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Report on the collaborative trial organised by the JRC on the determination of PVC and phthalates in textile products

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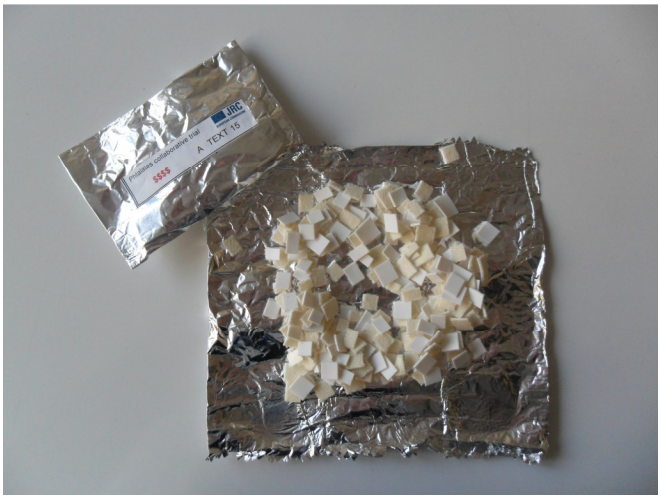

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1 Executive summary

On behalf of CEN/TC 248/WG 26 and ISO/TC 38/WG 22, the Joint Research Centre (JRC) organised a collaborative trial for the comparison and validation of four methods for the determination of phthalates and one method for the quantification of PVC in textile products. The first four methods investigated had been developed and used in both European and non-European countries, while the fifth method was developed by the JRC.

Methods 1, 2 and 3 were based on ultrasonic extraction of phthalates (with n-hexane/acetone 80/20 v/v, n-hexane and tert-butyl methyl ether, respectively); method 4 was based on the dissolution of PVC with tetrahydrofuran in an ultrasonic generator, followed by the re-precipitation of it with acetonitrile. In all cases, phthlates were then quantified by GC-MS.

Method 5 for the determination of PVC mass per cent was based on the dissolution of PVC with tetrahydrofuran in an ultrasonic generator, followed by the washing of the residue and its gravimetric determination.

The collaborative exercise was organised, according to ISO 5725-2, as a balanced uniform-level experiment, i.e. with the same number of test results in each laboratory, which each laboratory analysing the same levels of test samples. Out of the eighteen laboratories who had enrolled in the exercise, thirteen, 8 European and 5 from outside EU, provided results.

The Italian company MP S.p.A (Poggio a Caiano Prato, Italy) produced both the PVC samples and the textile ones, made by cotton spread with PVC layer. The softener used for PVC was diethyl hexyl adipate (DEHA). In the PVC formulation known quantities of the following seven phthalates were also added: bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), di-n-octyl phthalate (DNOP) and diisobutyl phthalate (DIBP).

The homogeneity test carried out by the JRC with method 2 proved that all samples could be considered ‘sufficiently homogeneous’ according to the IUPAC harmonised protocol for proficiency testing.

In total four textile samples spread with PVC layer and one PVC sample containing 7 phthalates (DEHP, DBP, BBP, DINP, DIDP, DNOP and DIBP) at 3 concentration levels and one sample, in which the PVC mass per cent had to be measured, were analysed by 13 laboratories, both European and non-European, in triplicates. Levels I, II and III refer to samples containing a specific phthalate in concentration of approximately 200, 1000 and 5000 mg of phthalate per kg of PVC. In the case of DIDP and DINP, level I corresponded to approximately 500 mg of phthalate per kg of PVC. These phthalate concentrations were selected in order to assess the precision of the analytical methods in the range of the current limits for toys and childcare articles. In fact, the regulation 1907/2006/EC, concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), forbad the use of DEHP, DBP, BBP, DINP, DIDP and DNOP at concentration higher than 0.1% by mass (1000 mg/kg) of the plasticised material, in toys and childcare articles. In the case of DINP, DIDP and DNOP the ban applies to toys and childcare articles which can be placed in the mouth by children.

In total, 4091 test results were collected. Out of the 104 data sets only 27 could be considered as being part of a normal distribution at 95 % probability level using the Shapiro-Wilk test. The situation improved after the elimination of outliers (47 data sets were normally distributed). The distribution of the mean values was proved to be normal in the majority of cases.

The results were statistically evaluated, according to ISO 5725-2 and ISO 5725-5, using the software Prolab. The consensus values and the precisions of the various methods, in terms of repeatability and reproducibility limits as well as repeatability and reproducibility relative standard deviations, were evaluated. Applying ISO 5725-2, the statistical outliers identified with Cochran's and Grubbs' tests were rejected, together with the results of laboratory LC0004 for method 4 and the ones of laboratory LC0005 for DIDP in methods 1-4, which were identified as outliers with Mandel's h statistics. According to ISO 5725-5, all test results were retained and robust statistics was used. These two alternative approaches gave results that could be considered in good agreement. Generally, the differences were lower than 35 %, except in few cases.

The best method in terms of phthalates' recovery was number 4 based on tetrahydrofuran, whereas method 2 was the worst one. Virtually the same extraction efficiency was shown by methods 1 and 3.

Considering phthalates, both the minimum and the maximum relative standard deviation of repeatability were obtained in method 4 (3.0 and 23.5 % respectively). Concerning the relative standard deviation of reproducibility, the minimum value 19.4 % was shown with method 3 and the highest 189.2 % with method 2. Results indicated that both the four methods for phthalates and the laboratories' performance have to be drastically improved. Poor repeatability was observed in the case of several laboratories and the large spread in the mean values calculated in the thirteen laboratories is responsible for the high observed relative standard deviation of reproducibility.

Two samples, one made of PVC and one made of cotton spread with PVC, were prepared starting from the same plastisol batch. Results were in good agreement when the phthalates' concentrations of both samples were expressed in mg of phthalate per kg of PVC.

Method 5 for the quantification of PVC showed good precision and can be considered validated for cotton samples spread with PVC. The repeatability and reproducibility relative standard deviations were 0.6 and 1.4 % respectively. These values are in line with the ones obtained in the case of similar dissolution methods validated in the context of quantification of fibre binary mixtures.

Even though the collaborative trial was not a proficiency test, the performances of the participating laboratories were evaluated. Laboratories LC0003 and LC0008 showed the best performance: their z-scores were in almost all cases good ($|z| < 1$) and in the others at least satisfactory ($|z| < 2$). On the contrary, laboratories LC0004 and LC0005 obtained the worst performance: they showed respectively 25 and 17 z-score considered questionable or unsatisfactory out of 104.

Considering the methods, after the elimination of outliers, method 4 showed 6.2 % of questionable or unsatisfactory z-scores. Methods 2, 1 and 3 followed with 5.9, 3.7 and 3.7 % respectively.

2 Introduction

Phthalates show softening properties and have been largely used as plasticisers in the production of plastisol and PVC. Some of them have been shown to exhibit negative effects both on health and environment and to migrate fairly easily from PVC into the environment. The European Regulation 1907/2006, concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) [1], prohibited the use of bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP) and benzyl butyl phthalate (BBP), at concentrations higher than 0.1 % by mass of the plasticised material, in toys and childcare articles. The same Regulation banned also the use of diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-n-octyl phthalate (DNOP), at concentrations higher than 0.1 % by mass of the plasticised material, in toys and childcare articles which can be placed in the mouth by children.

Nowadays, at worldwide level there is no standard method for the quantification of phthalates in textiles. At European level, the standard method exists (EN 15777 [2]) and is based on the extraction of phthalates in n-hexane by Soxhlet; however, due to difficulties experienced in getting good repeatability, CEN/TC 248/WG 26 (test methods for analysis of EC restricted substances in textiles) agreed to revise the standard.

There is the need to have a reliable standard method for the quantification of hazardous phthalates in textiles; in particular considering that textiles spread or coated with PVC are available on the market, such as for instance T-shirts and tablecloths, and could contain phthalates.

On the basis of the results of a small intercomparison exercise conducted by some members of CEN/TC 248/WG 26, the working group decided to standardise an approach based on extraction by ultrasonic bath. In fact, the results had shown that comparable or higher extraction could be obtained using ultrasonic bath instead of Soxhlet.

In the meantime, at ISO level a work item proposal was accepted for the development of a quantification method for phthalates in textiles. In view of harmonisation, CEN/TC 248/WG 26 and ISO/TC 38/WG 22 (composition and chemical testing of textiles) started to organise joint meetings to collaborate on this issue. Experts agreed to compare the performances of three methods based on ultrasonic extraction and one method based on the principle of dissolving the PVC layer and then re-precipitating it.

On behalf of CEN/TC 248/WG 26 and ISO/TC 38/WG 22, the Joint Research Centre (JRC) organised a collaborative trial for method validation, with the aim of evaluating the precision of the various methods, in terms of repeatability and reproducibility, in order to compare them and select the best one for standardisation purposes. The collaborative exercise was organised as a balanced uniform-level experiment, i.e. with the same number of test results in each laboratory, which each laboratory analysing the same levels of test samples, according to ISO 5725-2 [3]. The methods investigated had been developed and used in both European and non-European countries.

Contemporaneously, the JRC organised the validation of an in-house developed method for the quantification of the mass percentage of PVC in coated textiles, following the same ISO standard.

3 Test materials

3.1 Preparation

The five samples used in this study were provided by MP S.p.a. (Poggio a Caiano Prato, Italy), an Italian company specialised in textile processing, such as PVC spreading. They were prepared with laboratory scale equipment in order to better control the process.

Four cotton samples (coded A, B, C and D) were spread with PVC containing either five or six different phthalates at various levels of concentration. For each sample, 3 sheets of cotton coupled with PVC were prepared with the same batch of plastisol. The fifth sample (coded E) was entirely made of PVC containing five phthalates and it was provided in 5 sheets all prepared with the same batch of plastisol. It has to be noted that the same batch of plastisol was used to produce both samples A and E.

To avoid interferences in the analysis of phthalates and after preliminary tests, PVC was softened with diethyl hexyl adipate (DEHA). The following seven phthalates were added to the plastisol formulation: DEHP, DBP, BBP, DINP, DIDP, DNOP and DIBP. The first six phthalates are prohibited in toys and childcare articles, at concentrations higher than 0.1 % by mass of the plasticised material, and the seventh one will be most probably banned in the next future. They were added to get a final concentration of approximately 200 or 500, 1000 and 5000 mg/kg in the plastisol, corresponding to one fifth or half of the limit value, the limit value and five times it. In the following these concentrations will be referred as level I, II and III respectively. The plastisol composition is reported in Table 1 and the names and CAS numbers of its components are listed in Table 2.

A white pigment was used for samples A, B and E, whereas the PVC was colored with a yellow pigment in the case of samples C and D. Dioctyl stearate was used as carrier for pigments. MS 68 was a stabilizer containing magnesium and zinc.

Table 1: Plastisol composition (in grams).

	Sample A	Sample B	Sample C/F	Sample D	Sample E
PVC	602.41	602.41	602.41	602.41	602.41
BBP	0.212	5.042		1.010	0.212
DBP	1.012		0.230	5.015	1.012
DEHP		1.012	5.020	0.211	
DIBP	5.018	0.210		1.015	5.018
DIDP	0.521		1.018	5.005	0.521
DINP		1.020	5.005	0.515	
DNOP	1.057	5.005	0.212		1.057
DEHA	353.756	350.243	350.068	348.755	353.756
PIGMENT	24.13	24.1	24.1	24.13	24.13
MS 68	12.110	12.070	12.520	12.050	12.110
TOTAL	1000.226	1001.112	1000.583	1000.116	1000.226

Table 2: Description of plastisol components.

	Name	CAS
PVC	Polyvinyl chloride	9002-86-2
BBP	Butyl benzyl phtalate	85-68-7
DBP	Dibutyl phtalate	84-74-2
DEHP	Bis-(2-ethylhexyl) phtalate	117-81-7
DIBP	Di-iso-butyl phtalate	84-69-5
DIDP	Di-iso-decyl phtalate	26761-40-0
DINP	Di-iso-nonyl phtalate	28553-12-0
DNOP	Di-n-octyl phtalate	117-84-0
DEHA	Bis-(2-ethylhexyl) adipate	103-23-1

As some fumes were noticed during the sample production, this might have caused some loss of materials and subsequent deviations from the declared composition of the samples.

All sheets of the same sample were cut into small squares about 10 mm long, put into a 2 L glass bottle and mixed by means of a rotator drive (Stuart STR4, Staffordshire, UK) for 1 hour at 60 rpm.

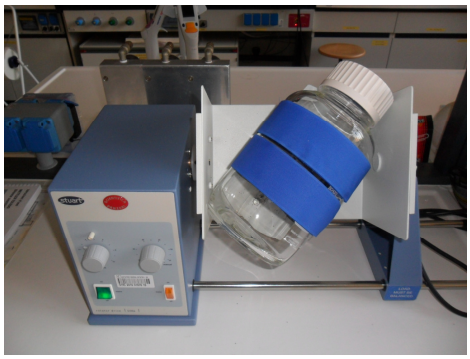

Figure 1: Rotator drive device for sample homogenisation.

The cut and mixed samples were packed in aluminium sheets, containing 8 grams each. Half of the provided quantity was necessary to perform the analyses of phthalates foreseen in the collaborative trial and the other half had to be considered as spare sample. The packages were randomly coded. Ten of them, randomly selected, were used for the homogeneity study and the others were sent to the participants.

Packages containing about 3 grams of the cut and mixed sample C were also prepared and provided to participants for the analysis of PVC content. These packages had to be used for the determination of the textile and PVC mass percentage. In order to avoid confusion, they were coded naming the sample F instead of C. The provided grams were sufficient to perform the determination in triplicate; however, in this case no spare sample was available.

Samples packages were marked with codes, such as BE – A – TXT or PVC – 1. Codes indicate the laboratory's nationality, the sample code, the sample material and a progressive number.

Figure 2: Samples packages to be sent to participants.

3.2 Homogeneity assessment

The Joint Research Centre carried out the homogeneity assessment on each sample, according to the test for 'sufficient homogeneity' established in the IUPAC harmonised protocol for proficiency testing [4]. Ten packages for each sample were randomly selected and, after mixing the content, two test portions from each package were analysed in a random order under repeatability conditions.

For practical reasons, method 2 was used to check the homogeneity, in terms of phthalate concentration, of samples A-E. This method foresees an ultrasonic extraction of the sample with n-hexane and is described in Chapter 4.

All the phthalates in the samples A, B, C, D and E were assessed for homogeneity and results are reported in Table 3. Results are expressed in mg of phthalate/kg of sample (including both the textile and the PVC part) for samples A-D and in mg of phthalate/kg of PVC for sample E, which is made by PVC only.

The homogeneity assessment of sample F, in terms of PVC mass percentage, was not performed due to the too little quantity available.

For the statistical evaluation the unrounded figures were used. First, the normality of the distribution of each set of data was evaluated by the Shapiro-Wilk test [5]. The null hypothesis for this test is that the data are normally distributed. If the chosen alpha level is 0.05 and the p-value is greater than 0.05, then the null hypothesis is not rejected. As reported in Table 4, all data set were considered normally distributed, except DIDP and DINP in sample C.

Data were then examined visually for pathologies (see Annex I). No trends or non-random distribution of differences between first and second test results were observed. Out of the 260 couples of results only four of them were considered outliers when Cochran's test was applied to the set of measurements. The estimates of sampling variance (s^2_{sam}, between variance) and analytical variance (s^2_{an}, within variance) were calculated with a single-factor analysis of variance (ANOVA). According to the test, samples can be considered 'sufficiently homogeneous' if the sampling variance is lower than a critical value c, where $c = 1.88\ \sigma^2_{all} + 1.01\ s^2_{an}$, considering ten testing specimens. The allowable variance (σ^2_{all}) is calculated following the formula $\sigma^2_{all} = 0.09 \times \sigma^2_p$, where σ^2_p is the target variance, an estimation of the expected variability of the trial.

As the reproducibility limit R of method 2 was unknown, the target relative standard deviation was calculated on the basis of the Horwitz equation RSR_R (%) = $2*C^{-0.15}$, using the concentration obtained during the homogeneity test [6]. The target standard deviation σ_p was then calculated multiplying the obtained value for the mean of the data set and dividing by 100 (σ_p =RSR_R (%) * mean / 100). All five samples (26 phthalates) could be considered 'sufficiently homogeneous' as their sampling variances were smaller than *c* (Table 4).

Table 3: Homogeneity study results.

		DIBP (mg/kg)		DBP (mg/kg)		BBP (mg/kg)		DEHP (mg/kg)		DNOP (mg/kg)		DIDP (mg/kg)		DINP (mg/kg)	
		Portion a	Portion b	Portion a	Portion b	Portion a	Portion b	Portion a	Portion b	Portion a	Portion b	Portion a	Portion b	Portion a	Portion b
Sample A	Package 1	3357.36	3425.70	868.15	878.21	117.21	119.64			976.10	1008.89	391.72	478.05		
	Package 2	3411.05	3368.13	893.22	918.80	143.16	136.57			1011.55	1031.55	384.79	388.92		
	Package 3	3461.96	3650.03	871.12	919.64	130.44	126.22			1011.34	967.01	359.57	406.20		
	Package 4	3464.26	3411.89	873.66	937.88	133.38	128.20			1002.58	1008.22	414.57	389.86		
	Package 5	3525.41	3701.61	939.06	983.85	112.76	137.23			995.42	1108.40	419.90	378.90		
	Package 6	3315.02	3466.15	851.33	903.82	126.74	126.16			940.24	970.12	369.52	406.70		
	Package 7	3573.01	3016.15	882.92	819.93	119.69	110.96			960.46	928.97	445.03	431.00		
	Package 8	3430.80	3426.59	929.86	875.69	133.64	122.51			1018.10	1009.75	426.80	478.11		
	Package 9	3209.67	3264.16	836.47	823.61	121.04	123.77			888.41	968.28	388.11	472.89		
	Package 10	2990.99	3325.86	765.10	837.99	110.51	114.21			879.88	939.00	405.24	466.46		
Sample B	Package 1	141.07	165.36			3818.07	3841.42	1043.36	1104.84	5080.41	5379.70			1177.34	1292.90
	Package 2	146.49	160.13			3610.19	3670.73	1019.92	1014.38	4772.23	4900.71			1104.82	1117.29
	Package 3	148.23	155.38			3712.66	4036.42	1062.41	1131.82	4962.89	5609.27			1104.48	1246.91
	Package 4	151.35	153.19			3709.13	3851.65	1056.55	1063.00	5192.34	5246.60			1204.07	1164.05
	Package 5	151.38	158.49			3750.15	3660.48	1094.48	1035.53	5290.02	5116.20			1141.27	1165.99
	Package 6	161.57	150.80			3788.76	3770.98	1073.97	1044.72	5136.66	5037.01			1156.63	1115.29
	Package 7	157.33	144.08			3811.54	3766.93	1078.98	1097.60	5232.95	5161.44			1186.59	1133.30
	Package 8	152.33	146.82			4009.14	3806.86	1090.46	1057.60	5387.20	5111.82			1196.98	1141.72
	Package 9	145.62	154.70			3433.66	3663.78	980.83	1034.28	4653.85	4903.14			1033.85	1071.37
	Package 10	151.71	150.84			3581.09	3659.42	1023.30	1041.39	4976.38	5080.65			1078.93	1121.04
Sample C	Package 1			109.02	84.48			3237.20	4060.79	100.57	118.50	819.98	760.23	3821.62	3637.53
	Package 2			79.76	106.15			3936.25	3766.26	113.08	101.06	786.89	926.91	3392.25	4203.40
	Package 3			106.36	81.89			3474.12	4106.69	101.30	122.00	835.07	778.18	3386.52	3635.64
	Package 4			85.07	92.06			4055.28	3546.45	121.94	116.00	737.42	743.47	3541.27	3528.64
	Package 5			94.29	85.15			3588.10	3633.04	99.28	107.89	722.91	720.32	3405.48	3293.94
	Package 6			101.75	96.33			3732.62	3698.81	106.70	99.23	767.92	761.62	3569.66	3275.87
	Package 7			99.39	100.16			3871.09	3725.68	114.44	103.85	802.47	738.79	3784.51	3415.99
	Package 8			74.19	98.69			3594.42	3102.78	103.15	113.44	695.89	699.32	3280.44	3306.93
	Package 9			91.61	90.02			3380.29	3678.68	98.13	105.05	716.72	735.85	3326.96	3323.70
	Package 10			100.23	91.73			3247.45	3860.51	108.12	125.50	840.16	716.14	3701.44	3668.56
Sample D	Package 1	391.10	423.29	2912.76	3377.88	498.72	576.67	201.15	237.37			3626.71	3997.90	605.11	786.21
	Package 2	342.74	441.27	3172.98	3133.50	548.44	500.46	216.22	195.35			3721.68	3595.53	732.44	662.40
	Package 3	296.88	400.56	3015.97	3237.39	530.07	573.39	205.61	220.43			4149.39	4014.38	772.19	802.57
	Package 4	448.44	365.37	3005.41	3352.25	526.13	623.39	192.48	249.59			3434.69	3668.54	645.13	818.82
	Package 5	340.55	384.15	3054.61	2941.20	516.25	487.07	200.99	188.88			3763.29	3465.38	725.53	685.39
	Package 6	442.41	405.70	3039.68	3108.87	547.78	542.09	207.87	223.30			3510.90	3645.75	676.11	760.41
	Package 7	420.22	413.06	2888.61	3141.73	532.53	542.37	194.59	208.51			3438.98	3871.53	698.39	742.53
	Package 8	330.89	426.64	3033.48	3012.60	551.54	537.27	208.07	186.12			3776.04	3352.93	760.58	643.05
	Package 9	377.73	403.23	2753.41	2812.67	536.28	598.66	208.67	200.45			3140.00	3633.67	635.19	732.36
	Package 10	440.74	320.17	2969.57	3061.16	554.06	569.51	181.12	191.36			3330.28	3427.90	602.15	612.05
Sample E	Package 1	3114.27	3211.84	358.04	278.07	72.54	65.90			721.98	702.28	273.39	305.42		
	Package 2	2856.67	2936.95	268.16	374.82	74.77	76.37			662.08	676.51	283.23	303.17		
	Package 3	3249.04	3094.30	332.13	312.25	75.50	71.70			739.98	709.66	292.20	272.66		
	Package 4	2760.85	3075.52	287.86	361.58	72.99	70.35			699.65	703.07	296.59	265.46		
	Package 5	2600.67	2708.74	312.57	333.78	60.68	64.94			603.83	592.64	234.10	249.88		
	Package 6	2090.37	3239.36	413.27	406.95	52.84	78.22			780.11	722.86	208.12	214.76		
	Package 7	2889.44	2835.03	369.77	361.95	71.68	82.30			668.94	629.89	237.92	262.46		
	Package 8	2975.00	3626.13	294.75	309.34	74.14	74.96			592.59	748.95	210.49	291.32		
	Package 9	2743.12	2773.79	283.87	278.16	63.99	71.66			556.79	695.07	264.02	338.48		
	Package 10	3233.70	3099.38	351.62	404.25	74.04	83.01			725.35	773.91	314.56	293.43		

Table 4: Samples' homogeneity evaluation.

		outliers	S_{sam}^2	c	homogeneity test	W	p	normality test
Sample A	DIBP	no	5.52E+03	3.07E+04	✓	0.94	0.204	✓
	DBP	no	1.42E+03	1.66E+03	✓	0.98	0.980	✓
	BBP	yes	4.15E+01	6.18E+01	✓	0.96	0.563	✓
	DNOP	no	1.35E+03	1.94E+03	✓	0.95	0.315	✓
	DIDP	no	-1.52E+01	1.49E+03	✓	0.93	0.124	✓
Sample B	DIBP	no	-2.78E+01	8.69E+01	✓	0.98	0.978	✓
	BBP	no	7.50E+03	1.72E+04	✓	0.96	0.613	✓
	DEHP	no	4.36E+02	1.48E+03	✓	0.99	0.998	✓
	DNOP	no	1.36E+04	4.50E+04	✓	0.99	0.997	✓
	DINP	no	1.41E+03	3.04E+03	✓	0.98	0.925	✓
Sample C	DBP	no	-4.80E+01	1.48E+02	✓	0.97	0.833	✓
	DEHP	no	-2.76E+04	1.11E+05	✓	0.97	0.731	✓
	DNOP	no	-8.18E+00	9.46E+01	✓	0.92	0.113	✓
	DINP	yes	6.62E+03	5.46E+04	✓	0.88	0.018	✋
	DIDP	no	1.01E+03	2.68E+03	✓	0.90	0.041	✋
Sample D	DIBP	no	-8.31E+02	2.94E+03	✓	0.93	0.180	✓
	DBP	no	1.29E+03	2.79E+04	✓	0.97	0.830	✓
	BBP	no	-1.67E+02	1.46E+03	✓	0.97	0.725	✓
	DEHP	no	-3.30E+01	3.63E+02	✓	0.93	0.166	✓
	DINP	no	-5.57E+02	5.49E+03	✓	0.95	0.403	✓
	DIDP	no	1.78E+04	5.29E+04	✓	0.98	0.931	✓
Sample E	DIBP	yes	5.50E+03	1.00E+05	✓	0.95	0.302	✓
	DBP	no	8.00E+02	1.46E+03	✓	0.94	0.234	✓
	BBP	yes	2.04E+00	5.57E+01	✓	0.93	0.174	✓
	DNOP	no	1.35E+03	2.93E+03	✓	0.95	0.318	✓
	DIDP	no	5.16E+02	8.76E+02	✓	0.96	0.615	✓

3.3 Distribution

The sample packages previously coded (see Table 5) were shipped from 23rd to 30th September 2011 to 18 laboratories, listed in Table 6. These participants are members of CEN/TC 248/WG 26 and/or ISO/TC 38/WG 22 (11 belonging to EU and 7 from outside EU), who had signed the registration form sent together with the invitation letter reported in Annex II.

Table 5: Distribution list of samples.

	Sample A			Sample B			Sample C			Sample D			Sample E			Sample F		
CH	A	TEXT	20	B	TEXT	6	C	TEXT	19	D	TEXT	25	E	PVC	18	F	TEXT	29
CN1	A	TEXT	16	B	TEXT	20	C	TEXT	15	D	TEXT	1	E	PVC	51	F	TEXT	33
CN2	A	TEXT	3	B	TEXT	12	C	TEXT	9	D	TEXT	8	E	PVC	46	F	TEXT	9
DE1	A	TEXT	13	B	TEXT	30	C	TEXT	31	D	TEXT	10	E	PVC	21	F	TEXT	2
DE2	A	TEXT	35	B	TEXT	2	C	TEXT	11	D	TEXT	3	E	PVC	32	F	TEXT	13
FR1	A	TEXT	32	B	TEXT	29	C	TEXT	28	D	TEXT	2	E	PVC	42	F	TEXT	1
FR2	A	TEXT	10	B	TEXT	3	C	TEXT	18	D	TEXT	7	E	PVC	34	F	TEXT	4
IT1	A	TEXT	21	B	TEXT	22	C	TEXT	25	D	TEXT	24	E	PVC	30	F	TEXT	3
IT2	A	TEXT	1	B	TEXT	31	C	TEXT	33	D	TEXT	35	E	PVC	25	F	TEXT	16
JP1	A	TEXT	33	B	TEXT	13	C	TEXT	5	D	TEXT	18	E	PVC	6	F	TEXT	23
JP2	A	TEXT	6	B	TEXT	23	C	TEXT	23	D	TEXT	28	E	PVC	50	F	TEXT	40
JP3	A	TEXT	2	B	TEXT	19	C	TEXT	1	D	TEXT	14	E	PVC	24	F	TEXT	31
JRC	A	TEXT	25	B	TEXT	11	C	TEXT	7	D	TEXT	22	E	PVC	37	F	TEXT	26
NL	A	TEXT	4	B	TEXT	10	C	TEXT	8	D	TEXT	23	E	PVC	5	F	TEXT	27
PT	A	TEXT	29	B	TEXT	28	C	TEXT	21	D	TEXT	30	E	PVC	3	F	TEXT	15
SE	A	TEXT	30	B	TEXT	14	C	TEXT	14	D	TEXT	5	E	PVC	20	F	TEXT	10
UK	A	TEXT	9	B	TEXT	9	C	TEXT	27	D	TEXT	32	E	PVC	2	F	TEXT	30
USA	A	TEXT	18	B	TEXT	33	C	TEXT	4	D	TEXT	11	E	PVC	29	F	TEXT	11

Table 6: Participants enrolled in the validation study.

JRC Code	Country	Laboratory
CH	Switzerland	UL-SSTR Testing & Inspection AG
CN1	China	CTTC - China National Textiles Supervision Testing Center
CN2	China	Technical Centre of Jilin Entry-Exit Inspection and Quarantine Bureau (JLCIQ)
DE1	Germany	TUV Rheinland LGA Products GmbH
DE2	Germany	Bureau Veritas CPS Germany
FR1	France	CTC
FR2	France	IFTH - Institut Français Textile - Habillement
IT1	Italy	ICQ Division of Italian Institute for Toy Safety
IT2	Italy	Centro Tessile Cotoniero e Abbigliamento S.p.A.
JP1	Japan	Japan textile products quality and technology center
JP2	Japan	KE'KEN Textile Testing & Certification Center
JP3	Japan	BOKEN Quality Evaluation Institute
JRC	Italy	European Commission - Joint Research Centre
NL	The Netherlands	Food and Consumer Product Safety Authority Region North
PT	Portugal	CITEVE - Centro Tecnológico das Indústria Têxtil e do Vestuário de Portugal
SE	Sweden	Swerea IVF
UK	United Kingdom	Shirley Technologies Limited
USA	USA	Vartest Laboratories, Inc.

Each participant received:

- five samples (A, B, C, D and E) for the quantification of phthalates;
- one sample (F) for the determination of PVC mass percentage;
- one vial containing about 2 ml of dipentyl phthalate (DPP), to be used as internal standard for the quantification of phthalates;
- two vials containing about 2 ml of diisononyl phthalate (DINP) and 2 ml of diisodecyl phthalate (DIDP) standards, respectively, in order to avoid

problems in their quantification (their isomeric composition can differ depending on the supplier);

- standard operating procedure for each method to be carefully and strictly applied (Annex III);
- an accompanying letter with instructions (Annexes IV and V);
- Excel sheets containing calculation formulas for reporting results (Annex VI);
- a form that had to be sent back after the sample reception to confirm their arrival (Annex VII);

3.4 Instructions

Instructions were given to all participants.

For the precision experiments the laboratories were asked to extract and analyse three specimens for each of the five samples (A-E) with each method (M1-M4), plus two blanks for each method. Seven phthalates had to be quantified (DEHP, DBP, BBP, DINP, DIDP, DNOP and DIBP). The extraction of the testing replicates for each sample and method had to be conducted in repeatability conditions. For each sample and method, the extraction solutions had to be analysed in a short time interval. In case of any problem during the extraction and analysis of some replicates, all the three replicates of the sample had to be repeated. Independent calibration curves, including six points each, had to be prepared for each method (M1-M4) in the solvent used in the extraction or re-precipitation step.

For method 5, participants were asked to analyse three specimens of sample F in repeatability conditions.

The results, including calibration curves, phthalates quantification in blanks and specimens, sample mass etc., had to be reported, by the end of October 2011, in Excel templates prepared by the JRC.

After the deadline, the JRC sent several reminders to laboratories that had not reported results. By 18th November 2011, thirteen laboratories had sent results and the collaborative trial was considered closed.

4 Methods

Four methods (M1-M4) for the quantification of phthalates in textiles and one (M5) for the determination of PVC mass per cent were under evaluation. Participants were asked to strictly follow the standard operating procedures of the five methods, which were provided by the Joint Research Centre and are reported in Annex III.

Methods 1, 2, 3 were based on ultrasonic extraction of phthalates (with n-hexane/acetone 80/20 v/v, n-hexane and tert-butyl methyl ether, respectively), followed by a centrifugation step, if needed, and a GC-MS analysis of the liquid phase. They were, respectively, similar to ISO/TS 16181 [7], developed for footwear materials, a method used in Germany and one applied in China. In each case, the extraction time was 1 h and the temperature of the water bath was 60 ºC for method 3 and 50 ºC for methods 1 and 2, due to the high volatility of the solvents employed. In all cases, the ratio sample/extraction solvent was 0.3 g/10 ml, in order to facilitate the comparison of the extraction properties of the various solvents.

Method 4 was based on the dissolution of PVC with tetrahydrofuran in an ultrasonic generator, followed by the re-precipitation of it with acetonitrile, the centrifugation, if needed, and a GC-MS analysis of the liquid phase. This procedure, similar to the American method CPSC-CH-C1001-09.2 [8], was in use in Germany and in The Netherlands. The dissolution of PVC was carried out in 1 h in an ultrasonic bath at 60 ºC, while the re-precipitation was performed at room temperature in half an hour.

Methods 1-4 foresaw the preparation and the analysis of blanks to exclude any phthalate contamination. The internal standard used in methods 1-4 was dipentyl phthalate (DPP) and it was dissolved in the solvents employed for extraction, dissolution and re-precipitation.

Table 7: Methods' experimental conditions.

	internal standard	sample mass g	extraction solvent	volume ml	time h	temperature ºC
Method 1	DPP	0.3	n-hexane/acetone 80/20 v/v	10	1	50
Method 2	DPP	0.3	n-hexane	10	1	50
Method 3	DPP	0.3	tert-butyl methyl ether	10	1	60

	internal standard	sample mass g	dissolution re-precipitation solvent	volume ml	time h	temperature ºC
Method 4	DPP	0.3	tetrahydrofuran	10	1	60
			acetonitrile	20	0.5	RT

	sample mass g	dissolution solvent	volume ml	time h	temperature ºC
Method 5	1.0	tetrahydrofuran	50	1	60

Method 5 for the determination of PVC mass per cent was based on the dissolution of PVC with tetrahydrofuran (THF) in an ultrasonic generator, followed by the washing of the residue and its gravimetric determination. One gram of sample was treated with 50 ml of THF for 1 h at 60 ºC in an ultrasonic bath. The textile residue was then washed with pre-heated THF and water, dried to constant mass and weighed.

5 Results and discussion

Laboratories were encoded to avoid identification. The results concerning the quantification of phthalates were received from 13 out of 18 laboratories to which samples had been sent, and from 12 in the case of the determination of PVC mass fraction. All participants reported as requested three replicate results under repeatability conditions, with the exception of LC0008 for DNOP in method 1. In total, 4091 test results were collected.

Levels I, II and III refer to samples containing a specific phthalate in concentration of approximately 200, 1000 and 5000 mg of phthalate per kg of PVC. In the case of DIDP and DINP, level I corresponded to approximately 500 mg of phthalate per kg of PVC.

Some deviations from instructions were reported. In particular, LC0011 did prepare the stock solutions for the calibration curve for method 4 in n-hexane instead of acetonitrile and experienced problems in the miscibility of solvents. In addition, LC0006 did quantify the phthalates with HPLC-MS instead of GC-MS. The comments of participants are reported in Annex VIII.

Participants were requested to specify how they had performed the quantification of phthalates. Six of them used SIM mode, three SCAN mode, one both SIM and SCAN modes and three laboratories did not answer this question.

Table 8 summarised the scheme of the collaborative trial, including samples, laboratories reporting results, methods, levels, measurands, and number of test results received.

Table 8: Number of test results per sample, method and measurand.

Method	Sample	Measurand	Level	Number of test results	Number of laboratories
1-4	A	DIBP	III	39	13
		DBP	II	39	13
		BBP	I	39	13
		DNOP	II	39	13
		DIDP	I	39	13
	B	DIBP	I	39	13
		BBP	III	39	13
		DEHP	II	39	13
		DNOP	III	39	13
		DINP	II	39	13
	C	DBP	I	39	13
		DEHP	III	39	13
		DNOP	I	39	13
		DIDP	II	39	13
		DINP	III	39	13
	D	DIBP	II	39	13
		DBP	III	39	13
		BBP	II	39	13
		DEHP	I	39	13
		DIDP	III	39	13
		DINP	I	39	13
	E	DIBP	III	39	13
		DBP	II	39	13
		BBP	I	39	13
		DNOP	II	39 (38 for M1)	13
		DIDP	I	39	13
5	F	% PVC		36	12

The results were statistically evaluated to determine the consensus value, the repeatability and reproducibility, following the rules laid down in ISO 5725-2 [3]. The software Prolab [9] was used to perform the statistic calculations.

The standard ISO 5725 assumes that the materials to be tested are homogeneous and that all laboratories (apart from very few outlier laboratories) have the same analytical performance, in order to guarantee that the test results are normally distributed.

ISO 5725-2 recommends the procedure described in the following for ouliers' identification. The consistency statistic, Mandel h, and the within-laboratory consistency statistic, Mandel k, are calculated for each laboratory within each level. Plots of h and k for each cell in order of laboratory, in groups for each level (separately grouped for the several levels examined by each laboratory) are prepared and evaluated.

Test results are then analysed first with Cochran's test to identify exceeding intra-laboratory standard deviations. Grubbs' test is successively applied for the outlier identification of individual test results (if $n > 2$) and laboratory mean values. The item tested (respectively standard deviation or mean) is:

- accepted as correct if the test statistic is less than or equal to its 5 % critical value;
- called straggler if the test statistic is comprised between 5 % and 1 % of the critical value;
- or called statistical outlier if the test statistic is greater than its 1 % critical value.

Straggler data are marked by a single asterisk and statistical outlier with a double asterisk. They are investigated and if possible replaced by the correct values. When any straggler and/or statistical outliers remain that cannot be either explained or rejected as belonging to an outlying laboratory, the stragglers are retained as correct items and the statistical outliers are discarded unless there are good reasons to retain them.

For the statistical evaluation the unrounded figures were used. Participants provided their results in the templates developed by the JRC. It appeared immediately evident that in many cases the calibration curves could not be considered linear. In order to harmonise as much as possible the data treatment, all calibration curves showing a correlation coefficient higher than 0.995 were considered linear, whereas the others were recalculated fitting quadratic curves which were used to calculate final concentrations of phthalates.

Table 9: Laboratories requested to verify results.

	Method 1	Method 2	Method 3	Method 4
LC0005	A-DIDP E-DIDP	A-DIDP E-DIDP	A-DIDP E-DIDP	A-DIDP E-DIDP
LC0006	-DIBP/DNOP/DIDP B-DINP D-DINP E-DNOP/DIDP			
LC0007	A-BBP D-BBP E-BBP	A-BBP D-BBP E-BBP	A-BBP D-BBP E-BBP	D-BBP E-BBP
LC0008				A-DBP/DNOP C-all phthalates
LC0009			A-DBP	
LC0010	A-BBP D-BBP E-BBP	A-BBP D-BBP E-BBP	A-BBP D-BBP E-BBP	A-BBP D-BBP E-BBP
LC0012		B-BBP		

The results, both in terms of individual results, means and standard deviations, were screened for suspect data and the laboratories who had reported suspect results were asked to check them (Table 9). After verification, all requested laboratories, but LC0005, found mistakes and reported corrected results by the end of December 2011.

The statistical analysis was performed on the corrected results presented in Annex IX. Tables A, B and C for each method report, respectively, the original data, the mean values and the standard deviation, corresponding to each phthalate, sample and laboratory. The results, which were corrected by participants after check, are highlighted in yellow and the original data are written nearby in parenthesis.

As a first step, the normality of the distribution of each set of data was evaluated by the Shapiro-Wilk test [5]. As shown in Table 10, out of the 104 data sets only 27 could be considered as being part of a normal distribution at 95 % probability level. No data sets related to method 4 passed this test. The Kernel density estimation (see Annex X) confirmed this fact, as in several cases data sets show a multimodal distribution.

It has to be noted that, in case of absence of normality of data sets, the statistical evaluation of results should be used with due care; however, as the distribution can be influenced by outliers, the test was repeated after their elimination showing an improvement (47 data sets normally distributed out of 104 corresponding to 45%), see Table 11.

Furthermore, the distribution of the mean values was found normal in the majority of cases (73.1 % in method 1, 69.2 % in method 2, 88.5 % in method 3 and 46.2 % in method 4). This situation further improved after the elimination of outliers, see Tables 12 and 13.

Table 10: Results of Shapiro-Wilk test for normality on original data.

	Method 1		normality	Method 2		normality
	W	p	test	W	p	test
A-DIBP	0.85	< 0.0001	✗	0.89	0.001	✗
A-DBP	0.94	0.055	✓	0.83	< 0.0001	✗
A-BBP	0.96	0.191	✓	0.92	0.009	✗
A-DNOP	0.54	< 0.0001	✗	0.87	< 0.0001	✗
A-DIDP	0.87	< 0.0001	✗	0.94	0.054	✓
B-DIBP	0.97	0.278	✓	0.95	0.060	✓
B-BBP	0.72	< 0.0001	✗	0.90	0.003	✗
B-DEHP	0.95	0.115	✓	0.95	0.100	✓
B-DNOP	0.93	0.018	✗	0.98	0.634	✓
B-DINP	0.92	0.008	✗	0.93	0.026	✗
C-DBP	0.90	0.003	✗	0.90	0.002	✗
C-DEHP	0.92	0.008	✗	0.94	0.051	✓
C-DNOP	0.83	< 0.0001	✗	0.83	< 0.0001	✗
C-DIDP	0.58	< 0.0001	✗	0.73	< 0.0001	✗
C-DINP	0.80	< 0.0001	✗	0.96	0.190	✓
D-DIBP	0.92	0.012	✗	0.86	< 0.0001	✗
D-DBP	0.91	0.005	✗	0.86	< 0.0001	✗
D-BBP	0.95	0.118	✓	0.97	0.410	✓
D-DEHP	0.93	0.017	✗	0.96	0.131	✓
D-DIDP	0.99	0.917	✓	0.84	< 0.0001	✗
D-DINP	0.78	< 0.0001	✗	0.88	0.001	✗
E-DIBP	0.97	0.372	✓	0.70	< 0.0001	✗
E-DBP	0.95	0.103	✓	0.85	< 0.0001	✗
E-BBP	0.96	0.153	✓	0.97	0.304	✓
E-DNOP	0.91	0.006	✗	0.86	< 0.0001	✗
E-DIDP	0.85	< 0.0001	✗	0.91	0.004	✗

	Method 3		normality	Method 4		normality
	W	p	test	W	p	test
A-DIBP	0.98	0.582	✓	0.63	< 0.0001	✗
A-DBP	0.92	0.009	✗	0.88	< 0.0001	✗
A-BBP	0.93	0.020	✗	0.91	0.004	✗
A-DNOP	0.92	0.008	✗	0.72	< 0.0001	✗
A-DIDP	0.88	0.001	✗	0.93	0.023	✗
B-DIBP	0.94	0.035	✗	0.73	< 0.0001	✗
B-BBP	0.92	0.010	✗	0.51	< 0.0001	✗
B-DEHP	0.89	0.001	✗	0.82	< 0.0001	✗
B-DNOP	0.96	0.198	✓	0.52	< 0.0001	✗
B-DINP	0.89	0.001	✗	0.81	< 0.0001	✗
C-DBP	0.90	0.002	✗	0.86	< 0.0001	✗
C-DEHP	0.91	0.004	✗	0.74	< 0.0001	✗
C-DNOP	0.82	< 0.0001	✗	0.91	0.004	✗
C-DIDP	0.68	< 0.0001	✗	0.89	0.001	✗
C-DINP	0.86	< 0.0001	✗	0.71	< 0.0001	✗
D-DIBP	0.95	0.059	✓	0.71	< 0.0001	✗
D-DBP	0.95	0.082	✓	0.94	0.030	✗
D-BBP	0.98	0.717	✓	0.84	< 0.0001	✗
D-DEHP	0.95	0.118	✓	0.89	0.001	✗
D-DIDP	0.95	0.077	✓	0.86	< 0.0001	✗
D-DINP	0.90	0.002	✗	0.88	< 0.0001	✗
E-DIBP	0.96	0.207	✓	0.69	< 0.0001	✗
E-DBP	0.91	0.005	✗	0.91	0.005	✗
E-BBP	0.93	0.021	✗	0.86	< 0.0001	✗
E-DNOP	0.95	0.088	✓	0.71	< 0.0001	✗
E-DIDP	0.91	0.005	✗	0.88	0.001	✗

Table 11: Results of Shapiro-Wilk test for normality on original data after outliers' elimination.

	Method 1		normality	Method 2		normality
	W	p	test	W	p	test
A-DIBP	0.92	0.011	✗	0.95	0.223	✓
A-DBP	0.94	0.055	✓	0.84	< 0.0001	✗
A-BBP	0.96	0.191	✓	0.92	0.009	✗
A-DNOP	0.9	0.003	✗	0.86	< 0.0001	✗
A-DIDP	0.96	0.191	✓	0.93	0.048	✗
B-DIBP	0.97	0.313	✓	0.94	0.060	✓
B-BBP	0.97	0.365	✓	0.91	0.006	✗
B-DEHP	0.95	0.115	✓	0.94	0.069	✓
B-DNOP	0.93	0.031	✗	0.96	0.272	✓
B-DINP	0.98	0.008	✗	0.93	0.028	✗
C-DBP	0.90	0.003	✗	0.90	0.002	✗
C-DEHP	0.92	0.008	✗	0.94	0.051	✓
C-DNOP	0.83	< 0.0001	✗	0.83	< 0.0001	✗
C-DIDP	0.97	0.443	✓	0.73	< 0.0001	✗
C-DINP	0.95	0.089	✓	0.95	0.148	✓
D-DIBP	0.92	0.012	✗	0.86	< 0.0001	✗
D-DBP	0.91	0.005	✗	0.86	< 0.0001	✗
D-BBP	0.95	0.104	✓	0.97	0.410	✓
D-DEHP	0.92	0.013	✗	0.96	0.190	✓
D-DIDP	0.99	0.917	✓	0.94	0.061	✓
D-DINP	0.94	0.070	✓	0.97	0.385	✓
E-DIBP	0.97	0.372	✓	0.84	< 0.0001	✗
E-DBP	0.95	0.103	✓	0.85	< 0.0001	✗
E-BBP	0.95	0.080	✓	0.96	0.326	✓
E-DNOP	0.9	0.005	✗	0.87	< 0.0001	✗
E-DIDP	0.86	< 0.0001	✗	0.92	0.015	✗

	Method 3		normality	Method 4		normality
	W	p	test	W	p	test
A-DIBP	0.98	0.582	✓	0.97	0.316	✓
A-DBP	0.92	0.009	✗	0.88	0.002	✗
A-BBP	0.93	0.020	✗	0.92	0.014	✗
A-DNOP	0.92	0.008	✗	0.93	0.020	✗
A-DIDP	0.97	0.447	✓	0.92	0.014	✗
B-DIBP	0.93	0.034	✗	0.94	0.072	✓
B-BBP	0.92	0.010	✗	0.95	0.135	✓
B-DEHP	0.89	0.001	✗	0.89	0.002	✗
B-DNOP	0.96	0.198	✓	0.93	0.018	✗
B-DINP	0.88	0.001	✗	0.92	0.016	✗
C-DBP	0.90	0.002	✗	0.88	0.001	✗
C-DEHP	0.90	0.005	✗	0.93	0.027	✗
C-DNOP	0.82	< 0.0001	✗	0.91	0.005	✗
C-DIDP	0.76	< 0.0001	✗	0.87	0.001	✗
C-DINP	0.97	0.503	✓	0.88	0.001	✗
D-DIBP	0.95	0.059	✓	0.86	0.003	✗
D-DBP	0.96	0.153	✓	0.91	0.009	✗
D-BBP	0.98	0.717	✓	0.80	< 0.0001	✗
D-DEHP	0.95	0.118	✓	0.93	0.063	✓
D-DIDP	0.90	0.005	✗	0.94	0.056	✓
D-DINP	0.88	0.001	✗	0.94	0.064	✓
E-DIBP	0.96	0.207	✓	0.95	0.106	✓
E-DBP	0.59	< 0.0001	✓	0.94	0.073	✓
E-BBP	0.93	0.021	✓	0.92	0.009	✗
E-DNOP	0.95	0.088	✓	0.97	0.471	✓
E-DIDP	0.91	0.005	✓	0.80	0.001	✗

Table 12: Results of Shapiro-Wilk test for normality on original mean values.

	Method 1		normality	Method 2		normality
	W	p	test	W	p	test
A-DIBP	0.85	0.030	✗	0.89	0.106	✓
A-DBP	0.95	0.589	✓	0.84	0.019	✗
A-BBP	0.96	0.820	✓	0.92	0.220	✓
A-DNOP	0.88	0.067	✓	0.86	0.035	✗
A-DIDP	0.88	0.070	✓	0.97	0.942	✓
B-DIBP	0.96	0.800	✓	0.96	0.715	✓
B-BBP	0.71	0.001	✗	0.92	0.234	✓
B-DEHP	0.96	0.811	✓	0.95	0.629	✓
B-DNOP	0.93	0.344	✓	0.98	0.957	✓
B-DINP	0.92	0.243	✓	0.94	0.489	✓
C-DBP	0.91	0.194	✓	0.91	0.207	✓
C-DEHP	0.93	0.310	✓	0.94	0.428	✓
C-DNOP	0.84	0.021	✗	0.84	0.020	✗
C-DIDP	0.59	< 0.0001	✗	0.74	0.001	✗
C-DINP	0.8	0.007	✗	0.96	0.720	✓
D-DIBP	0.93	0.379	✓	0.88	0.054	✓
D-DBP	0.92	0.224	✓	0.88	0.056	✓
D-BBP	0.95	0.626	✓	0.98	0.978	✓
D-DEHP	0.92	0.267	✓	0.97	0.896	✓
D-DIDP	0.98	0.995	✓	0.83	0.018	✗
D-DINP	0.78	0.004	✗	0.91	0.198	✓
E-DIBP	0.98	0.995	✓	0.70	0.001	✗
E-DBP	0.96	0.766	✓	0.87	0.048	✗
E-BBP	0.97	0.829	✓	0.98	0.983	✓
E-DNOP	0.9	0.129	✓	0.86	0.044	✗
E-DIDP	0.86	0.035	✗	0.92	0.247	✓

	Method 3		normality	Method 4		normality
	W	p	test	W	p	test
A-DIBP	0.97	0.913	✓	0.64	< 0.0001	✗
A-DBP	0.93	0.295	✓	0.89	0.101	✓
A-BBP	0.94	0.448	✓	0.92	0.291	✓
A-DNOP	0.93	0.319	✓	0.72	0.001	✗
A-DIDP	0.89	0.097	✓	0.95	0.539	✓
B-DIBP	0.93	0.348	✓	0.74	0.001	✗
B-BBP	0.92	0.257	✓	0.58	< 0.0001	✗
B-DEHP	0.90	0.134	✓	0.83	0.016	✗
B-DNOP	0.95	0.656	✓	0.52	< 0.0001	✗
B-DINP	0.89	0.097	✓	0.82	0.010	✗
C-DBP	0.90	0.137	✓	0.86	0.042	✗
C-DEHP	0.90	0.143	✓	0.74	0.001	✗
C-DNOP	0.82	0.011	✗	0.91	0.167	✓
C-DIDP	0.69	< 0.0001	✗	0.90	0.147	✓
C-DINP	0.83	0.018	✗	0.71	0.001	✗
D-DIBP	0.95	0.612	✓	0.71	0.001	✗
D-DBP	0.96	0.728	✓	0.94	0.468	✓
D-BBP	0.98	0.974	✓	0.85	0.025	✗
D-DEHP	0.96	0.726	✓	0.90	0.136	✓
D-DIDP	0.93	0.313	✓	0.87	0.055	✓
D-DINP	0.92	0.216	✓	0.88	0.075	✓
E-DIBP	0.96	0.827	✓	0.72	0.001	✗
E-DBP	0.89	0.085	✓	0.93	0.355	✓
E-BBP	0.94	0.481	✓	0.88	0.068	✓
E-DNOP	0.96	0.699	✓	0.70	0.001	✗
E-DIDP	0.93	0.330	✓	0.90	0.137	✓

Table 13: Results of Shapiro-Wilk test for normality on original means after outliers' elimination.

	Method 1		normality	Method 2		normality
	W	p	test	W	p	test
A-DIBP	0.85	0.030	✗	0.89	0.106	✓
A-DBP	0.95	0.589	✓	0.84	0.019	✗
A-BBP	0.96	0.820	✓	0.92	0.220	✓
A-DNOP	0.88	0.067	✓	0.86	0.035	✗
A-DIDP	0.97	0.927	✓	0.99	0.99	✓
B-DIBP	0.96	0.800	✓	0.96	0.715	✓
B-BBP	0.96	0.844	✓	0.92	0.234	✓
B-DEHP	0.96	0.811	✓	0.95	0.629	✓
B-DNOP	0.93	0.344	✓	0.98	0.957	✓
B-DINP	0.92	0.243	✓	0.94	0.489	✓
C-DBP	0.91	0.194	✓	0.91	0.207	✓
C-DEHP	0.93	0.310	✓	0.94	0.428	✓
C-DNOP	0.84	0.021	✗	0.84	0.020	✗
C-DIDP	0.7	0.001	✗	0.71	0.001	✗
C-DINP	0.94	0.550	✓	0.96	0.720	✓
D-DIBP	0.93	0.379	✓	0.88	0.054	✓
D-DBP	0.92	0.224	✓	0.88	0.056	✓
D-BBP	0.95	0.626	✓	0.98	0.978	✓
D-DEHP	0.92	0.267	✓	0.97	0.896	✓
D-DIDP	0.99	0.997	✓	0.93	0.403	✓
D-DINP	0.98	0.508	✓	0.91	0.198	✓
E-DIBP	0.98	0.995	✓	0.83	0.019	✗
E-DBP	0.96	0.766	✓	0.87	0.048	✗
E-BBP	0.97	0.829	✓	0.98	0.983	✓
E-DNOP	0.9	0.129	✓	0.86	0.044	✗
E-DIDP	0.86	0.045	✗	0.93	0.364	✓

	Method 3		normality	Method 4		normality
	W	p	test	W	p	test
A-DIBP	0.97	0.913	✓	0.96	0.740	✓
A-DBP	0.93	0.295	✓	0.91	0.200	✓
A-BBP	0.94	0.448	✓	0.97	0.921	✓
A-DNOP	0.93	0.319	✓	0.92	0.286	✓
A-DIDP	0.97	0.912	✓	0.93	0.398	✓
B-DIBP	0.93	0.348	✓	0.97	0.877	✓
B-BBP	0.92	0.257	✓	0.90	0.148	✓
B-DEHP	0.90	0.134	✓	0.95	0.658	✓
B-DNOP	0.95	0.656	✓	0.92	0.316	✓
B-DINP	0.89	0.097	✓	0.90	0.159	✓
C-DBP	0.90	0.137	✓	0.89	0.116	✓
C-DEHP	0.90	0.143	✓	0.94	0.529	✓
C-DNOP	0.93	0.418	✓	0.88	0.104	✓
C-DIDP	0.76	0.003	✗	0.89	0.103	✓
C-DINP	0.87	0.078	✓	0.92	0.254	✓
D-DIBP	0.95	0.612	✓	0.81	0.011	✗
D-DBP	0.96	0.728	✓	0.92	0.282	✓
D-BBP	0.98	0.974	✓	0.93	0.360	✓
D-DEHP	0.96	0.726	✓	0.63	0.001	✗
D-DIDP	0.90	0.166	✓	0.96	0.799	✓
D-DINP	0.92	0.216	✓	0.95	0.670	✓
E-DIBP	0.96	0.827	✓	0.93	0.392	✓
E-DBP	0.89	0.085	✓	0.95	0.683	✓
E-BBP	0.94	0.481	✓	0.95	0.601	✓
E-DNOP	0.96	0.699	✓	0.86	0.059	✓
E-DIDP	0.99	0.999	✓	0.98	0.980	✓

The evaluation of data was carried out with the Mandel's h and k statistics to assess laboratories' performances in terms of mean values and variances, respectively, for each method. The resulting plots are reported in Annex X. From the plots, it appeared evident that the laboratory LC0004 had some problems with method 4. Its results seemed to be affected by a systematic error; in fact the mean values for all phthalates in every sample were much higher than the means obtained by the other laboratories, as proved by the fact that, out of 26 mean values, 19 were identified as outliers (h**) and 4 as stragglers (h*) with Mandel's h parameter. In addition, the plots highlighted that the participant LC0005 encountered difficulties in quantifying DIDP, both at low (it could not quantify level I) and at high levels; out of 16 mean values for this phthalate, 11 averages were considered outliers and 3 were judged stragglers with Mandel's h parameter. On the basis of these findings, LC0004's results were rejected for all phthalates and samples analysed with method 4 and the ones of LC0005 for the quantification of DIDP in every sample and method. Furthermore, the analysis of Mandel's statistics makes evident that in all methods, but method 2, LC0011 constantly obtained mean values below the overall mean ones, independently from levels and phthalates, suggesting a systematic error. The results of this laboratory, however, were not identified as outliers or stragglers and were retained. In the case of method 5, with Mandel's tests LC0003 was recognised as straggler for the variance and LC0005 was identified as outlier for the mean value, however no decision was taken on this basis.

Table 14: Statistical outliers and stragglers according to Mandel's h and k, Cochran and Grubbs.

	M1				M2				M3				M4				total				M5
	C**	C*	k**	k*	C**	C*	k**	k*	C**	C*	k**	k*	C**	C*	k**	k*	C**	C*	k**	k*	k*
LC0000	1		4	1					2		2	2	1	2	1	3	4	2	7	6	
LC0001		2	4	1	1		3		1	1	5	1	2	1	1	1	4	4	13	3	
LC0002	4	3	5	3	4	1	3	5	2		1	4	4	2	5	2	14	6	14	14	
LC0003					1	1	4	1					1	1	1	2	2	2	5	3	1
LC0004	1	1	3	2	8	2	10	1	7		8	2	6	3	11	4	22	6	32	9	
LC0005							1												1		
LC0006	2	1	2	1	1	2	2						1				4	3	4	1	
LC0007									1		1	1				1	1		1	2	
LC0008					1		1						1		1		2		2		
LC0009											1	2	1	1	2	2	1	1	3	4	
LC0010	2		2	1		2		1				1	1			2	3	2	2	5	
LC0011		1	2		2		2	1	1					1	1		3	2	5	1	
LC0012				1				1		1	1	1						1	1	3	
outliers	10	8	22	10	18	8	26	10	14	2	19	14	18	11	23	17	60	29	90	51	1
%	3,0	2,4	6,5	3,0	5,3	2,4	7,7	3,0	4,1	0,6	5,6	4,1	5,3	3,3	6,8	5,0	4,4	2,1	6,7	3,8	8,3

	M1				M2				M3				M4				total				M5
	G**	G*	h**	h*	G**	G*	h**	h*	G**	G*	h**	h*	G**	G*	h**	h*	G**	G*	h**	h*	h**
LC0000	1		3	3											1		1		4	3	
LC0001					1	1	3	2		2	1	3					1	3	4	5	
LC0002				1								5								6	
LC0003																					1
LC0004													15		19	5	15		19	5	
LC0005	1	2	3	1		2	3	4	1	2	4			1		1	2	7	10	6	
LC0006			1	1			1	2			1	1							3	4	
LC0007	1			3		3	3	2				1					1	3	3	6	
LC0008																					
LC0009	2		3								1						2		4		
LC0010		1	2					3		1	1	1				1		2	3	5	
LC0011						1						1		1				2		1	
LC0012				1		1	1	1	1		1						1	1	2	2	
outliers	5	3	12	10	1	8	11	14	2	5	9	12	15	2	20	7	23	18	52	43	1
%	1.5	0.9	3.6	3.0	0.3	2.4	3.3	4.1	0.6	1.5	2.7	3.6	4.4	0.6	5.9	2.1	1.7	1.3	3.8	3.2	8.3

Table 15: Cochran's and Grubbs' statistical outliers per level and method.

	C**						G**					
	M1	M2	M3	M4	total	%	M1	M2	M3	M4	total	%
Level I	4	7	7	7	25	21.4	1	0	0	3	4	3.4
Level II	4	4	2	8	18	15.4	2	0	1	6	9	7.7
Level III	2	7	5	4	18	17.3	2	1	1	6	10	9.6

ISO 5725-2 assumes that between laboratories only small differences exist in the within-laboratory variances. To test the validity of this assumption the standard deviations obtained in each laboratory for every sample and phthalate were evaluated with Cochran's test to find outliers. Tables 14 and C in Annex IX report the results obtained. For methods 1-4, the statistical outliers (C**), 60 representing 4.4 % of all standard deviations, were rejected, whereas stragglers (C*), 29 corresponding to 2.1 %, were retained for further calculations. No Cochran's outliers or stragglers were identified in method 5.

No individual outliers were recognised on the basis of Grubbs' test. Grubbs' test was also applied to cell means and results are showed in Tables 14 and B in Annex IX. As with Cochran's test, statistical outliers (G**, 1.7 %) were rejected, whereas stragglers (G*, 1.3 %) were retained for further calculations. No Grubbs' outliers or stragglers were identified in method 5.

The analysis of the outliers supported the decision taken on the basis of Mandel's statistics. In fact, LC0004 was recognised as Grubbs' outlier in the case of 14 out of 26 cell means in method 4. In addition, LC0004 showed a very poor repeatability, when compared to other laboratories, particularly in method 4 but also in methods 2 and 3 (7, 8 and 7 Cochran's outliers were respectively identified out of 26 variances for each method). Also LC0002 showed a relatively poor repeatability considering that it was excluded in 4, 4, 2, and 4 phthalates in methods 1, 2, 3 and 4 respectively.

As shown in Table 15, for methods 1-4 among the Cochran's outliers there was a slight prevalence in level I, compared to levels II and III. On the contrary, in the case of cell means level III contained the highest number (10) of Grubbs' outliers, compared to level II (9) and I (4).

Table 16 presents the summary results in terms of number of outliers eliminated from each data set, mean values, repeatability and reproducibility limits as well as relative standard deviation for repeatability and reproducibility. The quantity of each phthalate is expressed in mg per kg of sample (which includes textile plus PVC for samples A-D and only PVC for sample E). Each data set, corresponding to one phthalate in one sample analysed with one method, was composed by 13 cell means or 13 standard deviations. It is generally accepted that a maximum of two outliers out of nine results can be rejected. This rule was respected on all 104 data sets, with the exception of DIBP in sample D analysed with method 4. In this case, the number of rejected outliers was 5. The graphical representation of final results is reported in Annex X.

It has to be noted that the results obtained by LC0006 were generally in good agreement with the final results of the study, despite the fact that this laboratory quantified phthalates with HPLC-MS technique instead of GC-MS.

Both the minimum and the maximum relative standard deviation of repeatability were obtained in method 4 (3.0 and 23.5 % respectively). Concerning the relative standard deviation of reproducibility, the minimum value 19.4 % was shown with method 3 and the highest 189.2 % with method 2. Generally speaking, results proved that both the methods and the laboratories' performances have to be drastically improved. Poor repeatability was observed in the case of several laboratories and the large spread in the mean values calculated in the thirteen laboratories is responsible for the observed relative standard deviation of reproducibility.

In some cases participants detected also phthalates that, according to the plastisol composition, were not present in the samples. These results are reported in Annex XI. It is remarkable the fact that all participants detected DEHP both in samples A and E; this could have possibly been caused by an initial contamination of the same plastisol used in the production of those two samples.

The percentage of PVC in sample A was determined by the JRC on five replicates applying method 5 and was equal to 88.87 %. Considering this value, the concentration of phthalates in sample A were recalculated in order to express them in terms of mg of phthalates per kg of PVC (sample A*). In this way, samples A* and E could be compared as they were prepared starting from the same plastisol batch. As shown in Table 18, results were in good agreement.

Table 16: Results of the collaborative trial for methods 1-4.

		DIBP						DBP					
		outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %	outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %
Sample A	Method 1	1	3256,5	353,5	10,9%	2104,0	64,6%	0	713,3	71,2	10,0%	594,7	83,4%
	Method 2	3	2554,1	199,3	7,8%	912,4	35,7%	1	566,5	62,5	11,0%	615,3	108,6%
	Method 3	0	3379,1	373,1	11,0%	1553,4	46,0%	0	736,7	86,1	11,7%	565,8	76,8%
	Method 4	1	3632,3	406,4	11,2%	1441,9	39,7%	2	738,3	54,6	7,4%	551,2	74,7%
Sample B	Method 1	1	120,7	17,4	14,4%	108,1	89,6%						
	Method 2	1	100,6	17,1	17,0%	92,6	92,1%						
	Method 3	2	135,8	22,4	16,5%	133,8	98,5%						
	Method 4	2	116,1	12,3	10,6%	79,5	68,5%						
Sample C	Method 1							0	133,9	14,9	11,1%	146,3	109,3%
	Method 2							0	112,8	18,6	16,5%	148,5	131,6%
	Method 3							0	143,5	18,7	13,0%	158,6	110,6%
	Method 4							1	136,3	25,7	18,9%	170,2	124,9%
Sample D	Method 1	0	579,7	76,3	13,2%	433,8	74,8%	0	3434,2	369,5	10,8%	2943,9	85,7%
	Method 2	0	535,4	61,8	11,5%	702,4	131,2%	0	2702,2	251,5	9,3%	2337,6	86,5%
	Method 3	0	642,7	70,9	11,0%	533,5	83,0%	1	3217,3	332,5	10,3%	2437,6	75,8%
	Method 4	5	635,8	19,0	3,0%	331,0	52,1%	3	3503,0	290,8	8,3%	2989,1	85,3%
Sample E	Method 1	0	3758,0	424,7	11,3%	2823,0	75,1%	0	776,2	74,5	9,6%	534,8	68,9%
	Method 2	2	2428,2	155,2	6,4%	1190,5	49,0%	0	605,9	56,7	9,4%	529,4	87,4%
	Method 3	1	3534,8	430,7	12,2%	2235,2	63,2%	0	787,8	78,7	10,0%	607,3	77,1%
	Method 4	1	4158,9	382,0	9,2%	1968,6	47,3%	2	803,0	54,5	6,8%	640,9	79,8%

		BBP						DEHP					
		outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %	outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %
Sample A	Method 1	0	131.1	19.7	15.0%	132.4	101.0%						
	Method 2	0	73.7	9.2	12.5%	75.0	101.7%						
	Method 3	0	129.0	12.4	9.6%	144.8	112.3%						
	Method 4	2	183.4	14.9	8.1%	177.1	96.5%						
Sample B	Method 1	1	3788.2	523.3	13.8%	1517.1	40.1%	0	848.3	139.6	16.5%	680.9	80.3%
	Method 2	1	2590.9	314.5	12.1%	3086.9	119.1%	1	795.8	104.4	13.1%	762.1	95.8%
	Method 3	0	4088.3	440.9	10.8%	2120.5	51.9%	0	888.2	81.5	9.2%	846.8	95.3%
	Method 4	2	4620.8	325.7	7.1%	1457.2	31.5%	1	982.8	90.1	9.2%	907.1	92.3%
Sample C	Method 1							0	4028.0	318.4	7.9%	3081.3	76.5%
	Method 2							0	3339.2	670.0	20.1%	1866.6	55.9%
	Method 3							1	3835.8	438.3	11.4%	2178.5	56.8%
	Method 4							1	4560.6	692.6	15.2%	2775.0	60.9%
Sample D	Method 1	1	755.1	54.5	7.2%	429.6	56.9%	1	217.4	15.5	7.1%	199.9	92.0%
	Method 2	0	520.9	65.2	12.5%	497.9	95.6%	2	172.8	9.5	5.5%	210.1	121.6%
	Method 3	1	797.0	101.1	12.7%	375.4	47.1%	0	219.0	39.0	17.8%	232.5	106.2%
	Method 4	1	1113.9	171.9	15.4%	1640.7	147.3%	1	242.5	10.5	4.3%	273.5	112.8%
Sample E	Method 1	1	147.7	14.5	9.8%	156.9	106.2%						
	Method 2	2	77.8	6.2	7.9%	71.0	91.3%						
	Method 3	0	155.7	26.3	16.9%	203.0	130.4%						
	Method 4	1	194.2	17.7	9.1%	175.5	90.4%						

		DNOP						DIDP					
		outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %	outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %
Sample A	Method 1	1	949,3	80,4	8,5%	774,2	81,6%	2	459,8	53,4	11,6%	307,9	67,0%
	Method 2	1	743,8	93,6	12,6%	608,1	81,8%	2	405,8	63,0	15,5%	323,0	79,6%
	Method 3	0	853,8	79,7	9,3%	637,6	74,7%	2	440,6	35,7	8,1%	307,1	69,7%
	Method 4	1	915,6	134,4	14,7%	598,1	65,3%	2	463,2	75,0	16,2%	337,4	72,8%
Sample B	Method 1	1	4370,4	476,8	10,9%	2101,1	48,1%						
	Method 2	1	3562,4	312,9	8,8%	1191,9	33,5%						
	Method 3	0	4223,5	418,9	9,9%	2036,5	48,2%						
	Method 4	1	4574,3	620,8	13,6%	1575,1	34,4%						
Sample C	Method 1	0	209,3	27,8	13,3%	326,9	156,2%	3	931,9	95,5	10,3%	364,6	39,1%
	Method 2	0	166,8	28,1	16,8%	279,3	167,4%	1	1135,7	87,0	7,7%	2149,1	189,2%
	Method 3	2	201,0	29,6	14,7%	309,3	153,9%	1	1174,1	234,7	20,0%	1563,5	133,2%
	Method 4	3	218,3	51,3	23,5%	362,3	165,9%	3	1385,1	211,7	15,3%	1636,5	118,2%
Sample D	Method 1							1	4611,1	647,8	14,1%	2004,9	43,5%
	Method 2							1	4017,5	451,4	11,2%	1596,3	39,7%
	Method 3							2	4685,4	624,2	13,3%	2431,3	51,9%
	Method 4							3	4527,3	497,3	11,0%	5007,4	110,6%
Sample E	Method 1	1	1017,6	89,7	8,8%	532,1	52,3%	1	535,6	79,2	14,8%	385,8	72,0%
	Method 2	0	841,2	52,2	6,2%	653,0	77,6%	1	425,2	90,5	21,3%	310,6	73,0%
	Method 3	0	960,5	106,0	11,0%	606,0	63,1%	1	507,8	52,9	10,4%	367,1	72,3%
	Method 4	1	963,5	185,1	19,2%	661,9	68,7%	2	501,4	81,2	16,2%	400,7	79,9%

		DINP					
		outlier	mean mg/kg	r mg/kg	RSDr %	R mg/kg	RSDR %
Sample A	Method 1						
	Method 2						
	Method 3						
	Method 4						
Sample B	Method 1	0	937.0	197.9	21.1%	840.4	89.7%
	Method 2	1	704.5	110.2	15.7%	478.9	68.0%
	Method 3	1	890.1	125.8	14.1%	571.5	64.2%
	Method 4	1	901.7	125.8	14.0%	938.8	104.1%
Sample C	Method 1	1	4797.8	533.9	11.1%	1765.0	36.8%
	Method 2	1	3913.3	427.1	10.9%	1783.3	45.6%
	Method 3	3	4225.4	385.2	9.1%	820.7	19.4%
	Method 4	1	4550.1	822.8	18.1%	3919.0	86.1%
Sample D	Method 1	1	642.7	110.6	17.2%	323.0	50.3%
	Method 2	1	480.2	59.6	12.4%	349.6	72.8%
	Method 3	1	641.3	111.3	17.4%	546.3	85.2%
	Method 4	2	665.7	124.2	18.7%	776.0	116.6%
Sample E	Method 1						
	Method 2						
	Method 3						
	Method 4						

Table 17: Ranges of repeatability and reproducibility relative standard deviations per method.

	RSDr %	RSDR %
Method 1	7.1-21.1	36.8-156.2
Method 2	5.5-21.3	33.5-189.2
Method 3	8.1-20.0	19.4-153.9
Method 4	3.0-23.5	31.5-165.9

Table 18: Comparison of results calculated as mg of phthalate per kg of PVC for sample A and E.

		DIBP mg/kg	DBP mg/kg	BBP mg/kg	DNOP mg/kg	DIDP mg/kg
Sample A*	Method 1	3664.3	802.6	147.5	1068.2	517.4
	Method 2	2874.0	637.5	83.0	836.9	456.7
	Method 3	3802.3	829.0	145.1	960.7	495.7
	Method 4	4087.3	830.7	206.4	1030.3	521.3
Sample E	Method 1	3758.0	776.2	147.7	1017.6	535.6
	Method 2	2428.2	605.9	77.8	841.2	425.2
	Method 3	3534.8	787.8	155.7	960.5	507.8
	Method 4	4158.9	803.0	194.2	963.5	501.4

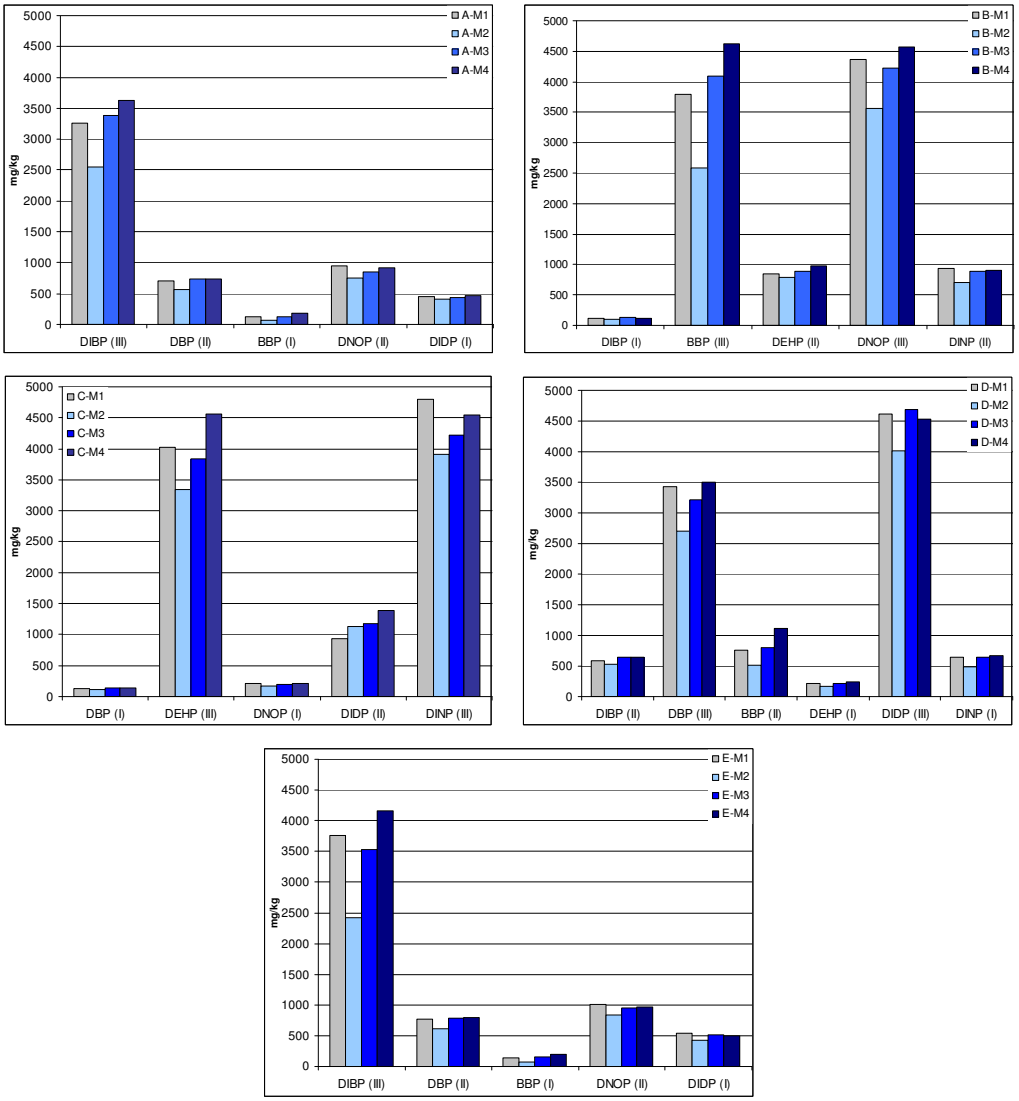

Figure 3: Mean values for samples A-E (from left to right, top to bottom).

Figure 3 represents graphically the average concentration of phthalates per sample and method. In several cases, method 4 gave higher results when compared to the other methods, in particular method 2.

In order to calculate the theoretical recovery of phthalates, the PVC mass fraction in all samples had to be measured with method 5 and, first of all, the *d* correction factor for cotton had to be established. This factor is the mass loss of the insoluble fibre (in this case cotton) in the conditions of the method used (method 5). For this purpose the JRC analysed five specimens of pure cotton with method 5 and calculated the correction factor dividing the dry mass of the sample after pre-treatment by the dry mass of the residue obtained applying the method.

$$d = \frac{m}{r} \qquad 5.1$$

where:

m is the dry mass of the specimen after pre-treatment
r is the dry mass of the residue

On the basis of the average of five replicates, the *d* factor 1.00, corresponding to a complete insolubility of cotton in THF, was established (Table 19) and used in all the calculations in method 5 to evaluate the PVC mass per cent.

Table 19: Determination of *d* correction factor for cotton in Method 5.

Specimen	Bottle + specimen (g)	Bottle (g)	Filter (g)	Filter + residue (g)	Sample (g)	Residue (g)	*d* factor
cotton_1a	102.5622	101.5962	67.4255	68.3887	0.9660	0.9632	1.0029
cotton_1b	100.9676	100.0054	68.9360	69.8971	0.9622	0.9611	1.0011
cotton_1c	106.9252	105.9646	68.1030	69.0596	0.9606	0.9566	1.0042
cotton_1d	103.2970	102.3263	65.8776	66.8467	0.9707	0.9691	1.0017
cotton_1e	106.5340	105.5640	69.2559	70.2219	0.9700	0.9660	1.0041
						average	1.0028
						SD	0.0014
						RSD%	0.14

Table 20: Determination of PVC mass percentage of samples A-D according to method 5.

Sample	Sample mass (g)	Residue (g)	% Cotton	% PVC	P1A% Cotton	P2A% PVC
A-1	1.0008	0.1046	10.45	89.55	11.24	88.76
A-2	0.9905	0.1003	10.13	89.87	10.89	89.11
A-3	1.0053	0.1068	10.62	89.38	11.42	88.58
A-4	0.9977	0.1029	10.31	89.69	11.09	88.91
A-5	0.9976	0.102	10.22	89.78	11.00	89.00
		average	10.35	89.65	11.13	88.87
		SD	0.20	0.20	0.21	0.21
		RSD	1.89	0.22	1.87	0.23
B-1	0.9953	0.1135	11.40	88.60	12.25	87.75
B-2	1.0054	0.1144	11.38	88.62	12.23	87.77
B-3	0.9981	0.1136	11.38	88.62	12.23	87.77
B-4	1.0034	0.1128	11.24	88.76	12.08	87.92
B-5	1.0076	0.1129	11.20	88.80	12.04	87.96
		average	11.32	88.68	12.17	87.83
		SD	0.09	0.09	0.10	0.10
		RSD	0.81	0.10	0.80	0.11
C-1	1.0099	0.1143	11.32	88.68	12.16	87.84
C-2	1.0672	0.1236	11.58	88.42	12.44	87.56
C-3	0.9985	0.1136	11.38	88.62	12.23	87.77
C-4	0.9876	0.1114	11.28	88.72	12.12	87.88
C-5	1.0053	0.1189	11.83	88.17	12.70	87.30
		average	11.48	88.52	12.33	87.67
		SD	0.23	0.23	0.24	0.24
		RSD	1.99	0.26	1.97	0.28
D-1	1.059	0.121	11.43	88.57	12.28	87.72
D-2	1.0186	0.116	11.39	88.61	12.24	87.76
D-3	1.0433	0.1177	11.28	88.72	12.12	87.88
D-4	1.0044	0.1138	11.33	88.67	12.18	87.82
D-5	1.0076	0.1129	11.20	88.80	12.04	87.96
		average	11.33	88.67	12.17	87.83
		SD	0.09	0.09	0.09	0.09
		RSD	0.77	0.10	0.76	0.11

Five replicates of each sample A-D were analysed with method 5 to measure the percentages of soluble (PVC) and insoluble (cotton) components (Table 20). Calculations were carried out following the formulas reported in the method protocol (see Annex III). At first, calculations were performed on a clean, dry mass basis and then corrected with adjustment by the agreed allowance a_1 (8.5 for cotton). The PVC mass per cent was 88.87 %, 87.83 %, 87.67 % and 87.83 % for samples A, B, C and D, respectively.

These values, apart from the one for sample C/F which was taken from the results obtained in the collaborative study (88.2 %), were used to calculate the theoretical recovery of the seven phthalates per sample and method, expressing the concentration in mg of phthalate per kg of PVC (Table 21).

Due to probable losses of phthalates during the sample preparation, recoveries cannot be regarded as exact values, however comparison among methods' efficiency can be done and conclusions can be drawn. Method 4 proved to be the best method in terms of phthalates' recovery in 18 out of 26 phthalate's determinations. The recoveries obtained with this method ranged from 62.2 to 154.3 %. On the contrary, method 2 was the worst one in all 26 phthalate's determinations but one, with recoveries ranging from 36.7 to 126.5. Practically the same extraction efficiency was shown by methods 1 and 3.

Table 21: Theoretical recovery of phthalates.

		DIBP			DBP			BBP			DEHP		
		expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %
Sample A	Method 1	5018.0	3664.3	73.0	1012.0	802.6	79.3	212.0	147.5	69.6			
	Method 2	5018.0	2874.0	57.3	1012.0	637.5	63.0	212.0	83.0	39.1			
	Method 3	5018.0	3802.3	75.8	1012.0	829.0	81.9	212.0	145.1	68.4			
	Method 4	5018.0	4087.3	81.5	1012.0	830.7	82.1	212.0	206.4	97.4			
Sample B	Method 1	210.0	135.9	64.7				5042.0	4264.6	84.6	1012.0	955.0	94.4
	Method 2	210.0	113.2	53.9				5042.0	2916.7	57.8	1012.0	895.8	88.5
	Method 3	210.0	152.9	72.8				5042.0	4602.3	91.3	1012.0	999.9	98.8
	Method 4	210.0	130.7	62.2				5042.0	5201.9	103.2	1012.0	1106.3	109.3
Sample C	Method 1				230.0	151.8	66.0				5020.0	4566.9	91.0
	Method 2				230.0	127.9	55.6				5020.0	3786.0	75.4
	Method 3				230.0	162.7	70.7				5020.0	4349.0	86.6
	Method 4				230.0	154.5	67.2				5020.0	5170.8	103.0
Sample D	Method 1	1015.0	661.5	65.2	5015.0	3919.0	78.1	1010.0	861.7	85.3	211.0	248.1	117.6
	Method 2	1015.0	611.0	60.2	5015.0	3083.6	61.5	1010.0	594.5	58.9	211.0	197.2	93.4
	Method 3	1015.0	733.4	72.3	5015.0	3671.5	73.2	1010.0	909.5	90.0	211.0	250.0	118.5
	Method 4	1015.0	725.6	71.5	5015.0	3997.5	79.7	1010.0	1271.2	125.9	211.0	276.8	131.2
Sample E	Method 1	5018.0	3758.0	74.9	1012.0	776.2	76.7	212.0	147.7	69.7			
	Method 2	5018.0	2428.2	48.4	1012.0	605.9	59.9	212.0	77.8	36.7			
	Method 3	5018.0	3534.8	70.4	1012.0	787.8	77.8	212.0	155.7	73.4			
	Method 4	5018.0	4158.9	82.9	1012.0	803.0	79.3	212.0	194.2	91.6			

		DNOP			DIDP			DINP		
		expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %
Sample A	Method 1	1057.0	1068.2	101.1	521.0	517.4	99.3			
	Method 2	1057.0	836.9	79.2	521.0	456.7	87.7			
	Method 3	1057.0	960.7	90.9	521.0	495.7	95.1			
	Method 4	1057.0	1030.3	97.5	521.0	521.3	100.1			
Sample B	Method 1	5005.0	4920.0	98.3				1020.0	1054.9	103.4
	Method 2	5005.0	4010.4	80.1				1020.0	793.0	77.7
	Method 3	5005.0	4754.6	95.0				1020.0	1002.1	98.2
	Method 4	5005.0	5149.5	102.9				1020.0	1015.1	99.5
Sample C	Method 1	212.0	237.3	111.9	1018.0	1056.6	103.8	5005.0	5439.7	108.7
	Method 2	212.0	189.1	89.2	1018.0	1287.6	126.5	5005.0	4436.9	88.6
	Method 3	212.0	227.9	107.5	1018.0	1331.2	130.8	5005.0	4790.7	95.7
	Method 4	212.0	247.5	116.8	1018.0	1570.4	154.3	5005.0	5158.9	103.1
Sample D	Method 1				5005.0	5262.0	105.1	515.0	733.4	142.4
	Method 2				5005.0	4584.6	91.6	515.0	548.0	106.4
	Method 3				5005.0	5346.8	106.8	515.0	731.9	142.1
	Method 4				5005.0	5166.4	103.2	515.0	759.7	147.5
Sample E	Method 1	1057.0	1017.6	96.3	521.0	535.6	102.8			
	Method 2	1057.0	841.2	79.6	521.0	425.2	81.6			
	Method 3	1057.0	960.5	90.9	521.0	507.8	97.5			
	Method 4	1057.0	963.5	91.2	521.0	501.4	96.2			

As a comparison, results, in terms of assigned values and precision parameters, were also calculated using Part-5 of the standard ISO 5725 [10]. This part describes alternative methods for the determination of precision of a standard measurement method. In ISO 5725-2, Mandel's h and k statistics and Cochran's and Grubbs' tests are performed to identify statistical outliers and stragglers; then the statistician has to take decisions on which results discard and which not. Of course, these decisions will have an impact on the calculated standard mean values and standard deviations for repeatability and reproducibility. In addition, quite often results from a precision experiment are at the border between stragglers and statistical outliers. The robust method proposed in Part 5 allows elaborating data without the need to take decisions as no data are rejected. In fact, the method calculates results in a way that they are not influenced much by data of low quality.

As reported in Table 22, a good agreement was observed among results calculated with Parts 2 and 5 of ISO 5725. Generally, the differences were always lower than 35 %, except in few cases which are highlighted in yellow.

Table 22: Comparison of results calculated with Parts 2 and 5 of ISO 5725.

		Sample A - Method 1			Sample A - Method 2			Sample A - Method 3			Sample A - Method 4		
		ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %
DBP	mean (mg/kg)	713.3	708.5	-0.7	566.5	518.6	-8.5	736.7	747.9	1.5	804.4	767.0	-4.7
	R (mg/kg)	594.7	642.6	8.0	615.3	453.9	-26.2	565.8	565.4	-0.1	824.2	562.0	-31.8
	r (mg/kg)	71.2	51.6	-27.6	62.5	69.9	11.9	86.1	76.1	-11.5	54.1	54.0	-0.2
	RSDR	83.4%	90.7%		0.0%	87.5%		76.8%	75.6%		74.7%	73.3%	
	RSDr	10.0%	7.3%		0.0%	13.5%		11.7%	10.2%		7.4%	7.0%	
BBP	mean (mg/kg)	131.1	131.1	0.0	73.7	72.6	-1.6	129.0	129.0	0.0	183.4	190.0	3.6
	R (mg/kg)	132.4	149.3	12.8	75.0	77.3	3.0	144.8	163.9	13.2	177.1	215.2	21.5
	r (mg/kg)	19.7	17.9	-9.2	9.2	5.7	-38.1	12.4	12.4	0.4	14.9	17.2	15.2
	RSDR	101.0%	113.9%		101.7%	106.5%		112.3%	127.1%		96.5%	113.3%	
	RSDr	15.0%	13.6%		12.5%	7.9%		9.6%	9.7%		8.1%	9.0%	
DNOP	mean (mg/kg)	949.3	993.3	4.6	743.8	739.8	-0.5	853.8	838.4	-1.8	915.6	943.9	3.1
	R (mg/kg)	774.2	975.7	26.0	608.1	637.3	4.8	637.6	600.5	-5.8	598.1	586.1	-2.0
	r (mg/kg)	80.4	89.2	11.0	93.6	76.5	-18.3	79.7	75.6	-5.2	134.4	151.9	13.0
	RSDR	81.6%	98.2%		81.8%	86.1%		74.7%	71.6%		65.3%	62.1%	
	RSDr	8.5%	9.0%		12.6%	10.3%		9.3%	9.0%		14.7%	16.1%	
DIDP	mean (mg/kg)	459.8	444.8	-3.3	405.8	360.9	-11.1	440.6	430.4	-2.3	463.2	463.2	0.0
	R (mg/kg)	307.9	317.5	3.1	323.0	462.6	43.2	307.1	378.1	23.1	337.4	478.4	41.8
	r (mg/kg)	53.4	53.3	-0.1	63.0	55.7	-11.6	35.7	35.3	-1.2	75.0	56.0	-25.3
	RSDR	67.0%	71.4%		79.6%	128.2%		69.7%	87.8%		72.8%	103.3%	
	RSDr	11.6%	12.0%		15.5%	15.4%		8.1%	8.2%		16.2%	12.1%	
DIBP	mean (mg/kg)	3256.5	3394.2	4.2	2554.1	2585.2	1.2	3379.1	3376.4	-0.1	3632.3	3712.3	2.2
	R (mg/kg)	2104.0	2455.3	16.7	912.4	1301.5	42.6	1553.4	1580.6	1.8	1441.9	1783.1	23.7
	r (mg/kg)	353.5	308.3	-12.8	199.3	267.1	34.0	373.1	393.3	5.4	406.4	336.2	-17.3
	RSDR	64.6%	72.3%		35.7%	50.3%		46.0%	46.8%		39.7%	48.0%	
	RSDr	10.9%	9.1%		7.8%	10.3%		11.0%	11.6%		11.2%	9.1%	

		Sample B - Method 1			Sample B - Method 2			Sample B - Method 3			Sample B - Method 4		
		ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %
BBP	mean (mg/kg)	3788.2	3873.6	2.3	2590.9	2557.0	-1.3	4088.3	4035.6	-1.3	4620.8	4724.5	2.2
	R (mg/kg)	1517.1	1845.7	21.7	3086.9	2004.9	-35.1	2120.5	1587.6	-25.1	1457.2	1565.7	7.4
	r (mg/kg)	523.3	577.9	10.4	314.5	294.4	-6.4	440.9	306.6	-30.5	325.7	315.9	-3.0
	RSDR	40.1%	47.7%		119.1%	78.4%		51.9%	39.3%		31.5%	33.1%	
	RSDr	13.8%	14.9%		12.1%	11.5%		10.8%	7.6%		7.1%	6.7%	
DEHP	mean (mg/kg)	848.3	841.0	-0.9	795.8	786.6	-1.2	888.2	886.2	-0.2	982.8	1034.3	5.2
	R (mg/kg)	680.9	637.3	-6.4	762.1	830.2	8.9	846.8	946.1	11.7	907.1	1142.9	26.0
	r (mg/kg)	139.6	105.1	-24.7	104.4	85.1	-18.5	81.5	59.4	-27.1	90.1	76.0	-15.6
	RSDR	80.3%	75.8%		95.8%	105.5%		95.3%	106.8%		92.3%	110.5%	
	RSDr	16.5%	12.5%		13.1%	10.8%		9.2%	6.7%		9.2%	7.3%	
DNOP	mean (mg/kg)	4370.4	4278.3	-2.1	3562.4	3557.4	-0.1	4223.5	4198.4	-0.6	4574.3	4659.4	1.9
	R (mg/kg)	2101.1	1653.8	-21.3	1191.9	1248.5	4.8	2036.5	1801.1	-11.6	1575.1	1926.8	22.3
	r (mg/kg)	476.8	522.0	9.5	312.9	335.4	7.2	418.9	322.9	-22.9	620.8	701.5	13.0
	RSDR	48.1%	38.7%		33.5%	35.1%		48.2%	42.9%		34.4%	41.4%	
	RSDr	10.9%	12.2%		8.8%	9.4%		9.9%	7.7%		13.6%	15.1%	
DINP	mean (mg/kg)	937.0	925.5	-1.2	704.5	731.7	3.9	890.1	870.2	-2.2	901.7	943.6	4.6
	R (mg/kg)	840.4	598.0	-28.8	478.9	399.7	-16.5	571.5	441.4	-22.8	938.8	1112.8	18.5
	r (mg/kg)	197.9	158.8	-19.8	110.2	123.0	11.6	125.8	124.8	-0.8	125.8	96.2	-23.5
	RSDR	89.7%	64.6%		68.0%	54.6%		64.2%	50.7%		104.1%	117.9%	
	RSDr	21.1%	17.2%		15.7%	16.8%		14.1%	14.3%		14.0%	10.2%	
DIBP	mean (mg/kg)	120.7	126.7	5.0	100.6	102.5	1.9	135.8	138.2	1.8	116.1	128.3	10.6
	R (mg/kg)	108.1	135.3	25.1	92.6	91.2	-1.5	133.8	144.4	7.9	79.5	124.7	57.0
	r (mg/kg)	17.4	17.8	2.5	17.1	12.3	-28.1	22.4	20.0	-10.7	12.3	14.8	20.9
	RSDR	89.6%	106.7%		92.1%	89.0%		98.5%	104.5%		68.5%	97.2%	
	RSDr	14.4%	14.1%		17.0%	12.0%		16.5%	14.5%		10.6%	11.6%	

		Sample C - Method 1			Sample C - Method 2			Sample C - Method 3			Sample C - Method 4		
		ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %
DBP	mean (mg/kg)	133.9	135.8	1.5	112.8	108.6	-3.7	143.5	143.5	0.0	136.3	141.2	3.6
	R (mg/kg)	146.3	153.1	4.7	148.5	119.2	-19.7	158.6	179.2	13.0	170.2	181.2	6.4
	r (mg/kg)	14.9	13.9	-6.8	18.6	16.3	-12.4	18.7	11.5	-38.5	25.7	24.3	-5.8
	RSDR	109.3%	112.7%		131.6%	109.7%		110.6%	124.9%		124.9%	128.4%	
	RSDr	11.1%	10.2%		16.5%	15.0%		13.0%	8.0%		18.9%	17.2%	
DEHP	mean (mg/kg)	4028.0	3987.9	-1.0	3339.2	3385.2	1.4	3835.8	3920.4	2.2	4560.6	4731.1	3.7
	R (mg/kg)	3081.3	2559.0	-17.0	1866.6	1515.0	-18.8	2178.5	1790.9	-17.8	2775.0	3280.7	18.2
	r (mg/kg)	318.4	300.0	-5.8	670.0	398.1	-40.6	438.3	486.6	11.0	692.6	400.6	-42.2
	RSDR	76.5%	64.2%		55.9%	44.8%		56.8%	45.7%		60.9%	69.3%	
	RSDr	7.9%	7.5%		20.1%	11.8%		11.4%	12.4%		15.2%	8.5%	
DNOP	mean (mg/kg)	209.3	189.1	-9.6	166.8	149.3	-10.5	201.0	186.6	-7.2	218.3	236.6	8.4
	R (mg/kg)	326.9	226.4	-30.8	279.3	184.4	-34.0	309.3	199.7	-35.4	362.3	443.1	22.3
	r (mg/kg)	27.8	25.0	-10.2	28.1	24.5	-12.8	29.6	29.3	-1.0	51.3	51.4	0.3
	RSDR	156.2%	119.7%		167.4%	123.5%		153.9%	107.0%		165.9%	187.3%	
	RSDr	13.3%	13.2%		16.8%	16.4%		14.7%	15.7%		23.5%	21.7%	
DINP	mean (mg/kg)	4797.8	4893.9	2.0	3913.3	3876.6	-0.9	4225.4	4265.9	1.0	4550.1	4603.0	1.2
	R (mg/kg)	1765.0	2171.4	23.0	1783.3	1771.3	-0.7	820.7	1195.6	45.7	3919.0	3839.7	-2.0
	r (mg/kg)	533.9	497.5	-6.8	427.1	453.3	6.1	385.2	463.5	20.3	822.8	746.3	-9.3
	RSDR	36.8%	44.4%		45.6%	45.7%		19.4%	28.0%		86.1%	83.4%	
	RSDr	11.1%	10.2%		10.9%	11.7%		9.1%	10.9%		18.1%	16.2%	
DIDP	mean (mg/kg)	931.9	1137.6	22.1	1135.7	1255.0	10.5	1174.1	1245.0	6.0	1385.1	1505.1	8.7
	R (mg/kg)	364.6	1278.2	250.6	2149.1	2432.5	13.2	1563.5	1858.9	18.9	1636.5	1939.4	18.5
	r (mg/kg)	95.5	108.4	13.5	87.0	105.5	21.3	234.7	199.1	-15.1	211.7	181.8	-14.2
	RSDR	39.1%	112.4%		189.2%	193.8%		133.2%	149.3%		118.2%	128.9%	
	RSDr	10.3%	9.5%		7.7%	8.4%		20.0%	16.0%		15.3%	12.1%	

		Sample D - Method 1			Sample D - Method 2			Sample D - Method 3			Sample D - Method 4		
		ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %
DBP	mean (mg/kg)	3434.2	3380.6	-1.6	2702.2	2622.1	-3.0	3217.3	3306.2	2.8	3503.0	3686.0	5.2
	R (mg/kg)	2943.9	2976.6	1.1	2337.6	1610.9	-31.1	2437.6	2662.7	9.2	2989.1	3237.3	8.3
	r (mg/kg)	369.5	255.5	-30.9	251.5	209.8	-16.6	332.5	375.8	13.0	290.8	335.7	15.5
	RSDR	85.7%	88.1%		86.5%	61.4%		75.8%	80.5%		85.3%	87.8%	
	RSDr	10.8%	7.6%		9.3%	8.0%		10.3%	11.4%		8.3%	9.1%	
BBP	mean (mg/kg)	755.1	769.9	2.0	520.9	523.2	0.4	797.0	801.7	0.6	1113.9	1153.9	3.6
	R (mg/kg)	429.6	494.4	15.1	497.9	460.4	-7.5	375.4	379.6	1.1	1640.7	1763.8	7.5
	r (mg/kg)	54.5	58.4	7.3	65.2	46.5	-28.6	101.1	103.9	2.8	171.9	110.1	-36.0
	RSDR	56.9%	64.2%		95.6%	88.0%		47.1%	47.4%		147.3%	152.9%	
	RSDr	7.2%	7.6%		12.5%	8.9%		12.7%	13.0%		15.4%	9.5%	
DEHP	mean (mg/kg)	217.4	207.5	-4.5	172.8	167.0	-3.3	219.0	214.8	-2.0	242.5	267.1	10.1
	R (mg/kg)	199.9	229.1	14.6	210.1	199.8	-4.9	232.5	233.9	0.6	273.5	356.7	30.4
	r (mg/kg)	15.5	16.9	9.4	9.5	11.9	24.5	39.0	33.3	-14.6	10.5	20.0	90.1
	RSDR	92.0%	110.4%		121.6%	119.6%		106.2%	108.9%		112.8%	133.5%	
	RSDr	7.1%	8.2%		5.5%	7.1%		17.8%	15.5%		4.3%	7.5%	
DINP	mean (mg/kg)	642.7	660.4	2.8	480.2	503.4	4.8	641.3	648.1	1.1	665.7	702.6	5.5
	R (mg/kg)	323.0	396.8	22.8	349.6	402.2	15.0	546.3	590.1	8.0	776.0	934.0	20.4
	r (mg/kg)	110.6	109.2	-1.3	59.6	62.8	5.5	111.3	119.7	7.6	124.2	139.2	12.1
	RSDR	50.3%	60.1%		72.8%	79.9%		85.2%	91.0%		116.6%	132.9%	
	RSDr	17.2%	16.5%		12.4%	12.5%		17.4%	18.5%		18.7%	19.8%	
DIDP	mean (mg/kg)	4611.1	4606.9	-0.1	4017.5	3939.7	-1.9	4685.4	4674.8	-0.2	4527.3	4554.5	0.6
	R (mg/kg)	2004.9	1774.3	-8.0	1596.3	1912.9	19.8	2431.3	3346.0	37.6	5007.4	6942.9	38.7
	r (mg/kg)	647.8	618.4	-7.1	451.4	400.7	-11.2	624.2	651.3	4.3	497.3	410.3	-17.5
	RSDR	43.5%	38.5%		39.7%	48.6%		51.9%	71.6%		110.6%	152.4%	
	RSDr	14.1%	13.4%		11.2%	10.2%		13.3%	13.9%		11.0%	9.0%	
DIBP	mean (mg/kg)	579.7	579.7	0.0	535.4	505.6	-5.6	642.7	642.7	0.0	635.8	693.8	9.1
	R (mg/kg)	433.8	487.8	12.4	702.4	545.6	-22.3	533.5	602.7	13.0	331.0	470.5	42.1
	r (mg/kg)	76.3	53.2	-30.3	61.8	55.2	-10.7	70.9	70.9	0.0	19.0	56.9	200.2
	RSDR	74.8%	84.1%		131.2%	107.9%		83.0%	93.8%		52.1%	67.8%	
	RSDr	13.2%	9.2%		11.5%	10.9%		11.0%	11.0%		3.0%	8.2%	

		Sample E - Method 1			Sample E - Method 2			Sample E - Method 3			Sample E - Method 4		
		ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %	ISO 5725 Part 2	ISO 5725 Part 5	Δ %
DBP	mean (mg/kg)	776.2	776.6	0.1	605.9	581.8	-4.0	787.8	818.6	3.9	803.0	876.7	9.2
	R (mg/kg)	534.8	601.3	12.4	529.4	411.9	-22.2	607.3	657.7	8.3	640.9	760.4	18.6
	r (mg/kg)	74.5	66.8	-10.3	56.7	49.4	-12.8	78.7	88.0	11.9	54.5	57.9	6.2
	RSDR	68.9%	77.4%		87.4%	70.8%		77.1%	80.3%		79.8%	86.7%	
	RSDr	9.6%	8.6%		9.4%	8.5%		10.0%	10.8%		6.8%	6.6%	
BBP	mean (mg/kg)	147.7	145.1	-1.8	77.8	85.8	10.2	155.7	150.3	-3.5	194.2	205.1	5.6
	R (mg/kg)	156.9	172.7	10.0	71.0	96.0	35.1	203.0	192.0	-5.4	175.5	212.3	21.0
	r (mg/kg)	14.5	11.4	-21.2	6.2	7.7	24.5	26.3	21.5	-18.3	17.7	18.1	1.8
	RSDR	106.2%	119.0%		91.3%	111.9%		130.4%	127.8%		90.4%	103.5%	
	RSDr	9.8%	7.9%		7.9%	9.0%		16.9%	14.3%		9.1%	8.8%	
DNOP	mean (mg/kg)	1017.6	986.3	-3.1	841.2	827.5	-1.6	960.5	958.7	-0.2	963.5	1004.2	4.2
	R (mg/kg)	532.1	430.8	-19.0	653.0	663.4	1.6	606.0	562.4	-7.2	661.9	780.2	17.9
	r (mg/kg)	89.7	90.8	1.2	52.2	57.6	10.2	106.0	111.7	5.4	185.1	184.2	-0.5
	RSDR	52.3%	43.7%		77.6%	80.2%		63.1%	58.7%		68.7%	77.7%	
	RSDr	8.8%	9.2%		6.2%	7.0%		11.0%	11.7%		19.2%	18.3%	
DIDP	mean (mg/kg)	535.6	510.5	-4.7	425.2	405.3	-4.7	507.8	484.3	-4.6	501.4	514.6	2.6
	R (mg/kg)	385.8	278.9	-27.7	310.6	354.3	14.1	367.1	433.2	18.0	400.7	569.2	42.0
	r (mg/kg)	79.2	72.1	-9.0	90.5	59.6	-34.1	52.9	48.9	-7.5	81.2	89.5	10.2
	RSDR	72.0%	54.6%		73.0%	87.4%		72.3%	89.4%		79.9%	110.6%	
	RSDr	14.8%	14.1%		21.3%	14.7%		10.4%	10.1%		16.2%	17.4%	
DIBP	mean (mg/kg)	3758.0	3752.7	-0.1	2428.2	2542.0	4.7	3534.8	3551.6	0.5	4158.9	4269.7	2.7
	R (mg/kg)	2823.0	3127.4	10.8	1190.5	1372.0	15.2	2235.2	2411.8	7.9	1968.6	2464.0	25.2
	r (mg/kg)	424.7	344.9	-18.8	155.2	178.1	14.8	430.7	407.8	-5.3	382.0	359.6	-5.9
	RSDR	75.1%	83.3%		49.0%	54.0%		63.2%	67.9%		47.3%	57.7%	
	RSDr	11.3%	9.2%		6.4%	7.0%		12.2%	11.5%		9.2%	8.4%	

Considering now method 5, Table 23 reports the summary of results of the collaborative trial. In this case, no statistical outliers were identified among the 12 reporting laboratories and all collected results were used for the calculations. As previously mentioned calculations were performed at first on a clean, dry mass basis and then corrected with adjustment by agreed allowances *a* (8.5 for cotton and zero for PVC). The *d* correction factor used for cotton was 1.00.

This method showed good precision both in terms of repeatability and reproducibility (0.6 and 1.4 % for RSD_r and RSD_R respectively) and can be considered validated. As a comparison, it has to be considered that similar dissolution methods, validated in the field of the quantification of textile binary mixtures, show relative standard deviations for reproducibility ranging from 1 to 2 %.

Table 23: Results of the collaborative trial for method 5.

		outlier	PVC %	r %	RSDr %	R %	RSDR %
Sample F	Method 5	0	88.2	0.5	0.6	1.2	1.4

Finally, even though the collaborative trial was not a proficiency test aimed to establish laboratory performances, the performances of the participating laboratories

were evaluated in terms of z-scores according to ISO 13528 [11] and the International Harmonised Protocol [4]. The z-scores compared the participants' deviation from the assigned value with the standard deviation obtained from the precision experiment. The usual interpretation of z-scores considers values above 3.0 or below -3.0 as unsatisfactory and above 2.0 or below -2.0 as questionable. The z-scores per laboratory, sample, phthalate and method are shown in Table 24, whereas the graphical presentation is reported in Annex X. In both cases, the absolute values are highlighted in red when higher than 3 and in yellow if higher than 2 but lower than 3.

Considering all data including outliers, the best performance was showed by LC0003 and LC0008; in fact, the z-scores for both of them were in the large majority of cases good ($|z| < 1$) and, in the others, at least satisfactory ($|z| < 2$). The worst performance was obtained by LC0004 and LC0005, who showed 25 and 17 z-scores considered questionable or unsatisfactory. This evidence confirmed once again that there were sufficient reasons to reject the results of LC0004 for method 4 and the ones of LC0005 for DIDP.

When data proved to be outliers are not taken into consideration, method 4 showed 19 questionable or unsatisfactory z-scores, corresponding to 6.2 % of all z-scores. Methods 2 follows immediately with 5.9 % of z-scores considered questionable or unsatisfactory. Both method 1 and 3 showed 3.7 % of z-scores higher than 2.

Table 24: z-scores per laboratory, sample, phthalate and method.

	LC0000	LC0001	LC0002	LC0003	LC0004	LC0005	LC0006	LC0007	LC0008	LC0009	LC0010	LC0011	LC0012
A-M1/DBP	0,25	0,33	-1,50	-0,28	0,20	-1,54	0,40	1,89	0,45	-0,63	1,46	-0,54	-0,49
A-M1/BBP	1,41	-0,25	-0,52	-0,51	0,64	-0,11	1,63	-1,41	-0,08	0,59	-1,59	-0,71	0,90
A-M1/DNOP	-0,59	1,38	-1,51	-0,41	-0,14	0,08	3,87 C**	1,47	0,11	-0,34	1,60	-0,76	-0,88
A-M1/DIDP	-0,41	0,46	0,32 C**	-0,83	-0,25	-4,13	0,11	0,84	0,53	-0,51	1,99	-1,86	-0,07
A-M1/DIBP	4,66 C**	0,65	-0,46	0,36	0,30	-1,79	1,56	0,85	0,63	-0,06	-0,24	-0,03	-1,77
B-M1/BBP	7,28 G**	0,74	-1,72	0,23	0,45	-1,43	0,77	-0,34	1,67	0,17	-0,38	0,49	-0,66
B-M1/DEHP	-0,22	0,10	-0,66	0,42	-0,13	0,35	-1,76	2,08	0,35	-0,60	1,37	-0,34	-0,96
B-M1/DNOP	2,33	0,76	-1,58	-0,06	-0,59 C**	-0,59	-0,19	0,29	-0,38	-0,11	0,43	0,22	-1,13
B-M1/DINP	-0,41	0,20	0,36	-0,31	-0,61	-1,96	-0,03	-0,46	-0,48	2,24	0,34	-0,03	1,16
B-M1/DIBP	0,38	0,22	-0,92	-0,15	0,42	-1,52	1,13	1,92	0,62	-0,54	2,00 C**	-1,23	-0,33
C-M1/DBP	0,43	0,71	-2,01	-0,28	0,23	-1,47	0,46	0,90	0,56	-0,39	1,33	-1,11	0,62
C-M1/DEHP	2,26	0,24	-1,10	0,26	0,11	-0,66	-1,86	0,72	0,41	-0,06	0,23	0,30	-0,85
C-M1/DNOP	-0,45	0,27	-1,28	-0,37	-0,28	-0,55	0,23	1,59	-0,26	-0,22	2,43	-0,94	-0,17
C-M1/DINP	1,03	-0,03	-1,19	-0,28	0,00	-0,89	-0,88	0,44	-1,15	5,15 G**	0,80	2,00	0,16
C-M1/DIDP	-0,19	1,29	0,38	0,57	1,26	31,42 G**	-0,59	9,91 G**	-0,79	-0,66	8,86 C**	0,52	-1,78
D-M1/DBP	2,10	1,49	-1,54	0,14	0,00	-1,46	0,23	-0,04	0,27	-0,24	0,07	-0,35	-0,67
D-M1/BBP	1,28	1,80	-1,46	-0,63	0,20	0,02	1,24 C**	0,41	0,50	0,07	0,22	-1,35	-1,07
D-M1/DEHP	0,23	-0,40	-1,53 C**	0,20	0,01	-0,17	-1,43	1,77	0,44	-0,62	1,64	-1,49	-0,18
D-M1/DINP	0,09	-0,84	1,31	-0,37	-0,04	0,24	-1,22	-1,10	-0,49	5,58 G**	-0,38	1,89	0,91
D-M1/DIDP	1,86	0,62	0,80	0,59	0,47	0,02	-0,47	-0,15	-1,05	-0,78	0,13	-0,24	-1,77
D-M1/DIBP	0,42	1,12	-1,04	0,21	0,45	-1,32	0,16	0,77	0,71	-0,47	1,58	-1,13	-1,46
E-M1/DBP	0,25	0,90	-1,71	0,07	0,21	-1,43	0,55	1,11	0,71	-0,68	1,53	-0,79	-0,71
E-M1/BBP	1,30	0,04	-0,61 C**	-0,39	0,58	0,03	1,49	-1,58	-0,15	0,48	-1,64	-0,81	0,65
E-M1/DNOP	-0,84	-0,11	-0,94 C**	-0,03	-0,08	0,57	-0,06	0,63	0,29	-0,25	2,42	-0,97	-1,46
E-M1/DIDP	-0,13	0,34	-0,40	-0,34	0,11	-3,84	0,01	2,51	0,07	-0,57	0,58	-1,78	-0,41
E-M1/DIBP	1,75	1,34	-0,90	0,53	-0,03	-1,33	0,80	-0,36	0,50	-0,12	0,00	-0,48	-1,69

	LC0000	LC0001	LC0002	LC0003	LC0004	LC0005	LC0006	LC0007	LC0008	LC0009	LC0010	LC0011	LC0012
A-M2/DBP	-0,17	-0,26	-0,92	-0,80	-0,91 C**	-1,14	-0,07	2,52	-0,09	-0,19	1,15	-0,43	0,38
A-M2/BBP	1,01	-0,64	-0,50	-0,81	-0,81	-0,45	2,05	-0,81	-0,03	0,39	-1,33	1,04	0,89
A-M2/DNOP	-0,44	1,30	-1,14	-0,97	-0,04 C**	-0,96	-0,37	1,67	-0,26	0,07	1,62	-0,34	-0,18
A-M2/DIDP	-1,05	0,10	0,19	-0,86	-2,33 C**	-3,48	-0,14	1,33	-0,38	-0,56	1,91	0,67	-1,23
A-M2/DIBP	-0,89	5,51 G**	1,04 C**	-1,25	-3,21 C**	-1,58	0,15	0,03	0,26	0,18	1,12	0,48	1,50
B-M2/BBP	0,35	2,15	0,31	-0,42	-0,27 C**	-0,77	0,55	-0,43	0,20	-0,03	-0,38	0,55	-2,09
B-M2/DEHP	0,14	1,48	-0,99	-0,43	-0,43 C**	-1,40	-1,49	1,23	-0,01	-0,05	1,01	0,82	-0,31
B-M2/DNOP	-0,75	0,27	-1,70	-0,74	-0,25 C**	-0,93	-0,50	-0,28	0,91	1,13	0,77	1,58	0,25
B-M2/DINP	-0,59	0,36	-0,09	-0,38	-0,57	-2,31	0,40	0,11	0,71	0,68	1,78	1,20 C**	-0,09
B-M2/DIBP	0,31	-0,10	-0,7 C**	-0,69	-1,21	-2,17	0,92	1,50	0,52	0,23	0,91	-0,04	0,51
C-M2/DBP	0,19	-0,27	-0,60	-0,54	-0,69	-1,62	-0,07	2,47	0,16	0,24	1,08	-0,73	0,37
C-M2/DEHP	-0,30	-0,65	0,22	0,25	-0,57	-0,57	-2,32	-0,10	0,39	0,78	0,29	1,01	1,57
C-M2/DNOP	-0,22	0,00	-0,76	-0,45	-0,76	-1,35	-0,16	1,87	-0,10	0,15	2,20	-0,55	0,11
C-M2/DINP	-1,29	0,01	0,20	-0,37 C**	-0,71	-1,60	-0,52	0,32	-0,07	0,13	1,86	1,36	0,33
C-M2/DIDP	-0,57	-0,38	0,03	-0,44	-0,51	2,59	-0,51	2,20	-0,38	-0,48	1,76	0,50	-0,71
D-M2/DBP	0,11	2,64	-0,83	-0,46	-0,90	-1,60	0,02	0,49	0,08	0,08	-0,13	-0,12	0,61
D-M2/BBP	0,09	1,90	0,08	-1,02	-0,92	-2,04	0,88	0,86	-0,34	-0,35	0,27	0,63	-0,05
D-M2/DEHP	0,78	-0,34	-0,94	-0,31	-0,49 C**	-1,54	-0,88	1,85	-0,04 C**	0,13	1,19	-0,34	0,41
D-M2/DINP	-0,40	0,80	1,69 C**	-0,29	-0,82	-2,02	-0,41	-0,80	0,67	0,89	0,30	4,00 C**	0,39
D-M2/DIDP	-1,08	0,69	1,11	-0,14	0,24	-4,43	-0,09	1,20	-0,18	-0,92	0,66	0,60	-2,08
D-M2/DIBP	-0,10	0,88	-0,45	-0,57	-0,98	-1,36	-0,62	0,62	-0,09	-0,03	0,04	0,00	2,65
E-M2/DBP	0,06	0,63	-0,25	-0,90	-0,86	-1,28	-0,13	2,68	-0,05	-0,16	0,14	-0,65	0,78
E-M2/BBP	1,60	-0,18	1,69	-0,87	-0,04	-0,18	2,92 C**	-1,32	0,32	0,53	-1,66	0,75	1,06
E-M2/DNOP	-0,59	1,44	-0,60	-1,19	-0,26	-1,09	-0,33	1,26	-0,36	0,00	1,89	-0,45	-0,04
E-M2/DIDP	-1,04	-0,23	0,19	-1,17	-0,48	-3,79	0,17	1,35	-0,15	-0,51	1,95	0,87	-0,95
E-M2/DIBP	0,52	7,35 C**	0,97 C**	-0,16	-1,74	-0,84	0,65	0,68	0,81	1,02	0,01	0,70	-1,66

	LC0000	LC0001	LC0002	LC0003	LC0004	LC0005	LC0006	LC0007	LC0008	LC0009	LC0010	LC0011	LC0012
A-M3/DBP	0,33	0,65	-2,13	-0,15	-0,35	-0,83	0,87	1,26	0,37	-0,14	0,92	-1,46	0,65
A-M3/BBP	1,03	-0,21	-1,32	0,13	0,22	0,41	1,66	-1,56	-0,25	0,90	-1,56	-0,03	0,59
A-M3/DNOP	0,15	1,93	-1,19	-0,49	-0,34	0,17	0,11	-0,58	0,49	-0,13	1,75	-1,60	-0,28
A-M3/DIDP	-0,59	0,91	-0,45	-1,07	0,75 C**	-3,97	0,32	0,92	0,61	0,08	1,59	-1,80	-0,52
A-M3/DIBP	-0,07	0,57	-1,79	0,67	-0,74	-0,59	1,85	0,06	0,77	-0,15	0,05	-1,41	0,79
B-M3/BBP	0,67	2,46	-1,70	0,19	-0,33	0,09	0,20	-0,93	0,78	-0,40	-0,10	-0,50	-0,44
B-M3/DEHP	-0,54	0,40	-0,51	-0,22	-0,58	1,75	-1,53	1,63	0,03	-0,27	1,28	-0,81	-0,63
B-M3/DNOP	0,22	2,17	-1,79	-0,10	-0,42	1,17	-0,38	-0,50	0,23	0,82	-0,05	-0,90	-0,46
B-M3/DINP	-0,74	2,50	0,29	-0,99	0,20 C**	-1,17	0,12	-0,25	-0,20	-0,31	0,54	-0,56	0,78
B-M3/DIBP	0,15	0,99	-1,17 C**	0,37	0,55 C**	-1,19	0,69	0,99	0,13	-0,81	1,42	-1,65	0,08
C-M3/DBP	0,55	1,06	-1,61	-0,12	-0,24	-1,50	0,21	1,39	0,32	0,01	0,78	-1,54	0,67
C-M3/DEHP	1,27	0,13 C**	-0,71	0,59	-0,84	0,55	-2,38	0,43	0,60	0,04	0,02	-0,46	0,90
C-M3/DNOP	-0,21	0,49	-0,65 C**	-0,44	-0,14 C**	-0,67	-0,11	0,85	-0,17	-0,26	2,63	-1,36	-0,12
C-M3/DINP	0,11	-1,42	-0,69	-0,10	1,51 C**	0,44	1,30	-0,15	-0,24	-0,84	1,58	-4,21 C**	7,45 G**
C-M3/DIDP	-0,58	0,16	-0,12	-0,82	0,14	5,74 G**	-0,56	1,82	-0,60	-0,51	2,18	-0,29	-0,83
D-M3/DBP	1,07 C**	0,83	-1,78	0,37	-0,28	-1,12	0,77	-0,33	0,61	0,26	0,25	-1,24	1,67
D-M3/BBP	0,21 C**	1,61	-2,00	-0,43	-0,61	0,84	1,35	-0,20	0,54	-0,21	-0,38	-1,04	0,32
D-M3/DEHP	0,05	-0,96	-0,31	-0,32	-0,24	1,28	-1,19	2,12	0,23	-0,17	0,81	-1,52	0,21
D-M3/DINP	-0,52	1,70	1,35	-0,87	0,51 C**	-0,54	-0,48	-1,27	-0,20	-0,09	-0,79	0,26	1,43
D-M3/DIDP	-0,70	1,16	0,87	-0,44	1,91 C**	-3,49	-0,35	1,67	-1,09	-0,65	0,92	-1,16	-0,22
D-M3/DIBP	0,64	0,86	-1,55	0,36	-0,43	-0,97	0,11	1,48	0,27	-0,69	0,55	-1,69	1,06
E-M3/DBP	0,82	0,79	-1,82	0,11	-0,26	-1,08	0,53	1,35	0,54	0,07	0,99	-1,62	0,92
E-M3/BBP	0,53	-0,25	-0,96	-0,03	0,17	0,34	1,12	-1,41	-0,29	2,30	-1,30	-0,35	0,13
E-M3/DNOP	-0,03	1,52	-0,84	-0,60	-0,33	0,42	0,07	-0,18	0,73	-0,25	1,88	-1,93	-0,47
E-M3/DIDP	-0,57	0,85	0,15	-1,01	1,95	-3,83	0,10	-0,40	0,54	-0,24	0,99	-1,76	-0,59
E-M3/DIBP	0,63	0,75	-1,86	0,86	-0,60	-1,01	1,51	-0,32 C**	0,90	0,37	-0,01	-1,35	0,11

	LC0000	LC0001	LC0002	LC0003	LC0004	LC0005	LC0006	LC0007	LC0008	LC0009	LC0010	LC0011	LC0012
A-M4/DBP	-0,77	0,59	-0,34	-0,62	3,99 G**	0,43	1,15	0,94	-0,36	-0,68 C**	0,56	-2,27	0,70
A-M4/BBP	-0,01	-1,50	0,54	-0,75	3,49	1,66	0,33	0,44	-0,64 C**	0,06	0,77	-1,77	0,23
A-M4/DNOP	-0,80	-0,17	2,12	-0,53	6,81 G**	0,27	0,02	-0,27	-0,05	0,13	1,03	-1,98	0,23
A-M4/DIDP	-0,58	0,90	1,28 C**	0,25	3,66 C**	-3,80	-0,16	-0,84	-0,14	-0,45	-1,09	-1,07	1,88
A-M4/DIBP	-0,03	0,28	-0,99	-0,57	9,41 G**	0,12	1,33	-0,48	0,33	-0,98	1,60	-1,57	0,96
B-M4/BBP	-0,42	0,26	0,30	-0,95	11,73 C**	1,15	-0,22	0,78	-0,06	-0,61	1,44	-2,17	0,50
B-M4/DEHP	-0,52	-0,41	1,97	-0,49	4,36 G**	1,69	-1,27	0,51	-0,23	-0,45	0,21	-1,16	0,15
B-M4/DNOP	-1,18	-0,40	1,10	-0,85	13,62 G**	-0,27	-0,21	-0,64	-0,77	-0,42	0,81	1,87	0,96
B-M4/DINP	-0,72	0,79	2,19	-0,05	4,82 G**	-1,39	-0,07	-1,33	-0,04	0,03	-0,37	-0,05	1,02
B-M4/DIBP	0,16	0,41	-0,80	-0,18	8,26 G**	-0,52	-0,81	1,45	1,08	-0,45	7,00 C**	-1,67	1,34
C-M4/DBP	-0,34	-0,17	-0,37	-0,54	3,15	-0,30	-0,68	2,37	-0,03	0,05	1,20	-1,58	0,40
C-M4/DEHP	-0,59	1,52	0,65	-0,67	6,59 G**	1,76	-1,87	-0,27	-0,24	-0,52	0,02	0,19	0,02
C-M4/DNOP	-0,57	-1,14	1,95 C**	-0,69	1,82 C**	-0,41	0,64	0,96	-0,36	-0,14	1,31	-1,22	-0,33
C-M4/DINP	-0,64	0,91	0,41	-0,53	6,23 G**	-1,37	-0,14	-0,76	-0,39	-0,16	-0,04	2,51	0,21
C-M4/DIDP	-0,80	-0,21	0,38 C**	-0,69	1,66	0,98	-0,94	0,55	-0,96	-0,91	1,95	1,33	0,30
D-M4/DBP	-2,00	1,45	-0,13	-0,06 C**	2,83 C**	0,19	0,24	1,17	-0,27	-0,09	0,44	-1,41	0,34
D-M4/BBP	-0,45	-0,82	0,19	-0,64	1,48	0,16	-0,22	1,80	-0,43	-0,33	2,17	-1,09	-0,32
D-M4/DEHP	-0,18	-0,35	1,86	-0,58	3,63	1,99	-0,86	0,75	0,05	-0,47	0,26	-1,51	0,09
D-M4/DINP	-0,35	0,58	2,15	-0,34	3,87 C**	-1,16	-0,57	-1,28	0,11	0,48	-0,92	0,22	1,09
D-M4/DIDP	-1,98	0,96	0,51	-0,10	4,67 C**	-1,90	-0,16	-0,97	-0,26	-0,30	0,03	1,89	0,38
D-M4/DIBP	10,14 C**	1,45 C**	-0,76 C**	-0,44	7,94 C**	0,13	0,00 C**	0,73	0,64	-0,54	0,44	-2,05	1,08
E-M4/DBP	-0,67	1,46 C**	-0,14	-0,71	4,01 G**	0,83	0,34	1,58	-0,26	-0,48	0,83	-2,04	0,73
E-M4/BBP	0,17	-1,24	0,86	-1,12	4,18 G**	1,81	0,52	0,31	-0,10	0,13	0,22	-1,88	0,30
E-M4/DNOP	-0,58	-0,20	1,91	-1,17	7,25 G**	0,19	0,27	-0,38	0,02	0,31	0,91	-1,88	0,59
E-M4/DIDP	-0,29	1,53	1,00	-0,57	4,77 G**	-3,46	-0,11	-0,71	0,08	-0,35	-0,96	-0,64	2,01
E-M4/DIBP	-0,86	2,02	-0,85	-0,74	7,44 G**	-0,12	0,61	1,33	0,10	-0,58	-0,05	-1,36	0,50

	LC0000	LC0001	LC0002	LC0003	LC0004	LC0005	LC0006	LC0007	LC0008	LC0009	LC0010	LC0011
F-M5/ % PVC	-1.09	-0.37	-0.33	0.28	-0.17	2.22	-1	1.11	-0.42	0.57	0.02	-0.82

Table 25: z-scores per laboratory and method.

	|z| > 3	2 < |z| > 3	|z| > 2
LC0000	3	3	6
LC0001	2	6	8
LC0002	0	5	5
LC0003	0	0	0
LC0004	23	2	25
LC0005	12	5	17
LC0006	1	4	5
LC0007	1	8	9
LC0008	0	0	0
LC0009	2	2	4
LC0010	2	7	9
LC0011	2	5	7
LC0012	1	4	5
M 1	10	10	20
M 2	7	19	26
M 3	6	9	15
M 4	26	13	39
M 5	0	1	1

6 Conclusions

A collaborative study was organised by the JRC on behalf of CEN/TC 248/WG 26 and ISO/TC 38/WG 22. The aim was the comparison and validation of four methods for the determination of phthalates (based on n-hexane/acetone 80/20 v/v, n-hexane, tert-butyl methyl ether and tetrahydrofuran, respectively) and one method for the quantification of PVC in textile products.

ISO 5725-2 was followed to organise a balanced uniform-level experiment. Seven phthalates (DEHP, DBP, BBP, DINP, DIDP, DNOP and DIBP) had to be determined in three levels of concentration (200 or 500, 1000 and 5000 mg/kg of PVC) in five samples (A-E). In addition, the PVC mass per cent had to be measured on another sample (F). All specimens were produced by the Italian company MP S.p.A. The JRC carried out the homogeneity assessment and proved that all samples could be considered 'sufficiently homogeneous' according to the IUPAC harmonised protocol for proficiency testing.

Thirteen laboratories, out of eighteen participants, did report results. The Shapiro-Wilk test showed that, out of the 104 data sets, 47 could be considered as being part of a normal distribution at 95 % probability level after the elimination of outliers. As not all data set were normally distributed, both ISO 5725 parts 2 and 5 were used to statistically evaluate the test results. These two alternative approaches gave results that could be considered in good agreement and are reported in Table 22. Generally, the differences were always lower than 35 %, except in few cases.

Considering phthalates, results proved that both the four methods and the laboratories' performance have to be drastically improved. In fact, the relative standard deviations of repeatability and reproducibility ranged from 3.0 to 23.5 % and from 19.4 and 189.9 % respectively. Poor repeatability was observed in the case of several laboratories and the large spread in the mean values calculated in the 13 laboratories is responsible for the high observed relative standard deviation of reproducibility. Method 4 (tetrahydrofuran) proved to be the best one in terms of phthalates' recovery, whereas method 2 was the worst one. Practically the same extraction efficiency was shown by methods 1 and 3.

Method 5 for the quantification of PVC showed good precision and can be considered validated, the repeatability and reproducibility relative standard deviations being 0.6 and 1.4 % respectively. These values are in line with the ones obtained in the case of similar dissolution methods validated in the context of quantification of fibre binary mixtures.

Even though the collaborative trial was not a proficiency test, the performances of the participating laboratories were evaluated without eliminating the outliers. The best performance was showed by laboratories LC0003 and LC0008; in fact, the z-scores of both of them were in the large majority of cases good ($|z| < 1$) and, in the others, at least satisfactory ($|z| < 2$). The worst performance was obtained by laboratories LC0004 and LC0005, who showed 25 and 17 z-scores considered questionable or unsatisfactory out of 104. Considering the methods, after the elimination of outliers, method 4 showed 6.2 % of questionable or unsatisfactory z-scores. Methods 2, 1 and 3 followed with 5.9, 3.7 and 3.7 % respectively.

7 Acknowledgments

The authors would like to thank MP S.p.A. (Poggio a Caiano Prato, Italy) for providing the samples and the following laboratories, members of CEN/TC 248/WG 26 or ISO/TC 38/WG 22, for their participation in the collaborative study:

Switzerland – UL-SSTR Testing & Inspection AG; China – CTTC China National Textiles Supervision Testing Center; China – Technical Centre of Jilin Entry-Exit Inspection and Quarantine Bureau (JLCIQ); Germany – Bureau veritas CPS Germany; France - CTC; Italy – ICQ Division of Italian Institute for Toy Safety; Italy – Centro Tessile Cotoniero e Abbigliamento S.p.A; Japan - Japan Textile Products Quality and Technology Center; Japan - KE'KEN Textile Testing & Certification Center; The Netherlands- Food and Consumer Product Safety Authority Region North; Sweden- Swerea IVF; United Kingdom - Shirley Technologies Ltd.

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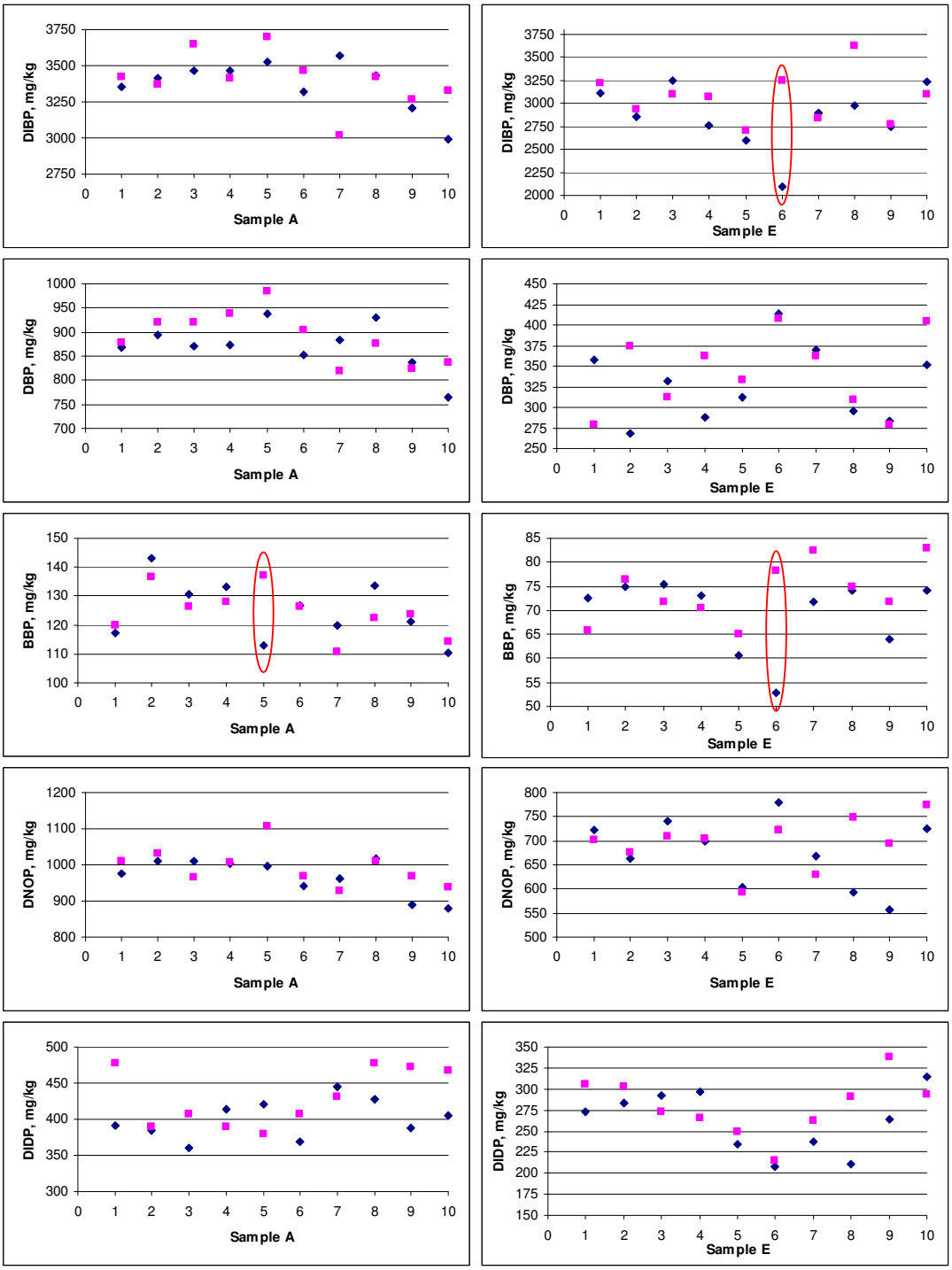
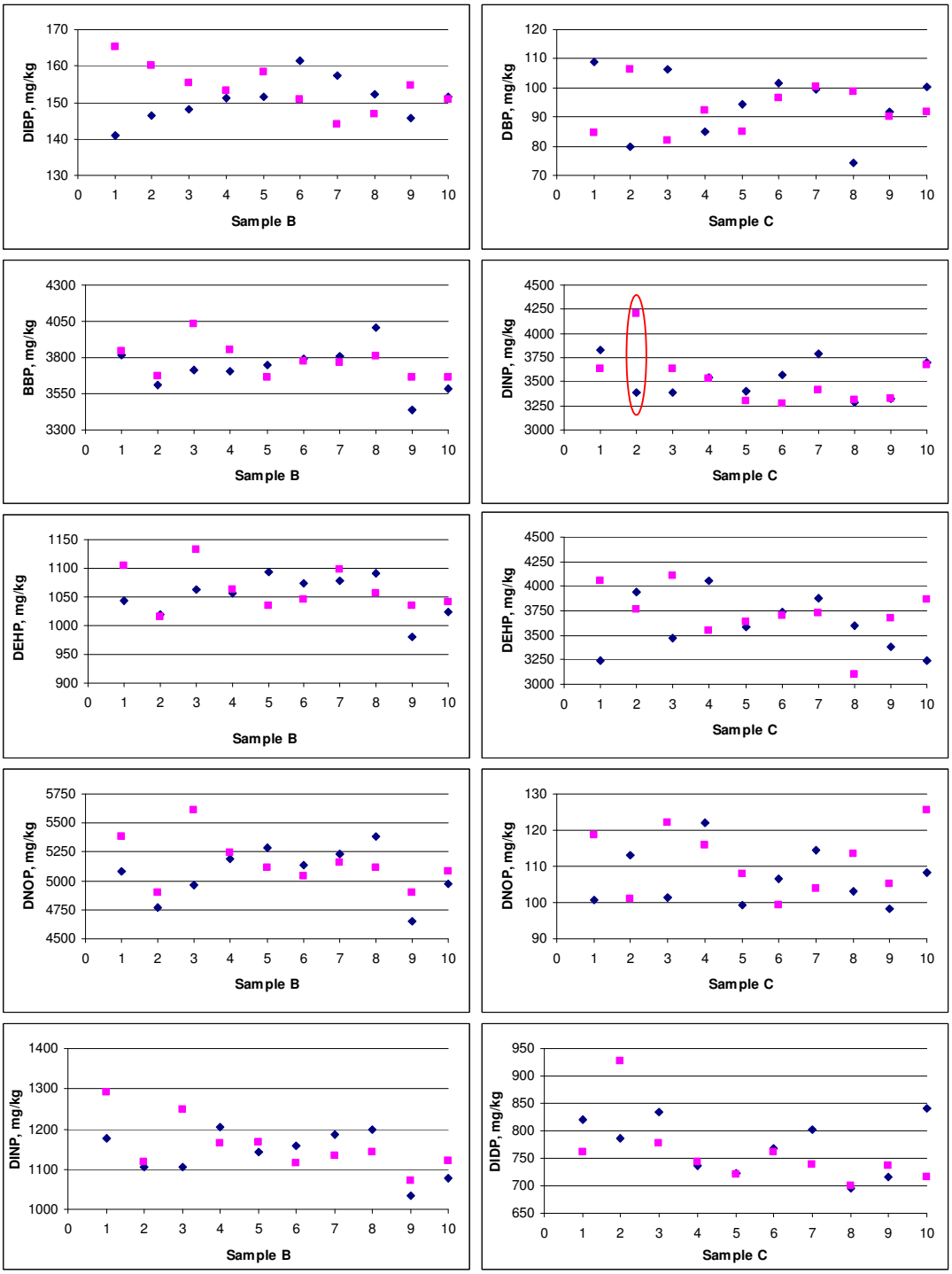
ANNEX I

Homogeneity

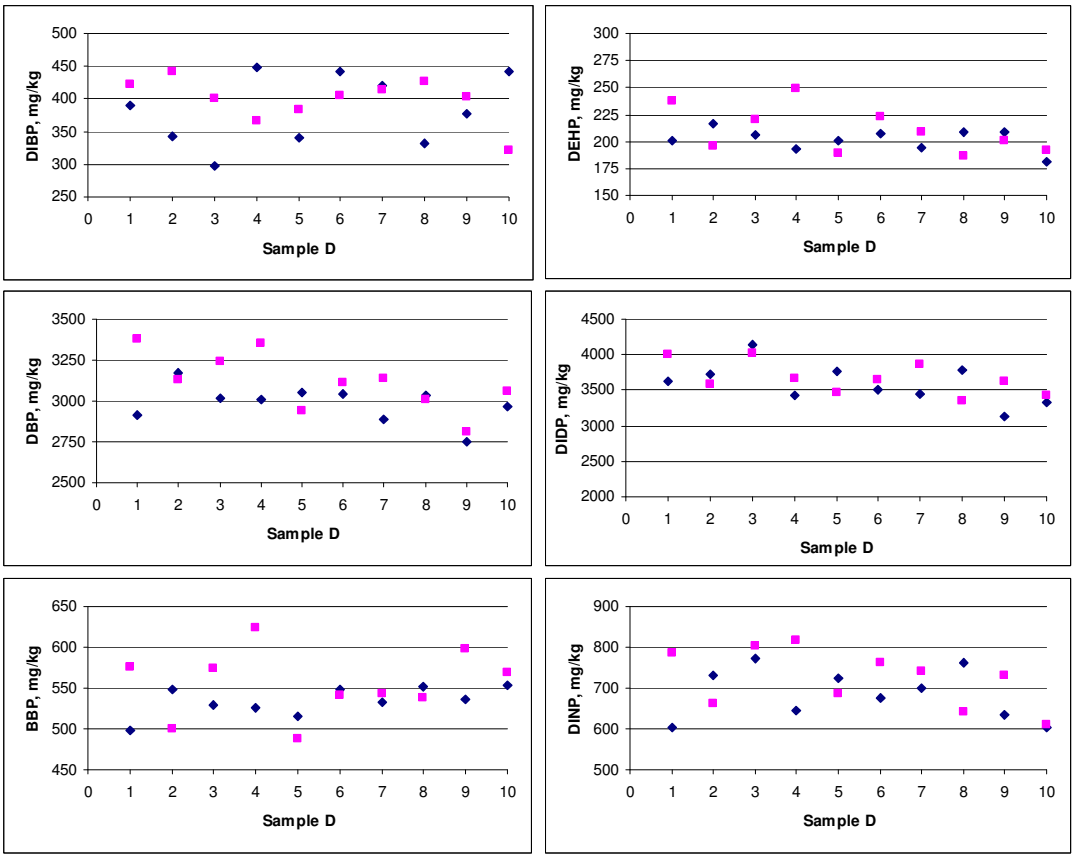
Graphic presentation of the homogeneity study carried out on samples A-E according to method 2.



Graphic presentation of the homogeneity study carried out on samples B-C according to method 2.



Graphic presentation of the homogeneity study carried out on sample D according to method 2.



ANNEX II

Invitation letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Health and Consumer Protection
Chemical Assessment and Testing Unit

Ispra, 20th September 2011

Dear Expert,

As agreed during last joint meeting of CEN/TC 248/WG 26 and ISO/TC 38/WG 22 in Paris on 6th April 2011, the JRC is organising a collaborative trial to validate the method for the quantification of phthalates in textiles (DIBP, DBP, BBP, DEHP, DNOP, DIDP, DINP).

Four different methods will be tested:

1. the first is based on ultrasonic extraction with n-hexane/acetone 80/20 (similar to ISO/TS 16181 developed for footwear materials);
2. the second uses ultrasonic extraction with methyl tert-butyl ether (German proposal)
3. the third is based on ultrasonic extraction with n-hexane (Chinese proposal)
4. the forth dissolves pvc with tetrahydrofuran in a ultrasonic generator and then re-precipitate it with acetonitrile (German/Dutch proposal).

Five samples will be distributed and must be analysed in triplicate with each method. In total 60 specimens will have to be tested*. For each method and sample, the replicates should be analysed by the same operator, under the same conditions and at the same time (repeatability conditions).

As agreed, four independent calibration curves, with 6 points each, must be prepared with the same solvents used in the four different methods.

Finally, one sample must be tested in triplicate to evaluate the mass percentage of the textile and pvc part.

Each participant will receive specimens by carrier and will have to analyse them at the latest by the end of October 2011.

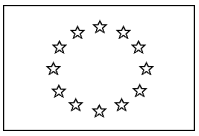
I would kindly ask you to fill in the following registration form in capital letters with all details and to send it back to me, together with this letter, by fax (+39-0332-785707) or e-mail (paola.piccinini@jrc.ec.europa.eu), so that we can post samples by the end of this month.

I would like to thank you very much for your precious collaboration.

Best regards,

Paola Piccinini

* Specimens to be analysed by participants:
15 specimens with method 1 (3 specimens for each of the 5 samples)
15 specimens with method 2 (3 specimens for each of the 5 samples)
15 specimens with method 3 (3 specimens for each of the 5 samples)
15 specimens with method 4 (3 specimens for each of the 5 samples)



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Health and Consumer Protection
Chemical Assessment and Testing Unit

COLLABORATIVE TRIAL'S REGISTRATION FORM

Contact person: ……

Institution: ……

Address: ……

Postal code: ……...

City: ……..

State: …….

Phone: ……

Fax: ……

E-mail: ……...

- ☐ I accept to take part in the ring trial for the determination of phthalates
- ☐ I do not accept to take part in the ring trial for the determination of phthalates

Signature: ……

Date: ……

ANNEX III

Methods’ protocols

METHOD 1 (n-hexane-acetone 80/20)

Before starting the analysis, please carefully read the Excel data reporting sheet in order to collect all required data.

1 Principle

The aim of the method is to extract phthalates in materials such as textile, polymer, coated materials or others. This method uses an ultrasonic bath as extraction apparatus with n-hexane/acetone as solvent.
The total n-hexane/acetone extractable phthalate plasticizer content is calculated by weight with gas chromatography-mass spectrometry (GC-MS) detection to identify and quantify individual phthalates.

2 Apparatus and reagents

2.1 Apparatus

2.1.1 Analytical balance, resolution of 0.1 mg.
2.1.2 Vial, 20-25 ml.
2.1.3 Thermostatic ultrasonic bath.
2.1.4 Volumetric or automatic pipette, 10 ml.
2.1.5 Calibrated volumetric flasks of suitable volume.
2.1.6 Graduated or automatic pipettes of suitable volume.
2.1.7 Gas chromatograph with mass-selective detector (GC-MSD).

Avoid direct contact between the samples and glassware and/or equipment used in order to minimize cross-contamination. Glassware, after washing, should be given an extra rinse with 0.1 N nitric acid and finally with acetone. Glassware should be completely dried before use.

WARNING — The vapour of the organic solvents are highly flammable, especially at high temperature. Allow glassware to cool down before use.

2.2 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

2.2.1 n-Hexane, CAS number: 110-54-3.
2.2.2 Acetone, CAS number: 67-64-1.
2.2.3 Mixture of n-hexane/acetone, 80 /20 v/v volume fraction.
2.2.4 Di-iso-nonyl phthalate (DINP), CAS number: 28553-12-0 or 68515-48-0.
2.2.5 Di-(2-ethylhexyl) phthalate (DEHP), CAS number: 117-81-7.
2.2.6 Di-n-octyl phthalate (DNOP), CAS number: 117-84-0.
2.2.7 Di-iso-decyl phthalate (DIDP), CAS number: 26761-40-0 or 68515-49-1.
2.2.8 Butyl benzyl phthalate (BBP), CAS number: 85-68-7.
2.2.9 Di-butyl phthalate (DBP), CAS number: 84-74-2.
2.2.10 Di-isobutyl phthalate (DIBP), CAS number: 84-69-5.
2.2.11 Di-pentyl phtalate (DPP), CAS number: 131-18-0, Internal Standard.

3 Sampling

Use the specimens as received.

4 Test procedure

4.1 Reagents (standard solutions)

4.1.1 Preparation of the standard solutions

Prepare the **individual stock solutions** of the different phthalates and of the internal standard **in n-hexane** by weighing approximately 50.0 mg of phthalate (report the exact amount in the excel calculation sheet) in a 50 ml volumetric flask (theoric concentration, 1000 mg/l). Fill the volumetric flask up to the mark with n-hexane and mix thoroughly to dissolve completely the substance.

Table 1 — Stock solutions

Phthalate	**DIDP**	**DINP**	**DBP**	**BBP**	**DNOP**	**DEHP**	**DIBP**	**DPP**
Concentration, µg/ml	1 000	1 000	1 000	1 000	1 000	1 000	1 000	1 000

4.1.2 Preparation of the calibration solutions

From the individual stock standard solutions, prepare the following six calibration solutions (theoric concentration 1, 3, 15, 30, 90, 180 mg/l) in n-hexane/acetone 80/20 v/v containing all the phthalates. In the case of the level 180 mg/l, two calibration solutions have to be prepared containing respectively three and four different phthalates.

1 mg/l	Add 0.1 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.
3 mg/l	Add 0.3 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.
15 mg/l	Add 0.75 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.
30 mg/l	Add 1.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.
90 mg/l	Add 4.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.

180 mg/l	Add 4.5 ml of each of three phthalate stock solutions in 25 ml volumetric flask plus 0.125 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.
180 mg/l	Add 4.5 ml of each of four phthalate stock solutions in 25 ml volumetric flask plus 0.125 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane/acetone 80/20 v/v.

NOTE: the target ions to be chosen for each phthalate are indicated in Annex A, DIDP and DINP overlap in the chromatogram.

4.2 Extraction of phthalates

4.2.1 Ultrasonic extraction

Weigh accurately (0.3 ± 0.01) g of the pieces of a representative specimen into a 20-25 ml vial (2.1.2) fitted with teflon stopcock. Add, with a volumetric or automatic pipette (2.1.4), 10 ml of n-hexane/acetone (2.2.3) containing 5 mg/l of internal standard (DPP).
Extract the phthalate in the ultrasonic bath (2.1.3) for 1 h at 50 °C .If necessary centrifuge at 2500 rpm for 5 minutes and transfer a volume of organic phase into a suitable GC sampling vial and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of extraction solvent containing 5 mg/l of the internal standard.

4.2.2 Blank

For each series of tests, blank in duplicate shall be prepared to exclude any contamination.

Note: attention to the chosen stopcock, make sure it remains tight for the whole extraction process in the ultrasonic bath.

4.3 Calculation of results

From the calibration graph, determine the response of each phthalate, corrected for the internal standard peak and interpolate the concentration (*C*) in mg/l solution using linear regression correcting for any dilutions. Subtract the blank concentration from the specimen concentration. The concentration P (w/w %) of each phthalate in the sample is calculated as follows:

$$P = \frac{(C - C_b) \times V}{m \times 1000} \times 100 \qquad (1)$$

where

C is the concentration of phthalate in the solution used for extracting sample (in mg/l);
C_b is the concentration of phthalate in the solution used for extracting blank (in mg/l);
V is the total volume of n-hexane/acetone added for the extraction, in millilitres (take into consideration dilution if any);
m is the mass of the specimen, in milligrams.

Note: the Excel sheet to report results contains all the calculations.

5 Test report

Please report any deviations in the Excel sheet.

METHOD 2 (n-hexane)

Before starting the analysis, please carefully read the Excel data reporting sheet in order to collect all required data.

1 Principle

The aim of the method is to extract phthalates in materials such as textile, polymer, coated materials or others. This method uses an ultrasonic bath as extraction apparatus with n-hexane as solvent.
The total n-hexane extractable phthalate plasticizer content is calculated by weight with gas chromatography-mass spectrometry (GC-MS) detection to identify and quantify individual phthalates.

2 Apparatus and reagents

2.1 Apparatus

2.1.1 Analytical balance, resolution of 0.1 mg.
2.1.2 Vial, 20-25 ml.
2.1.3 Thermostatic ultrasonic bath.
2.1.4 Volumetric or automatic pipette, 10 ml.
2.1.5 Calibrated volumetric flasks of suitable volume.
2.1.6 Graduated or automatic pipettes of suitable volume.
2.1.7 Gas chromatograph with mass-selective detector (GC-MSD).

Avoid direct contact between the samples and glassware and/or equipment used in order to minimize cross-contamination. Glassware, after washing, should be given an extra rinse with 0,1 N nitric acid and finally with acetone. Glassware should be completely dried before use.

WARNING — The vapour of the organic solvents are highly flammable, especially at high temperature. Allow glassware to cool down before use.

2.2 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

2.2.1 n-Hexane, CAS number: 110-54-3.
2.2.2 Di-iso-nonyl phthalate (DINP), CAS number: 28553-12-0 or 68515-48-0.
2.2.3 Di-(2-ethylhexyl) phthalate (DEHP), CAS number: 117-81-7.
2.2.4 Di-n-octyl phthalate (DNOP), CAS number: 117-84-0.
2.2.5 Di-iso-decyl phthalate (DIDP), CAS number: 26761-40-0 or 68515-49-1.
2.2.6 Butyl benzyl phthalate (BBP), CAS number: 85-68-7.
2.2.7 Di-butyl phthalate (DBP), CAS number: 84-74-2.
2.2.8 Di-isobutyl phthalate (DIBP), CAS number: 84-69-5.
2.2.9 Di-pentyl phtalate (DPP), CAS number: 131-18-0, Internal Standard.

3 Sampling

Use the specimens as received.

4 Test procedure

4.1 Reagent (standard solutions)

4.1.1 Preparation of the standard solutions

Prepare the **individual stock solutions** of the different phthalates and of the internal standard **in n-hexane** by weighing approximately 50.0 mg of phthalate (report the exact amount in the excel calculation sheet) in a 50 ml volumetric flask (theoric concentration, 1000 mg/l). Fill the volumetric flask up to the mark with n-hexane and mix thoroughly to dissolve completely the substance.

Table 1 — Stock solutions

Phthalate	**DIDP**	**DINP**	**DBP**	**BBP**	**DNOP**	**DEHP**	**DIBP**	**DPP**
Concentration, µg/ml	1 000	1 000	1 000	1 000	1 000	1 000	1 000	1 000

4.1.2 Preparation of the calibration solutions

From the individual stock standard solutions, prepare the following six calibration solutions (theoric concentration 1, 3, 15, 30, 90, 180 mg/l) in n-hexane containing all the phthalates. In the case of the level 180 mg/l, two calibration solutions have to be prepared containing respectively three and four different phthalates.

1 mg/l	Add 0.1 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.
3 mg/l	Add 0.3 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.
15 mg/l	Add 0.75 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.
30 mg/l	Add 1.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.
90 mg/l	Add 4.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.
180 mg/l	Add 4.5 ml of each of three phthalate stock solutions in 25 ml volumetric flask plus 0.125 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.
180 mg/l	Add 4.5 ml of each of four phthalate stock solutions in 25 ml volumetric flask plus 0.125 ml of the internal standard (DPP) stock solution then fill up to the mark with n-hexane.

NOTE: the target ions to be chosen for each phthalate are indicated in Annex A, DIDP and DINP overlap in the chromatogram.

4.2 Extraction of phthalates

4.2.1 Ultrasonic extraction

Weigh accurately (0.3 ± 0.01) g of the pieces of a representative specimen into a 20-25 ml vial (2.1.2) fitted with teflon stopcock. Add, with a volumetric or automatic pipette (2.1.4), 10 ml of n-hexane containing 5 mg/l of internal standard (DPP).
Extract the phthalate in the ultrasonic bath (2.1.3) for 1 h at 50 °C .If necessary centrifuge at 2500 rpm for 5 minutes and transfer a volume of organic phase into a suitable GC sampling vial and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of extraction solvent containing 5 mg/l of the internal standard.

4.2.2 Blank

For each series of tests, blank in duplicate shall be prepared to exclude any contamination.

Note: attention to the chosen stopcock, make sure that it remains tight for the whole extraction process in the ultrasonic bath.

4.3 Calculation of results

From the calibration graph, determine the response of each phthalate, corrected for the internal standard peak and interpolate the concentration (*C*) in mg/l solution using linear regression correcting for any dilutions. Subtract the blank concentration from the specimen concentration. The concentration P (w/w %) of each phthalate in the sample is calculated as follows:

$$P = \frac{(C - C_b) \times V}{m \times 1000} \times 100 \qquad (1)$$

where

C is the concentration of phthalate in the solution used for extracting sample (in mg/l);
C_b is the concentration of phtalate in the solution used for extracting blank (in mg/l);
V is the total volume of n-hexane added for the extraction, in millilitres (take into consideration dilution if any);
m is the mass of the specimen, in milligrams;

Note: the Excel sheet to report results contains all the calculations.

5 Test report

Please report any deviations in the Excel sheet.

METHOD 3 (methyl tert-butyl ether MTBE)

Before starting the analysis, please carefully read the Excel data reporting sheet in order to collect all required data.

1 Principle

The aim of the method is to extract phthalates in materials such as textile, polymer, coated materials or others. This method uses an ultrasonic bath as extraction apparatus with methyl tert-butyl ether (MTBE) as solvent.
The total MTBE extractable phthalate plasticizer content is calculated by weight with gas chromatography-mass spectrometry (GC-MS) detection to identify and quantify individual phthalates.

2 Apparatus and reagents

2.1 Apparatus

2.1.1 Analytical balance, resolution of 0.1 mg.
2.1.2 Vial, 20-25 ml.
2.1.3 Thermostatic ultrasonic bath.
2.1.4 Volumetric or automatic pipette, 10 ml.
2.1.5 Calibrated volumetric flasks of suitable volume.
2.1.6 Graduated or automatic pipettes of suitable volume.
2.1.7 Gas chromatograph with mass-selective detector (GC-MSD).

Avoid direct contact between the samples and glassware and/or equipment used in order to minimize cross-contamination. Glassware, after washing, should be given an extra rinse with 0,1 N nitric acid and finally with acetone. Glassware should be completely dried before use.

WARNING — The vapour of the organic solvents are highly flammable, especially at high temperature. Allow glassware to cool down before use.

2.2 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

2.2.1 Methyl tert-butyl ether (MTBE), CAS number: 1634-04-4.
2.2.2 Di-iso-nonyl phthalate (DINP), CAS number: 28553-12-0 or 68515-48-0.
2.2.3 Di-(2-ethylhexyl) phthalate (DEHP), CAS number: 117-81-7.
2.2.4 Di-n-octyl phthalate (DNOP), CAS number: 117-84-0.
2.2.5 Di-iso-decyl phthalate (DIDP), CAS number: 26761-40-0 or 68515-49-1.
2.2.6 Butyl benzyl phthalate (BBP), CAS number: 85-68-7.
2.2.7 Di-butyl phthalate (DBP), CAS number: 84-74-2.
2.2.8 Di-isobutyl phthalate (DIBP), CAS number: 84-69-5.
2.2.9 Di-pentyl phtalate (DPP), CAS number: 131-18-0, Internal Standard.

3 Sampling

Use the specimens as received.

4 Test procedure

4.1 Reagent (standard solutions)

4.1.1 Preparation of the standard solutions

Prepare the **individual stock solutions** of the different phthalates and of the internal standard **in n-hexane** by weighing approximately 50.0 mg of phthalate (report the exact amount in the excel calculation sheet) in a 50 ml volumetric flask (theoric concentration, 1000 mg/l). Fill the volumetric flask up to the mark with n-hexane and mix thoroughly to dissolve completely the substance.

Table 1 — Stock solutions

Phthalate	**DIDP**	**DINP**	**DBP**	**BBP**	**DNOP**	**DEHP**	**DIBP**	**DPP**
Concentration, µg/ml	1 000	1 000	1 000	1 000	1 000	1 000	1 000	1 000

4.1.2 Preparation of the calibration solutions

From the individual stock standard solutions, prepare the following six calibration solutions (theoric concentration 1, 3, 15, 30, 90, 180 mg/l) in n-hexane/acetone 80/20 v/v containing all the phthalates. In the case of the level 180 mg/l, two calibration solutions have to be prepared containing respectively three and four different phthalates.

1 mg/l	Add 0.1 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.
3 mg/l	Add 0.3 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.
15 mg/l	Add 0.75 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.
30 mg/l	Add 1.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.
90 mg/l	Add 4.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.
180 mg/l	Add 4.5 ml of each of three phthalate stock solutions in 25 ml volumetric flask plus 0.125 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.

180 mg/l	Add 4.5 ml of each of four phthalate stock solutions in 25 ml volumetric flask plus 0.125 ml of the internal standard (DPP) stock solution then fill up to the mark with MTBE.

NOTE: the target ions to be chosen for each phthalate are indicated in Annex A, DIDP and DINP overlap in the chromatogram.

4.2 Extraction of phthalates

4.2.1 Ultrasonic extraction

Weigh accurately (0.3 ± 0.01) g of the pieces of a representative specimen into a 20-25 ml vial (2.1.2) fitted with teflon stopcock. Add, with a volumetric or automatic pipette (2.1.4), 10 ml of MTBE (2.2.1) containing 5 mg/l of internal standard (DPP). Extract the phthalate in the ultrasonic bath (2.1.3) for 1 h at 60 °C .If necessary centrifuge at 2500 rpm for 5 minutes and transfer a volume of organic phase into a suitable GC sampling vial and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of extraction solvent containing 5 mg/l of the internal standard.

4.2.2 Blank

For each series of tests, blank in duplicate shall be prepared to exclude any contamination.

Note: attention to the chosen stopcock, make sure that it remains tight for the whole extraction process in the ultrasonic bath.

4.3 Calculation of results

From the calibration graph, determine the response of each phthalate, corrected for the internal standard peak and interpolate the concentration (C) in mg/l solution using linear regression correcting for any dilutions. Subtract the blank concentration from the specimen concentration. The concentration P (w/w %) of each phthalate in the sample is calculated as follows:

$$P = \frac{(C - C_b) \times V}{m \times 1000} \times 100 \qquad (1)$$

where

C is the concentration of phthalate in the solution used for extracting sample (in mg/l);
C_b is the concentration of phthalate in the solution used for extracting blank (in mg/l);
V is the total volume of MTBE added for the extraction, in millilitres (take into consideration dilution if any);
m is the mass of the specimen, in milligrams.

Note: the Excel sheet to report results contains all the calculations.

5 Test report

Please report any deviations in the Excel sheet.

METHOD 4 (tetrahydrofuran-acetonitrile)

Before starting the analysis, please carefully read the Excel data reporting sheet in order to collect all required data.

1 Principle

The aim of the method is to extract phthalates in materials such as textile, polymer, coated materials or others. PVC is dissolved in tetrahydrofuran and then precipitated with acetonitrile.
The total extractable phthalate plasticizer content is calculated by weight with gas chromatography-mass spectrometry (GC-MS) detection to identify and quantify individual phthalates.

2 Apparatus and reagents

2.1 Apparatus

2.1.1 Analytical balance, resolution of 0.1 mg.
2.1.2 Vial, 40 ml.
2.1.3 Thermostatic ultrasonic bath.
2.1.4 Volumetric or automatic pipette, 10 and 20 ml.
2.1.5 Calibrated volumetric flasks of suitable volume.
2.1.6 Graduated or automatic pipettes of suitable volume.
2.1.7 Gas chromatograph with mass-selective detector (GC-MSD).

Avoid direct contact between the samples and glassware and/or equipment used in order to minimize cross-contamination. Glassware, after washing, should be given an extra rinse with 0.1 N nitric acid and finally with acetone. Glassware should be completely dried before use.

WARNING — The vapour of the organic solvents are highly flammable, especially at high temperature. Allow glassware to cool down before use.

3.2 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

2.2.1 Tetrahydrofuran (THF), CAS number: 109-99-9.
2.2.2 Acetonitrile (ACN), CAS number: 75-05-8.
2.2.3 Di-iso-nonyl phthalate (DINP), CAS number: 28553-12-0 or 68515-48-0.
2.2.4 Di-(2-ethylhexyl) phthalate (DEHP), CAS number: 117-81-7.
2.2.5 Di-n-octyl phthalate (DNOP), CAS number: 117-84-0.
2.2.6 Di-iso-decyl phthalate (DIDP), CAS number: 26761-40-0 or 68515-49-1.
2.2.7 Butyl benzyl phthalate (BBP), CAS number: 85-68-7.
2.2.8 Di-butyl phthalate (DBP), CAS number: 84-74-2.
2.2.9 Di-isobutyl phthalate (DIBP), CAS number: 84-69-5.
2.2.10 Di-pentyl phtalate (DPP), CAS number: 131-18-0, Internal Standard.

3 Sampling

Use the specimens as received.

4 Test procedure

4.1 Reagent (standard solutions)

4.1.1 Preparation of the standard solutions

Prepare the **individual stock solutions** of the different phthalates and of the internal standard **in acetonitrile** by weighing approximately 50.0 mg of phthalate (report the exact amount in the excel calculation sheet) in a 50 ml volumetric flask (theoric concentration, 1000 mg/l). Fill the volumetric flask up to the mark with acetonitrile and mix thoroughly to dissolve completely the substance.

Table 1 — Stock solutions

Phthalate	**DIDP**	**DINP**	**DBP**	**BBP**	**DNOP**	**DEHP**	**DIBP**	**DPP**
Concentration, µg/ml	1 000	1 000	1 000	1 000	1 000	1 000	1 000	1 000

4.1.2 Preparation of the calibration solutions

From the individual stock standard solutions, prepare the following five calibration solutions (theoric concentration 1, 3, 15, 30, 90 mg/l) in n-hexane containing all the phthalates. From the stock standard solutions, prepare appropriate phthalate calibration solutions in tetrahydrofuran / acetonitrile 33/66 v/v.

1 mg/l	Add 0.1 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran / acetonitrile 33/66 v/v.
3 mg/l	Add 0.3 ml of each phthalate stock solution in 100 ml volumetric flask plus 0.5 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran / acetonitrile 33/66 v/v.
15 mg/l	Add 0.75 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran / acetonitrile 33/66 v/v.
30 mg/l	Add 1.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran / acetonitrile 33/66 v/v.
90 mg/l	Add 4.5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0.25 ml of the internal standard (DPP) stock solution

then fill up to the mark with tetrahydrofuran / acetonitrile 33/66 v/v.

NOTE: the target ions to be chosen for each phthalate are indicated in Annex A, DIDP and DINP overlap in the chromatogram.

4.2 Extraction of phthalates

4.2.1 Ultrasonic extraction

Weigh accurately (0.3 ± 0.01) g of the pieces of a representative specimen into a 40 ml vial (2.1.2) fitted with teflon stopcock. Add, with a volumetric or automatic pipette (2.1.4), 10 ml of tetrahydrofuran (2.2.1) containing 5 mg/l of internal standard (DPP).
Dissolve the PVC in the ultrasonic bath (2.1.3) for 1 h at 60 °C and wait until the sample is at room temperature. Precipitate the polymer by adding dropwise 20 ml (measured with a volumetric or automatic pipette) of acetonitrile containing 5 mg/l of internal standard (DPP).
Shake vigorously the vial (better with a vortex for at least 30 seconds) and wait 30 minutes to allow the precipitation of PVC.
Centrifuge at 2500 rpm for 10 minutes and transfer a volume of organic phase into a suitable GC sampling vial and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of tetrahydrofuran / acetonitrile 33/66 v/v containing 5 mg/l of the internal standard.

4.2.2 Blank

For each series of tests, blank in duplicate shall be prepared to exclude any contamination.

Note: attention to the chosen stopcock, make sure that it remains tight for the whole dissolution process in the ultrasonic bath.

4.3 Calculation of results

From the calibration graph, determine the response of each phthalate, corrected for the internal standard peak and interpolate the concentration (C) in mg/l solution using linear regression correcting for any dilutions. Subtract the blank concentration from the specimen concentration.
The concentration P (w/w %) of each phthalate in the sample is calculated as follows:

$$P = \frac{(C - C_b) \times V}{m \times 1000} \times 100 \qquad (1)$$

where

C is the concentration of phthalate in the final tetrahydrofuran / acetonitrile solution used for sample (in mg/l);
C_b is the concentration of phtalate in the final tetrahydrofuran / acetonitrile solution used for blank (in mg/l);
V is the total volume of tetrahydrofuran and acetonitrile added for the extraction, in millilitres (take into consideration dilution if any);
m is the mass of the specimen, in milligrams.

Note: the Excel sheet to report results contains all the calculations.

5 Test report

Please report any deviations in the Excel sheet.

Annex A
(informative)
Suitable gas chromatography-mass spectrometry (GC-MS) apparatus, method and precision data for determination of phthalate plasticizers

A.1 General

The following equipment, column and operating conditions have been found suitable:

Equipment: 6890 gas chromatograph (GC) mass-selective device (MSD), quadrupole.

Column: 5 % phenyl methyl siloxane for MS; length 30 m; 0.32 mm interior diameter and 0.25 μm film thickness.

Carrier gas: helium.

Flow rate: 2.0 ml/min.

Injector temperature: 250 °C, mode splitless or split.

Injection volume: 1 mm^3 (μl).

Temperature programme: 150 °C for 1 min.
up to 250 °C at 8 °C/min.
up to 290 °C at 3 °C/min.
isothermal 5.00 min.
Total programme time: 34 min.

Transfer line temperature: 280 °C.

MSD mode: Electron impact.

Typical quantification ions for phthalate plasticizers are shown in Table A.1.

Table A.1 — Typical quantification ions for phthalate plasticizers

Phthalate plasticizers	Target ion	Q1	Q2
Di-butyl phthalate (DBP)	149	150	223
Butyl benzyl phthalate (BBP)	149	206	150
Di-(2-ethylhexyl) phthalate (DEHP)	149	167	279
Di-n-octyl phthalate (DNOP)	149	279	261
Di-iso-nonyl phthalate (DINP)	293		
Di-iso-decyl phthalate (DIDP)	307		

Di-cyclohexyl phthalate (DPP) (internal standard)	149	219	237
Di-isobutyl phthalate (DIBP)	149	167	223

Depending on the type of equipment used, the appropriate operating conditions may need to be established.

METHOD 5 (determination of PVC mass percentage)

Before starting the analysis, please carefully read the Excel data reporting sheet in order to collect all required data.

1 Principle

The PVC layer is dissolved out from a known dry mass of the sample, with tetrahydrofuran. The textile residue is collected, washed, dried and weighed; its mass, corrected if necessary, is expressed as a percentage of the dry mass of the sample. The percentage of dry PVC is found by difference.

2 Apparatus and reagents

2.1 Apparatus

2.1.1 Weighing bottle or any other apparatus giving identical results.
2.1.2 Filter crucibles.
2.1.3 Desiccator containing self-indicating silica gel.
2.1.4 Ventilated oven for drying specimens at 105 ± 3 °C.
2.1.5 Analytical balance, accurate to 0,0002 g.
2.1.6 Glass conical flasks fitted with screw teflon cap of at least 100 ml capacity.
2.1.7 Thermostatic ultrasonic bath.
2.1.8 Graduated cylinder, 50 ml.

2.2 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

2.2.1 Tetrahydrofuran (THF), CAS number: 109-99-9.
2.2.2 Deionised water.

3 Sampling

Use the specimens as received.

4 Test procedure

Dry three specimens of 1 gram each, each one in a different weighing bottle, in a ventilated oven (105 °C) for 14-16 hours.
At the same time dry three filter crucibles in three weighing bottles in a ventilated oven (105 °C) for 14-16 hours.
Cool all the mentioned weighing bottles, containing specimens and filter crucibles, in a desiccator for at least 2 hours.
Weigh weighing bottles containing specimens.
Transfer quantitatively specimens in the glass conical flask fitted with screw teflon cap of at least 100 ml capacity, that will be used for the method, and then weigh empty weighing bottles (the difference is the weight of specimens, sample mass).
Weigh filter crucibles.

To each specimen contained in the glass conical flask, add 50 ml of tetrahydrofuran per gram of specimen. Dissolve the PVC in the ultrasonic bath (2.1.7) for 1 h at 60 °C

and then decant immediately the liquid through the weighed filter crucible. Transfer the residue to the filter crucible. Wash twice the residue in the filter crucible with 30 ml tetrahydrofuran pre-heated at 60 °C and allow draining under gravity. Then rinse thoroughly with water and allow draining under gravity. Finally, drain the crucible with suction.

Dry filter crucibles with residues in weighing bottle in a ventilated oven (105 °C) for 14-16 hours
Cool them in a desiccator for at least 2 hours.
Weigh filter crucibles with residues (the difference with empty filter crucibles is the weigh of residues, residue mass)

Some key points of the procedure are recalled in the following:

Drying
Avoid handling crucibles and weighing bottles, specimens or residues with bare hands during the drying, cooling and weighing operations. Always wear gloves when weighing.

Cooling
Conduct all cooling operations in a desiccator placed beside the balance.

Weighing
After cooling, complete the weighing of weighing bottles within two minutes of its removal from the desiccator.

Make sure that specimens are washed with plenty of water in the end of the procedure to avoid tetrahydrofuran smell when residues are dried in the oven.

4.3 Calculation of results

Calculate the results as described in the following:

$$P_1\ \% \ = \ \frac{100\ r\ d}{m} \qquad (1)$$

where:
P_1 is the percentage of clean, dry insoluble textile component
m is the dry mass of the specimen
r is the dry mass of the textile residue
d is the correction factor for loss of mass of the insoluble textile component in the reagent during analysis

Then calculate the percentage of the insoluble textile component on clean, dry mass basis, with adjustment by conventional factors (agreed allowances) using the following formula:

$$P_{1A}\ \% \ = \ \frac{100\ \ P_1\left(1+\frac{a_1}{100}\right)}{P_1\left(1+\frac{a_1}{100}\right)+\left(100-P_1\right)} \qquad (2)$$

where:
P_{1A} is the percentage of insoluble component, adjusted by agreed allowance.
P_1 is the percentage of clean, dry insoluble component as calculated from equation 1.
a_1 is the agreed allowance for the insoluble component, in this case cotton (listed in Annex V to the Directive 2008/121/EC on textile names)

The percentage of the soluble component, in this case PVC, (P_{2A} %) is obtained by difference.

Note: the Excel sheet to report results contains all the calculations.

ANNEX IV

Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Health and Consumer Protection (IHCP)
Chemical Assessment and Testing Unit (CAT)

Ispra, 28th September 2011

Dear Expert,

Today collaborative trial's samples containing phthalates have been sent by carrier. Please notice that experimental results must be reported by the end of October 2011 at the latest.

As soon as you receive the samples please send us back by fax (+39-0332-785707) or e-mail (paola.piccinini@jrc.ec.europa.eu) the acknowledgement form you can find in attachment.

The methods' protocols and the provided instructions should allow you to perform the analysis. However, if you experience any problems please contact us and we will be willing to help you.

In attachment you will find:

- acknowledgement form to be sent by fax or e-mail as soon as you receive the samples;
- five protocols;
- general requirements and instructions about how to conduct the analysis of the collaborative trial;
- Excel sheets to report results.

I would like to thank you very much for your collaboration.

Best regards,

Paola Piccinini

ANNEX V

Instructions

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Health and Consumer Protection (IHCP)
Chemical Assessment and Testing Unit (CAT)

GENERAL REQUIREMENTS AND INSTRUCTIONS

Before starting the analysis, please carefully read the Excel data reporting sheet in order to collect all required data.

Provided samples

About 8 grams for each of five different samples (A, B, C, D, E) are provided. Samples A – D are textile samples covered with a PVC layer, whereas sample E is made of PVC. The provided quantity is enough to carry out all the determinations of phthalates (4 grams) and, if necessary, also some additional ones.

Samples are marked with codes, e.g. BE – A – TXT or PVC – 1. Codes indicate the laboratory's nationality, the sample code, the sample material and a progressive number.

In addition, about 3 grams of a textile sample (F composition) is provided for the determination of the textile and PVC mass percentage. This quantity allows performing the determination in triplicate. Unfortunately, no spare specimens are available for this sample.

Instructions

The provided five methods have to be strictly applied.

Three vials containing the internal standard dipentyl phthalate (DPP), the diisononyl phthalate (DINP) and the diisodecyl phthalate are also provided. Please use them to prepare the stock solutions.

The extraction of the testing replicates for each sample and method **must** be performed in the same laboratory by the same operator, using the same equipment and at the same time, taking care of respecting the foreseen contact time. In other words, test results for replicates have to be obtained in **repeatability conditions**. For each sample and method, the extraction solutions **must** be analysed in a short time interval.

In case of any problem during the extraction and analysis of some replicates, please be aware that all the three replicates of the sample must be repeated.

Reporting

The following five Excel files are available and must be filled-in with results:

1. "Phthalates template results method 1 hexane acetone"
2. "Phthalates template results method 2 hexane"
3. "Phthalates template results method 3 MTBE"
4. "Phthalates template results method 4 THF ACN"

5. “Phthalates template results method 5 textile mass percentage”

The first four Excel files contain seven Excel Worksheets each, which refer to calibration curves, blanks and samples A – E respectively.

Using these worksheets the phthalates’ mass percentage and concentration in mg/kg of the whole sample (textile + PVC layer) will be automatically calculated, as well as the mass percentage of the textile and PVC part.

Please return the filled-in Excel files and your comments and remarks by e-mail (paola.piccinini@jrc.ec.europa.eu) by 31st October 2011 at the latest.

ANNEX VI

Excel templates

Stock solution:	in n-hexane
Dilutions from stock solution:	in n-hexane/acetone 80/20 v/v

Remarks

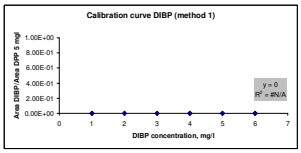
PLEASE FILL IN ALL THE YELLOW CELLS

DIBP CAS 84-69-5

retention time (min)
mass of DIBP weighed for stock solution (mg)
volume of stock solution (ml)
theoric stock solution concentration (mg/l) 1000
actual stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DIBP 149-167-223	Area/Area ISTD
1				
3				
15				
30				
90				
180				

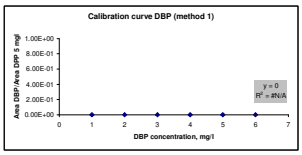


DBP CAS 84-74-2

retention time (min)
mass of DBP weighed for stock solution (mg)
volume of stock solution (ml)
teoric stock solution concentration (mg/l) 1000
theoric stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DBP 149-150-223	Area/Area ISTD
1				
3				
15				
30				
90				
180				

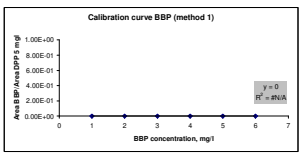


BBP CAS 85-68-7

retention time (min)
mass of BBP weighed for stock solution (mg)
volume of stock solution (ml)
teoric stock solution concentration (mg/l) 1000
theoric stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area BBP 149-150-206	Area/Area ISTD
1				
3				
15				
30				
90				
180				

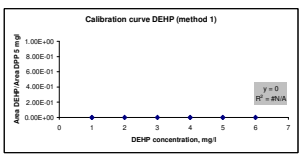


DEHP CAS 117-81-7

retention time (min)
mass of DEHP weighed for stock solution (mg)
volume of stock solution (ml)
teoric stock solution concentration (mg/l) 1000
theoric stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DEHP 149-167-279	Area/Area ISTD
1				
3				
15				
30				
90				
180				

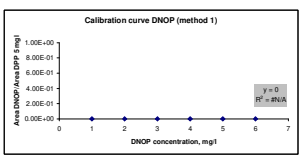


DNOP CAS 117-84-0

retention time (min)
mass of DNOP weighed for stock solution (mg)
volume of stock solution (ml)
teoric stock solution concentration (mg/l) 1000
theoric stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DNOP 149-261-279	Area/Area ISTD
1				
3				
15				
30				
90				
180				

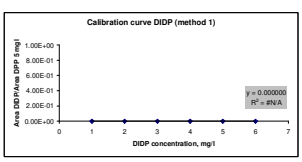


DIDP CAS 26761-40-0

retention time (min)
mass of DIDP weighed for stock solution (mg)
volume of stock solution (ml)
teoric stock solution concentration (mg/l) 1000
theoric stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DIDP 307	Area/Area ISTD
1				
3				
15				
30				
90				
180				

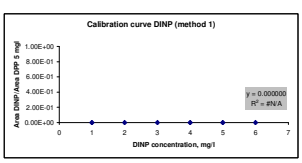


DINP CAS 28553-12-0

retention time (min)
mass of DINP weighed for stock solution (mg)
volume of stock solution (ml)
teoric stock solution concentration (mg/l) 1000
theoric stock solution concentration (mg/l)
correction factor (CF)

calibration curve slope (from the cal curve graph)
calibration curve correlation coefficient (from the cal curve graph)

mg/l	mg/l*CF	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DINP 293	Area/Area ISTD
1				
3				
15				
30				
90				
180				



Sample code: BLANK

Method: 1 (hexane / acetone 80/20 v/v)

Remarks

PLEASE FILL IN ALL THE YELLOW CELLS

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DIBP 149-167-223	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	DIBP				
	blank_M1_b	DIBP				
					average	
					SD	
					RSD	

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DBP 149-150-223	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	DBP				
	blank_M1_b	DBP				
					average	
					SD	
					RSD	

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area BBP 149-150-206	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	BBP				
	blank_M1_b	BBP				
					average	
					SD	
					RSD	

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DEHP 149-167-279	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	DEHP				
	blank_M1_b	DEHP				
					average	
					SD	
					RSD	

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DNOP 149-261-279	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	DNOP				
	blank_M1_b	DNOP				
					average	
					SD	
					RSD	

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DIDP 307	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	DIDP				
	blank_M1_b	DIDP				
					average	
					SD	
					RSD	

Laboratory code	sample code	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DINP 293	Area/Area ISTD	cal curve slope 0 conc. mg/l
	blank_M1_a	DINP				
	blank_M1_b	DINP				
					average	
					SD	
					RSD	

JRC EUROPEAN COMMISSION

CEN/TC 248/WG 26 on test methods for analysis of EC restricted substances 38/WG 22 on composition and chemical testing | ISO/TC | Phthalates Collaborative Trial | September 2011

Sample code: A TEXT

Method: 1 (hexane / acetone 80/20 v/v)

Sample type: textile

Remarks

PLEASE FILL IN THE YELLOW CELLS

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DIBP 149-167-223	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		DIBP						#VALUE!	'Blanks_Method 1'!$G$61					
	Sample A_TEXT_M1_b		DIBP						#VALUE!	'Blanks_Method 1'!$G$61					
	Sample A_TEXT_M1_c		DIBP						#VALUE!	'Blanks_Method 1'!$G$61					
											average				
											SD				
											RSD				

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DBP 149-150-223	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		DBP						#VALUE!	'Blanks_Method 1'!$G$62					
	Sample A_TEXT_M1_b		DBP						#VALUE!	'Blanks_Method 1'!$G$62					
	Sample A_TEXT_M1_c		DBP						#VALUE!	'Blanks_Method 1'!$G$62					
											average				
											SD				
											RSD				

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area BBP 149-150-205	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		BBP						#VALUE!	'Blanks_Method 1'!$G$63					
	Sample A_TEXT_M1_b		BBP						#VALUE!	'Blanks_Method 1'!$G$63					
	Sample A_TEXT_M1_c		BBP						#VALUE!	'Blanks_Method 1'!$G$63					
											average				
											SD				
											RSD				

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DEHP 149-167-279	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		DEHP						#VALUE!	'Blanks_Method 1'!$G$64					
	Sample A_TEXT_M1_b		DEHP						#VALUE!	'Blanks_Method 1'!$G$64					
	Sample A_TEXT_M1_c		DEHP						#VALUE!	'Blanks_Method 1'!$G$64					
											average				
											SD				
											RSD				

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DNOP 149-261-279	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		DNOP						#VALUE!	'Blanks_Method 1'!$G$65					
	Sample A_TEXT_M1_b		DNOP						#VALUE!	'Blanks_Method 1'!$G$65					
	Sample A_TEXT_M1_c		DNOP						#VALUE!	'Blanks_Method 1'!$G$65					
											average				
											SD				
											RSD				

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DIDP 307	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		DIDP						#VALUE!	'Blanks_Method 1'!$G$66					
	Sample A_TEXT_M1_b		DIDP						#VALUE!	'Blanks_Method 1'!$G$66					
	Sample A_TEXT_M1_c		DIDP						#VALUE!	'Blanks_Method 1'!$G$66					
											average				
											SD				
											RSD				

cal curve slope 0

Laboratory Code	sample code	sample mass (g)	phthalate	Peak area ISTD DPP (5 mg/l) ion 149-219-237	Peak area DINP 293	Area/Area ISTD	conc. mg/l	dilution factor	corrected for dilution conc. mg/l	conc. blank mg/l	conc. (sample-blank) mg/l	conc. mg/Kg	phtalate mass (mg)	sample mass (mg)	%weight
	Sample A_TEXT_M1_a		DINP						#VALUE!	'Blanks_Method 1'!$G$67					
	Sample A_TEXT_M1_b		DINP						#VALUE!	'Blanks_Method 1'!$G$67					
	Sample A_TEXT_M1_c		DINP						#VALUE!	'Blanks_Method 1'!$G$67					
											average				
											SD				
											RSD				

JRC EUROPEAN COMMISSION

CEN/TC 248/WG 26 on test methods for analysis of EC restricted substances 38/WG 22 on composition and chemical testing | ISO/TC | Phthalates Collaborative Trial September 2011

Sample code: F COMPOSITION

Method: M5 determination of textile mass percentage

Sample type: TEXT

Remarks

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Laboratory Code	sample code	Bottle + Specimen (g)	Bottle (g)	Sample mass (g)	Filter (g)	Filter + Residue (g)	Residue (g)	% Cotton	% PVC	P1A% Cotton	P2A% PVC
	Sample F_composition_M5_a										
	Sample F_composition_M5_b										
	Sample F_composition_M5_c										
							average				
							SD				
							RSD				

ANNEX VII

Confirmation of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Health and Consumer Protection (IHCP)
Chemical Assessment and Testing Unit (CAT)

SAMPLES ACKNOWLEDGMENT FORM

Please fill in this form in capital letters and send it back by fax (+39-0332-785707) or e-mail (paola.piccinini@jrc.ec.europa.eu), as soon as you receive the samples.

Contact person: ……
Institution: ……
E-mail: ……...

I declare that I received the samples for the collaborative trial to validate a quantification method for phthalates in textiles.

Date, ____ /____ / 2011.

Signature: ……..

ANNEX VIII

Participants' comments

Participant Code	SIM/SCAN	Split/splitless	Column	Standard 180 mg/L
LC0000	no comment	no comment	no comment	no comment
LC0001	SIM mode	Splitless mode	DB 35 MS 60m×0.25mm×0.25um	no comment
LC0002	We used SCAN mode about DIBP,DBP,BBP,DEHP,DNOP. And we used SIM mode about DINP,DIDP.	We injected in Split mode.	We used colum about DB-5(Length 50m, I.D. 0.320mm, Film 0.25Ï¼m).	One group that we divided into is DBP,DNOP,DINP and another group is DIBP,BBP,DEHP,DIDP.We converted one group of peak area ISTD DPP to another group of peak area ISTD DPP.
LC0003	SIM mode on ions 149, 293 and	Split injection with ratio 1:25. The	Zebron ZB-5 (similar to standard	First 180 standard is DINP,DEHP and DNOP. Second
LC0004	no comment	no comment	no comment	no comment
LC0005	Sim Mode	Split Mode Ratio: 20-1	HP-5 length: 30m I.D: Ø	Mix A: DIDP; DNOP; BBP; DBP.
LC0006	no comment	no comment	no comment	no comment
LC0007	SIM mode	Splitless mode	DB 5 MS 30m×0.25mm×0.25um	Method1 area of DPP: 4.04×108 (DIDP, DBP, BBP) area of DPP:3.87×108 (DINP, DNOP, DEHP, DIBP) Method2 area of DPP:4.24×108 (DIDP, DBP, BBP) area of DPP:3.73×108 (DINP, DNOP, DEHP, DIBP) Method3 area of DPP:2.84×108 (DIDP, DBP, BBP) area of DPP:2.77×108 (DINP, DNOP, DEHP, DIBP) Besides, the dilution factor 3 we inserted in the template for results of method 4 (tetrahydrofuran/acetonitrile) is due to the fact that we just followed the protocol ending up with a final volume of the solution of 30 ml.
LC0008	SIM mode, using the ions specified (and some more, specifically 127 and 141 for reference ions of DINP and DIDP and 91 for BBP. These correspond the the alcohol group decomposition during ionisation.	Split mode, 8:1	Phenomenex ZB-5 ms 30m x 0.25mm x 0.25u with integrated 5m guard column section.	As mentioned previously, I did not have the time to prepare individual stock solutions therefore I prepared mixed stocks. This meant all components could be calibrated in one run at the 180mg/L level. (with the exception of those overloading the detector in my case)
LC0009	SCAN mode	Splitless mode	Thermo TR-50 MS 30m×0.25mm×0.25um	Method1 area of DPP: 2465278 (DIBP,DBP,DEHP,DINP) area of DPP: 2302663 (BBP,DNOP,DIDP) Method2 area of DPP: 2029397 (DIBP,DBP,DNOP,DIDP) area of DPP: 2030919 (BBP, DEHP, DINP) Method3 area of DPP: 1632905 (DIBP,DBP,DNOP,DIDP) area of DPP: 1388047 (BBP, DEHP, DINP) Method4 std 180 mg/l not prepared
LC0010	SCAN mode	Splitless mode	DB 5 MS 30m×0.25mm×0.25um	Method1 area of DPP: 70830 (DIDP, DBP, BBP) area of DPP: 66532 (DINP, DNOP, DEHP, DIBP) Method2 area of DPP: 80223 (DIDP, DBP, BBP) area of DPP: 77032 (DINP, DNOP, DEHP, DIBP) Method3 area of DPP: 81052 (DIDP, DBP, BBP) area of DPP: 80032 (DINP, DNOP, DEHP, DIBP) NOTE: It would be pointed that the DIDP and DINP could not be auto integrated by the software, so we integrated them manually, and the numbers we inserted in the template for the results of DIDP and DINP are the response values instead of the areas of the peaks. Meanwhile, all the calibration standards and the test results were the response values. Besides, the dilution factor 3 we inserted in the template for results of method 4 (tetrahydrofuran/acetonitrile) is due to the fact that we just followed the protocol ending up with a final volume of the solution of 30 ml.
LC0011	SCAN mode	Split Mode Ratio: 20-1	Zebron ZB 35 length: 15m I.D: Ø 0.50mm film: 0.25µm	Method1 area of DPP: 2905554 (DBP,DEHP,DIDP) area of DPP: 2457443 (DIBP,BBP, DNOP, DINP) Method2 area of DPP: 2289876 (DBP,DEHP,DIDP) area of DPP: 2023726 (DIBP,BBP, DNOP, DINP) Method3 area of DPP: 2009168 (DBP,DEHP,DIDP) area of DPP: 1951113 (DIBP,BBP, DNOP, DINP) Method4 area of DPP: 2428400 (DBP,DEHP,DIDP) area of DPP: 3559930 (DIBP,BBP, DNOP, DINP)
LC0012	SIM mode for quantification; SCAN mode for qualification	Spitless mode	DB-35-MS length: 30m I.D: Ø 0.25mm film: 0.25µm	All the targets compounds are quantified under the same internal standard.
LC0013	no comment	no comment	no comment	no comment

Participant Code	General Comments
LC0000	Noi abbiamo utilizzato una colonna dal diametro più piccolo (0.25 mm) che non ci ha consentito di utilizzare splittaggi elevati e quindi abbiamo lavorato in splitless come ns routine; questo purtroppo ha creato una marcata deviazione dalla linearità per i punti ad alta concentrazione (90 e 180 ppm) ad eccezione dei risultati in n-esano. Abbiamo elaborato i dati anche senza i punti che deviavano, trovate i risultati ottenuti in questa maniera nei fail nominati modCTC. Non so se vi possano essere utili; in goni caso abbiamo provveduto ad opportune diluizioni degli estratti in modo tale da rientrare nel range di linearità della curva.I risultati con la curva a sei punti e quella a 4 risultano abbastanza differenti; fatemi sapere se avete bisogno di ulteriori delucidazioni in merito. Inoltre abbiamo utilizzato un flusso pari a 1.5 ml/min e la programmata di temperatura risulta di 32 min anziché 34.
LC0001	no comment
LC0002	no comment
LC0003	The use of automatic pipettes is difficult on solvents having low evaporation pressure specially on the higher volumes (10 ml).For blanks the extraction fluid with internal standard was used. This is not specified in method descriptions.Results all methods, Formula error (missing) in calibration for DEHP and DNOP.I could not access the calibration graph for method 4. The 180 mg/l was removed by entering 0. Hopefully this does not affect the slope curve.
LC0004	no comment
LC0005	no comment
LC0006	La tecnica strumentale da noi utilizzata risulta essere LC-MS/MS in quanto è la tecnica da noi impiegata in maniera routinaria per la determinazione del contenuto di ftalati in consumer products. Di seguito sono a dettagliare le transizioni impiegate per la determinazione LC-MS/MS DPP = 307.4 --> 149 BBP = 313.2 --> 91 DINP = 419.3 --> 149 DIDP = 447.4 --> 85.1 DEHP = 391.3 --> 149 DNOP = 391.3 --> 149 DiBP = 279.2 --> 149 DBP = 279.2 --> 149 In merito al file excel relativo al metodo ACN/THF ed in particolare al fattore di diluizione we set the value on 3 to consider the final volume on 30 ml instead 10ml of the other methods
LC0007	for GC scan mode, JICIQ used SIM
LC0008	The corrections/alterations I made to the sheets are highlighted in red. (mainly for removing the top calibration level).Analyses which required diluting 1:1 are clearly highlighted in blue. dilution factor calculation (x2) was put in "column H".General Comments. 1. Methods.Use of a mixed stock solution is strongly recommended, single stock solutions takes too long to prepare and used too much solvent and glassware.Full calibration range specified was not achievable, 180mg/L is too high for DBP, DIBP and DNOP when detecting 1mg/L of DINP and DIDP.Also some of the samples needed diluting. MTBE is difficult to work with volumetrically due to its low viscosity and high volatility. Mixing hexane and acetone causes cooling and contraction, this must be done well in advance of extraction and dilutions and be allowed to stabilise.Solvent choice does not affect the chromatography therefore any solvent can be used for calibration of any of the four methods. 2. Excel evaluation .After fixing errors with missing formulas etc. some concerns still persist. All calibrations are set as zero intercept, in some cases this does not apply. This causes less accurate quantification and R-square values to deviate. Manually transferred calibration coefficients are at different accuracies (between 3 and 6 decimal places).
LC0009	There are some mistakes in your excelfiles, but we put our results in it. And you can do only lineair regression, most of our calibration curves are quadratic.
LC0010	for GC scan mode, CTTC used SCAN
LC0011	no comment
LC0012	As you will see all the sheet doesn't work because you subtract our blanks values And I think that the denomination of the cell is wrong
LC0013	in accordance with CPSC-CH-C1001-09.1.Based on our review of the various protocols used in this round trial it appears that the CPSC protocol is most aggressive with respect to phthalate removal from the substrate/coating combination and hence reported phthalate values expressed by the GCMS should also be highest. As mentioned a specific block of text devoted to how to deal with the textile substrate in the denominator of the PPM phthalate calculation would probably be useful.

Participant Code	M1 - hexane/acetone	M2 - hexane	M3 - MTBE	M4 - THF/CAN	M5 - gravimetric
LC0000	Calibrazione: problema con punti ad alta concentrazione: non si miscelano acn e hexane; elaborata retta escludendo gli ultimi due punti per avere maggiore linearità	no comment	Calibration: Attention: a new sheet was made without the last point of the calibration curve of BBP e DEHP because they aren't linear with the others.	no comment	no comment
LC0001	no comment	no comment	no comment	no comment	no comment
LC0002	no comment	no comment	no comment	no comment	no comment
LC0003	Calibration: Peak area for DPP second 180 (4-7) mg/l is 1353774.Blanks: extraction DPP n-hex/acet 80/20 v/v. Method 1 material D sample c might be faulty	Calibration: Peak area for DPP second 180 (4-7) mg/l is 1247035. Method 2 Material C sample b might be faulty	Calibration: Method 3 Calibration for BBP 30 mg/l might be faulty. Peak area for DPP second 180 (4-7) mg/l is 1974777	Calibration: The 180 mg/l was removed by entering 0. Hopefully this does not affect the slope curve.Method 4 material C sample a is faulty due to a leakage of THF after extraction. For method 4, samples were not centrifuged due to lack of equipment. liquid was quite clear and was no problem for our GC. For method 4, standard 180 mg/l is not included in method giving corrupt calibration curves in result template.	Sample name was F composition 14. Samples in filter crucibles gained weight rather quickly after removal from desiccator, but all samples was weighed within 2 min. Possible error should be in the last decimal of sample b and c. For method 5 Acetonitrile is listed as a reagent but was not mentioned in test procedure.
LC0004	no comment	no comment	no comment	no comment	no comment
LC0005	no comment	no comment	no comment	no comment	no comment
LC0006	no comment	no comment	no comment	no comment	no comment
LC0007	Blanks: the peak area of phthalates is so little that it can be ignored.	Blanks: the peak area of phthalates is so little that it can be ignored.	Blanks: the peak area of phthalates is so little that it can be ignored.	Blanks: the peak area of phthalates is so little that it can be ignored.	no comment
LC0008	Calibration: Tuning the method to detect DINP and DIDP at 1mg/L meant that at 180mg/L, DIBP, DBP and DNOP overloaded the detector. This also affected DINP and DIDP at this level. Blanks: No peaks detected. Sample A: BLUE = sample was diluted by a factor of two, formula in column H adjusted Sample E: BLUE = sample was diluted by a factor of two, formula in column H adjusted	Blanks: no peak detected.	Sample A: BLUE = sample was diluted by a factor of two, formula in column H adjusted Sample E: BLUE = sample was diluted by a factor of two, formula in column H adjusted	no comment	no comment
LC0009	no comment	no comment	no comment	no comment	no comment
LC0010	no comment	no comment	no comment	no comment	no comment
LC0011	no comment	Calibration: For the Peak Area only the 149 or the other first mass mentioned were used. In the field for the weighed mass for stock solution, I multiplied the mass with the purity of the substance.Blank: For the Peak Area only the 149 or the other first mass mentioned were used. For all samples: For the Peak Area only the 149 or the other first mass mentioned were used.	Calibration: For the Peak Area only the 149 or the other first mass mentioned were used. In the field for the weighed mass for stock solution, I multiplied the mass with the purity of the substance.Blank: For the Peak Area only the 149 or the other first mass mentioned were used. For all samples: For the Peak Area only the 149 or the other first mass mentioned were used.	Calibration: due to a mistake by the lab technican, the stock solution in hexan was used!!! We had no time do redo it correctly. Sorry!Blank: For the Peak Area only the 149 or the other first mass mentioned were used. For all samples: For the Peak Area only the 149 or the other first mass mentioned were used.	no comment
LC0012	no comment	no comment	no comment	no comment	no comment
LC0013	no comment	no comment	no comment	no comment	no comment

ANNEX IX

Results

Tables A, B, C (Method 1): original values, cell means and cell standard deviations, respectively.

	Sample A – Method					Sample B - Method 1				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP	DIBP	BBP	DEHP	DNOP	DINP
Level	III	II	I	II	I	I	III	II	III	II
LC0000	6191.73	779.69	205.31	793.32	405.58	137.42	8325.64	777.00	6447.13	763.29
	6355.46	753.39	195.84	780.61	418.66	133.42	7614.06	810.70	6126.66	836.29
	7839.04	767.17	194.43	777.57	417.50	135.33	7394.20	794.27	5834.17	834.02
LC0001	3793.20	788.70	117.46	1337.29	508.96	120.40	4360.58	864.41	5105.52	986.42
	3739.24	789.77	122.79	1327.61	520.26	129.30	4173.15	858.65	4912.17	1001.63
	3711.31	771.60	117.81	1338.57	504.40	137.91	4043.82	892.60	4815.97	1005.57
LC0002	3094.38	459.12	124.30	578.26	581.83	77.89	2905.07	674.92	3338.00	1031.81
	2885.14	350.00	101.07	497.19	494.96	84.28	2729.12	606.17	2975.18	968.33
	2743.78	367.64	94.09	503.63	409.86	92.49	2912.24	778.11	3204.61	1142.27
LC0003	3498.98	645.95	105.87	827.74	328.88	114.14	3942.32	954.21	4346.65	833.12
	3544.10	650.95	107.03	837.41	384.06	115.08	3900.69	950.83	4300.65	842.99
	3549.60	660.42	107.69	839.01	391.03	115.23	3897.54	950.59	4318.44	850.49
LC0004	3525.00	768.91	170.46	950.57	429.46	128.70	3672.54	677.00	3099.01	581.63
	3726.37	785.35	164.91	930.43	432.35	137.36	4201.58	885.11	4377.48	856.88
	3196.64	715.17	150.09	851.46	434.83	145.50	4236.61	883.70	4297.29	813.45
LC0005	1939.43	388.39	127.33	981.30	(0) (0)	60.54	2984.93	929.19	3904.69	356.96
	1859.11	376.88	126.18	968.42	(0) (0)	61.33	3007.47	932.61	3926.94	325.40
	1900.29	381.98	124.46	961.18	(0) (0)	62.38	3028.40	943.39	3934.22	346.15
LC0006	4404.99 (440,49)	815.45	219.24	971.51	489.77 (4897,7)	179.70	4459.66	436.15	4466.02	1039.00 (4825,36)
	4522.59	793.44	205.72	872.96	473.98	153.59	4204.35	404.58	4072.67	918.32
	4393.72	790.23	201.32	4250.78 (4250,78)	453.14	161.62	3968.58	404.69	4150.36	822.11
LC0007	3937.55	1124.01	60.99 (0)	1374.40	563.36	186.45	3631.96	1301.72	4584.14	767.81
	3865.31	1130.91	65.83 (0)	1345.14	546.03	199.64	3598.90	1371.20	4651.27	819.76
	3901.44	1099.77	64.65 (0)	1358.63	548.81	201.00	3570.90	1407.88	4541.96	807.47
LC0008	3734.56	815.94	135.84	948.82	493.32	145.44	4673.34	925.88	3961.84	764.86
	3756.33	812.75	127.42	964.92	518.22	145.45	4739.11	937.93	4109.32	799.34
	3719.01	798.05	118.31	1030.32	543.80	143.45	4695.20	939.21	4166.41	814.35
LC0009	3154.24	577.56	159.08	822.42	395.58	100.99	3845.64	699.17	4222.00	1584.03
	3244.71	576.65	160.32	863.66	408.41	101.26	3928.15	712.19	4316.73	1654.84
	3229.38	577.37	157.82	875.43	405.46	96.30	3870.90	693.67	4329.07	1610.41
LC0010	3128.36	1043.09	53.20 (0)	1421.97	687.13	222.14	3669.95	1215.71	4782.27	1081.71
	3053.47	1032.08	54.86 (0)	1387.53	655.33	186.00	3677.56	1111.24	4762.32	1001.77
	3047.82	1007.50	56.92 (0)	1379.14	700.12	188.68	3388.66	1231.50	4556.05	1036.15
LC0011	3370.03	619.29	97.57	727.32	256.02	75.34	4427.71	821.66	4763.19	1044.45
	3209.40	597.50	98.68	743.71	249.50	71.54	3999.60	745.26	4436.49	788.66
	3123.77	578.46	95.47	737.61	253.49	71.55	3743.51	726.88	4421.48	949.57
LC0012	1753.64	659.72	179.81	735.21	484.85	107.45	3394.04	610.02	3464.69	1296.36
	1779.34	568.86	164.52	658.48	417.18	104.85	3164.16	594.77	3244.22	1242.05
	2196.94	598.27	178.18	719.95	453.14	110.80	3728.09	630.27	3842.07	1324.39

	Sample A - Method 1					Sample B - Method 1				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP	DIBP	BBP	DEHP	DNOP	DINP
Level	III	II	I	II	I	I	III	II	III	II
LC0000	6795.41 h**	766.75	198.52	783.84	413.91	135.39	7777.96 G**, h**	793.99	6135.99 h**	811.20
LC0001	3747.92	783.36	119.35	1334.49	511.21	129.20	4192.52	871.89	4944.55	997.87
LC0002	2907.77	392.25	106.48	526.36	495.55	84.89	2848.81	686.40	3172.59	1047.47
LC0003	3530.89	652.44	106.87	834.72	367.99	114.82	3913.52	951.88	4321.91	842.20
LC0004	3482.67	756.48	161.82	910.82	432.21	137.19	4036.91	815.27	3924.59	750.65
LC0005	1899.61	382.42	125.99	970.30	0.00 G*, h**	61.41	3006.93	935.06	3921.95	342.84 h*
LC0006	4440.44	799.71	208.76	2031.75 h**	472.30	164.97	4210.87	415.14	4229.68	926.47
LC0007	3901.43	1118.23 h*	63.82	1359.39	552.74	195.69	3600.59	1360.27 h*	4592.46	798.35
LC0008	3736.63	808.91	127.19	981.36	518.45	144.78	4702.55	934.34	4079.19	792.85
LC0009	3209.44	577.19	159.07	853.84	403.15	99.52	3881.56	701.67	4289.27	1616.43 h**
LC0010	3076.55	1027.56	54.99	1396.21	680.86	198.94	3578.72	1186.15	4700.21	1039.88
LC0011	3234.40	598.42	97.24	736.21	253.00	72.81	4056.94	764.60	4540.39	927.56
LC0012	1909.97	608.95	174.17	704.55	451.72	107.70	3428.76	611.69	3516.99	1287.60

	Sample A - Method 1					Sample B - Method 1				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP	DIBP	BBP	DEHP	DNOP	DINP
Level	III	II	I	II	I	I	III	II	III	II
LC0000	907.51 C**, k**	13.16	5.92	8.35	7.24	2.00	486.87 k**	16.85	306.59	41.51
LC0001	41.63	10.20	2.99	5.99	8.16	8.75	159.26	18.17	147.47	10.11
LC0002	176.39	58.57 C*, k**	15.82 C*, k**	45.06	85.99 C**	7.32	103.72	86.54 k*	183.52	88.03
LC0003	27.77	7.35	0.92	6.10	34.05	0.59	24.99	2.03	23.19	8.71
LC0004	267.39	36.71	10.53	52.39	2.68	8.40	316.04	119.75 C*, k**	716.10 C**, k**	147.98 k**
LC0005	40.16	5.77	1.45	10.19	0.00	0.92	21.74	7.41	15.38	16.03
LC0006	71.37	13.73	9.34	1922.36 C**, k*	18.37	13.37	245.60	18.19	208.33	108.67
LC0007	36.12	16.35	2.52	14.65	9.31	8.04	30.57	53.92	55.12	27.15
LC0008	18.75	9.54	8.77	43.16	25.24	1.15	33.50	7.36	105.56	25.38
LC0009	48.42	0.48	1.25	27.84	6.72	2.79	42.28	9.51	58.58	35.79
LC0010	44.96	18.22	1.86	22.69	23.05	20.14 C**, k**	164.65	65.35	125.25	40.10
LC0011	125.02	20.43	1.63	8.28	3.29	2.19	345.69	50.26	193.10	129.31 k**
LC0012	248.85	46.36 k*	8.40	40.62	33.86	2.98	283.57	17.81	302.34	41.86

	Sample C - Method 1					Sample D - Method 1					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	156.17	6297.83	152.15	873.49	5286.61	661.62	5928.00	961.00	236.60	6263.97	632.21
	158.02	6776.11	158.00	926.13	5925.57	631.11	5490.62	938.01	231.64	5770.47	654.98
	156.07	6553.28	158.15	920.77	5148.31	641.91	5575.82	962.39	234.36	5834.89	671.19
LC0001	160.43	4202.72	222.82	1037.11	4702.14	717.00	4669.37	1050.02	194.73	5113.62	550.33
	182.44	4456.32	252.72	1142.64	4996.97	814.34	5142.69	1012.83	179.37	4745.09	545.60
	171.98	4234.75	246.41	1124.20	4637.84	732.55	5228.14	1041.21	191.36	5318.82	536.80
LC0002	24.79	2794.50	54.59	1013.93	3995.32	482.21	1985.37	493.15	102.62	4968.25	702.28
	22.27	2988.61	49.36	932.92	4262.92	367.04	1772.46	524.11	131.72	5419.89	805.84
	35.90	2635.85	72.15	997.51	3856.43	401.98	1649.60	569.71	86.90	5178.17	878.06
LC0003	119.85	4342.86	165.96	1061.57	4639.00	619.43	3642.27	668.32	229.10	5078.25	609.53
	120.90	4345.35	165.53	986.43	4661.92	608.41	3564.07	661.01	224.00	5027.62	595.39
	117.18	4275.75	165.03	974.12	4555.56	611.59	3539.19	644.87	241.27	5015.58	594.76
LC0004	139.46	4032.12	194.56	1091.18	4783.31	650.98	3518.31	803.02	214.89	4806.72	620.64
	156.08	4323.80	178.55	1149.30	5042.97	648.41	3452.69	785.37	225.23	4813.60	602.57
	143.09	4092.41	157.01	1050.90	4570.07	651.85	3333.53	768.51	214.85	5227.73	692.23
LC0005	56.13	3317.49	133.98	5112.75	4237.93	367.69	1868.04	756.12	204.36	4276.50	633.74
	56.49	3271.81	147.42	5014.65	4221.85	368.67	1867.43	757.85	205.29	4755.99	720.38
	56.87	3285.21	151.54	5074.80	4229.25	381.08	1915.35	761.50	206.20	4846.94	656.86
LC0006	154.79	2028.43	235.98	867.87	4326.21	643.71	3825.76	1014.35	122.49	4358.87	552.80 (5528)
	165.24	1953.29	234.13	858.01	4248.05	613.33	3746.85	935.99	117.73	4257.49	472.44
	154.49	1882.10	238.66 (465,23)	836.86	4127.67	558.50	3460.57	892.21	102.43	4202.79	475.58
LC0007	175.32	4790.74	402.19	2229.92	5017.88	675.32	3394.20	788.10 (0)	346.35	4469.54	505.00
	183.19	4869.37	395.47	2233.14	5135.41	716.34	3424.24	849.72 (0)	350.63	4585.80	522.78
	185.43	4814.50	394.17	2244.12	5087.98	707.50	3354.00	819.07 (0)	337.75	4446.13	513.78
LC0008	166.96	4507.36	181.20	825.75	4105.18	698.73	3755.71	826.03	249.33	3714.80	557.31
	162.03	4458.04	177.85	836.64	4044.76	686.07	3704.17	845.46	251.26	4092.87	629.58
	162.01	4471.37	177.85	823.08	4040.18	688.57	3698.26	827.09	245.83	3735.64	569.09
LC0009	112.77	3853.07	178.16	836.58	7930.96	495.08	3129.72	768.24	171.96	4071.61	1249.19
	112.83	3981.73	182.83	851.31	8041.80	518.28	3199.73	765.08	174.55	4014.19	1273.58
	114.02	4051.94	188.21	846.76	8266.40	506.88	3223.01	762.83	171.17	4051.63	1358.35
LC0010	202.46	4332.38	479.82	2231.91	5493.11	811.91	3490.63	766.40 (0)	338.34	4535.07	625.65
	202.34	4223.90	492.81	2007.80	5153.82	853.11	3494.90	823.85 (0)	332.73	4658.03	601.40
	207.83	4297.72	515.09	2053.07	5280.22	816.77	3536.14	776.55 (0)	336.44	4932.72	569.22
LC0011	72.29	4420.00	104.39	976.52	6015.97	406.76	3070.35	546.59	110.03	4751.97	858.52
	75.53	4404.96	99.32	1015.05	5851.12	387.50	3019.53	552.74	113.57	3823.19	911.14
	77.17	4272.88	89.55	1009.23	6348.62	412.22	3090.55	537.67	106.63	4733.61	820.65
LC0012	168.41	3119.75	189.46	699.47	4943.05	359.95	2672.76	580.44	202.66	3426.74	744.62
	160.78	2966.49	183.13	672.54	4715.60	354.21	2764.22	596.68	206.66	3305.05	755.30
	171.38	3166.02	195.93	719.88	5033.25	339.26	2736.92	592.10	203.55	3248.73	748.03

	Sample C - Method 1					Sample D - Method 1					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	156.75	6542.41 h*	156.10	906.80	5453.49	644.88	5664.81 h*	953.80	234.20	5956.44 h*	652.80
LC0001	171.62	4297.93	240.65	1101.32	4778.98	754.63	5013.40	1034.69	188.49	5059.18	544.24
LC0002	27.65 h*	2806.32	58.70	981.45	4038.22	417.08	1802.48	528.99	107.08	5188.77	795.39
LC0003	119.31	4321.32	165.50	1007.37	4618.83	613.14	3581.84	658.06	231.45	5040.48	599.89
LC0004	146.21	4149.44	176.71	1097.13	4798.79	650.41	3434.84	785.63	218.32	4949.35	638.48
LC0005	56.50	3291.50	144.32	5067.40 G**, h**	4229.68	372.48	1883.61	758.49	205.28	4626.48	670.33
LC0006	158.17	1954.61 h*	236.26	854.25	4233.98	605.18	3677.73	947.52	114.21	4273.05	500.27
LC0007	181.31	4824.87	397.28	2235.73 G**	5080.42	699.72	3390.81	818.96	344.91	4500.49	513.85
LC0008	163.67	4478.93	178.97	828.49	4063.37	691.12	3719.38	832.86	248.81	3847.77	585.33
LC0009	113.21	3962.25	183.06	844.88	8079.72 G**, h**	506.75	3184.15	765.38	172.56	4045.81	1293.71 G**, h**
LC0010	204.21	4284.66	495.91 h**	2097.59	5309.05	827.26	3507.23	788.93	335.84	4708.61	598.75
LC0011	75.00	4365.95	97.75	1000.27	6071.91	402.16	3060.15	545.67	110.08	4436.26	863.44
LC0012	166.86	3084.08	189.51	697.29	4897.30	351.14	2724.63	589.74	204.29	3326.84 h*	749.32

	Sample C - Method 1					Sample D - Method 1					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	1.10	239.33 k**	3.42	28.96	414.63 k**	15.47	231.87 k*	13.69	2.48	268.27	19.58
LC0001	11.01 k**	138.10	15.76	56.36	191.50	52.29 k*	300.99 C*, k**	19.43	8.07	290.71	6.87
LC0002	7.25	176.68	11.94	42.82	206.62	59.06 k**	169.88	38.51	22.74 C**, k**	226.01	88.36 C*, k**
LC0003	1.92	39.49	0.46	47.34	55.98	5.67	53.79	12.00	8.87	33.26	8.35
LC0004	8.74	153.98	18.85 k*	49.47	236.83	1.79	93.68	17.26	5.99	241.11	47.42
LC0005	0.37	23.48	9.18	49.47	8.05	7.46	27.49	2.75	0.92	306.48	44.86
LC0006	6.12	73.17	2.28	15.84	100.01	43.19	192.16	61.88 C**, k**	10.48	79.20	45.51
LC0007	5.31	40.33	4.31	7.45	59.12	21.59	35.24	30.81	6.56	74.80	8.89
LC0008	2.85	25.51	1.93	7.19	36.28	6.70	31.60	10.92	2.75	212.52	38.77
LC0009	0.71	100.86	5.03	7.54	170.90	11.60	48.56	2.71	1.77	29.15	57.30
LC0010	3.13	55.40	17.84 k*	118.51 C**, k**	171.48	22.52	25.13	30.66	2.85	203.59	28.31
LC0011	2.48	80.95	7.54	20.77	253.42	12.99	36.59	7.58	3.47	531.01 C*, k**	45.45
LC0012	5.47	104.44	6.40	23.74	163.70	10.68	46.95	8.37	2.10	90.98	5.46

	Sample E – Method 1				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**
Level	**III**	**II**	**I**	**II**	**I**
LC0000	5688.27	836.26	220.72	844.80	497.53
	5543.91	816.34	221.02	852.83	522.19
	5385.62	821.17	223.07	869.88	533.65
LC0001	4750.44	923.39	143.56	1033.73	576.33
	5260.81	903.59	145.00	946.80	565.96
	5355.07	1020.83	161.02	1009.86	605.66
LC0002	3037.61	449.59	95.37	685.39	526.09
	2500.16	472.28	132.04	969.72	482.34
	2998.28	416.25	111.94	857.75	430.14
LC0003	4229.40	784.92	127.80	1014.02	478.67
	4265.30	781.61	126.46	1006.92	487.90
	4387.61	802.35	123.03	1012.32	499.38
LC0004	3599.63	803.14	179.96	991.35	529.79
	3746.04	841.64	184.51	999.33	517.06
	3843.31	808.10	177.13	1015.94	608.02
LC0005	2256.37	470.25	148.26	1107.73	(0) (0)
	2405.89	498.04	147.51	1124.16	(0) (0)
	2544.24	530.46	151.96	1148.11	(0) (0)
LC0006	4712.06	914.11	245.81	1074.13	574.13 (4215,65)
	4519.44	869.95	229.44	998.89	537.12
	4487.38	861.01	221.70	943.26 (4326,56)	500.83
LC0007	3406.55	968.58	58.15 (0)	1110.49	841.70
	3396.50	970.28	52.56 (0)	1113.31	927.32
	3377.75	1032.04	64.27 (0)	1190.84	884.91
LC0008	4224.96	902.28	138.94	1068.30	552.11
	4295.64	917.82	140.31	1079.65	536.15
	4275.99	917.02	139.18		548.12
LC0009	3500.62	632.03	172.04	956.34	457.78
	3732.07	651.07	176.51	974.40	446.01
	3664.93	651.55	175.40	979.70	464.25
LC0010	3689.68	1064.37	52.76 (0)	1528.35	614.43
	3735.99	1075.24	52.79 (0)	1489.93	637.73
	3845.13	1074.55	58.05 (0)	1426.75	597.91
LC0011	3174.20	611.60	100.83	834.58	297.94
	3325.48	631.04	101.82	831.66	279.60
	3293.78	626.69	102.93	828.71	287.28
LC0012	2016.05	638.04	184.80	735.71	479.40
	2013.94	615.86	182.45	727.75	458.44
	2075.45	666.11	185.93	745.68	498.14

	Sample E - Method 1				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**
Level	**III**	**II**	**I**	**II**	**I**
LC0000	5539.27	824.59	221.60	855.84	517.79
LC0001	5122.11	949.27	149.86	996.80	582.65
LC0002	2845.35	446.04	113.12	837.62	479.52
LC0003	4294.10	789.62	125.76	1011.09	488.65
LC0004	3729.66	817.62	180.53	1002.21	551.62
LC0005	2402.17	499.58	149.24	1126.66	0.00 G*, h**
LC0006	4572.96	881.69	232.32	1005.43	537.36
LC0007	3393.60	990.30	58.33	1138.22	884.65 h*
LC0008	4265.53	912.37	139.48	1073.97	545.46
LC0009	3632.54	644.88	174.65	970.15	456.01
LC0010	3756.93	1071.39	54.53	1481.67 G*, h**	616.69
LC0011	3264.48	623.11	101.86	831.65	288.27
LC0012	2035.15	640.00	184.39	736.38	478.66

	Sample E - Method 1				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**
Level	**III**	**II**	**I**	**II**	**I**
LC0000	151.38	10.39	1.28	12.81	18.46
LC0001	325.31 k**	62.75 C*, k**	9.69	44.91	20.59
LC0002	299.59 k*	28.19	18.36 C**, k**	143.23 C**, k**	48.04 k*
LC0003	82.94	11.14	2.46	3.71	10.38
LC0004	122.66	20.95	3.72	12.54	49.25 k*
LC0005	143.97	30.14	2.38	20.31	0.00
LC0006	121.53	28.43	12.31 C*, k*	65.68	36.65
LC0007	14.62	36.16	5.86	45.60	42.81
LC0008	36.48	8.75	0.73	8.03	8.30
LC0009	119.08	11.14	2.33	12.25	9.25
LC0010	79.81	6.09	3.05	51.30	20.01
LC0011	79.78	10.20	1.05	2.93	9.21
LC0012	34.92	25.18	1.77	8.98	19.86

Tables A, B, C (Method 2): original values, cell means and cell standard deviations, respectively.

	Sample A - Method 2					Sample B – Method 2				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	2241.67	528.54	100.12	638.47	272.52	113.56	3120.76	846.54	3306.80	607.46
	2317.17	537.79	102.64	653.97	293.52	110.47	2937.44	829.30	3203.44	604.85
	2220.07	519.60	100.76	646.43	285.13	108.67	2887.17	830.93	3214.16	595.81
LC0001	4440.76	513.77	55.42	1043.56	418.35	101.78	4785.08	1132.99	3887.04	815.95
	4231.45	489.75	55.65	986.78	409.14	97.70	5148.11	1261.14	3589.58	760.40
	4435.05	522.75	57.76	1055.55	425.33	92.67	5022.63	1211.50	3556.48	726.12
LC0002	2637.32	351.21	60.46	501.28	434.14	88.62	2889.27	466.93	3084.71	667.85
	2808.23	331.58	60.53	501.75	378.84	61.07	2700.34	569.54	2671.60	630.21
	3242.14	405.48	59.74	475.66	471.61	81.73	3210.67	535.26	2738.77	767.17
LC0003	2186.46	402.07	59.76	541.14	327.02	82.20	2156.23	690.76	3326.53	660.89
	2148.59	386.57	48.58	529.45	305.35	76.78	2096.45	677.62	3241.04	654.80
	2090.53	377.78	47.10	523.54	284.68	74.01	2127.11	661.28	3165.90	600.18
LC0004	2003.36	454.07	48.63	945.37	7.36	66.25	2766.30	887.19	4635.48	653.91
	1315.60	326.50	57.18	611.75	153.23	58.22	2079.41	565.68	2849.85	554.41
	1169.61	312.56	49.93	648.33	242.74	55.60	2019.58	576.31	2884.40	610.65
LC0005	2118.00	318.46	62.78	542.54	(0) (0)	27.74	1728.58	406.16	3139.10	321.84
	2027.72	317.96	60.84	534.50	(0) (0)	28.33	1740.81	412.92	3175.75	301.79
	1957.47	306.44	60.75	523.82	(0) (0)	28.30	1734.63	413.99	3173.24	289.78
LC0006	2606.13	552.80	137.22	683.47	400.67	130.35	3231.16	386.56	3268.16	780.10
	2521.76	534.71	122.51	630.23	373.18	131.01	3045.22	371.14	3234.43	730.02
	2684.24	568.05	128.34	670.79	393.80	132.84	3328.83	397.94	3533.87	810.99
LC0007	2584.86	1113.38	51.27 (0)	1113.71	553.47	153.91	2106.42	1109.43	3404.38	700.26
	2572.80	1158.90	52.16 (0)	1115.77	572.53	151.30	2120.06	1167.97	3452.61	754.23
	2531.39	1109.04	52.15 (0)	1103.39	557.19	146.58	2114.34	1125.45	3465.89	713.64
LC0008	2623.05	546.44	71.34	689.41	362.72	119.53	2849.71	799.39	3913.01	807.72
	2642.42	541.54	73.08	679.32	362.53	116.77	2816.77	790.84	3975.54	826.76
	2657.99	554.32	73.95	689.62	360.41	117.25	2788.86	785.40	3967.26	846.59
LC0009	2484.96	479.16	82.35	729.28	340.88	100.80	2432.72	755.28	3893.93	784.30
	2653.80	553.86	86.60	788.81	355.87	113.40	2582.22	780.58	4159.10	852.53
	2699.21	540.76	84.01	757.73	326.54	110.60	2643.57	807.30	4088.27	827.53
LC0010	2882.04	801.44	35.14 (0)	1017.45	605.00	143.17	2175.67	1173.50	3952.48	1077.04
	2995.60	854.07	39.99 (0)	1173.98	607.34	131.32	2116.69	1046.16	3850.87	1007.78
	2895.28	807.22	37.62 (0)	1108.59	674.84	118.55	2209.15	1003.87	3879.59	950.82
LC0011	2674.51	468.86	102.07	640.21	452.25	98.94	3240.18	1037.81	4313.37	807.27
	2688.10	465.79	101.66	628.36	503.91	99.00	3152.41	1014.70	4199.56	1079.05
	2777.85	479.92	102.02	741.70	495.82	100.22	3233.19	1014.23	4213.46	848.97
LC0012	3174.07	674.43	98.68	701.41	266.56	118.02	271.34	716.12	3743.37	689.67
	3010.62	651.33	98.78	717.15	258.24	115.86	266.61	709.98	3676.68	690.76
	2955.59	629.05	95.74	696.86	263.50	119.39	263.68 (2636,85)	707.25	3586.22	686.01

	Sample A - Method 2					Sample B - Method 2				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	2259.64	528.65	101.17	646.29	283.72	110.90	2981.79	835.59	3241.47	602.71
LC0001	4369.09 G**, h**	508.75	56.27	1028.63	417.61	97.39	4985.27 h*	1201.88	3677.70	767.49
LC0002	2895.90	362.75	60.24	492.90	428.20	77.14	2933.43	523.91	2831.69	688.41
LC0003	2141.86	388.81	51.81	531.37	305.68	77.66	2126.60	676.55	3244.49	638.62
LC0004	1496.19	364.38	51.91	735.15	134.44	60.02	2288.43	676.39	3456.58	606.32
LC0005	2034.40	314.29	61.46	533.62	0.00 h*	28.12 h*	1734.67	411.02	3162.70	304.47 h**
LC0006	2604.05	551.85	129.36 h*	661.50	389.22	131.40	3201.74	385.22	3345.49	773.70
LC0007	2563.01	1127.10 G*, h**	51.86	1110.96	561.07	150.60	2113.61	1134.28	3440.96	722.71
LC0008	2641.15	547.43	72.79	686.12	361.89	117.85	2818.45	791.87	3951.94	827.02
LC0009	2612.66	524.59	84.32	758.61	341.10	108.27	2552.84	781.05	4047.10	821.45
LC0010	2924.31	820.91	37.58	1100.01	629.06	131.01	2167.17	1074.51	3894.31	1011.88
LC0011	2713.49	471.52	101.92	670.09	483.99	99.39	3208.59	1022.24	4242.13	911.76
LC0012	3046.76	651.61	97.74	705.14	262.76	117.76	267.21 h*	711.12	3668.76	688.81

	Sample A - Method 2					Sample B - Method 2				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	50.98	9.10	1.31	7.75	10.57	2.47	122.95	9.52	56.83	6.11
LC0001	119.23	17.06	1.29	36.74	8.12	4.56	184.37	64.62	182.05	45.33
LC0002	311.80 C**, k*	38.28	0.44	14.93	46.67	14.33 C**, k**	258.01 C*	52.24	221.68	70.75
LC0003	48.32	12.30	6.92 k**	8.96	21.17	4.16	29.89	14.76	80.37	33.43
LC0004	445.24 C**, k**	77.99 C**, k**	4.61	182.97 C**, k**	118.81 C**, k**	5.55	414.93 C**, k**	182.63 C**, k**	1021.11 C**, k*	49.89
LC0005	80.47	6.80	1.14	9.39	0.00	0.33	6.12	4.25	20.48	16.20
LC0006	81.26	16.69	7.41 C*, k**	27.81	14.31	1.29	144.08	13.45	164.02	40.86
LC0007	28.05	27.62	0.51	6.63	10.10	3.72	6.85	30.26	32.36	28.11
LC0008	17.50	6.45	1.33	5.88	1.28	1.48	30.46	7.05	33.96	19.43
LC0009	112.89	39.89	2.14	29.77	14.66	6.62	108.45	26.01	137.30	34.52
LC0010	62.09	28.86	2.42	78.62 C*	39.67	12.31 k*	46.82	88.30 C*	52.38	63.21
LC0011	56.15	7.43	0.22	62.30	27.79	0.73	48.79	13.48	62.09	146.37 C**, k**
LC0012	113.64	22.69	1.73	10.64	4.21	1.78	3.87	4.54	78.87	2.49

	Sample C . Method 2					Sample D . Method 2					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	III	I	III	I
LC0000	123.80	3137.01	148.48	679.44	3073.39	513.99	2832.21	542.38	232.80	3355.52	436.17
	121.42	3129.63	143.21	697.04	3095.81	508.80	2779.44	534.82	232.58	3409.30	431.14
	123.61	3141.73	143.63	695.04	3080.72	507.20	2769.76	534.42	229.88	3422.77	421.35
LC0001	101.72	2824.63	170.73	838.29	3842.28	736.46	4878.42	851.75	143.18	4384.75	588.53
	99.97	2827.97	159.24	821.98	3739.55	802.79	4830.71	816.76	145.90	4299.49	570.87
	93.85	3044.83	171.01	872.78	4169.32	739.65	5084.37	916.84	151.12	4556.78	585.17
LC0002	71.48	3470.13	100.10	1218.05	4182.84	421.76	1831.01	538.79	94.87	4913.84	656.74
	78.22	3326.63	78.19	1093.90	3879.20	452.14	2032.27	493.12	107.72	4715.49	687.95
	92.75	3655.60	93.34	1166.29	4058.50	386.36	2135.65	576.37	101.19	4342.63	735.74
LC0003	75.46	3286.99	109.18	785.60	3348.87	391.75	2313.27	333.62	152.13	4052.31	454.43
	100.70	4070.83	147.80	794.72	4237.50	395.80	2338.07	343.51	149.20	3984.81	458.28
	75.01	3175.35	106.40	794.73	3439.33	385.03	2289.22	336.28	147.08	3781.18	419.40
LC0004	74.37	3590.12	106.00	787.97	3811.66	303.41	2161.60	353.87	147.79	3801.04	336.44
	75.23	2698.90	80.73	719.87	3270.51	281.23	1878.25	353.18	134.53	4320.69	380.01
	77.10	2569.23	84.14	704.51	3283.18	275.48	1791.36	360.41	125.22	4342.39	413.65
LC0005	25.98	3137.52	32.69	3266.35	2969.11	188.06	1341.57	153.92	55.83	1374.71	213.66
	26.42	2927.70	30.63	3122.87	2952.03	189.76	1343.71	152.84	54.80	1461.05	235.49
	26.08	2806.46	29.93	3044.93	2725.70	195.12	1377.90	157.92	57.46	1552.38	227.23
LC0006	108.64	1800.61	151.81	744.46	3646.57	374.39	2621.69	694.89	109.28	4062.03	438.64
	107.43	1735.03	154.64	726.17	3498.98	387.54	2733.00	644.68	101.29	3770.04	404.98
	110.95	1801.84	147.04	744.47	3586.30	376.08	2790.21	698.82	106.73	4061.87	440.46
LC0007	245.22	3293.74	355.68	2840.00	4093.20	673.23	3097.09	659.03 (0)	312.60	4707.92	379.06
	244.28	3284.43	354.24	2848.34	4140.26	698.16	3079.99	683.07 (0)	319.06	4709.59	377.70
	245.97	3236.44	355.15	2833.36	4123.86	705.30	3162.13	682.01 (0)	307.87	4714.12	379.74
LC0008	126.45	3736.90	165.26	865.71	4050.15	518.97	2772.25	446.64	192.07	3921.07	567.13
	120.10	3624.24	158.70	849.80	3903.19	507.21	2780.77	462.00	191.13	3774.46	559.56
	117.72	3453.44	147.66	798.26	3650.38	515.46	2767.82	472.33	126.54	4043.89	567.02
LC0009	130.93	3840.39	180.43	779.87	4048.58	536.95	2786.33	467.54	182.35	3690.44	591.87
	121.53	3892.87	185.84	766.90	4018.59	525.92	2762.08	452.36	182.89	3397.00	597.84
	124.33	3868.43	178.86	745.92	3917.42	518.32	2763.66	454.93	183.29	3368.20	587.56
LC0010	161.83	3602.30	378.24	2556.11	5138.56	586.99	2601.74	537.98 (0)	262.97	4383.23	519.61
	172.64	3475.20	406.73	2475.59	5177.34	536.24	2625.66	607.92 (0)	264.05	4434.90	539.43
	177.38	3522.26	382.04	2468.31	5012.66	516.37	2558.72	561.88 (0)	260.91	4368.60	496.11
LC0011	72.61	4211.51	116.38	1638.37	4931.82	516.92	2541.24	635.25	150.39	4222.85	1075.46
	80.15	4218.30	114.03	1448.47	4844.95	546.31	2636.79	647.73	146.10	4355.48	1125.04
	68.50	3628.86	105.20	1473.15	4591.54	542.70	2636.75	621.42	144.63	4509.49	756.11
LC0012	141.31	4406.40	170.33	577.49	4181.05	1254.57	3120.79	508.77	203.06	2769.96	560.26
	134.17	4395.30	184.55	598.65	4025.05	1192.16	3202.49	519.19	202.72	2821.17	525.43
	122.72	4379.96	177.66	588.72	4164.59	1177.49	3335.12	507.09	205.27	2859.48	503.25

	Sample C - Method 2					Sample D - Method 2					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	122.94	3136.12	145.11	690.51	3083.30	509.99	2793.80	537.21	231.75	3395.86	429.55
LC0001	98.51	2899.14	166.99	844.35	3917.05	759.63	4931.17 G*, h**	861.78 h*	146.73	4413.67	581.52
LC0002	80.82	3484.12	90.54	1159.41	4040.18	420.09	1999.64	536.10	101.26	4657.32	693.48
LC0003	83.72	3511.05	121.13	791.68	3675.23	390.86	2313.52	337.81	149.47	3939.43	444.04
LC0004	75.57	2952.75	90.29	737.45	3455.12	286.71	1943.74	355.82	135.85	4154.71	376.70
LC0005	26.16	2957.23	31.08	3144.71 h*	2882.28	190.98	1354.39	154.89 h*	56.03	1462.71 G*, h**	225.46
LC0006	109.01	1779.16 h**	151.16	738.37	3577.29	379.34	2714.96	679.47	105.77	3964.65	428.03
LC0007	245.16 G*, h**	3271.54	355.02 h*	2840.57	4119.11	692.23	3113.07	674.71	313.17 h*	4710.54	378.83
LC0008	121.42	3604.86	157.21	837.92	3867.91	513.88	2773.61	460.33	169.91	3913.14	564.57
LC0009	125.60	3867.23	181.71	764.23	3994.86	527.06	2770.69	458.28	182.84	3485.22	592.42
LC0010	170.62	3533.25	389.00 h*	2500.01	5109.52 h*	546.53	2595.37	569.26	262.64	4395.58	518.38
LC0011	73.75	4019.56	111.87	1520.00	4789.44	535.31	2604.93	634.80	147.04	4362.61	985.54 h**
LC0012	132.73	4393.89	177.51	588.29	4123.57	1208.08 G*, h**	3219.47	511.68	203.68	2816.87	529.65

	Sample C - Method 2					Sample D - Method 2					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	1.32	6.10	2.93	9.64	11.43	3.55	33.61	4.49	1.63	35.58	7.54
LC0001	4.14	126.18	6.72	25.94	224.43	37.41	134.80	50.79 k**	4.04	131.06	9.38
LC0002	10.87	164.93	11.22	62.36	152.65	32.92	154.92 k**	41.69 k*	6.42	290.02 k*	39.79
LC0003	14.71 k**	487.98 k*	23.14 C*, k**	5.27	489.03 C**, k**	5.44	24.43	5.12	2.54	141.15	21.42
LC0004	1.40	555.77 C*, k**	13.71	44.42	308.84	14.75	193.61 k**	3.99	11.34 C**	306.47 k*	38.71
LC0005	0.23	167.49	1.44	112.32 k**	135.87	3.68	20.38	2.67	1.34	88.85	11.02
LC0006	1.79	38.22	3.84	10.56	74.21	7.15	85.70	30.19	4.08	168.54	19.98
LC0007	0.85	30.75	0.73	7.50	23.89	16.84	43.34	13.58	5.62	3.21	1.04
LC0008	4.51	142.72	8.90	35.26	202.21	6.03	6.58	12.93	37.56 C**, k**	134.89	4.34
LC0009	4.82	26.26	3.66	17.13	68.72	9.37	13.57	8.13	0.47	178.32	5.16
LC0010	7.97	64.26	15.47	48.73	86.09	36.42	33.92	35.55	1.60	34.83	21.69
LC0011	5.91	338.37	5.89	103.25 k*	176.80	16.03	55.15	13.16	3.00	143.45	200.23 C**, k**
LC0012	9.38	13.28	7.11	10.59	85.71	40.93 k*	108.17	6.56	1.38	44.91	28.74

	Sample E – Method 2				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP
Level	III	II	I	II	I
LC0000	2729.49	638.11	123.29	708.04	296.94
	2615.38	609.17	116.68	700.40	324.72
	2614.22	606.79	116.67	698.52	305.04
LC0001	5864.85	759.76	73.92	1189.39	397.92
	5713.22	742.41	72.33	1152.59	394.06
	5180.22	675.81	73.65	1201.91	406.03
LC0002	2906.95	554.00	134.94	704.03	489.43
	2626.58	524.67	138.90	730.64	477.41
	2998.26	594.26	89.34	661.93	374.28
LC0003	2365.72	436.91	56.71	566.20	295.10
	2318.33	424.49	54.41	555.38	298.92
	2390.56	437.71	55.08	560.74	289.23
LC0004	1813.50	467.93	73.03	759.70	294.68
	1647.27	432.91	77.14	777.34	399.32
	1577.49	424.74	79.91	800.55	418.49
LC0005	2003.78	352.22	73.19	585.91	(0) (0)
	2112.28	373.05	75.30	594.19	(0) (0)
	2090.44	358.17	70.76	574.38	(0) (0)
LC0006	2698.87	584.84	163.88	818.64	471.57
	2750.06	568.77	137.13	677.79	390.98
	2679.31	588.32	157.45	793.21	471.08
LC0007	2703.44	1105.65	42.87 (0)	1142.13	576.68
	2770.94	1135.90	46.12 (0)	1152.94	601.79
	2682.04	1109.98	43.04 (0)	1122.26	552.39
LC0008	2748.13	590.63	85.53	765.49	425.39
	2781.88	600.43	86.45	745.67	398.22
	2804.13	599.01	86.26	755.29	400.26
LC0009	2832.65	544.78	92.99	865.23	393.46
	2881.53	589.93	87.41	828.38	358.10
	2890.78	590.96	93.60	830.97	351.78
LC0010	2445.04	641.47	33.62 (0)	1315.32	638.53
	2452.75	636.74	36.99 (0)	1278.40	666.81
	2399.47	621.96	35.27 (0)	1263.71	626.19
LC0011	2713.76	477.98	97.07	741.60	515.75
	2735.55	482.37	96.31	720.29	532.04
	2740.24	482.94	98.04	740.92	519.62
LC0012	1770.09	754.20	105.90	829.32	308.45
	1731.58	760.83	105.52	816.93	328.91
	1639.55	747.43	103.22	846.22	317.31

	Sample E - Method 2				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP
Level	III	II	I	II	I
LC0000	2653.03	618.02	118.88	702.32	308.90
LC0001	5586.10 h**	725.99	73.30	1181.30	399.34
LC0002	2843.93	557.64	121.06	698.87	447.04
LC0003	2358.20	433.03	55.40	560.77	294.42
LC0004	1679.42	441.86	76.69	779.20	370.83
LC0005	2068.83	361.15	73.09	584.83	0.00 G*, h**
LC0006	2709.41	580.64	152.82 h*	763.21	444.55
LC0007	2718.80	1117.18 G*, h**	44.01	1139.11	576.96
LC0008	2778.05	596.69	86.08	755.48	407.96
LC0009	2868.32	575.22	91.33	841.53	367.78
LC0010	2432.42	633.39	35.29	1285.81 h*	643.84
LC0011	2729.85	481.10	97.14	734.27	522.47
LC0012	1713.74	754.15	104.88	830.82	318.22

	Sample E - Method 2				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP
Level	III	II	I	II	I
LC0000	66.22	17.44	3.82	5.04	14.29
LC0001	359.58 C**, k**	44.32 k**	0.85	25.64	6.11
LC0002	193.69 C**	34.94 k*	27.54 C**, k**	34.64	63.30 k*
LC0003	36.69	7.41	1.18	5.41	4.88
LC0004	121.25 C*	22.94	3.46	20.49	66.64 k**
LC0005	57.39	10.73	2.27	9.95	0.00
LC0006	36.53	10.43	13.97 C**	75.06 C*, k**	46.39
LC0007	46.40	16.36	1.83	15.56	24.70
LC0008	28.20	5.30	0.48	9.91	15.13
LC0009	31.24	26.37	3.41	20.57	22.46
LC0010	28.79	10.18	1.69	26.59	20.82
LC0011	14.13	2.72	0.87	12.11	8.51
LC0012	67.07	6.70	1.45	14.71	10.26

Tables A, B, C (Method 3): original values, cell means and cell standard deviations, respectively.

	Sample A - Method 3					Sample B - Method 3				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	3474.18	826.67	189.72	894.52	362.33	142.38	4487.92	741.03	4308.26	731.83
	3153.84	777.90	177.97	872.77	373.68	143.81	4565.35	721.54	4349.23	757.32
	3389.81	808.64	180.49	899.18	388.56	143.41	4752.22	709.38	4497.12	723.23
LC0001	3710.10	820.05	113.72	1303.80	538.28	178.02	6380.51	1051.50	6171.11	1432.15
	3500.12	849.23	119.16	1248.69	532.30	184.29	5746.67	948.41	5666.69	1467.22
	3893.69	938.25	120.75	1344.57	553.17	188.56	5780.39	1035.00	5612.94	1317.22
LC0002	2202.62	317.18	63.39	644.95	419.77	58.10	2773.06	759.95	2769.56	948.69
	2508.09	258.51	50.43	549.85	368.90	85.67	2761.33	708.73	2993.50	855.46
	2406.90	330.36	65.32	545.34	384.76	93.78	2825.67	731.24	2953.78	1043.75
LC0003	3735.77	699.66	135.41	741.92	325.49	158.42	4219.05	816.56	4099.12	680.16
	3742.20	707.51	136.22	740.59	322.97	151.64	4272.84	833.16	4221.62	698.92
	3787.41	710.67	134.84	737.47	317.00	150.34	4213.49	810.34	4131.42	679.49
LC0004	3163.15	694.33	141.22	801.05	470.86	174.03	4072.00	728.56	4223.08	866.91
	2898.19	651.13	140.41	745.38	532.65	199.22	3509.75	687.71	3707.98	825.00
	2827.71	647.92	139.37	782.86	566.25	114.58	3933.56	720.07	3811.67	1100.73
LC0005	3265.57	578.72	147.59	904.35	(0) (0)	76.72	4258.04	1442.82	5124.45	690.35
	3006.28	572.11	152.48	893.46	(0) (0)	78.32	4103.74	1409.57	5055.54	636.28
	2875.73	550.23	151.39	882.92	(0) (0)	79.72	4113.20	1420.25	5074.82	617.52
LC0006	4403.90	917.92	220.23	891.97	484.15	171.91	4454.00	439.24	4172.21	966.65
	4488.97	928.77	219.69	893.33	484.09	164.70	3982.25	397.76	3674.42	853.85
	4354.44	899.52	207.55	854.19	461.18	170.58	4295.64	423.30	3984.05	925.55
LC0007	3468.22	995.67	53.10 (0)	710.55	537.75	170.78	3412.88	1380.88	3898.61	824.22
	3375.65	1000.55	44.80 (0)	726.98	531.36	192.52	3413.72	1393.54	3822.40	885.98
	3397.28	988.28	43.75 (0)	722.65	559.18	187.33	3312.16	1382.74	3850.64	803.19
LC0008	3856.39	823.45	118.98	942.24	514.36	142.93	4689.47	897.10	4362.09	858.81
	3775.38	802.89	116.90	982.67	505.44	143.53	4671.22	892.44	4328.09	836.64
	3796.29	810.99	112.38	976.53	504.84	140.56	4697.22	898.93	4480.71	853.29
LC0009	3214.27	647.90 (0)	178.60	798.90	452.32	90.01	3755.51	803.73	4717.21	847.11
	3443.65	764.09 (0)	172.55	865.85	449.37	101.99	3773.19	799.06	4836.68	828.05
	3219.30	714.84 (0)	176.97	806.57	444.90	98.72	3824.44	811.17	4917.30	804.81
LC0010	3386.43	936.58	46.10 (0)	1275.25	627.34	211.66	3932.78	1293.00	4142.26	1004.00
	3308.87	916.77	47.31 (0)	1223.13	602.44	189.14	3969.93	1256.28	4263.76	978.45
	3522.18	918.38	49.29 (0)	1269.84	620.90	212.60	4131.22	1287.74	4164.27	1021.31
LC0011	2687.86	450.95	125.91	483.67	236.55	55.16	3647.45	628.43	3527.40	778.97
	2585.36	437.11	130.26	490.62	249.47	53.62	3658.35	624.11	3492.26	730.85
	2497.20	427.40	125.97	480.74	235.43	59.40	3801.16	665.93	3656.41	813.03
LC0012	3990.65	914.84	165.54	823.38	396.40	141.87	3822.10	737.58	3971.29	1051.29
	3810.28	864.49	157.93	781.49	384.16	142.23	3656.97	614.85	3859.34	1047.78
	3661.23	832.12	155.57	764.11	369.30	135.22	3771.81	734.93	3822.78	1051.70

	Sample A - Method 3					Sample B - Method 3				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	3339.28	804.41	182.73	888.82	374.86	143.20	4601.83	723.98	4384.87	737.46
LC0001	3701.30	869.18	117.88	1299.02 h*	541.25	183.62	5969.19 G*, h**	1011.64	5816.91 h*	1405.53 G*, h*
LC0002	2372.54	302.02 h*	59.71	580.05	391.15	79.18	2786.69	733.31	2905.61	949.30
LC0003	3755.13	705.95	135.49	739.99	321.82	153.47	4235.13	820.02	4150.72	686.19
LC0004	2963.01	664.46	140.33	776.43	523.25	162.61	3838.44	712.11	3914.24	930.88
LC0005	3049.19	567.02	150.48	893.58	0.00 G*, h**	78.25	4158.32	1424.21	5084.94	648.05
LC0006	4415.77 h*	915.41	215.82	879.83	476.47	169.06	4243.97	420.10	3943.56	915.35
LC0007	3413.72	994.83	47.22	720.06	542.76	183.54	3379.58	1385.72	3857.22	837.80
LC0008	3809.35	812.44	116.09	967.14	508.21	142.34	4685.97	896.15	4390.30	849.58
LC0009	3292.41	708.94	176.04	823.78	448.87	96.91	3784.38	804.66	4823.73	826.66
LC0010	3405.82	923.91	47.57	1256.07	616.89	204.46	4011.31	1279.01	4190.10	1001.26
LC0011	2590.14	438.49	127.38	485.01	240.48	56.06	3702.32	639.49	3558.69	774.28
LC0012	3820.72	870.48	159.68	789.66	383.29	139.77	3750.29	695.78	3884.47	1050.26

	Sample A - Method 3					Sample B - Method 3				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	166.04	24.66	6.19	14.10	13.16	0.74	135.88	15.96	99.35	17.73
LC0001	196.93	61.57 k*	3.69	48.12	10.75	5.30	356.61 C*, k**	55.38 k**	307.92 k**	78.46
LC0002	155.61	38.25	8.10 k*	56.25 k*	26.03	18.71 C**	34.26	25.67	119.49	94.15
LC0003	28.14	5.67	0.70	2.29	4.36	4.34	32.78	11.80	63.49	11.03
LC0004	176.87	25.92	0.93	28.39	48.38 C**, k**	43.46 C**, k**	292.95 k*	21.56	272.44 k*	148.58 C**, k**
LC0005	198.43	14.92	2.57	10.72	0.00	1.50	86.48	16.98	35.55	37.82
LC0006	68.05	14.79	7.17	22.21	13.25	3.83	240.08	20.92	251.35	57.09
LC0007	48.43	6.17	5.13	8.51	14.57	11.35	58.39	6.84	38.53	43.03
LC0008	42.06	10.36	3.38	21.79	5.33	1.57	13.35	3.35	80.12	11.54
LC0009	131.01	58.32 k*	3.13	36.64	3.74	6.19	35.80	6.11	100.67	21.18
LC0010	107.97	11.00	1.61	28.66	12.92	13.28	105.49	19.85	64.73	21.56
LC0011	95.42	11.84	2.50	5.08	7.80	2.99	85.77	23.00	86.43	41.29
LC0012	164.96	41.68	5.21	30.47	13.57	3.95	84.64	70.11 C*, k**	77.38	2.16

	Sample C - Method 3					Sample D - Method 3					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	174.25	5137.99	177.17	840.69	4572.03	729.05	3925.38	855.64	194.39	3940.13	525.70
	173.07	4571.15	178.02	821.95	4083.71	747.26	3948.21	779.43	224.52	3840.34	517.43
	178.14	4797.30	179.08	880.65	4122.40	820.82	4598.51	841.28	250.59	4442.05	574.14
LC0001	203.58	3402.92	266.86	1294.85	3650.92	842.24	3900.32	1049.32	147.35	5990.65	1006.26
	207.76	4495.88	257.10	1257.60	3941.63	787.88	3840.07	997.04	137.00	5528.15	929.12
	201.78	3919.90	244.23	1249.16	3823.06	797.69	4090.93	1000.89	132.17	5587.60	996.43
LC0002	58.48	3461.09	113.74	1154.68	3966.47	372.88	1825.65	514.79	190.29	5545.92	937.46
	59.77	3297.48	115.72	1221.97	4073.20	356.22	1653.86	508.79	167.57	5336.41	837.55
	35.83	3062.62	156.27	949.39	4023.75	300.64	1480.75	556.11	222.40	5475.13	950.04
LC0003	136.84	4299.09	155.23	815.89	4320.58	737.45	3713.61	769.13	199.87	4556.69	432.09
	136.68	4278.67	150.18	636.80	4137.63	685.98	3360.56	711.93	188.23	4234.97	514.77
	137.12	4320.71	150.63	682.48	4129.58	711.95	3565.93	734.94	188.26	4099.50	461.61
LC0004	128.37	3243.37	153.64	1069.22	3407.90	552.21	2806.27	704.58	209.08	3313.69	545.87
	128.82	3303.66	241.57	1421.88	5851.92	554.82	2955.50	688.12	181.58	7476.25	808.88
	131.43	2970.04	160.12	1265.05	4754.75	570.96	3153.53	752.15	206.97	8286.26	869.43
LC0005	57.55	4406.50	131.48	4364.50	4449.55	477.09	2311.90	934.09	337.40	1691.78	568.83
	57.15	4191.17	123.72	4430.12	4340.23	434.59	2140.81	877.73	312.15	1562.88	503.32
	57.32	4213.34	123.82	4447.90	4280.73	456.34	2233.29	920.36	329.55	1620.36	534.09
LC0006	157.34	1978.28	185.03	895.09	4796.99	671.76	3921.52	1045.48	128.51	4695.83	582.23
	159.28	1992.45	195.58	849.35	4596.19	655.41	3872.23	942.01	114.50	4152.58	526.53
	150.07	1927.54	186.98	829.63	4435.25	665.67	3888.53	952.71	114.18	4275.64	530.15
LC0007	226.87	4098.98	303.81	2267.78	4195.83	892.54	2890.51	698.90 (0)	379.25	6122.43	392.49
	216.82	4100.34	279.86	2090.21	4149.62	948.79	2919.28	822.32 (0)	403.05	6154.48	368.66
	225.98	4314.55	304.03	2245.39	4198.13	941.73	2966.82	790.10 (0)	407.63	6165.88	408.91
LC0008	163.93	4303.60	184.19	849.24	4224.97	693.53	3715.99	845.31	239.18	3773.40	582.92
	161.08	4299.39	188.92	851.50	4238.31	689.21	3730.48	909.99	236.94	3724.77	629.67
	161.15	4308.75	173.44	806.93	4003.45	702.51	3802.84	853.28	239.95	3677.03	596.08
LC0009	134.46	3780.82	170.36	869.11	3916.17	499.38	3327.82	755.38	202.67	4069.03	626.69
	139.57	4006.58	181.95	933.94	4152.37	538.18	3648.25	806.32	218.31	4323.83	647.28
	158.10	3805.02	164.68	861.71	3857.07	494.25	3369.55	742.10	193.63	3950.67	596.32
LC0010	203.55	3810.69	511.29	2352.57	4727.66	720.27	3384.85	750.73 (0)	283.44	5599.96	491.41
	181.36	3896.18	483.18	2454.09	4692.72	755.69	3412.51	710.64 (0)	282.33	5558.14	497.05
	180.36	3842.79	487.80	2406.46	4661.36	769.61	3506.01	775.11 (0)	295.01	5327.62	470.77
LC0011	56.09	3666.21	44.62	1034.90	2683.15	333.84	2261.81	679.92	93.67	3643.05	747.78
	55.22	3496.82	50.08	1018.54	3712.54	306.70	2046.21	632.36	90.30	3564.73	728.73
	54.50	3268.50	52.19	981.77	2538.11	309.80	2058.72	653.90	91.18	3784.56	603.74
LC0012	179.46	4366.84	181.87	798.29	6319.53	839.88	4622.02	841.94	237.81	4780.94	952.01
	183.00	4822.67	190.47	697.05	6418.11	861.59	4738.40	840.04	232.85	4675.99	933.16
	183.77	4447.75	191.69	613.35	6558.68	837.92	4707.04	837.15	238.78	4018.91	887.12

	Sample C - Method 3					Sample D - Method 3					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	175.15	4835.48	178.09	847.76	4259.38	765.71	4157.36	825.45	223.17	4074.17	539.09
LC0001	204.37	3939.57	256.07	1267.20	3805.20	809.27	3943.77	1015.75	138.84	5702.13	977.27
LC0002	51.36	3273.73	128.57	1108.68	4021.14	343.24	1653.42 h*	526.56 h*	193.42	5452.49	908.35
LC0003	136.88	4299.49	152.01	711.72	4195.93	711.79	3546.70	738.67	192.12	4297.05	469.49
LC0004	129.54	3172.36	185.11	1252.05	4671.53	559.33	2971.77	714.95	199.21	6358.73	741.39
LC0005	57.34	4270.34	126.34	4414.17 G**, h**	4356.84	456.01	2228.66	910.73	326.37	1625.01 h**	535.41
LC0006	155.57	1966.09 h**	189.20	858.02	4609.48	664.28	3894.10	980.07	119.07	4374.68	546.30
LC0007	223.22	4171.29	295.90	2201.12	4181.19	927.69	2925.54	770.44	396.64 h*	6147.60	390.02
LC0008	162.05	4303.91	182.19	835.89	4155.58	695.08	3749.77	869.53	238.69	3725.07	602.89
LC0009	144.05	3864.14	172.33	888.25	3975.20	510.60	3448.54	767.94	204.87	4114.51	623.43
LC0010	188.42	3849.88	494.09 G*, h**	2404.37	4693.91	748.52	3434.46	745.50	286.93	5495.24	486.41
LC0011	55.27	3477.18	48.96	1011.74	2977.93	316.78	2122.24	655.39	91.72	3664.11	693.42
LC0012	182.08	4545.76	188.01	702.90	6432.10 G**, h**	846.47	4689.15	839.71	236.48	4491.95	924.10

	Sample C - Method 3					Sample D - Method 3					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	2.65	285.34	0.96	29.98	271.45	48.59 k*	382.21 C**, k**	40.50 C**	28.13 k*	322.48	30.64
LC0001	3.07	546.75 C**, k**	11.35	24.31	146.17	28.97	130.95	29.13	7.76	251.63	41.99
LC0002	13.47 k*	200.30	24.00 C**	141.99 k**	53.41	37.83	172.45	25.76	27.55 k*	106.57	61.64
LC0003	0.23	21.02	2.80	93.06	108.03	25.74	177.31	28.78	6.71	234.83	41.90
LC0004	1.65	177.78	49.00 C**, k**	176.69 k**	1224.13 C**, k**	10.16	174.20	33.25	15.30	2668.01 C**, k**	172.01 C**, k**
LC0005	0.20	118.44	4.45	43.93	85.62	21.26	85.64	29.39	12.92	64.58	32.78
LC0006	4.85	34.13	5.61	33.58	181.24	8.26	25.11	56.90	8.18	284.85	31.16
LC0007	5.56	124.07	13.89	96.71	27.37	30.64	38.54	64.02 k*	15.24	22.53	20.24
LC0008	1.62	4.69	7.93	25.10	131.91	6.78	46.53	35.27	1.56	48.19	24.10
LC0009	12.44 k*	123.95	8.80	39.73	156.25	24.02	174.21	33.90	12.49	190.69	25.63
LC0010	13.11 k*	43.18	15.08	50.79	33.16	25.44	63.49	32.55	7.02	146.66	13.84
LC0011	0.80	199.58	3.91	27.21	640.31 C**	14.86	121.03	23.81	1.75	111.42	78.24
LC0012	2.30	243.21	5.35	92.61	120.19	13.14	60.21	2.41	3.18	413.01	33.38

	Sample E – Method 3				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP
Level	III	II	I	II	I
LC0000	4347.89	1016.05	205.34	1003.54	457.95
	3709.48	915.72	182.70	893.95	405.60
	4076.69	968.05	196.38	966.68	433.18
LC0001	4121.69	969.68	133.75	1248.44	577.88
	4022.30	952.20	137.44	1326.61	635.21
	4275.57	963.00	141.57	1302.82	649.70
LC0002	1938.80	417.23	90.77	776.10	531.94
	2109.98	377.78	85.45	739.29	537.96
	2050.04	371.43	80.56	812.14	512.85
LC0003	4179.03	809.91	157.28	837.23	390.04
	4162.59	791.43	148.06	817.43	362.84
	4354.61	834.29	154.27	833.36	368.78
LC0004	3129.87	775.31	175.09	841.34	738.38
	2802.52	684.22	163.32	865.64	770.09
	3226.58	732.87	165.28	956.85	790.37
LC0005	2668.65	537.73	178.49	1030.83	(0) (0)
	2702.78	553.62	183.96	1079.52	(0) (0)
	2791.73	564.80	180.10	1048.44	(0) (0)
LC0006	4618.93	905.11	247.87	1012.29	533.88
	4687.94	917.88	239.48	1002.16	533.86
	4948.32	886.87	225.98	916.08	495.55
LC0007	3392.42	1105.81	46.18 (0)	927.82	460.26
	3297.65	1276.23	53.79 (0)	919.67	445.62
	3147.30	868.47	56.27 (0)	912.85	457.56
LC0008	4295.70	912.34	134.23	1089.09	578.22
	4154.64	880.09	131.98	1136.86	581.25
	4343.53	923.48	137.52	1137.75	576.96
LC0009	3775.60	749.44	301.96	883.58	473.74
	3895.80	837.37	337.96	962.19	493.82
	3817.67	824.88	332.74	873.95	458.86
LC0010	3518.85	996.16	58.87 (0)	1422.42	630.57
	3467.12	999.68	57.55 (0)	1344.95	651.22
	3601.00	1021.58	64.06 (0)	1344.74	635.78
LC0011	2406.25	426.78	125.53	532.05	276.51
	2442.79	432.81	132.53	557.69	280.71
	2491.89	438.83	132.09	526.23	266.60
LC0012	3431.76	968.83	171.43	853.54	420.59
	3553.62	1013.75	143.88	877.93	424.47
	3895.82	988.78	180.61	843.94	443.40

	Sample E - Method 3				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP
Level	III	II	I	II	I
LC0000	4044.69	966.61	194.81	954.73	432.24
LC0001	4139.85	961.63	137.59	1292.62	620.93
LC0002	2032.94 h*	388.81 h*	85.59	775.84	527.58
LC0003	4232.08	811.88	153.20	829.34	373.89
LC0004	3052.99	730.80	167.90	887.94	766.28
LC0005	2721.05	552.05	180.85	1052.93	0.00 G*, h**
LC0006	4751.73	903.29	237.77	976.84	521.09
LC0007	3279.13	1083.50	52.08	920.11	454.48
LC0008	4264.62	905.30	134.58	1121.23	578.81
LC0009	3829.69	803.90	324.22 h**	906.57	475.47
LC0010	3528.99	1005.81	60.16	1370.70 h*	639.19
LC0011	2446.98	432.81	130.05	538.66 h*	274.61
LC0012	3627.07	990.46	165.31	858.47	429.49

	Sample E - Method 3				
Laboratory	DIBP	DBP	BBP	DNOP	DIDP
Level	III	II	I	II	I
LC0000	320.41 k**	50.18	11.41	55.76	26.19
LC0001	127.61	8.82	3.91	40.07	37.98 k**
LC0002	86.86	24.81	5.10	36.43	13.11
LC0003	106.44	21.50	4.70	10.49	14.30
LC0004	222.24	45.58	6.31	60.90	26.20
LC0005	63.55	13.60	2.81	24.66	0.00
LC0006	173.71	15.58	11.04	52.87	22.12
LC0007	123.61 C**	204.79 k**	5.26	7.50	7.79
LC0008	98.20	22.54	2.78	27.84	2.20
LC0009	60.99	47.57	19.45 k**	48.41	17.54
LC0010	67.51	13.77	3.44	44.79	10.74
LC0011	42.98	6.02	3.92	16.74	7.25
LC0012	240.59	22.51	19.11 k*	17.52	12.20

Tables A, B, C (Method 4): original values, cell means and cell standard deviations, respectively.

	Sample A - Method 4					Sample B - Method 4				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	3613.96	589.76	183.30	720.47	385.31	120.85	4312.01	808.84	3697.57	610.14
	3699.80	585.24	184.71	717.92	402.48	119.20	4699.72	818.25	4136.12	683.29
	3530.17	577.71	181.25	790.51	388.54	121.61	4189.82	811.62	3873.39	677.42
LC0001	3702.25	846.12	83.75	892.78	566.82	131.48	4607.79	845.64	4593.02	1128.97
	3808.27	866.47	87.13	802.33	576.99	119.60	4703.38	824.68	4248.18	1142.37
	3825.87	854.92	91.06	938.89	574.80	132.35	4957.56	877.60	4207.00	1240.10
LC0002	3059.90	658.47	229.02	1360.52	660.27	100.92	4900.06	1700.62	5107.45	1664.05
	2942.67	634.80	213.74	1372.85	645.67	89.69	4672.52	1548.53	4921.95	1659.24
	3356.00	718.99	211.59	1387.17	553.05	89.10	4757.74	1629.79	5575.48	1611.05
LC0003	3464.12	636.99	142.41	777.33	492.98	113.34	4052.74	821.40	4040.12	885.87
	3326.79	613.95	132.04	782.81	500.72	109.42	4133.81	824.75	4082.56	868.40
	3219.62	593.31	131.93	846.14	489.04	110.33	4173.90	820.60	4148.03	903.16
LC0004	8450.73	1534.39	418.47	2384.17	1021.74	345.72	10637.42	2375.68	11786.20	2518.66
	8647.01	1548.56	390.33	2250.32	795.80	362.12	11235.37	2489.25	12394.45	2529.12
	8498.17	1513.45	410.22	2521.43	908.67	351.51	10495.01	2369.42	12782.28	2556.38
LC0005	3816.14	821.26	294.12	988.48	(0) (0)	102.07	5280.45	1556.79	4325.36	454.26
	3666.19	823.72	288.88	929.21	(0) (0)	100.98	5212.97	1536.68	4267.93	428.75
	3603.17	827.21	285.75	1002.84	(0) (0)	100.20	5187.38	1513.56	4665.42	406.29
LC0006	4140.59	971.74	206.32	897.11	443.53	96.07	4661.52	591.33	4449.26	901.37
	4382.98	937.72	203.74	888.22	450.95	91.15	4502.75	567.73	4372.85	871.13
	4448.57	988.92	202.72	972.57	438.53	91.64	4348.01	539.20	4547.13	856.66
LC0007	3391.52	902.58	224.12	857.12	375.70	160.03	5065.96	1190.43	4055.22	480.01
	3439.20	958.79	210.07	817.10	354.14	158.97	5026.25	1148.87	4071.27	431.07
	3321.21	914.69	201.27	899.81	354.70	154.00	5004.31	1112.05	4501.82	440.65
LC0008	3749.71	657.24	97.98	858.28	445.64	150.23	4606.17	905.73	4119.34	891.90
	3825.24	668.05	163.72	887.66	439.11	144.46	4551.49	905.31	4198.50	886.81
	3831.20	671.89	165.33	969.12	452.25	146.61	4605.39	911.65	4094.96	885.43
LC0009	3487.79	683.63 (68,36)	187.87	981.95 (98,19)	463.52	97.82	4392.17	902.64	4518.52	997.27
	3074.18	587.97	188.50	893.46	382.96	113.28	4292.72	798.92	4123.20	888.29
	2803.31	535.29	185.44	956.96	379.70	98.07	4221.05	808.16	4359.82	847.57
LC0010	4547.97	853.35	229.02 (0)	1105.41	342.03	344.19	5437.68	1048.67	4919.94	777.22
	4302.17	848.18	234.97 (0)	1084.82	325.43	316.81	5363.11	1062.17	4856.40	752.37
	4547.17	849.45	233.39 (0)	1221.23	324.51	289.92	5342.15	1042.50	5330.88	794.91
LC0011	2784.69	285.71	72.26	488.64	357.97	67.05	3434.23	597.68	5348.97	837.69
	2815.77	286.90	70.82	485.28	311.68	68.06	3492.38	610.95	5583.37	815.94
	2837.52	285.62	67.98	490.61	330.69	69.12	3513.02	602.16	5979.26	996.10
LC0012	4190.04	891.23	198.49	935.91	663.31	153.28	4804.04	1027.12	4955.66	1247.11
	4120.43	870.13	199.74	922.66	734.89	152.19	4904.88	1036.70	4989.59	1267.96
	4088.30	871.42	195.42	1037.08	679.18	157.76	4938.30	1029.89	5410.87	1230.60

	Sample A - Method 4					Sample B - Method 4				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	3614.64	584.24	183.09	742.97	392.11	120.55	4400.52	812.90	3902.36	656.95
LC0001	3778.80	855.84	87.31	878.00	572.87	127.81	4756.24	849.31	4349.40	1170.48
LC0002	3119.52	670.75	218.12	1373.51	619.66	93.24	4776.77	1626.31	5201.63	1644.78
LC0003	3336.85	614.75	135.46	802.09	494.25	111.03	4120.15	822.25	4090.24	885.81
LC0004	8531.97 G**, h**	1532.13 G**, h**	406.34 h**	2385.31 G**, h**	908.74 h*	353.12 G**, h**	10789.26 G**, h**	2411.45 G**, h**	12320.98 G**, h**	2534.72 G**, h**
LC0005	3695.16	824.06	289.59	973.51	0.00 G*, h*	101.08	5226.94	1535.68	4419.57	429.76
LC0006	4324.05	966.13	204.26	919.30	444.34	92.95	4504.09	566.09	4456.41	876.38
LC0007	3383.98	925.35	211.82	858.01	361.52	157.67	5032.18	1150.45	4209.44	450.58
LC0008	3802.05	665.72	142.34	905.02	445.66	147.10	4587.68	907.56	4137.60	888.05
LC0009	3121.76	602.30	187.27	944.13	408.73	103.06	4301.98	836.57	4333.84	911.04
LC0010	4465.77	850.33	232.46	1137.15	330.66	316.98 h*	5380.98	1051.11	5035.74	774.84
LC0011	2812.66	286.08	70.36	488.17	333.44	68.08	3479.88	603.60	5637.20	883.24
LC0012	4132.92	877.59	197.88	965.22	692.46	154.41	4882.41	1031.24	5118.70	1248.56

	Sample A - Method 4					Sample B - Method 4				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**	**DIBP**	**BBP**	**DEHP**	**DNOP**	**DINP**
Level	**III**	**II**	**I**	**II**	**I**	**I**	**III**	**II**	**III**	**II**
LC0000	84.82	6.09	1.74	41.19	9.13	1.23	266.22 C*, k*	4.83	220.71	40.64
LC0001	66.87	10.20	3.66	69.47	5.35	7.12	180.78	26.65	211.98	60.66
LC0002	213.02	43.42 C*	9.51	13.34	58.15 C**	6.66	114.96	76.11 k**	336.79	29.31
LC0003	122.56	21.85	6.02	38.25	5.94	2.05	61.72	2.20	54.36	17.38
LC0004	102.41	17.67	14.46 C*	135.56 k**	112.97 C**, k**	8.32	392.85 C**, k**	67.45 k**	502.09 k*	19.47
LC0005	109.40	2.99	4.23	39.03	0.00	0.94	48.08	21.64	214.84	24.00
LC0006	162.23	26.06	1.85	46.35	6.25	2.71	156.76	26.10	87.36	22.81
LC0007	59.35	29.58	11.52	41.36	12.29	3.22	31.25	39.21	253.34	25.94
LC0008	45.43	7.59	38.43 C**, k**	57.42	6.57	2.91	31.34	3.55	54.13	3.40
LC0009	344.71 C*, k**	75.20 C**, k**	1.61	45.62	47.48	8.86	85.94	57.40	198.94	77.40 k*
LC0010	141.68	2.69	3.08	73.54	9.86	27.14 C**, k*	50.21	10.06	257.57	21.37
LC0011	26.55	0.71	2.18	2.69	23.27	1.04	40.86	6.75	318.58	98.34 C*, k**
LC0012	52.00	11.83	2.22	62.59	37.59	2.95	69.89	4.93	253.59	18.72

	Sample C - Method 4					Sample D - Method 4					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	115.23	3488.56	142.57	916.88	3182.89	1804.28	1365.99	837.85	224.52	983.07	583.34
	115.08	4579.41	136.88	924.39	4319.13	1695.99	1305.14	853.56	225.01	936.66	586.27
	116.73	3855.72	150.81	895.56	3434.53	2040.88	1370.70	849.28	223.90	950.24	535.61
LC0001	122.85	5972.63	69.27	1231.43	5561.49	860.37	5230.99	640.01	220.46	6680.29	846.01
	121.54	6114.03	68.10	1262.27	5883.33	774.13	5027.49	633.95	208.34	6134.03	796.79
	132.18	6154.60	70.01	1283.31	6055.50	792.59	4949.35	611.98	194.11	5976.31	844.46
LC0002	108.67	5410.15	505.31	1752.90	5431.34	504.03	3113.33	1172.18	394.91	5362.95	1226.67
	107.33	5307.98	487.17	1645.34	5368.79	515.96	3127.40	1227.90	418.33	5713.29	1340.48
	124.29	4918.39	427.64	1430.75	4571.11	614.19	3841.36	1275.21	465.52	5267.22	1236.53
LC0003	84.05	3231.01	105.85	912.42	3173.98	582.45	3410.34	722.40	184.06	4256.60	489.84
	110.07	4213.53	140.48	970.70	4155.27	583.23	3454.47	735.73	185.44	4437.36	647.50
	114.25	4216.26	137.36	1054.68	4055.42	584.23	3453.35	738.93	186.26	4319.79	572.17
LC0004	352.00	11674.54	374.79	1959.27	12575.24	1729.56	7187.24	2180.94	613.04	12983.85	1639.72
	307.98	11051.57	479.57	2555.68	13852.07	1474.63	6133.81	1839.93	558.46	12408.68	1611.46
	330.06	10749.39	513.31	2579.87	13682.65	1550.91	6344.95	1956.33	632.22	13541.18	2000.36
LC0005	115.92	6284.22	161.68	2021.39	2646.44	652.59	3702.24	1220.59	441.22	1128.06	353.32
	119.88	6354.01	159.27	1946.23	2543.78	650.33	3719.01	1206.37	437.55	1028.26	307.83
	116.97	6318.22	173.29	1927.98	2654.02	652.09	3708.97	1192.53	438.22	1129.54	363.75
LC0006	100.82	2703.91	305.61	838.53	4367.02	662.76	3673.12	982.39	158.90	4193.09	507.87
	95.32	2693.06	279.72	830.94	4312.11	610.90	3754.35	989.42	151.88	4263.92	505.29
	88.16	2658.26	321.63	825.81	4361.60	632.83	3845.57	981.05	162.31	4281.46	508.07
LC0007	287.79	4301.47	323.19	1730.08	3488.03	713.16	4515.35	2080.83 (0)	316.67	2837.99	301.71
	269.84	4274.44	331.21	1683.78	3458.54	722.71	4850.39	2347.90 (0)	309.41	2641.40	304.55
	288.67	4293.45	376.02	1721.34	3462.17	732.60	4916.44	2110.90 (0)	324.38	2839.11	311.83
LC0008	135.83	4354.59	171.39	832.67	4038.29	704.65	3177.10	891.78	245.86	3939.19	684.35
	132.90	4320.35	172.91	807.53	4014.41	712.98	3211.39	804.34	247.62	4172.73	723.37
	134.01	4294.59	170.59	806.74	3953.97	720.84	3249.78	875.52	247.59	4034.98	678.40
LC0009	160.21	4014.67	207.19	890.39	4404.94	578.59	3327.55	897.35	202.64	4053.58	795.70
	120.32	3997.33	191.58	818.73	4261.71	558.97	3625.42	959.02	213.72	4291.82	862.01
	137.02 (13,7)	4104.57 (410,45)	199.50 (19,95)	835.86 (83,56)	4304.78 (430,47)	577.34	3256.30	903.29	170.95	3631.98	738.57
LC0010	219.90	4556.86	382.50	2473.81	4521.38	690.56	3995.24	2244.70 (0)	273.74	4530.91	385.62
	205.62	4606.33	373.96	2566.00	4603.10	690.68	3962.22	2468.53 (0)	266.55	4651.00	420.99
	203.65	4587.39	411.97	2563.61	4374.47	682.70	3982.87	2475.87 (0)	264.16	4558.40	417.57
LC0011	39.72	4941.70	69.21	2267.30	8441.68	394.82	1988.18	473.21	91.28	7901.15	765.28
	40.28	4722.81	56.86	2105.91	7872.61	390.78	1988.53	457.94	94.27	7972.16	646.26
	38.17	4602.28	51.97	2143.28	7989.33	388.62	1963.96	465.70	94.61	7959.11	767.49
LC0012	158.39	4576.34	165.03	1471.22	4852.25	769.19	3934.60	948.74	250.63	5231.23	1012.90
	162.11	4660.97	170.48	1720.80	4887.55	755.82	3876.46	889.68	254.38	5287.10	968.87
	162.09	4498.93	191.32	1491.92	4798.33	769.48	3805.48	934.93	247.97	5112.22	927.26

	Sample C - Method 4					Sample D - Method 4					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	115.68	3974.56	143.42	912.28	3645.52	1847.05 h**	1347.28	846.90	224.48	956.66	568.41
LC0001	125.52	6080.42	69.12	1259.00	5833.44	809.03	5069.28	628.65	207.64	6263.54	829.09
LC0002	113.43	5212.17	473.37	1609.66	5123.75	544.73	3360.70	1225.10	426.25	5447.82	1267.89
LC0003	102.79	3886.93	127.90	979.27	3794.89	583.30	3439.39	732.35	185.26	4337.91	569.84
LC0004	330.01 h*	11158.50 G**, h**	455.89	2364.94	13369.99 G**, h**	1585.03 h*	6555.33 h*	1992.40	601.24 h**	12977.90 h**	1750.52 h**
LC0005	117.59	6318.82	164.75	1965.20	2614.75	651.67	3710.07	1206.49	438.99	1095.29	341.63
LC0006	94.77	2685.08	302.32	831.76	4346.91	635.50	3757.68	984.29	157.69	4246.15	507.08
LC0007	282.10	4289.79	343.47	1711.73	3469.58	722.82	4760.73	2179.88	316.82	2772.83	306.03
LC0008	134.25	4323.18	171.63	815.64	4002.23	712.82	3212.76	857.21	247.02	4048.97	695.37
LC0009	139.18	4038.85	199.42	848.33	4323.81	571.64	3403.09	919.89	195.77	3992.46	798.76
LC0010	209.72	4583.53	389.48	2534.48	4499.65	687.98	3980.11	2396.36 h*	268.15	4580.10	408.06
LC0011	39.39	4755.60	59.35	2172.17	8101.21 G*	391.41	1980.22	465.61	93.39	7944.14	726.34
LC0012	160.86	4578.75	175.61	1561.31	4846.04	764.83	3872.18	924.45	250.99	5210.18	969.68

	Sample C - Method 4					Sample D - Method 4					
Laboratory	DBP	DEHP	DNOP	DIDP	DINP	DIBP	DBP	BBP	DEHP	DIDP	DINP
Level	I	III	I	II	III	II	III	II	I	III	I
LC0000	0.92	555.05 C*, k*	7.01	14.96	596.78 k*	176.37 C**, k**	36.57	8.12	0.55	23.86	28.44
LC0001	5.80	95.53	0.96	26.09 C*	250.76	45.41 C**	145.40	14.75	13.19	369.43	27.98
LC0002	9.43	259.50	40.63 C**	164.01	479.62	60.45 C**	416.33 C**, k*	51.57	35.96 k**	234.84	63.06
LC0003	16.36	568.05 C*, k**	19.15	71.52 C**, k**	540.04 k*	0.89	25.16	8.77	1.11	91.73	78.86
LC0004	22.01 k**	471.75 k*	72.24 C**, k**	351.53	693.46	130.85 C**, k*	557.34 C**, k**	173.34 C*, k**	38.27 C*, k**	566.28 C**, k**	216.84 C**, k**
LC0005	2.05	34.89	7.50	49.51	61.58	1.19	8.44	14.03	1.95	58.05	29.74
LC0006	6.35	23.85	21.14	6.40	30.26	26.03 C**	86.27	4.50	5.32	46.79	1.55
LC0007	10.63	13.88	28.47	24.60	16.08	9.72	215.05	146.28 k*	7.49	113.83	5.22
LC0008	1.48	30.10	1.18	14.75	43.46	8.10	36.36	46.51	1.01	117.40	24.43
LC0009	20.03 k*	57.57	7.81	37.42	73.49	10.99	195.81	34.02	22.20	334.14	61.78
LC0010	8.87	24.96	19.94	52.55	115.85	4.57	16.68	131.40 k*	4.99	62.92	19.51
LC0011	1.09	172.07	8.89	84.48	300.58	3.14	14.08	7.63	1.83	37.80	69.36
LC0012	2.14	81.04	13.87	138.51	44.93	7.81	64.66	30.89	3.22	89.32	42.83

	Sample E - Method 4				
Laboratory	**DIBP**	**DBP**	**BBP**	**DNOP**	**DIDP**
Level	**III**	**II**	**I**	**II**	**I**
LC0000	3431.16	649.42	204.87	797.44	467.37
	3402.40	654.57	206.40	797.69	469.77
	3808.06	639.39	203.52	882.87	443.26
LC0001	5790.02	1223.47	120.13	936.11	775.58
	5686.05	1093.37	111.31	855.18	689.19
	5313.60	1105.26	115.65	956.35	701.90
LC0002	3473.13	747.74	233.38	1345.97	638.11
	3398.64	750.43	255.53	1591.65	769.10
	3794.33	813.53	257.93	1322.65	531.92
LC0003	3667.25	645.08	120.63	681.06	448.36
	3712.73	657.70	132.81	733.90	440.49
	3522.19	615.21	117.00	638.37	367.97
LC0004	9375.66	1723.27	473.96	2587.47	1227.15
	9402.13	1719.77	458.35	2664.71	1201.63
	9567.19	1747.36	444.14	2833.79	1146.75
LC0005	3989.42	989.98	307.05	957.11	(0) (0)
	4090.52	1003.52	309.27	979.33	(0) (0)
	4142.82	990.98	310.61	1086.74	(0) (0)
LC0006	4625.88	887.40	229.60	1000.90	481.22
	4535.00	878.61	226.91	988.26	492.63
	4614.23	877.08	225.65	1091.53	484.19
LC0007	5103.33	1157.22	217.94 (0)	834.57	385.62
	5120.66	1196.79	214.69 (0)	829.24	403.77
	5092.28	1148.40	209.84 (0)	957.75	405.33
LC0008	4241.46	747.09	188.60	987.95	517.85
	4194.55	731.77	187.81	959.93	523.09
	4244.24	747.90	187.79	956.07	496.09
LC0009	3935.58	700.67	190.87	1038.34	468.35
	3701.47	710.39	209.86	1093.71	467.64
	3595.52	665.69	207.05	983.26	418.15
LC0010	4163.71	1002.09	201.08 (0)	1180.52	357.82
	4109.96	989.21	208.16 (0)	1135.70	376.61
	4106.96	996.04	215.38 (0)	1229.69	355.12
LC0011	3129.54	324.23	71.95	501.11	376.15
	3207.54	333.55	77.51	492.92	380.27
	3230.61	332.23	74.89	552.11	471.02
LC0012	4663.22	1001.90	218.84	1087.02	795.24
	4431.04	942.59	207.79	1050.50	785.74
	4452.43	968.97	212.81	1172.88	796.94

	Sample E - Method 4									
Laboratory	**DIBP**		**DBP**		**BBP**		**DNOP**		**DIDP**	
Level	**III**		**II**		**I**		**II**		**I**	
LC0000	3547.21		647.80		204.93		826.00		460.13	
LC0001	5596.56		1140.70		115.70		915.88		722.22	
LC0002	3555.37		770.57		248.95		1420.09		646.38	
LC0003	3634.06		639.33		123.48		684.44		418.94	
LC0004	9448.33	G**, h**	1730.13	G**, h**	458.82	G**, h**	2695.32	G**, h**	1191.84	G**, h**
LC0005	4074.25		994.83		308.97		1007.73		0.00	h*
LC0006	4591.71		881.03		227.39		1026.90		486.01	
LC0007	5105.42		1167.47		214.16		873.85		398.24	
LC0008	4226.75		742.25		188.07		967.98		512.34	
LC0009	3744.19		692.25		202.59		1038.44		451.38	
LC0010	4126.88		995.78		208.20		1181.97		363.18	
LC0011	3189.23		330.00		74.78		515.38		409.15	
LC0012	4515.56		971.16		213.15		1103.47		792.64	

	Sample E - Method 4									
Laboratory	**DIBP**		**DBP**		**BBP**		**DNOP**		**DIDP**	
Level	**III**		**II**		**I**		**II**		**I**	
LC0000	226.36		7.72		1.44		49.25		14.66	
LC0001	250.50	k*	71.93	C**, k**	4.41		53.53		46.65	
LC0002	210.27		37.23		13.53	k*	149.03	C*, k**	118.80	K**
LC0003	99.51		21.82		8.28		47.85		44.32	
LC0004	103.78		15.02		14.92	k*	125.98	k*	41.09	
LC0005	77.98		7.54		1.80		69.32		0.00	
LC0006	49.45		5.57		2.02		56.33		5.92	
LC0007	14.30		25.77		4.07		72.71		10.95	
LC0008	27.92		9.08		0.46		17.40		14.32	
LC0009	174.01		23.51		10.25		55.23		28.78	
LC0010	31.93		6.45		7.15		47.01		11.71	
LC0011	52.96		5.04		2.78		32.07		53.62	
LC0012	128.32		29.72		5.54		62.82		6.04	

Tables A, B, C (Method 5): original values, cell means and cell standard deviations, respectively.

	Sample F - Method 5
Laboratory	**% PVC**
LC0000	87.80
	87.70
	87.56
LC0001	88.07
	87.84
	88.10
LC0002	88.01
	88.03
	88.03
LC0003	88.26
	88.62
	88.00
LC0004	88.13
	87.91
	88.25
LC0005	89.22
	89.01
	89.23
LC0006	87.48
	87.88
	87.81
LC0007	88.48
	88.86
	88.65
LC0008	88.16
	87.90
	87.89
LC0009	88.40
	88.59
	88.28
LC0010	88.27
	88.05
	88.23
LC0011	87.79
	87.59
	88.04

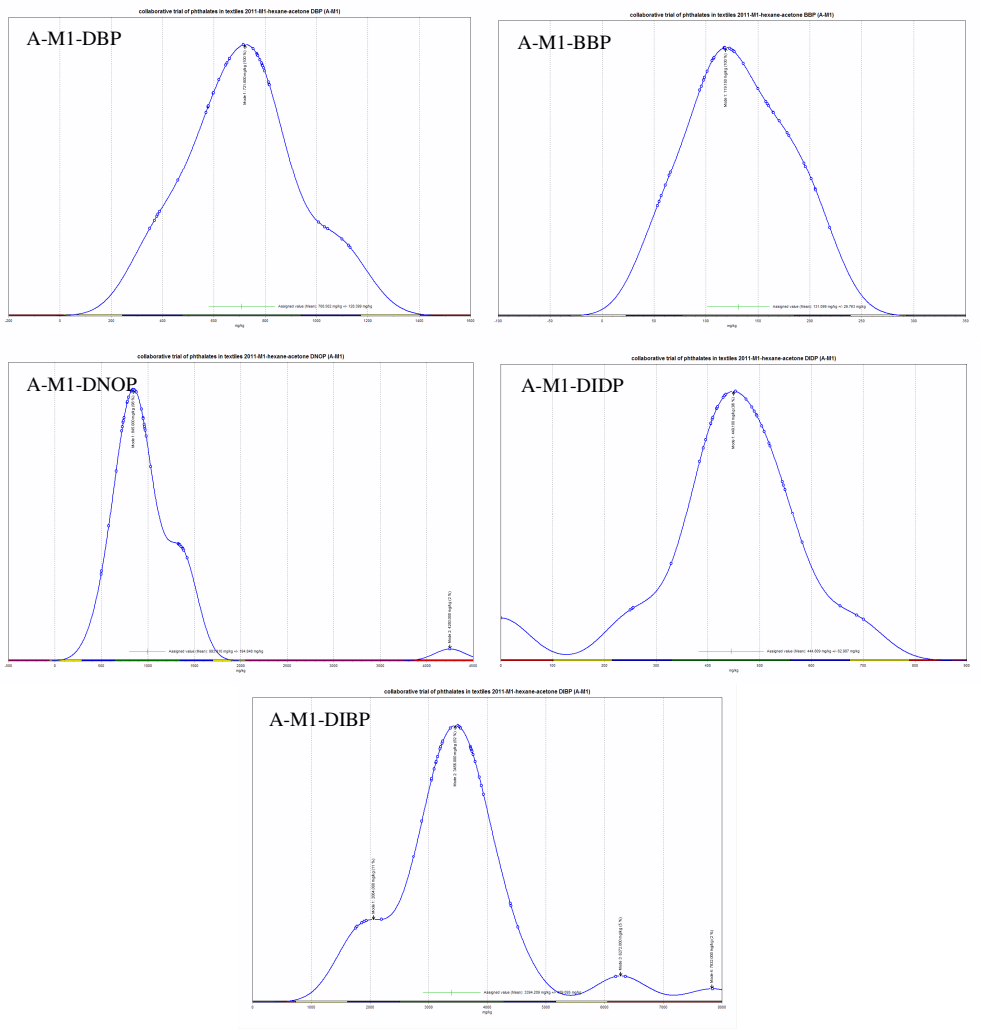
mean	Sample F - Method 5	
Laboratory	**% PVC**	
LC0000	87.69	
LC0001	88.00	
LC0002	88.03	
LC0003	88.29	
LC0004	88.09	
LC0005	89.15	h**
LC0006	87.73	
LC0007	88.66	
LC0008	87.99	
LC0009	88.42	
LC0010	88.18	
LC0011	87.81	

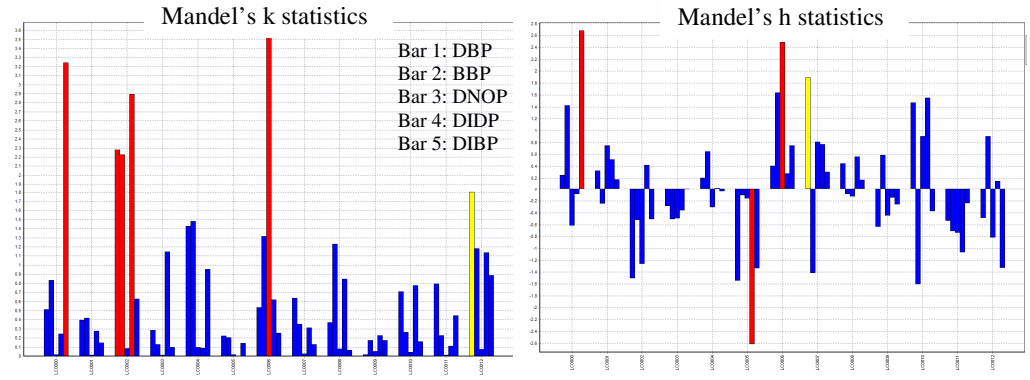
SD	Sample F - Method 5	
Laboratory	**% PVC**	
LC0000	0.12	
LC0001	0.14	
LC0002	0.01	
LC0003	0.31	k*
LC0004	0.17	
LC0005	0.12	
LC0006	0.21	
LC0007	0.19	
LC0008	0.15	
LC0009	0.16	
LC0010	0.12	
LC0011	0.22	

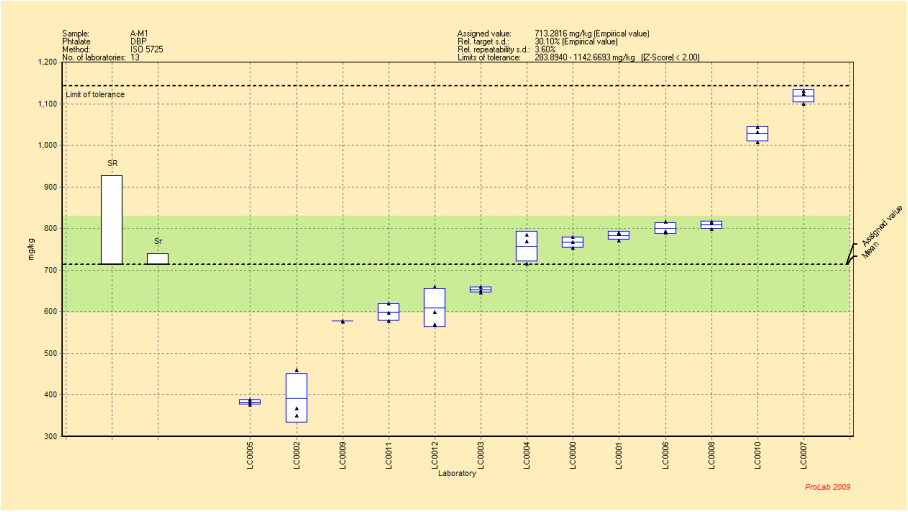
ANNEX X

Kernel’s density, Mandel’s statistics, final results and z-scores

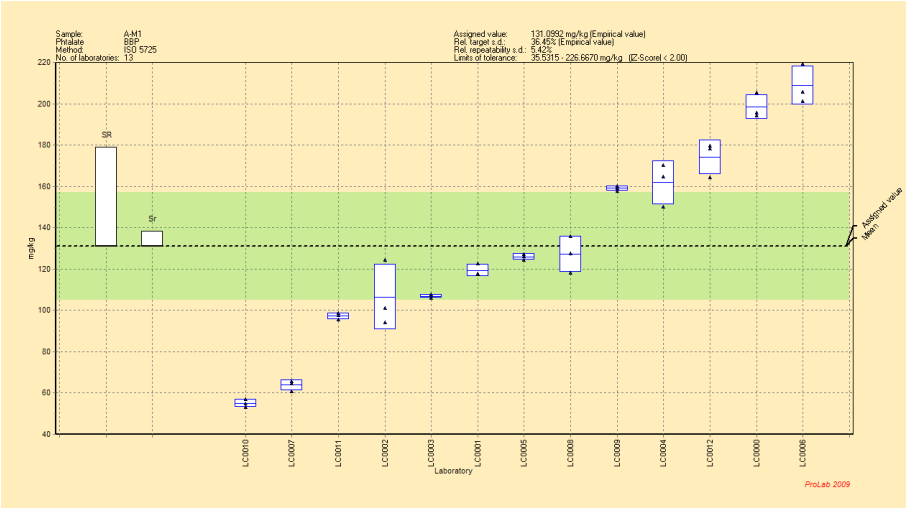
Sample A – Method 1



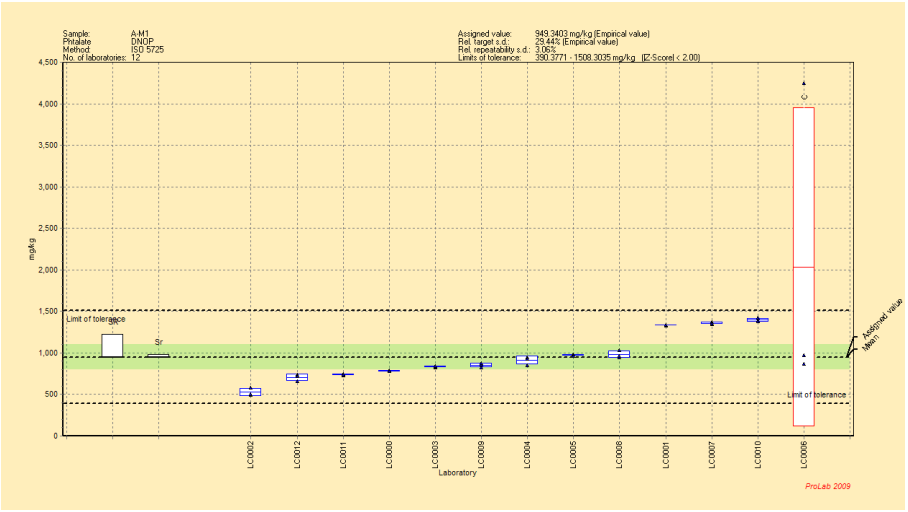




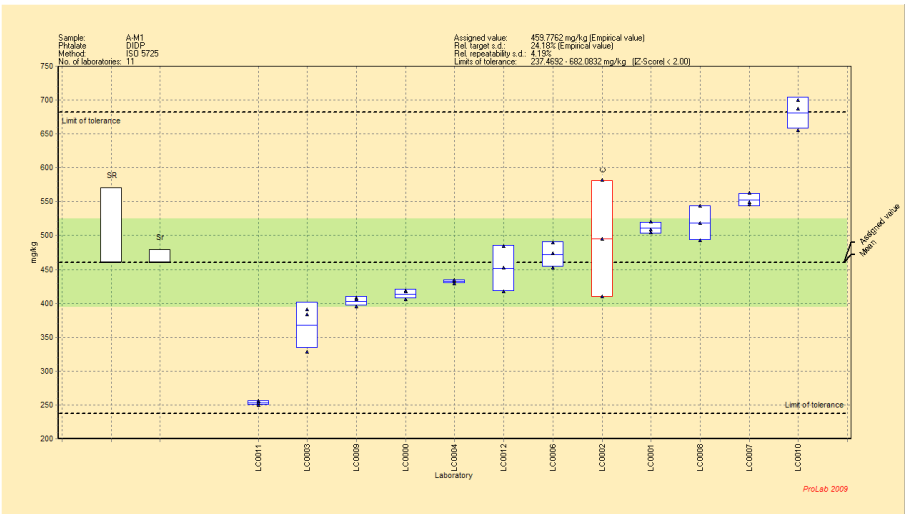
A-M1-DBP
Nr.Labs: 13
Mean (mg/kg): 713.3
SD_r (mg/kg): 25.7
SD_R (mg/kg): 214.7



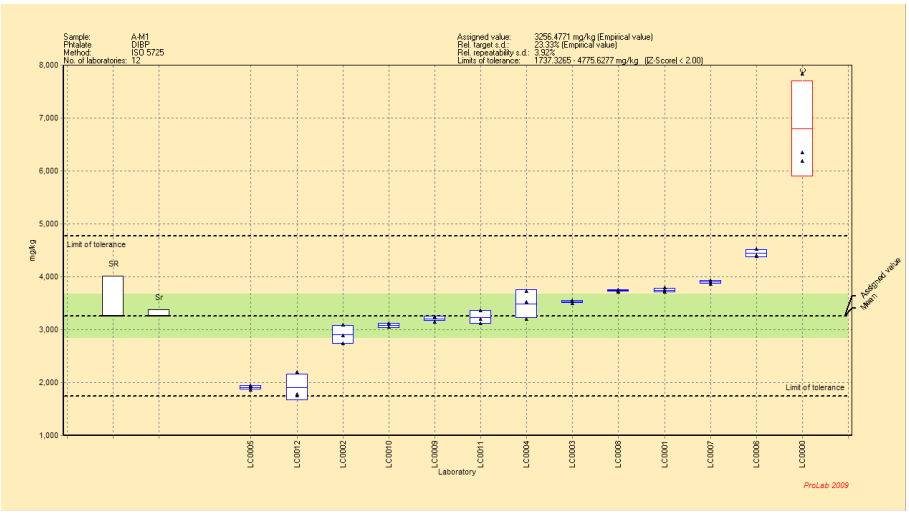
A-M1-BBP
Nr.Labs: 13
Mean (mg/kg): 131.1
SD_r (mg/kg): 7.1
SD_R (mg/kg): 47.8



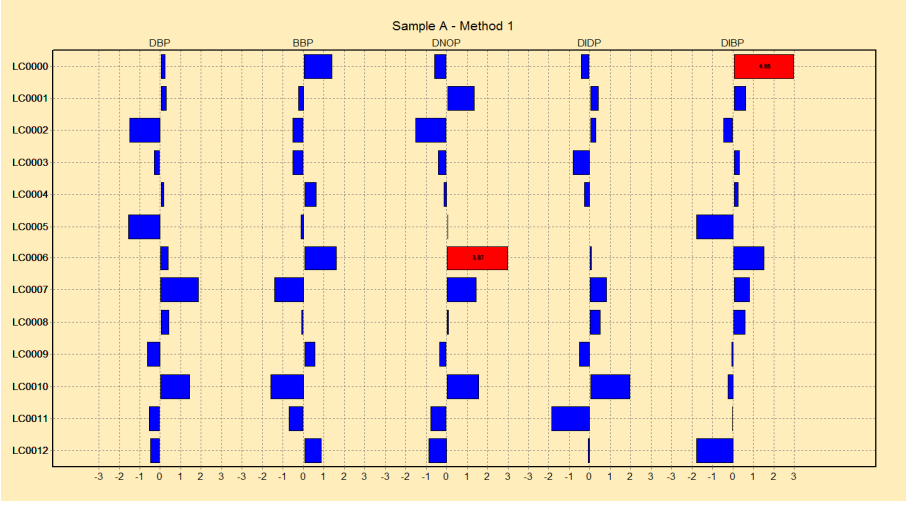
A-M1-DNOP
Nr.Labs: 12
Mean (mg/kg): 949.3
SD_r (mg/kg): 29.0
SD_R (mg/kg): 279.5



A-M1-DIDP
Nr.Labs: 11
Mean (mg/kg): 459.8
SD_r (mg/kg): 19.3
SD_R (mg/kg): 111.2

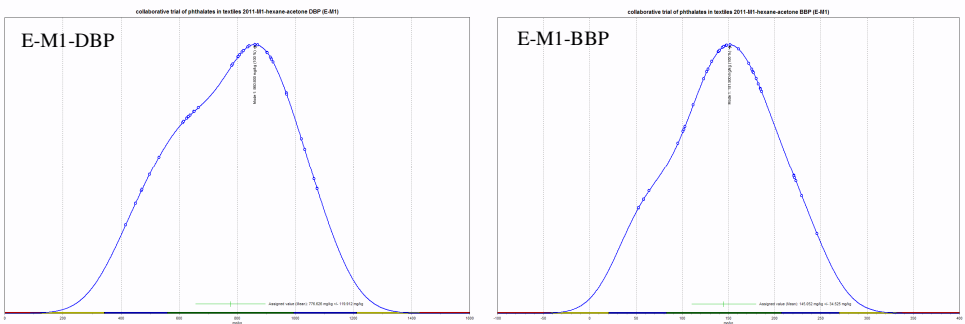


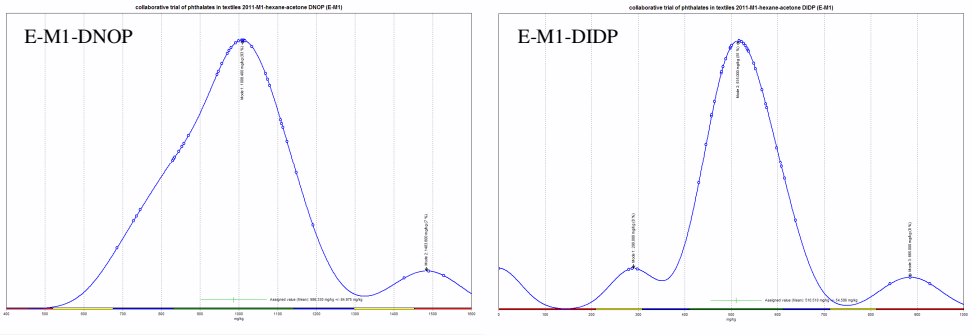
A-M1-DIBP
Nr.Labs: 12
Mean (mg/kg): 3256.5
SD_r (mg/kg): 127.6
SD_R (mg/kg): 759.6

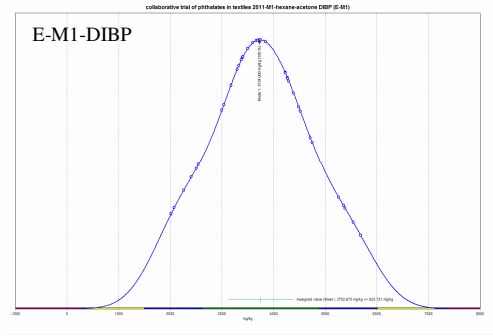


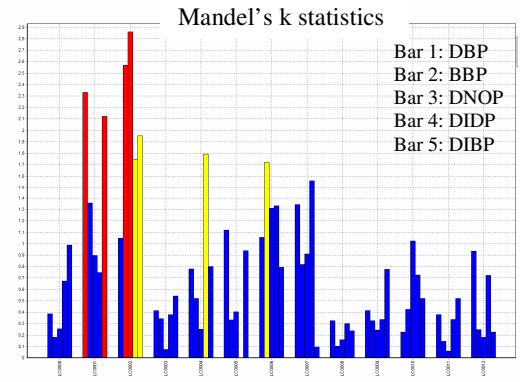
Z-scores

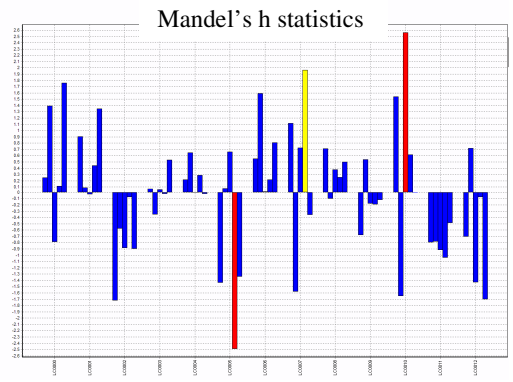
Sample E – Method 1

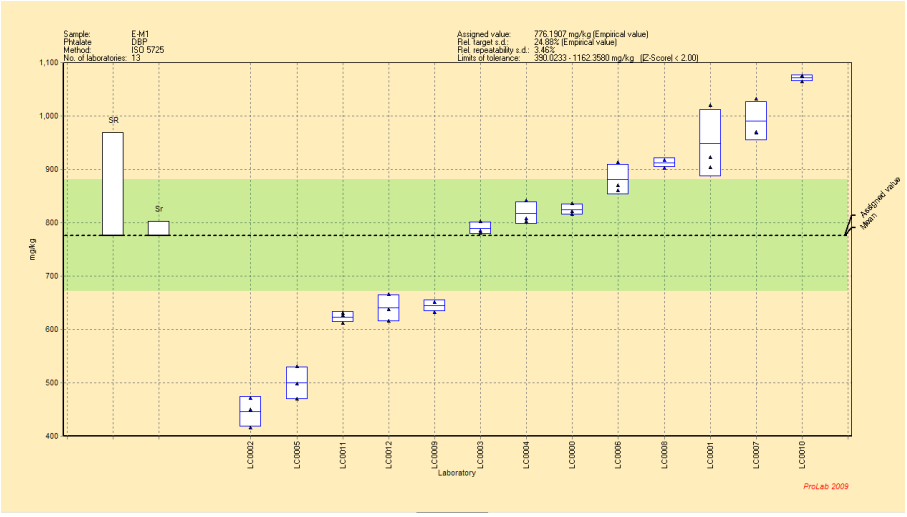




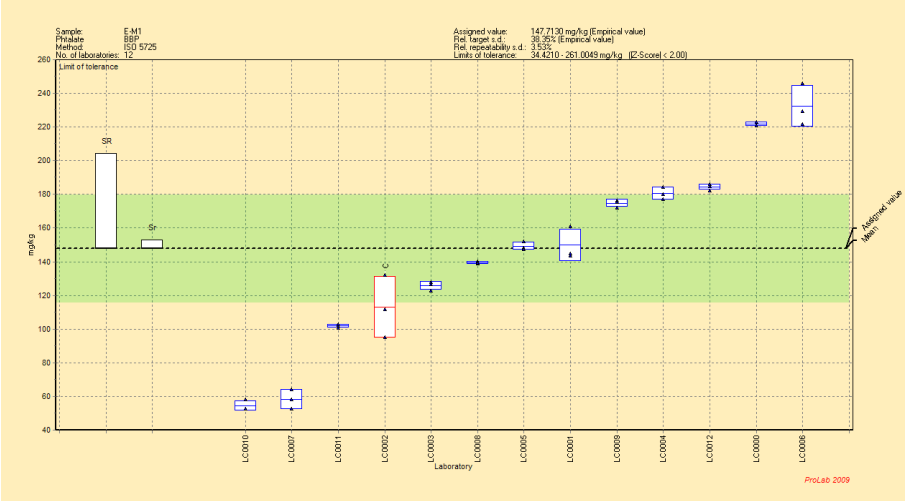




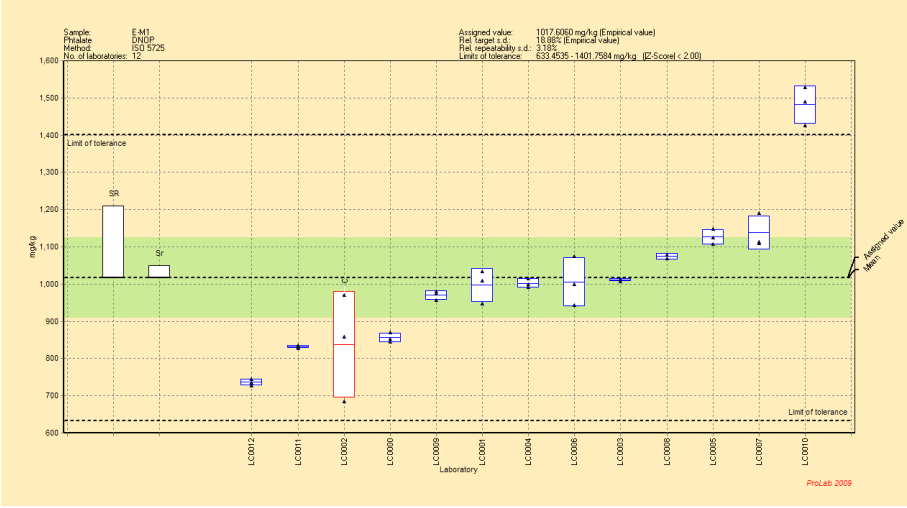




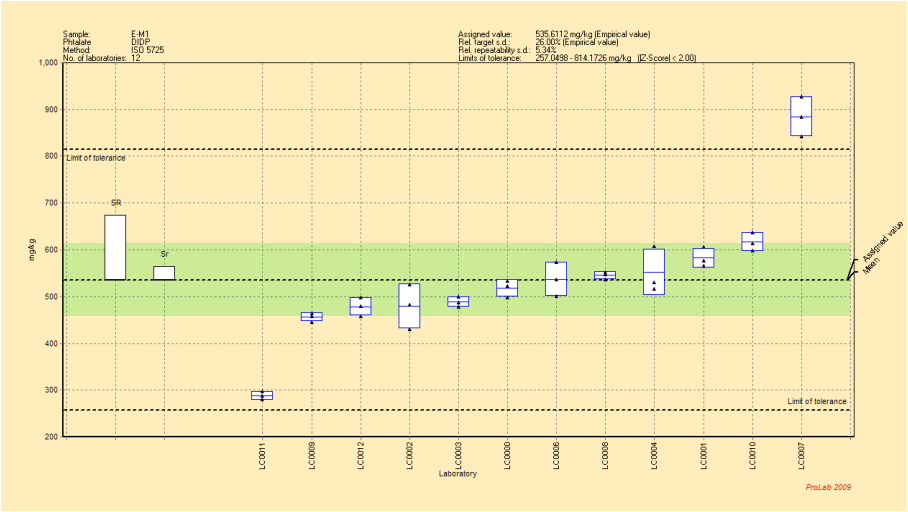
E-M1-DBP
Nr.Labs: 13
Mean (mg/kg): 776.2
SD_r (mg/kg): 26.9
SD_R (mg/kg): 193.1



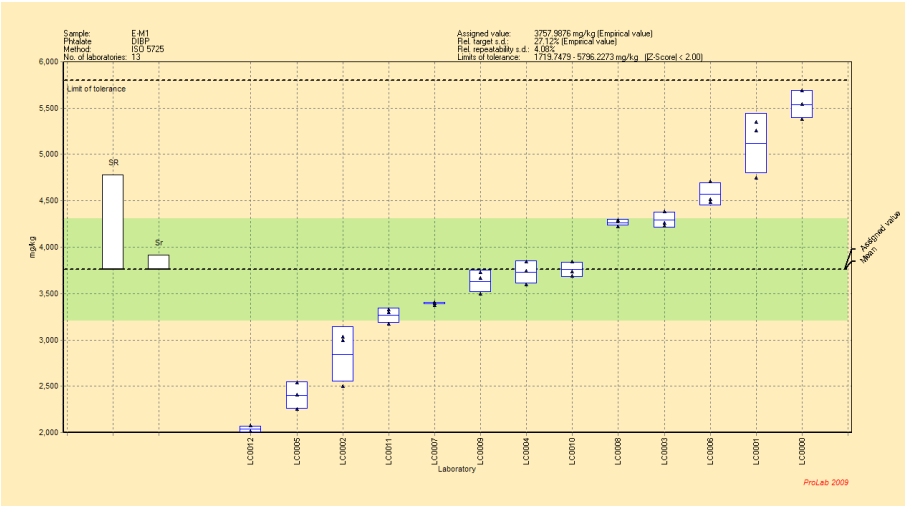
E-M1-BBP
Nr.Labs: 12
Mean (mg/kg): 147.7
SD_r (mg/kg): 5.2
SD_R (mg/kg): 56.6



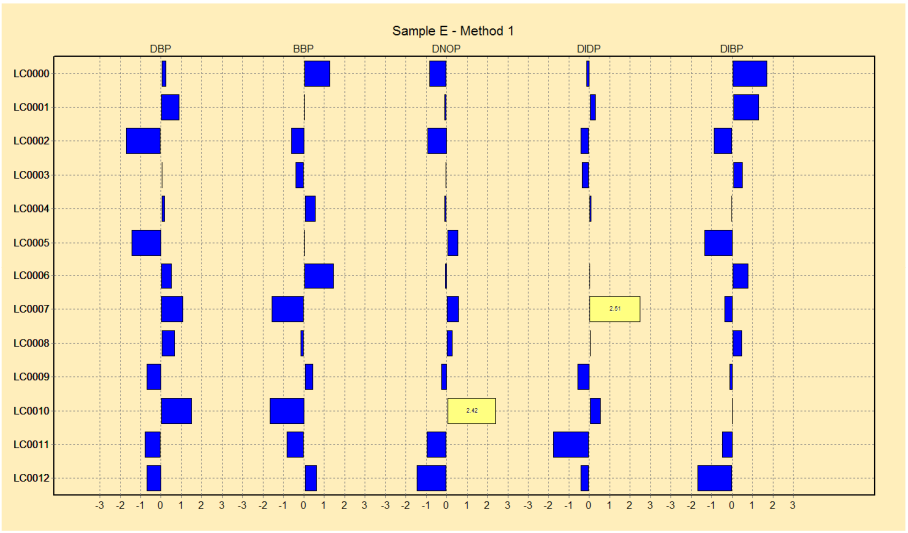
E-M1-DNOP
Nr.Labs: 12
Mean (mg/kg): 1017.6
SD_r (mg/kg): 32.4
SD_R (mg/kg): 192.1



E-M1-DIDP
Nr.Labs: 12
Mean (mg/kg): 535.6
SD_r (mg/kg): 28.6
SD_R (mg/kg): 139.3

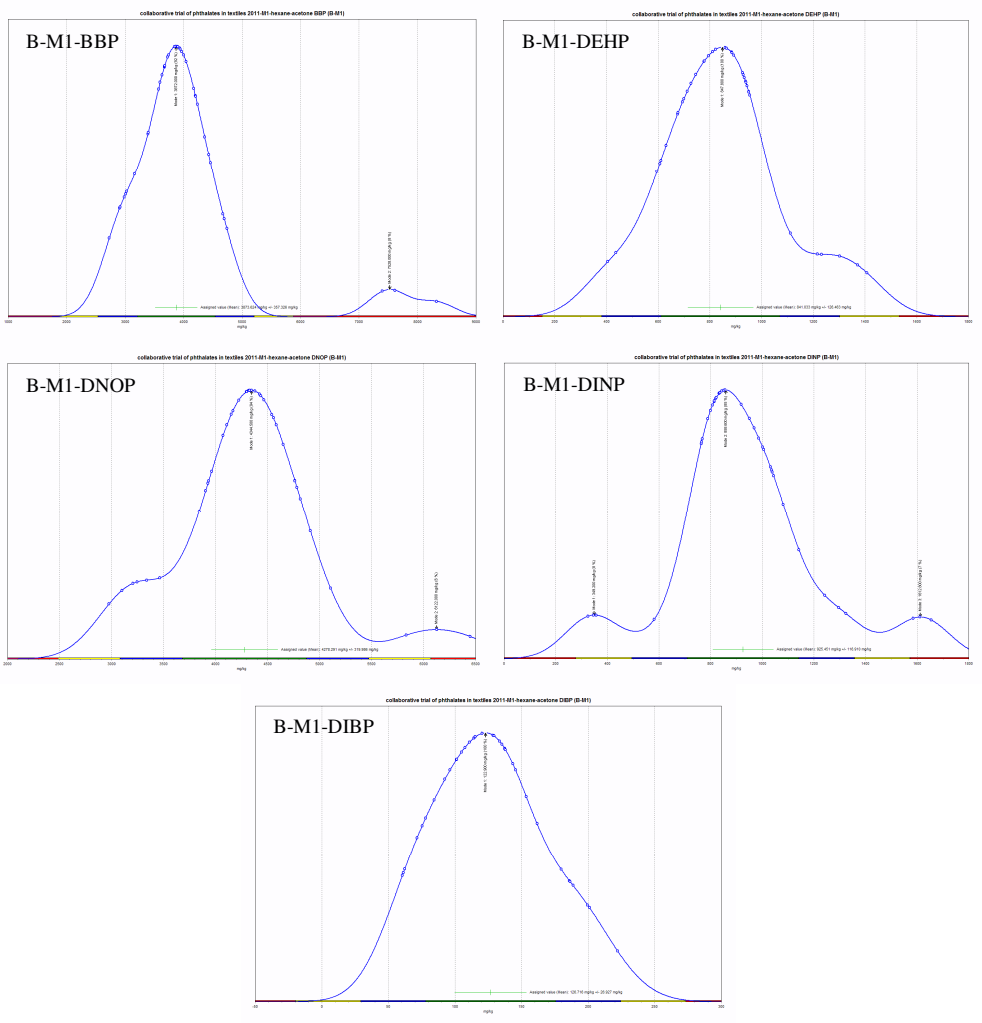


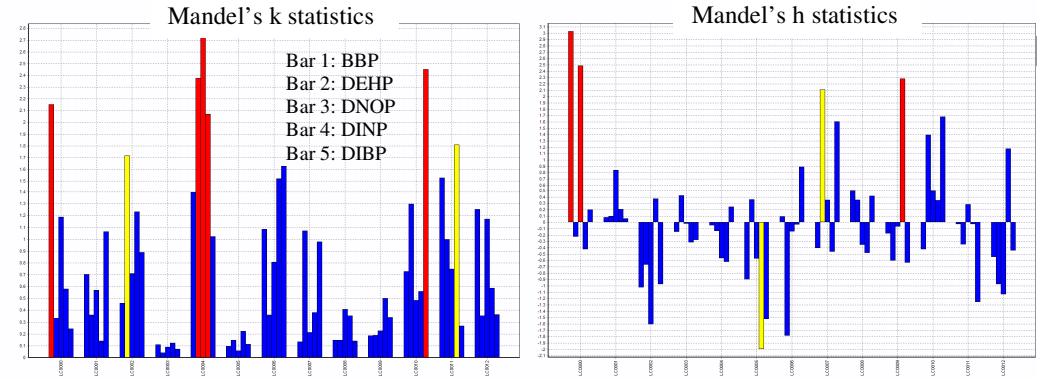
E-M1-DIBP
Nr.Labs: 13
Mean (mg/kg): 3758.0
SD_r (mg/kg): 153.3
SD_R (mg/kg): 1019.1

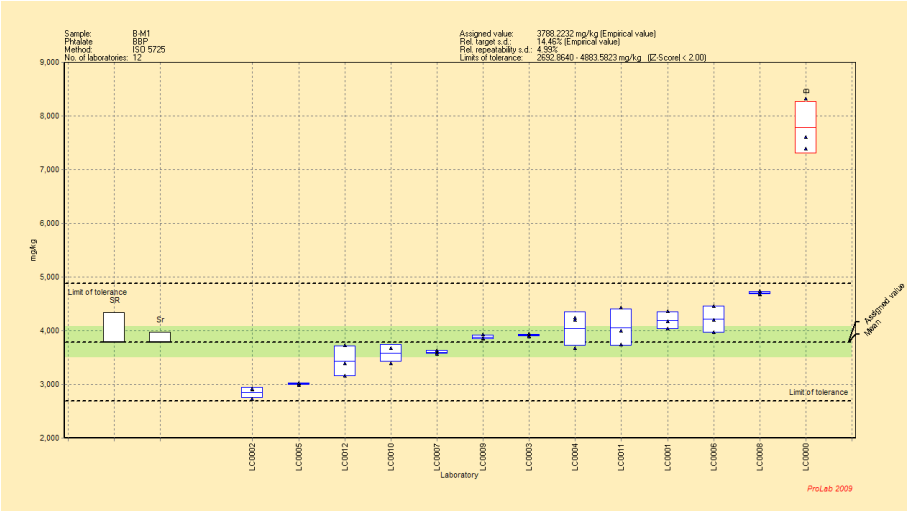


Z-scores

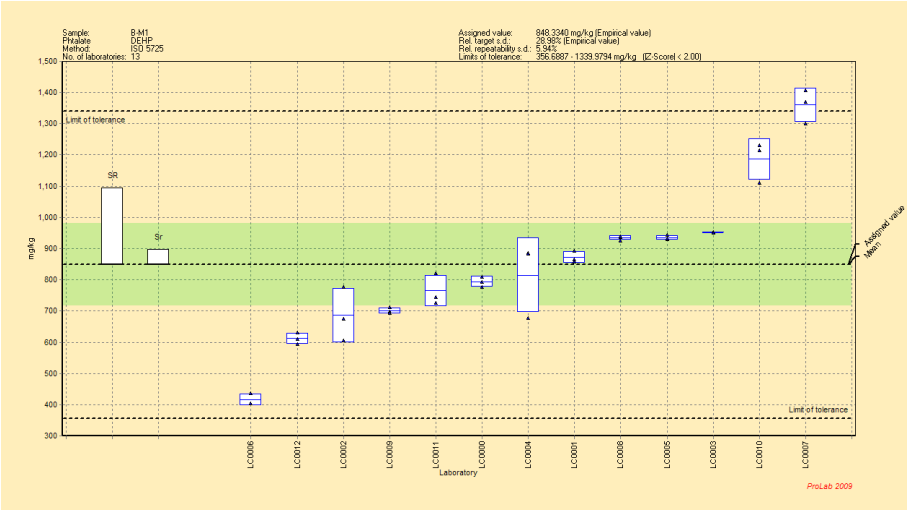
Sample B – Method 1



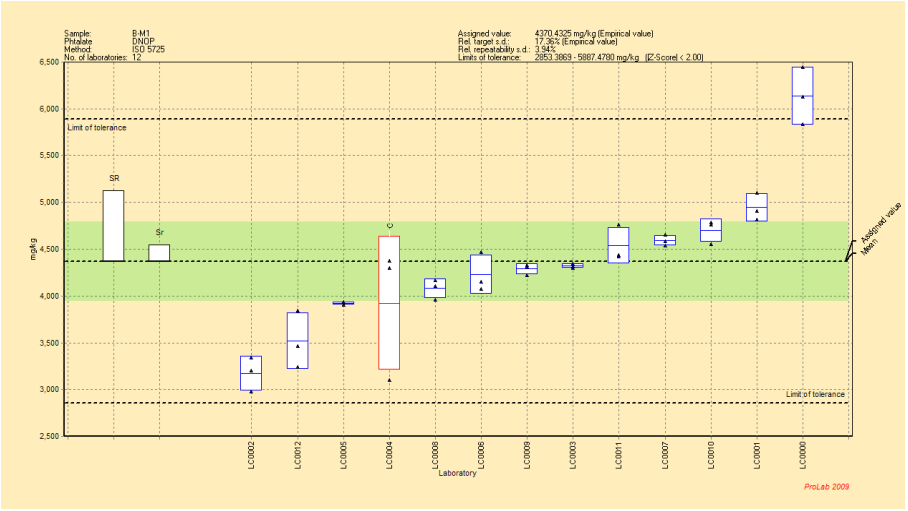




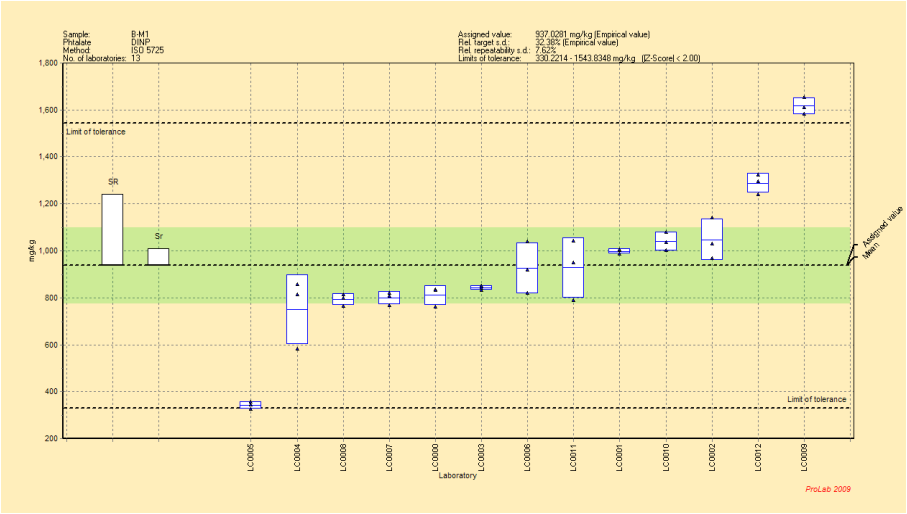
B-M1-BBP
Nr.Labs: 12
Mean (mg/kg): 3788.2
SD_r (mg/kg): 188.9
SD_R (mg/kg): 547.7



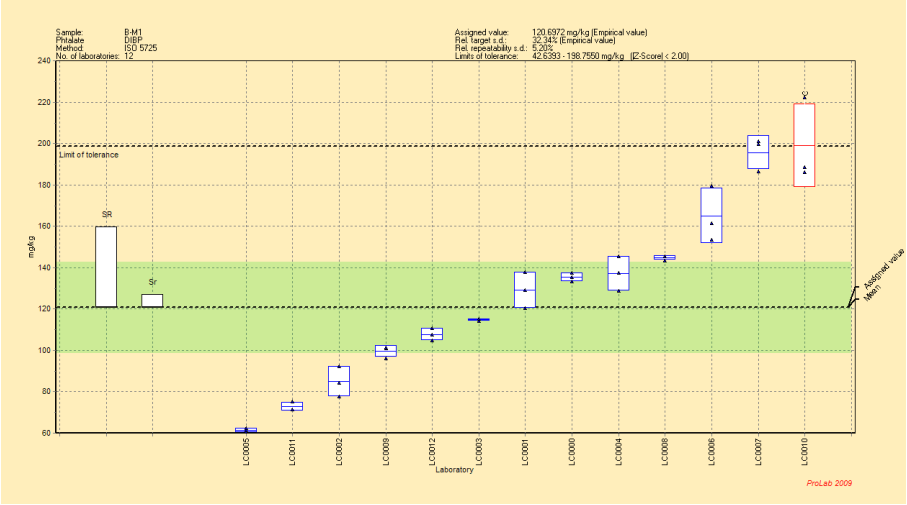
B-M1-DEHP
Nr.Labs: 13
Mean (mg/kg): 848.3
SD_r (mg/kg): 50.4
SD_R (mg/kg): 245.8



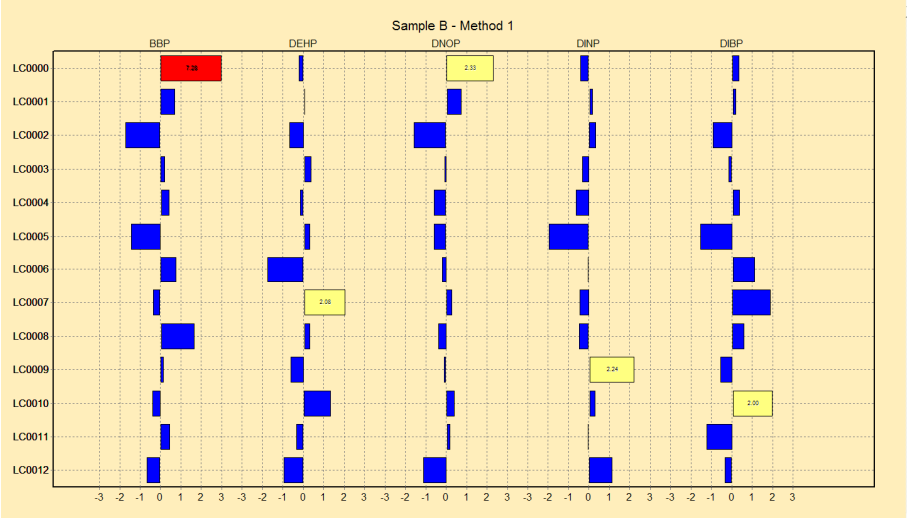
B-M1-DNOP
Nr.Labs: 12
Mean (mg/kg): 4370.4
SD_r (mg/kg): 172.1
SD_R (mg/kg): 758.5



B-M1-DINP
Nr.Labs: 13
Mean (mg/kg): 937.0
SD_r (mg/kg): 71.4
SD_R (mg/kg): 303.4

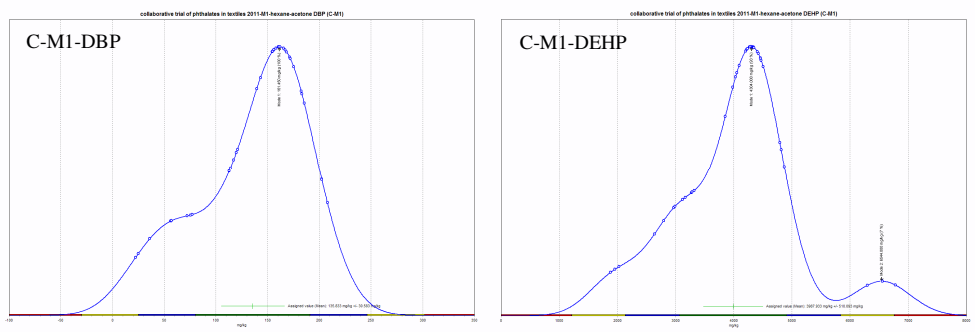


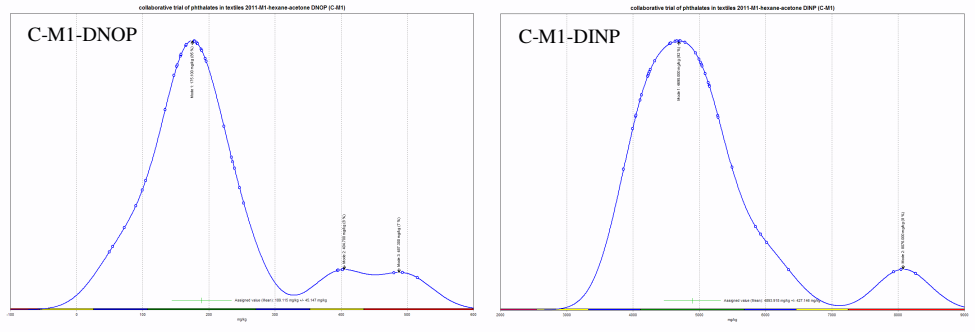
B-M1-DIBP
Nr.Labs: 12
Mean (mg/kg): 120.7
SD_r (mg/kg): 6.3
SD_R (mg/kg): 39.0

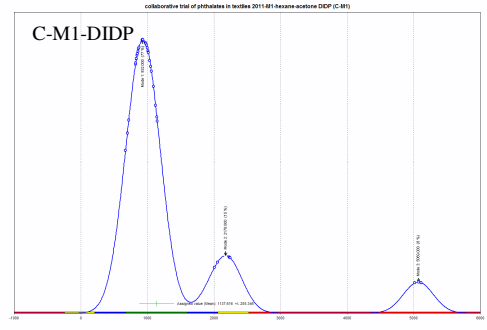


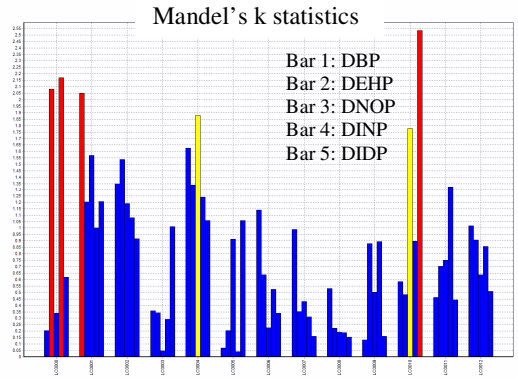
Z-scores

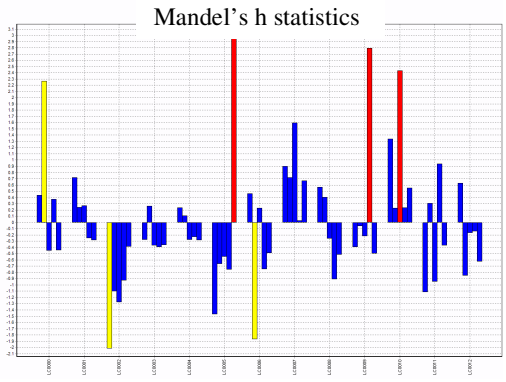
Sample C – Method 1

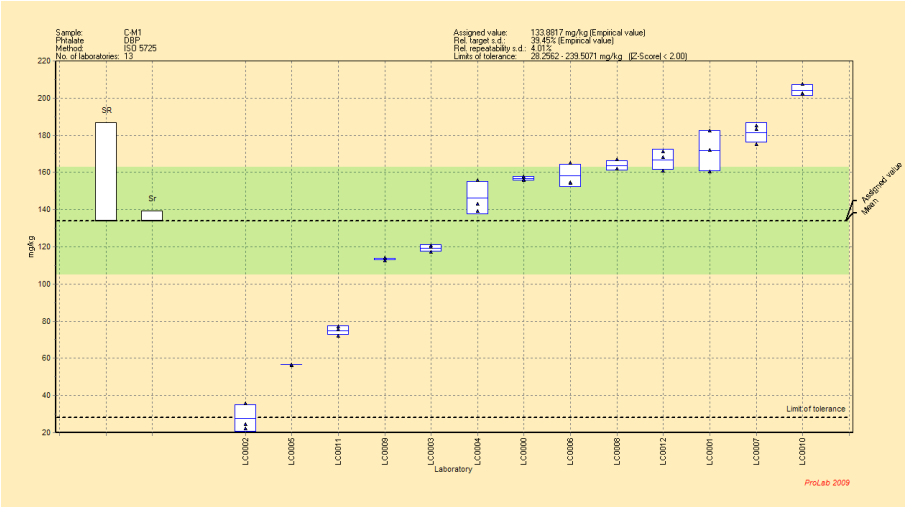




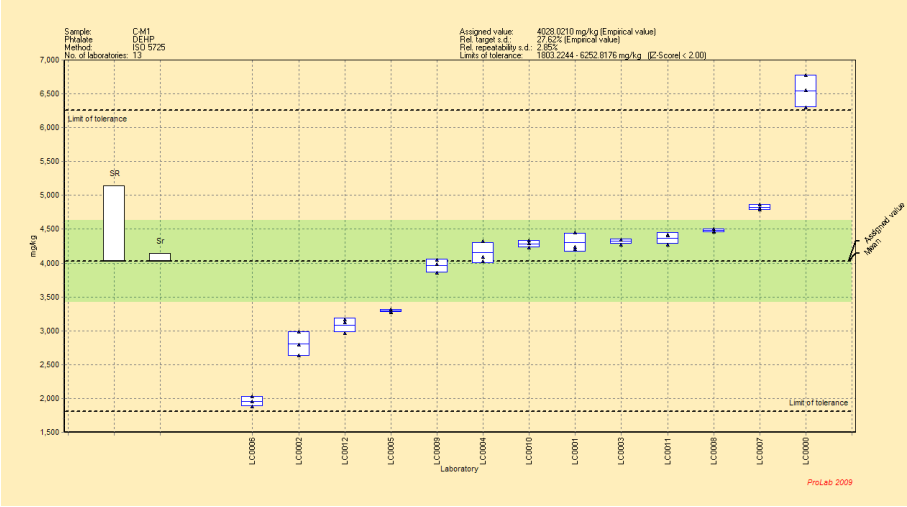




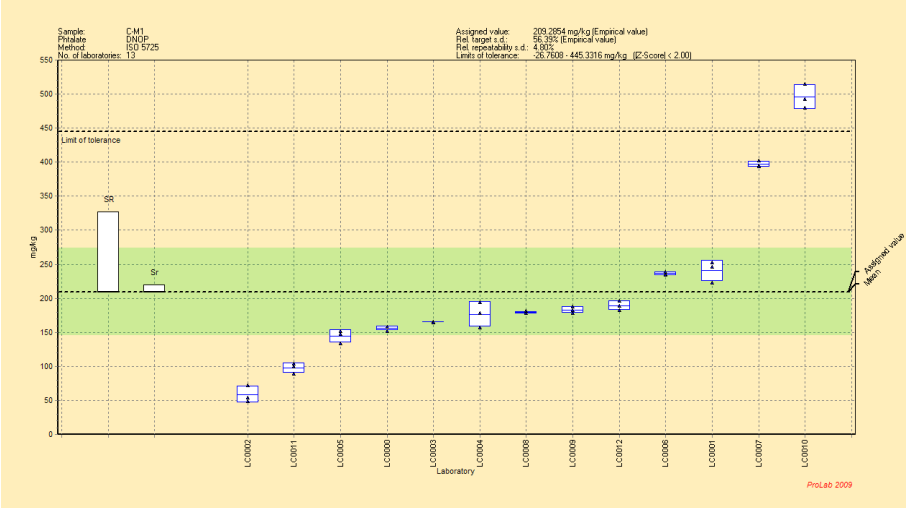




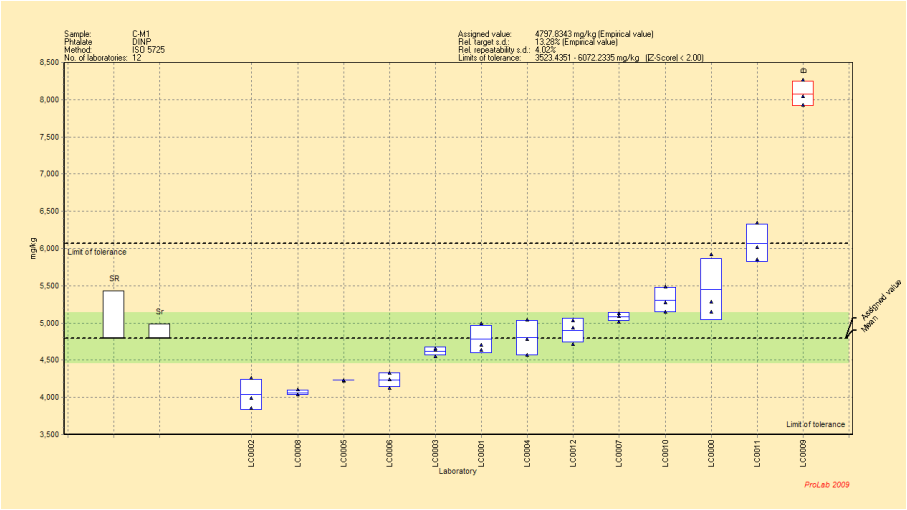
C-M1-DBP
Nr.Labs: 13
Mean (mg/kg): 133.9
SD_r (mg/kg): 5.4
SD_R (mg/kg): 52.8



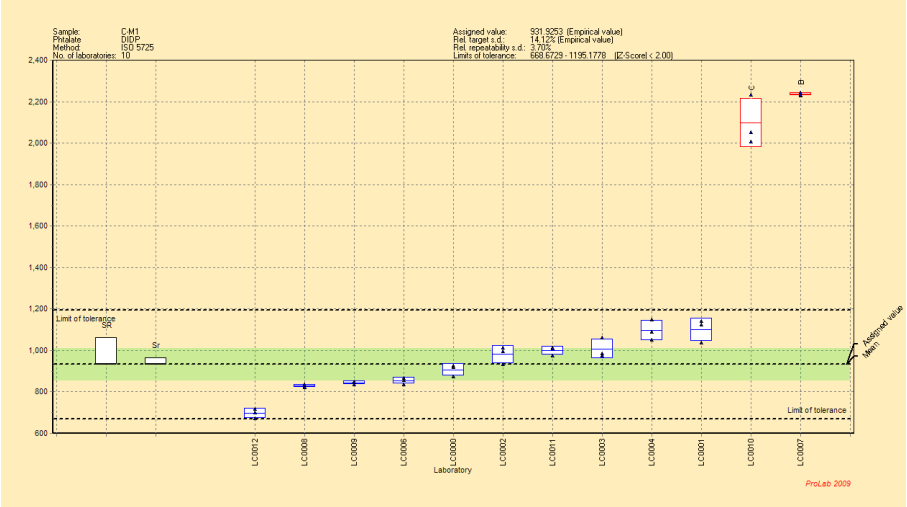
C-M1-DEHP
Nr.Labs: 13
Mean (mg/kg): 4028.0
SD_r (mg/kg): 114.9
SD_R (mg/kg): 1112.4



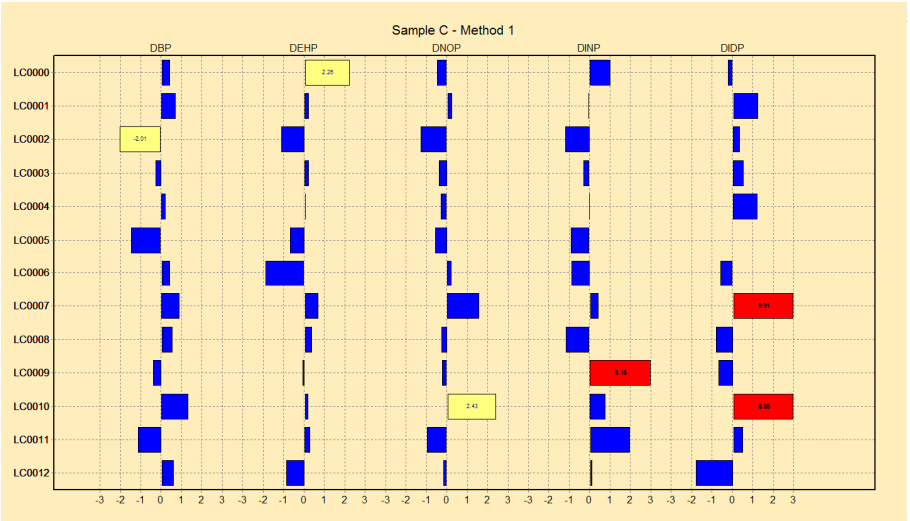
C-M1-DNOP
Nr.Labs: 13
Mean (mg/kg): 209.3
SD_r (mg/kg): 10.0
SD_R (mg/kg): 118.0



C-M1-DINP
Nr.Labs: 12
Mean (mg/kg): 4797.8
SD_r (mg/kg): 192.7
SD_R (mg/kg): 637.2

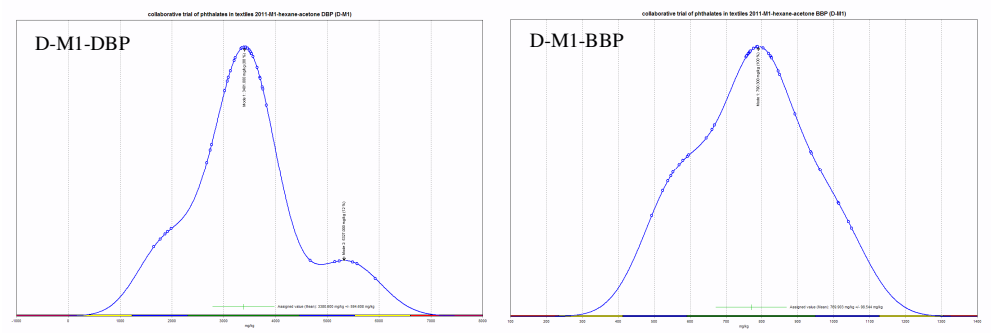


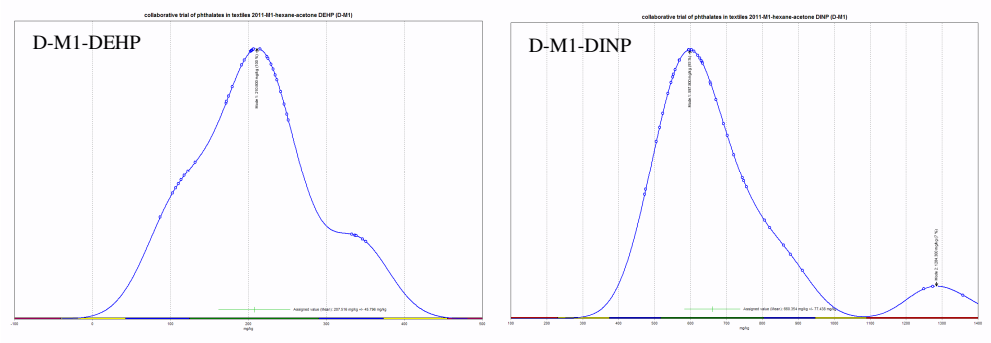
C-M1-DIDP
Nr.Labs: 10
Mean (mg/kg): 931.9
SD_r (mg/kg): 34.5
SD_R (mg/kg): 131.6

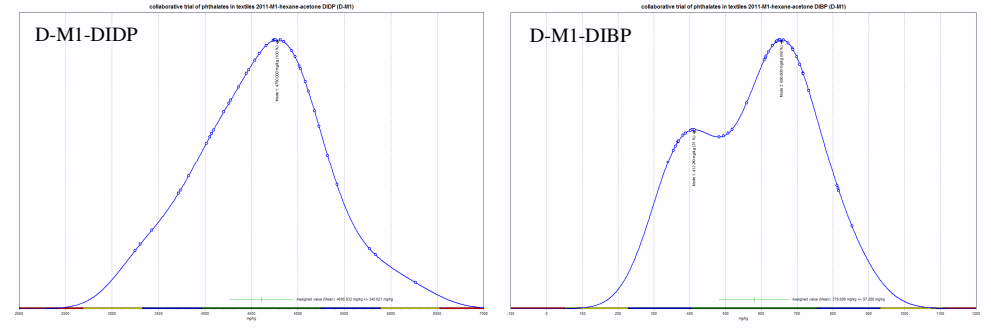


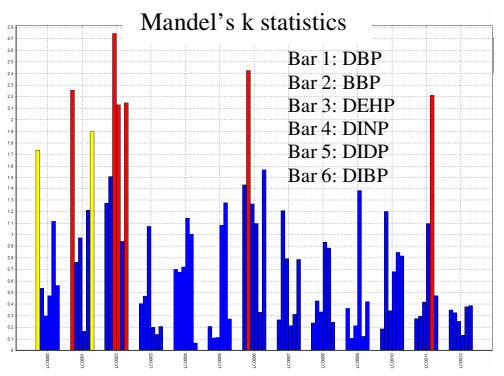
Z-scores

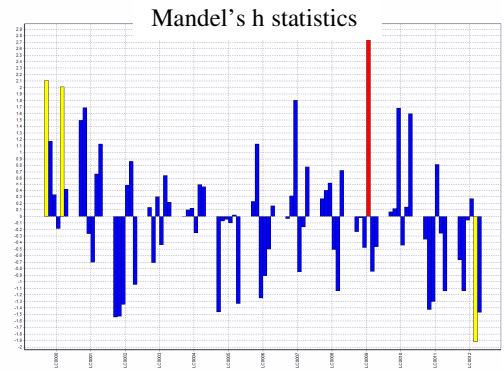
Sample D – Method 1

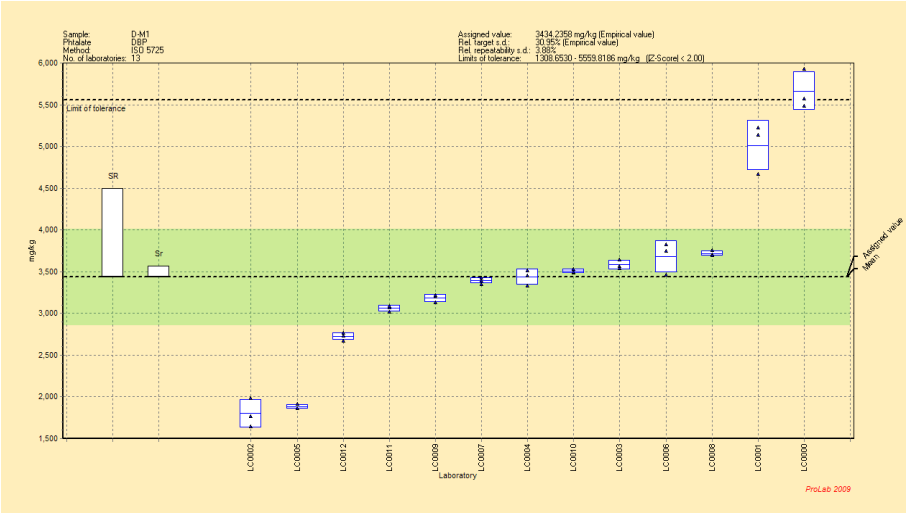




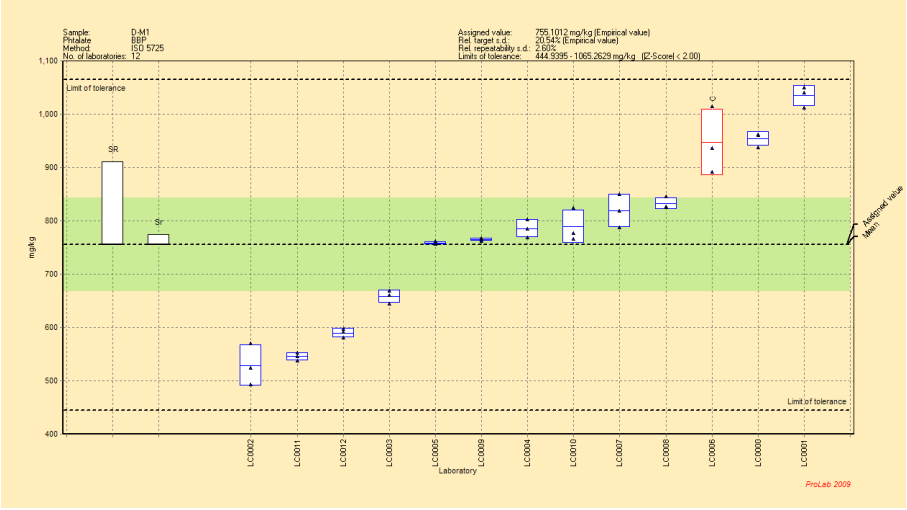




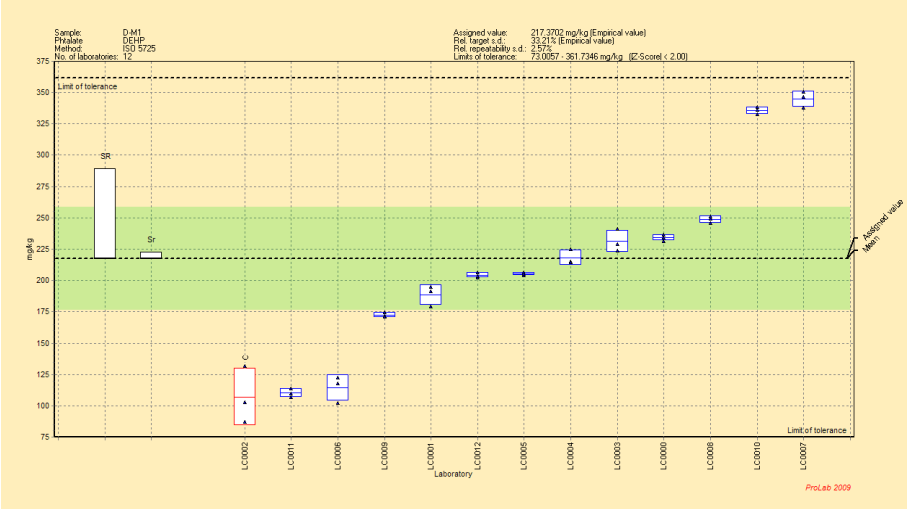




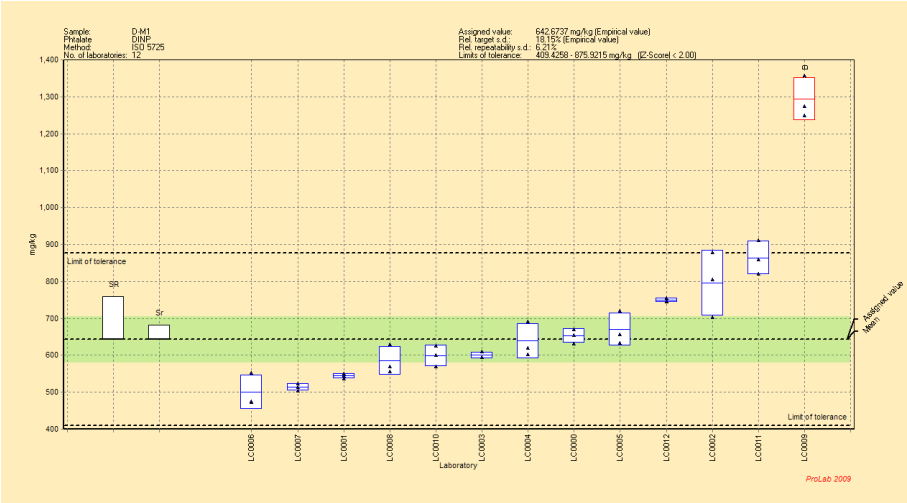
D-M1-DBP
Nr.Labs: 13
Mean (mg/kg): 3434.2
SD_r (mg/kg): 133.4
SD_R (mg/kg): 1062.8



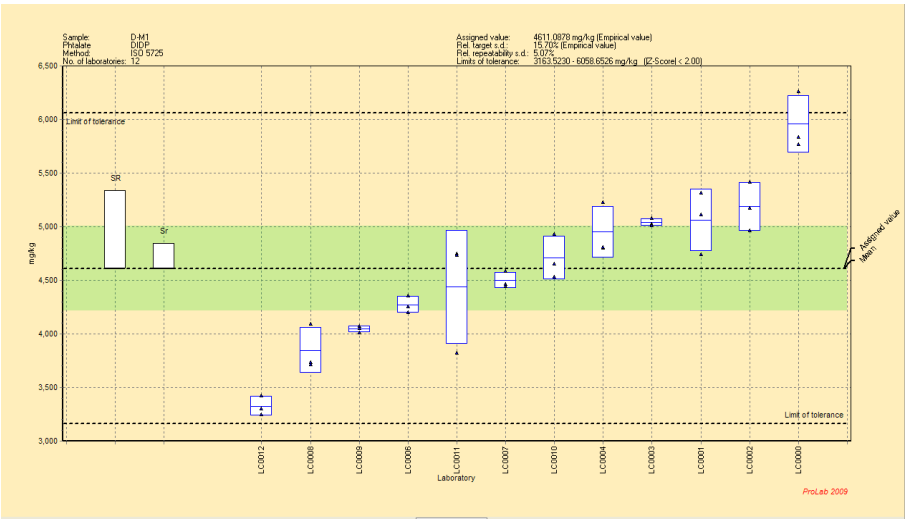
D-M1-BBP
Nr.Labs: 12
Mean (mg/kg): 755.1
SD_r (mg/kg): 19.7
SD_R (mg/kg): 155.1



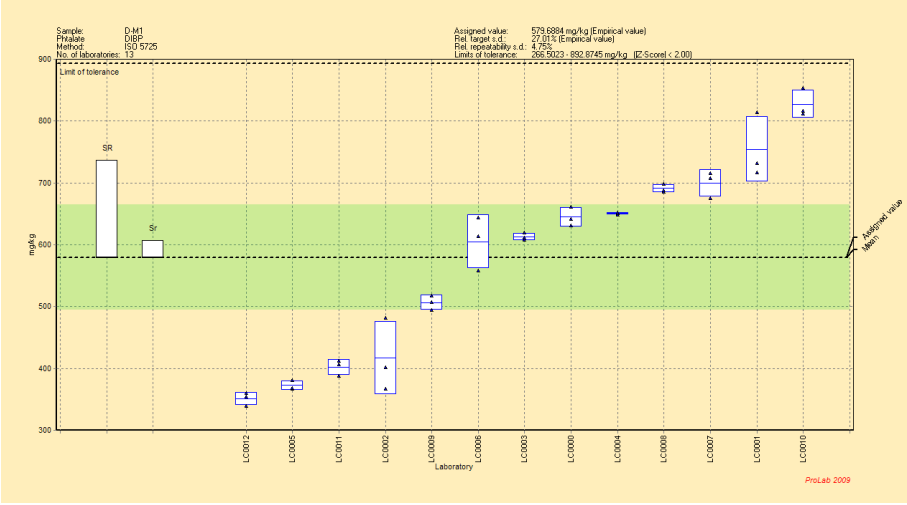
D-M1-DEHP
Nr.Labs: 12
Mean (mg/kg): 217.4
SD_r (mg/kg): 5.6
SD_R (mg/kg): 72.2



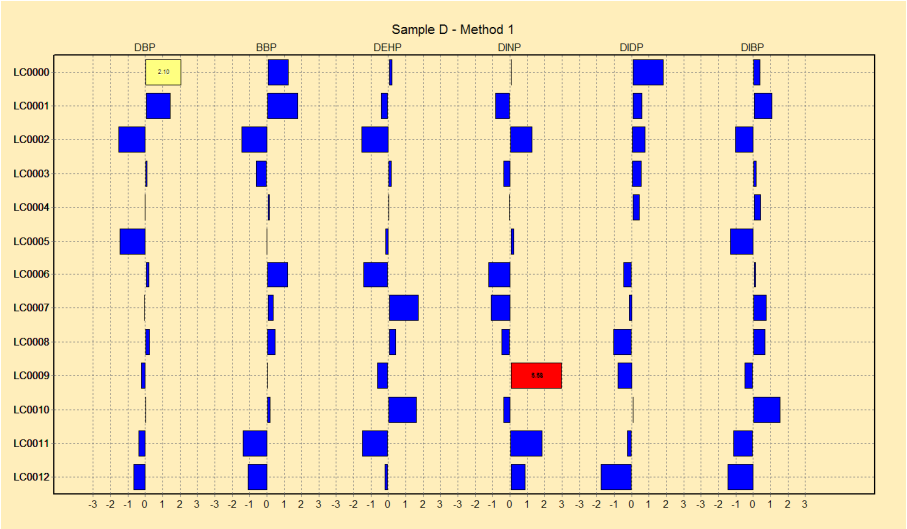
D-M1-DINP
Nr.Labs: 12
Mean (mg/kg): 642.7
SD_r (mg/kg): 39.9
SD_R (mg/kg): 116.6



D-M1-DIDP
Nr.Labs: 12
Mean (mg/kg): 4611.1
SD_r (mg/kg): 233.9
SD_R (mg/kg): 723.8

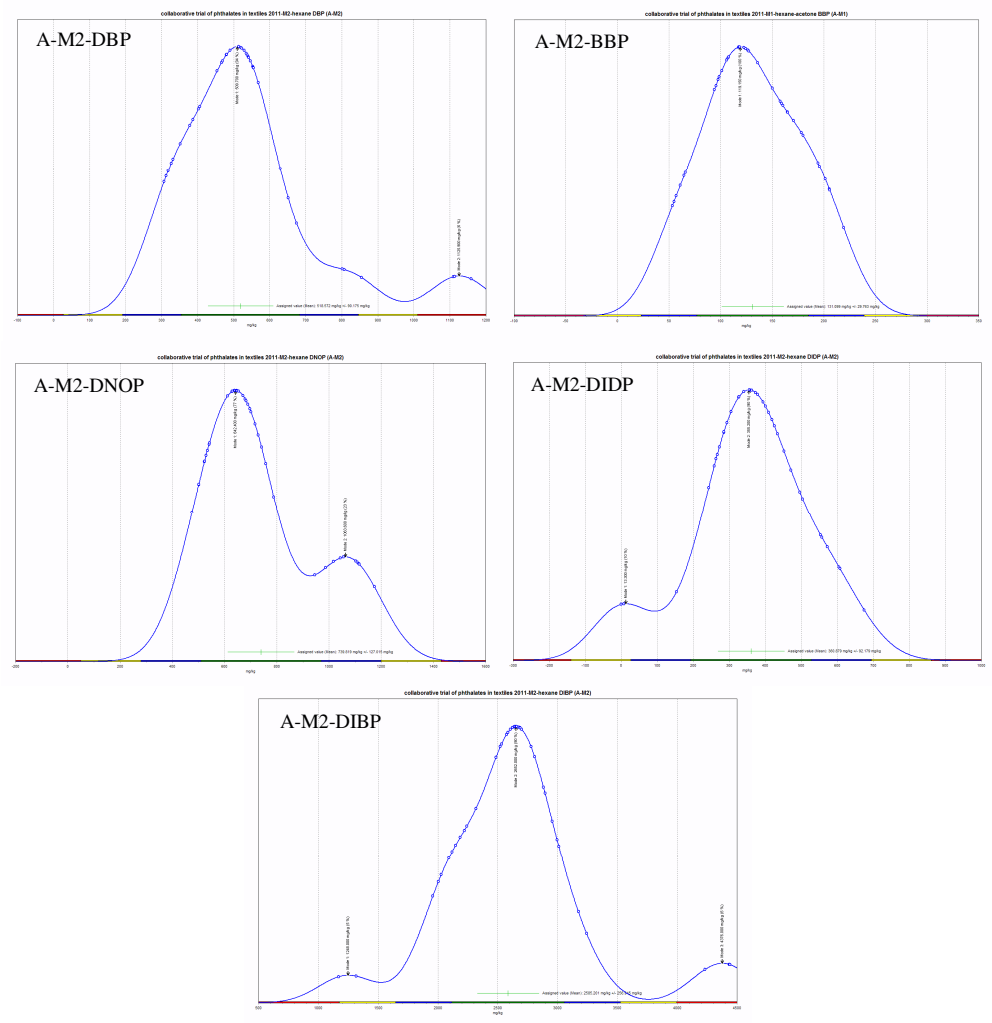


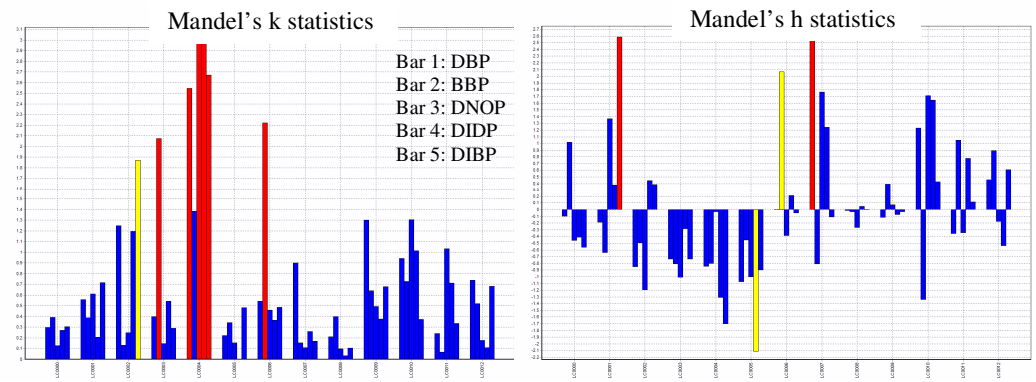
D-M1-DIBP
Nr.Labs: 13
Mean (mg/kg): 579.7
SD_r (mg/kg): 27.5
SD_R (mg/kg): 156.6

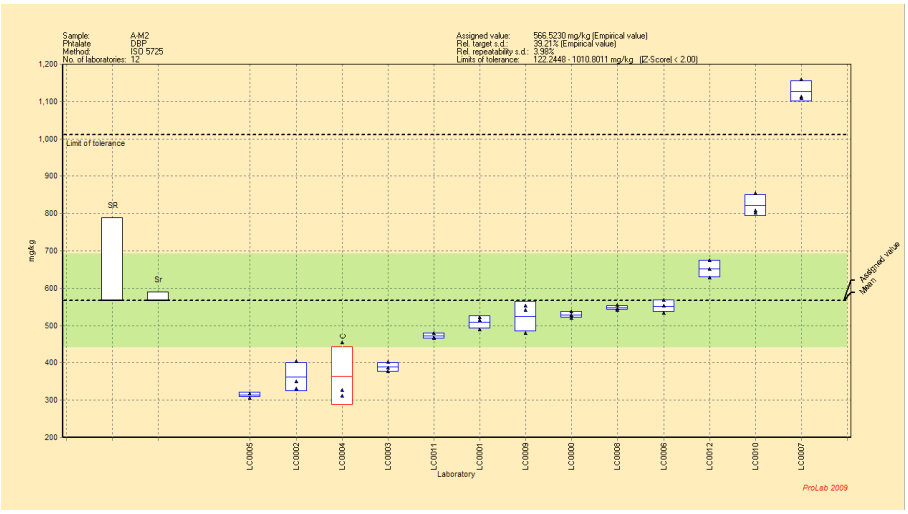

Sample D - Method 1
DBP
BBP
DEHP
DINP
DIDP
DIBP
LC0000
LC0001
LC0002
LC0003
LC0004
LC0005
LC0006
LC0007
LC0008
LC0009
LC0010
LC0011
LC0012
2.10
5.55
-3 -2 -1 0 1 2 3

Z-scores

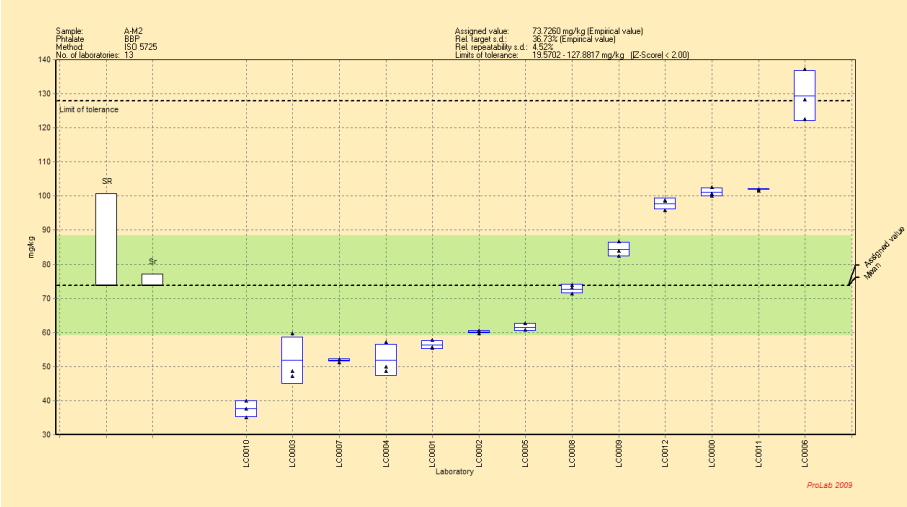
Sample A – Method 2



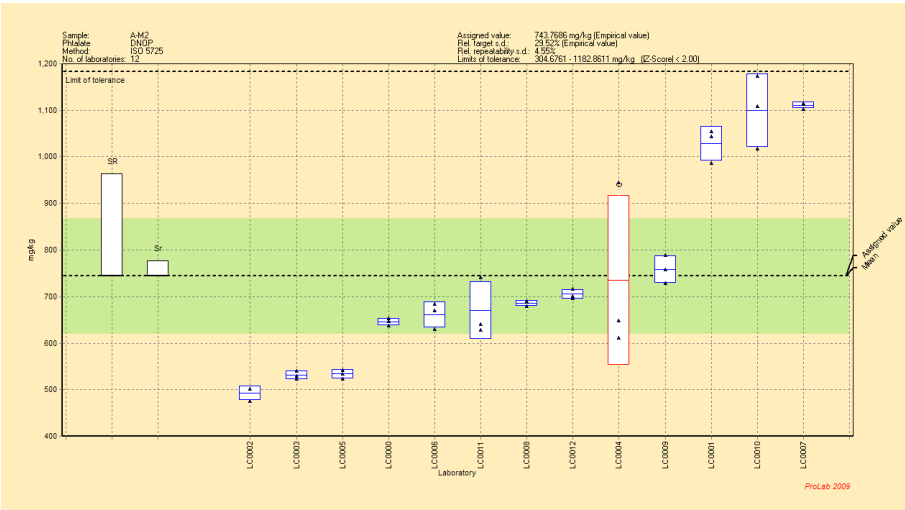




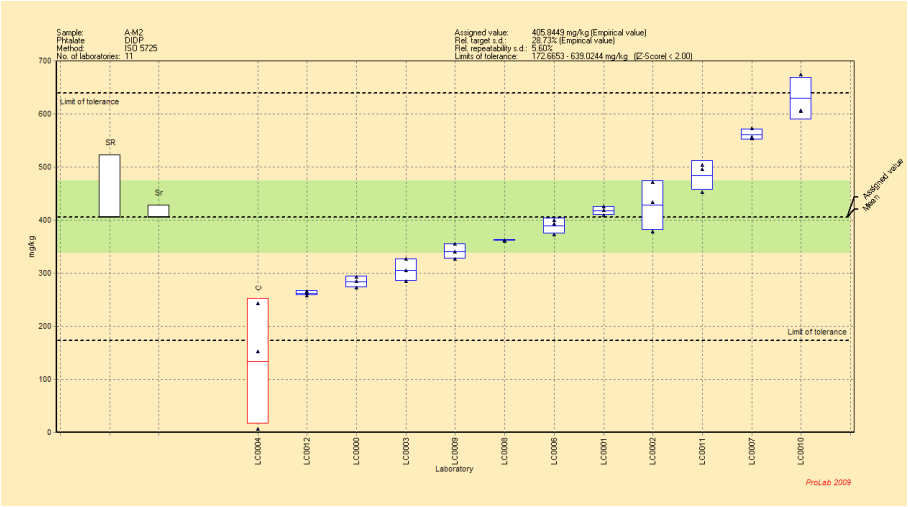
A-M2-DBP
Nr.Labs: 12
Mean (mg/kg): 566.5
SD_r (mg/kg): 22.6
SD_R (mg/kg): 222.1



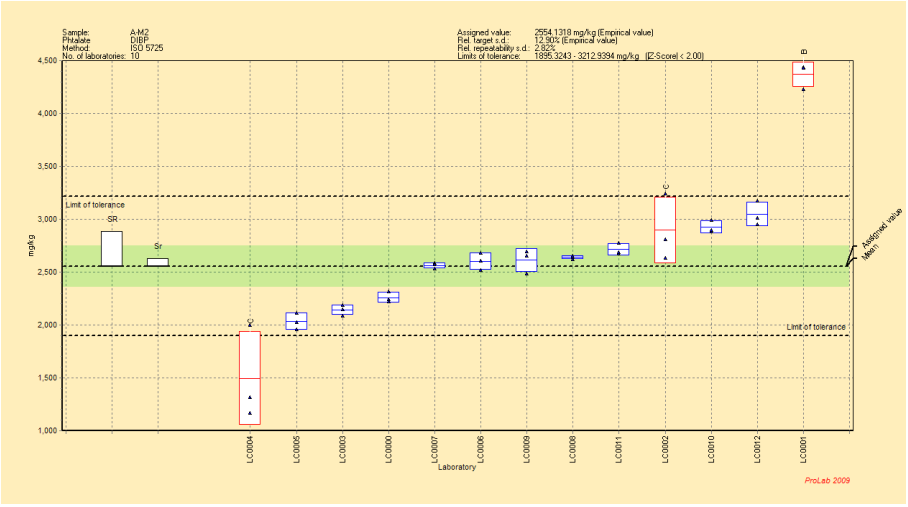
A-M2-BBP
Nr.Labs: 13
Mean (mg/kg): 73.7
SD_r (mg/kg): 3.3
SD_R (mg/kg): 27.1



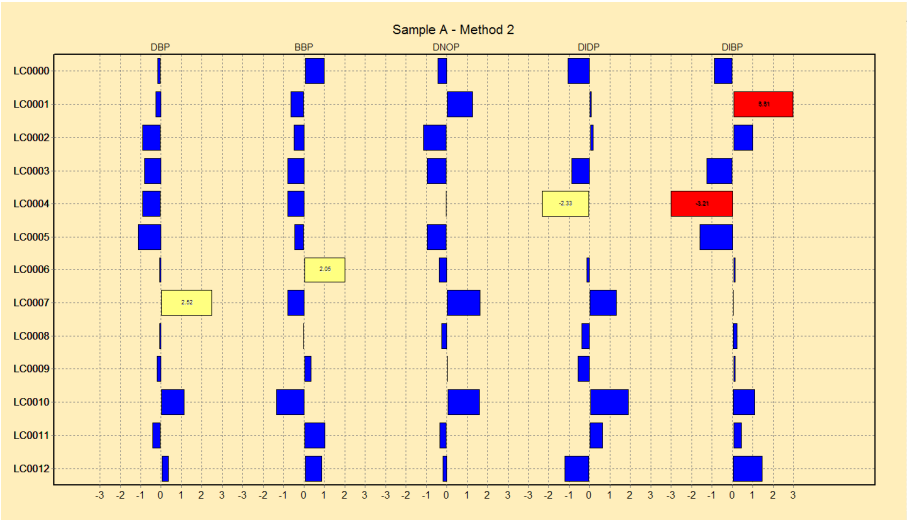
A-M2-DNOP
Nr.Labs: 12
Mean (mg/kg): 743.8
SD_r (mg/kg): 33.8
SD_R (mg/kg): 219.5



A-M2-DIDP
Nr.Labs: 11
Mean (mg/kg): 405.8
SD_r (mg/kg): 22.7
SD_R (mg/kg): 116.6

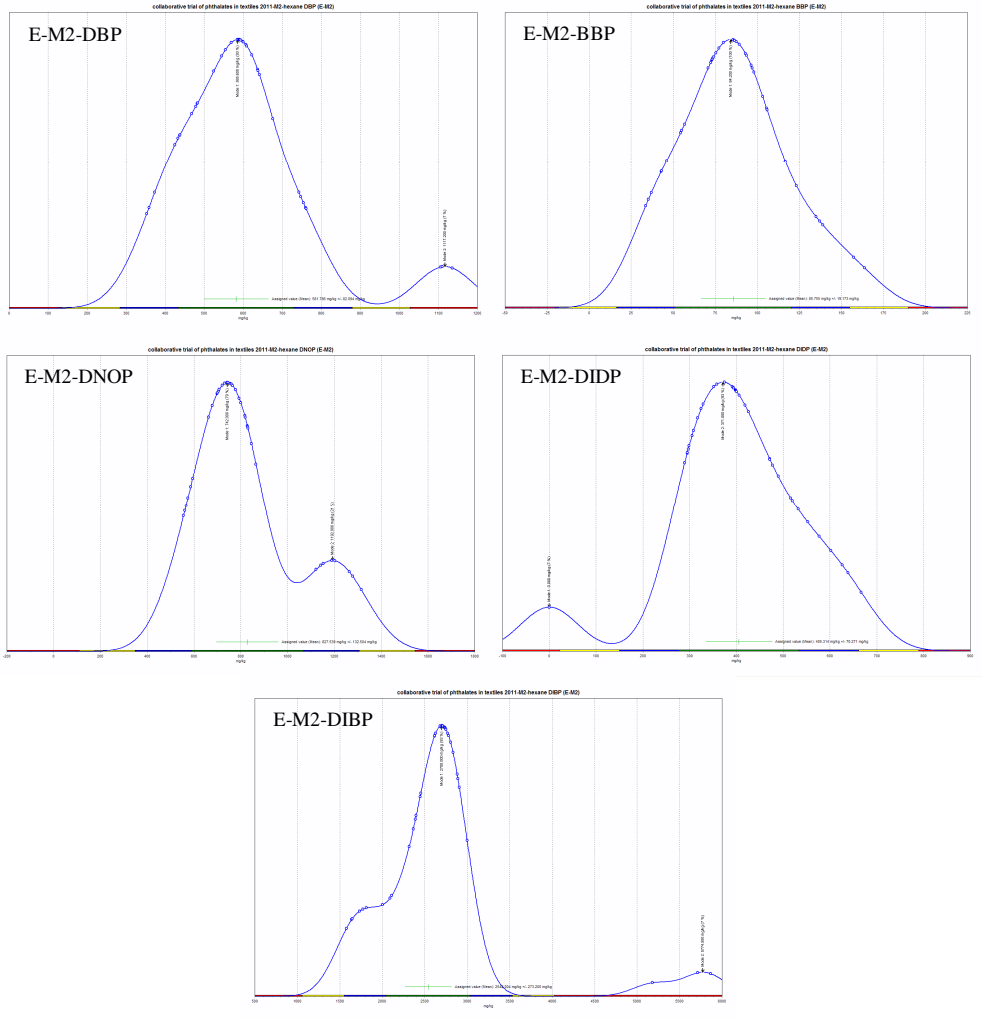


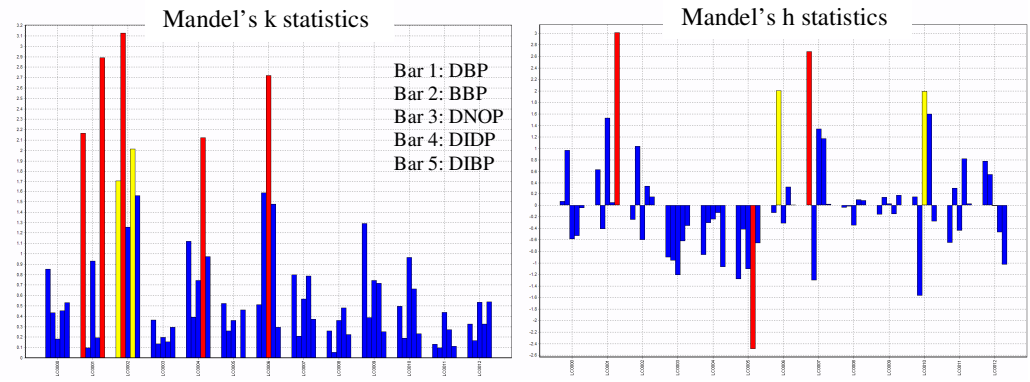
A-M2-DIBP
Nr.Labs: 10
Mean (mg/kg): 2554.1
SD_r (mg/kg): 72.0
SD_R (mg/kg): 324.4

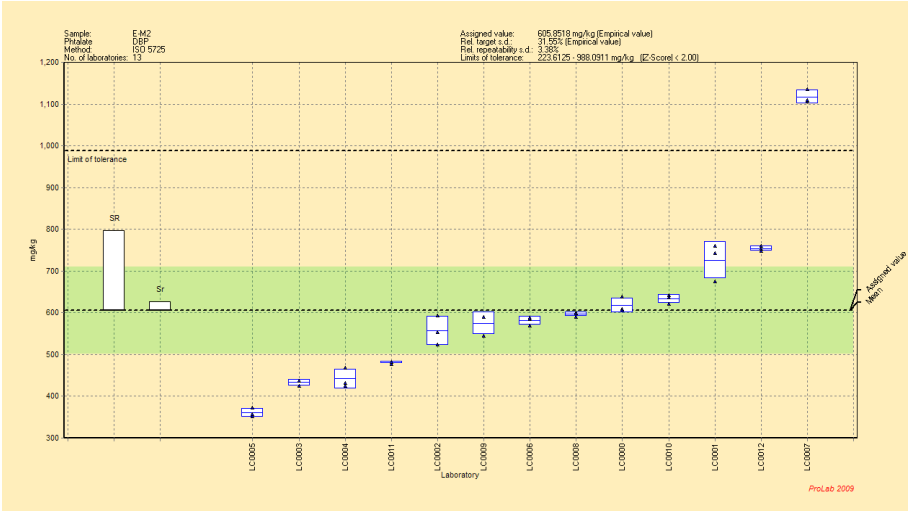


Z-scores

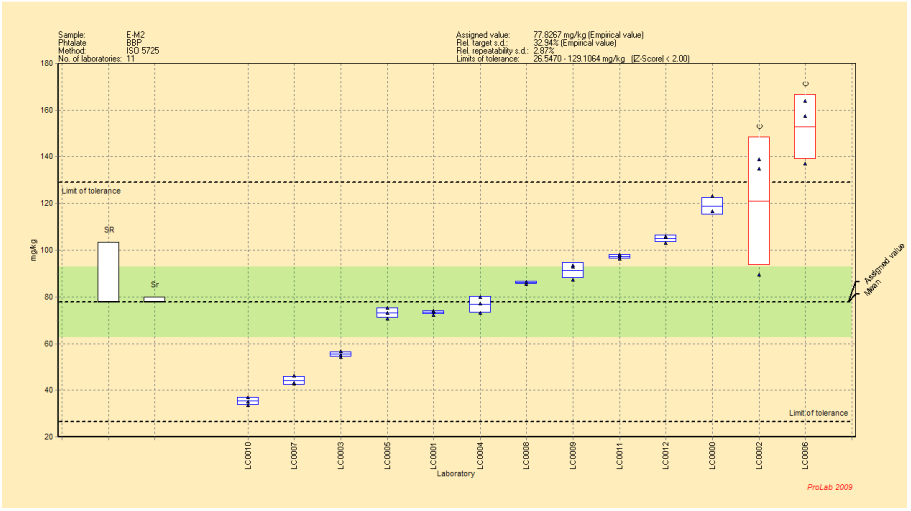
Sample E – Method 2



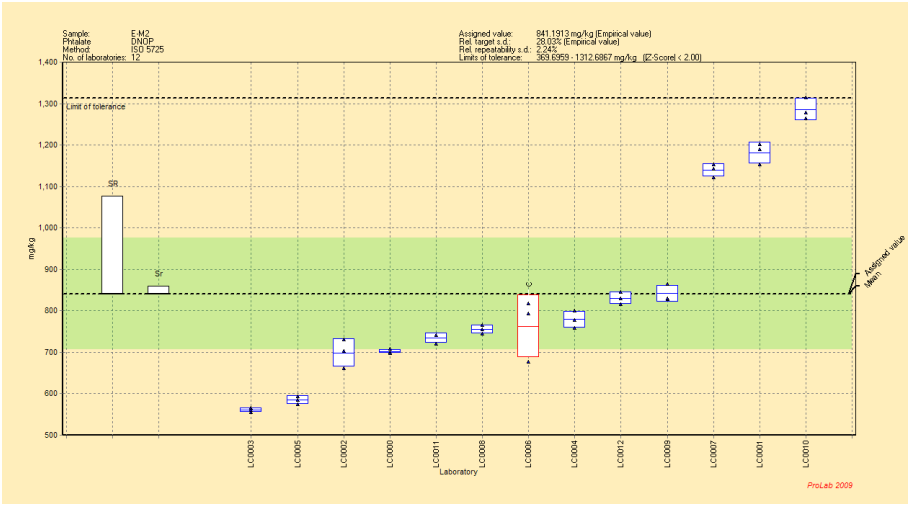




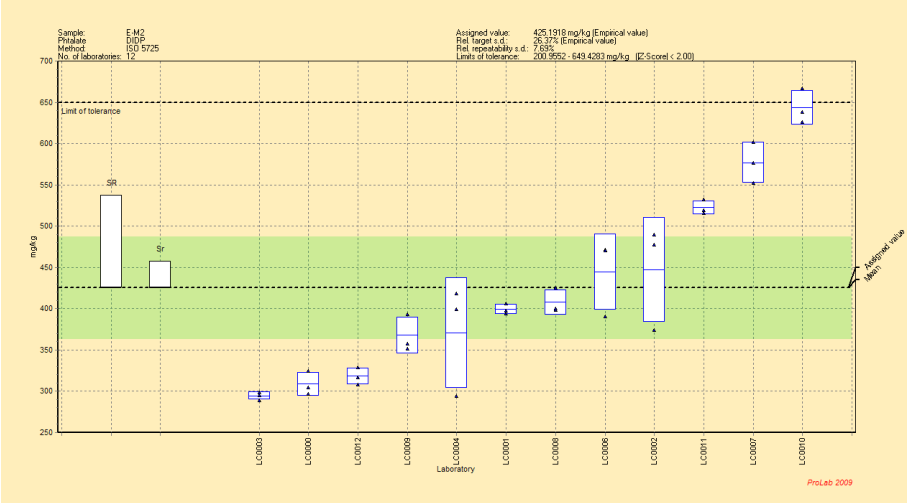
E-M2-DBP
Nr.Labs: 13
Mean (mg/kg): 605.9
SD_r (mg/kg): 20.5
SD_R (mg/kg): 191.1



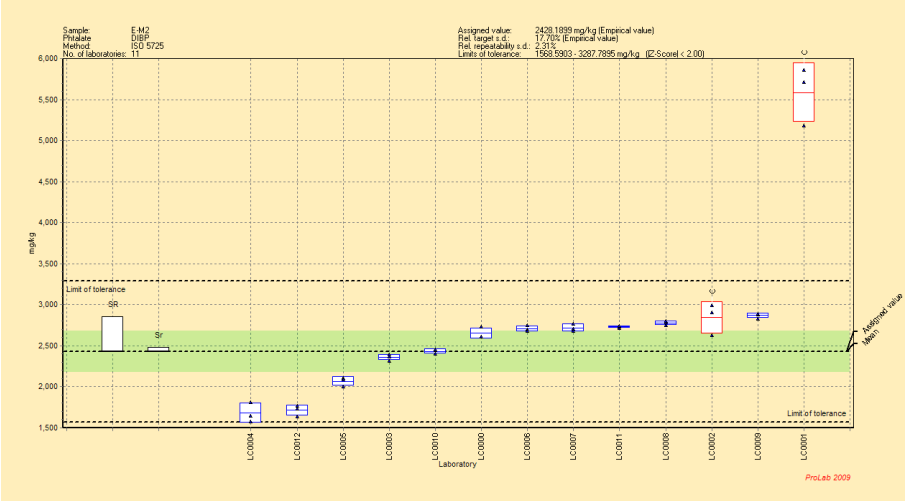
E-M2-BBP
Nr.Labs: 11
Mean (mg/kg): 77.8
SD_r (mg/kg): 2.3
SD_R (mg/kg): 26.3



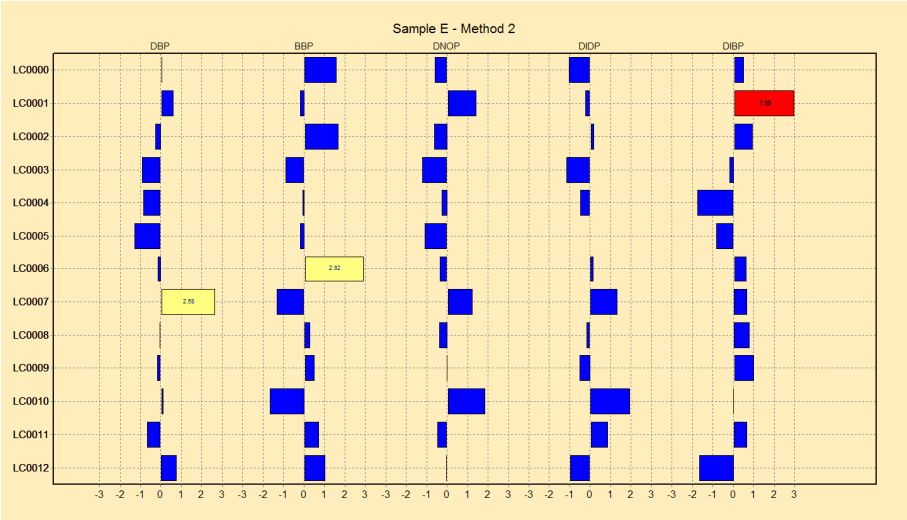
E-M2-DNOP
Nr.Labs: 12
Mean (mg/kg): 841.2
SD_r (mg/kg): 18.9
SD_R (mg/kg): 235.7



E-M2-DIDP
Nr.Labs: 12
Mean (mg/kg): 425.2
SD_r (mg/kg): 32.7
SD_R (mg/kg): 112.1

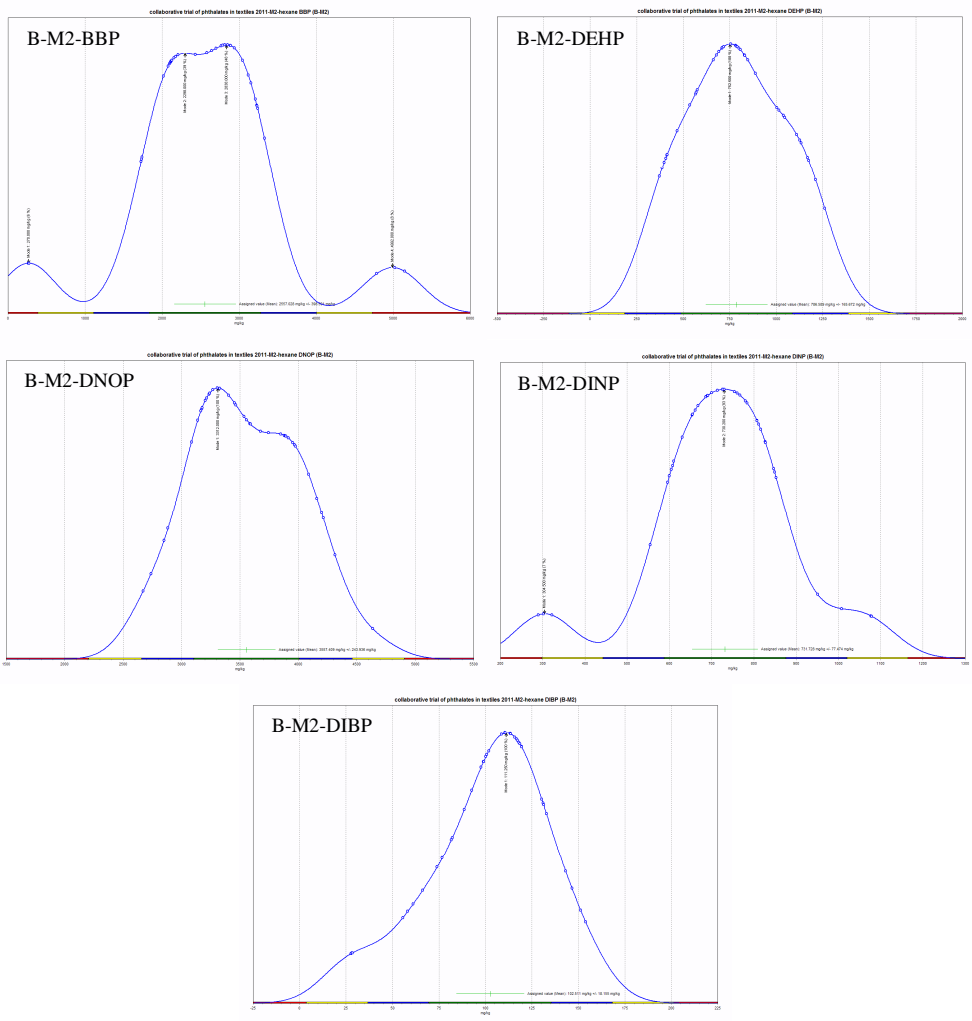


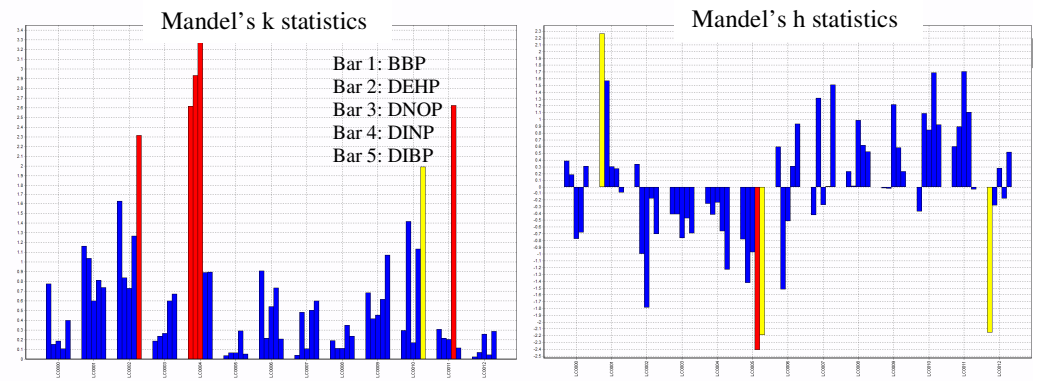
E-M2-DIBP
Nr.Labs: 11
Mean (mg/kg): 2428.2
SD_r (mg/kg): 56.0
SD_R (mg/kg): 429.8

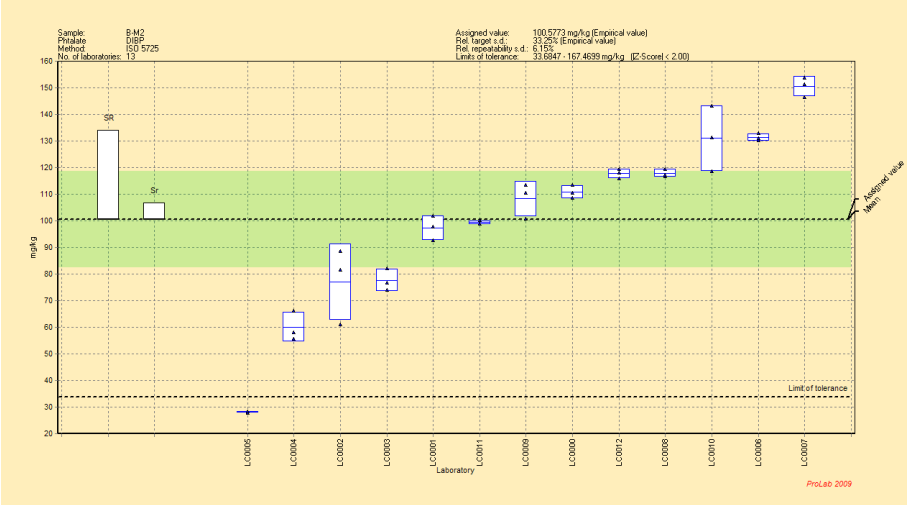


Z-scores

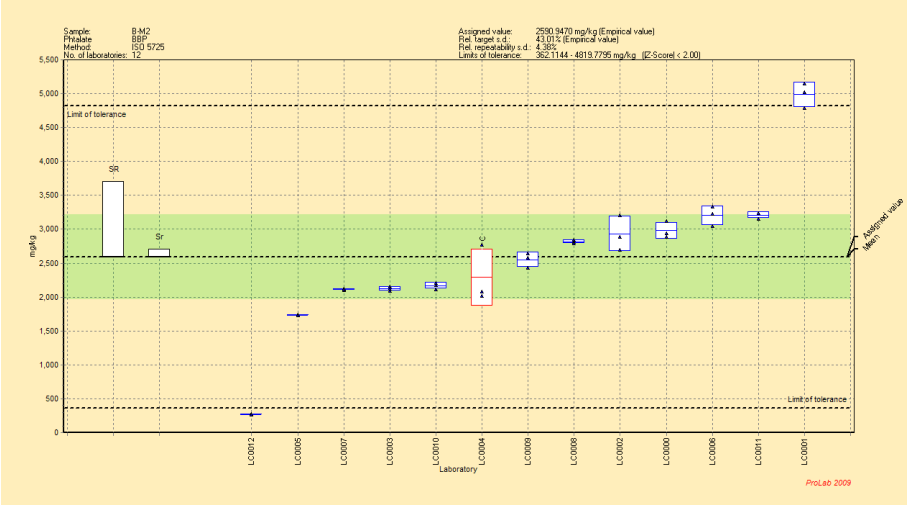
Sample B – Method 2



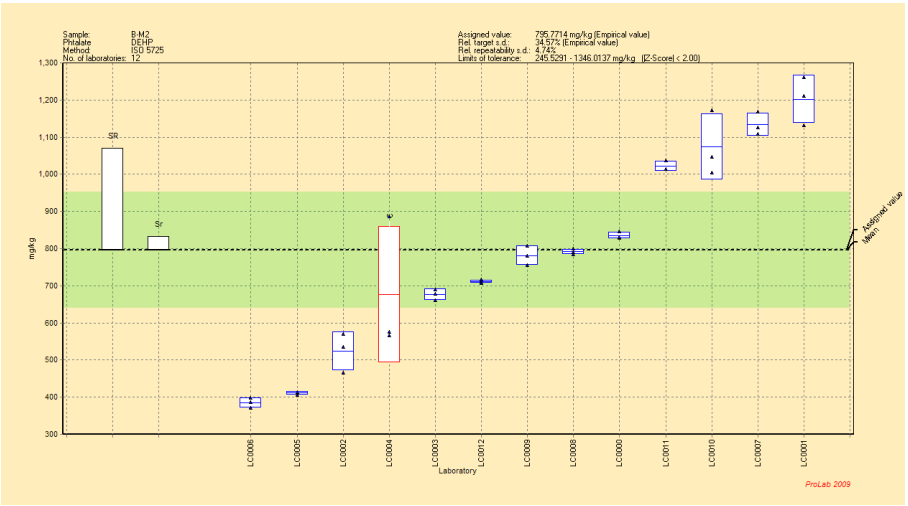




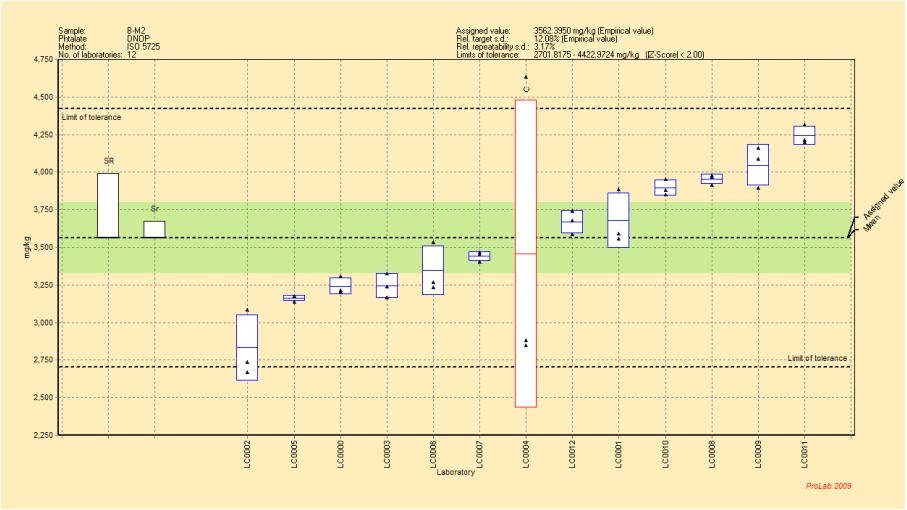
B-M2-DIBP
Nr.Labs: 13
Mean (mg/kg): 100.6
SD_r (mg/kg): 6.2
SD_R (mg/kg): 33.4



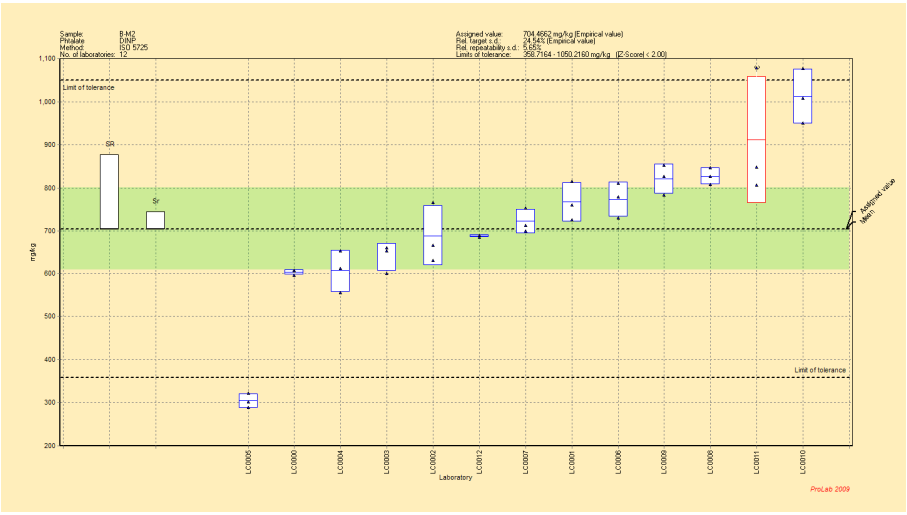
B-M2-BBP
Nr.Labs: 12
Mean (mg/kg): 2590.9
SD_r (mg/kg): 113.5
SD_R (mg/kg): 1114.4



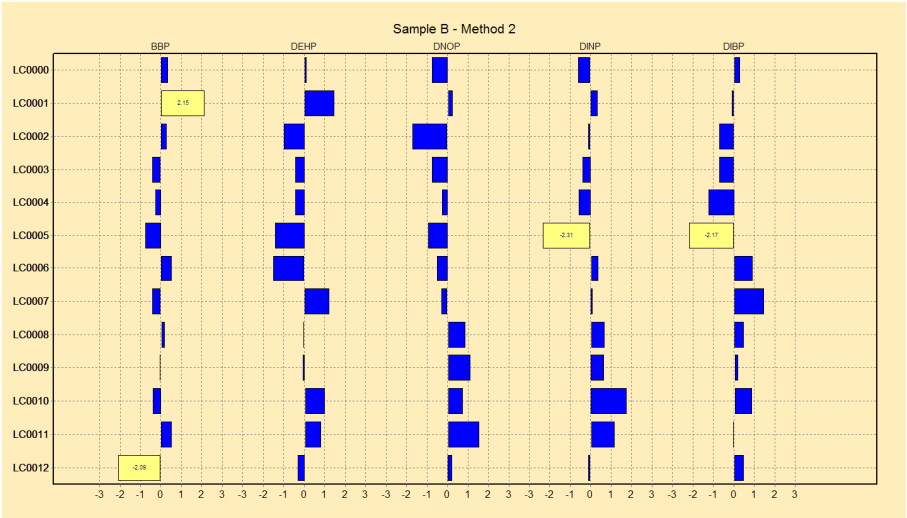
B-M2-DEHP
Nr.Labs: 12
Mean (mg/kg): 795.8
SD_r (mg/kg): 37.7
SD_R (mg/kg): 275.1



B-M2-DNOP
Nr.Labs: 12
Mean (mg/kg): 3562.4
SD_r (mg/kg): 113.0
SD_R (mg/kg): 430.3

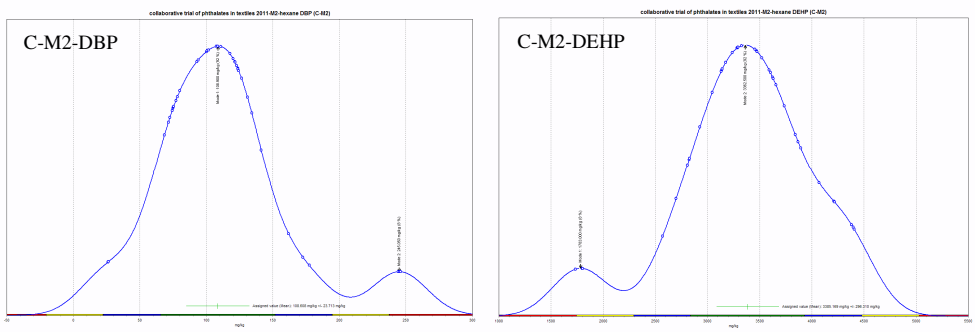


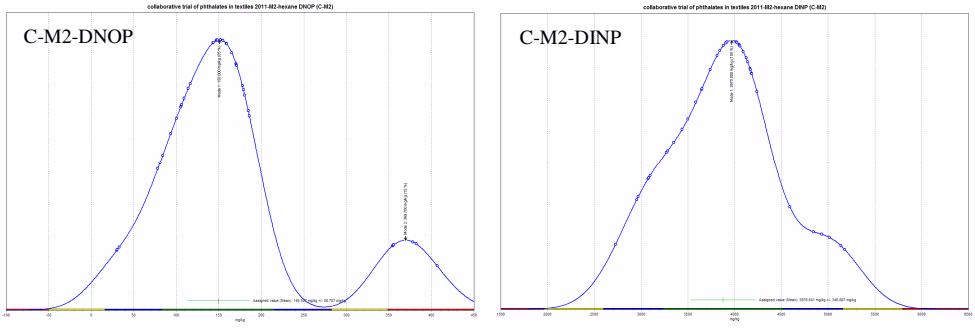
B-M2-DINP
Nr.Labs: 12
Mean (mg/kg): 704.5
SD_r (mg/kg): 39.8
SD_R (mg/kg): 172.9

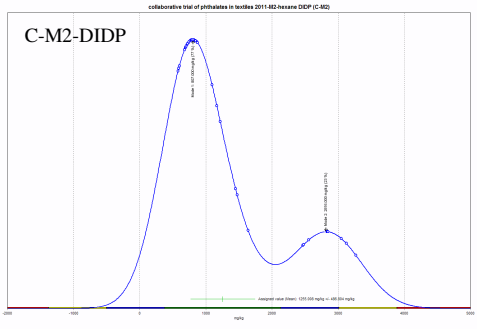


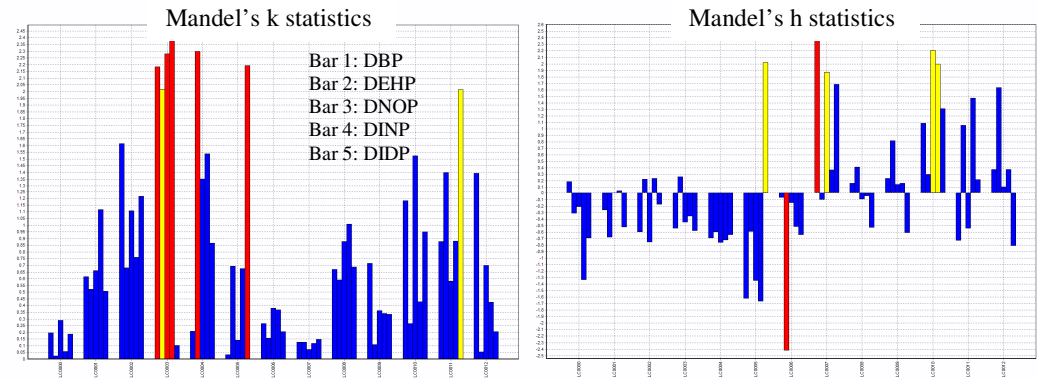
Z-scores

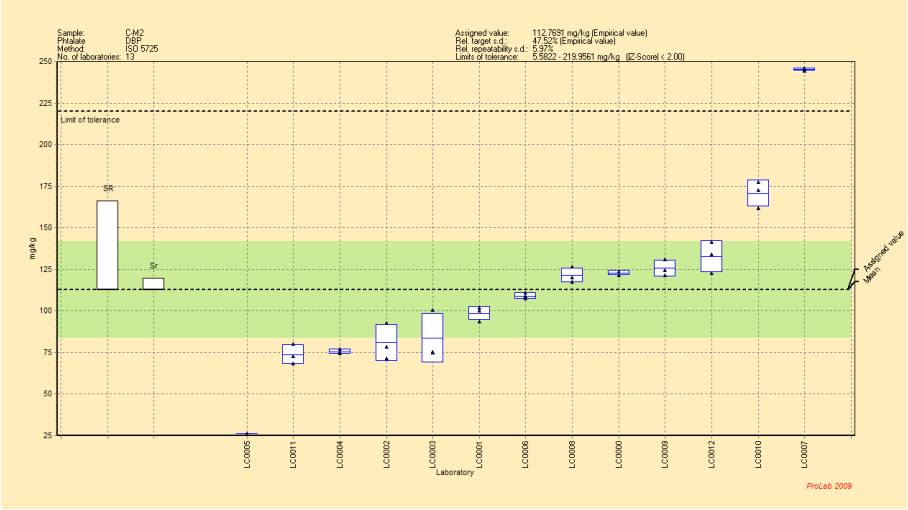
Sample C – Method 2



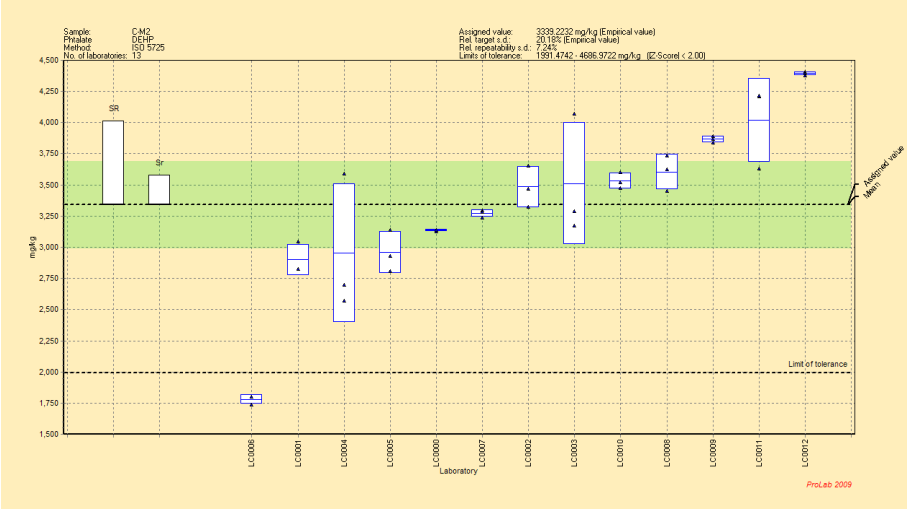




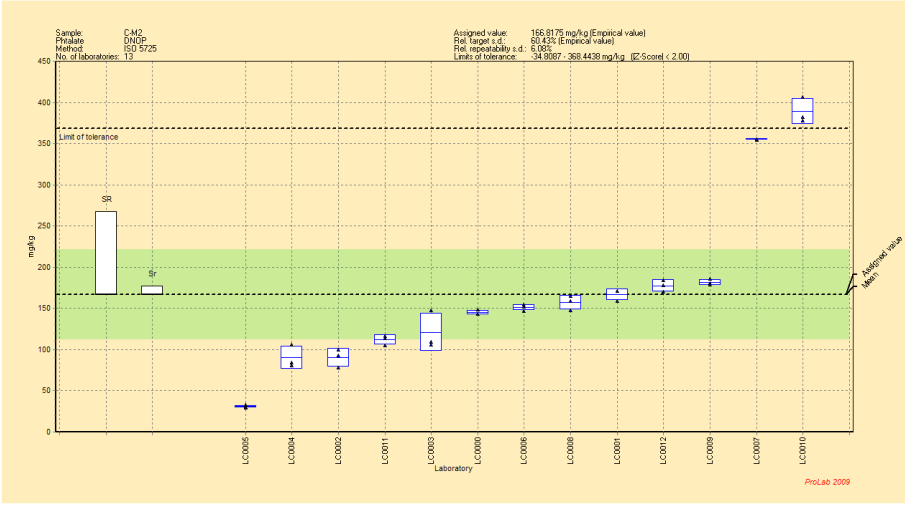




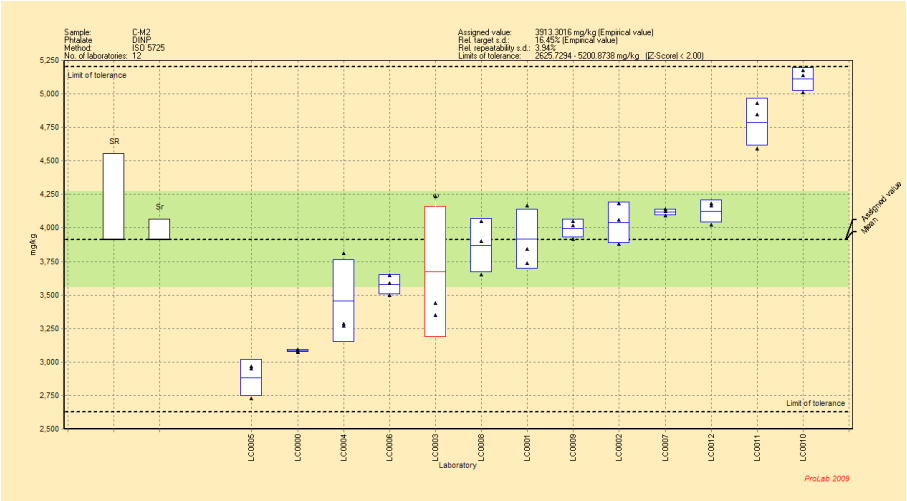
C-M2-DBP
Nr.Labs: 13
Mean (mg/kg): 112.8
SD_r (mg/kg): 6.7
SD_R (mg/kg): 53.6



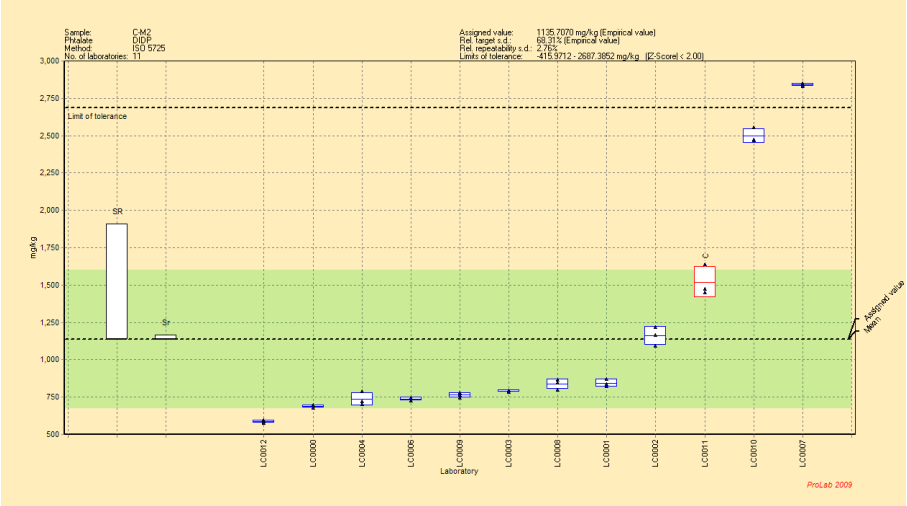
C-M2-DEHP
Nr.Labs: 13
Mean (mg/kg): 3339.2
SD_r (mg/kg): 241.9
SD_R (mg/kg): 673.9



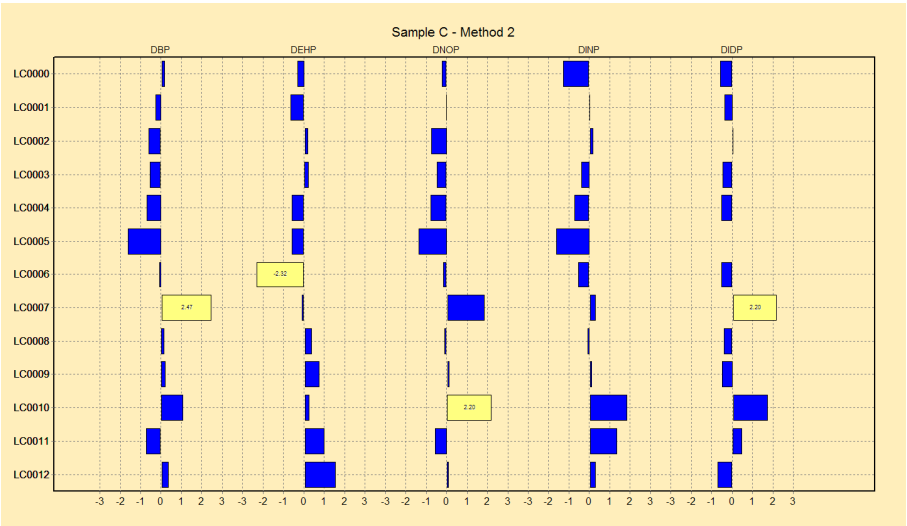
C-M2-DNOP
Nr.Labs: 13
Mean (mg/kg): 166.8
SD_r (mg/kg): 10.1
SD_R (mg/kg): 100.8



C-M2-DINP
Nr.Labs: 12
Mean (mg/kg): 3913.3
SD_r (mg/kg): 154.2
SD_R (mg/kg): 643.8

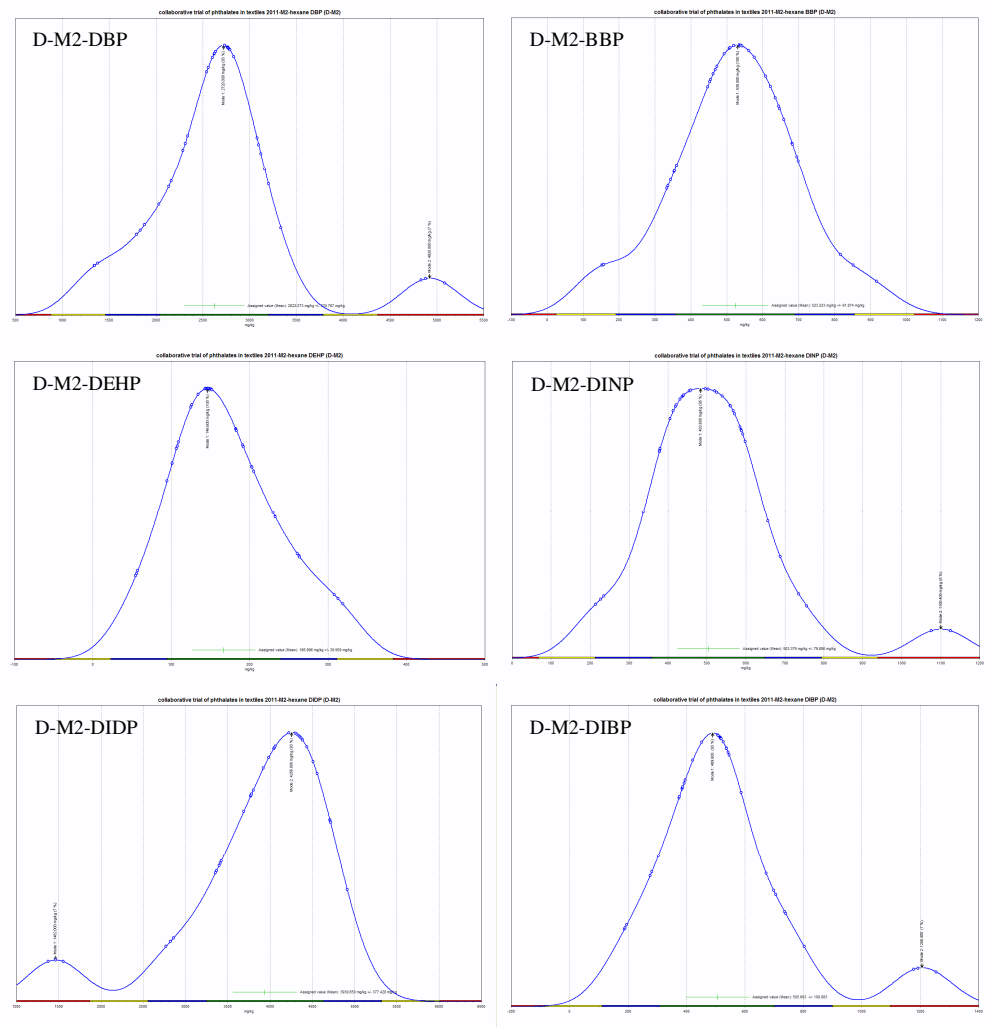


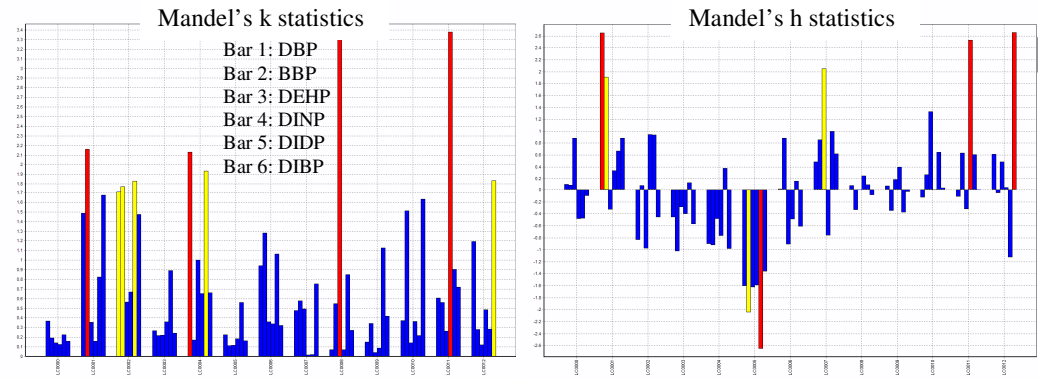
C-M2-DIDP
Nr.Labs: 11
Mean (mg/kg): 1135.7
SD_r (mg/kg): 31.4
SD_R (mg/kg): 775.8

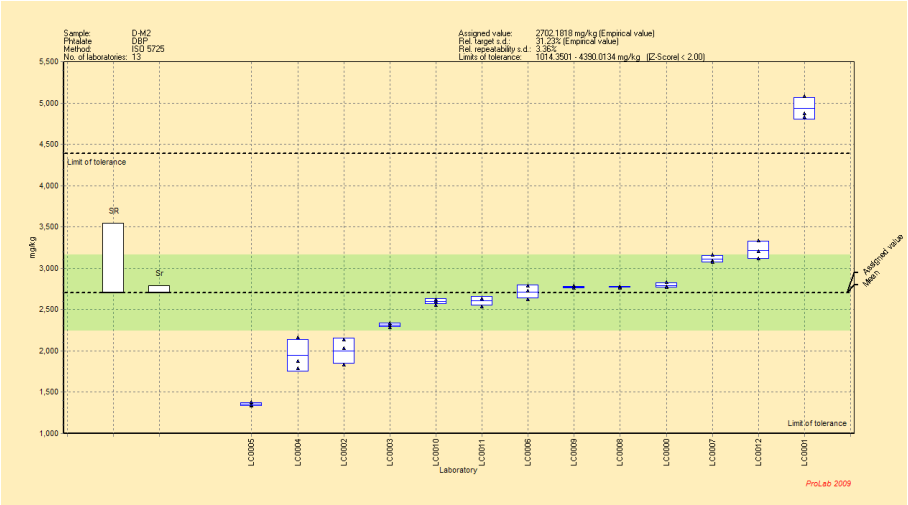


Z-scores

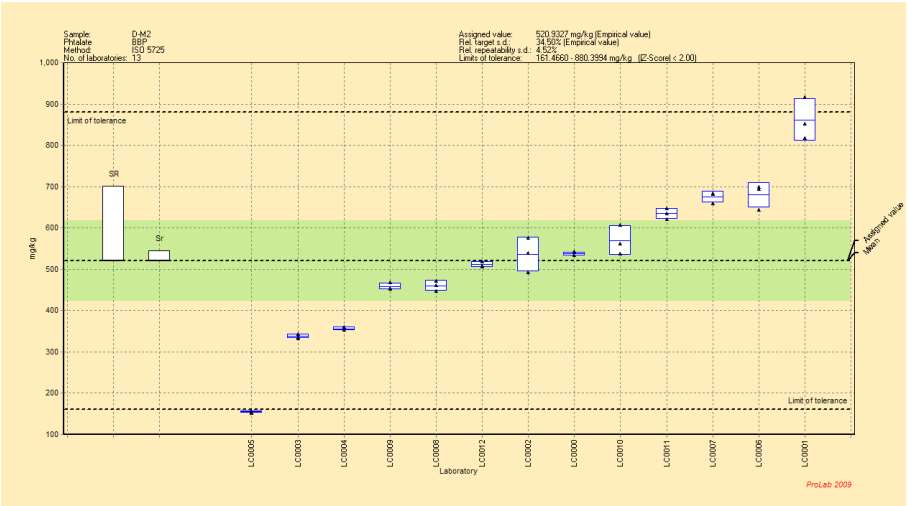
Sample D – Method 2



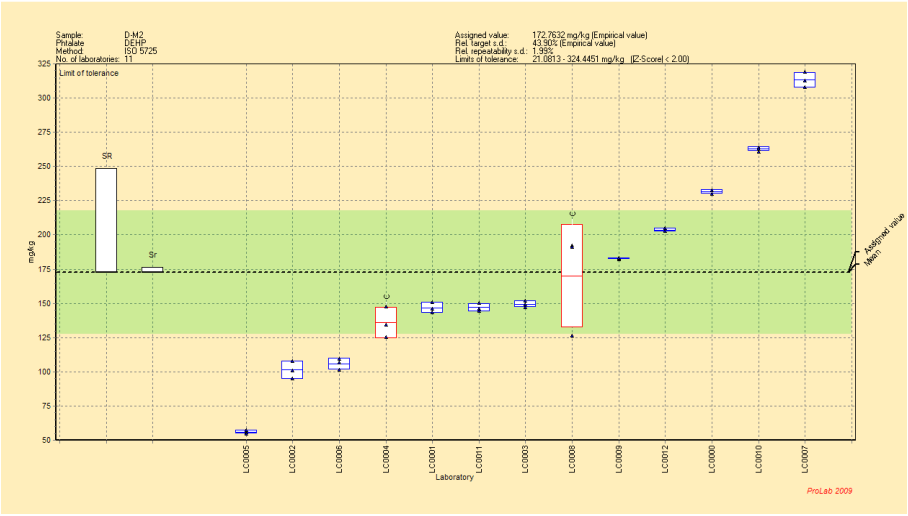




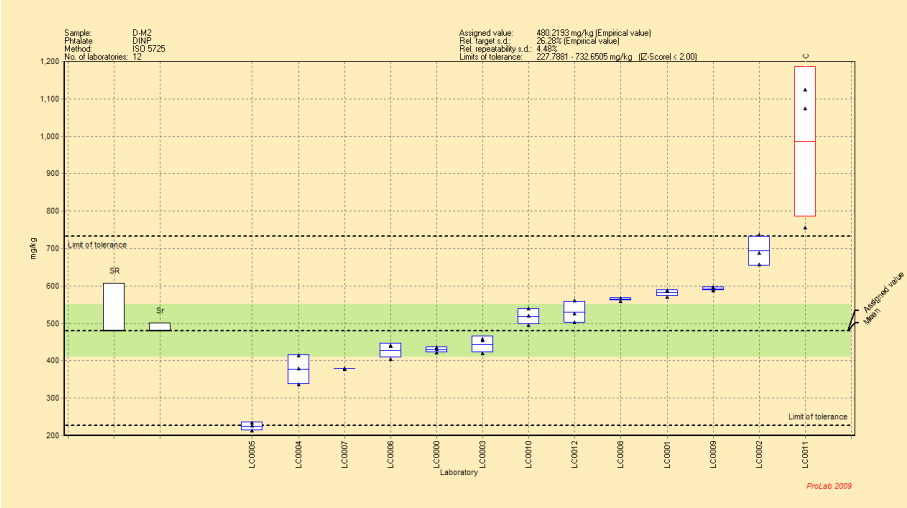
D-M2-DBP
Nr.Labs: 13
Mean (mg/kg): 2702.2
SD_r (mg/kg): 90.8
SD_R (mg/kg): 843.6



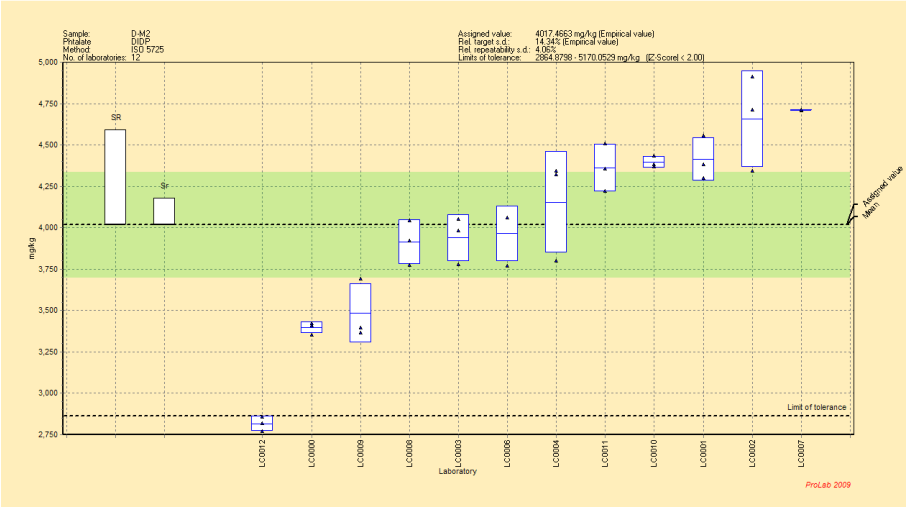
D-M2-BBP
Nr.Labs: 13
Mean (mg/kg): 520.9
SD_r (mg/kg): 23.5
SD_R (mg/kg): 179.7



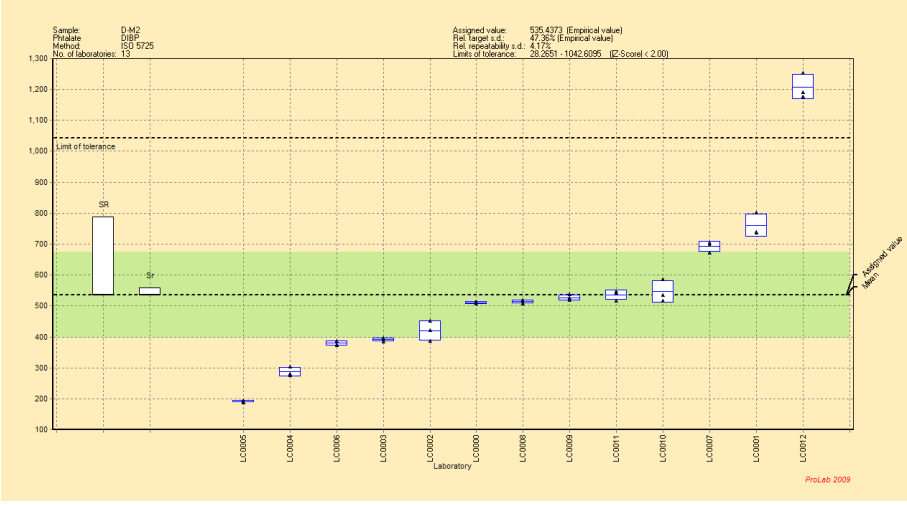
D-M2-DEHP
Nr.Labs: 11
Mean (mg/kg): 172.8
SD_r (mg/kg): 3.4
SD_R (mg/kg): 75.8



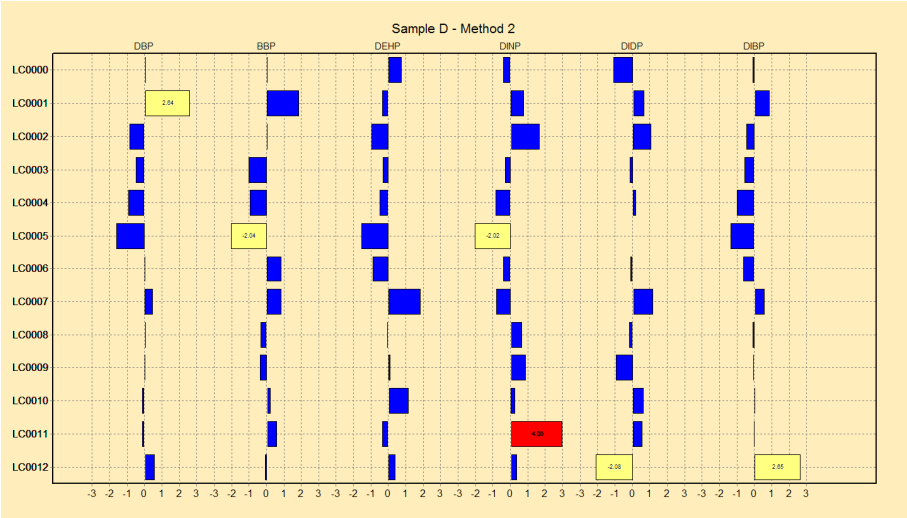
D-M2-DINP
Nr.Labs: 12
Mean (mg/kg): 480.2
SD_r (mg/kg): 21.6
SD_R (mg/kg): 126.2



D-M2-DIDP
Nr.Labs: 12
Mean (mg/kg): 4017.5
SD_r (mg/kg): 162.9
SD_R (mg/kg): 576.3

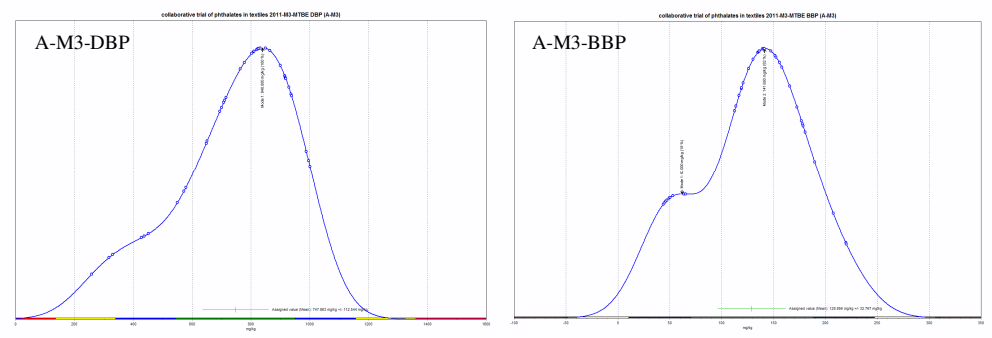


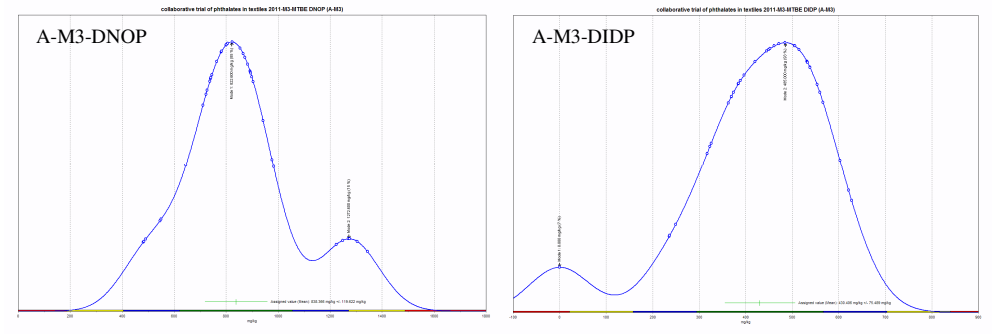
D-M2-DIBP
Nr.Labs: 13
Mean (mg/kg): 535.4
SD_r (mg/kg): 22.3
SD_R (mg/kg): 253.6

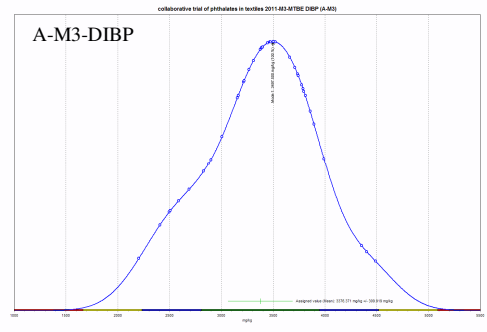

Sample D - Method 2
DBP
BBP
DEHP
DINP
DIDP
DIBP
LC0000
LC0001
LC0002
LC0003
LC0004
LC0005
LC0006
LC0007
LC0008
LC0009
LC0010
LC0011
LC0012
2.64
-2.04
-2.02
4.99
-2.06
2.66

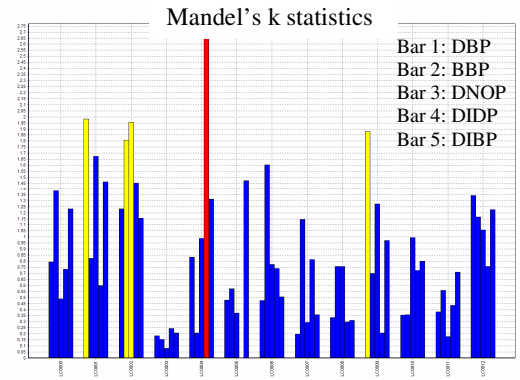
Z-scores

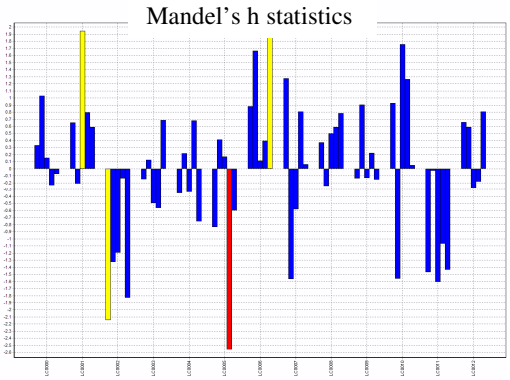
Sample A – Method 3

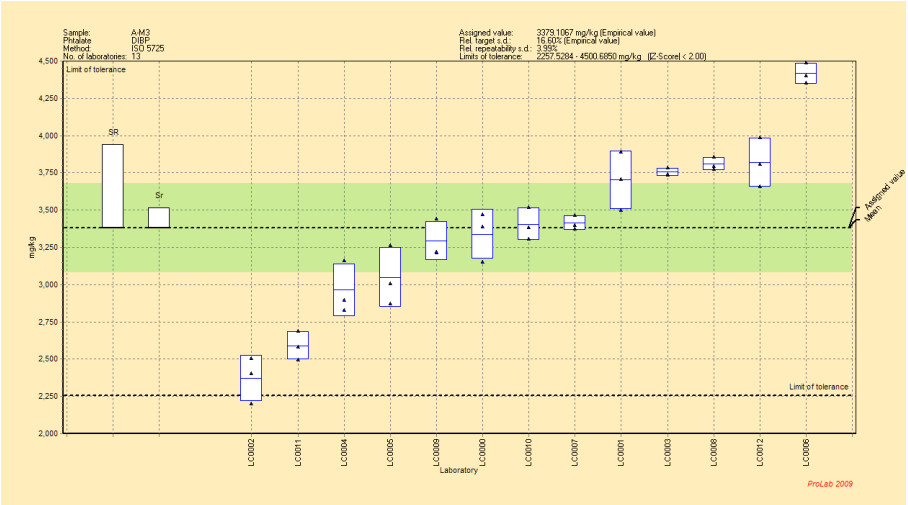




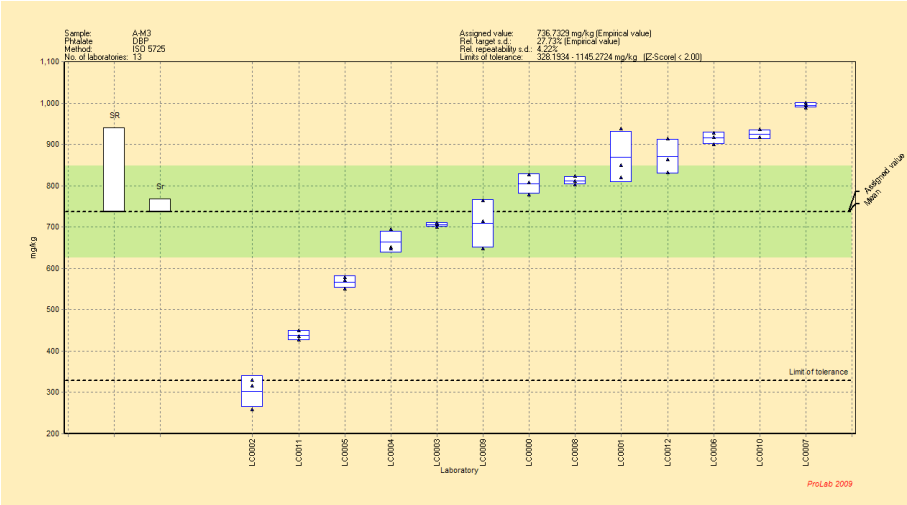




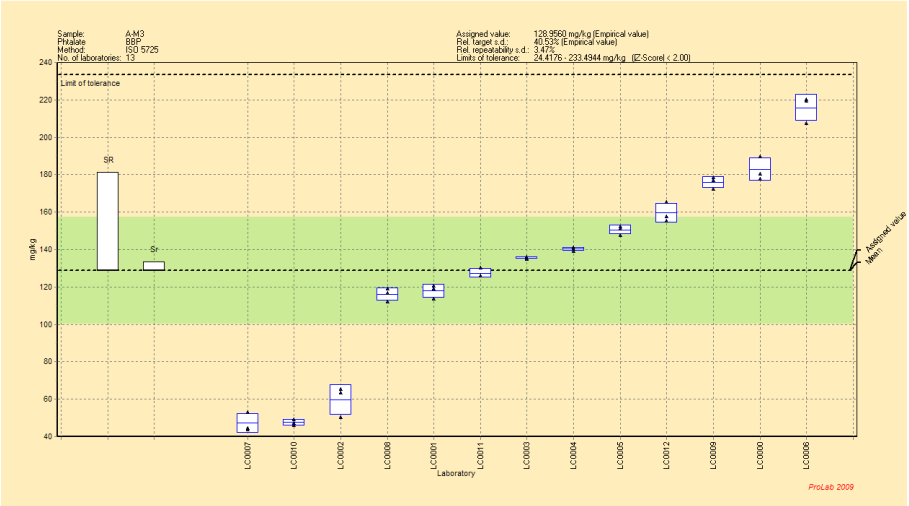




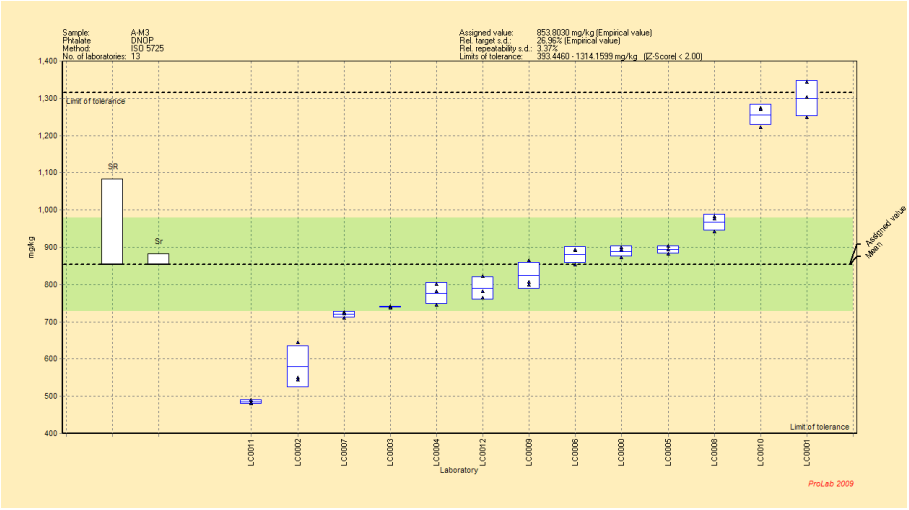
A-M3-DIBP
Nr.Labs: 13
Mean (mg/kg): 3379.1
SD_r (mg/kg): 134.7
SD_R (mg/kg): 560.8



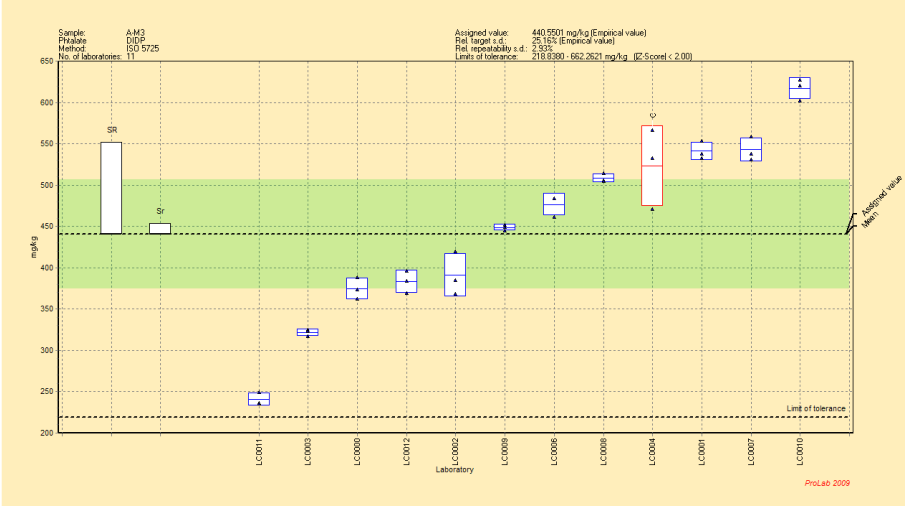
A-M3-DBP
Nr.Labs: 13
Mean (mg/kg): 736.7
SD_r (mg/kg): 31.1
SD_R (mg/kg): 204.3



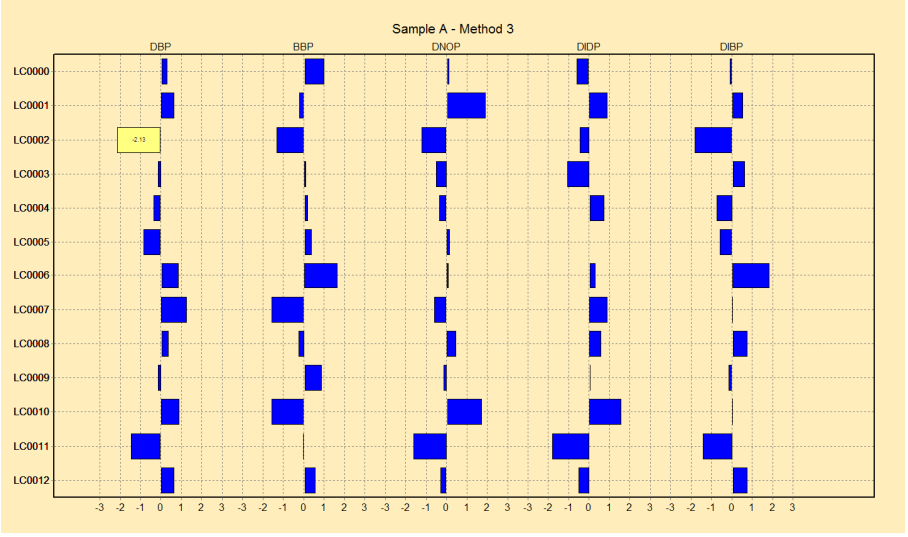
A-M3-BBP
Nr.Labs: 13
Mean (mg/kg): 128.9
SD_r (mg/kg): 4.5
SD_R (mg/kg): 52.3



A-M3-DNOP
Nr.Labs: 13
Mean (mg/kg): 853.8
SD_r (mg/kg): 28.8
SD_R (mg/kg): 230.2

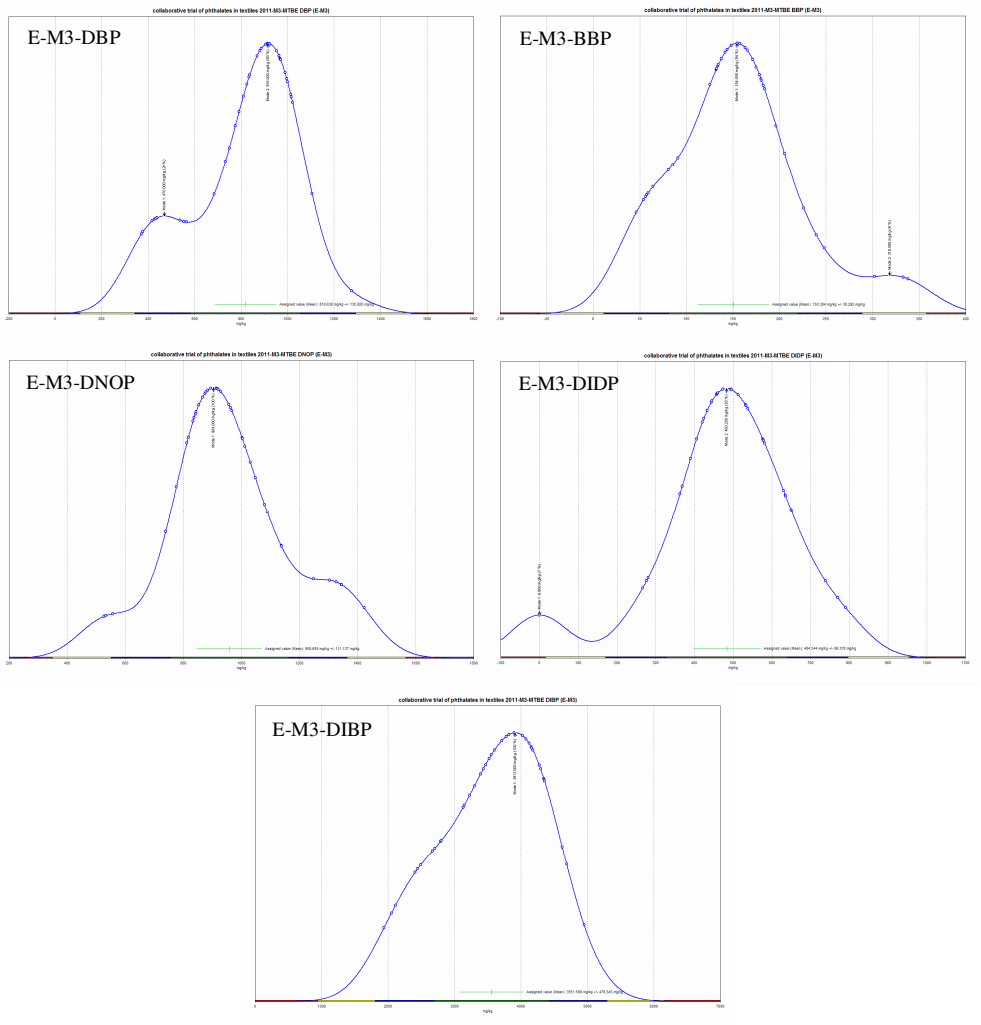


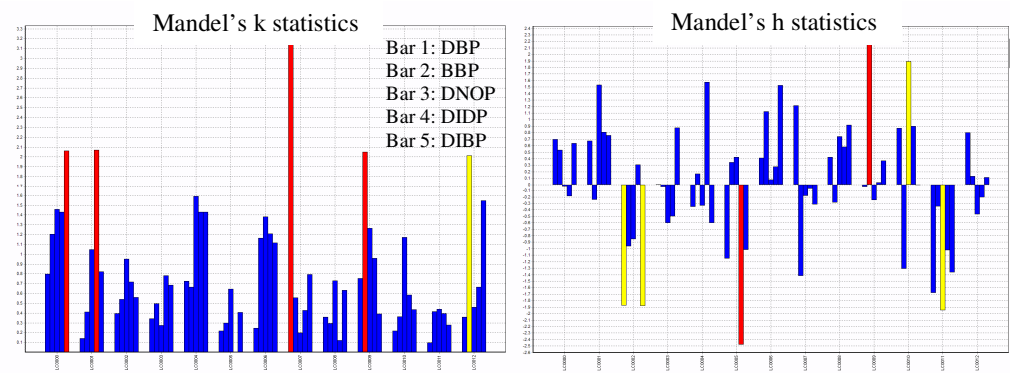
A-M3-DIDP
Nr.Labs: 11
Mean (mg/kg): 440.5
SD_r (mg/kg): 12.9
SD_R (mg/kg): 110.9

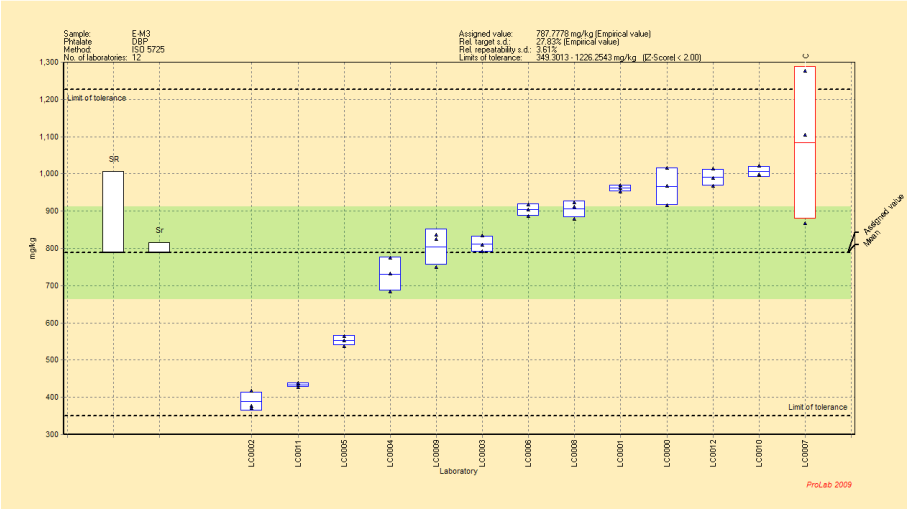


Z-scores

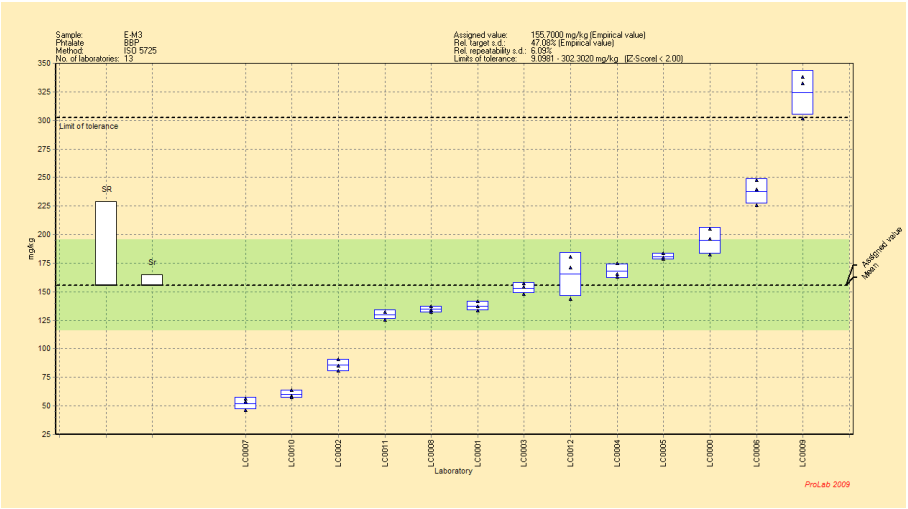
Sample E – Method 3



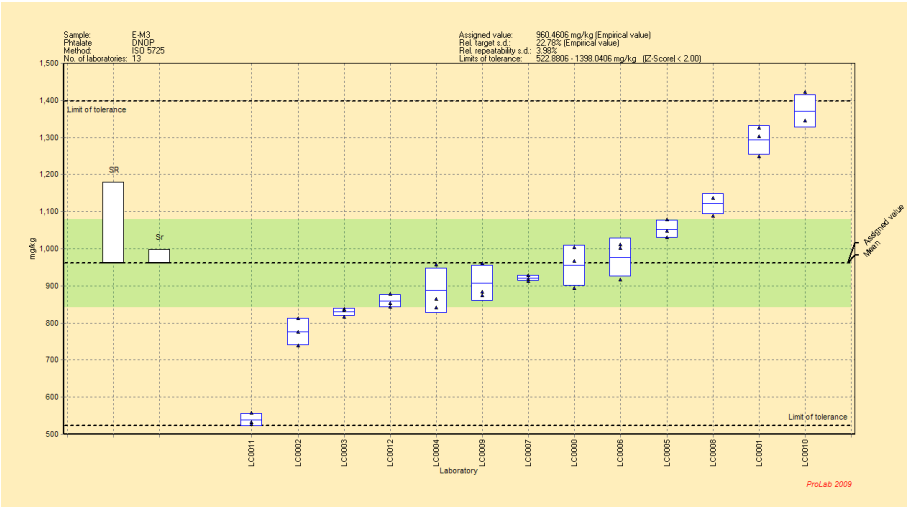




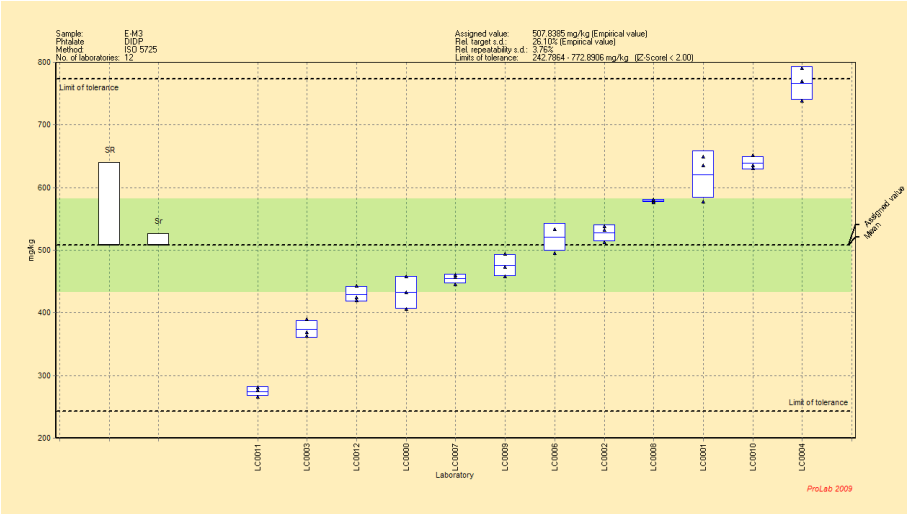
E-M3-DBP
Nr.Labs: 12
Mean (mg/kg): 787.8
SD_r (mg/kg): 28.4
SD_R (mg/kg): 219.2



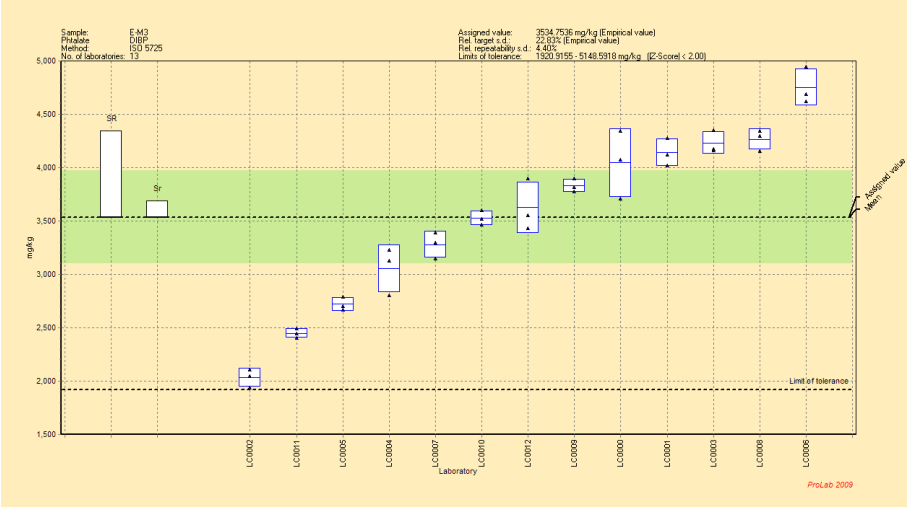
E-M3-BBP
Nr.Labs: 13
Mean (mg/kg): 155.7
SD_r (mg/kg): 9.5
SD_R (mg/kg): 73.3



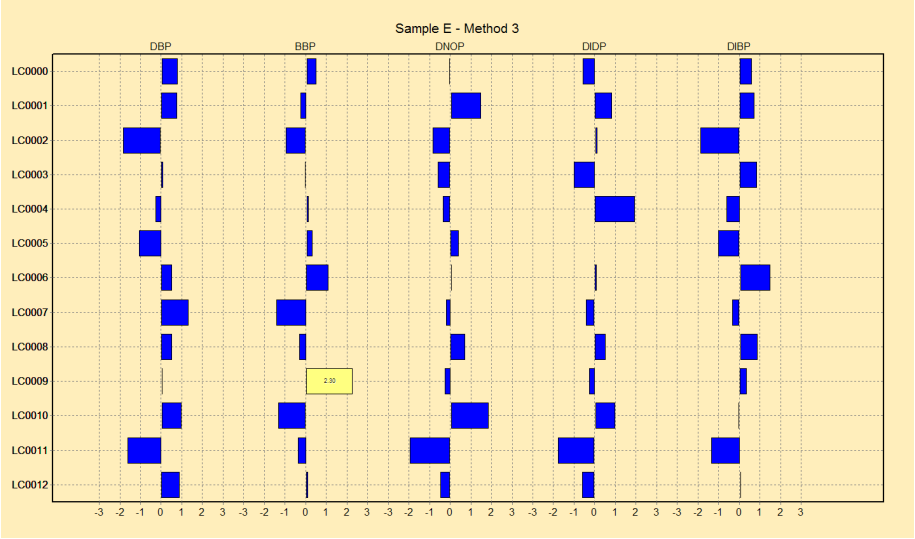
E-M3-DNOP
Nr.Labs: 13
Mean (mg/kg): 960.5
SD_r (mg/kg): 38.3
SD_R (mg/kg): 218.8



E-M3-DIDP
Nr.Labs: 12
Mean (mg/kg): 507.8
SD_r (mg/kg): 19.1
SD_R (mg/kg): 132.5

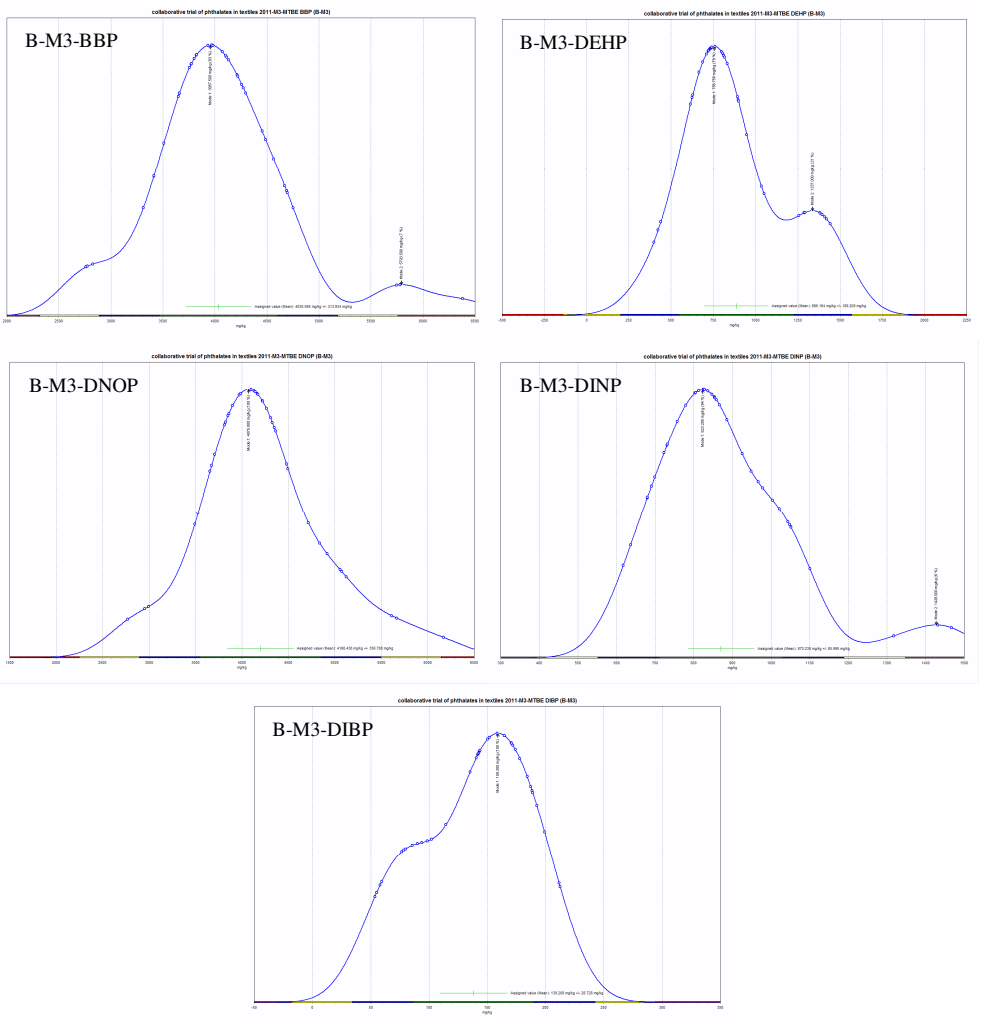


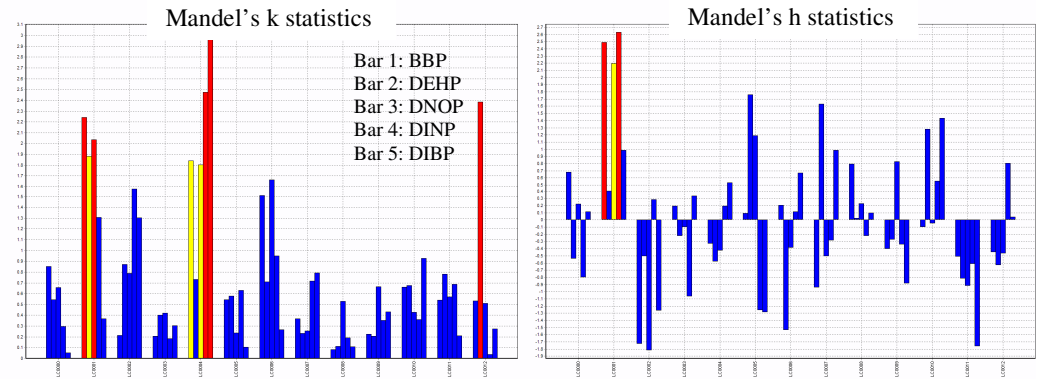
E-M3-DIBP
Nr.Labs: 13
Mean (mg/kg): 3534.7
SD_r (mg/kg): 155.5
SD_R (mg/kg): 806.9

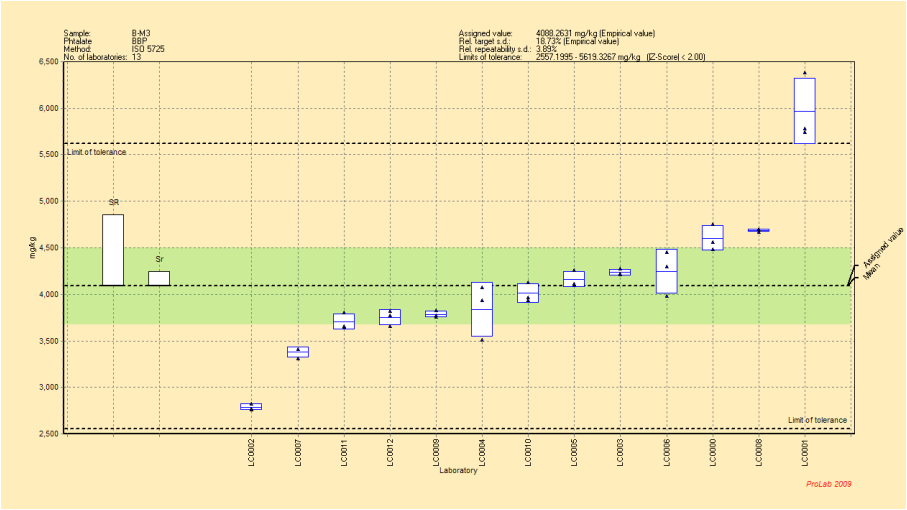


Z-scores

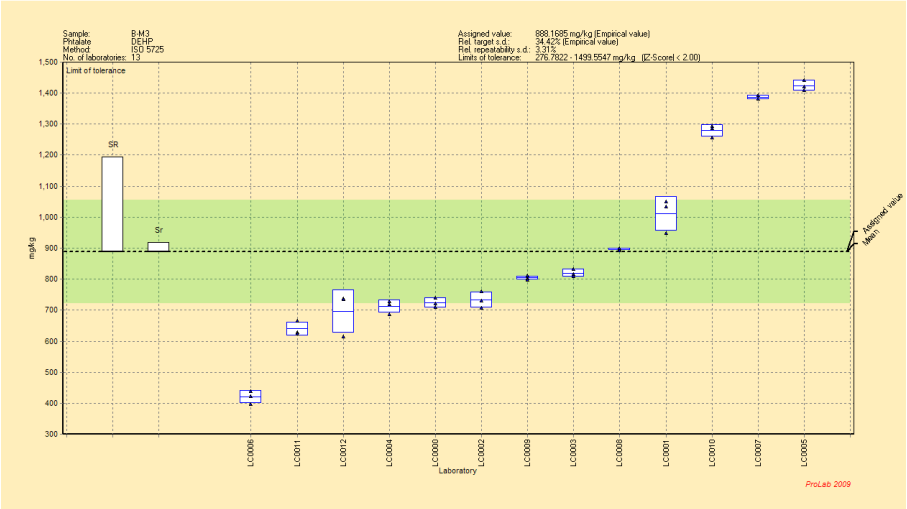
Sample B – Method 3



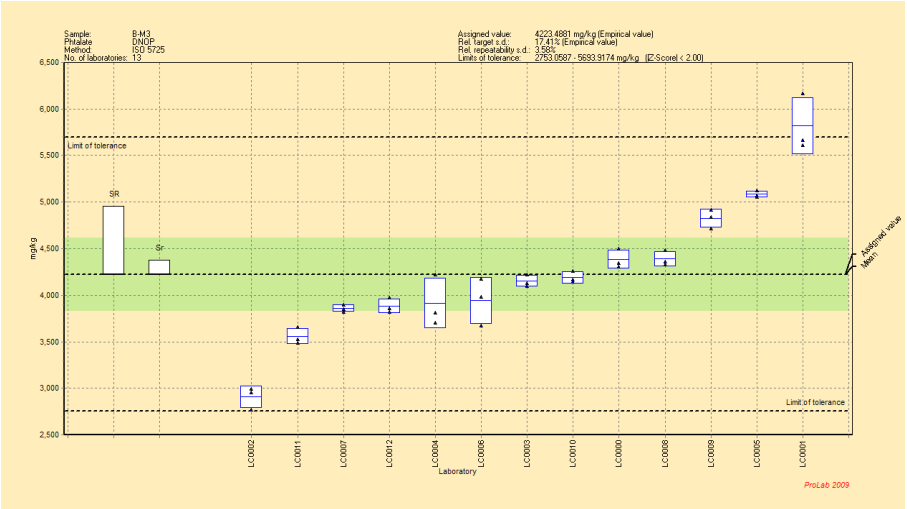




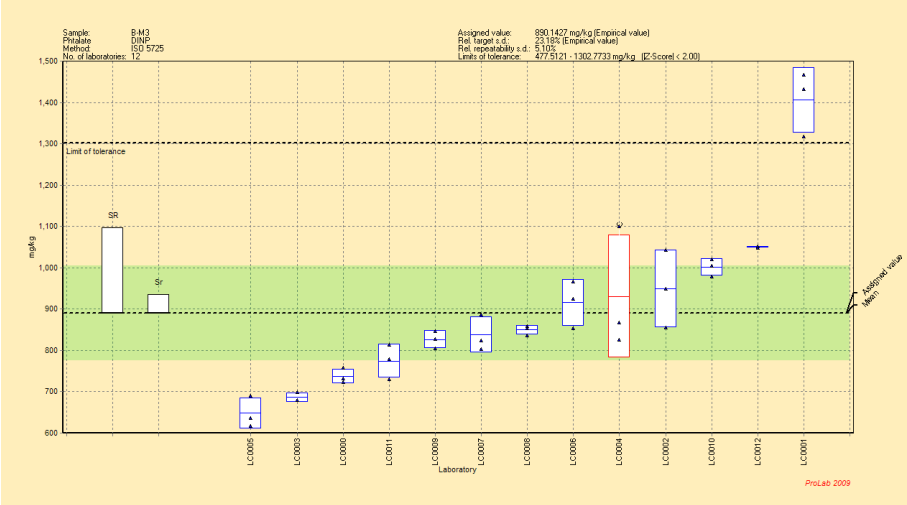
B-M3-BBP
Nr.Labs: 13
Mean (mg/kg): 4088.3
SD_r (mg/kg): 159.2
SD_R (mg/kg): 765.5



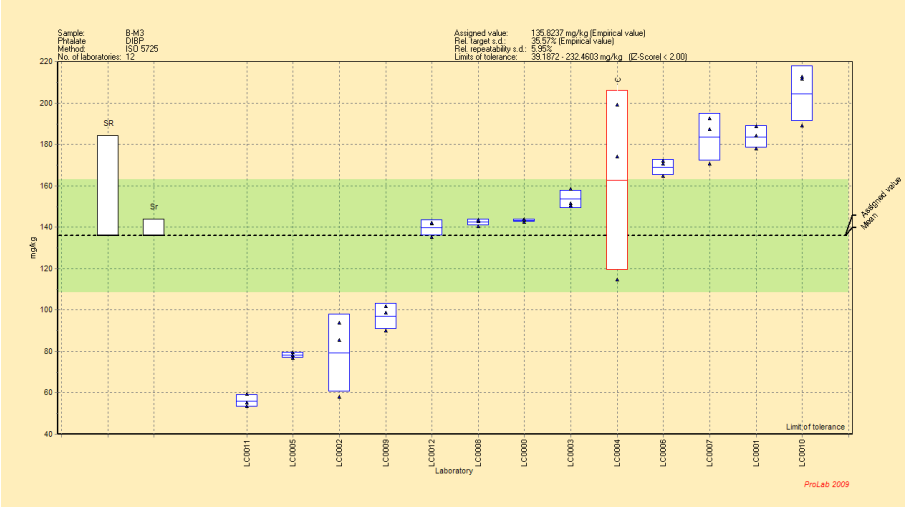
B-M3-DEHP
Nr.Labs: 13
Mean (mg/kg): 888.2
SD_r (mg/kg): 29.4
SD_R (mg/kg): 305.7



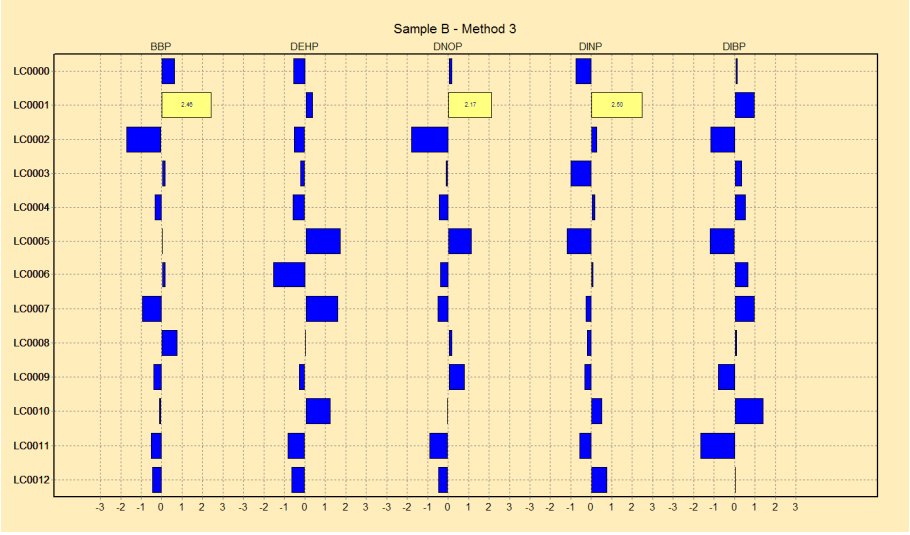
B-M3-DNOP
Nr.Labs: 13
Mean (mg/kg): 4223.5
SD_r (mg/kg): 151.2
SD_R (mg/kg): 735.2



B-M3-DINP
Nr.Labs: 12
Mean (mg/kg): 890.1
SD_r (mg/kg): 45.4
SD_R (mg/kg): 206.3

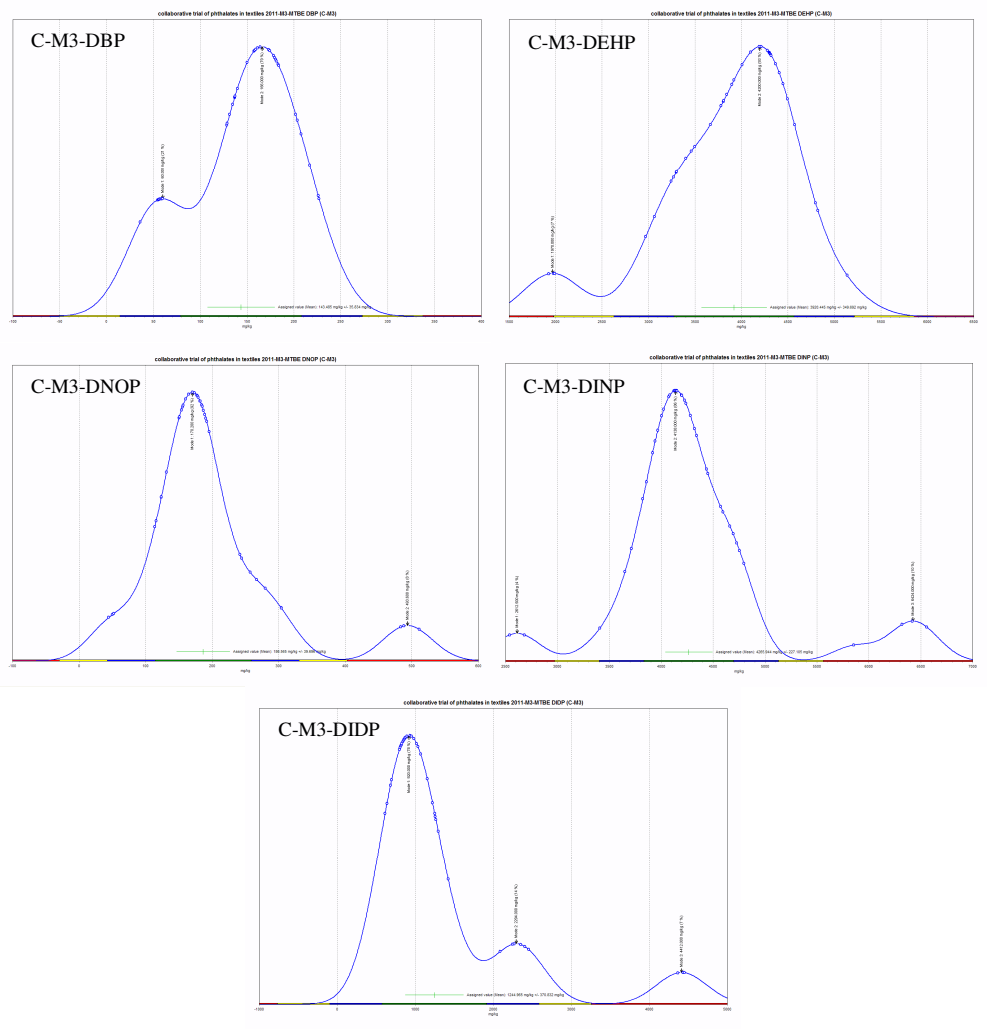


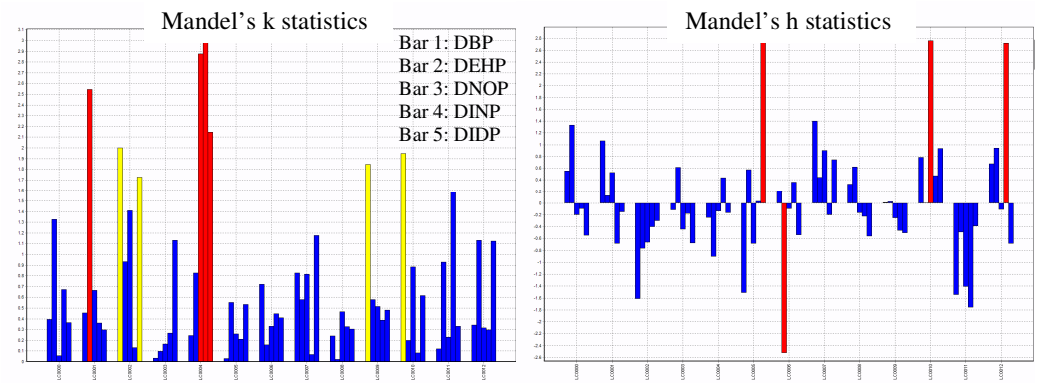
B-M3-DIBP
Nr.Labs: 12
Mean (mg/kg): 135.8
SD_r (mg/kg): 8.1
SD_R (mg/kg): 48.3

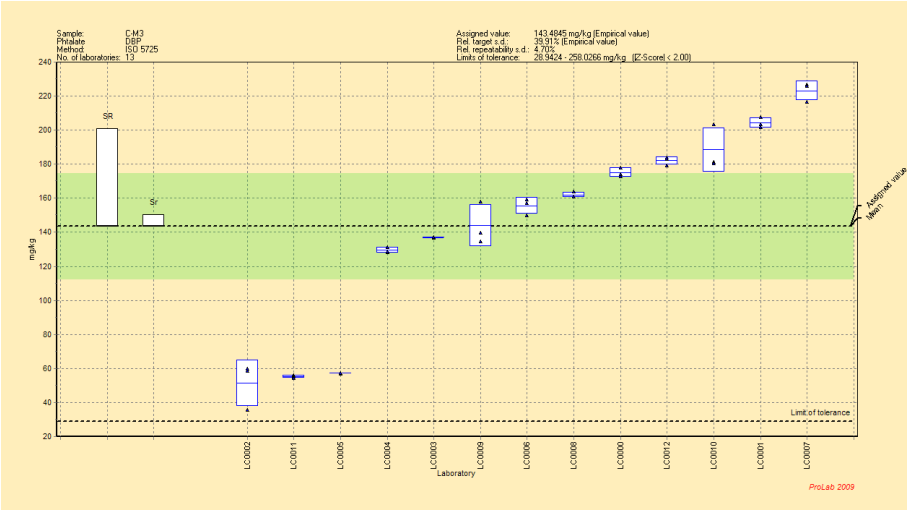


Z-scores

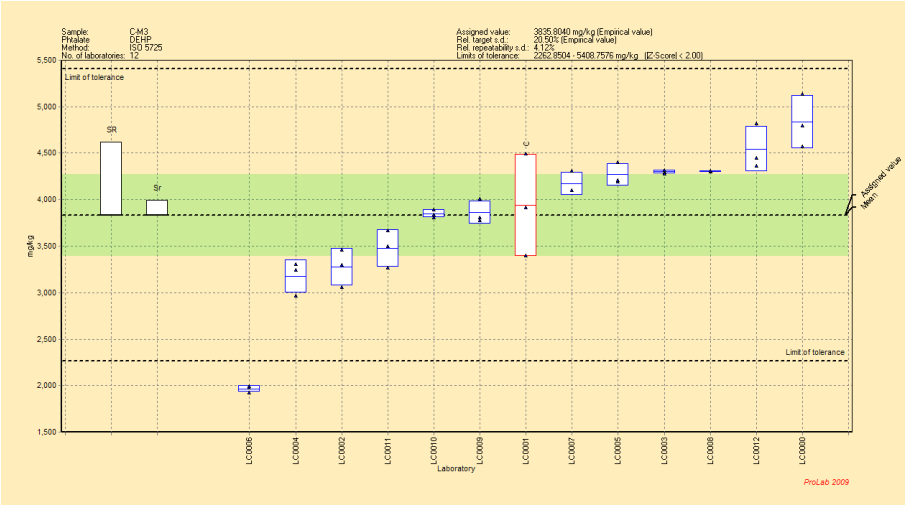
Sample C – Method 3



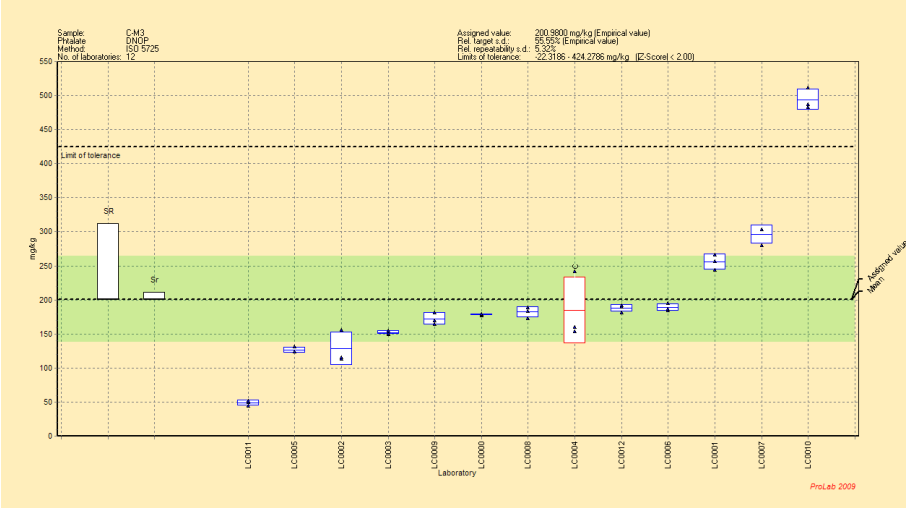


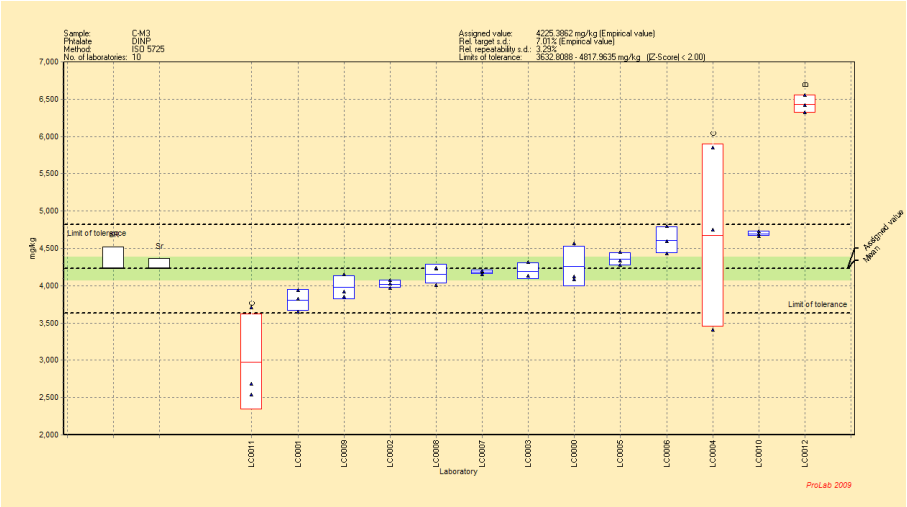


C-M3-DBP
Nr.Labs: 13
Mean (mg/kg): 143.5
SD_r (mg/kg): 6.7
SD_R (mg/kg): 57.3

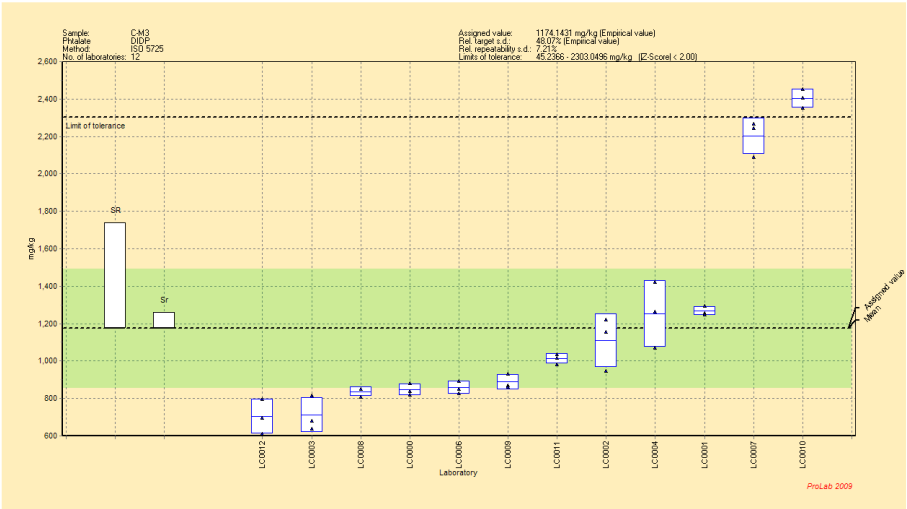


C-M3-DNOP
Nr.Labs: 12
Mean (mg/kg): 201.0
SD_r (mg/kg): 10.7
SD_R (mg/kg): 111.6

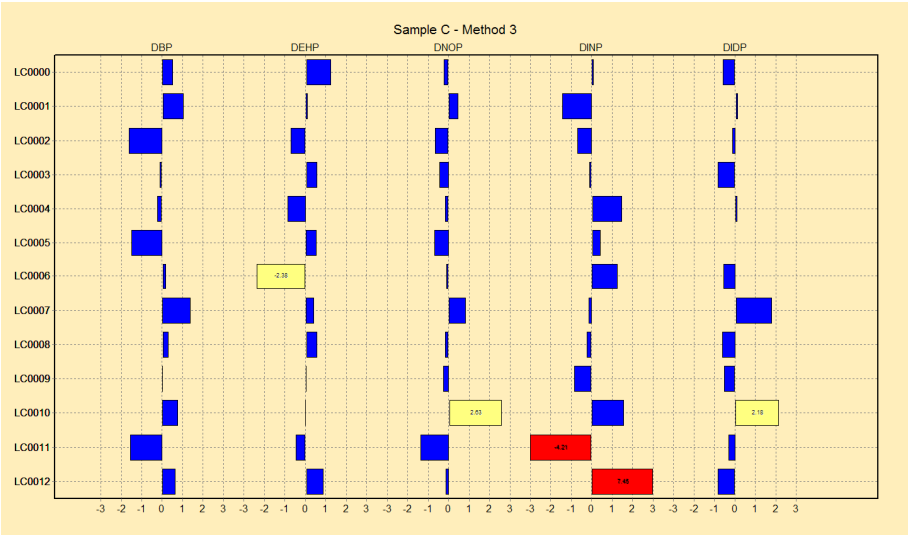




C-M3-DINP
Nr.Labs: 10
Mean (mg/kg): 4225.4
SD_r (mg/kg): 139.1
SD_R (mg/kg): 296.3

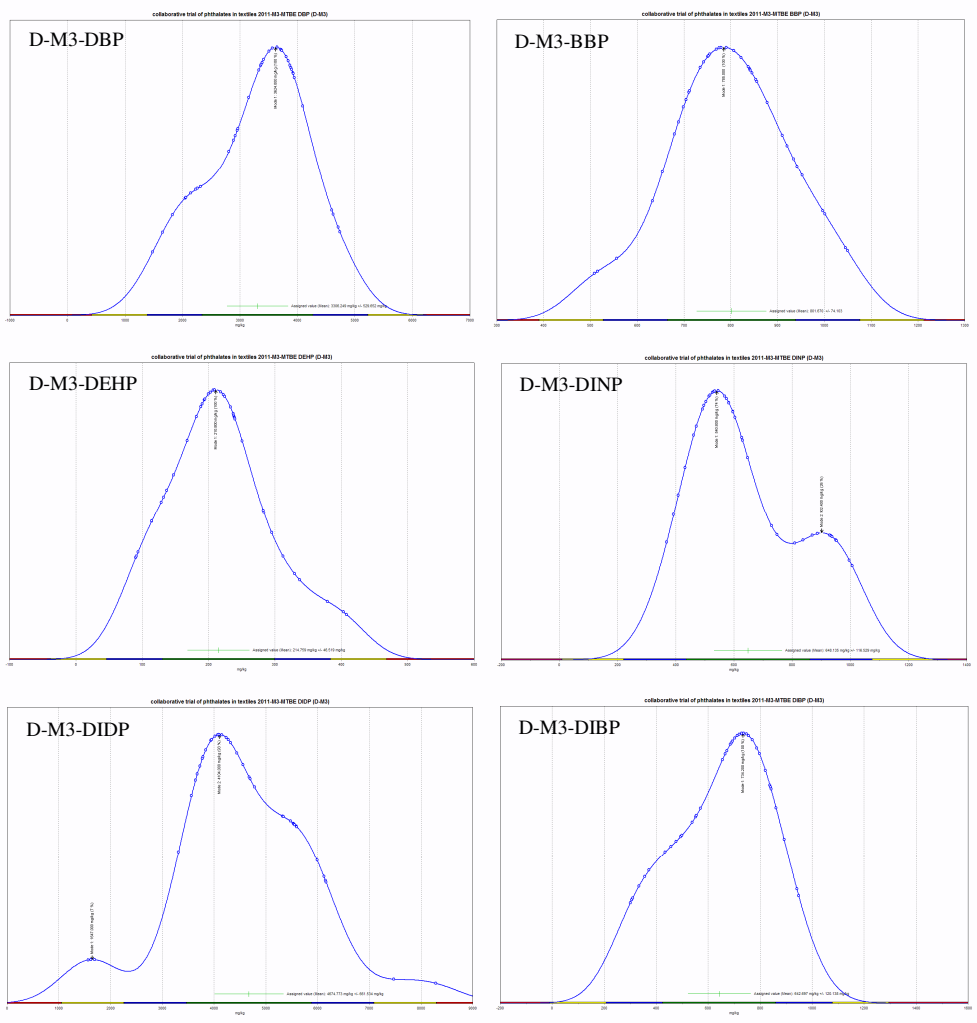


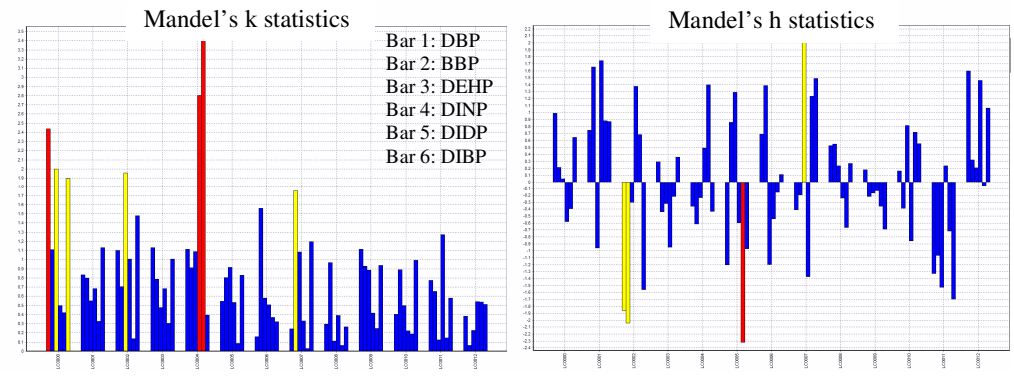
C-M3-DIDP
Nr.Labs: 12
Mean (mg/kg): 1174.1
SD_r (mg/kg): 84.7
SD_R (mg/kg): 564.5

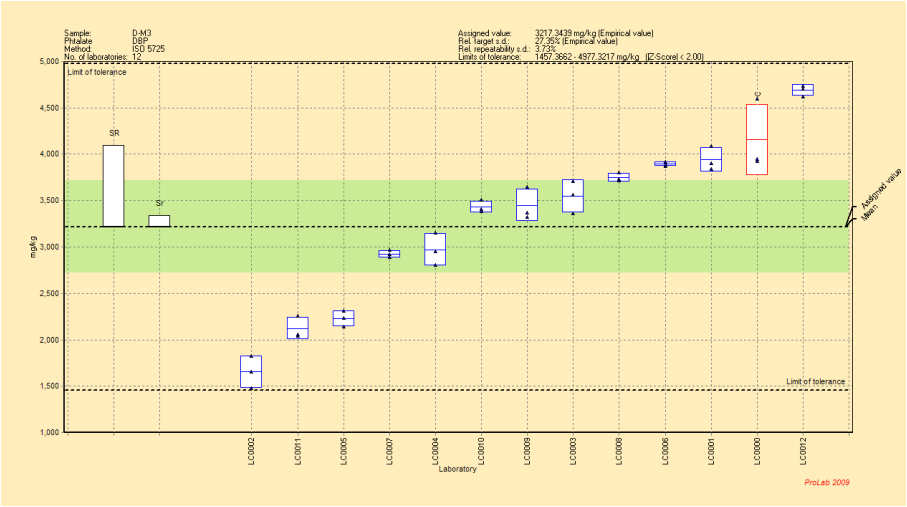


Z-scores

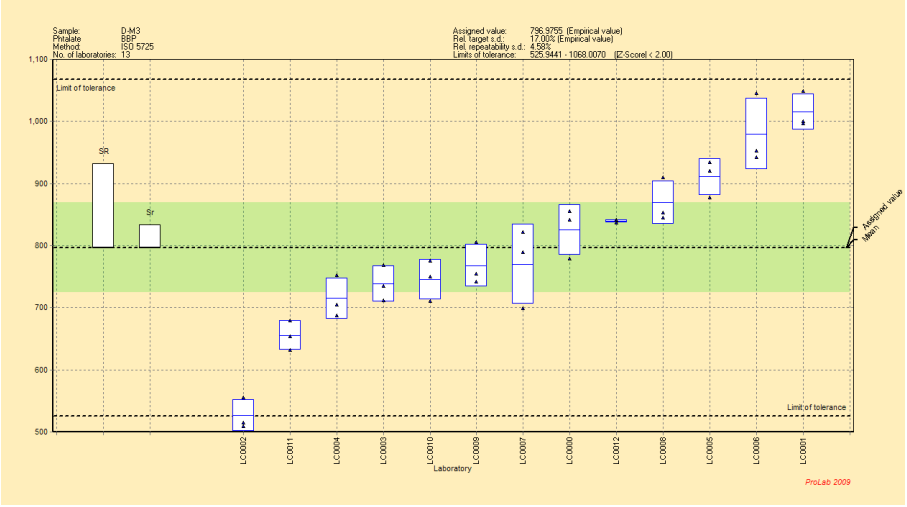
Sample D – Method 3



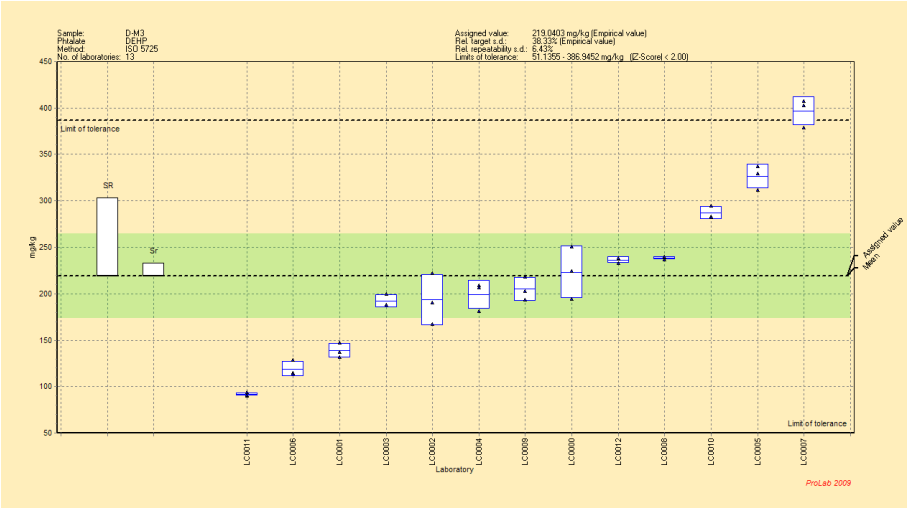




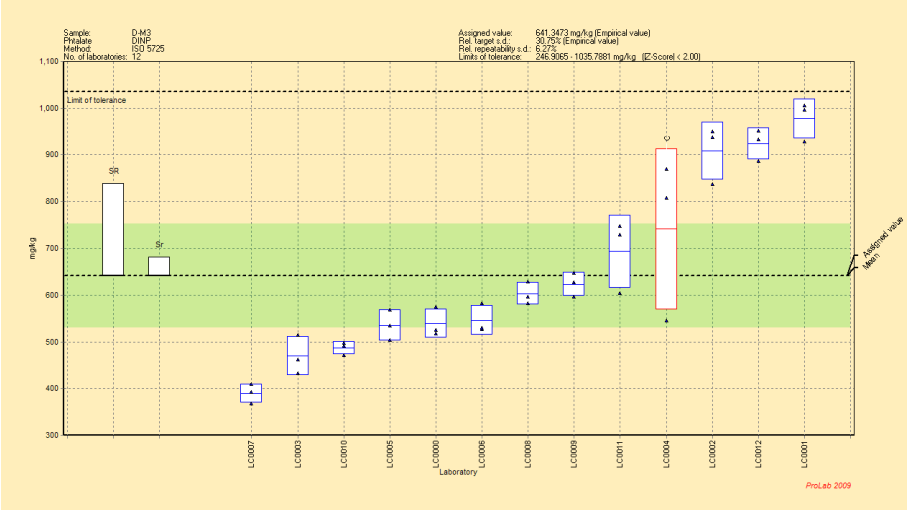
D-M3-DBP
Nr.Labs: 12
Mean (mg/kg): 3217.3
SD_r (mg/kg): 120.0
SD_R (mg/kg): 880.0



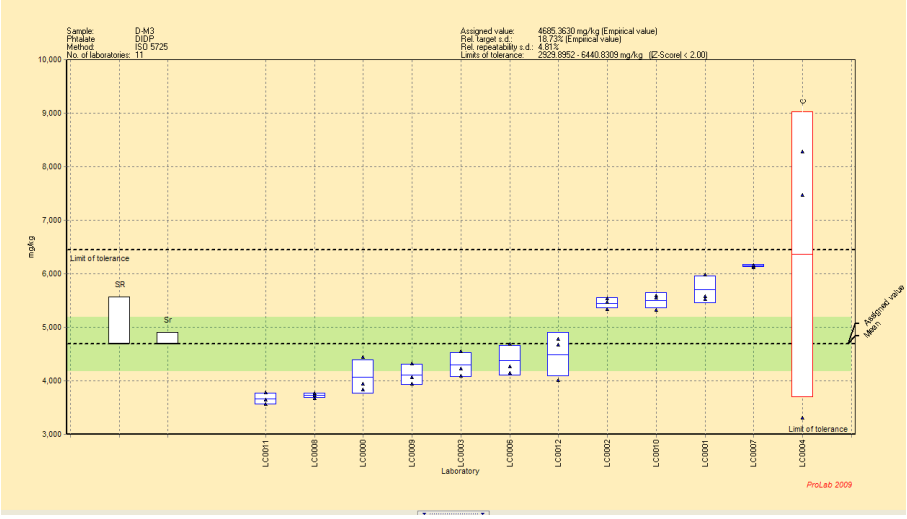
D-M3-BBP
Nr.Labs: 13
Mean (mg/kg): 797.0
SD_r (mg/kg): 36.5
SD_R (mg/kg): 135.5



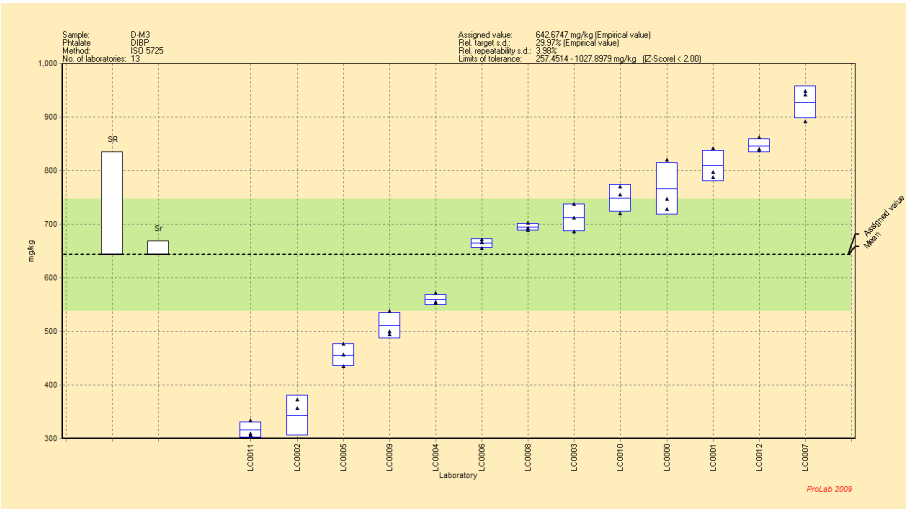
D-M3-DEHP
Nr.Labs: 13
Mean (mg/kg): 219.0
SD_r (mg/kg): 14.1
SD_R (mg/kg): 84.0

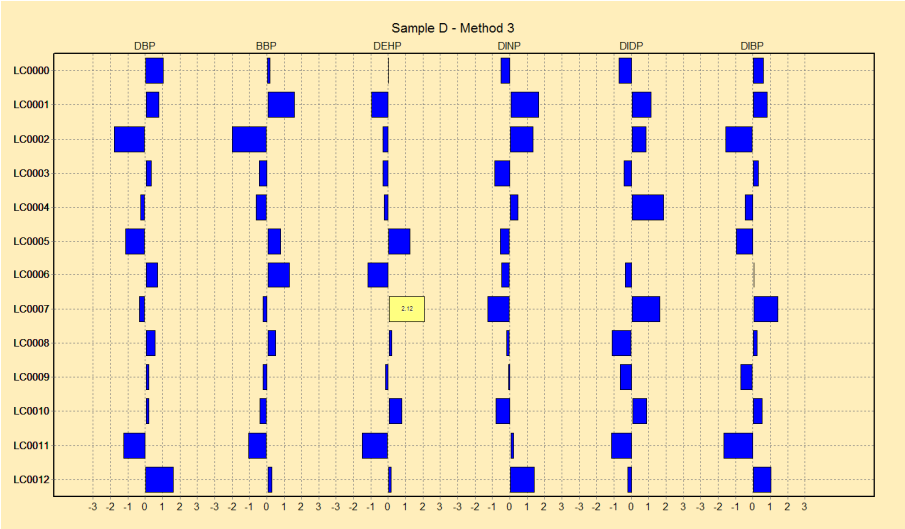


D-M3-DINP
Nr.Labs: 12
Mean (mg/kg): 641.3
SD_r (mg/kg): 40.2
SD_R (mg/kg): 197.2



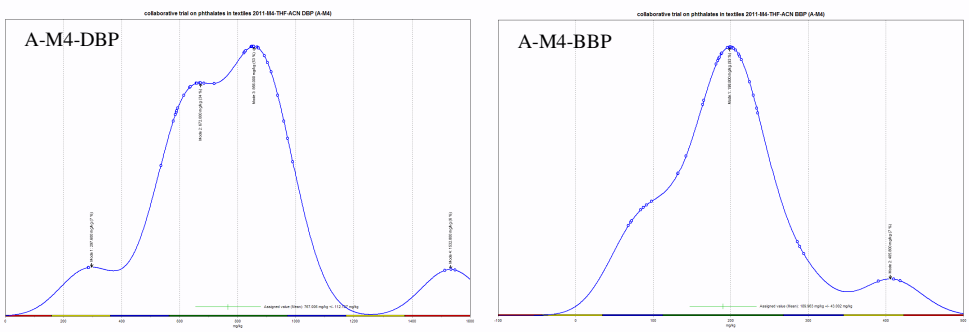
D-M3-DIBP
Nr.Labs: 13
Mean (mg/kg): 642.7
SD_r (mg/kg): 25.6
SD_R (mg/kg): 192.6

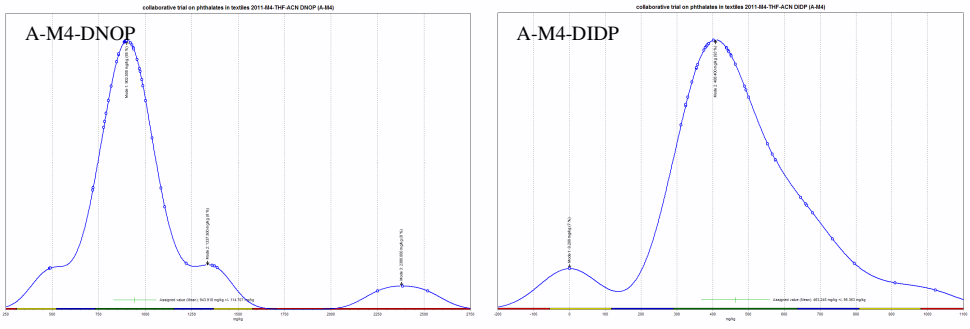


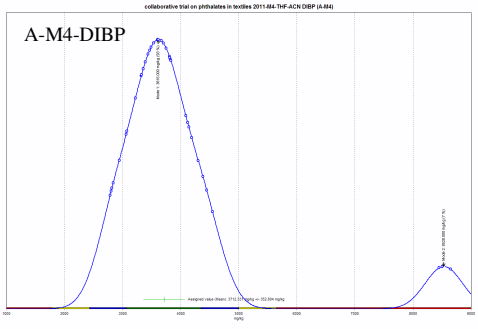

Sample D - Method 3
DBP
BBP
DEHP
DINP
DIDP
DIBP
LC0000
LC0001
LC0002
LC0003
LC0004
LC0005
LC0006
LC0007
LC0008
LC0009
LC0010
LC0011
LC0012
-3 -2 -1 0 1 2 3

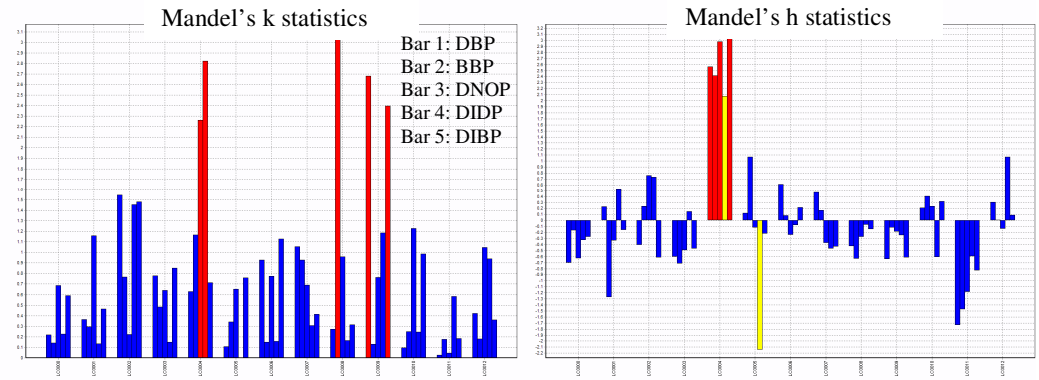
Z-scores

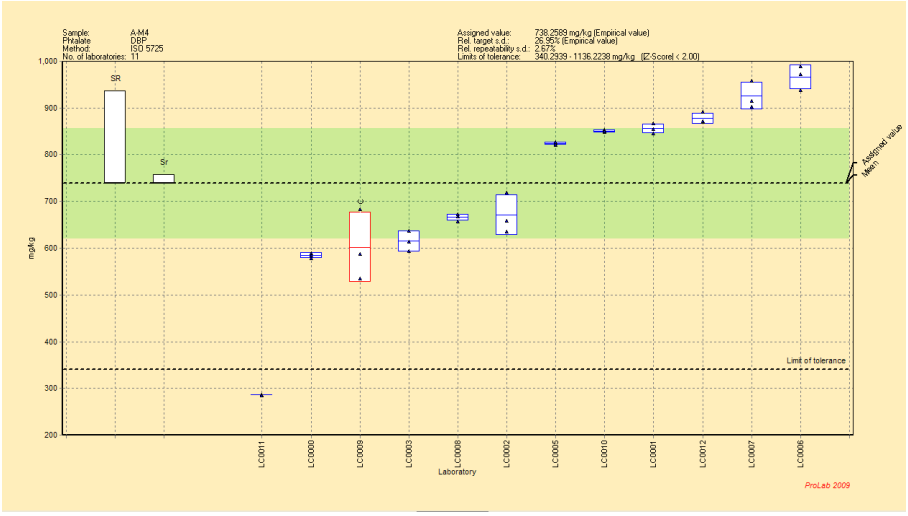
Sample A – Method 4



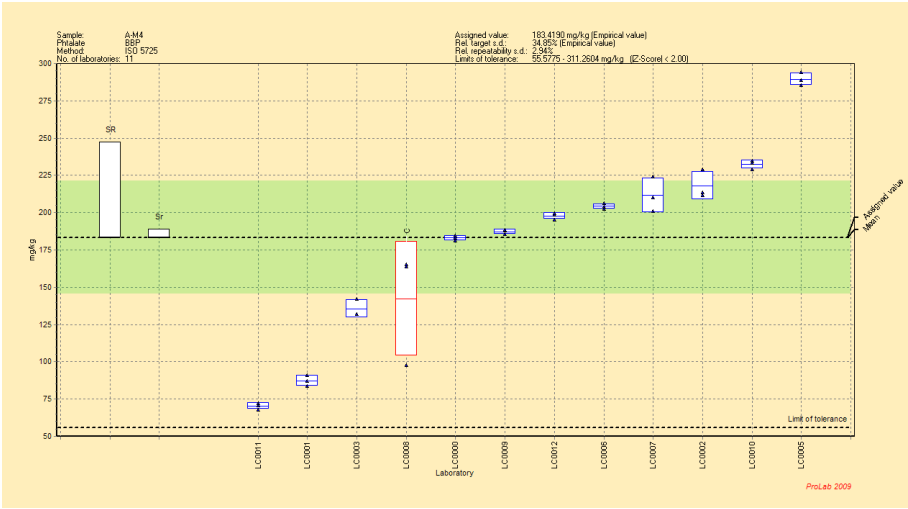




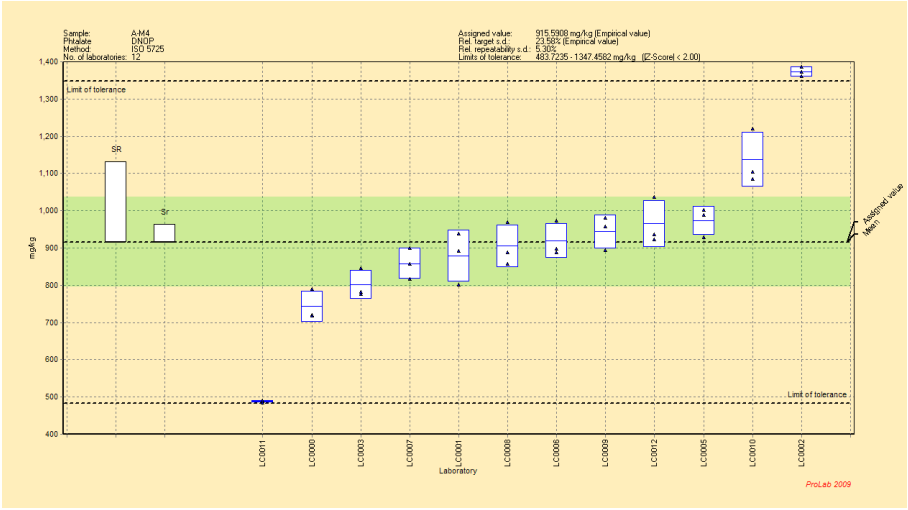




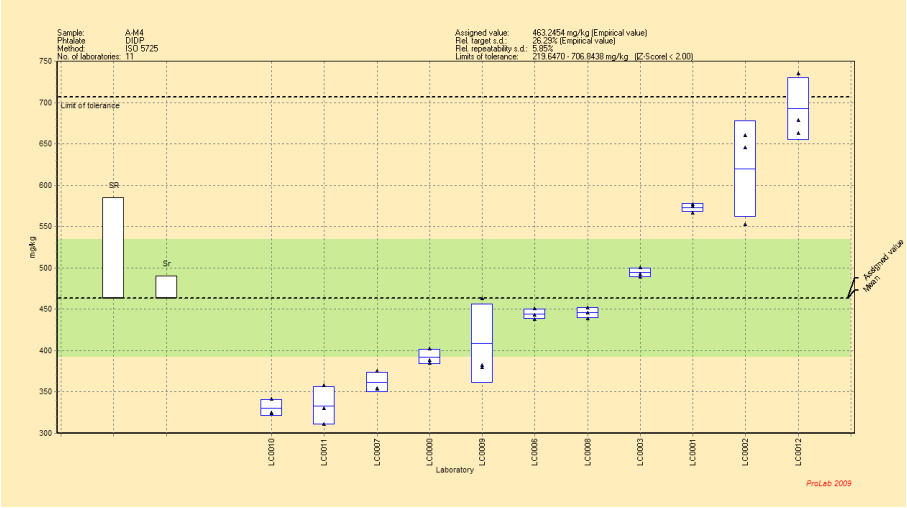
A-M4-DBP
Nr.Labs: 11
Mean (mg/kg): 738.26
SD_r (mg/kg): 19.7
SD_R (mg/kg): 199.0



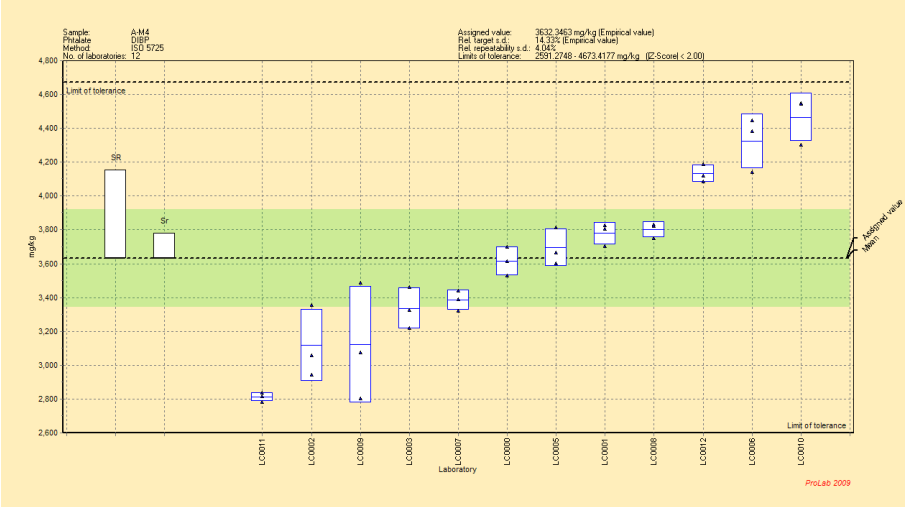
A-M4-BBP
Nr.Labs: 11
Mean (mg/kg): 183.4
SD_r (mg/kg): 5.4
SD_R (mg/kg): 63.9



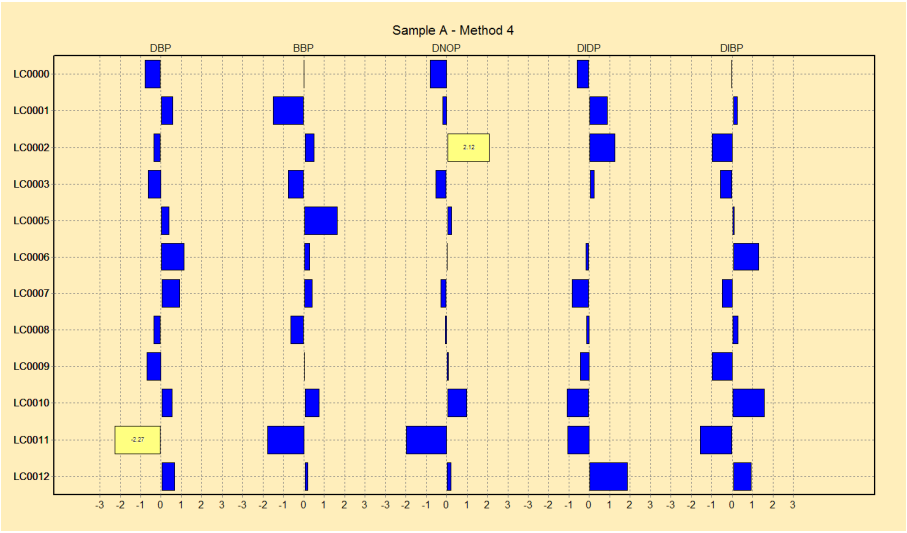
A-M4-DNOP
Nr.Labs: 12
Mean (mg/kg): 915.6
SD_r (mg/kg): 48.5
SD_R (mg/kg): 215.9



A-M4-DIDP
Nr.Labs: 11
Mean (mg/kg): 463.2
SD_r (mg/kg): 27.1
SD_R (mg/kg): 110.9

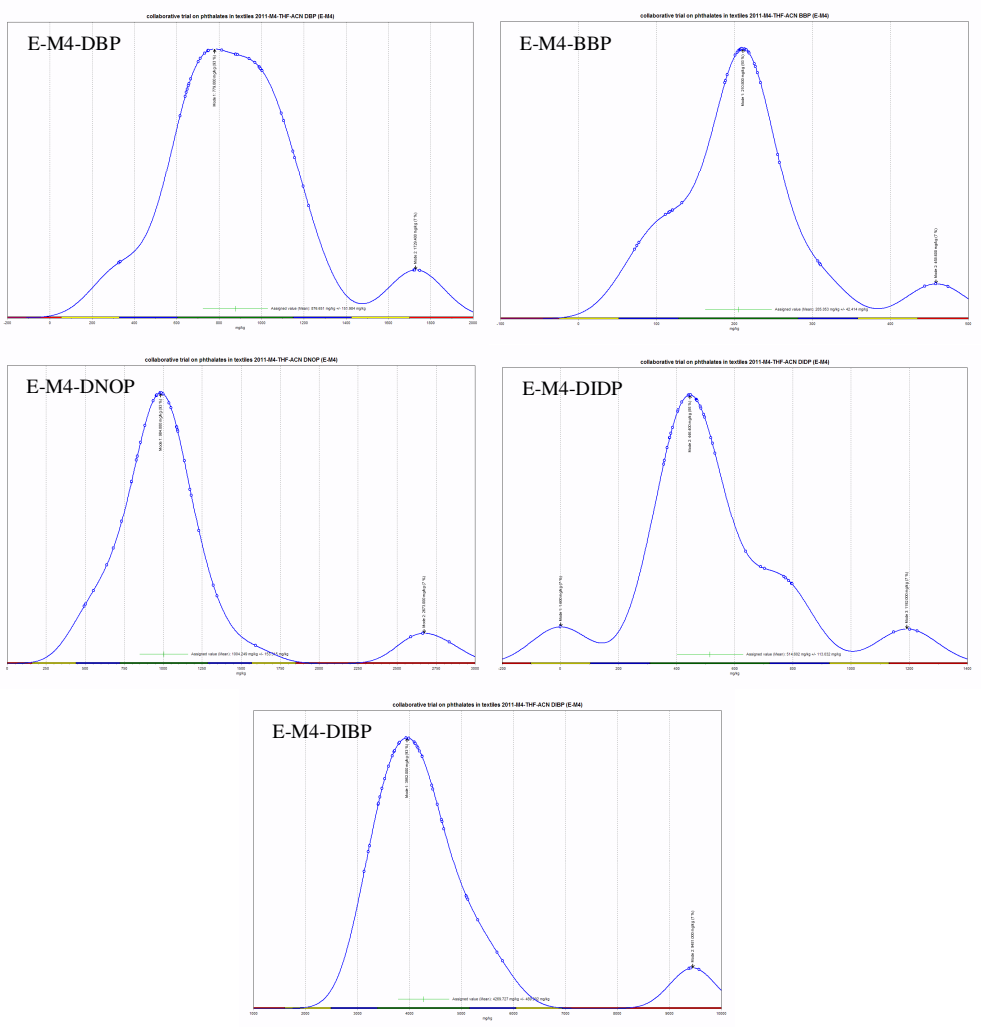


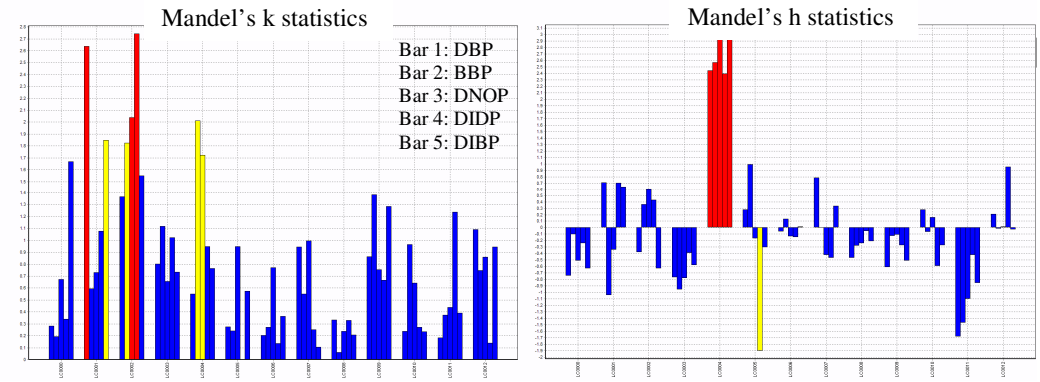
A-M4-DIBP
Nr.Labs: 12
Mean (mg/kg): 3632.3
SD_r (mg/kg): 146.7
SD_R (mg/kg): 560.8

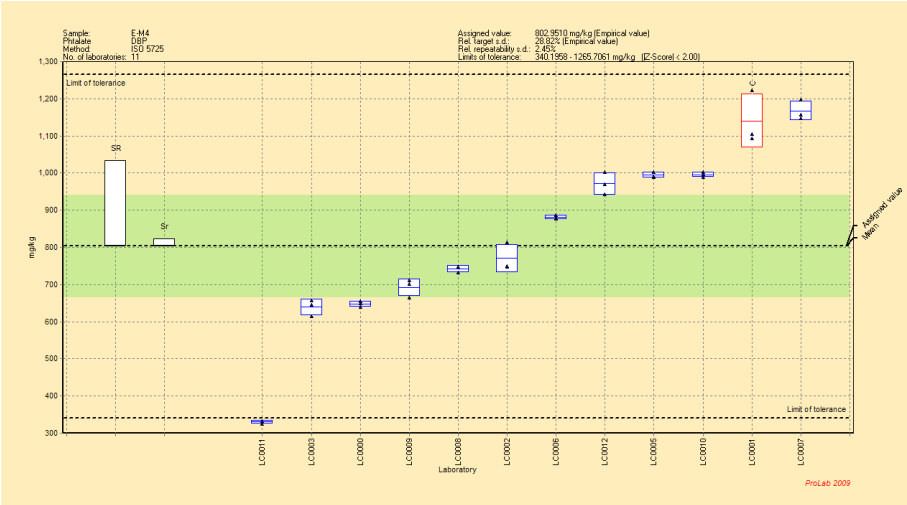


Z-scores

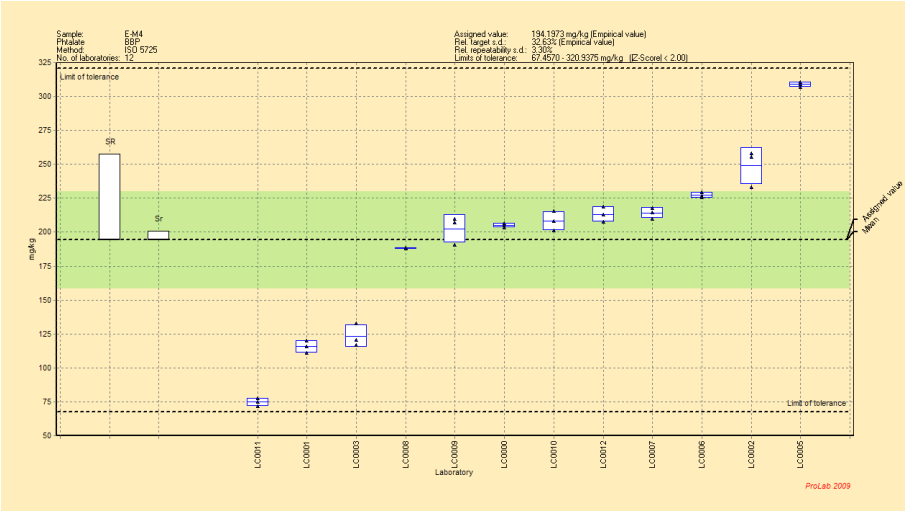
Sample E – Method 4



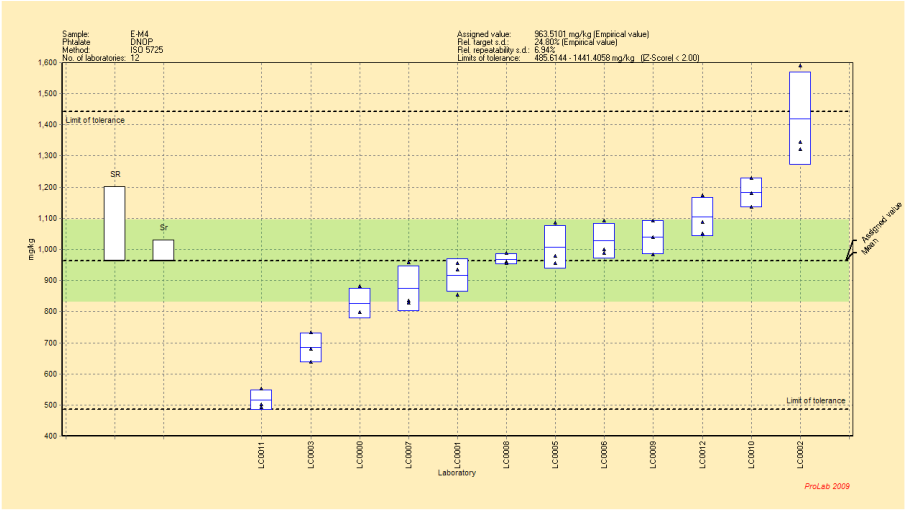




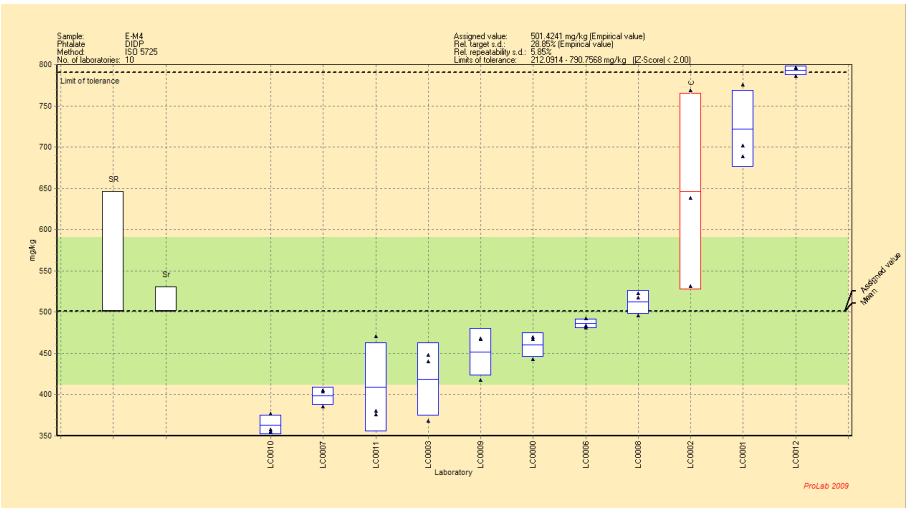
E-M4-DBP
Nr.Labs: 11
Mean (mg/kg): 802.9
SD_r (mg/kg): 19.7
SD_R (mg/kg): 231.4



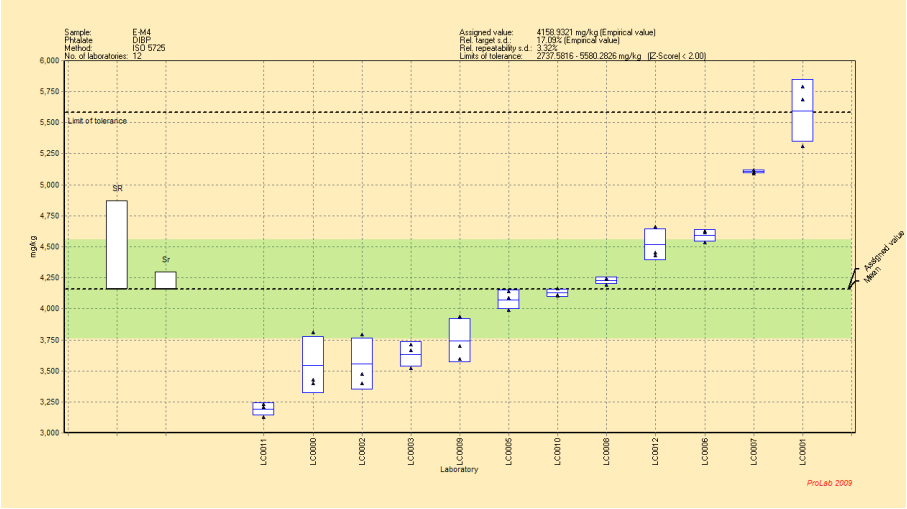
E-M4-BBP
Nr.Labs: 12
Mean (mg/kg): 194.2
SD_r (mg/kg): 6.4
SD_R (mg/kg): 63.4



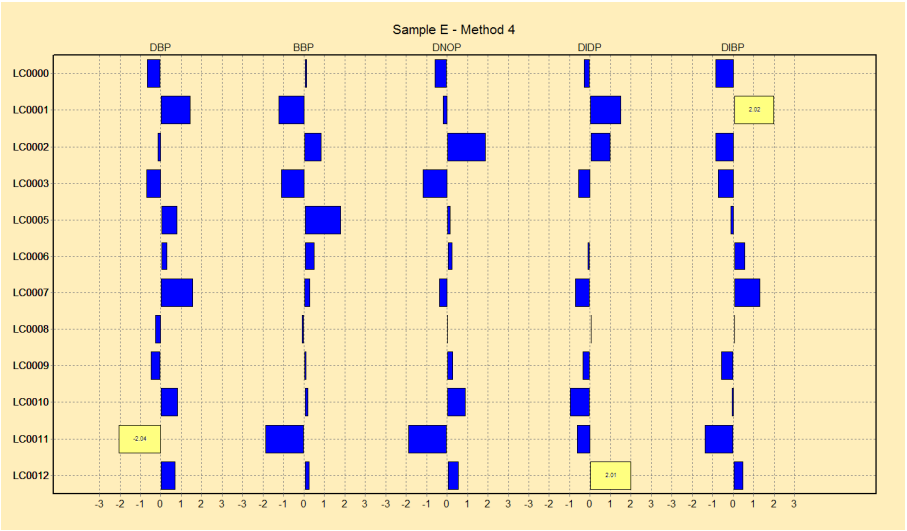
E-M4-DNOP
Nr.Labs: 12
Mean (mg/kg): 963.5
SD_r (mg/kg): 66.8
SD_R (mg/kg): 238.9



E-M4-DIDP
Nr.Labs: 10
Mean (mg/kg): 501.4
SD_r (mg/kg): 29.3
SD_R (mg/kg): 144.7

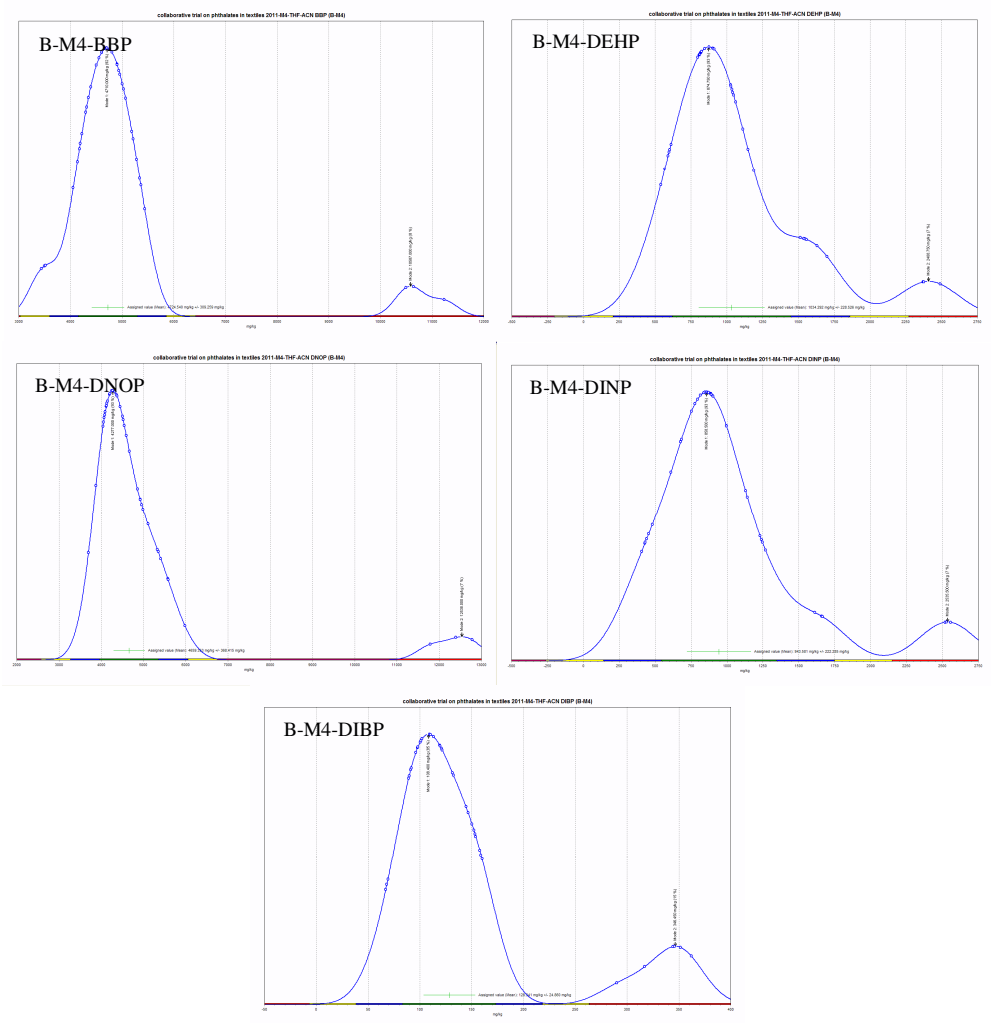


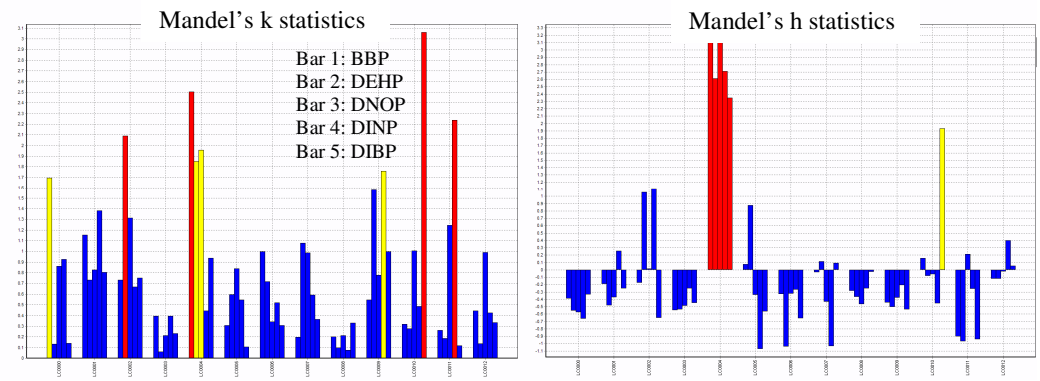
E-M4-DIBP
Nr.Labs: 12
Mean (mg/kg): 4158.9
SD_r (mg/kg): 137.9
SD_R (mg/kg): 710.7

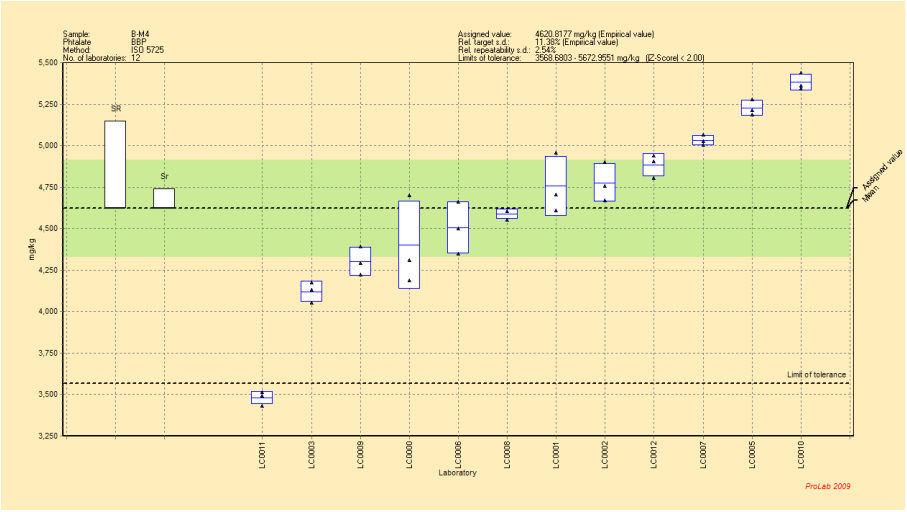


Z-scores

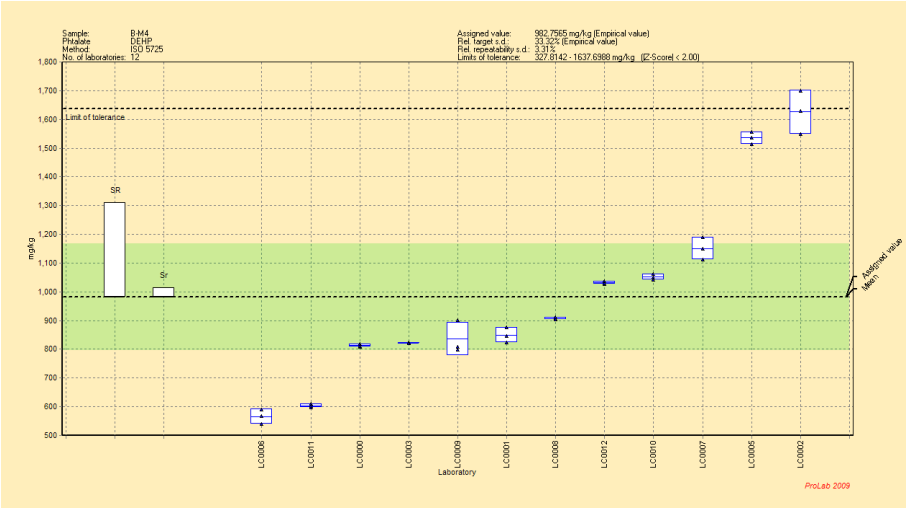
Sample B – Method 4



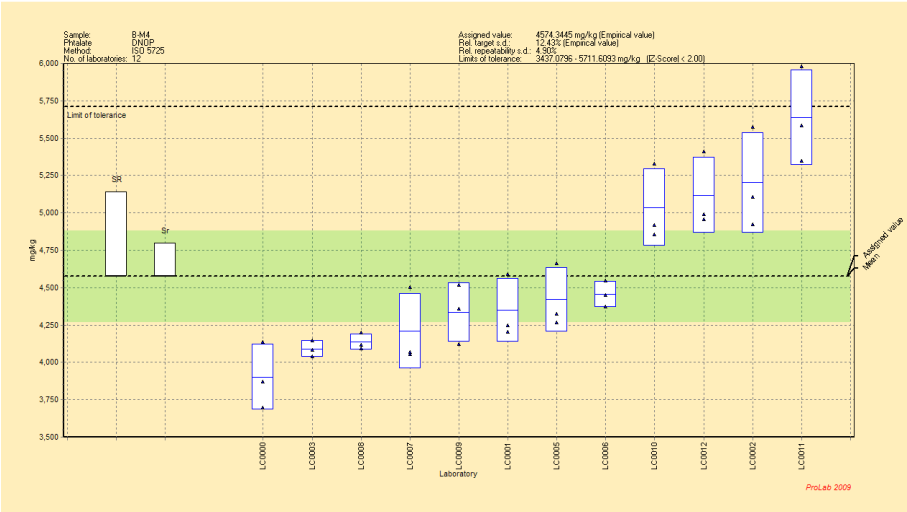




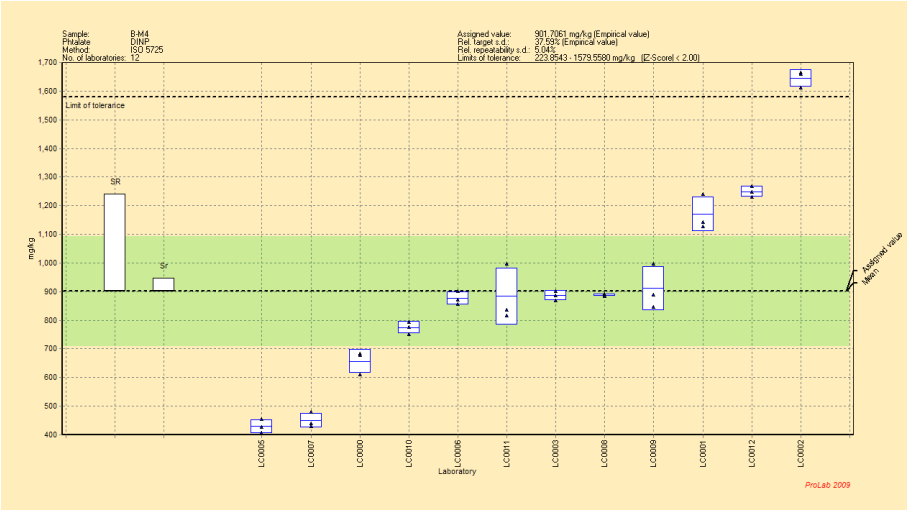
B-M4-BBP
Nr.Labs: 12
Mean (mg/kg): 4620.8
SD_r (mg/kg): 117.6
SD_R (mg/kg): 526.1



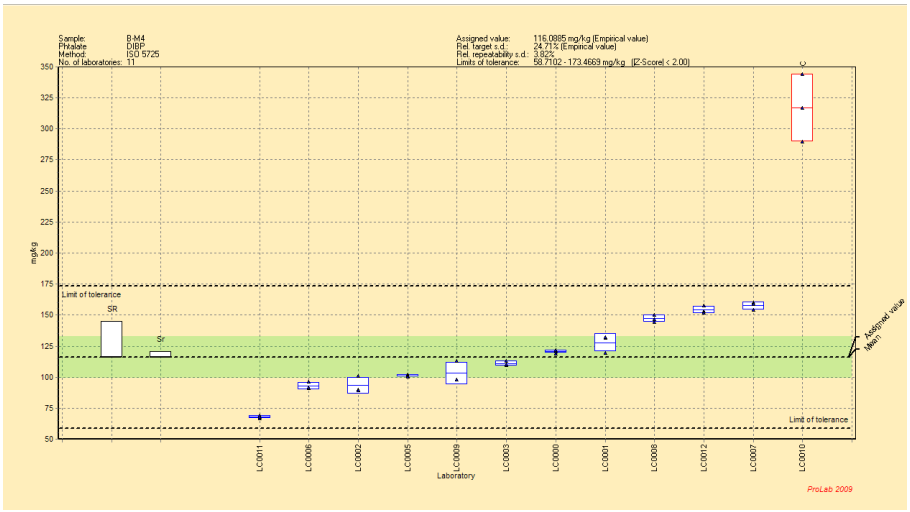
B-M4-DEHP
Nr.Labs: 12
Mean (mg/kg): 982.8
SD_r (mg/kg): 32.5
SD_R (mg/kg): 327.5



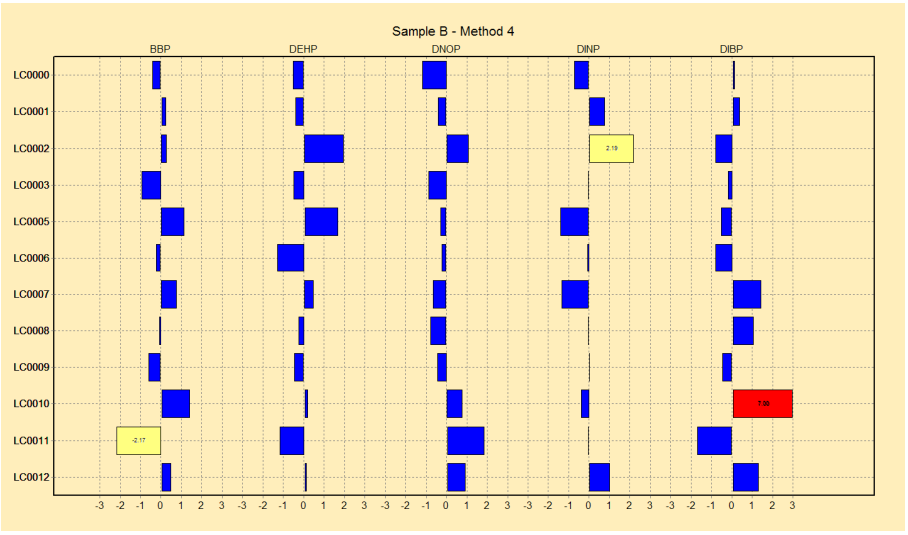
B-M4-DNOP
Nr.Labs: 12
Mean (mg/kg): 4574.3
SD_r (mg/kg): 224.1
SD_R (mg/kg): 568.6



B-M4-DINP
Nr.Labs: 12
Mean (mg/kg): 901.7
SD_r (mg/kg): 45.4
SD_R (mg/kg): 338.9

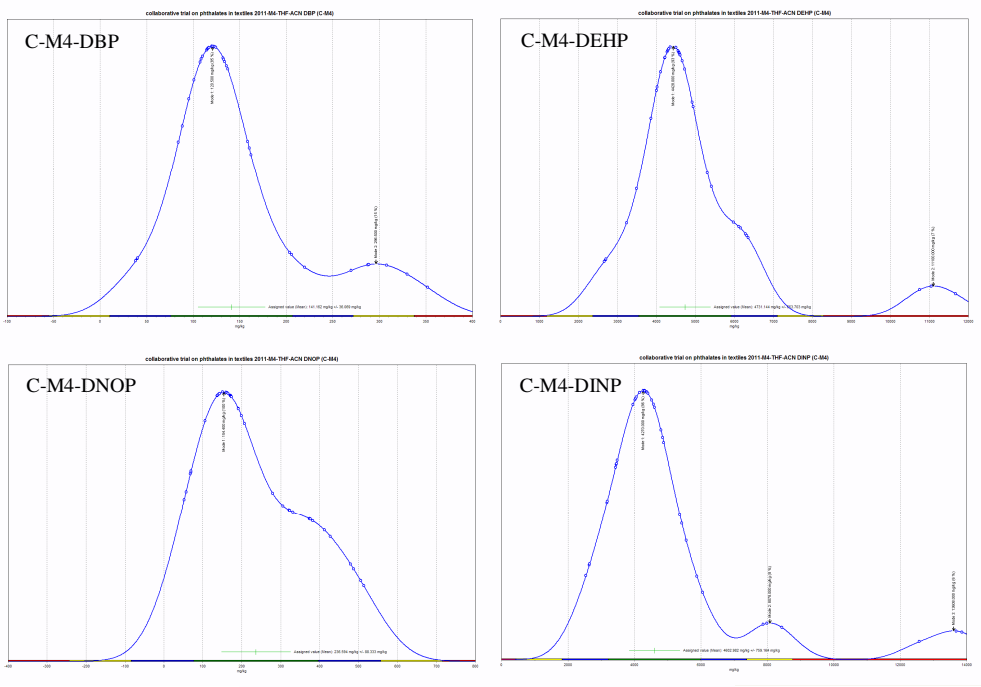


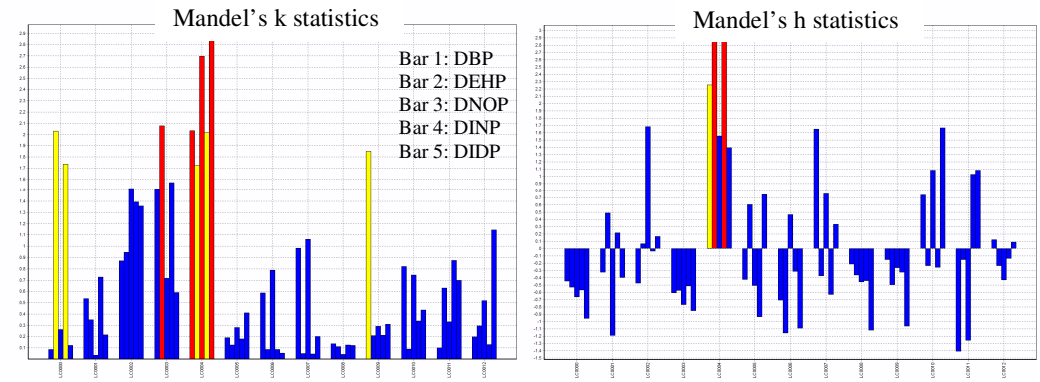
B-M4-DIBP
Nr.Labs: 11
Mean (mg/kg): 116.1
SD_r (mg/kg): 4.4
SD_R (mg/kg): 28.7

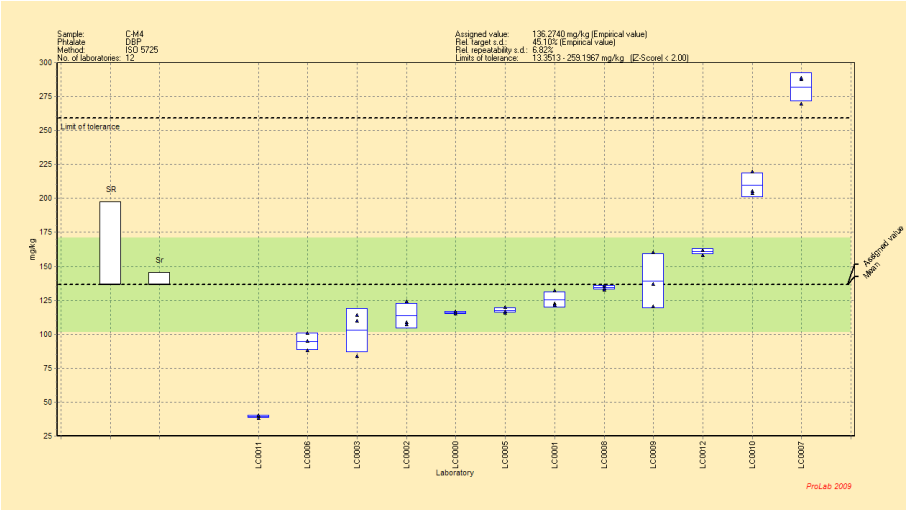


Z-scores

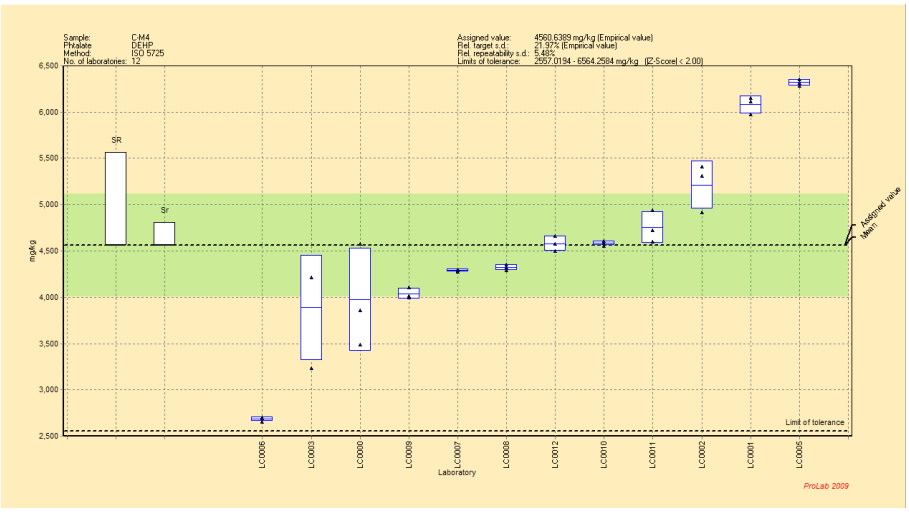
Sample C – Method 4



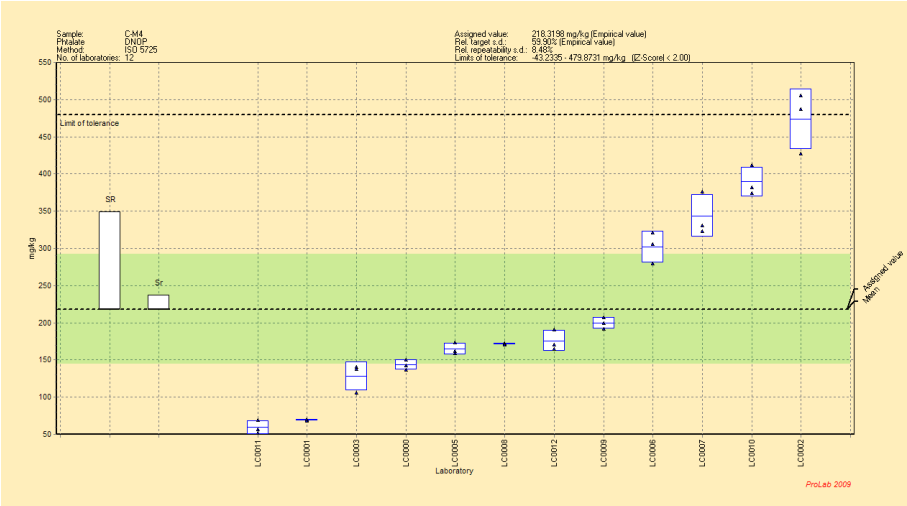




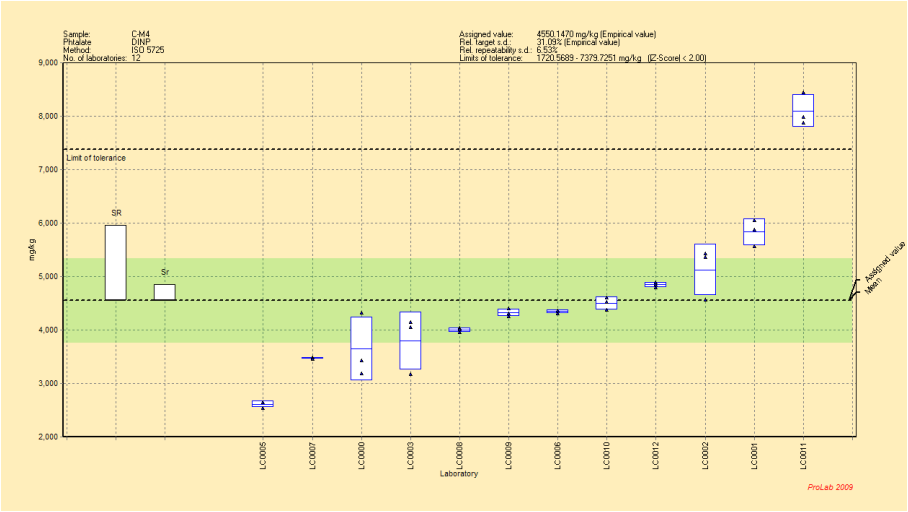
C-M4-DBP
Nr.Labs: 12
Mean (mg/kg): 136.3
SD_r (mg/kg): 9.3
SD_R (mg/kg): 61.5



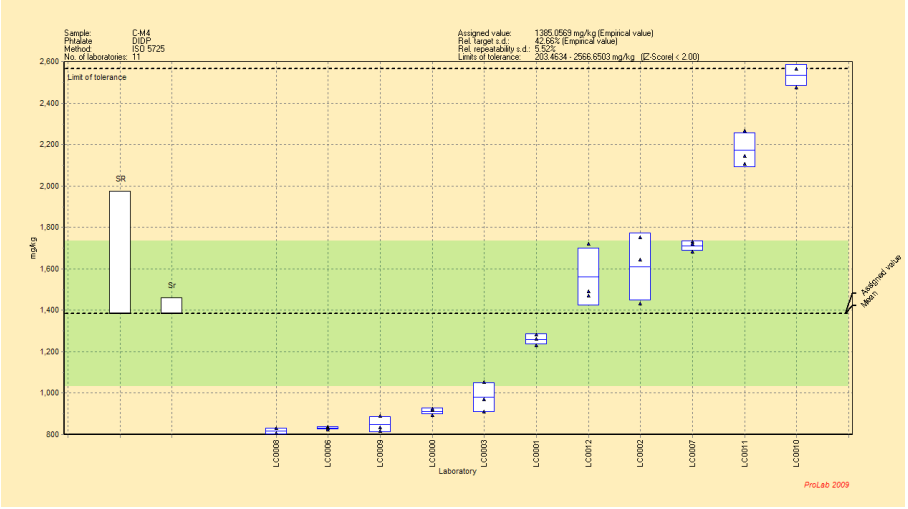
C-M4-DEHP
Nr.Labs: 12
Mean (mg/kg): 4560.6
SD_r (mg/kg): 250.0
SD_R (mg/kg): 1001.8



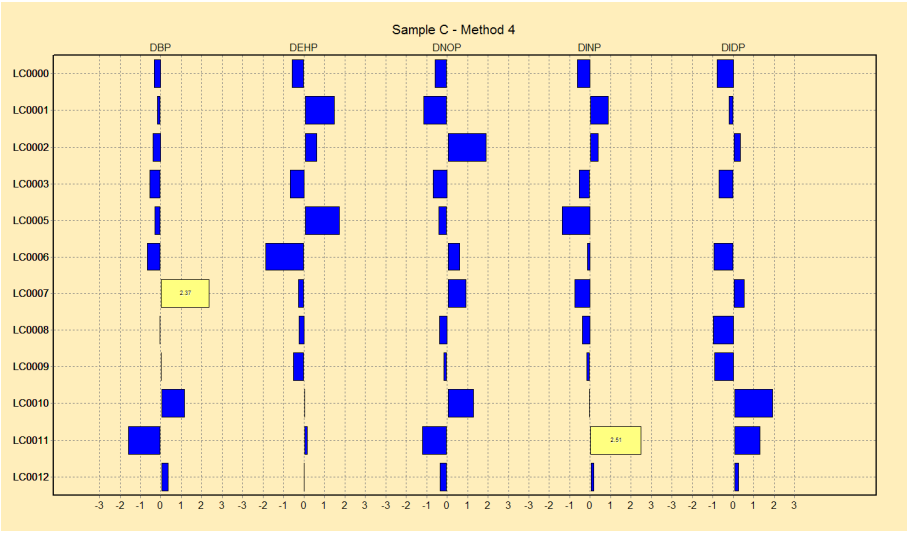
C-M4-DNOP
Nr.Labs: 12
Mean (mg/kg): 218.3
SD_r (mg/kg): 18.5
SD_R (mg/kg): 130.8



C-M4-DINP
Nr.Labs: 12
Mean (mg/kg): 4550.1
SD_r (mg/kg): 297.0
SD_R (mg/kg): 1414.8

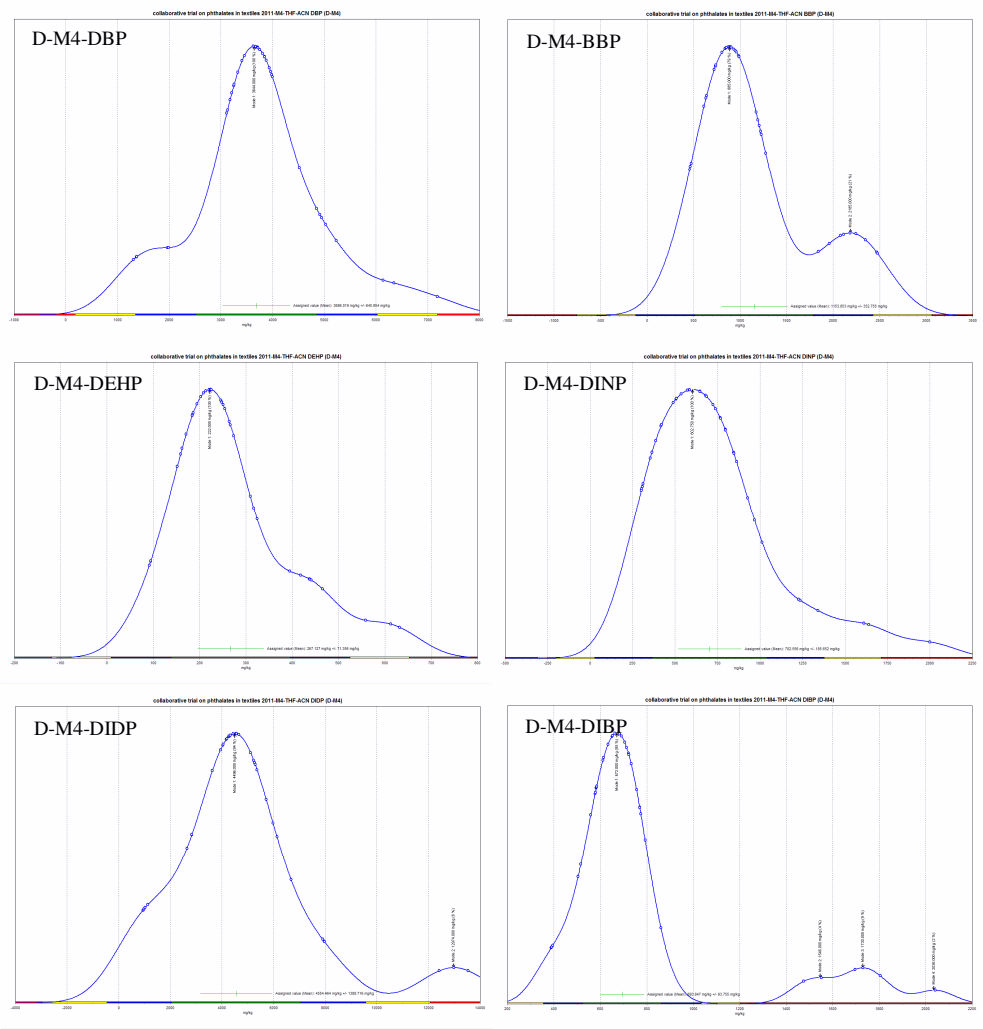


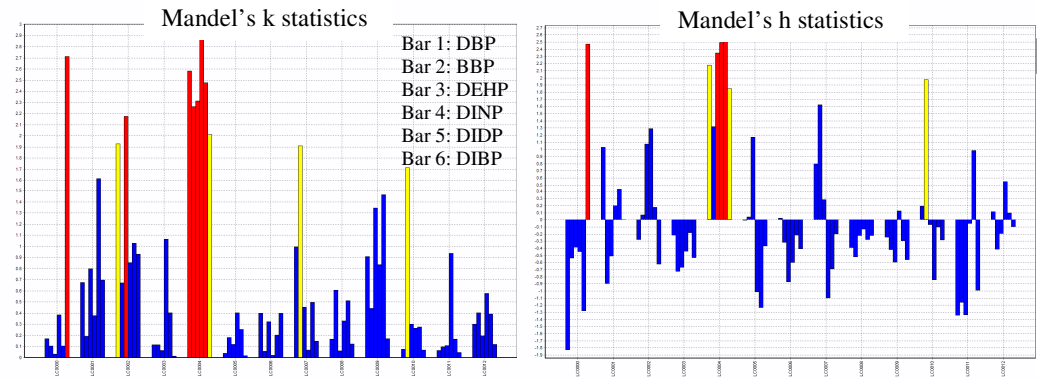
C-M4-DIDP
Nr.Labs: 11
Mean (mg/kg): 1385.1
SD_r (mg/kg): 76.4
SD_R (mg/kg): 590.8

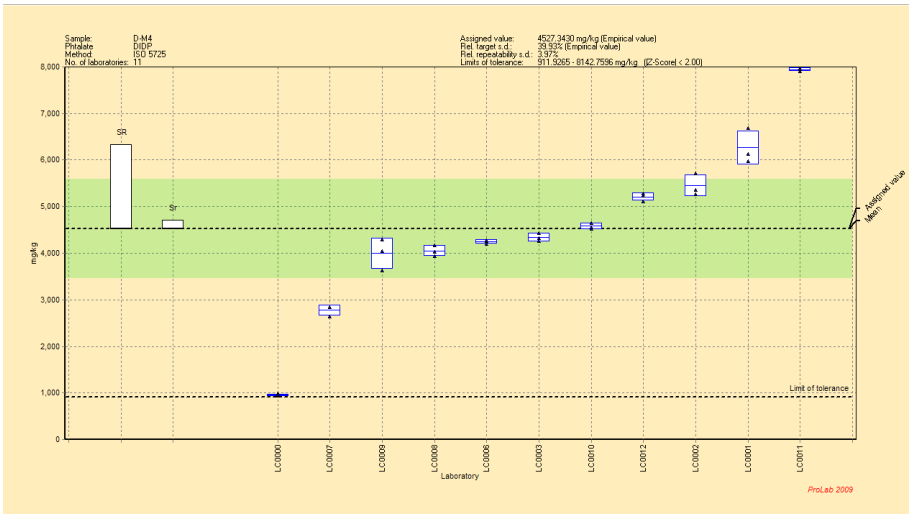


Z-scores

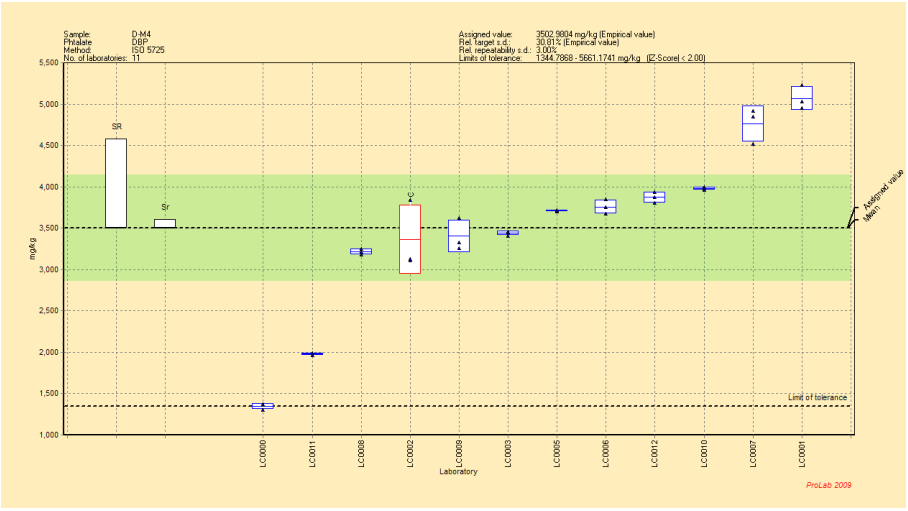
Sample D – Method 4



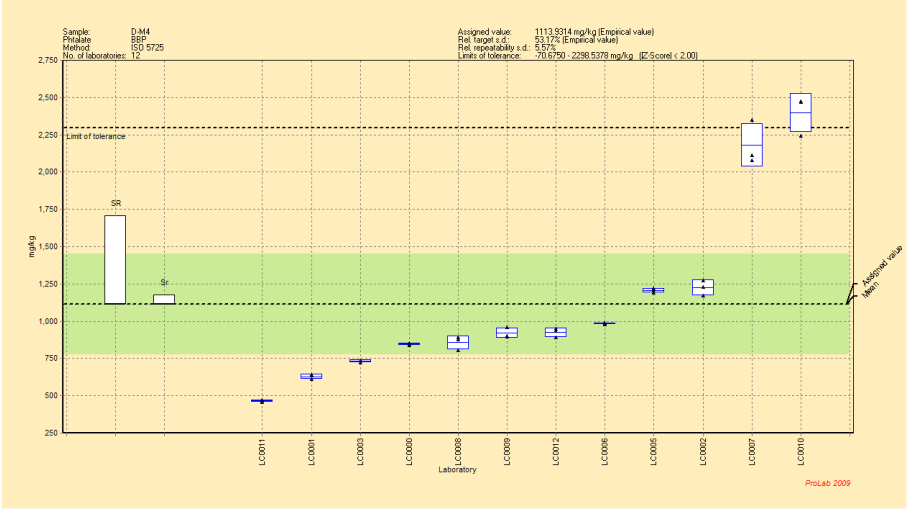




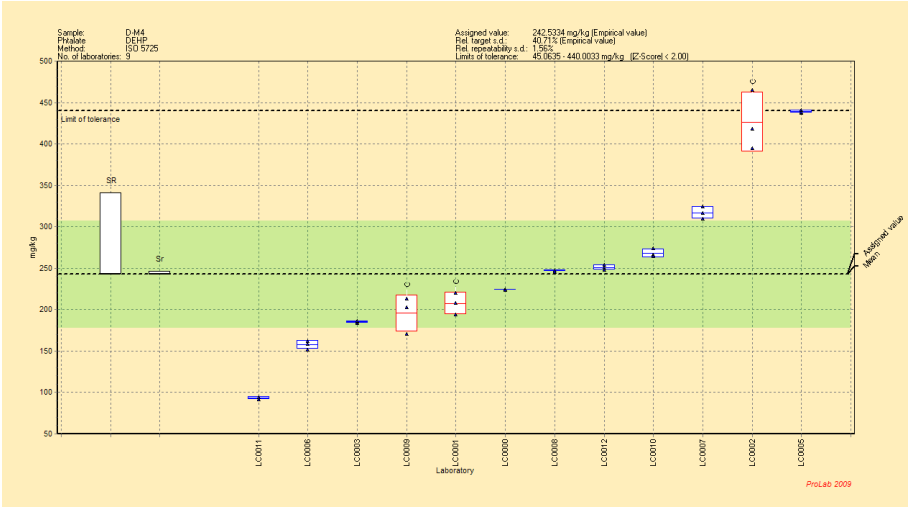
D-M4-DIDP
Nr.Labs: 11
Mean (mg/kg): 4527.3
SD_r (mg/kg): 179.7
SD_R (mg/kg): 1807.7



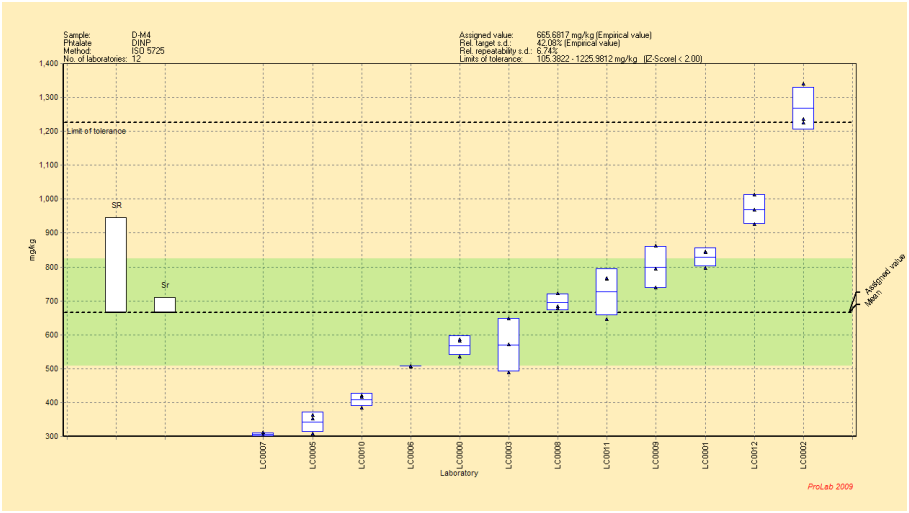
D-M4-DBP
Nr.Labs: 11
Mean (mg/kg): 3503.0
SD_r (mg/kg): 105.0
SD_R (mg/kg): 1079.1



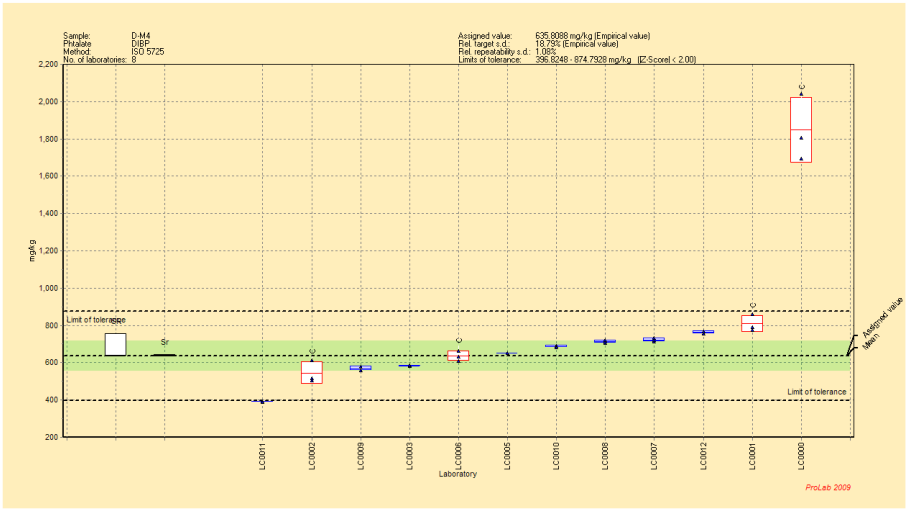
D-M4-BBP
Nr.Labs: 12
Mean (mg/kg): 1113.9
SD_r (mg/kg): 62.1
SD_R (mg/kg): 592.3



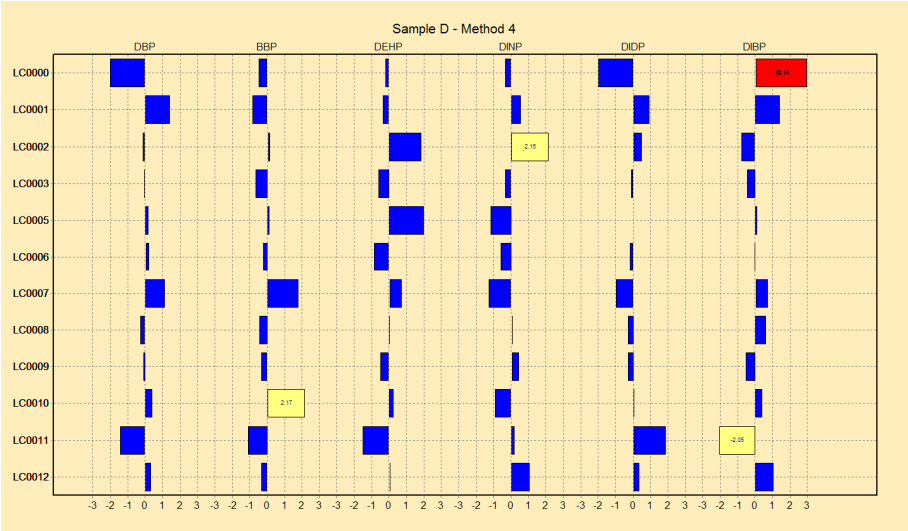
D-M4-DEHP
Nr.Labs: 9
Mean (mg/kg): 242.5
SD_r (mg/kg): 3.8
SD_R (mg/kg): 98.7



D-M4-DINP
Nr.Labs: 12
Mean (mg/kg): 665.7
SD_r (mg/kg): 44.9
SD_R (mg/kg): 280.1

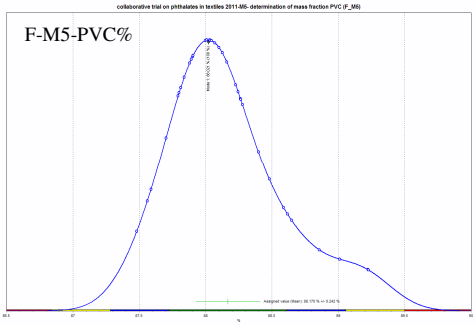


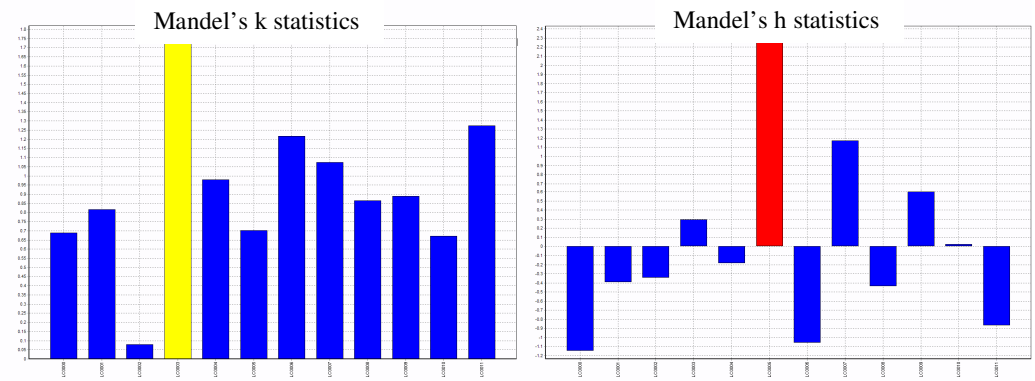
D-M4-DIBP
Nr.Labs: 8
Mean (mg/kg): 635.8
SD_r (mg/kg): 6.8
SD_R (mg/kg): 119.5

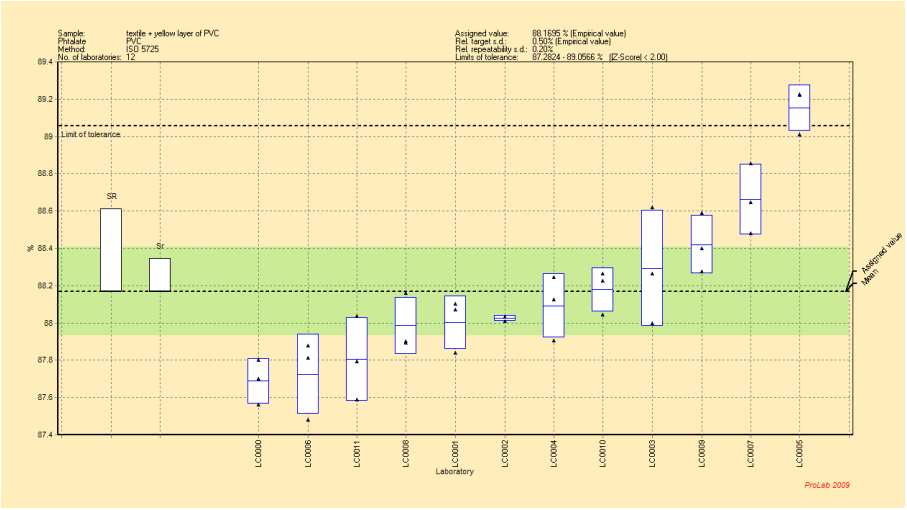


Z-scores

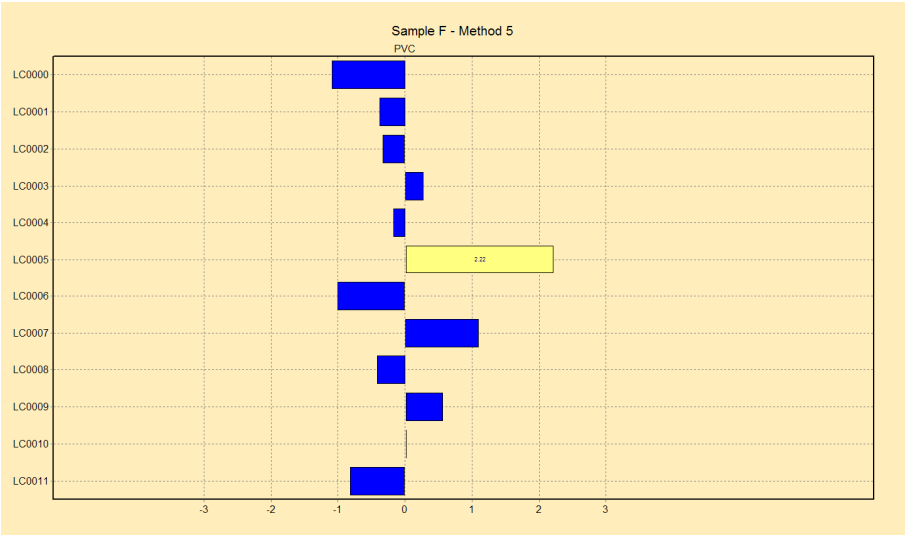
Sample F – Method 5







F-M5-%PVC
Nr.Labs: 12
Mean (%): 88.2
SDr (%): 0.2
SDR (%): 0.4



Z-scores

ANNEX XI

Other phthalates detected

Tables A, B, C (Method 1): Other phthalates detected by participants: original values, cell means and cell standard deviations, respectively.

	Sample A - M1		Sample B - M1		Sample C - M1		Sample D - M1	Sample E - M1	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	65.48		6.24		0.79			69.17	76.24
	63.13		6.52		1.11			69.38	86.25
	62.75		6.68		1.01			70.31	81.09
LC0001	40.61		3.52		0.60			48.90	
	39.81		3.54		0.57			48.53	
	41.06		3.81		0.59			51.73	
LC0002	35.93	21.42			5.68			30.50	75.46
	31.57	1.10			5.99			17.51	60.34
	30.92	45.44			3.72			27.08	112.10
LC0003	47.67							60.50	106.62
	48.69							60.36	69.92
	49.19							58.23	74.43
LC0004	55.32	13.62	11.01		4.38	37.62	8.20	61.83	35.55
	50.81	19.05	14.59		8.20	18.51	5.26	63.12	20.77
	50.73	14.21	16.53		4.14	14.34	4.15	63.53	33.16
LC0005	35.04		1.75	1203.19				44.29	
	35.12		1.80	1213.34				43.45	
	34.37		1.70	1175.42				45.81	
LC0006	25.91	8.49		4441.72		2.45	0.00	30.95	4520.92
	24.96	7.96		2.31		1.74	0.00	26.00	87.02
	24.53	6.97		5.34		1.52	3818.38	26.07	48.04
LC0007	104.92		10.34	7.31			111.00	99.80	31.48
	102.97		10.13	7.79			112.19	100.48	30.91
	108.50		10.82	8.24			112.72	99.90	31.46
LC0008	95.97	114.80	6.93	24.95				84.14	166.93
	84.08	109.01	6.68	27.46				84.59	163.39
	78.26	111.85	6.73	24.83				83.31	159.20
LC0009	43.70		4.82				7.48	45.88	162.60
	43.07		4.03				0.00	49.56	196.93
	40.68		2.90				0.00	45.39	242.85
LC0010	95.08		11.42		3.17			98.15	82.62
	94.77		6.48		0.00			97.88	78.80
	97.93		9.27		2.37			98.34	78.10
LC0011	18.50							19.95	62.02
	19.67							19.17	105.17
	17.73							19.95	46.48
LC0012	74.29	393.16	10.73	14.70	1.29	25.52	18.55	75.21	98.47
	66.48	33.69	11.10	136.73	1.02	20.90	18.51	74.08	82.67
	72.18	33.24	11.21	15.31	1.15	23.98	18.27	76.51	73.34

mean	Sample A - M1		Sample B - M1		Sample C - M1		Sample D - M1	Sample E - M1	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	63.79		6.48		0.97			69.62	81.19
LC0001	40.50		3.63		0.59			49.72	
LC0002	32.81	22.65			5.13			25.03	82.63
LC0003	48.52							59.70	83.66
LC0004	52.29	15.63	14.04		5.57	23.49	5.87	62.83	29.82
LC0005	34.85		1.75	1197.32				44.52	
LC0006	25.14	7.81		1483.12		1.90	1272.79	27.67	1551.99
LC0007	105.46		10.43	7.78			111.97	100.06	31.28
LC0008	86.10	111.89	6.78	25.75				84.01	163.17
LC0009	42.48		3.92				2.49	46.94	200.79
LC0010	95.92		9.05		1.85			98.12	79.84
LC0011	18.63							19.69	71.22
LC0012	70.98	153.36	11.01	55.58	1.15	23.47	18.44	75.27	84.83

SD	Sample A - M1		Sample B - M1		Sample C - M1		Sample D - M1	Sample E - M1	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	1.48		0.22		0.17			0.61	5.01
LC0001	0.63		0.16		0.02			1.75	
LC0002	2.72	22.20			1.23			6.73	26.61
LC0003	0.78							1.27	20.01
LC0004	2.63	2.98	2.80		2.28	12.41	2.10	0.89	7.93
LC0005	0.41		0.05	19.63				1.20	
LC0006	0.70	0.77		2562.22		0.49	2204.54	2.83	2571.24
LC0007	2.81		0.35	0.46			0.88	0.37	0.32
LC0008	9.03	2.90	0.13	1.49				0.65	3.87
LC0009	1.59		0.96				4.32	2.28	40.26
LC0010	1.74		2.48		1.65			0.23	2.43
LC0011	0.98							0.45	30.41
LC0012	4.04	207.67	0.25	70.27	0.14	2.35	0.15	1.21	12.70

Tables A, B, C (Method 2): Other phthalates detected by participants: original values, cell means and cell standard deviations, respectively.

	Sample A - M2		Sample B - M2		Sample C - M2		Sample D - M2	Sample E - M2	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	57.05		4.64		0.60			60.65	54.25
	57.47		5.04		0.62			60.37	46.35
	56.56		5.22		0.79			59.28	48.13
LC0001	30.97		4.22					32.47	
	30.02		4.18					33.03	
	32.52		4.56					32.79	
LC0002	22.14	6.37	3.07	5.59	7.90			24.79	45.41
	22.00	16.27	2.42	5.21	6.88			13.97	47.30
	22.50	8.77	4.04	5.06	12.51			11.94	45.85
LC0003	33.89	55.42	3.71					32.79	56.50
	31.17	0.00	3.16					32.03	36.25
	30.58	0.00	3.57					32.18	24.81
LC0004	52.09		4.14		0.00	3.89		38.22	
	33.58		4.53		0.46	2.88		42.50	
	35.96		4.45		0.00	6.01		45.94	
LC0005	37.03		0.87	474.42				33.63	
	34.88		0.86	483.01				35.30	
	34.41		0.87	550.23				35.93	
LC0006	22.42	3.40		3.62		0.82		28.95	46.44
	19.39	5.11		3.30		1.62		20.86	49.99
	20.54	5.60		2.36		0.85		28.37	80.22
LC0007	78.77	6.26	13.16	5.43	2.50		12.91	81.44	28.46
	79.83	7.11	11.85	5.59	2.25		12.56	80.95	27.47
	77.83	6.33	11.25	5.35	2.29		12.21	78.61	28.34
LC0008	52.26	37.13	5.44	26.50		2.64		48.05	70.31
	51.95	36.11	5.47	13.31		2.63		48.35	73.30
	51.03	38.97	5.39	17.78		2.54		48.35	81.48
LC0009	42.39	57.44					10.24	41.92	99.12
	38.70	57.95					0.00	44.27	98.64
	33.62	0.00					10.19	36.24	88.23
LC0010	50.33				9.00			69.42	61.01
	56.46				1.38			70.05	63.33
	54.46				4.50			68.48	66.16
LC0011	26.08		2.88					26.03	
	26.90		2.69					25.96	
	26.63		2.62					25.65	
LC0012	49.74	15.09	5.68	10.10	0.09	17.74	2.49	58.09	71.54
	50.46	15.44	5.44	10.10	0.07	17.58	2.52	59.90	73.27
	49.29	15.44	5.31	10.08	0.06	18.34	2.67	59.49	71.46

mean	Sample A - M2		Sample B - M2		Sample C - M2		Sample D - M2	Sample E - M2	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	57.03		4.97		0.67			60.10	49.58
LC0001	31.17		4.32					32.76	
LC0002	22.21	10.47	3.17	5.28	9.10			16.90	46.19
LC0003	31.88	18.47	3.48					32.34	39.19
LC0004	40.55		4.37		0.15	4.26		42.22	
LC0005	35.44		0.86	502.55				34.95	
LC0006	20.78	4.70		3.09		1.10		26.06	58.88
LC0007	78.81	6.57	12.08	5.45	2.35		12.56	80.33	28.09
LC0008	51.75	37.40	5.43	19.19		2.60		48.25	75.03
LC0009	38.24	38.46					6.81	40.81	95.33
LC0010	53.75				4.96			69.32	63.50
LC0011	26.54		2.73					25.88	
LC0012	49.83	15.32	5.48	10.09	0.07	17.89	2.56	59.16	72.09

SD	Sample A - M2		Sample B - M2		Sample C - M2		Sample D - M2	Sample E - M2	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	0.46		0.29		0.10			0.72	4.15
LC0001	1.26		0.21					0.28	
LC0002	0.25	5.17	0.81	0.27	3.00			6.91	0.99
LC0003	1.77	32.00	0.29					0.40	16.05
LC0004	10.07		0.21		0.26	1.60		3.87	
LC0005	1.40		0.01	41.52				1.19	
LC0006	1.53	1.15		0.65		0.45		4.51	18.57
LC0007	1.00	0.47	0.97	0.12	0.13		0.35	1.51	0.54
LC0008	0.64	1.45	0.04	6.71		0.05		0.17	5.78
LC0009	4.40	33.31					5.90	4.13	6.16
LC0010	3.12				3.83			0.79	2.58
LC0011	0.42		0.13					0.20	
LC0012	0.59	0.20	0.19	0.01	0.02	0.40	0.10	0.95	1.02

Tables A, B, C (Method 3): Other phthalates detected by participants: original values, cell means and cell standard deviations, respectively.

	Sample A - M3		Sample B - M3		Sample C - M3		Sample D - M3	Sample E - M3	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	53.87		7.01		1.24			63.78	52.50
	51.82		7.70		0.84			56.02	48.15
	56.78		8.00		0.84			60.48	55.48
LC0001	42.55		2.97		1.53			51.37	153.99
	44.84		2.90		1.26			52.91	174.74
	46.77		2.74		0.85			52.95	161.00
LC0002	37.45	17.38	1.61		0.00		7.87	44.56	142.59
	29.30	18.30	7.76		0.00		8.51	42.58	115.80
	31.63	10.29	2.46		8.71		19.50	47.29	83.83
LC0003	45.69		6.07					51.64	57.98
	45.44		5.70					49.55	44.30
	45.14		5.16					50.78	39.30
LC0004	38.51		27.26		4.95	21.21	9.43	58.17	0.00
	42.92		60.96		12.96	85.48	3.48	52.09	36.86
	43.81		10.44		2.28	34.57	8.27	54.55	41.01
LC0005	85.66		1.91	544.33				82.41	
	80.77		1.71	499.01				86.30	
	79.18		1.75	531.27				87.59	
LC0006	26.37	35.48		4.88		1.56		29.72	141.95
	27.17	29.66		5.75		1.36		28.78	130.24
	24.38	26.82		6.77		1.11		26.41	89.75
LC0007	65.81	7.14	10.23	3.94	3.31	0.53	8.24	95.62	9.76
	70.46	8.43	11.61	4.44	3.11	0.86	9.61	105.12	10.93
	68.44	8.16	10.42	4.58	3.42	0.71	9.36	94.43	9.91
LC0008	70.01	84.58	6.63	29.44		2.85		76.52	143.44
	69.35	87.12	6.56	11.78		2.75		75.40	164.32
	69.75	79.07	6.39	20.63		2.67		77.64	125.89
LC0009	61.60	124.65	9.85		0.00		8.09	55.43	134.21
	45.90	78.74	4.65		4.05		9.72	55.66	96.09
	51.62	86.19	11.61		0.00		9.35	57.67	103.76
LC0010	92.92		8.62		17.60			82.20	65.88
	89.75		7.43		8.02			83.80	60.95
	90.28		9.55		7.29			85.82	64.25
LC0011	15.52							17.00	
	16.95							17.42	
	14.28							17.99	
LC0012	55.38	32.92	6.80	13.94	0.23	19.48	2.81	59.43	99.00
	53.85	31.46	6.56	14.28	0.35	19.17	2.81	60.62	97.41
	51.63	29.48	6.59	14.01	0.43	19.90	3.02	62.75	81.19

mean	Sample A - M3		Sample B - M3		Sample C - M3		Sample D - M3	Sample E - M3	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	54.16		7.57		0.97			60.09	52.04
LC0001	44.72		2.87		1.21			52.41	163.24
LC0002	32.79	15.32	3.94		2.90		11.96	44.81	114.07
LC0003	45.42		5.65					50.66	47.20
LC0004	41.75		32.89		6.73	47.08	7.06	54.93	25.95
LC0005	81.87		1.79	524.87				85.43	
LC0006	25.97	30.65		5.80		1.34		28.30	120.65
LC0007	68.24	7.91	10.75	4.32	3.28	0.70	9.07	98.39	10.20
LC0008	69.70	83.59	6.53	20.62		2.76		76.52	144.55
LC0009	53.04	96.53	8.70		1.35		9.05	56.25	111.36
LC0010	90.98		8.54		10.97			83.94	63.69
LC0011	15.58							17.47	
LC0012	53.62	31.28	6.65	14.08	0.34	19.52	2.88	60.93	92.53

SD	Sample A - M3		Sample B - M3		Sample C - M3		Sample D - M3	Sample E - M3	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	2.50		0.51		0.23			3.89	3.69
LC0001	2.11		0.11		0.34			0.90	10.56
LC0002	4.20	4.38	3.33		5.03		6.54	2.36	29.42
LC0003	0.28		0.46					1.05	9.67
LC0004	2.84		25.72		5.56	33.91	3.15	3.06	22.57
LC0005	3.38		0.10	23.33				2.70	
LC0006	1.44	4.42		0.95		0.23		1.71	27.39
LC0007	2.33	0.68	0.75	0.34	0.15	0.17	0.73	5.86	0.63
LC0008	0.33	4.11	0.12	8.83		0.09		1.12	19.24
LC0009	7.94	24.64	3.62		2.34		0.85	1.23	20.16
LC0010	1.70		1.06		5.75			1.81	2.51
LC0011	1.34							0.50	
LC0012	1.89	1.73	0.13	0.18	0.10	0.37	0.12	1.69	9.86

Tables A, B, C (Method 4): Other phthalates detected by participants: original values, cell means and cell standard deviations, respectively.

	Sample A - M4		Sample B - M4		Sample C - M4		Sample D - M4	Sample E - M4	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	59.18		4.85		1.35		838.67	69.27	25.08
	57.57		4.75		1.39		795.25	64.29	31.69
	56.36		5.12		0.70		946.32	63.71	18.67
LC0001	41.98		5.75		2.32			59.82	
	42.47		5.49		2.51			55.68	
	44.30		5.56		2.24			55.46	
LC0002	88.96	45.65	10.42		0.12		0.81	99.89	53.28
	92.58	52.44	9.81		0.98		2.71	111.50	261.08
	92.23	24.34	13.41		0.41		4.36	129.93	145.74
LC0003	50.69		8.68					42.75	98.68
	47.65		7.81					44.55	119.91
	47.32		7.86					40.29	81.82
LC0004	151.95	40.10	24.34		9.09	20.95	7.30	150.49	116.35
	136.38	15.19	30.55		10.40	29.25	13.15	170.70	137.13
	142.64	27.84	36.86		11.64	32.37	17.42	162.59	91.96
LC0005	132.85			398.95				128.33	
	126.52			364.24				135.22	
	121.25			343.30				136.40	
LC0006	35.11	3.39		7.42		1.88		37.30	65.24
	34.19	5.76		6.35		1.10		36.22	49.85
	34.07	6.08		5.17		1.60		37.51	43.10
LC0007	94.12	3.36	11.66	3.13	2.30	0.55	10.00	88.01	11.16
	85.25	3.48	10.13	2.92	2.20	0.58	8.82	85.98	10.67
	82.14	3.18	9.89	2.98	2.46	0.61	10.22	87.02	10.88
LC0008	67.62	77.60	6.29	18.43		854.10	4.66	73.25	161.52
	66.46	99.01	5.98	50.67		840.70	5.24	73.67	166.61
	67.53	103.06	6.08	29.71		835.81	8.58	72.94	152.16
LC0009	65.12	0.00						57.75	212.21
	49.95	0.00						58.42	201.58
	47.22	117.06						55.22	187.92
LC0010	64.35		11.11		12.70			75.91	
	61.99		7.02		13.96			72.51	
	60.60		7.35		14.87			74.31	
LC0011	20.88							21.28	
	18.93							21.68	
	21.52							17.98	
LC0012	56.99	42.32	5.99	36.39	0.85	20.36	1.23	68.51	107.89
	58.48	40.65	6.39	36.84	0.75	21.01	1.33	71.82	112.70
	59.04	39.16	6.82	37.88	0.30	20.29	1.50	68.33	152.15

mean	Sample A - M4		Sample B - M4		Sample C - M4		Sample D - M4	Sample E - M4	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	57.70		4.91		1.15		860.08	65.76	25.15
LC0001	42.92		5.60		2.36			56.99	
LC0002	91.26	40.81	11.21		0.50		2.63	113.77	153.37
LC0003	48.55		8.12					42.53	100.14
LC0004	143.65	27.71	30.58		10.38	27.53	12.62	161.26	115.14
LC0005	126.87			368.83				133.32	
LC0006	34.46	5.08		6.32		1.53		37.01	52.73
LC0007	87.17	3.34	10.56	3.01	2.32	0.58	9.68	87.01	10.90
LC0008	67.20	93.22	6.12	32.94		843.54	6.16	73.29	160.10
LC0009	54.10	39.02						57.13	200.57
LC0010	62.31		8.49		13.84			74.24	
LC0011	20.44							20.31	
LC0012	58.17	40.71	6.40	37.03	0.63	20.55	1.35	69.55	124.25

SD	Sample A - M4		Sample B - M4		Sample C - M4		Sample D - M4	Sample E - M4	
Laboratory	DEHP	DINP	DBP	DIDP	DIBP	BBP	DNOP	DEHP	DINP
LC0000	1.42		0.19		0.38		77.78	3.06	6.51
LC0001	1.22		0.13		0.14			2.46	
LC0002	2.00	14.66	1.92		0.44		1.78	15.15	104.11
LC0003	1.86		0.49					2.14	19.09
LC0004	7.84	12.46	6.26		1.27	5.90	5.08	10.17	22.61
LC0005	5.81			28.11				4.36	
LC0006	0.57	1.47		1.12		0.39		0.69	11.35
LC0007	6.22	0.15	0.96	0.11	0.13	0.03	0.76	1.01	0.25
LC0008	0.65	13.68	0.16	16.36		9.47	2.12	0.37	7.33
LC0009	9.64	67.58						1.69	12.17
LC0010	1.90		2.27		1.09			1.70	
LC0011	1.35							2.03	
LC0012	1.06	1.58	0.42	0.76	0.29	0.40	0.13	1.96	24.28

European Commission
EUR 25674 EN – Joint Research Centre – Institute for Health and Consumer Protection

Title: Report on the collaborative trial organised by the JRC on the determination of PVC and phthalates in textile products

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Abstract

On behalf of CEN/TC 248/WG 26 and ISO/TC 38/WG 22, the European Commission's Joint Research Center (JRC) organised a collaborative study on the determination of PVC and phthalates in textiles products.
The purpose of the study was the comparison and validation of four methods for the determination of phthalates and the validation of one method to determine the content of PVC in textile products. Methods 1, 2 and 3 were based on ultrasonic extraction of phthalates with n-hexane/acetone 80/20 v/v, n-hexane, tert-butyl methyl ether, respectively, and method 4 foresaw PVC dissolution in tetrahydrofuran and re-precipitation with acetonitrile. One method for the quantification of PVC in textile products based on the dissolution of PVC with tetrahydrofuran, followed by the washing of the residue and its gravimetric determination was also investigated (method 5).
The collaborative exercise was organised, according to ISO 5725-2, as a balanced uniform-level experiment with the same number of test results in each laboratory, which each laboratory analysing the same levels of test samples. Thirteen laboratories both European and non-European participated to this study.
The Italian company MP S.p.A produced both the PVC samples and the textile ones, made by cotton spread with PVC layer. Four textile and one PVC samples containing in total 7 phthalates (DEHP, DBP, BBP, DINP, DIDP, DNOP and DIBP) at 3 concentration levels and one sample, in which the PVC mass per cent had to be measured were analysed in triplicates. Levels I, II and III refer to samples containing a specific phthalate in concentrations of approximately 200, 1000 and 5000 mg/kg. In the case of DIDP and DINP, level I corresponded to approximately 500 mg/kg of PVC. These phthalate concentrations were selected in order to assess the precision of the analytical methods in the range of the current limits for toys and childcare articles.
The homogeneity study was carried out by the JRC and all samples could be considered 'sufficiently homogeneous' according to the IUPAC harmonised protocol for proficiency testing. Results were statistically evaluated following the rules laid down in ISO 5725 parts 2 and 5. The consensus values and the precisions of the various methods, in terms of repeatability and reproducibility limits as well as repeatability and reproducibility relative standard deviations, were evaluated. Applying ISO 5725-2, the statistical outliers identified with Cochran's and Grubbs' tests were rejected, together with the results of LC0004 for method 4 and the ones of LC0005 for DIDP in methods 1-4, which were identified as outliers with Mandel's h statistics. On the contrary, considering ISO 5725-5, all test results were retained and robust statistics was used. These two alternative approaches gave results that could be considered in good agreement. Generally, the differences were always lower than 35 %, except in few cases.
Concerning the extraction efficiency, method 4 proved to be the best one in terms of phthalates' recovery, whereas method 2 was the worst one. Practically the same recovery rate was shown by methods 1 and 3. Relative standard deviations of repeatability and reproducibility ranged from 3.0 to 23.5 % and from 19.4 and 189.9 % respectively. This means that both the four methods and the laboratories' performance have to be drastically improved. Poor repeatability was observed in the case of several laboratories and the large spread in the mean values calculated in the 13 laboratories is responsible for the high observed relative standard deviation of reproducibility.
Regarding method 5 for the quantification of PVC, repeatability and reproducibility relative standard deviations were 0.6 and 1.4% respectively. Considering that these values are in the same range of the values obtained with similar dissolution methods validated in the context of quantification of fibre binary mixtures, this method can be considered validated.

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