

**Results of Proficiency Test
Phthalates in PVC
March 2003**

Organised by: Institute for Interlaboratory Studies
Dordrecht, the Netherlands

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1 INTRODUCTION

Phthalates act as softeners and are commonly used as plasticizers in PVC. Phthalates may migrate fairly easily from PVC because they are not chemically bond with PVC. Because phthalates have negative effects on health and the environment, regulations have been set up.

In ASTM F963:96a (standard consumer safety specification on toy safety) § 4.3.8 is stated: "Pacifiers, rattles and teethingers shall not intentionally contain DEHP (DOP)".

In Europe, the Commissioner for Industrial Affairs of the EC is responsible for toy regulations. The manufacture and import of toys is regulated by the European Union's Toy Directive (88/378), with in addition the general product safety, which is covered by EU directive 2001/95. These regulations govern conditions related to toys intended for children under 36 months of age (this group often suck or chew on toys and phthalates migrate easily). The regulations for migration are covered by EU directive 98/485, which described the maximum tolerance extractable quantity of migrated phthalates from toys for children under 36 months of age. Beside the migration tolerance, manufactures are not allowed to bring toys into the EC market which are (partly) made of soft PVC and contain more than 0.1 %M/M of one of the following phthalates:

| | | |
|---------------------------------------------------|-------------------|----------------------|
| • di-isononylphthalate (DINP) | CASno. 28553-12-0 | EINECS no. 249-079-5 |
| • bis(2-ethylhexyl)phthalate (DEHP) ¹⁾ | CASno. 117-81-7 | EINECS no. 204-211-0 |
| • di-n-octylphthalate (DNOP) | CASno. 117-84-0 | EINECS no. 204-214-7 |
| • di-isodecylphthalate (DIDP) | CASno. 26761-40-0 | EINECS no. 247-977-1 |
| • benzylbutylphthalate (BBP) | CASno. 85-68-7 | EINECS no. 201-622-7 |
| • dibutylphthalate (DBP) | CASno. 84-74-2 | EINECS no. 201-557-4 |

Further more on request of one of the participants the following phthalates were added to the test scope of this PT:

| | | |
|--------------------------------|------------------|----------------------|
| • dipropylphthalate (DPrP) | CASno. 131-16-8 | |
| • dipentylphthalate (DPP) | CASno. 131-18-0 | |
| • dicyclohexylphthalate (DCHP) | CASno. 84-61-7 | |
| • diethylphthalate (DEP) | CASno. 84-66-2 | EINECS no. 201-550-6 |
| • diheptylphthalate (DHP) | CASno. 3648-21-3 | EINECS no. 222-885-4 |

¹⁾ DEHP is also known as dioctylphthalate (DOP).

Especially the determination of phthalates in PVC is known to give problems with the comparability of laboratory results. However, no appropriate PVC reference materials are available.

As an alternative, participation in a proficiency test may enable laboratories to check this comparability. Therefore, a proficiency test (laboratory-evaluating interlaboratory study) for the determination of total and individual phthalates in pvc was organised by the Institute for Interlaboratory Studies in March 2003.

In the international interlaboratory study of March 2003, 26 laboratories in 12 different countries have participated. See appendix 3 for a list of the number of participating laboratories per countries. In this report the results of the proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies (i.i.s.) in Dordrecht, The Netherlands, was the organiser of this proficiency test. Participants were requested to report results with one extra significant figure. These results with an extra figure are preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Dordrecht, the Netherlands, is accredited in agreement with ISO-guide 43 and ILAC –G13:2000, since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie).

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of August 1998 (iis98protocol, version 2.0).

The participants were asked to report the analytical results using the indicated units on the report form.

2.3 SAMPLES

Three samples were prepared from three different bulk materials. The first bulk material (#0314) was a green PVC ball. The second bulk material (#0315) was purple PVC inflatable chair and the last bulk material (#0316) was a yellow PVC swim-toy. All bulk materials were obtained from a local Dutch market. The bulk materials of #0314, #0315 and #0316 were cut into pieces and thoroughly mixed and subsequently distributed over plastic bags at random. The homogeneity of the subsamples was checked by determination of the total phthalates content by extraction of 4 stratified random selected subsamples using an in house method.

| <i>Total phthalates content in %M/M</i> | | |
|-----------------------------------------|---------------------------|---------------------------|
| <i>Subsamples of 0314</i> | <i>Subsamples of 0315</i> | <i>Subsamples of 0316</i> |
| 31.5 | 15.3 | 17.8 |
| 31.4 | 15.5 | 17.8 |
| 32.0 | 15.0 | 18.0 |
| 30.6 | 14.8 | 18.1 |

table 1: results of the homogeneity test on the subsamples 0314, 0315 and 0316

From the results of the homogeneity tests, the repeatability was calculated:

| | <i>observed repeatability in %M/M</i> |
|--------------------|-------------------------------------------|
| Subsamples of 0314 | 1.6 |
| Subsamples of 0315 | 0.7 |
| Subsamples of 0316 | 0.6 |

table 2: repeatability of the phthalate content of the subsamples 0314, 0315 and 0316

For the determination of total phthalates content an in house extraction/GC-MS method was used. The calculated repeatability is in good agreement with the usual repeatability of the laboratory that performed the homogeneity tests. Therefore, homogeneity of subsamples 0314, 0315 and 0316 was assumed.

To each of the participating laboratories 3 samples were sent on February 19, 2003.

2.4 ANALYSIS

The participants were requested to determine eleven individual phthalates (DINP, DEHP, DNOP, DIDP, BBP, DBP, DprP, DPP, DCHP, DEP and DHP) and other (OP) and total phthalates (TP) of each sample (0314, 0315 and 0316). They were explicitly asked to treat the samples as if they were routine samples and to report the analytical results using the indicated units on the report form and not to round the results, but report as much significant figures as possible. They were also asked not to report 'less than' results which are above the detection limit, because such results can not be used for meaningful statistical calculations.

To get comparable results a detailed report form, on which the units were prescribed, was sent together with each set of samples. Also a letter of instructions was added to the package. The laboratories were asked to complete the report form with the requested details of the methods used.

3 RESULTS

During four weeks after sample despatch the results of the individual laboratories were received. The original data are tabulated per sample in the appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after deadline, a reminder fax 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.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of August 1998 (iis98protocol, version 2.0).

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers this check was repeated. All data sets proved to have a normal distribution.

In accordance with ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs 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. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs 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.

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 average of the reported data is presented by a straight line. The reproducibility limits of the selected standard, calculated as mean \pm target reproducibility, are presented by two striped lines parallel to the average line. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

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 literature reproducibility by division with 2.8. The z-scores were calculated in accordance with:

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

The $z_{(\text{target})}$ scores are listed in the 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 |
| $ z > 3$ | unsatisfactory |

4 EVALUATION

In this interlaboratory study some problems were encountered during the execution. Four participants had not received the samples after three weeks, thus new samples were sent. All other participants received the samples on time. Finally all the 26 reporting participating laboratories did send in 190 numerical results. Observed were 6 outlying results, which is 3.2%. In proficiency studies outlier percentages of 3 % - 7.5 % are quite normal.

4.1 EVALUATION PER SAMPLE

In this section the results are discussed per sample.

For comparison of the results of this Interlaboratory Study, the requirements from a standardised method like ASTM D3421:75, "Extraction and analysis of plasticizer mixtures from vinyl chloride plastics" should be used. Unfortunately, this method was discontinued in 1987, although it is still referred in ASTM F963:96a § 4.3.8 and no other validated determinations are published yet. However, in this method, the scope of the reproducibility requirements is not mentioned. From the previous round robins of Phthalates in PVC it could be learned that the requirements may only be valid for a high concentration ($\pm 15\%$). Unfortunately, the concentrations of the phthalates, determined in the samples used in this proficiency test, deviate very much from 15% (see also §4.2). Therefore, the spreads found in this proficiency test are compared with the spreads estimated from the Horwitz equation.

As only a few participants reported a value for the "Total Phthalates", therefore a manual summation was made for evaluation.

A few participants reported for all three samples a significantly lower result for DEHP than the other participants. It was noticed that these participants used release/extract techniques (see appendix 2), which deviated significantly from the literature methods: ASTM D3421 and Chromatographia No.784 (S.C. Rastogi). Deviations were noticed for "Temperature" and "type of Solvent". These participants had to be excluded manually in order to get unbiased averages.

sample 0314: This sample was positive on DEHP (DOP). The determination of DEHP is very problematic. Fourteen (!) of the twenty-two reported results were outside the estimated reproducibility limits and the calculated reproducibility is, after rejection of the statistical outliers, not at all agreement with the requirements estimated from the Horwitz equation.

For Total Phthalates "as reported", only two results were within the estimated reproducibility limits. The calculated reproducibility is not at all in agreement with the requirements estimated from the Horwitz equation. When the calculated reproducibilities for the Total Phthalates "as reported" are compared with "after manual summation", a small improvement is noticed.

This material contained only very low concentrations of all the other investigated phthalates. Some laboratories reported a numerical result for DBP, although it was very near to the detection limit of the method used. Most participants reported a 'less than'-result or 'not detected'.

sample 0315: This sample contains beside a high concentration of DEHP also a small amount of DINP. For DEHP thirteen (!) of the twenty-two reported results were outside the estimated reproducibility limits and the calculated reproducibility is, after rejection of the statistical outliers, not at all in agreement with the requirements estimated from the Horwitz equation. For DINP only four of the seventeen results were within the estimated reproducibility limits. The calculated reproducibility is not at all in agreement with the requirements estimated from the Horwitz equation. For Total phthalates "as reported" four results were outside the estimated reproducibility limits and the calculated reproducibility is, after rejection of the statistical outlier, not at all in agreement with the requirements estimated from the Horwitz equation. When the calculated reproducibilities for the Total Phthalates "as reported" are compared with "after manual summation", a small improvement is noticed. This material contained only very low concentrations of all the other investigated phthalates. Nine laboratories reported a numerical result for DBP, although it was very near to the detection limit of the method used. Most participants reported a 'less than'-result or 'not detected'

sample 0316: This sample was positive on DINP and DEHP. For DEHP twelve of the twenty-two reported results were outside the estimated reproducibility limits and the calculated reproducibility is, after rejection of the statistical outlier, not at all in agreement with the requirements estimated from the Horwitz equation. For DINP only three results were within the estimated reproducibility limits. The calculated reproducibility is not at all in agreement with the requirements estimated from the Horwitz equation. Only one result for Total phthalates "as reported" was within the reproducibility limits. The calculated reproducibility is not at all in agreement with the requirements estimated from the Horwitz equation. When the calculated reproducibilities for the Total Phthalates "as reported" are compared with "after manual summation", a small improvement is noticed. This material contained only very low concentrations of all the other investigated phthalates. Ten laboratories reported a numerical result for DBP, although it was very near to the detection limit of the method used. Most participants reported a 'less than'-result or 'not detected'. Some participants reported some false positive results, which may be caused by incorrect identification of components.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility for DEHP (= DOP), Total phthalates (both declared by the standard ASTM D3421:75), DINP and DIDP (both estimated from the standard ASTM3421:75) and the reproducibility as found for the group of participating laboratories. The “observed reproducibilities” and the reproducibilities, derived and estimated from ASTM D3421:75 are compared in the next tables:

| Parameter | <i>unit</i> | <i>n</i> | <i>average</i> | <i>2.8 * sd</i> | <i>R (Target)</i> |
|------------------------------|-------------|----------|----------------|-----------------|-------------------|
| DBP | %M/M | 7 | 0.005 | 0.012 | 0.001 |
| DEHP | %M/M | 19 | 49.254 | 11.601 | 3.068 |
| Total Phthalates as reported | %M/M | 5 | 49.944 | 13.121 | 3.105 |
| Total Phthalates *) | %M/M | 19 | 49.324 | 11.711 | 3.072 |

table 3 : sample 0314

| Parameter | <i>unit</i> | <i>n</i> | <i>average</i> | <i>2.8 * sd</i> | <i>R (target)</i> |
|------------------------------|-------------|----------|----------------|-----------------|-------------------|
| DINP | %M/M | 17 | 0.233 | 0.321 | 0.033 |
| DBP | %M/M | 8 | 0.005 | 0.010 | 0.001 |
| DEHP | %M/M | 19 | 29.574 | 7.801 | 1.989 |
| Total Phthalates as reported | %M/M | 5 | 29.235 | 9.652 | 1.970 |
| Total Phthalates *) | %M/M | 19 | 29.774 | 7.976 | 2.001 |

table 4: sample 0315

| Parameter | <i>unit</i> | <i>n</i> | <i>Average</i> | <i>2.8 * sd</i> | <i>R (target)</i> |
|------------------------------|-------------|----------|----------------|-----------------|-------------------|
| DINP | %M/M | 16 | 0.489 | 1.009 | 0.061 |
| DBP | %M/M | 9 | 0.006 | 0.009 | 0.001 |
| DEHP | %M/M | 19 | 30.600 | 8.154 | 1.912 |
| Total Phthalates as reported | %M/M | 4 | 30.265 | 9.967 | 2.029 |
| Total Phthalates *) | %M/M | 19 | 31.021 | 8.217 | 2.072 |

table 5: sample 0316

*) = after manually summing-up

The average results found for “Total Phthalates as reported”, for all the samples, are not in agreement with the sum of the individual phthalates. However, when the results are manually summarised, the “Total Phthalates” are in agreement with the other figures.

4.3 COMPARISON WITH INTERLABORATORY STUDY OF MARCH 2002

The performance of the group in 2003 was compared with the performance in March 2002 for the individual determinations in the following table:

| <i>2003 better than 2002</i> | <i>2003 the same as 2002</i> | <i>2003 worse than 2002</i> |
|------------------------------|------------------------------|-----------------------------|
| | DBP | DINP |
| | Total phthalates | DEHP (=DOP) |
| | | |

5 CONCLUSIONS

The determination of phthalates in PVC seems problematic for this group of participants. The reported details of the methods, which were used by the participants, are listed in appendix 2. The technique to release the phthalates used by the participants was rather diverse, although a lot of participants used a method, which was related to ASTM D3421-75. However, for detecting and quantifying more common techniques were used: GCMS and GC/FID.

The samples which were used in this proficiency test were relatively difficult, because of the extremely high concentrations for DEHP. These high concentrations made it for some participants impossible to quantify the phthalates with concentrations below or near the limit of 0.1%. Some participants reported false positive results.

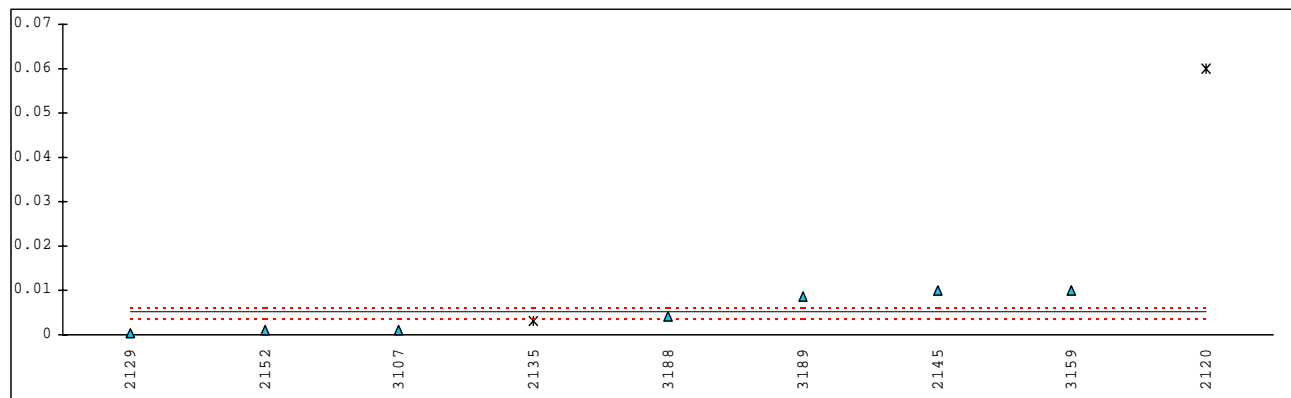
In comparison with last year's round, the performance of this group of participants did not improve. This may partially be explained by the participation of several new participants, who joined the proficiency test scheme for the first time.

Finally, from the details of the analyses provided by the participants (see appendix 4) it is clear that the participants that adhered close to the ASTM D3421:75 or to the method described in Chromatographia Vol.47, No.784 (S.C.Rastogi) reported values that are close to the mean values. The important parameters are type of solvent, temperature and time. Therefore, it is advised to use a chlorinated solvent like Dichloromethane or Chloroform and to use Soxhlet extraction as mentioned in ASTM D3421 and Chromatographia No.784.

APPENDIX 1

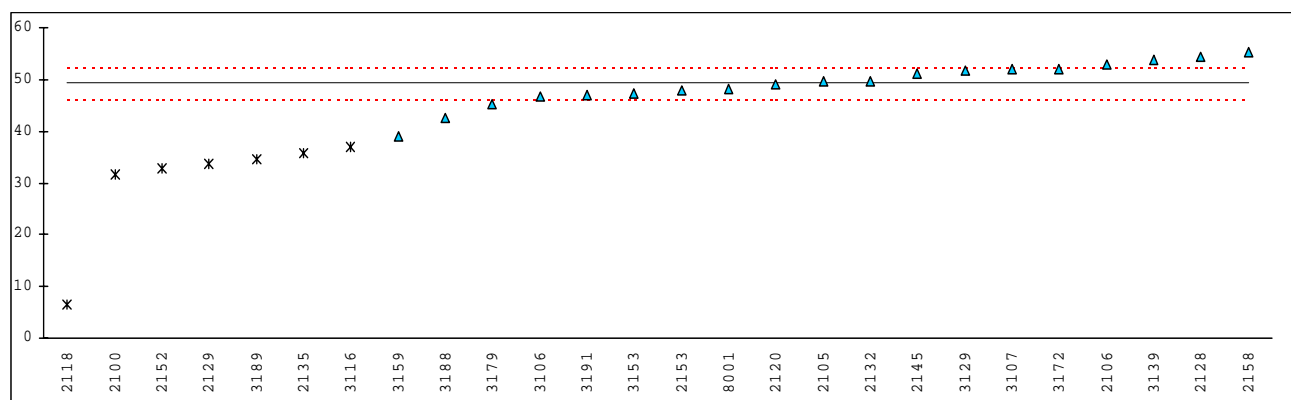
Determination of DBP on sample 0314; results in %M/M

| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|---------|------------------------------|---------|------------------------------------|
| 2100 | | ---- | | ---- | |
| 2105 | | ---- | | ---- | |
| 2106 | inhouse | nd | | ---- | |
| 2118 | | ---- | | ---- | |
| 2120 | inhouse | 0.06 | G(0.01) | 128.30 | |
| 2128 | Oko-tex | <0.002 | | ---- | |
| 2129 | inhouse | 0.0004 | | -10.77 | |
| 2132 | inhouse | <0.005 | | ---- | |
| 2135 | Oko-tex 100 | 0.003 | ex | -4.70 | Manually excluded, (see § 4.1 & 5) |
| 2145 | inhouse | 0.01 | | 11.63 | |
| 2152 | D3421 | 0.001 | | -9.37 | |
| 2153 | inhouse | <0.01 | | ---- | |
| 2158 | | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | ---- | |
| 3107 | S.C. Rastogi | 0.001 | | -9.37 | |
| 3116 | inhouse | <0.01 | ex | ---- | Manually excluded, (see § 4.1 & 5) |
| 3129 | | ---- | | ---- | |
| 3139 | inhouse | <0.02 | | ---- | |
| 3153 | inhouse | <0.01 | | ---- | |
| 3159 | inhouse | 0.01 | | 11.63 | |
| 3172 | | <0.05 | | ---- | |
| 3179 | | ---- | | ---- | |
| 3188 | eec1999-815 | 0.004 | | -2.37 | |
| 3189 | inhouse | 0.0087 | | 8.60 | |
| 3191 | inhouse | <0.01 | | ---- | |
| 8001 | | ---- | | ---- | |
| | | | | | |
| normality | | OK | | | |
| n | | 7 | | | |
| outliers | | 2 | | | |
| mean (n) | | 0.0050 | | | |
| st.dev. (n) | | 0.0044 | | | |
| R(calc.) | | 0.01241 | | | |
| R(Horwitz) | | 0.0012 | Compare R(D3421:75) = 3.3000 | | |



Determination of DEHP (DOP) on sample 0314; results in %M/M

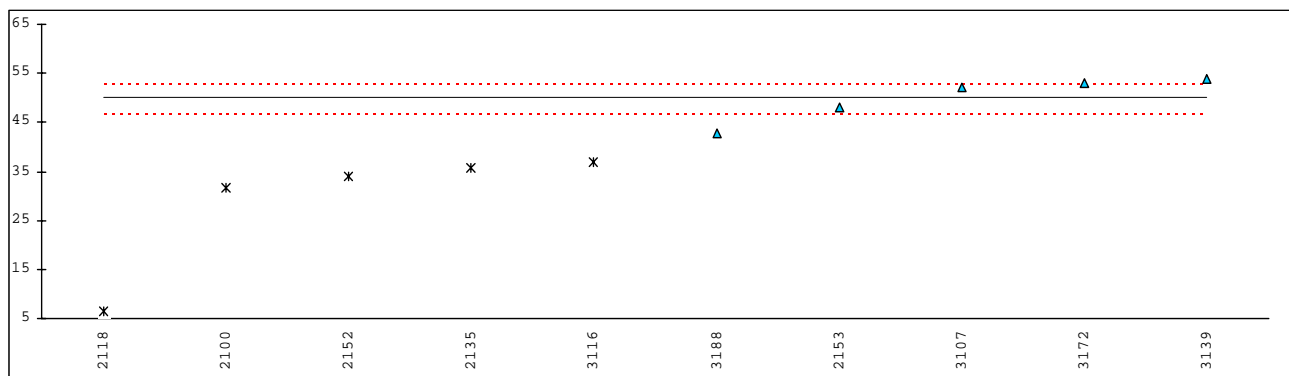
| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|--------|----------|---------|------------------------------------|
| 2100 | In house | 31.5 | ex | -16.20 | Manually excluded, (see § 4.1 & 5) |
| 2105 | D3421 | 49.60 | | 0.32 | |
| 2106 | In house | 52.9 | | 3.33 | |
| 2118 | In house | 6.56 | ex | -38.96 | Manually excluded, (see § 4.1 & 5) |
| 2120 | In house | 49.0 | | -0.23 | |
| 2128 | Oko-tex | 54.5 | | 4.79 | |
| 2129 | In house | 33.7 | DG(0.05) | -14.20 | |
| 2132 | In house | 49.8 | | 0.50 | |
| 2135 | Oko-tex 100 | 35.7 | ex | -12.37 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | 51.22 | | 1.79 | |
| 2152 | D3421 | 32.91 | G(0.01) | -14.92 | |
| 2153 | In house | 47.99 | | -1.15 | |
| 2158 | D3421 | 55.35 | | 5.56 | |
| 3106 | D3421 | 46.65 | | -2.38 | |
| 3107 | S.C. Rastogi | 51.97 | | 2.48 | |
| 3116 | In house | 36.98 | ex | -11.20 | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | 51.6 | | 2.14 | |
| 3139 | In house | 53.92 | | 4.26 | |
| 3153 | In house | 47.3 | | -1.78 | |
| 3159 | In house | 39 | | -9.36 | |
| 3172 | | 52.0 | | 2.51 | |
| 3179 | In house | 45.2 | | -3.70 | |
| 3188 | D3421 | 42.6 | | -6.07 | |
| 3189 | In house | 34.55 | DG(0.05) | -13.42 | |
| 3191 | D3421 | 46.9 | | -2.15 | |
| 8001 | D3421 | 48.32 | | -0.85 | |
| normality | | OK | | | |
| n | | 19 | | | |
| outliers | | 3 | | | |
| mean (n) | | 49.254 | | | |
| st.dev. (n) | | 4.1431 | | | |
| R(calc.) | | 11.601 | | | |
| R(Horwitz) | | 3.068 | | | Compare R(D3421:75) = 3.300 |



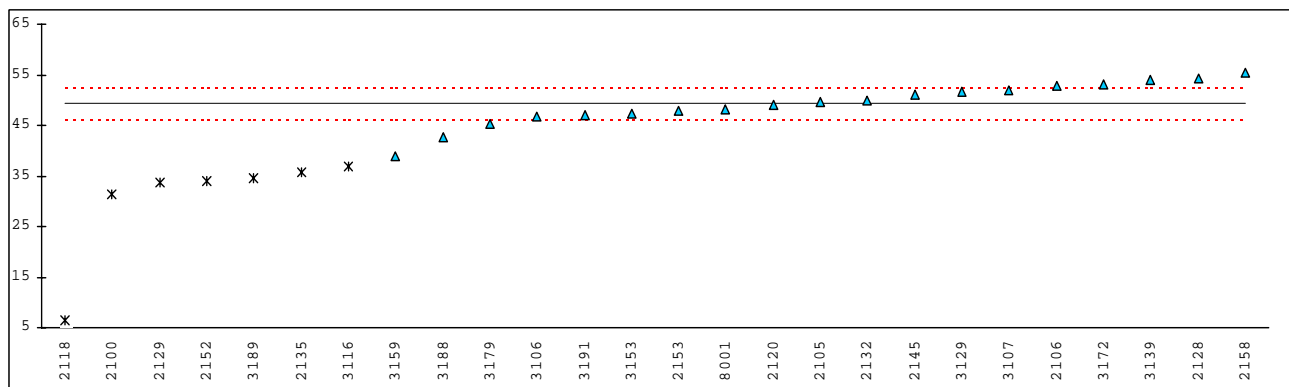
Determination of Total phthalates on sample 0314; results in %M/M

| lab | method | value | mark | Z(target) | value *) | mark | Z(target) | Remarks |
|-------------|--------------|--------|---------|-----------|----------|----------|-----------|------------------------------------|
| 2100 | In house | 31.5 | ex | -16.63 | 31.5 | ex | -16.25 | Manually excluded, (see § 4.1 & 5) |
| 2105 | D3421 | ---- | | ---- | 49.61 | | 0.26 | |
| 2106 | In house | ---- | | ---- | 52.9 | | 3.26 | |
| 2118 | In house | 6.56 | ex | -39.12 | 6.56 | ex | -38.98 | Manually excluded, (see § 4.1 & 5) |
| 2120 | In house | ---- | | ---- | 49.06 | | -0.24 | |
| 2128 | Oko-tex | ---- | | ---- | 54.41 | | 4.64 | |
| 2129 | In house | ---- | | ---- | 33.7 | G(0.01) | -14.24 | |
| 2132 | In house | ---- | | ---- | 49.8 | | 0.43 | |
| 2135 | Oko-tex 100 | 35.7 | ex | -12.85 | 35.7 | ex | -12.42 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | ---- | | ---- | 51.22 | | 1.73 | |
| 2152 | D3421 | 33.94 | G(0.01) | -14.43 | 33.94 | DG(0.05) | -14.02 | |
| 2153 | In house | 47.99 | | -1.76 | 47.99 | | -1.22 | |
| 2158 | D3421 | ---- | | ---- | 55.35 | | 5.49 | |
| 3106 | D3421 | ---- | | ---- | 46.68 | | -2.41 | |
| 3107 | S.C. Rastogi | 52.092 | | 1.94 | 52.092 | | 2.52 | |
| 3116 | In house | 36.98 | ex | -11.69 | 36.98 | ex | -11.25 | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ---- | | ---- | 51.6 | | 2.07 | |
| 3139 | In house | 53.92 | | 3.59 | 53.92 | | 4.19 | |
| 3153 | In house | ---- | | ---- | 47.3 | | -1.85 | |
| 3159 | In house | ---- | | ---- | 39.01 | | -9.40 | |
| 3172 | | 53.1 | | 2.85 | 53.1 | | 3.44 | |
| 3179 | In house | ---- | | ---- | 45.2 | | -3.76 | |
| 3188 | D3421 | 42.62 | | -6.60 | 42.62 | | -6.11 | |
| 3189 | In house | ---- | | ---- | 34.57 | DG(0.05) | -13.45 | |
| 3191 | D3421 | ---- | | ---- | 46.98 | | -2.14 | |
| 8001 | D3421 | ---- | | ---- | 48.32 | | -0.92 | |
| normality | | OK | | | OK | | | |
| n | | 5 | | | 19 | | | |
| outliers | | 1 | | | 3 | | | |
| mean (n) | | 49.944 | | | 49.324 | | | |
| st.dev. (n) | | 4.6862 | | | 4.1824 | | | |
| R(calc.) | | 13.121 | | | 11.711 | | | |
| R(D3421:75) | | 3.105 | | | 3.072 | | | Compare R(D3421:75) = 4.900 |

*) after manual summation



Only reported data

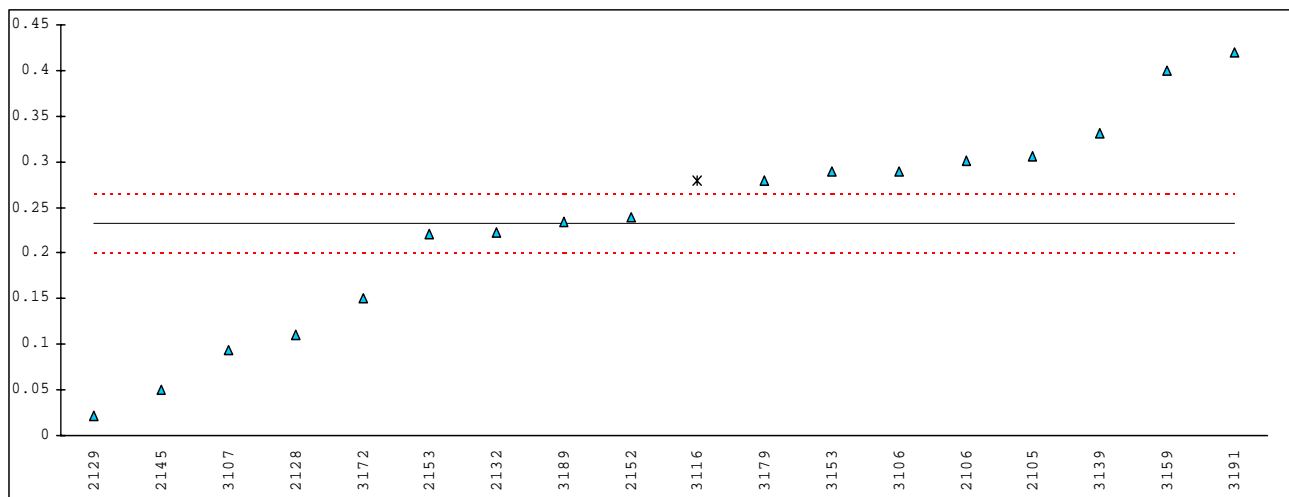


All data after manual summation

Determination of DINP on sample 0315; results in %M/M

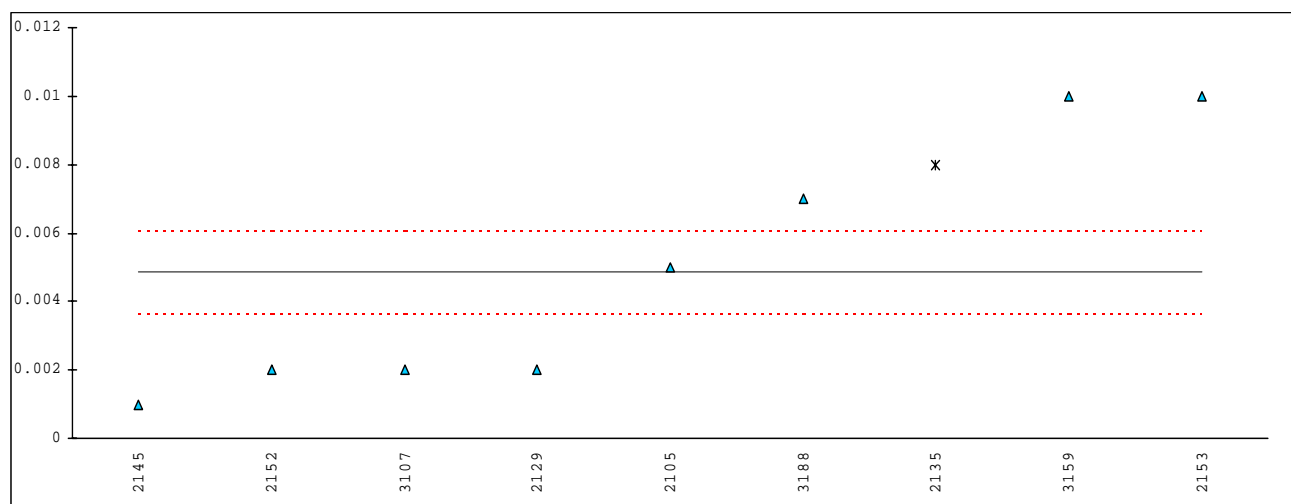
| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|----------|-------|---------|---------------------------------------------------------|
| 2100 | In house | ----- | | ----- | |
| 2105 | D3421 | 0.306 | | 6.29 | |
| 2106 | In house | 0.301 | | 5.86 | |
| 2118 | In house | ----- | | ----- | |
| 2120 | In house | positive | | ----- | |
| 2128 | Oko-tex | 0.11 | | -10.60 | |
| 2129 | In house | 0.022 | C | -18.18 | First reported 0.022 |
| 2132 | In house | 0.222 | | -0.95 | |
| 2135 | Oko-tex 100 | ----- | | ----- | |
| 2145 | S.C. Rastogi | 0.05 | | -15.77 | |
| 2152 | D3421 | 0.240 | | 0.60 | |
| 2153 | In house | 0.22 | | -1.12 | |
| 2158 | D3421 | ----- | | ----- | |
| 3106 | D3421 | 0.29 | | 4.91 | |
| 3107 | S.C. Rastogi | 0.094 | | -11.98 | |
| 3116 | In house | 0.28 | ex, C | 4.05 | First reported 0.53, Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ----- | | ----- | |
| 3139 | In house | 0.331 | | 8.44 | |
| 3153 | In house | 0.29 | | 4.91 | |
| 3159 | In house | 0.40 | | 14.39 | |
| 3172 | In house | 0.15 | | -7.15 | |
| 3179 | In house | 0.28 | | 4.05 | |
| 3188 | D3421 | nd | | ----- | False negative |
| 3189 | In house | 0.235 | | 0.17 | |
| 3191 | D3421 | 0.42 | | 16.11 | |
| 8001 | D3421 | ----- | | ----- | |
| | | | | | |
| normality | OK | | | | |
| n | 17 | | | | |
| outliers | 0 | | | | |
| mean (n) | 0.233 | | | | |
| st.dev. (n) | 0.1148 | | | | |
| R(calc.) | 0.321 | | | | |
| R(Horwitz) | 0.033 | | | | |

Compare R(D3421:75) = 3.300



Determination of DBP on sample 0315; results in %M/M

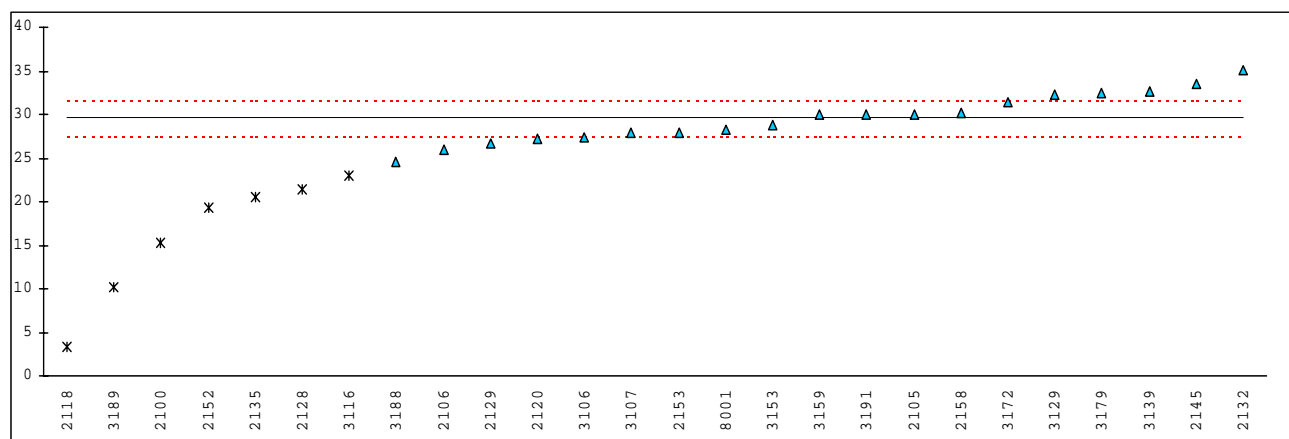
| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|---------|------|---------|------------------------------------|
| 2100 | In house | ---- | | ---- | |
| 2105 | D3421 | 0.005 | | 0.29 | |
| 2106 | In house | nd | | ---- | |
| 2118 | In house | ---- | | ---- | |
| 2120 | In house | <0.03 | | ---- | |
| 2128 | Oko-tex | <0.002 | | ---- | |
| 2129 | In house | 0.002 | | -6.71 | |
| 2132 | In house | <0.005 | | ---- | |
| 2135 | Oko-tex 100 | 0.008 | ex | 7.29 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | 0.001 | | -9.04 | |
| 2152 | D3421 | 0.002 | | -6.71 | |
| 2153 | In house | 0.01 | | 11.96 | |
| 2158 | D3421 | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | ---- | |
| 3107 | S.C. Rastogi | 0.002 | | -6.71 | |
| 3116 | In house | <0.01 | ex | ---- | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ---- | | ---- | |
| 3139 | In house | <0.02 | | ---- | |
| 3153 | In house | <0.01 | | ---- | |
| 3159 | In house | 0.01 | | 11.96 | |
| 3172 | | <0.05 | | ---- | |
| 3179 | In house | ---- | | ---- | |
| 3188 | D3421 | 0.007 | | 4.96 | |
| 3189 | In house | <0.0020 | | ---- | |
| 3191 | D3421 | <0.01 | | ---- | |
| 8001 | D3421 | ---- | | ---- | |
| normality | | OK | | | |
| n | | 8 | | | |
| outliers | | 0 | | | |
| mean (n) | | 0.0049 | | | |
| st.dev. (n) | | 0.00372 | | | |
| R(calc.) | | 0.0104 | | | |
| R(Horwitz) | | 0.0012 | | | Compare R(D3421:75) = 3.3000 |



Determination of DEHP (DOP) on sample 0315; results in %M/M

| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|--------|------------|---------|---------------------------------------------------------|
| 2100 | In house | 15.2 | ex | -20.23 | Manually excluded, (see § 4.1 & 5) |
| 2105 | D3421 | 30.01 | | 0.61 | |
| 2106 | In house | 25.9 | C | -5.17 | First reported 38.5 |
| 2118 | In house | 3.31 | ex, C | -36.97 | First reported 0.33, Manually excluded, (see § 4.1 & 5) |
| 2120 | In house | 27.2 | | -3.34 | |
| 2128 | Oko-tex | 21.4 | C, G(0.05) | -11.51 | First reported 14.4 |
| 2129 | In house | 26.6 | | -4.19 | |
| 2132 | In house | 35.073 | | 7.74 | |
| 2135 | Oko-tex 100 | 20.6 | ex | -12.63 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | 33.51 | | 5.54 | |
| 2152 | D3421 | 19.22 | (G(0.01) | -14.58 | |
| 2153 | In house | 27.98 | | -2.24 | |
| 2158 | D3421 | 30.19 | | 0.87 | |
| 3106 | D3421 | 27.32 | | -3.17 | |
| 3107 | S.C. Rastogi | 27.85 | | -2.43 | |
| 3116 | In house | 23.01 | ex | -9.24 | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | 32.2 | | 3.70 | |
| 3139 | In house | 32.61 | | 4.27 | |
| 3153 | In house | 28.8 | | -1.09 | |
| 3159 | In house | 30 | | 0.60 | |
| 3172 | | 31.4 | | 2.57 | |
| 3179 | In house | 32.4 | | 3.98 | |
| 3188 | D3421 | 24.6 | | -7.00 | |
| 3189 | In house | 10.1 | G(0.01) | -27.41 | First reported 14.6 |
| 3191 | D3421 | 30.0 | | 0.60 | |
| 8001 | D3421 | 28.26 | | -1.85 | |
| normality | | OK | | | |
| n | | 19 | | | |
| outliers | | 3 | | | |
| mean (n) | | 29.574 | | | |
| st.dev. (n) | | 2.7862 | | | |
| R(calc.) | | 7.801 | | | |
| R(Horwitz) | | 1.989 | | | |

Compare R(D3421:75) = 3.300



Determination of Total phthalates on sample 0315; results in %M/M

| lab | method | value | mark | Z(targ) | value *) | mark | Z(targ) | Remarks |
|------|--------------|--------|---------|---------|----------|---------|---------|------------------------------------|
| 2100 | In house | 15.2 | ex | -19.95 | 15.2 | ex | -20.39 | Manually excluded, (see § 4.1 & 5) |
| 2105 | D3421 | ---- | | ---- | 30.321 | | 0.77 | |
| 2106 | In house | ---- | | ---- | 25.9 | | -5.42 | |
| 2118 | In house | 3.31 | ex | -36.85 | 3.31 | ex | -37.03 | Manually excluded, (see § 4.1 & 5) |
| 2120 | In house | ---- | | ---- | 27.2 | | -3.60 | |
| 2128 | Oko-tex | ---- | | ---- | 24.51 | G(0.05) | -7.37 | |
| 2129 | In house | ---- | | ---- | 26.62 | | -4.41 | |
| 2132 | In house | ---- | | ---- | 35.073 | | 7.41 | |
| 2135 | Oko-tex 100 | 20.6 | ex | -12.27 | 20.6 | ex | -12.84 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | ---- | | ---- | 33.56 | | 5.30 | |
| 2152 | D3421 | 19.47 | G(0.01) | -13.88 | 19.47 | G(0.01) | -14.42 | |
| 2153 | In house | 28.21 | | -1.46 | 28.21 | | -2.19 | |
| 2158 | D3421 | ---- | | ---- | 30.19 | | 0.58 | |
| 3106 | D3421 | ---- | | ---- | 27.61 | | -3.03 | |
| 3107 | S.C. Rastogi | 27.996 | | -1.76 | 27.996 | | -2.49 | |
| 3116 | In house | 23.29 | ex | -8.45 | 23.29 | ex | -9.07 | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ---- | | ---- | 32.2 | | 3.39 | |
| 3139 | In house | 32.94 | | 5.27 | 32.94 | | 4.43 | |
| 3153 | In house | ---- | | ---- | 29.09 | | -0.96 | |
| 3159 | In house | ---- | | ---- | 30.41 | | 0.89 | |
| 3172 | | 32.4 | | 4.50 | 32.4 | | 3.67 | |
| 3179 | In house | ---- | | ---- | 32.68 | | 4.07 | |
| 3188 | D3421 | 24.63 | | -6.55 | 24.63 | | -7.20 | |
| 3189 | In house | ---- | | ---- | 10.34 | G(0.01) | -27.19 | |
| 3191 | D3421 | ---- | | ---- | 30.42 | | 0.90 | |
| 8001 | D3421 | ---- | | ---- | 28.26 | | -2.12 | |

normality

OK

OK

n

5

19

outliers

1

3

mean (n)

29.235

29.774

st.dev. (n)

3.4473

2.8485

R(calc.)

9.652

7.976

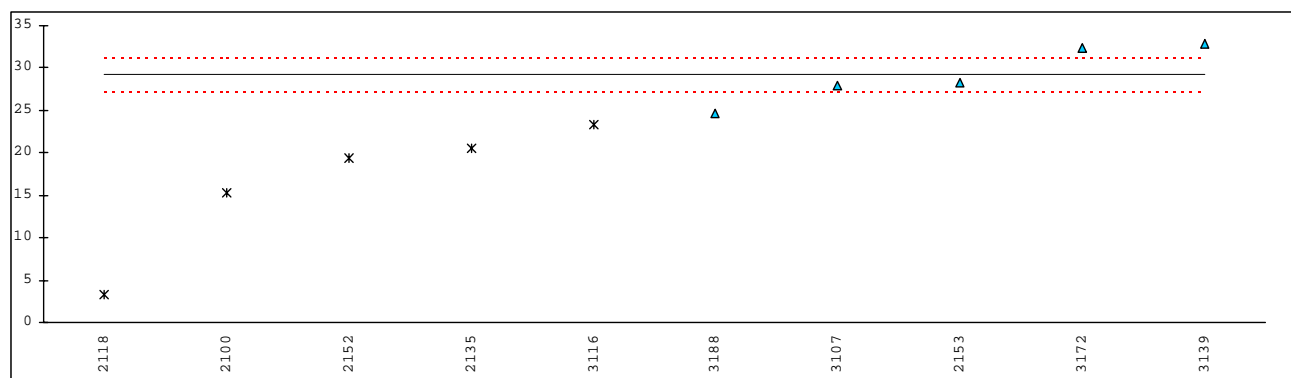
R(D3421:75)

1.970

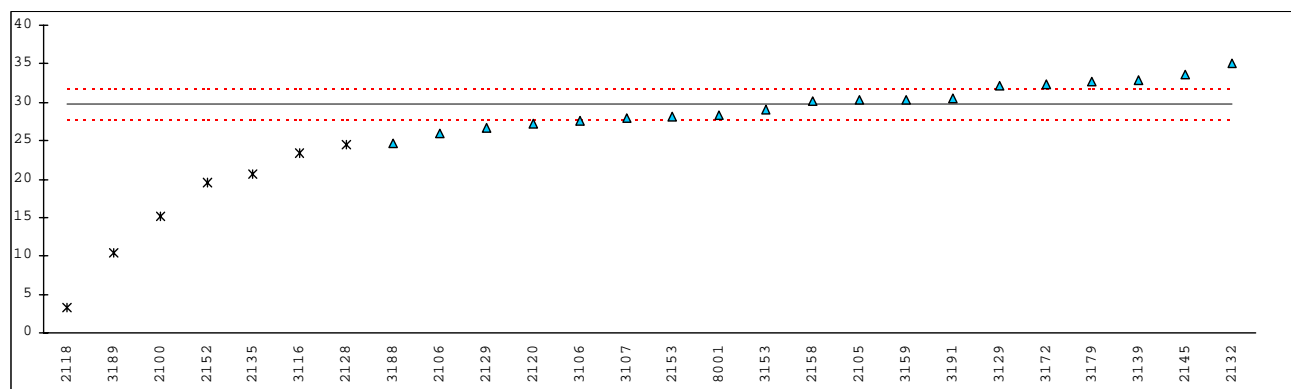
2.001

Compare R(Horwitz) = 4.900

*) after manual summation



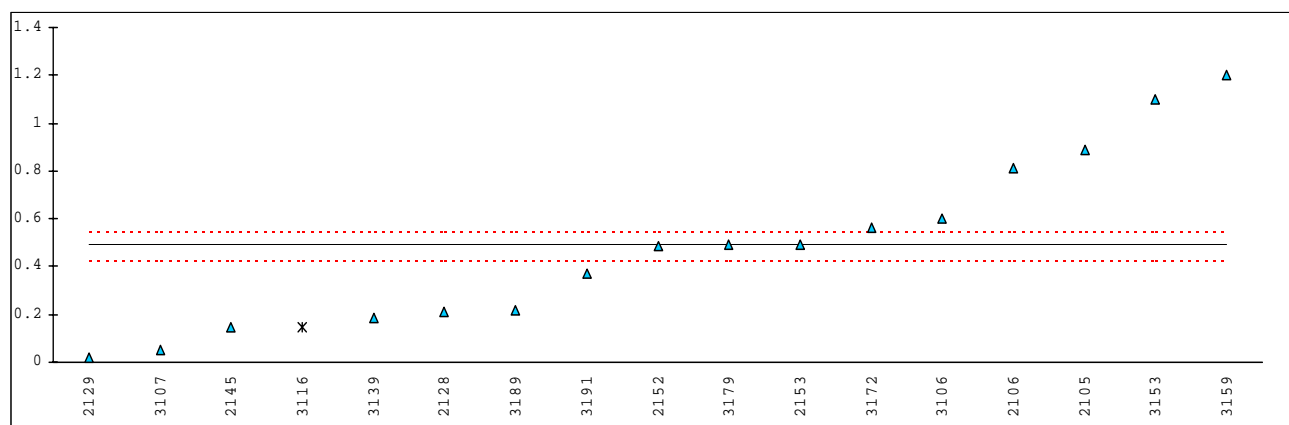
Only reported data



All data after manual summation

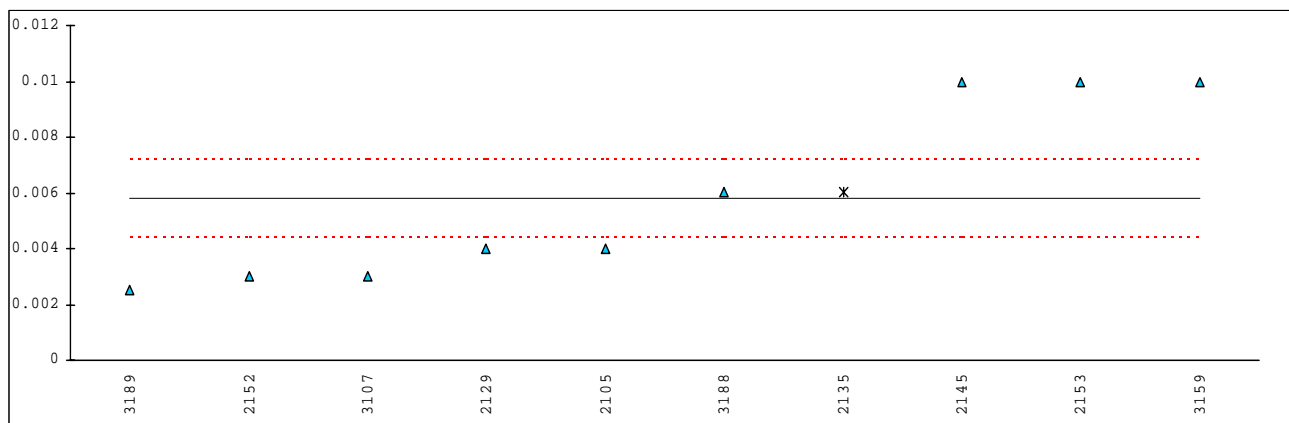
Determination of DINP on sample 0316; results in %M/M

| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|----------|------|-----------------------------|---------------------------------------------------------|
| 2100 | In house | ----- | | ----- | |
| 2105 | D3421 | 0.889 | | 18.35 | |
| 2106 | In house | 0.810 | | 14.73 | |
| 2118 | In house | ----- | | ----- | |
| 2120 | In house | positive | | ----- | |
| 2128 | Oko-tex | 0.21 | | -12.81 | |
| 2129 | In house | 0.018 | | -21.63 | |
| 2132 | In house | <0.005 | | <-22.22 | false negative |
| 2135 | Oko-tex 100 | ----- | | ----- | |
| 2145 | S.C. Rastogi | 0.15 | | -15.57 | |
| 2152 | D3421 | 0.485 | | -0.19 | |
| 2153 | In house | 0.49 | | 0.04 | |
| 2158 | D3421 | ----- | | ----- | |
| 3106 | D3421 | 0.60 | | 5.09 | |
| 3107 | S.C. Rastogi | 0.048 | | -20.25 | |
| 3116 | In house | 0.15 | ex | -15.57 | First reported 2.51, Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ----- | | ----- | |
| 3139 | In house | 0.186 | | -13.91 | |
| 3153 | In house | 1.1 | | 28.04 | |
| 3159 | In house | 1.2 | | 32.63 | |
| 3172 | | 0.56 | | 3.25 | |
| 3179 | In house | 0.49 | | 0.04 | |
| 3188 | D3421 | nd | | ----- | false negative |
| 3189 | In house | 0.220 | | -12.35 | |
| 3191 | D3421 | 0.37 | | -5.47 | |
| 8001 | D3421 | ----- | | ----- | |
| | | | | | |
| normality | | OK | | | |
| n | | 16 | | | |
| outliers | | 0 | | | |
| mean (n) | | 0.489 | | | |
| st.dev. (n) | | 0.3602 | | | |
| R(calc.) | | 1.009 | | | |
| R(Horwitz) | | 0.061 | | | |
| | | | | Compare R(D3421:75) = 3.300 | |



Determination of DBP on sample 0316; results in %M/M

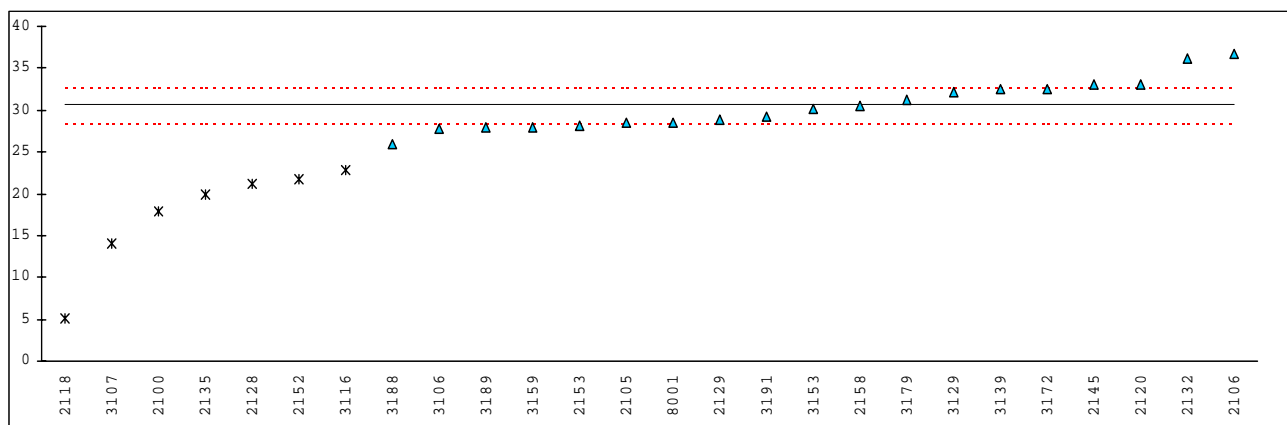
| lab | method | value | mark | Z(targ) | remarks |
|------|--------------|----------|------|---------|------------------------------------|
| 2100 | In house | ---- | | ---- | |
| 2105 | D3421 | 0.004 | | -3.67 | |
| 2106 | In house | nd | | ---- | |
| 2118 | In house | ---- | | ---- | |
| 2120 | In house | positive | | ---- | |
| 2128 | Oko-tex | <0.002 | | ---- | |
| 2129 | In house | 0.004 | | -3.67 | |
| 2132 | In house | <0.005 | | ---- | |
| 2135 | Oko-tex 100 | 0.006 | ex | 0.33 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | 0.01 | | 8.33 | |
| 2152 | D3421 | 0.003 | | -5.67 | |
| 2153 | In house | 0.01 | | 8.33 | |
| 2158 | D3421 | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | ---- | |
| 3107 | S.C. Rastogi | 0.003 | | -5.67 | |
| 3116 | In house | <0.01 | ex | ---- | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ---- | | ---- | |
| 3139 | In house | <0.02 | | ---- | |
| 3153 | In house | <0.01 | | ---- | |
| 3159 | In house | 0.01 | | 8.33 | |
| 3172 | | <0.05 | | ---- | |
| 3179 | In house | ---- | | ---- | |
| 3188 | D3421 | 0.006 | | 0.33 | |
| 3189 | In house | 0.0025 | | -6.67 | |
| 3191 | D3421 | <0.01 | | ---- | |
| 8001 | D3421 | ---- | | ---- | |
| | | | | | |
| | normality | OK | | | |
| | n | 9 | | | |
| | outliers | 0 | | | |
| | mean (n) | 0.0058 | | | |
| | st.dev. (n) | 0.00328 | | | |
| | R(calc.) | 0.0092 | | | |
| | R(Horwitz) | 0.0014 | | | Compare R(D3421:75) = 3.3000 |



Determination of DEHP (DOP) on sample 0316; results in %M/M

| lab | method | value | mark | Z(targ) | remarks |
|-------------|--------------|--------|-------------|---------|---------------------------------------------------------|
| 2100 | In house | 17.9 | ex | -17.36 | Manually excluded, (see § 4.1 & 5) |
| 2105 | D3421 | 28.57 | | -2.78 | |
| 2106 | In house | 36.7 | | 8.34 | |
| 2118 | In house | 5.09 | ex | -34.88 | First reported 0.51, Manually excluded, (see § 4.1 & 5) |
| 2120 | In house | 33.1 | | 3.42 | |
| 2128 | Oko-tex | 21.1 | C, DG(0.05) | -12.99 | First reported 13.4 |
| 2129 | In house | 28.9 | | -2.32 | |
| 2132 | In house | 36.159 | | 7.60 | |
| 2135 | Oko-tex 100 | 19.9 | ex | -14.63 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | 33.08 | | 3.39 | |
| 2152 | D3421 | 21.662 | DG(0.05) | -12.22 | |
| 2153 | In house | 28.17 | | -3.32 | |
| 2158 | D3421 | 30.58 | | -0.03 | |
| 3106 | D3421 | 27.84 | | -3.77 | |
| 3107 | S.C. Rastogi | 14.00 | G(0.05) | -22.70 | |
| 3116 | In house | 22.88 | ex | -10.56 | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | 32.2 | | 2.19 | |
| 3139 | In house | 32.47 | | 2.56 | |
| 3153 | In house | 30.1 | | -0.68 | |
| 3159 | In house | 28 | | -3.56 | |
| 3172 | | 32.5 | | 2.60 | |
| 3179 | In house | 31.3 | | 0.96 | |
| 3188 | D3421 | 26.0 | | -6.29 | |
| 3189 | In house | 27.86 | | -3.75 | |
| 3191 | D3421 | 29.3 | | -1.78 | |
| 8001 | D3421 | 28.58 | | -2.76 | |
| normality | | OK | | | |
| n | | 19 | | | |
| outliers | | 3 | | | |
| mean (n) | | 30.600 | | | |
| st.dev. (n) | | 2.9122 | | | |
| R(calc.) | | 8.154 | | | |
| R(Horwitz) | | 2.048 | | | |

Compare R(D3421:75) = 3.300



Determination of Total phthalates on sample 0316; results in %M/M

| lab | method | value | mark | Z(targ) | value *) | mark | Z(targ) | Remarks |
|------|--------------|--------|---------|---------|----------|---------|---------|------------------------------------|
| 2100 | In house | 17.9 | ex | -17.06 | 17.9 | ex | -17.73 | Manually excluded, (see § 4.1 & 5) |
| 2105 | D3421 | ----- | | ----- | 29.463 | | -2.11 | |
| 2106 | In house | ----- | | ----- | 37.531 | | 8.80 | |
| 2118 | In house | 5.09 | ex | -34.74 | 5.09 | ex | -35.04 | Manually excluded, (see § 4.1 & 5) |
| 2120 | In house | ----- | | ----- | 33.1 | | 2.81 | |
| 2128 | Oko-tex | ----- | | ----- | 21.31 | G(0.05) | -13.12 | |
| 2129 | In house | ----- | | ----- | 28.93 | | -2.83 | |
| 2132 | In house | ----- | | ----- | 36.296 | | 7.13 | |
| 2135 | Oko-tex 100 | 19.9 | ex | -14.30 | 19.9 | ex | -15.03 | Manually excluded, (see § 4.1 & 5) |
| 2145 | S.C. Rastogi | ----- | | ----- | 33.24 | | 3.00 | |
| 2152 | D3421 | 22.156 | G(0.05) | -11.19 | 22.156 | G(0.05) | -11.98 | |
| 2153 | In house | 28.67 | | -2.20 | 28.67 | | -3.18 | |
| 2158 | D3421 | ----- | | ----- | 30.58 | | -0.60 | |
| 3106 | D3421 | ----- | | ----- | 28.44 | | -3.49 | |
| 3107 | S.C. Rastogi | 14.089 | (G0.01) | -22.32 | 14.089 | (G0.01) | -22.88 | |
| 3116 | In house | 23.03 | ex | -9.98 | 23.03 | ex | -10.80 | Manually excluded, (see § 4.1 & 5) |
| 3129 | In house | ----- | | ----- | 32.2 | | 1.59 | |
| 3139 | In house | 32.66 | | 3.31 | 32.66 | | 2.21 | |
| 3153 | In house | ----- | | ----- | 31.22 | | 0.27 | |
| 3159 | In house | ----- | | ----- | 29.21 | | -2.45 | |
| 3172 | In house | 33.7 | | 4.74 | 33.7 | | 3.62 | |
| 3179 | In house | ----- | | ----- | 31.79 | | 1.04 | |
| 3188 | D3421 | 26.03 | | -5.84 | 26.03 | | -6.74 | |
| 3189 | In house | ----- | | ----- | 28.09 | | -3.96 | |
| 3191 | D3421 | ----- | | ----- | 29.67 | | -1.83 | |
| 8001 | D3421 | ----- | | ----- | 28.58 | | -3.30 | |

normality OK

OK

n 4

19

outliers 2

7

mean (n) 30.265

31.021

st.dev. (n) 3.5597

2.9353

R(calc.) 9.967

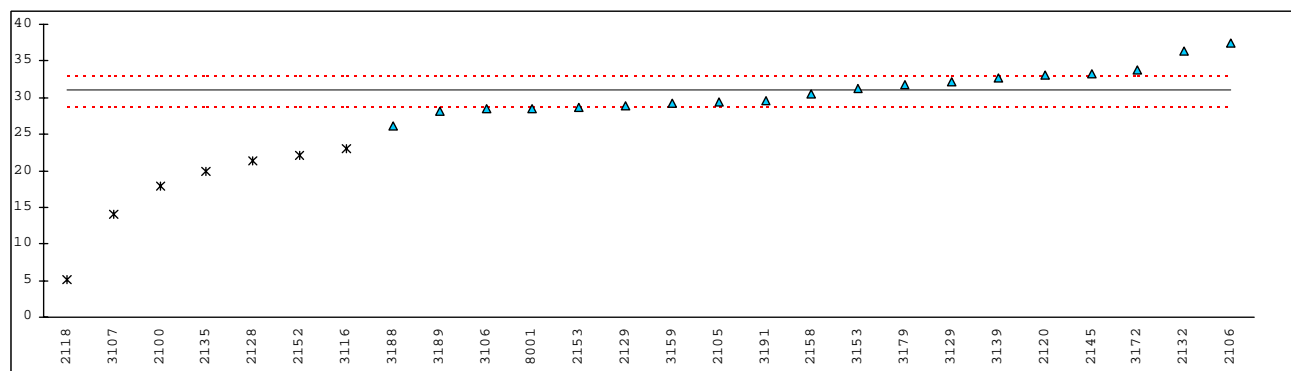
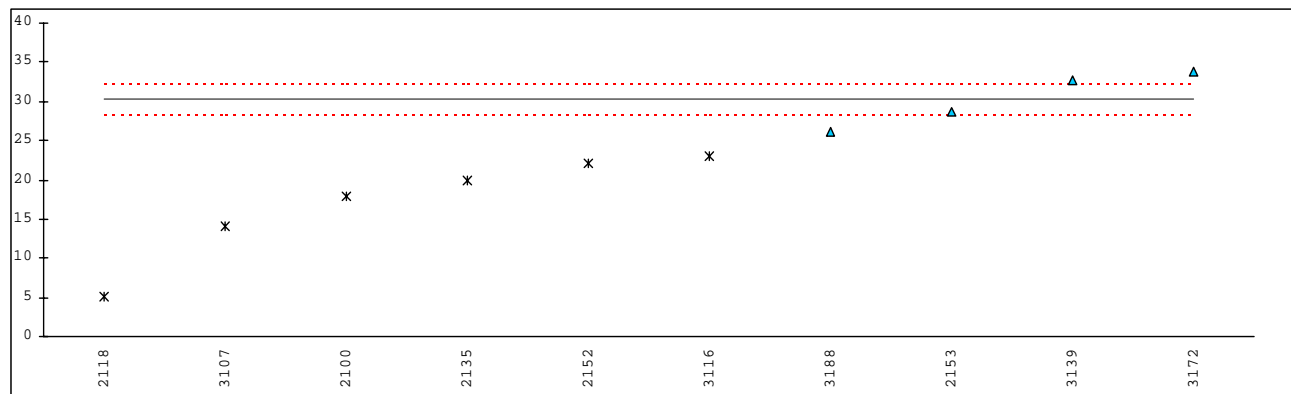
8.219

R(Horwitz) 2.029

2.072

Compare R(D3421:75) = 4.900

*) after manual summation



Determination of phthalates on sample 0314; results in %M/M

| lab | method | DINP | mark | BBP | mark | DIDP | mark | DNOP | mark | DPrP | mark | DDP | mark |
|------|--------------|---------|------|---------|------|---------|------|---------|------|---------|------|---------|------|
| 2100 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2105 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2106 | In house | nd | | nd | | nd | | nd | | ---- | | ---- | |
| 2118 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2120 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2128 | Oko-tex | <0.01 | | 0.009 | | <0.002 | | <0.01 | | ---- | | ---- | |
| 2129 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2132 | In house | <0.005 | | <0.005 | | <0.005 | | <0.005 | | ---- | | ---- | |
| 2135 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2145 | S.C. Rastogi | <0.001 | | <0.001 | | <0.001 | | <0.001 | | ---- | | ---- | |
| 2152 | D3421 | 0.027 | | nd | | nd | | nd | | nd | | nd | |
| 2153 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 2158 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3106 | D3421 | 0.03 | | <0.01 | | <0.02 | | <0.01 | | <0.01 | | <0.01 | |
| 3107 | S.C. Rastogi | nd | | 0.121 | | nd | | nd | | ---- | | ---- | |
| 3116 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3129 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3139 | In house | <0.02 | | <0.02 | | <0.02 | | <0.02 | | <0.02 | | <0.02 | |
| 3153 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3159 | In house | nd | | nd | | nd | | nd | | ---- | | ---- | |
| 3172 | | 0.05 | | <0.05 | | <0.05 | | <0.05 | | ---- | | ---- | |
| 3179 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3188 | eec1999-815 | nd | | nd | | nd | | nd | | ---- | | ---- | |
| 3189 | In house | 0.0055 | | <0.0020 | | <0.0020 | | <0.0020 | | <0.0020 | | <0.0020 | |
| 3191 | D3421 | 0.075 | | <0.01 | | <0.01 | | <0.01 | | ---- | | ---- | |
| 8001 | D3421 | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| | normality | OK | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | n | 5 | | 2 | | 0 | | 0 | | 0 | | 0 | |
| | outliers | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | |
| | mean (n) | 0.038 | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | st.dev. (n) | 0.0262 | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(calc.) | 0.073 | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(lit) | unknown | | unknown | | unknown | | unknown | | unknown | | unknown | |

Determination of phthalates on sample 0314; results in %M/M

| lab | method | DCHP | mark | DEP | mark | DHP | mark | Others | mark |
|------|-------------|----------|------|---------|------|---------|------|----------|------|
| 2100 | | ---- | | ---- | | ---- | | ---- | |
| 2105 | D3421 | ---- | | ---- | | ---- | | 0.009 | |
| 2106 | | ---- | | ---- | | ---- | | ---- | |
| 2118 | | ---- | | ---- | | ---- | | ---- | |
| 2120 | | ---- | | ---- | | ---- | | ---- | |
| 2128 | Oko-tex | ---- | | <0.002 | | ---- | | <0.002 | |
| 2129 | In house | positive | | ---- | | ---- | | positive | |
| 2132 | | ---- | | ---- | | ---- | | ---- | |
| 2135 | | ---- | | ---- | | ---- | | ---- | |
| 2145 | | ---- | | ---- | | ---- | | ---- | |
| 2152 | D3421 | nd | | nd | | nd | | ---- | |
| 2153 | In house | <0.01 | | <0.01 | | ---- | | ---- | |
| 2158 | | ---- | | ---- | | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | <0.01 | | ---- | | <0.01 | |
| 3107 | | ---- | | ---- | | ---- | | ---- | |
| 3116 | In house | <0.01 | | <0.01 | | <0.01 | | ---- | |
| 3129 | | ---- | | ---- | | ---- | | ---- | |
| 3139 | In house | <0.02 | | <0.02 | | ---- | | ---- | |
| 3153 | In house | <0.01 | | <0.01 | | ---- | | ---- | |
| 3159 | | ---- | | ---- | | ---- | | ---- | |
| 3172 | | ---- | | ---- | | ---- | | ---- | |
| 3179 | | ---- | | ---- | | ---- | | ---- | |
| 3188 | | ---- | | ---- | | ---- | | ---- | |
| 3189 | In house | <0.0020 | | <0.0020 | | ---- | | 0.0040 | |
| 3191 | D3421 | ---- | | <0.01 | | ---- | | ---- | |
| 8001 | | ---- | | ---- | | ---- | | ---- | |
| | normality | n.a. | | n.a. | | n.a. | | n.a. | |
| | n | 0 | | 0 | | 0 | | 2 | |
| | outliers | 0 | | 0 | | 0 | | 0 | |
| | mean (n) | n.a. | | n.a. | | n.a. | | n.a. | |
| | st.dev. (n) | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(calc.) | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(lit) | unknown | | unknown | | unknown | | unknown | |

Determination of phthalates on sample 0315: results in %M/M

| lab | method | BBP | mark | DIDP | mark | DNOP | mark | DPrP | mark | DDP | mark | DCHP | mark |
|------|--------------|---------|------|----------|------|---------|------|---------|------|---------|------|----------|------|
| 2100 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2105 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2106 | In house | nd | | nd | | nd | | ---- | | ---- | | ---- | |
| 2118 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2120 | In house | ---- | | positive | | ---- | | ---- | | ---- | | ---- | |
| 2128 | Oko-tex | <0.002 | | <0.002 | | <0.01 | | ---- | | ---- | | ---- | |
| 2129 | In house | ---- | | ---- | | ---- | | ---- | | ---- | | positive | |
| 2132 | In house | <0.005 | | <0.005 | | <0.005 | | ---- | | ---- | | ---- | |
| 2135 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2145 | S.C. Rastogi | <0.001 | | <0.001 | | <0.001 | | ---- | | ---- | | ---- | |
| 2152 | D3421 | nd | | nd | | nd | | nd | | nd | | nd | |
| 2153 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 2158 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | <0.02 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3107 | S.C. Rastogi | 0.050 | | nd | | nd | | ---- | | ---- | | ---- | |
| 3116 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3129 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3139 | In house | <0.02 | | <0.02 | | <0.02 | | <0.02 | | <0.02 | | <0.02 | |
| 3153 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3159 | In house | nd | | nd | | nd | | ---- | | ---- | | ---- | |
| 3172 | | <0.05 | | <0.05 | | <0.05 | | ---- | | ---- | | ---- | |
| 3179 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3188 | eec1999-815 | nd | | nd | | nd | | ---- | | ---- | | ---- | |
| 3189 | In house | <0.0020 | | <0.0020 | | <0.0020 | | <0.0020 | | <0.0020 | | <0.0020 | |
| 3191 | D3421 | <0.01 | | <0.01 | | <0.01 | | ---- | | ---- | | ---- | |
| 8001 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| | normality | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | n | 1 | | 0 | | 0 | | 0 | | 0 | | 0 | |
| | outliers | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | |
| | mean (n) | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | st.dev. (n) | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(calc.) | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(lit) | unknown | | unknown | | unknown | | unknown | | unknown | | unknown | |

Determination of phthalates on sample 0315: results in %M/M

| lab | method | DEP | mark | DHP | mark | Others | mark |
|------|-------------|---------|------|---------|------|---------|------|
| 2100 | | ---- | | ---- | | ---- | |
| 2105 | | ---- | | ---- | | ---- | |
| 2106 | | ---- | | ---- | | ---- | |
| 2118 | | ---- | | ---- | | ---- | |
| 2120 | | ---- | | ---- | | ---- | |
| 2128 | Oko-tex | <0.002 | | ---- | | <0.002 | |
| 2129 | | ---- | | ---- | | ---- | |
| 2132 | | ---- | | ---- | | ---- | |
| 2135 | | ---- | | ---- | | ---- | |
| 2145 | | ---- | | ---- | | ---- | |
| 2152 | D3421 | nd | | nd | | ---- | |
| 2153 | In house | <0.01 | | ---- | | ---- | |
| 2158 | | ---- | | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | ---- | | <0.01 | |
| 3107 | | ---- | | ---- | | ---- | |
| 3116 | In house | <0.01 | | <0.01 | | ---- | |
| 3129 | | ---- | | ---- | | ---- | |
| 3139 | In house | <0.02 | | ---- | | ---- | |
| 3153 | In house | <0.01 | | ---- | | ---- | |
| 3159 | | ---- | | ---- | | ---- | |
| 3172 | | ---- | | ---- | | ---- | |
| 3179 | | ---- | | ---- | | ---- | |
| 3188 | | ---- | | ---- | | ---- | |
| 3189 | In house | <0.0020 | | ---- | | 0.0056 | |
| 3191 | D3421 | <0.01 | | ---- | | ---- | |
| 8001 | | ---- | | ---- | | ---- | |
| | normality | n.a. | | n.a. | | n.a. | |
| | n | 0 | | 0 | | 0 | |
| | outliers | 0 | | 0 | | 0 | |
| | mean (n) | n.a. | | n.a. | | n.a. | |
| | st.dev. (n) | n.a. | | n.a. | | n.a. | |
| | R(calc.) | n.a. | | n.a. | | n.a. | |
| | R(lit) | unknown | | unknown | | unknown | |

Determination of phthalates on sample 0316: results in %M/M

| lab | method | BBP | mark | DIDP | mark | DNOP | mark | DPrP | mark | DDP | mark | DCHP | mark |
|------|--------------|---------|------|----------|------|---------|------|---------|------|---------|------|----------|------|
| 2100 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2105 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2106 | In house | nd | | 0.021 | | nd | | ---- | | ---- | | ---- | |
| 2118 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2120 | In house | ---- | | positive | | ---- | | ---- | | ---- | | ---- | |
| 2128 | Oko-tex | <0.002 | | <0.002 | | <0.01 | | ---- | | ---- | | ---- | |
| 2129 | In house | ---- | | 0.009 | | ---- | | ---- | | ---- | | positive | |
| 2132 | In house | <0.005 | | 0.137 | f.p. | <0.005 | | ---- | | ---- | | ---- | |
| 2135 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 2145 | S.C. Rastogi | <0.001 | | <0.001 | | <0.001 | | ---- | | ---- | | ---- | |
| 2152 | D3421 | nd | | 0.006 | | 21.66 | f.p. | nd | | nd | | nd | |
| 2153 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 2158 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | <0.02 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3107 | S.C. Rastogi | 0.038 | | nd | | nd | | ---- | | ---- | | ---- | |
| 3116 | In house | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3129 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3139 | In house | <0.02 | | <0.02 | | <0.02 | | <0.02 | | <0.02 | | <0.02 | |
| 3153 | In house | <0.01 | | 0.02 | | <0.01 | | <0.01 | | <0.01 | | <0.01 | |
| 3159 | In house | nd | | nd | | nd | | ---- | | ---- | | ---- | |
| 3172 | | <0.05 | | <0.05 | | <0.05 | | ---- | | ---- | | ---- | |
| 3179 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| 3188 | eec1999-815 | 0.004 | | 0.004 | | 0.006 | | ---- | | ---- | | ---- | |
| 3189 | In house | <0.0020 | | <0.0020 | | <0.0020 | | <0.002 | | <0.0020 | | <0.0020 | |
| 3191 | D3421 | <0.01 | | <0.01 | | <0.01 | | ---- | | ---- | | ---- | |
| 8001 | | ---- | | ---- | | ---- | | ---- | | ---- | | ---- | |
| | normality | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | n | 2 | | 6 | | 2 | | 0 | | 0 | | 0 | |
| | outliers | 0 | | 0 | | 0 | | 0 | | 0 | | 0 | |
| | mean (n) | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | st.dev. (n) | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(calc.) | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | | n.a. | |
| | R(lit) | unknown | | unknown | | unknown | | unknown | | unknown | | unknown | |

Determination of phthalates on sample 0316: results in %M/M

| lab | method | DEP | mark | DHP | mark | Others | mark |
|------|-------------|---------|------|----------|------|---------|------|
| 2100 | | ---- | | ---- | | ---- | |
| 2105 | | ---- | | ---- | | ---- | |
| 2106 | | ---- | | ---- | | ---- | |
| 2118 | | ---- | | ---- | | ---- | |
| 2120 | | ---- | | ---- | | ---- | |
| 2128 | Oko-tex | <0.002 | | ---- | | <0.002 | |
| 2129 | In house | 0.0003 | | positive | | ---- | |
| 2132 | | ---- | | ---- | | ---- | |
| 2135 | | ---- | | ---- | | ---- | |
| 2145 | | ---- | | ---- | | ---- | |
| 2152 | D3421 | 0.0003 | | nd | | ---- | |
| 2153 | In house | <0.01 | | ---- | | ---- | |
| 2158 | | ---- | | ---- | | ---- | |
| 3106 | D3421 | <0.01 | | ---- | | <0.01 | |
| 3107 | | ---- | | ---- | | ---- | |
| 3116 | In house | <0.01 | | <0.01 | | ---- | |
| 3129 | | ---- | | ---- | | ---- | |
| 3139 | In house | <0.02 | | ---- | | ---- | |
| 3153 | In house | <0.01 | | ---- | | ---- | |
| 3159 | | ---- | | ---- | | ---- | |
| 3172 | | ---- | | ---- | | ---- | |
| 3179 | | ---- | | ---- | | ---- | |
| 3188 | | ---- | | ---- | | ---- | |
| 3189 | In house | <0.0020 | | ---- | | 0.0072 | |
| 3191 | D3421 | <0.01 | | ---- | | ---- | |
| 8001 | D3421 | ---- | | ---- | | ---- | |
| | normality | n.a. | | n.a. | | n.a. | |
| | n | 2 | | 0 | | 1 | |
| | outliers | 0 | | 0 | | 0 | |
| | mean (n) | n.a. | | n.a. | | n.a. | |
| | st.dev. (n) | n.a. | | n.a. | | n.a. | |
| | R(calc.) | n.a. | | n.a. | | n.a. | |
| | R(lit) | unknown | | unknown | | unknown | |

APPENDIX 2

Method information

| Lab | Analysis method | Technique to release/extract | Technique to detect and quantify | Calibration used | Corrected for recovery |
|------|----------------------------|--------------------------------------------------------------------|----------------------------------|------------------|------------------------|
| 2100 | in house | extraction by boiling with PE | GC/MS | int.st. | no |
| 2105 | ASTM D3421-75 | soxhlet extraction, solvent methanol/dichloromethane 1:1 | GC/MS | ext. st. | no |
| 2106 | in house | soxhlet extraction, solvent dichloromethane | GC/MS | ext. st. | no |
| 2118 | in house | ASE | GC/MS | int. st. | no |
| 2120 | in house | solvent chloroform, room temp. for 1 hour | GC/MS | int. st. | no |
| 2128 | Öko-Tex standard | extraction with acetone, 5 hours | PLC / GC/MS | ext. st. | no |
| 2129 | In house | ultrasonic extraction with dichloromethane, 30 min. | GC/MS (Sim/scan) | ext. st. | no |
| 2132 | in house | extraction with chloroform at room temperature for 30 min. | GC/MSD | int. + ext. st. | no |
| 2135 | Öko-Tex standard 100 | soxhlet extraction with n-hexane. | GC/MS | ext. st. | no |
| 2145 | S.C.Rastogi | Dichloromethane extraction | GC | ext. st. | no |
| 2152 | ASTM D3421-75 | soxhlet extraction, solvent dichloromethane/methanol 2:1, 16 hours | GC/MSD | ext. st. | no |
| 2153 | in house | soxhlet extraction, solvent methanol/chloroform 1:2 | GC/MSD | ext. st. | no |
| 2158 | ASTM D3421-75 | soxhlet extraction, solvent carbontetra/methanol 2:1, 16 hours | GC | int. st. | no |
| 3106 | ASTM D3421-75 | soxhlet | GC-FID/GC-MSD | int.st./ext.st. | no |
| 3107 | S.C.Rastogi | soxhlet extraction, dichloromethane, 16 hours | GC/MS (SIM) | ext. st. | no |
| 3116 | in house | solvent extraction, dichloromethane, room temp. | GC/MS | ext. st. | no |
| 3129 | in house | solubility in THF/ethylacetate | GC/MS | ext.+int. st. | no |
| 3139 | in house | soxhlet extraction with acetone | GC-FID/GC-MS | int. st. | no |
| 3153 | in house | soxhlet extraction | GC-MSD/GC-FID | ext. st. | no |
| 3159 | in house | dissolve in THF, precipitate with acetonitril | LC/MS (scan & SIM mode) | ext. st. | no |
| 3172 | not mentioned | ---- | ---- | ---- | ---- |
| 3179 | in house | extraction with t-butylmethylether, 16 hours at 60°C | GC/MS | ext.+ int. st. | no |
| 3188 | ASTM D3421-75/ EEC1999/815 | soxhlet extraction, dichloromethane/methano 1:1 | GC/MS | ---- | ---- |
| 3189 | in house | soxhlet extraction, methanol/chloroform 1:2 | GC/MS | ext. st. | no |
| 3191 | ASTM D3421-75 mod. | soxhlet extraction, dichloromethane by 2 hours | GC-FID / GC-MS | ext. st. | no |
| 8001 | ASTM D3421-75 mod. | methanol/dichloromethane 1:1 | GC/FID | int. st | no |

APPENDIX 3**List of participating countries**

| Country | Number of laboratories |
|------------------|-------------------------------|
| Belgium | 1 |
| Germany | 4 |
| Hong Kong R.O.C. | 9 |
| Italy | 2 |
| Portugal | 1 |
| P.R. of China | 3 |
| Sweden | 1 |
| Taiwan R.O.C. | 1 |
| Thailand | 1 |
| The Netherlands | 1 |
| Turkey | 1 |
| United Kingdom | 1 |

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 |
| DG(0.01) | = outlier in Double Grubbs' outlier test |
| DG(0.05) | = straggler in Double Grubbs' outlier test |
| n.a. | = not applicable |
| nd | = not detected |

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