Results of Proficiency Test
Phosphorus Flame Retardants, total
in Polymers
February 2020

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

1 INTRODUCTION 3

2 SET UP 3

2.1 ACCREDITATION 3

2.2 PROTOCOL 3

2.3 CONFIDENTIALITY STATEMENT 4

2.4 SAMPLES 4

2.5 ANALYZES 5

3 RESULTS 6

3.1 STATISTICS 6

3.2 GRAPHICS 7

3.3 Z-SCORES 7

4 EVALUATION 8

4.1 EVALUATION PER SAMPLE AND PER COMPONENT 8

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES 10

4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2020 AGAINST PREVIOUS PTS 10

4.4 EVALUATION ANALYTICAL DETAILS 11

5 DISCUSSION 12

6 CONCLUSION 12

Appendices:

1. Data, statistical and graphic results 13
2. Determination of other Phosphorus Flame Retardants 19
3. Analytical details 21
4. Number of participants per country 23
5. Abbreviations and literature 24

1 INTRODUCTION

Organophosphate esters (OPs) are widely used as flame retardants in various consumer and industrial products, such as plastics, electronic equipment, furniture, textiles and building materials. However, production and use has been in decline since the 1980s, when Tris(2-chloro-ethyl) phosphate (TCEP) has been progressively replaced by other flame retardants. TCEP was comprehensively evaluated under the EU existing substances regulation (EEC) 793/93 in 2009. TCEP is classified under Regulation (EC) No 1272/2008 as a carcinogenic, mutagenic and toxic substance. Furthermore, the limits have been set under Regulation 2014/79/EU for TCEP, TCPP and TDCP (5 mg/kg from 21 December 2015).

Since 2014, the Institute for Interlaboratory Studies organizes a proficiency scheme for the determination of Phosphorus Flame Retardants in polymers every year. During the annual proficiency testing program 2019/2020, it was decided to continue the PT for the analysis of Phosphorus Flame retardants. In this interlaboratory study, 37 laboratories from 17 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the results of the 2020 proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send two polymer samples both positive on Phosphorus Flame retardants of 3 grams each and labelled #20500 and #20501 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/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 organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

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

2.4 SAMPLES

The first batch of brown colored PVC blocks was artificially fortified to be positive for TCEP, TCPP and TDCPP. The batch was divided over 60 plastic bags, approximately 3 grams each and labelled #20500. The homogeneity of subsamples #20500 was checked by determination of TCEP and TDCPP by an in-house test method on eight stratified randomly selected subsamples.

	TCEP in mg/kg	TDCPP in mg/kg
Sample #20500-1	807	487
Sample #20500-2	812	483
Sample #20500-3	830	504
Sample #20500-4	806	515
Sample #20500-5	793	484
Sample #20500-6	836	508
Sample #20500-7	826	504
Sample #20500-8	818	512

Table 1: homogeneity test results of subsamples #20500

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

	TCEP in mg/kg	TDCPP in mg/kg
r (observed)	40.0	36.3
reference test method	EN71-11:05	EN71-11:05
r (ref. test method)	59.4	36.4

Table 2: evaluation of the repeatabilities of subsamples #20500

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

The second batch of green colored PVC rings was artificially fortified to be positive for TBP, TCP and TCEP. The batch was divided over 60 plastic bags, approximately 3 grams each and labelled #20501. The homogeneity of subsamples #20501 was checked by determination of TBP and TCEP by an in-house method on eight stratified randomly selected subsamples.

	TBP in mg/kg	TCEP in mg/kg
Sample #20501-1	482	947
Sample #20501-2	466	958
Sample #20501-3	466	932
Sample #20501-4	458	894
Sample #20501-5	459	918
Sample #20501-6	461	910
Sample #20501-7	451	906
Sample #20501-8	446	888

Table 3: homogeneity test results of subsamples #20501

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

	TBP in mg/kg	TCEP in mg/kg
r (observed)	30.5	69.5
reference test method	EN71-11:05	EN71-11:05
r (ref. test method)	33.6	66.9

Table 4: evaluation of the repeatabilities of subsamples #20501

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

To each of the participating laboratories one subsample labelled #20500 and one subsample labelled #20501 of 3 grams each were sent on January 15, 2020.

2.5 ANALYZES

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

- Tri-o-cresyl phosphate (ToCP) (CAS No. 78-30-8)

ToCP and TCP were combined and evaluated as TCP, see also the discussion in paragraph 5.

Also, it was requested to report some analytical details. It was noted in the instructions of this PT to use no less than 0.5 grams per determination to ensure the homogeneity.
It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test results, but to report as much significant figures as possible. It was also requested not report 'less than' results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

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

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 or 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 reanalysis). Additional or corrected test results are used for data analysis and original test results are placed under 'Remarks' in the test result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5).

For the statistical evaluation, the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<…' or '>…' were not used in the statistical evaluation.

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

According to ISO5725 the original test results per determination were submitted to Dixon’s, Grubbs’ and/or Rosner’s outlier tests. Outliers are marked by D(0.01) for the Dixon’s test, by G(0.01) or DG(0.01) for the Grubbs’ test and by R(0.01) for the Rosner’s test. Stragglers are marked by D(0.05) for the Dixon’s test, by G(0.05) or DG(0.05) for the Grubbs’ test and by R(0.05) for the Rosner’s test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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

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

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis.

The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation of this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used. In some cases, a reproducibility based on former iis proficiency tests could be used.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.
The z-scores were calculated according to:

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

The $z_{(target)}$ scores are listed in the test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

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

4 EVALUATION

During the execution of this proficiency test no problems occurred with the dispatch of the samples. Two participants did not report any test results and six other participants reported the test results after the final reporting date. Not all laboratories were able to report all components requested. In total 35 laboratories reported 169 numerical test results. Observed were 16 outlying test results, which is 9.5%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

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

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section the reported test results are discussed per sample and per component. The test methods, which were reported to use by the laboratories were taken into account for explaining the observed differences when possible and applicable. These methods are also in the table together with the original data. The abbreviations, used in these tables, are explained in appendix 5.

Unfortunately, no standard test method is available for the determination of Phosphorus Flame retardants (e.g. TCEP, TDCPP, TCPP, TPP) in polymers. Most participating laboratories reported to use an in-house method. This consists of a preparation/extraction step and an analytical step. Some participants performed ISO17881-2, which is method for textiles. Method EN71-11 describes the analytical determination of TCEP after migration/extraction and has a precision statement for TCEP. Therefore, EN71-11 is used as reference test method for the evaluation of the test results. 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 for the evaluation of the other Phosphorus Flame Retardants.
Regretfully in EN71-11:05, 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.

The test results for TCP and ToCP were combined and evaluated as TCP, see paragraph 5 for the discussion.

Sample #20500

TCEP: The determination of this component may be problematic at the measured level of 668 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility of EN71-11:2005.

TCPP: The determination of this component may be very problematic at the measured level of 327 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the estimated target reproducibility of EN71-11:2005.

TDCPP: The determination of this component may be problematic at the measured level of 422 mg/kg. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility of EN71-11:2005.

Other components: All participants agreed on a content close to or below the limit of quantification for all other components. Therefore, no z-scores are calculated. The test results are given in appendix 2.

Sample #20501

TBP: The determination of this component may be problematic at the measured level of 456 mg/kg. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility of EN71-11:2005.

Total of TCP and ToCP: The determination of the sum of components may be very problematic at the measured level of 202 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the estimated target reproducibility of EN71-11:2005. See for more discussion paragraph 5.

TCEP: The determination of this component may be problematic at the measured level of 896 mg/kg. Five statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility of EN71-11:2005.

Other components: All participants agreed on a content close to or below the limit of quantification for all other components. Therefore, no z-scores are calculated. The test results are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

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

Component	unit	n	average	2.8 * sd	R (target)
TCEP	mg/kg	31	668	213	146
TCPP	mg/kg	28	327	166	71
TDCPP	mg/kg	28	422	132	92

Table 5: reproducibilities of components in sample #20500

Component	unit	n	average	2.8 * sd	R (target)
TBP	mg/kg	14	456	147	100
Total of TCP and ToCP	mg/kg	23	202	92	41
TCEP	mg/kg	29	896	276	196

Table 6: reproducibilities of components in sample #20501

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

4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2020 AGAINST PREVIOUS PTS

	February 2020	February 2019	February 2018	February 2017	February 2016
Number of reporting labs	35	29	44	40	31
Number of results reported	169	92	158	239	61
Number of statistical outliers	16	6	18	18	9
Percentage outliers	9.5%	6.5%	11.4%	7.5%	14.8%

Table 7: comparison with previous proficiency tests

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

The uncertainty (RSD) in the test results of all tested Phosphorus Flame Retardants, except TCP, improved or remained the same. TBP in the iis20P01 was determined for the first time.

Component	February 2020	February 2019	February 2018	February 2017	2016 - 2014	Est. EN71-11
TBP	11%	n.e.	n.e.	n.e.	n.e.	8%
TCP	16%	12%	n.e.	n.e.	n.e.	8%
TCEP	11%	15%	17%	13%	9-23%	8%
TCPP	18%	n.e.	19%	13-15%	n.e.	8%
TDCPP	11%	19%	10%	13-14%	15%	8%
TPP	n.e.	17%	14%	n.e.	n.e.	8%

Table 8: development of the uncertainties over the years

4.4 EVALUATION ANALYTICAL DETAILS

For this PT, some analytical details were requested (see appendix 3).
Of the reporting participants 66% mentioned that they are accredited for determination of P-flame retardants in polymer.
Twenty-six of the thirty-two participants mentioned that they have cut/grinded the samples before use, six other participants used the samples as received.
Twenty-two participants reported to have used a sample of 0.5 g or more, while six reported to have used a sample smaller than 0.5 g.
The majority of the participants (87%) reported to have used ultrasonic as technique to release/extract the analytes. Other techniques mentioned were Mechanical Shaking, Soxhlet extraction, Thermal Desorption and Microwave Digestion by only one participant.
Seven participants used Acetone as extraction solvent, six used Toluene or Toluene mixtures as extraction solvent, six used a combination of Acrylonitrile with THF and five used a combination of Hexane with Ethyl Acetate. The other participants used solvents such as Dichloromethane, Methanol, or Methylbenzene.

When evaluating the above differences in the execution of the test, no clear correlation was found between these test conditions and the reported test result. Please note that the number of test results is somewhat limited for in-depth analyzes.

5 DISCUSSION

Sample #20501 was made positive for Tri-o-Cresyl Phosphate (ToCP). This is the ortho-isomer of Tricresyl Phosphate (TCP). TCP is in the list of reported components with CAS no. 1330-78-5 for the mixture of isomers. Unfortunately, iis added ToCP (single isomer, CAS no. 78-30-8) to the list of reported components. One of the participants pointed iis to this. We decided to take the sum of both components and evaluated it as TCP and to correct the list of Phosphorus Flame Retardants for next year PT.

The materials used in this PT were PVC squares and PVC rings. To extract the requested components from a polymer, the extraction solvent, the extraction conditions and the contact surface area could be important variables. In previous proficiency tests on Phosphorus Flame retardants it appeared that the choice of the extraction solvent (see PT report iis14P01) and the grain size of the granulate (see PT report iis15P01) were important variables. This was mainly caused by the matrix of the samples used in these proficiency tests. This effect is less demonstrated in other polymer materials, like PVC. However, the number of data is somewhat limited to perform more in-depth analyzes.

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

6 CONCLUSION

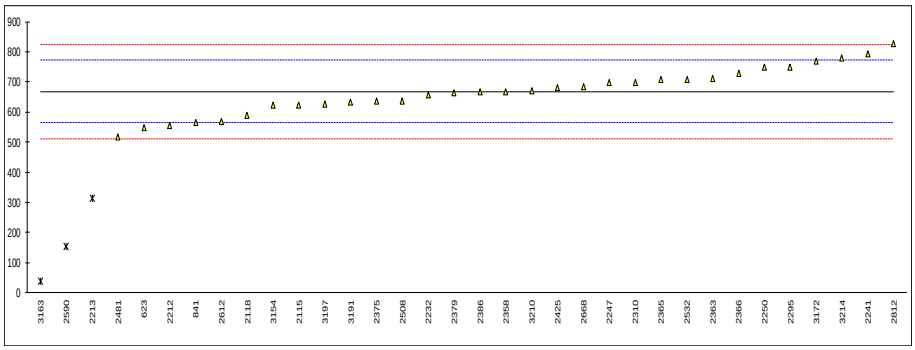
In the PT of 2020, most of the laboratories identified all added Phosphorus Flame retardants correctly: sample #20500 contained TCEP, TCPP and TDCPP and sample #20501 contained TBP, TCP (ToCP) and TCEP.

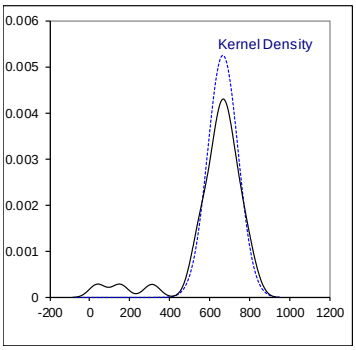
The large variations observed in this interlaboratory study can be caused by the preparation or the conditioning of the sample and/or by the performance of the analysis by the participating laboratory. Consequently, the reproducibility cannot be improved by only one change in the analysis. Each laboratory 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 #20500; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	546.77		-2.33	
841	In house	564.09		-2.00	
2115	ISO17881-2	622.21		-0.89	
2118	ISO17881-2	589.7		-1.51	
2212	In house	555.26		-2.17	
2213	ISO17881-2	313	R(0.01)	-6.82	
2232	ISO17881-2	656.61871		-0.23	
2241	In house	791.67		2.36	
2247	ISO17881-2	696.78		0.54	
2250	In house	749.99		1.57	
2293		-----		-----	
2295	In house	750.0		1.57	
2310	ISO17881-2	699		0.59	
2358	In house	666.94		-0.03	
2363	In house	710		0.80	
2365	In house	706.8		0.74	
2366	In house	727.57		1.14	
2375	ISO17881-2	637.0		-0.60	
2379	In house	663.0516		-0.10	
2386	In house	666.7		-0.03	
2390		-----		-----	
2425	In house	680.1		0.22	
2481	In house	517.0		-2.90	
2508	ISO17881-2	637.15		-0.60	
2532	ISO17881-2	708		0.76	
2590	ISO17881-2	151.984	C,R(0.01)	-9.91	first reported: 188.717
2612	EN71-11	569.03		-1.91	
2668		684.01		0.30	
2812	ISO17881-2	827.00		3.04	
3154	ISO17881-2	622.07		-0.89	
3163	In house	39	R(0.01)	-12.07	
3172	ISO17881-2	769.38		1.94	
3191	GB/T36922	631.43		-0.71	
3197	ISO17881-2	625.7		-0.82	
3210	In house	669.41		0.02	
3214	ISO17881-2	779.7		2.14	
	normality	OK			
	n	31			
	outliers	3			
	mean (n)	668.391			
	st.dev. (n)	76.0959	RSD = 11%		
	R(calc.)	213.068			
	st.dev.(EN71-11:05)	52.1345			
	R(EN71-11:05)	145.977			



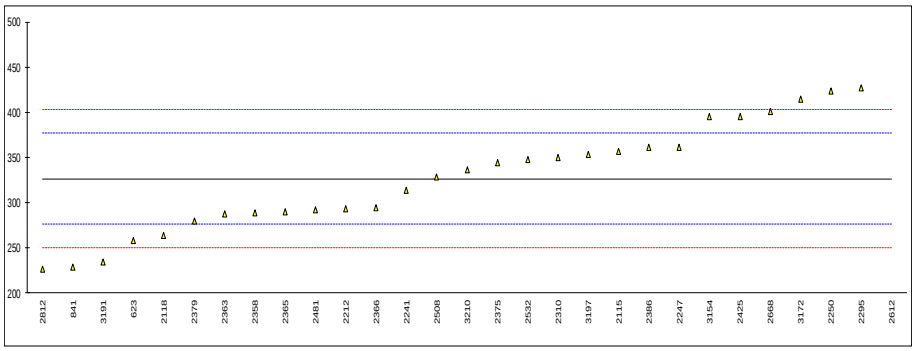


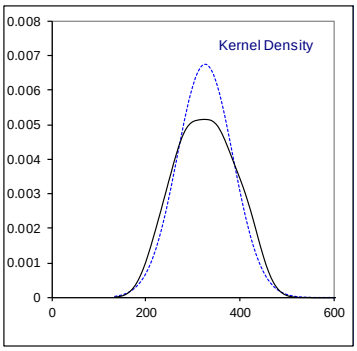
Determination of Tris(1-chloro-2-propyl) phosphate (TCPP) CAS no. 13674-84-5 in sample #20500; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	258.47		-2.67	
841	In house	228.24		-3.86	
2115	ISO17881-2	356.26		1.17	
2118	ISO17881-2	263.25		-2.49	
2212	In house	293.08		-1.31	
2213		-----		-----	
2232		-----		-----	
2241	In house	313.73		-0.50	
2247	ISO17881-2	361.21		1.36	
2250	In house	424	C	3.83	first reported: 76.35
2293		-----		-----	
2295	In house	427.0		3.94	
2310	ISO17881-2	350		0.92	
2358	In house	288.13		-1.51	
2363	In house	288		-1.51	
2365	In house	290.0		-1.44	
2366	In house	294.71		-1.25	
2375	ISO17881-2	344.0		0.68	
2379	In house	279.1891		-1.86	
2386	In house	360.9		1.35	
2390		-----		-----	
2425	In house	395.5		2.71	
2481	In house	292.0		-1.36	
2508	ISO17881-2	328.03		0.06	
2532	ISO17881-2	347.1		0.81	
2590		-----		-----	
2612	EN71-11	2823.87	R(0.01)	98.04	
2668		401.33		2.94	
2812	ISO17881-2	226.71		-3.92	
3154	ISO17881-2	394.73		2.68	
3163		-----		-----	
3172	ISO17881-2	414.85		3.47	
3191	GB/T36922	234.17		-3.63	
3197	ISO17881-2	352.9		1.03	
3210	In house	336.19		0.38	
3214		-----		-----	

normality	OK
n	28
outliers	1
mean (n)	326.560
st.dev. (n)	59.1765
R(calc.)	165.694
st.dev.(EN71-11:05)	25.4717
R(EN71-11:05)	71.321

RSD = 18%



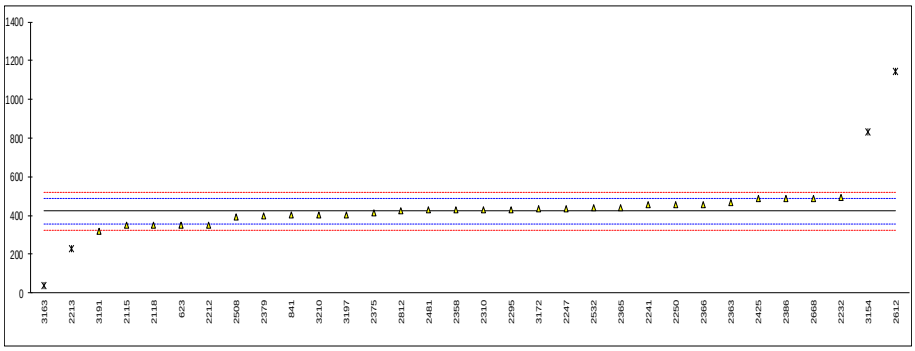


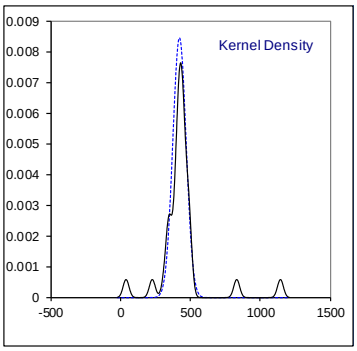
Determination of Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) CAS no.13674-87-8 in sample #20500; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	347.95		-2.24	
841	In house	402.19		-0.59	
2115	ISO17881-2	347.53		-2.26	
2118	ISO17881-2	347.9		-2.24	
2212	In house	352.34		-2.11	
2213	ISO17881-2	227.5	R(0.05)	-5.90	
2232	ISO17881-2	494.23204		2.20	
2241	In house	455.88		1.04	
2247	ISO17881-2	434.89		0.40	
2250	In house	456	C	1.04	first reported: 73.08
2293		-----		-----	
2295	In house	430.0		0.25	
2310	ISO17881-2	430		0.25	
2358	In house	428.87		0.22	
2363	In house	465		1.31	
2365	In house	440.0		0.55	
2366	In house	458.47		1.12	
2375	ISO17881-2	412.0		-0.30	
2379	In house	397.2866		-0.74	
2386	In house	490.0		2.07	
2390		-----		-----	
2425	In house	485.3		1.93	
2481	In house	427.9		0.19	
2508	ISO17881-2	393.60		-0.86	
2532	ISO17881-2	438.3		0.50	
2590		-----		-----	
2612	EN71-11	1143.35	R(0.01)	21.94	
2668		490.06		2.08	
2812	ISO17881-2	426		0.13	
3154	ISO17881-2	830.99	R(0.01)	12.44	
3163	In house	40	R(0.01)	-11.60	
3172	ISO17881-2	434.41		0.38	
3191	GB/T36922	316.37		-3.20	
3197	ISO17881-2	404.1		-0.54	
3210	In house	402.43		-0.59	
3214		-----		-----	

normality	OK
n	28
outliers	4
mean (n)	421.750
st.dev. (n)	47.2350
R(calc.)	132.258
st.dev.(EN71-11:05)	32.8966
R(EN71-11:05)	92.110

RSD = 11%

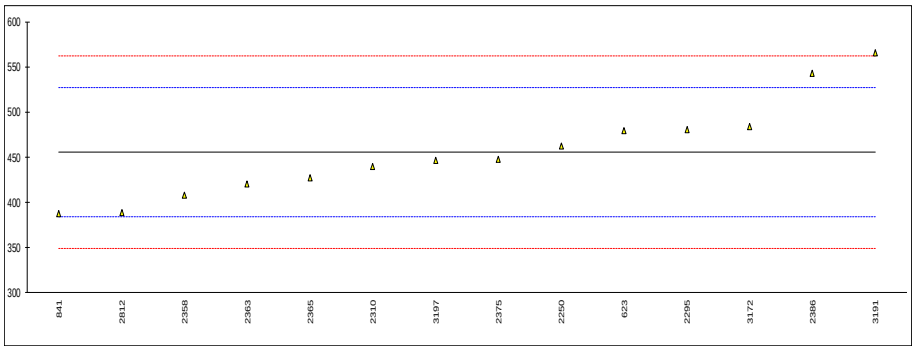


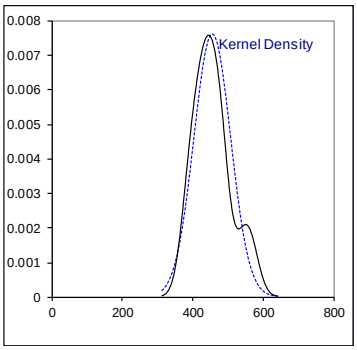


Determination of Tributyl phosphate (TBP) CAS no. 126-73-8 in sample #20501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	479.57		0.67	
841	In house	387.89		-1.91	
2115		-----		-----	
2118		-----		-----	
2212		-----		-----	
2213		-----		-----	
2232		-----		-----	
2241		-----		-----	
2247		-----		-----	
2250	In house	462.5		0.19	
2293		-----		-----	
2295	In house	480.0		0.69	
2310	ISO17881-2	440		-0.44	
2358	In house	408.34		-1.33	
2363	In house	420		-1.00	
2365	In house	426.7		-0.81	
2366		-----		-----	
2375	ISO17881-2	447.0		-0.24	
2379		-----		-----	
2386	In house	542.8		2.45	
2390		-----		-----	
2425		-----		-----	
2481		-----		-----	
2508		-----		-----	
2532		-----		-----	
2590		-----		-----	
2612		-----		-----	
2668		-----		-----	
2812	ISO17881-2	388.20		-1.90	
3154		-----		-----	
3163		-----		-----	
3172	ISO17881-2	483.65		0.79	
3191	GB/T36922	565.92	C	3.10	first reported: <1.00
3197	ISO17881-2	446.4		-0.26	
3210		-----		-----	
3214		-----		-----	

	normality	OK
	n	14
	outliers	0
	mean (n)	455.641
	st.dev. (n)	52.3627 RSD = 11%
	R(calc.)	146.616
	st.dev.(EN71-11:05)	35.540
	R(EN71-11:05)	99.5119



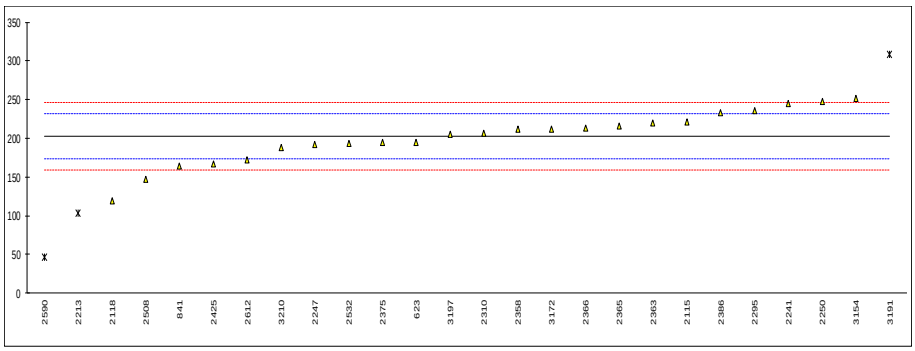


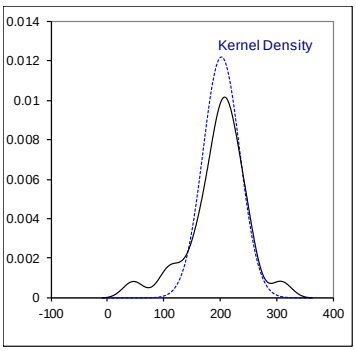
Determination of Tricresyl phosphate (Total of TCP and ToCP) in sample #20501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	194.53		-0.51	
841	In house	164.27		-2.59	
2115	ISO17881-2	220.72		1.29	
2118	ISO17881-2	118.667		-5.73	
2212		-----		-----	
2213	ISO17881-2	104	R(0.05)	-6.74	
2232		-----		-----	
2241	In house	245.29		2.98	
2247	ISO17881-2	191.43		-0.73	
2250	In house	247.15		3.10	
2293		-----		-----	
2295	In house	235.0		2.27	
2310	ISO17881-2	207		0.34	
2358	In house	211.19		0.63	
2363	In house	220		1.24	
2365	In house	215.3		0.91	
2366	In house	212.85		0.75	
2375	ISO17881-2	194.0		-0.55	
2379		-----		-----	
2386	In house	232.7		2.11	
2390		-----		-----	
2425	In house	167.5		-2.37	reported for TCP 96 and for ToCP 71.5, sum is 167.5
2481		-----		-----	
2508	ISO17881-2	147.54		-3.75	
2532	ISO17881-2	192.8		-0.63	
2590	ISO17881-2	45.895	C,R(0.05)	-10.73	first reported: 66.262
2612	EN71-11	172.31		-2.04	
2668		-----		-----	
2812		-----	W	-----	First reported: 144.20
3154	ISO17881-2	252.15		3.45	
3163		-----		-----	
3172	ISO17881-2	211.44		0.65	
3191	GB/T36922	307.72	C,R(0.05)	7.27	first reported: <1.00
3197	ISO17881-2	205.0		0.21	
3210	In house	187.41		-1.00	
3214		-----		-----	

normality	OK
n	23
outliers	3
mean (n)	202.011
st.dev. (n)	32.7319
R(calc.)	91.649
st.dev.(EN71-11:05)	14.5448
R(EN71-11:05)	40.725

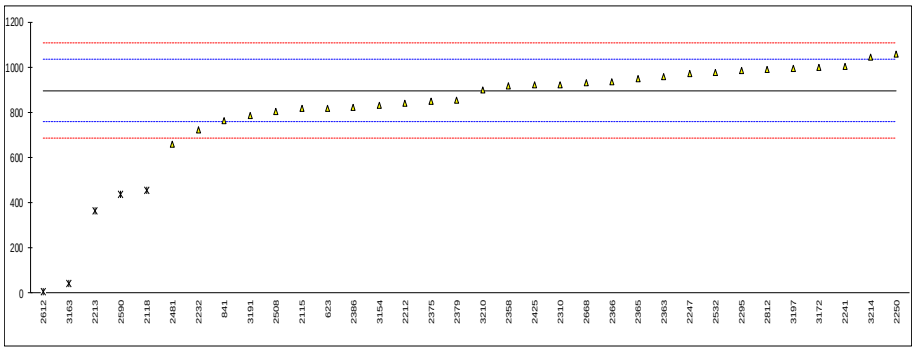
RSD = 16%

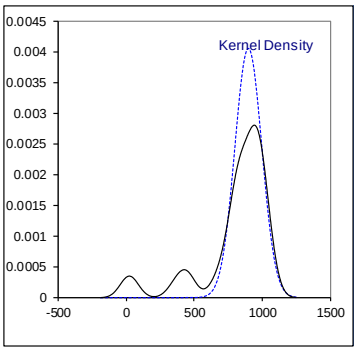




Determination of Tris(2-chloroethyl) phosphate (TCEP) CAS no. 115-96-8 in sample #20501; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	In house	818.04		-1.12	
841	In house	762.87		-1.91	
2115	ISO17881-2	817.96		-1.12	
2118	ISO17881-2	455.6	C,R(0.01)	-6.30	first reported: 615.867
2212	In house	840.00		-0.80	
2213	ISO17881-2	362	R(0.01)	-7.64	
2232	ISO17881-2	719.81055		-2.52	
2241	In house	1000.99		1.50	
2247	ISO17881-2	972.49		1.09	
2250	In house	1055.69		2.28	
2293		-----		-----	
2295	In house	984.0		1.26	
2310	ISO17881-2	920		0.34	
2358	In house	918.62		0.32	
2363	In house	958		0.88	
2365	In house	949.3		0.76	
2366	In house	933.47		0.53	
2375	ISO17881-2	847.0		-0.70	
2379	In house	851.7144		-0.64	
2386	In house	822.9		-1.05	
2390		-----		-----	
2425	In house	919.0		0.33	
2481	In house	660.0		-3.38	
2508	ISO17881-2	801.60		-1.35	
2532	ISO17881-2	974.2		1.12	
2590	ISO17881-2	437.100	C,R(0.01)	-6.57	first reported: 392.684
2612	EN71-11	5.03	R(0.01)	-12.75	
2668		930.03		0.48	
2812	ISO17881-2	987.10		1.30	
3154	ISO17881-2	831.56		-0.93	
3163	In house	40	R(0.01)	-12.25	
3172	ISO17881-2	997.78		1.45	
3191	GB/T36922	783.89		-1.61	
3197	ISO17881-2	991.9		1.37	
3210	In house	896.46		0.00	
3214	ISO17881-2	1044.2		2.12	
	normality	OK			
	n	29			
	outliers	5			
	mean (n)	896.227			
	st.dev. (n)	98.5645	RSD = 11%		
	R(calc.)	275.981			
	st.dev.(EN71-11:05)	69.9057			
	R(EN71-11:05)	195.736			





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

Sample #20500

Lab	TBEP	TBP	TCP (+ ToCP)	TPP	IPTPP
339	< 1	-----	-----	-----	-----
623	n.d.	n.d.	n.d.	n.d.	n.d.
841	ND	7.85	ND	ND	ND
2115	-----	-----	-----	-----	-----
2118	-----	-----	-----	-----	-----
2212	-----	-----	-----	-----	-----
2213	-----	-----	<5	<5	-----
2232	-----	-----	-----	-----	-----
2241	-----	-----	<5	<5	-----
2247	-----	-----	ND	ND	-----
2250	-----	2.1	-----	-----	-----
2293	-----	-----	-----	-----	-----
2295	-----	-----	-----	-----	-----
2310	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
2358	n.d.	n.d.	n.d.	n.d.	N/A
2363	ND	ND	ND	ND	ND
2365	<5	<5	<5	<5	<5
2366	-----	-----	<5	<5	-----
2375	-----	-----	-----	-----	-----
2379	-----	-----	-----	Not detected	-----
2386	<5	<5	<5	<5	-----
2390	-----	-----	-----	-----	-----
2425	-----	-----	Not Detected	-----	-----
2481	-----	-----	-----	-----	-----
2508	-----	-----	0.32	-----	-----
2532	-----	-----	<5	<5	<5
2590	-----	-----	-----	-----	-----
2612	-----	-----	1.49	-----	-----
2668	-----	-----	Not detected	Not detected	-----
2812	-----	-----	-----	-----	-----
3154	-----	-----	-----	0.66	-----
3163	-----	-----	-----	-----	-----
3172	n.d.	n.d.	n.d.	n.d.	n.d.
3191	<1.00	<1.00	<1.00	<1.00	<1.00
3197	-----	<10	<10	<10	<10
3210	-----	-----	-----	1.125	-----
3214	-----	-----	-----	-----	-----

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

TBP = Tributyl phosphate CAS no.126-73-8

TCP (ToCP) = Tricresyl phosphate (+Tri-o-cresyl phosphate), see paragraph 4

TPP = Triphenyl phosphate CAS no.115-86-6

IPTPP = Isopropylated Triphenyl phosphate CAS no.68937-41-7

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

Sample #20501

Lab	TBEP	TCPP	TDCPP	TPP	IPTPP
339	< 1	-----	-----	-----	-----
623	n.d.	n.d.	n.d.	n.d.	n.d.
841	ND	ND	ND	ND	ND
2115	-----	0.62	-----	-----	-----
2118	-----	-----	-----	-----	-----
2212	-----	<100	<100	-----	-----
2213	-----	-----	<5	<5	-----
2232	-----	-----	-----	-----	-----
2241	-----	<5	<5	<5	-----
2247	-----	ND	ND	ND	-----
2250	-----	-----	-----	-----	-----
2293	-----	-----	-----	-----	-----
2295	-----	-----	-----	-----	-----
2310	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
2358	n.d.	n.d.	n.d.	n.d.	N/A
2363	ND	ND	ND	ND	ND
2365	<5	<5	<5	<5	<5
2366	-----	<5	<5	<5	-----
2375	-----	-----	-----	-----	-----
2379	-----	Not detected	Not detected	Not detected	-----
2386	<5	<5	<5	<5	-----
2390	-----	-----	-----	-----	-----
2425	-----	Not Detected	Not Detected	-----	-----
2481	-----	-----	-----	-----	-----
2508	-----	1.34	0.50	-----	-----
2532	-----	<5	<5	<5	<5
2590	-----	-----	-----	-----	-----
2612	-----	2925.22	< 5	-----	-----
2668	-----	BDL	Not detected	Not detected	-----
2812	-----	-----	-----	-----	-----
3154	-----	1.86	-----	-----	-----
3163	-----	-----	-----	-----	-----
3172	n.d.	n.d.	n.d.	n.d.	n.d.
3191	<1.00	<1.00	<1.00	<1.00	<1.00
3197	-----	<10	<10	<10	<10
3210	-----	2.085	-----	-----	-----
3214	-----	-----	-----	-----	-----

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

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

APPENDIX 3 Analytical details

Lab	ISO17025 accr.	Sample preparation	Final estimated particle size	Sample intake (in grams)
339	No	Used as received		
623	No	Further Cut	2mm x 2mm	1 g
841	---	---		
2115	No	Further Cut	1.5 mm	0.2 g
2118	No	Used as received	used as received	0.75 g
2212	Yes	Further Cut	2mm x 2mm	0.06g
2213	Yes	Used as received		1 g
2232	Yes	Used as received	5mmx5mm	1g
2241	Yes	Further Cut	2mm*2mm	0.3g
2247	Yes	Further Cut	2mm x 2mm	0.2 g
2250	Yes	Further Cut	1 - 2 mm	LC-MS: 0,1 GC-MS: 0,25
2293	---	---		
2295	Yes	Further Cut		1 gram
2310	No	Further Cut		1 gram
2358	Yes	Used as received	5 mm X 5 mm	0.5 g
2363	Yes	Further Cut	1 mm*1 mm	0.5g
2365	Yes	Further Cut	1mm*1mm	0.3g
2366	---	---		
2375	Yes	Further Cut	1cmX1cm	0,5
2379	No	Further Cut	2 mm x 2mm.	0.5 g
2386	Yes	Further Cut	2*2mm	0,5
2390	---	---		
2425	Yes	Further Cut	2 mm (As minimum size as possible)	0.5 g
2481	No	Further Cut	<3mm	0.5 g
2508	No	Used as received	used as received	0.5
2532	Yes	Further Cut	2mm * 2mm	0.2 grams
2590	Yes	Further Cut		
2612	Yes	Further Cut	1x1 to 2x2 mm	0,5 g
2668	Yes	Further Cut	2 mm	0.5 gms
2812	No	Further Cut		
3154	---	---		
3163	No	Further Cut	0.5mg	0.5mg
3172	Yes	Further Cut	0.5x0.5 mm	0.5
3191	Yes	Further Cut	5mm*5mm	1.0g
3197	Yes	Further Cut	2*2 mm	0,2 grams
3210	No	Further Cut		0.5
3214	Yes	Further Grinded	500 um	1 gram

Analytical details (continued)

Lab	Extraction technique	Solvent to release/extract the analyte(s)	Extraction time (min)	Extraction temp. (°C)
339	---			
623	Ultrasonic	Ethyl acetate: Hexane(1:1)	60 mins	50°C
841	---			
2115	Ultrasonic	acetone	60 min	40°C
2118	Ultrasonic	acetone	60 min	40 °C
2212	Mechanical Shaking	Tetrahydrofuran follow by n-Hexane	60 minutes	Room Temperature
2213	Ultrasonic	Acetone	60 mins	40 C
2232	Ultrasonic	Acetone	40+20=60mins in total	40°C
2241	Ultrasonic	dichloromethane	60	room temperature
2247	Ultrasonic	THF:CAN (1:2)	60 mins	70°C
2250	Ultrasonic	GC-MS: Aceton LC-MS: ACN or Methanol	GC-MS:30 LC-MS:60	GC-MS:RT LC-MS:40
2293	---			
2295	Ultrasonic	Methanol	60 minutes	room temperature
2310	Ultrasonic	Ethyl acetate: Hexane(1:1)	1 hour	50°C
2358	Ultrasonic	Ethyl acetate:Hexane(1:1)	60 minutes	50°C
2363	Ultrasonic	toluene	60 min	60°C
2365	Ultrasonic	Toluene	60min	60°C
2366	---			
2375	Ultrasonic	Toluene	60	60
2379	Ultrasonic	EA : Hexane (1:1)	60 min	50 C
2386	Ultrasonic	Ethylacetat/Hexan 1:1	60	50
2390	---			
2425	Ultrasonic	THF + ACN	60 minutes	70° C
2481	microwave extraction	Toluene/ethanol 3/1	40	125
2508	Ultrasonic	Acetone	2 x 20	40
2532	Ultrasonic	THF/ACN	30 mints + 30 mints	70 °C
2590	Ultrasonic	Acetone	40'	40°C
2612	Ultrasonic	Acetonitrile	60 min	60 °C
2668	Ultrasonic	THF:Acetonitrile	60 min	70C
2812	Ultrasonic		40	40
3154	---			
3163	Thermal Desorption			
3172	Ultrasonic	Toluene-Acetone 1:1	40	40
3191	Soxhlet	Methylbenzene	3 hours	40℃-50℃
3197	Ultrasonic	THF/ACN	30 + 30 minutes	70C
3210	Ultrasonic	Toluene	60 minutes	60°C
3214	Ultrasonic	THF/ACN	60 mins	70°C

APPENDIX 4

Number of participants per country

1 lab in BANGLADESH

1 lab in BELGIUM

3 labs in FRANCE

5 labs in GERMANY

1 lab in GUATEMALA

2 labs in HONG KONG

5 labs in INDIA

1 lab in INDONESIA

3 labs in ITALY

5 labs in P.R. of CHINA

1 lab in PAKISTAN

1 lab in SINGAPORE

1 lab in TAIWAN R.O.C.

1 lab in THAILAND

1 lab in THE NETHERLANDS

4 labs in TURKEY

1 lab in VIETNAM

APPENDIX 5

Abbreviations

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

Literature

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