# Results of Proficiency Test
# Phosphorus Flame retardants
# in Polymers
# February 2016

**Organised 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. Well known organophosphate esters are: Tris(2-chloroethyl)phosphate (TCEP), Tris(1,3-dichloroisopropyl)phosphate (TDCPP) and Tris(chloropropyl)phosphate (TCPP).
However, production and use has been in decline since the 1980s, when TCEP has been progressively replaced by other flame retardants. TCEP was comprehensively evaluated under the EU existing substances regulation (EEC) 793/93 in 2009. TCEP is classified under Regulation (EC) No 1272/2008 as a carcinogenic, mutagenic and toxic substance. In March 2012, the European Union decided to lower the limit of TCEP in toys (5 mg/kg) .

Regretfully, no certified reference materials (CRMs) for TCEP, TDCPP and TCPP are available to optimise the determination of Phosphorus flame retardants. As an alternative, participation in a proficiency test may enable the laboratories to check their performance and thus to increase this comparability.

Therefore, a proficiency testing scheme (laboratory-evaluating interlaboratory study) for the determination of Phosphorus flame retardants was started by the Institute for Interlaboratory Studies in 2014. During this proficiency test in 2014 only TCEP was requested to be analyzed. This proficiency test was continued in the 2014/2015 program.
During the annual proficiency testing program 2015/2016, it was decided to continue the PT for the analysis of Phosphorus Flame retardants and to extend the scope with TDCPP and TCPP. In the international interlaboratory study of February 2016, 34 laboratories from 16 different countries participated (See appendix 3). In this report the results of the 2016 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

## 2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organizer of this proficiency test. It was decided to send 1 plastic sample positive on TCEP and TDCPP of approx. 3 grams and labelled #16500. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO17025 accredited laboratory. Participants were requested to report rounded and unrounded test results. These unrounded test results were preferably used for statistical evaluation. The participants were asked to report the analytical results using the indicated units on the report form.

## 2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC 17043:2010. 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 a 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 April 2014 (iis-protocol, version 3.3). This protocol is electronically available through the iis internet site 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

Small plastic (green) pieces, artificially fortified to be positive on TCEP and TDCPP, were selected. Samples of approx. 3 gram each were prepared. Seven stratified randomly selected samples were tested using EN71-11 to check the homogeneity of the batch.

| | *TCEP in mg/kg* |
|---|---|
| Sample #16500-1 | 430 |
| Sample #16500-2 | 422 |
| Sample #16500-3 | 423 |
| Sample #16500-4 | 428 |
| Sample #16500-5 | 433 |
| Sample #16500-6 | 428 |
| Sample #16500-7 | 440 |

Table 1: homogeneity test results of subsamples #16500

From the test results of table 1, the repeatability was calculated and compared with 0.3 times the corresponding estimated target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

| | *TCEP in mg/kg* |
|---|---|
| r (observed) | 17 |
| reference test method | EN71-11:2005 |
| 0.3 x R (reference test method) | 28 |

Table 2: repeatability of subsamples #16500

The calculated repeatability of the test results was in agreement with 0.3 times the estimated reproducibility mentioned in the reference method EN71-11.
Therefore, homogeneity of the subsamples was assumed.
Approx. 3 grams of sample #16500 was sent to each of the participating laboratories on January 20, 2016.

### 2.5 ANALYSES

The participants were asked to determine the concentration of Tris(2-chloroethyl)phosphate (TCEP) (CAS No. 115-96-8), Tris(1,3-dichloroisopropyl)phosphate (TDCPP) (CAS No. 13674-87-8) and Tris(chloropropyl)phosphate (TCPP) (CAS No. 13674-84-5) applying the analysis procedure that is routinely used in the laboratory.
To get comparable results a detailed report form, on which the units were prescribed as well as the reference standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. A form to confirm receipt of the samples and a letter of instructions were added to the samples.

## 3 RESULTS

During five weeks after sample despatch, the results of the individual laboratories were gathered via the data entry portal www.kmpd.co.uk/sgs-iis-cts/. The reported test results are tabulated per sample in appendix 1 of this report. The laboratories are represented by the code numbers.
Directly after the deadline, a reminder was sent to those laboratories that did not report results at that moment.
Shortly after the deadline, the available results were screened for suspect data. A 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 results. Additional or corrected results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1.
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 organisation of this proficiency test is described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3).

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. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 the original results per determination were submitted subsequently to Dixon, Grubbs and or Rosner General ESD outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.
Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have significant consequences for the evaluation of the test results.

### 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 analysis results are plotted. The corresponding laboratory numbers are under 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 standard. 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 spread of this interlaboratory study.

The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) by division with 2.8.
The z-scores were calculated in accordance with:

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

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

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 should be done in order to evaluate whether the reported test results are fit-for-purpose.

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 reporting problems occurred. Thirty-one participants reported a test result of which one participant after the deadline. Three other participants did not report any test results. Finally, the 31 participants did report 61 numerical results. Observed were 9 outlying results, which is 14.8% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

For the determination of TCEP and TDCPP no standard method is available. Most participating laboratories therefore had to perform an in house method. This will consist of a preparation/extraction step and an analytical step. Method EN71-11 describes the analytical determination of TCEP after extraction and has a precision statement for TCEP. That is the reason that in this report EN71-11 is used as reference method (for the analytical determination). It is also possible to use the estimated reproducibility calculated with the

Horwitz equation. It was decided to use for TDCPP also the precision statement for TCEP in EN71-11 as reference.

Regretfully in EN71-11:2005, no reproducibility requirements for TCEP are mentioned, but only the standard deviation for the repeatability. The target reproducibility is estimated as follows: the standard deviation was multiplied with 2.8 to get the target repeatability. This was multiplied with 3 to get an estimate of the target reproducibility.
For comparison also the Horwitz equation was used to estimate a target reproducibility. This estimated Horwitz reproducibility was smaller than the estimated reproducibility of EN71-11 for both TCEP and TDCPP.

Both original data sets proved to have a normal Gaussian distribution.

### 4.1 EVALUATION PER COMPONENT

In this section, the results are discussed per component. All statistical results reported on the sample #16500 are summarised in appendix 1 and analytical details provided by the participants are summarised in appendix 2.

TCEP: The determination of this component was problematic for a number of laboratories. Five statistical outliers were observed. The observed reproducibility after rejection of the statistical outliers was almost in agreement with the estimated target reproducibility of EN71-11:2005, but not in agreement with the estimated reproducibility calculated using the Horwitz equation.

TDCPP: The determination of this component was problematic. Four statistical outliers were observed. The observed reproducibility after rejection of the statistical outliers was not in agreement with the estimated target reproducibility of EN71-11:2005 and not in agreement with the estimated reproducibility calculated using the Horwitz equation.

TCPP: All participants reported a “less than” or not detected as test result. Therefore no significant conclusions were drawn.

### 4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard method and the reproducibility as found for the group of participating laboratories.

The number of significant results, the average result, the calculated reproducibility (standard deviation*2.8) and the target reproducibility, derived (or estimated) from the reference test method EN71-11 are presented in the next table.

| Parameter | unit | n | Average | 2.8 * sd | R(target) |
|---|---|---|---|---|---|
| TCEP | mg/kg | 26 | 479 | 117 | 105 |
| TDCPP | mg/kg | 26 | 325 | 139 | 71 |
| TCPP | mg/kg | 19 | n.d. | n.a. | n.a. |

Table 3: performance overview for sample #16500

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

### 4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2016 WITH THE PREVIOUS PT

| | February 2016 | February 2015 | February 2014 |
|---|---|---|---|
| Number of reporting labs | 31 | 33 | 23 |
| Number of results reported | 61 | 32 | 23 |
| Number of statistical outliers | 9 | 2 | 1 |
| Percentage outliers | 14.8% | 6.3% | 4.3% |

Table 4: Comparison with previous proficiency test

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

The uncertainty in the test results of TCEP in the iis16P01 PT are improved compared to the previous PTs, and almost in line with the uncertainty of the reference method.

| Parameter | February 2016 | February 2015 | February 2014 | Est. EN71-11 |
|---|---|---|---|---|
| TCEP | 8.8% | 12.4% | 23.0% | 7.8% |
| TDCPP | 15.3% | n.e. | n.e. | 7.8% |

Table 5: Development of relative uncertainties over the years

## 5 DISCUSSION

The material for this PT was a plastic granulate. In order to extract TCEP and TDCPP from a solid like a polymer, the extraction solvent, the extraction conditions and the surface area will be important variables. The choice of the extraction solvent was the most important variable in the PT of 2014, since TCEP had to be extracted from a low density foam. The conclusion in this 2014 PT was that the use of Acetonitrile as a solvent gave a much smaller spread of the test results than the use of other solvents.

In the PT of 2015, the solvent and extraction conditions appeared to be less important than the surface area. This was to be expected as the sample was a hard high density plastic, not foam. Therefore the total data set was compared in the PT of 2015 to the test results of only the participants that reduced the grain size of the granulate (see also final report: TCEP in plastics: iis15P01).

In the PT of 2016, for the TCEP determination, the calculated reproducibility is almost in agreement with the estimated reproducibility limits of EN71-11. It is therefore remarkable to see that the size of granulate and the choice of extraction solvent appeared not to be important as it was in previous rounds.

Due to the lack of a suitable test method, with precision data for the determination of TDCPP, it was decided to compare the group performance for the TDCPP determination with the precision statement for TCEP of EN71-11. As it was the first time this component was requested to be determined, it turned out that the choice of using this precision data was acceptable.

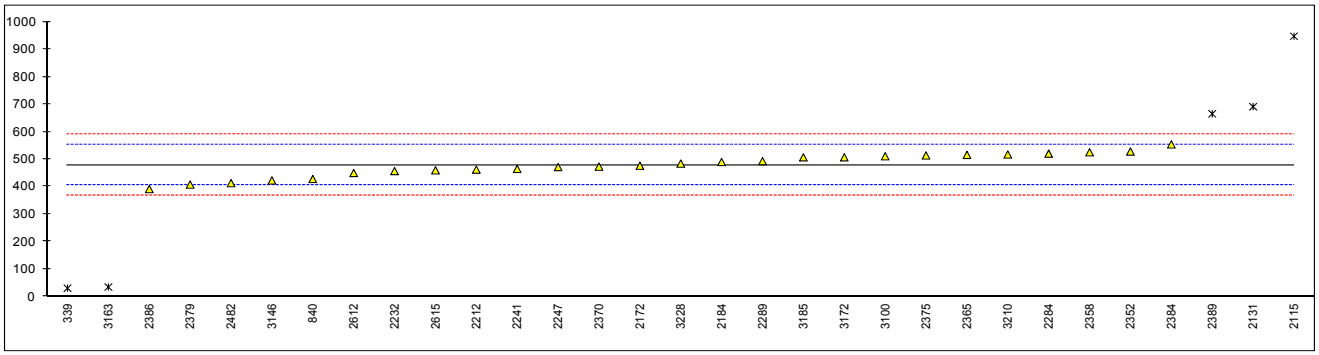
## 6 CONCLUSION

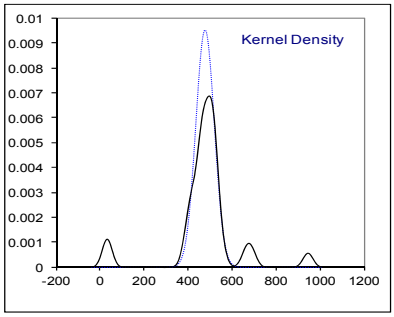
In this proficiency test the TCEP and TDCPP in polymers were determined. The spreads observed in this interlaboratory study can be caused by the preparation or the conditioning of the sample and/or by the performance of the analysis. Consequently, the reproducibility cannot be improved by only one change 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 #16500; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 110 | | ----- | | ----- | |
| 339 | In house | 30.9 | R(0.01) | -11.99 | |
| 840 | In house | 428 | | -1.35 | |
| 2115 | EN71-11 | 947.2 | R(0.01) | 12.56 | |
| 2131 | In house | 691 | R(0.01) | 5.69 | |
| 2172 | INH-65 | 476.31 | | -0.06 | |
| 2184 | In house | 489.8 | | 0.30 | |
| 2212 | In house | 462.2 | | -0.44 | |
| 2216 | | ----- | | ----- | |
| 2232 | In house | 456.8 | | -0.58 | |
| 2241 | EN71-11 | 464.7 | | -0.37 | |
| 2247 | In house | 471.4 | | -0.19 | |
| 2284 | In house | 520.2 | | 1.12 | |
| 2289 | EN71-11 | 493 | | 0.39 | |
| 2295 | | ----- | | ----- | |
| 2352 | In house | 528.0 | | 1.33 | |
| 2358 | In house | 525.14 | | 1.25 | |
| 2365 | EPA3550C | 515.8 | | 1.00 | |
| 2370 | EPA3550C | 473 | | -0.15 | |
| 2375 | In house | 513.65 | | 0.94 | |
| 2379 | INH-256 | 407.759 | | -1.90 | |
| 2384 | In house | 553.8 | | 2.02 | |
| 2386 | In house | 391.5 | | -2.33 | |
| 2389 | In house | 665 | C,R(0.01) | 5.00 | First reported 622.6 |
| 2482 | In house | 412.928 | | -1.76 | |
| 2612 | In house | 449.8 | | -0.77 | |
| 2615 | EN71-11 | 459.538 | | -0.51 | |
| 3100 | In house | 510.7 | | 0.86 | |
| 3146 | EN71-11 | 422.7 | | -1.50 | |
| 3163 | In house | 35 | R(0.01) | -11.88 | |
| 3172 | GB/T24279 | 507 | | 0.76 | |
| 3185 | In house | 506.9 | | 0.76 | |
| 3210 | In house | 517.1 | | 1.03 | |
| 3228 | In house | 484 | | 0.15 | |
| | normality | OK | | | |
| | n | 26 | | | |
| | Outliers | 5 | | | |
| | mean (n) | 478.528 | | | |
| | st.dev. (n) | 41.9083 | | | |
| | R(calc.) | 117.343 | | | |
| | R(EN71-11:05) | 104.510 | | | Compare R(Horwitz) = 84.687 |

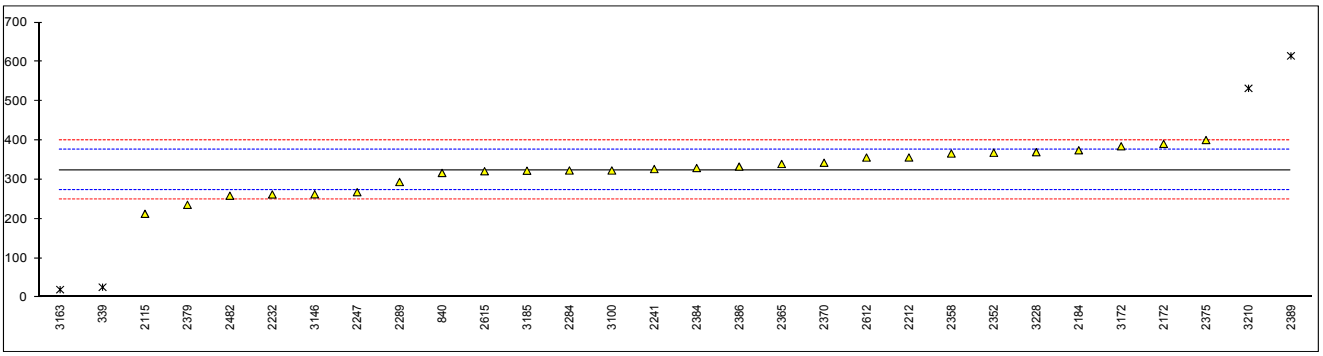


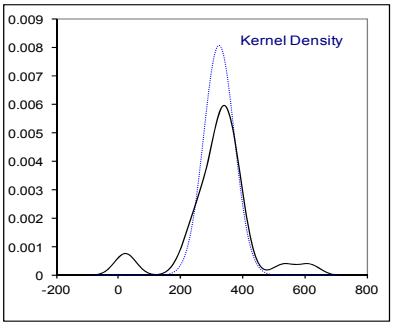



Determination of Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) CAS no.13674-87-8 in sample #16500; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 110 | | ----- | | ----- | |
| 339 | In house | 26.1 | R(0.01) | -11.79 | |
| 840 | In house | 317 | | -0.31 | |
| 2115 | EN71-11 | 213.0 | | -4.41 | |
| 2131 | | ----- | | ----- | |
| 2172 | INH-65 | 391.11 | | 2.62 | |
| 2184 | In house | 374.8 | | 1.97 | |
| 2212 | In house | 356.5 | | 1.25 | |
| 2216 | | ----- | | ----- | |
| 2232 | In house | 262.3 | | -2.47 | |
| 2241 | EN71-11 | 326.9 | | 0.08 | |
| 2247 | In house | 268.0 | | -2.24 | |
| 2284 | In house | 323.3 | | -0.06 | |
| 2289 | EN71-11 | 294 | | -1.22 | |
| 2295 | | ----- | | ----- | |
| 2352 | In house | 368.5 | | 1.72 | |
| 2358 | In house | 366.54 | | 1.65 | |
| 2365 | EPA3550C | 339.9 | | 0.60 | |
| 2370 | EPA3550C | 343 | | 0.72 | |
| 2375 | In house | 400.83 | | 3.00 | |
| 2379 | INH-256 | 235.893 | | -3.51 | |
| 2384 | In house | 329.6 | | 0.19 | |
| 2386 | In house | 333.2 | | 0.33 | |
| 2389 | In house | 615 | C,R(0.01) | 11.45 | First reported 539.81 |
| 2482 | In house | 259.037 | | -2.60 | |
| 2612 | In house | 356.2 | | 1.24 | |
| 2615 | EN71-11 | 321.426 | | -0.13 | |
| 3100 | In house | 323.3 | | -0.06 | |
| 3146 | EN71-11 | 262.8 | | -2.45 | |
| 3163 | In house | 20 | R(0.01) | -12.03 | |
| 3172 | GB/T24279 | 385 | | 2.38 | |
| 3185 | In house | 322.7 | | -0.08 | |
| 3210 | In house | 532.4 | R(0.05) | 8.19 | |
| 3228 | In house | 370 | | 1.78 | |

| | | |
|---|---|---|
| normality | OK | |
| n | 26 | |
| outliers | 4 | |
| mean (n) | 324.801 | |
| st.dev. (n) | 49.5497 | |
| R(calc.) | 138.739 | |
| R(EN71-11:05) | 70.937 | Compare R(Horwitz) = 60.934 |



Determination of Tris(1-chloro-2-propyl)phosphate (TCPP) CAS no.13674-84-5 in sample #16500; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 110 | | ----- | | ----- | |
| 339 | In house | <1 | | ----- | |
| 840 | In house | ND | | ----- | |
| 2115 | | ----- | | ----- | |
| 2131 | | ----- | | ----- | |
| 2172 | | ----- | | ----- | |
| 2184 | | ----- | | ----- | |
| 2212 | In house | <100 | | ----- | |
| 2216 | | ----- | | ----- | |
| 2232 | | ----- | | ----- | |
| 2241 | EN71-11 | <5 | | ----- | |
| 2247 | | ----- | | ----- | |
| 2284 | | ----- | | ----- | |
| 2289 | EN71-11 | ND | | ----- | |
| 2295 | | ----- | | ----- | |
| 2352 | In house | 0 | | ----- | |
| 2358 | In house | n.d. (<5) | | ----- | |
| 2365 | EPA3550C | ND | | ----- | |
| 2370 | EPA3550C | n.d. | | ----- | |
| 2375 | In house | ND | | ----- | |
| 2379 | INH-256 | Not detect | | ----- | |
| 2384 | In house | not detected | | ----- | |
| 2386 | In house | < 5 | | ----- | |
| 2389 | In house | N.D | | ----- | |
| 2482 | | ----- | | ----- | |
| 2612 | In house | < 5 | | ----- | |
| 2615 | EN71-11 | <5 | | ----- | |
| 3100 | In house | not detected | | ----- | |
| 3146 | | ----- | | ----- | |
| 3163 | In house | 0 | | ----- | |
| 3172 | GB/T24279 | < 1 | | ----- | |
| 3185 | | ----- | | ----- | |
| 3210 | | ----- | | ----- | |
| 3228 | In house | Not applicable | | ----- | |
| | | | | | |
| | normality | n.a. | | | |
| | n | 19 | | | |
| | outliers | n.a. | | | |
| | mean (n) | n.d. | | | |
| | st.dev. (n) | n.a. | | | |
| | R(calc.) | n.a. | | | |
| | R(lit) | n.a. | | | |

## APPENDIX 2
Analytical details

| lab | grinded/cut | Size (mm) | extraction solvent | time | detection technique | recovery |
|---|---|---|---|---|---|---|
| 110 | --- | --- | --- | --- | --- | --- |
| 339 | as received | ≤ 1 mm | Toluene | 1h, 60°C | GC-MS | No |
| 840 | Cut | ≤ 1 mm | Ethyl acetat : n-Hexane 1:1 | 1h, 60°C | GC-MS | --- |
| 2115 | as received | >1 mm | Acetonitrile | 1h, 40°C | Lc-MS/MS | --- |
| 2131 | as received | --- | Acetone | 40min,40°C | LC/MS/MS | --- |
| 2172 | Grinded | ≤ 0.5 mm | toluene | 2hrs, 70°C | GC-MS&LC-MS | --- |
| 2184 | Cut | >1 mm | Hexane: Acetone: Methanol (1:1:1) | 3hrs, 60°C | GCMS | --- |
| 2212 | Cut | ≤ 1 mm | Tetrahydrofuran | 1h, room temp | GCMS | Yes, >80% |
| 2216 | --- | --- | --- | --- | --- | --- |
| 2232 | as received | >1 mm | ACN | 1h, 40°C | LCMS | Yes |
| 2241 | Cut | >1 mm | Acetonitrile | 1h, 40°C | Int.std. | --- |
| 2247 | Cut | >1 mm | THF , ACN | 1h, 70°C | LCMS MS | 90 to 110 |
| 2284 | Cut | >1 mm | THF | 1h, 40°C | LC/MS | --- |
| 2289 | Cut | >1 mm | Acetonitrile/tetrahydrofurane | 30min.70°C | GC/MS | --- |
| 2295 | --- | --- | --- | --- | --- | --- |
| 2352 | Cut | ≤ 1 mm | Toluene | 1h, 60°C | GC-MS | 91%, 93.5%, 92.5% |
| 2358 | as received | >1 mm | ethyl acetate / hexane (1:1 v:v) | 1h, 50°C | GC/MS | 80-120% |
| 2365 | Cut | ≤ 1 mm | toluene | 1h, 60°C | GC-MS | 105%, 96%,102% |
| 2370 | Cut | >1 mm | Ethylacetate:n-Hexane 1:1 | 1h, 50°C | GC/MS | 98.9%,98.5%,105% |
| 2375 | Cut | >1 mm | Ethylacetate:Hexane (1:1) | 1h, 50°C | GC-MS | 96%, 93%, 93% |
| 2379 | Cut | >1 mm | Ethyl acetate : n-hexane (1:1) | 1h, 50°C | GC-MS | 100.1%, 97.6% |
| 2384 | Cut | >1 mm | Toluene (Soxhlet) | 21h, 80°C | GCMS | 93%, 107% |
| 2386 | Milled | ≤ 1 mm | Ethylacetate /n-Hexane 1:1 (v/v) | 1h, 50°C | Ultrasonic | 83%,95%, 87% |
| 2389 | as received | --- | n-Hexane + Ethyl acetate | 1h, 50°C | GCMS | 98%, 97.7% |
| 2482 | Cut | >1 mm | Toluene | 1 hr | LC-MS/MS | No |
| 2612 | Cut | 2 mm | Acetonitrile | 1h, 40°C | GC/MSD | no |
| 2615 | Cut | ≤ 0.5 mm | Acetonitrile | 1h, 40°C | GC-MS/MS | No |
| 3100 | Cut | >1 mm | TFH and ACN | 30min.70°C | LC-MS-MS | No |
| 3146 | --- | --- | --- | --- | --- | --- |
| 3163 | Cut | --- | none | none | GCMS | no |
| 3172 | Cut | >1 mm | n-Hexane-Acetone 7:3 (v/v) | 1h, room temp | GC-MS | No |
| 3185 | Cut | >1 mm | Tetrahydrofuran/Acetonitrile | 1h, 70°C | HPLC/MS/MS | 105%, 90% |
| 3210 | Cut | ≤ 1 mm | THF/ Hexane | 30 min, 60°C | GC/MS | yes above 95% |
| 3228 | Cut | >1 mm | Acetone/Hexane/MTBE 1:1:1 | 3hrs, 60°C | GC/MS | No. |

## APPENDIX 3

### Number of participants per country

2 labs in FRANCE

4 labs in GERMANY

3 labs in HONG KONG

1 lab in INDIA

2 labs in ITALY

1 lab in MALAYSIA

10 labs in P.R. of CHINA

1 lab in PAKISTAN

1 lab in SINGAPORE

1 lab in SWITZERLAND

1 lab in TAIWAN R.O.C.

1 lab in THAILAND

1 lab in THE NETHERLANDS

2 labs in TURKEY

2 labs in U.S.A.

1 lab in VIETNAM

## APPENDIX 4

**Abbreviations**:

C = final result after checking of first reported suspect 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
R(0.01) = outlier in Rosner outlier test
R(0.05) = straggler in Rosner outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
ex = test result excluded from calculations
n.a. = not applicable
n.d. = not detected
n.e. = not evaluated

**Literature**:

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