Results of Proficiency Test Phthalates in PVC March 2002

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 migrate fairly easily from PVC because they do 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 teethers 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). 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). In addition general product safety is covered by EU directive 92/59.

It is 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:

•	dipropylphthalate (DPrP)	CASno. 131-16-8	
•	dipentylphthalate (DPP)	CASno. 131-18-0	
•	dicyclohexylphthalate (DCHP)	CASno. 84-61-7	
٠	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) or di-isooctylphthalate (DIOP).

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 2002.

In the international interlaboratory study of March 2002, 20 laboratories in 13 different countries have participated. See appendix 3 for a list of participating 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 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.

2.2 SAMPLES

Three samples with different phthalates content were prepared from three different bulk materials. The first bulk material (#0210) was transparent PVC. The second bulk material (#0211) was yellow PVC frog toy and the last bulk material (#0212) was orange PVC. All bulk materials were obtained from a local dutch market. The bulk materials of #0210, #0211 and #0212 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.

Total phthalates content in %M/M					
Subsamples of 0210	Subsamples of 0211	Subsamples of 0212			
9.1	0.64	0.31			
8.9	0.60	0.28			
9.4	0.63	0.32			
8.8	0.70	0.30			

table 1: results of the homogeneity test on the subsamples 0210, 0211 and 0212

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

	observed repeatability in %M/M
Subsamples of 0210	0.74
Subsamples of 0211	0.12
Subsamples of 0212	0.048

table 2: repeatability of the phthalate content of the subsamples 0210, 0211 and 0212

For the determination of total phthalates content an in house extraction/gravimetric 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 0210, 0211 and 0212 was assumed.

To each of the participating laboratories 3 samples were sent on February 20, 2002.

2.3 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 (0210, 0211 and 0212). 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. All 20 participants but one reported results, thus 19 sets of results were accepted. 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 reproduciblities 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 ± 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:

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

The z (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:

 $\begin{array}{l|l} |z| < 1 & good \\ 1 < |z| < 2 & satisfactory \\ 2 < |z| < 3 & questionable \\ |z| > 3 & unsatisfactory \end{array}$

4 EVALUATION

In this interlaboratory study some problems were encountered during the execution. Three participants had not received the samples after two weeks, thus new samples were sent. All other participants received the samples on time. All participants but one submitted analysis results. The 19 reporting participating laboratories did send in 134 numerical results. Observed were 9 outlying results, which is 6.7 %. 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.

The literature requirements were taken from ASTM D3421:75, "Extraction and analysis of plasticizer mixtures from vinyl chloride plastics". This method was discontinued in1987, but is still referred to in ASTM F963:96a (see § 4.3.8) and no other validated determinations are published yet. In ASTM D3421:75 only figures for variance were given for DEHP and total phthalates. Therefor the variance for all other individual phthalates were estimated the same as for DEHP.

sample 0210: This sample was positive on DEHP (DOP). The determination of DEHP is problematic for some individual labs. Four results were outside the reproducibility limits. The calculated reproducibility is, after rejection of the statistical outliers, in agreement with the requirements of ASTM D3421:75. Only two results were outside the reproducibility limits for Total phthalates. However the calculated reproducibility is not at all in agreement with the requirements of ASTM D3421:75. The low number of results reported for total phthalates may explain this disagreement. This material contained only very low concentrations of all the other

investigated phthalates. Some laboratories reported a numerical result although perhaps very near to the detection limit of the method used, but most participants reported a 'less than'-result or 'not detected'.

sample 0211: This sample contained small amounts of DINP and DEHP (DOP). For DEHP no results were outside the reproducibility limits. The calculated reproducibility is, after rejection of the statistical outliers, in good agreement with the requirements of ASTM D3421:75.

For DINP no results were outside the reproducibility limits. The calculated reproducibility is in good agreement with the requirements estimated from ASTM D3421:75.

Also for Total phthalates no results outside the reproducibility limits were found. The calculated reproducibility is in good agreement with the requirements of ASTM D3421:75.

This material contained only very low concentrations of all the other investigated phthalates. Some laboratories reported a numerical result although perhaps very near to the detection limit of the method used but most participants reported a 'less than'-result or 'not detected'.

sample 0212: This sample was positive on DINP, DIDP and DEHP (DOP). For DEHP no results were outside the reproducibility limits. The calculated reproducibility is, after rejection of the statistical outliers, in good agreement with the requirements of ASTM D3421:75.
 For DINP no results outside the reproducibility limits were found. Also for DIDP no results outside the reproducibility limits were found. For DINP and

DIDP as well the calculated reproducibility is in good agreement with the requirements estimated from ASTM D3421:75.

The results for Total phthalates were found within the reproducibility limits. The calculated reproducibility is in good agreement with the requirements of ASTM D3421:75.

This material contained only very low concentrations of all other requested phthalates. Some laboratories reported a numerical result although perhaps very near to the detection limit of the method used but most participants reported a 'less than'-result or 'not detected'. Some participants reported some false positive results, maybe 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	unit	n	average	2.8 * sd	R (target)	
DEHP	%M/M	15	16.790	2.747	3.300	
Total phthalates	%M/M	8	16.086	11.348	4.900	

table 3 : sample210

Parameter	unit	n	average	2.8 * sd	R (target)
DEHP	%M/M	7	0.0104	0.0187	3.3000
DINP	%/M/M	13	0.629	0.760	3.300
Total phthalates	%M/M	8	0.597	0.756	4.900

table 4: sample 211

Parameter	unit	n	Average	2.8 * sd	R (target)
DEHP	%M/M	13	0.284	0.388	3.300
DINP	%M/M	12	0.928	1.150	3.300
DIDP	%M/M	10	0.494	0.814	3.300
Total phthalates	%M/M	8	1.084	1.626	4.9

table 5: sample 212

The average result found for total phthalates, for sample 212, is not in agreement with the som of the individual phthalates. The low number of reported results for total phthalates could explain this.

Without further statistical calculations it can be concluded that the determination of Phthalates in PVC in not very problematic for the group of participating laboratories. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON WITH INTERLABORATORY STUDY OF FEBRUARY 2001

The performance of the group in 2002 was compared with the performance in February 2001 for the individual determinations in the following table:

2002 better than 2001	2002 the same as 2001	2002 worse than 2001
DEHP (=DOP)	DIDP	Total phthalates
DINP		

5 CONCLUSIONS

The determination of phthalates in PVC is not very problematic. The reported details of the methods, which were used by the participants, are listed in appendix 2. Almost all participants used a method that was, one way or another, derived from ASTM D3421. The technique to release the phthalates was very divers. And various techniques (GCMS, GC/FID and HPLC) were used to detect and quantify the phthalates. Despite of the various techniques and solvents, there was an acceptable spread noticed. Only 2 participants did correct for recovery. These laboratories did not report significantly deviating results.

Although the samples were relatively difficult, with concentrations below the limit of 0.1% (except for DEHP in sample 0210), some false positive and negative results were reported. In comparison with last years round, the performance of the group of participants has improved. The observed reproducibilities were now all (except for Total phthalates in sample 0210) in good agreement with the requirements of ASTM D3421:75.

In order to improve the concrete conclusions, the number of participants should be expanded.

Determination of DEHP (DOP) on sample 0210; results in %M/M

lab	method	value	mark	Z(targ) remarks	
2100	inhouse	15.3		-1.26	
2105	D3421	16.945		0.13	
2106	inhouse	19.1	С	1.96 first reported 21.4	
2117	inhouse	15.5		-1.09	
2120	inhouse	10	G(0.01)	-5.76	
2132	inhouse	16.232		-0.47	
2147	inhouse	17.3		0.43	
2148	EPA 8016A	23.89	G(0.05)	6.02	
2153	inhouse	17		0.18	
3107	inhouse	0.958	G(0.01)	-13.43	
3116	inhouse	12.5	C,G(0.05)	-3.64 first reported 9.53	
3153	inhouse	16.5		-0.25	
3159	inhouse	17.04		0.21	
3161	inhouse	15.6		-1.01	
3165	to be a second				
3166	Innouse	17.1		0.26	
3167	D3421	17.2		0.35	
3109	D3421	17.74		0.67	
3172	inhouse	10		-0.87	
3175	Innouse	17.3		0.43	
	normality	OK			
	n	15			
	outliers	4			
	mean (n)	16.790			
	st.dev. (n)	0.9810			
	R(calc.)	2.747			
	R(D3421:75)	3.300			
²⁵ т					
22					*
23					



Determination of Total phthalates on sample 0210; results in %M/M

2100 inhouse 15.3 -0.45 2105 2106 2117 2120 inhouse 10.00135 -3.48 2132 2147 2148 EPA 8016A 23.89 4.46 2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND 3161 inhouse 15.6 -0.28 3165	
2105 2106 2117 2120 inhouse 10.00135 -3.48 2132 2147 2148 EPA 8016A 23.89 4.46 2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND 3161 inhouse 15.6 -0.28 3165	
2106 2117 2120 inhouse 10.00135 -3.48 2132 2147 2148 EPA 8016A 23.89 4.46 2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND 3161 inhouse 15.6 -0.28 3165	
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2132 2147 2148 EPA 8016A 23.89 4.46 2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND 3161 inhouse 15.6 -0.28 3165	
2147 2148 EPA 8016A 23.89 4.46 2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND false negative? 3161 inhouse 15.6 -0.28 3165	
2148 EPA 8016A 23.89 4.46 2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND false negative? 3159 3161 inhouse 15.6 -0.28 3165	
2153 inhouse 17 0.52 3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND false negative? 3159 3161 inhouse 15.6 -0.28 3165	
3107 inhouse 0.963 ex -8.64 manual excluded due to low DEHP result 3116 inhouse 12.5 -2.05 3153 inhouse ND false negative? 3159 3161 inhouse 15.6 -0.28 3165	
3116 inhouse 12.5 -2.05 3153 inhouse ND false negative? 3159 3161 inhouse 15.6 -0.28 3165	
3153 inhouse ND false negative? 3159 3161 inhouse 15.6 -0.28 3165	
3159 3161 inhouse 15.6 -0.28 3165	
3161 inhouse 15.6 -0.28 3165	
3165	
3166 inhouse 17.1 0.58	
3167	
3169	
3172	
3175 inhouse 17.3 0.69	
normality OK	
n 8	
outliers 1	
mean (n) 16.086	
st.dev. (n) 4.0528	
R(calc.) 11.348	
R(D3421:75) 4.900	



Determination of DINP on sample 0211; results in %M/M

lab method	value	mark	Z(targ) remarks
2100 inhouse	0.3		-0.28
2105 D3421	0.963		0.28
2106 inhouse	0.89		0.22
2117 inhouse	0.6		-0.02
2120 inhouse	0.18		-0.38
2132 inhouse	0.625	С	0.00 first reported 0.621
2147			
2148			
2153 inhouse	0.95		0.27
3107 inhouse	0.793		0.14
3116 inhouse	0.793		0.14
3153 inhouse	0.6		-0.02
3159 inhouse	ND		false negative?
3161			
3165			
3100			
3107 D3421 3160	0.8		0.15
3109 3172 inhouse	0.2	C	 0.26 first reported 0.065
	0.2	C	
	0.40		-0.15
normality	OK		
n	13		
outliers	0		
mean (n)	0 629		
st dev (n)	0.023		
R(calc.)	0.760		
R(D3421:75)	3.300		
1(00121110)	0.000		
4.5			
I.J			
4 -			
2 6			
3.3			
3 -			
2.5 -			
2			
1 5			
L			
1			
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Determination of DEHP (DOP) on sample 0211; results in %M/M

lab	method	value	mark	Z(targ) r	remarks				
2100 2105 2106 2117 2120 2132 2147 2148 2153 3107 3116 3153 3159 3161 3165 3166 3167 3169 3172 3175	D3421 inhouse inhouse inhouse EPA 8016A inhouse inhouse inhouse inhouse inhouse inhouse junhouse D3421 D3421 inhouse inhouse inhouse	0.004 ND 0.0025 0.019 0.4 0.51 <0.01 <0.01 <0.01 <0.01 <0.01 ND 0.0054 <0.002 <0.0005 0.017 0.015	C DG(0.01) DG(0.01)	-0.01 -0.01 0.01 f 0.33 0.42 0.00 0.00 0.00 0.00	irst reported 0.301				
	normality n outliers mean (n) st.dev. (n) R(calc.) R(D3421:75)	OK 7 2 0.0104 0.00667 0.0187 3.3000							
0.03									
0.025									
0.015	-				۵	۵	۵		
0.01				A					
0.005	▲	۵	۵						
0	- 1 5 120	2105	3166	3107	3175	3172	2132	2147	2148

Determination of Total phthalates on sample 0211; results in %M/M

lab	method	value	mark	Z(targ) remarks
2100	inhouse	0.3		-0.17
2105				
2106				
2117				
2120	inhouse	0.1852		-0.24
2132				
2147				
2148	EPA 8016A	0.51		-0.05
2153	innouse	0.95		0.20
2116	inhouse	0.640		0.14
3153	inhouse	0.793 ND		U. I I false negative?
3150	IIIIOuse			
3161				reported total extract - 31.3 %M/M
3165				
3166	inhouse	0.694		0.06
3167				
3169				
3172				
3175	inhouse	0.495		-0.06
	normality	OK		
	n	8		
	outliers	0		
	mean (n)	0.597		
	st.dev. (n)	0.2700		
	R(calc.)	0.756		
	R(D3421:75)	4.900		
^{1.2} T				
1 -				۵.
0.8 -				Δ
				Δ
0.6				
				A
			Δ	-
0.4				
		۵		
0.2	۵			
o				

Determination of DINP on sample 0212; results in %M/M

lab method	value	mark	Z(targ) remarks	
2100				
2105 D3421	1.243		0.27	
2106 inhouse	1.06		0.11	
2117 inhouse	0.6		-0.28	
2120 inhouse	0.046		-0.75	
2132 inhouse	0.621	С	-0.26 first reported 0.625	
2147				
2148				
2153 inhouse	0.91		-0.02	
3107 inhouse	0.693	0	-0.20	
3116 inhouse	1.257	C	0.28 first reported <0.01	
3153 inhouse	0.73	С	-0.17 first reported <0.01	
3159 inhouse	1.37		0.37	
3161				
3165				
3100	1 5	C		
3107 D3421	1.5	C	0.49 hist reported <0.01	
3172 inhouse	<0.02		< 0.77 falso pogativo 2	
	1 11			
	1.11		0.10	
normality	OK			
n	12			
outliers	0			
mean (n)	0.928			
st.dev. (n	0.4107			
R(calc.)	, 1.150			
R(D3421	:75) 3.300			
4.5 -				



Determination of DIDP on sample 0212; results in %M/M

lab	method	value	mark	Z(targ) re	marks
2100					
2105	D3421	0.478		-0.01	
2106	inhouse	0.44		-0.05	
2117	inhouse	0.2		-0.25	
2120	inhouse	0.15		-0.29	
2132	inhouse	0.198	С	-0.25 firs	st reported <0.005
2147					
2148	EPA 8016A	0.95		0.39	
2153	inhouse	0.48		-0.01	
3107	inhouse	0.531		0.03	
3116	inhouse	<0.01		<-0.41 fal	lse negative ?
3153	inhouse	0.51	С	0.01 firs	st reported <0.01
3159	inhouse	ND		fal	lse negative ?
3161	inhouse	3.2	G(0.01)	2.30	
3165					
3166			-		
3167	D3421	1	С	0.43 firs	st reported <0.01
3169					
3172	inhouse	< 0.02		<-0.40 fal	Ise negative ?
3175	inhouse	ND		fal	Ise negative ?
	a successful to a				
	normality	UK 10			
	n autliana	10			
	outliers	1			
	mean (n)	0.494			
	SLUEV. (II)	0.2909			
		0.814			
	R(D3421:75)	3.300			



Determination of DEHP (DOP) on sample 0212; results in %M/M

lab	method	value	mark	Z(targ)	remarks
2100	inhouse	0.06	С	-0.19	first reported 0.03
2105	D3421	0.335		0.04	
2106	inhouse	0.4		0.10	
2117	inhouse	0.2		-0.07	
2120	inhouse	0.18		-0.09	
2132	inhouse	0.301	С	0.01	first reported 0.019
2147	inhouse	2.7	DG(0.01)	2.05	
2148					
2153	inhouse	0.29		0.01	
3107	inhouse	0.292		0.01	
3116	inhouse	0.069	С	-0.18	first reported 0.036
3153	inhouse	0.34		0.05	
3159	inhouse	ND			
3161					
3165					
3166	inhouse	0.293		0.01	
3167	D3421	0.59		0.26	
3169	D3421	2.56	C,DG(0.01)	1.93	first reported <0.0005
3172	inhouse	<0.01			
3175	inhouse	0.34		0.05	
	normality	OK			
	n	13			
	outliers	2			
	mean (n)	0.284			
	st.dev. (n)	0.1387			
	R(calc.)	0.388			
	R(D3421:75)	3.300			
1 T					
0.9 -					
0.8					
0.0					
0.7 -					
0.6 -					A
					-
0.5 -					
0.4 -					٨
0 3					
T T			▲	A	
0.2		A	۵		
0.1					
	Δ Δ				
1 0 -					

Determination of Total phthalates on sample 0212; results in %M/M

lab	method	value	mark	Z(targ) remarks
2100	inhouse	0.06	С	-0.58 first reported 0.03
2105				
2106				
2117				
2120	inhouse	0.3763		-0.40
2132				
2147				
2148	EPA 8016A	0.95		-0.08
2153	inhouse	1.68		0.34
3107	inhouse	1.536		0.26
3116	inhouse	1.317		0.13
3153	inhouse	ND		false negative?
3159				
3161				reported total extract = 49.7 %M/M
3165				
3166	inhouse	1.3		0.12
3167				
3169				
3172				
3175	inhouse	1.45		0.21
	normality	ОК		
	n	8		
	outliers	0		
	mean (n)	1.084		
	st.dev. (n)	0.5809		
	R(calc.)	1.626		
	R(D3421:75)	4.900		



lab method	DINP	mark DBP	mark BBP	mark DIDP	mark DNOP	mark DPrP	mark
2100							
2105 D3421	<0.01	< 0.003	< 0.005	<0.01	<0.01		
2106 inhouse	0.0101	ND	ND	ND	ND	ND	
2117							
2120 inhouse	0.00085	0.0005	ND	ND	ND		
2132 inhouse	<0.005	<0.005	<0.005	< 0.005	< 0.005		
2147 inhouse	<0.10	<0.10	<0.10	<0.10	<0.10		
2148							
2153 inhouse	<0.05	<0.01	<0.01	< 0.05	<0.01	0.001	
3107 inhouse	0.002	0.001	0	0.002	0		
3116 inhouse	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
3153 inhouse	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
3159 inhouse	ND	ND	ND	ND	ND		
3161							
3165							
3166							
3167 D3421	<0.01	<0.002	< 0.002	<0.01	<0.005	< 0.002	
3169							
3172 inhouse	<0.02	<0.01	<0.01	< 0.02	<0.01	<0.01	
3175 inhouse	<0.1	<0.01	<0.01	<0.1	<0.01	<0.01	
normality	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
n	3	2	1	1	1	1	
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(litt)	unknown	ı unknowı	n unknow	n unknowr	n unknown	unknowr	۱

Determination of phthalates on sample 0210; results in %M/M

Determination of phthalates on sample 0210; results in %M/M

lab method	DDP	mark DCHP	mark DEP	mark DHP	mark Others mark
2100					
2105					
2106 inhouse	ND	ND	ND	ND	
2117					
2120					
2132					
2147					
2148					
2153 inhouse			<0.01		
3107					
3116 inhouse	<0.01	<0.01	<0.01	<0.01	<0.01
3153 inhouse	<0.01	<0.01	<0.01	NS	NS
3159					
3161					
3165					
3166					
3167 D3421	<0.002		< 0.002	<0.002	
3169					
3172 inhouse	<0.01	<0.01	<0.01	0.01	
3175 inhouse	<0.01	<0.01	<0.01	<0.01	<0.01
normality	n.a.	n.a.	n.a.	n.a.	n.a.
n	0	0	0	1	0
outliers	0	0	0	0	0
mean (n)	n.a.	n.a.	n.a.	n.a.	n.a.
st.dev. (n) n.a.	n.a.	n.a.	n.a.	n.a.
R(calc.)	n.a.	n.a.	n.a.	n.a.	n.a.
R(litt)	unknown	unknown	unknowr	n unknown	unknown

lab	method	DBP ma	rk BBP	mark DIDP	mark	DNOP	mark	DPrP	mark
2100							-		
2105	D3421	0.021	< 0.005	<0.01		<0.01	-		
2106	inhouse	ND	ND	ND		ND	1	ND	
2117							-		
2120	inhouse	0.0007	ND	ND		0.002	-		
2132	inhouse	<0.005	<0.005	<0.005	C(0.198)	<0.005	-		
2147	inhouse	<0.10	<0.10				-		
2148							-		
2153	inhouse	0.001	<0.01	< 0.05		<0.01		<0.01	
3107	inhouse	0.004	0.001	0.004		0.034	-		
3116	inhouse	<0.01	<0.01	<0.01		<0.01		<0.01	
3153	inhouse	<0.01	<0.01	<0.01		<0.01		<0.01	
3159	inhouse	ND	ND	ND		ND	-		
3161	inhouse			0.45		1	-		
3165							-		
3166							-		
3167	D3421	<0.002	<0.002	<0.01		<0.005		<0.002	
3169							-		
3172	inhouse	<0.01	<0.01	<0.01		<0.01		<0.01	
3175	inhouse	<0.01	<0.01	ND		<0.05		<0.01	
	normality	n.a.	n.a.	n.a.		n.a.	1	n.a.	
	n	4	1	2		3	(C	
	outliers	0	0	0		0	(C	
	mean (n)	n.a.	n.a.	n.a.		n.a.	1	n.a.	
	st.dev. (n)	n.a.	n.a.	n.a.		n.a.	1	n.a.	
	R(calc.)	n.a.	n.a.	n.a.		n.a.	I	n.a.	
	R(litt)	unknown	unknown	unknow	/n	unknown	l	unknown	

Determination of phthalates on sample 0211: results in %M/M

Determination of phthalates on sample 0211: results in %M/M

lab	method	DPP mar	k DCHP	mark	DEP	mark	DHP	mark	Others	mark
2100)			-						
2105	5			-						
2106	inhouse	ND	ND	1	ND		ND			
2117	,			-						
2120)			-						
2132	2			-						
2147	,			-						
2148	3			-						
2153	3 inhouse			(0.001					
3107	,			-						
3116	inhouse	<0.01	<0.01		<0.01		<0.01		<0.01	
3153	3 inhouse	<0.01	<0.01	•	<0.01		NS		NS	
3159)			-						
3161				-						
3165	5			-						
3166	inhouse			-					0.689	
3167	′ D3421	<0.002		(0.002		<0.002			
3169)			-						
3172	2 inhouse	<0.01	<0.01	•	<0.01		<0.01			
3175	5 inhouse	<0.01	<0.01	•	<0.01		<0.01		<0.01	
	normality	n.a.	n.a.	1	n.a.		n.a.		n.a.	
	n	0	0		2		0		1	
	outliers	0	0	()		0		0	
	mean (n)	n.a.	n.a.	r	n.a.		n.a.		n.a.	
	st.dev. (n)	n.a.	n.a.	r	n.a.		n.a.		n.a.	
	R(calc.)	n.a.	n.a.	1	n.a.		n.a.		n.a.	
	R(litt)	unknown	unknown	i (unknowr	ו	unknown	1	unknown	

lab r	method	DBP ma	rk BBP m	ark DNOP	mark DPrP	mark DPP	mark DCHP	mark
2100								
2105 E	D3421	0.003	<0.005	<0.01				
2106 i	nhouse	ND	ND	ND				
2117								
2120 i	nhouse	0.0003	ND	ND				
2132 i	nhouse	<0.005	<0.005	<0.005				
2147 i	nhouse	<0.10	<0.10					
2148								
2153 i	nhouse	<0.01	<0.01	<0.01	<0.01			
3107 i	nhouse	0.002	0	0.018				
3116 i	nhouse	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
3153 i	nhouse	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
3159 i	nhouse	ND	ND	ND				
3161 i	nhouse						4.2	
3165								
3166								
3167 [D3421	<0.002	<0.002	<0.005	< 0.002	< 0.002		
3169								
3172 i	nhouse	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
3175 i	nhouse	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	
r	ormality	na	na	na	na	na	na	
1 r	normanity	11.a. 3	11.a. 1	11.a.	n.a. 0	11.a. 0	11.a.	
1	outliere	0	0	0	0	0	0	
	moon (n)	0	0	0	0	0	0	
۱ د	st dev (n)	n.a.	n.a.	na.	na.	n.a.	na.	
с Г	R(calc)	n.a.	n.a.	na.	n.a.	n.a.	n.a.	
F	R(litt)	unknown	unknown	unknown	unknown	unknown	unknown	I

Determination of phthalates on sample 0212: results in %M/M

Determination of phthalates on sample 0212: results in %M/M

lab method	DEP	mark	DHP	mark	Others	mark
2100						
2105						
2106						
2117						
2120						
2132						
2147						
2148						
2153 inhouse	<0.01					
3107						
3116 inhouse	<0.01		<0.01		<0.01	
3153 inhouse	<0.01		NS		NS	
3159						
3161 inhouse	2.6					
3165						
3166 inhouse					1.01	
3167 D3421	<0.002		<0.002			
3169						
3172 inhouse	<0.01		<0.01			
3175 inhouse	<0.01		<0.01		<0.01	
normality	n.a.		n.a.		n.a.	
n	1		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(litt)	unknown		unknown	1	unknown	1

Method information

Lab	Analysis method	Technique to release/extract	Technique to detect and quantify	Calibration used	Corrected for recovery
2100	in house	extraction, solvent diethylether	gravimetric	no	no
2105	ASTM D3421-75	soxhlet extraction, solvent methanol/ dichloromethane 1:1	GC/MS	ext. st.	no
2106	in house	soxhlet extraction, solvent diethylether	GC/MS	ext. st.	no
2117	in house	soxhlet extraction, solvent diethylether	GC/MS	ext. st.	no
2120	in house	soxhlet extraction, solvent chloroform	GC/MS	int. st.	no
2132	in house	extraction with chloroform at room temperature for 30 min.	GC/MSD	int. + ext. st.	no
2147	in house	soxhlet extraction, solvent methanol/chloroform 1:2	GC/FID		no
2148	EPA 8061A	soxhlet extraction, solvent acetone/dichloromethane 1:1	GC/MS (scan & SIM mode)	ext. st.	yes
2153	in house	soxhlet extraction, solvent methanol/chloroform 1:2	GC/MS	ext. st.	no
3107	in house	soxhlet extraction, dichloromethane	GC/MS	ext. st.	no
3116	in house	solvent extraction, dichloromethane	detection: GC/MS + HPLC quantification	ext. 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
3161	in house	soxhlet extraction, solvent diethylether	GC/FID	ext. st.	no
3166	in house	soxhlet extraction, dichloromethane	GC/MS	ext. st.	no
3167	ASTM D3421-75	soxhlet extraction, solvent methanol/ carbontetra 2:1	GC/MS	ext. st.	no
3169	ASTM D3421-75	soxhlet extraction, solvent methanol/ carbontetra 2:1	GC/MS	ext. st.	no
3172	in house	dissolve in THF, precipitate with acetonitril	HPLC-DAD	ext. st.	no
3175	in house	dissolve in Dimethylacetamide, precipitate with methanol	GC/MS	int. st	yes

List of participating countries

Country	Number of laboratories
Austria	1
France	1
Germany	2
Hong Kong	6
Italy	1
Korea	1
Portugal	1
P.R. of China	2
Switzerland	1
Taiwan	1
The Netherlands	1
U.S.A.	1
United Kingdom	1

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

Literature:

- i.i.s. Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, August 1998
 ASTM D3421:75: "extraction and analysis of plasticizer mixtures from vinyl chloride plastics".
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