	----	Not detected	Not detected	Not detected	----

## APPENDIX 3 Analytical Details

lab	ISO17025 accredited	sample preparation	intake (g)	release technique	release/extract solvent	extraction time (min)	extraction temp (°C)
623	Yes	Further cut	1 gram	Ultrasonic	Ethyl acetate : n hexane	60	50
841	Yes	Further cut	1 g	Ultrasonic	Ethyl acetate:n-Hexane	60	50
1099	---	---		---			
2115	---	---		---			
2230	Yes	Further cut	1g	Ultrasonic	acetone	60	40
2236	Yes	Further cut	0.5012/0.1025 and 0.5008/0.110	Ultrasonic	Toluene	60	60
2241	Yes	Further cut	0.3g	Ultrasonic	Dichloromethane	60mins	room temperature
2250	Yes	Used as received	0,3 g	Ultrasonic	THF/MeOH	60 min	60°C
2265	---	---		---			
2295	Yes	Further cut	1 gram	Ultrasonic	Methanol	60 minutes	app. 20 C
2347	No	Further cut	0.3g	Ultrasonic	ethyl acetate:hexane 1:1	60min	50
2358	Yes	Further cut	1.0g	Ultrasonic	Ethyl acetate: Hexane (1:1)	60	50
2363	Yes	Further grinded	2g	Ultrasonic	Toluene	60mins	60°C
2365	Yes	Further cut	0.3 g	Ultrasonic	Toluene	60 min	60°C
2366	No	Further cut		Ultrasonic	EA : hexane=1 : 1	60min	50
2375	Yes	Further cut	0,5 gram	Ultrasonic	Toluene	60 min	60 C
2386	Yes	Used as received	1 g	Ultrasonic	Ethylacetate/ n-Hexan 1/1	60 min	50°C
2424	No	---	0.1	Ultrasonic	1:1:1 acetone:MTBE:Hexane	180	60
2426	---	---		---			
2488	Yes	Further cut	0,5 g	Ultrasonic	Acetonitrile	1 hour	40°C
2590	No	Further cut	0.5 g	Ultrasonic	toluene:DCM, acetone:DCM	360 min	Not applicable
2602	Yes	Further cut	0,1	Ultrasonic	acetonitrile, diluted with toluene after extraction	60	40
2971	Yes	Used as received	0.3g	Ultrasonic	Methanol	60	60
3018	Yes	Used as received	0,5 g	Ultrasonic	toluene	60 min	approx.45°C
3153	No	Further cut	0.3 gram	Ultrasonic	THF and ACN	30 minutes + 30 minutes	60°C
3163	---	---		---			
3179	Yes	#23530: 0,5g (further cut) #23531: 0,15g (used as received)	#23530: 0,5g #23531: 0,15g	heating block	toluene	120min	100°C
3210	Yes	Further cut	0.5	Ultrasonic	Toluene	60	60

## **APPENDIX 4**

### **Number of participants per country**

1 lab in FRANCE  
6 labs in GERMANY  
2 labs in HONG KONG  
1 lab in INDONESIA  
2 labs in ITALY  
5 labs in P.R. of CHINA  
1 lab in PAKISTAN  
1 lab in POLAND  
1 lab in TAIWAN  
1 lab in THE NETHERLANDS  
3 labs in TURKEY  
2 labs in U.S.A.  
2 labs in VIETNAM

## APPENDIX 5

### Abbreviations

C	= final test result after checking of first reported suspect test result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
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
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

### Literature

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
- 2 ISO5725:86
- 3 ISO5725 parts 1-6:94
- 4 ISO13528:05
- 5 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
- 6 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
- 7 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
- 8 J.N. Miller, Analyst, 118, 455, (1993)
- 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)
- 11 W. Horwitz and R. Albert, J. AOAC Int, 79.3, 589-621, (1996)
- 12 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
- 13 iis memo 2102: precision data of Phosphorus Flame Retardants in polymers