CCQM-K133

Low-Polarity Analytes in Plastics :

Phthalate esters in Polyvinyl Chloride (PVC)

Key Comparison
Track C

Draft B Report
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SUMMARY

Phthalate esters (phthalates, PAEs) are widely used as plasticizers to enhance the durability, flexibility, and workability of plastics, especially Polyvinyl Chloride (PVC). Due to the nature of the physical binding of PAEs to polymers (via secondary molecular interactions), they can easily be released from various products. These compounds have become ubiquitous in water, sediment, as well as food products and are classified as endocrine-disrupting chemicals because of their potential effect on wild animals and human beings. Recently, many countries prohibit or restrict the use of phthalates in electrical and electronic products, toys and children articles. Evidence of successful participation in formal, relevant international comparisons is needed to document measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs). To enable NMIs and DIs to update or establish, the CCQM Organic Analysis Working Group sponsored CCQM-K133 "Low-Polarity Analytes in Plastics: Phthalate esters in Polyvinyl Chloride (PVC)".

Nine National Metrology Institutes participated in the Track C Key Comparison CCQM-K133: Phthalate esters in PVC. Participants were requested to evaluate the mass fractions, expressed in mg/kg, of BBP in a low concentration PVC sample, and DBP, BBP and DEHP in a high concentration PVC sample, termed LCPVC and HCPVC. The consensus summary mass fractions for the four measurands are in the range of (95 to 905) mg/kg with relative standard deviation of (4 to 8) %.

Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, having low polarity $pK_{ow} < -2$, in mass fraction range from10 mg/kg to 5000 mg/kg in plastics: (i) value assignment of primary reference standards; (ii) value assignment of calibration solutions; (iii) extraction of analyte of interest from the matrix; (iv) clean-up and separation of analyte of interest from other interfering matrix or extract components; (v) separation and quantification using techniques such as GC-IDMS, GC-IDHRMS, HPLC-DAD or LC-IDMS/MS.

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ACRONYMS

ANOVA	analysis of variance
BBP	Benzyl Butyl Phthalate
CAS	Chemical Abstracts Service
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CIL	Cambridge Isotope Laboratories, Inc.
CMC	Calibration and Measurement Capability
CRM	certified reference material
CV	coefficient of variation, expressed in %: CV = $100 \cdot s/\bar{x}$
D4-BBP	Ring- four Deuterium labelled BBP
DBP	Di-*n*-butyl Phthalate
D4-DBP	Ring- four Deuterium labelled DBP
DEHP	Bis (2-ethylhexyl) Phthalate
D4-DEHP	Ring- four Deuterium labelled DEHP
DI	designated institute
DoE	degrees of equivalence
EXHM	Chemical Metrology Laboratory, DI: Greece
GC	gas chromatography
GC-FID	gas chromatography with flame ionization detector
GC-IDHRMS	gas chromatography isotope dilution high-resolution mass spectrometry
GC-IDMS	gas chromatography isotope dilution mass spectrometry
GC-IDMS/MS	gas chromatography isotope dilution tandem mass spectrometry
GC-MS	gas chromatography with mass spectrometry detection
GLHK	Government Laboratory, Hong Kong, DI: Hong Kong
DnOP	di-*n*-octyl phthalate
GC-IDTOFMS	gas chromatography isotope dilution time-of-flight mass spectrometry
HCPVC	high concentration PVC sample
HPLC-DAD	high pressure liquid chromatography with diode array detection
ID	isotope dilution
IDMS	isotope dilution mass spectrometry
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia, NMI: Brazil
KC	Key Comparison
KCRV	Key Comparison Reference Value
KEBS	Kenya Bureau of Standards, NMI: Kenya
KRISS	Korea Research Institute of Standards and Science, NMI: Republic of Korea
LC	liquid chromatography
LCPVC	low concentration PVC sample
LGC	Laboratory of the Government Chemist, Teddington, Middlesex UK
LC-IDMS/MS	liquid chromatography isotope dilution tandem mass spectrometry
LC-MS/MS	liquid chromatography with tandem mass spectrometry detection

LTSS	long-term stability study
MADe	median absolute deviation from the median (MAD)-based estimate of s: MADe = 1.4826·MAD, where MAD = median($\|x_i$-median(x_i)$\|$)
MRM	multiple reaction monitoring
NIM	National Institute of Metrology, NMI: China
NMI	national metrology institute
NMIJ	National Metrology Institute of Japan, NMI: Japan
NMISA	National Metrology Institute South Africa, NMI: South Africa
NMR	nuclear magnetic resonance spectroscopy
OAWG	Organic Analysis Working Group
PAEs	Phthalate esters
pK_{ow}	Negative base-10 logarithm of the octanol-water partition coefficient
PVC	Polyvinyl Chloride
qNMR	quantitative nuclear magnetic resonance spectroscopy
RSD	relative standard deviation
SD	standard deviation
SIM	selected ion monitoring
SRM	Selected reaction monitoring
STSS	short-term stability study
TBD	To Be Determined
TCI	Tokyo Chemical Industry
THF	Tetrahydrofuran
UME	National Metrology Institute of Turkey, NMI: Turkey
VNIIM	D.I. Mendeleyev Institute for Metrology, NMI: Russia

SYMBOLS

d_i	degree of equivalence: x_i - KCRV
$\%d_i$	percent relative degree of equivalence: $100 \cdot d_i/\text{KCRV}$
k	coverage factor: $U(x) = k \cdot u(x)$
n	number of quantity values in a series of quantity values
s	standard deviation of a series of quantity values: $s = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$
t_s	Student's *t*-distribution expansion factor
$u(x_i)$	standard uncertainty of quantity value x_i
$\bar{u}(x)$	pooled uncertainty: $\bar{u}(x) = \sqrt{\sum_{i=1}^{n} u^2(x_i)/n}$
$U(x)$	expanded uncertainty
$U_{95}(x)$	expanded uncertainty defined such that $x \pm U_{95}(x)$ is asserted to include the true value of the quantity with an approximate 95 % level of confidence
$U_{k=2}(x)$	expanded uncertainty defined as $U_{k=2}(x) = 2 \cdot u(x)$
x	a quantity value
x_i	the i^{th} member of a series of quantity values
$\bar{x}$	mean of a series of quantity values: $\bar{x} = \sum_{i=1}^{n} x_i/n$

INTRODUCTION

Phthalate esters (phthalates, PAEs) are widely used as plasticizers for Polyvinyl Chloride (PVC). However, some research articles have reported the effect of phthalates on wild animals and human beings. [1-4] Recently, many countries have restricted the use of phthalates for toys and children articles. [5-6] Especially, the European Union (EU) directive on "the reduction of certain hazardous substances in electrical and electronic equipment" (RoHS II) [7-8] will restrict four phthalates in 2019. Di-*n*-butyl Phthalate (DBP), Di-*iso*-butyl Phthalate (DiBP), Benzyl Butyl Phthalate (BBP) and Bis (2-ethylhexyl) Phthalate (DEHP) will be prohibited from being used in electronic and electrical equipment.

At the CCQM Organic Analysis Working Group meeting held in Tsukuba in October 2014, possibilities for new studies in the organic field were discussed, including selected phthalates in PVC. NMIJ and NIM offered the provision of a suitable study material and were requested to review possibilities for coordinating a study in that field. It was agreed that CCQM-K133 would be held in parallel with a pilot study, CCQM-P170.

Appendices A to G are the Protocol, the Registration Form, the Reporting Form, the Core Competency Form, the Full details of the analytical methods employed by participants, the Full details of the uncertainty budgets estimated by participants and the Core competency claimed by participant for this key comparison, respectively.

TIMELINE

Table 1. Timeline for CCQM-K133

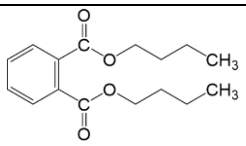
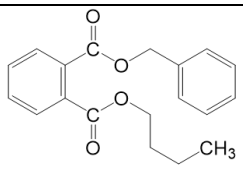
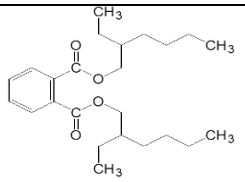
Date	Action
Oct. 2014	Proposed to CCQM
Oct. 2014	OAWG authorized CCQM-K133 as a Track C Key Comparison.
Apr. 2018	The protocol of CCQM-K133 was approved and authorized by OAWG.
Apr. 2018	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
Aug. 2018	Results due to coordinating laboratory
Mar. 2019	Draft A report distributed to OAWG
Oct. 2019	Draft B report distributed to OAWG
TBD	Final report approved by OAWG

MEASURANDS

Minimum reporting requirements for participants in CCQM-K133/P170 are the mass fractions of DBP, BBP and DEHP in the high concentration PVC sample (HCPVC) and BBP in the low concentration PVC sample (LCPVC). Relevant characteristic information of study measurands is listed in Table 2.

DBP, BBP and DEHP are restricted materials in the RoHS directive in EU. Although DiBP is also a restricted material and its molar mass is the same as DBP, DBP is a more popular plasticizer for PVC. DEHP exists as a number of enantiomers; because it is difficult to separate the enantiomers with versatile GC and LC columns, the reported mass fraction of DEHP shall include all enantiomers.

Table 2, Selected phthalates as study measurands for CCQM-K133/P170

Congener		DBP	BBP	DEHP
CAS		84-74-2	85-68-7	117-81-7
Molecular weight		278.344	312.360	390.556
pK_{ow} (-log K_{ow})		-4.50	-4.73	-7.5 (EUR23384 EN/2)
Structural Formula				
Measurand	LCPVC from NMIJ	No (Included, but unnecessary to report)	Yes	No (Included, but unnecessary to report)
	HCPVC from NIM	Yes	Yes	Yes

STUDY MATERIAL

Two types of PVC pellets (about 2 mm - 3 mm in diameter) in glass bottles were provided for CCQM-K133/170. Two bottles for each of the low and high concentration PVC samples were shipped together from NMIJ (NIM sent the HCPVC to NMIJ in advance). The PVC pellets were prepared by mixing and pelleting the available PVC, phthalates and other polymer additives.

The concentration range of LCPVC from NMIJ was from 30 mg/kg to 200 mg/kg, and for the HCPVC from NIM was from 300 mg/kg to 1200 mg/kg.

The HCPVC material required storage in a freezer. The LCPVC material required storage under 30 ºC.

Homogeneity and stability assessment of study material:
The coordinating laboratories carried out homogeneity studies, long-term stability monitoring and short-term stability monitoring. The results indicate that all study materials are homogenous and stable. The results and other detailed information are included in appendix A.

PARTICIPANTS, SAMPLE DISTRIBUTION AND STUDY GUIDELINES

Ten NMIs participated in CCQM-K133 and three NMIs/DI participated in CCQM-P170. Five bottles of sample (3 bottles of LCPVC and one blank bottle, 3 bottles of HCPVC and one blank bottle) were sent to each participant via couriers at the end of April 2018. Participants reported results for two bottles for each level. Each bottle (both high and low levels) contained approximately 10 g of PVC pellets. A temperature strip was attached on each bottle for the purpose of monitoring the maximum temperature exposure during

the transportation. A sample receipt form was sent together with samples and sent back by e-mail to s.matsuyama@aist.go.jp after receiving samples. Participants were asked to check the physical condition of the samples upon receipt of the sample pack and store two low level samples at room temperature and two high samples in a freezer until usage. All laboratories received the samples in good condition in 2-7 days. Additional bottles were sent to one laboratory on request during June 2018.

Other relevant documents, including Technical Protocol, Result Report Form and Competency Template were sent to participants by e-mail before or at the same time of sample dispatching.

Participants were requested to report the mass fractions (mg/kg) of DBP (in HCPVC), BBP (in LCPVC and HCPVC) and DEHP (in HCPVC) in the study material using their preferred analytical methodology, with the following recommendation additionally given by the coordinator:
- The minimum sample intake must be at least 0.1 g.
-All bottles at each level can be used for reporting. Participating laboratories shall report results obtained from each bottle. It was recommended that three subsamples are prepared and analysed for each bottle.

The participants were requested to provide the following information in the reporting sheet to s.matsuyama@aist.go.jp or shaomw@nim.ac.cn (together with the Core competency table) before the deadline for submission (extended to 31st August 2018):
(i) Participant's details.
(ii) Mass fractions (mg/kg) of each individual measurand (see Table 2) in the study materials.
(iii) Standard and expanded measurement uncertainties, with a detailed description/breakdown of the full uncertainty budget.
(iv) Description of the analytical procedure employed (extraction, clean-up, separation/detection and quantification) as well as details concerning the calibration and internal standards used (purity statement or verifications done at the laboratory's premises, etc…), especially if not mentioned in the Core competency table.
(v) Detailed information on blank testing (testing result, how to remove possible contaminations and so on).

Table 3 shows the participating institutes and contact persons in CCQM-K133. All institutes were registered to test all measurands. Finally, all participants submitted their results except KEBS.

Table 3 Participating institutes and contact persons

No.	Institute	Country	Contact person
1	NMIJ	Japan	Shigetomo Matsuyama
2	VNIIM	Russia	Anatoliy Krylov
3	GLHK	Hong Kong, China	Po-on TANG
4	UME	Turkey	Mine Bilsel
5	KRISS	Korea	Song-Yee BAEK
6	EXHM	Greece	Elias Kakoulides
7	NIM	China	Shao Mingwu
8	INMETRO	Brazil	Eliane Rego
9	NMISA	South Africa	Désirée Prevoo-Franzsen
10	KEBS	Kenya	Boniface Mbithi Muendo

RESULTS

Nine institutions submitted their results of CCQM-K133as required. In addition to the quantitative results, participants were instructed to describe their analytical methods, approach to uncertainty estimation, and the Core Competencies they felt were demonstrated in this comparison.

Calibrants' Traceability

The information on the calibration standards used by the participants in CCQM-K133 are given in Table 4.

Table 4. Calibrants used by the participants

Participant	Calibrants' Source	Determined purity or certified value where not assessed in house	Purity assessment	Evidence of competence
KRISS	TCI, neat	DBP:99.53% ± 0.26% BBP: 98.37% ± 0.26% DEHP: 99.52% ± 0.19%	Purity was assayed by KRISS with mass-balance method and verified with qNMR	The capability is underpinned by participating in CCQM-K55 series.
GLHK	NIM Solution CRM	DBP: GBW (E) 100224 (164.0 ± 4.9)μg/mL BBP: GBW (E) 100226 (160.0 ± 4.0) μg/mL DEHP: GBW (E) 100223 (202 ± 8.0) μg/mL	N/A	N/A
VNIIM	Sigma-Aldrich neat	DBP:99.6% ± 0.3% BBP: 98.3% ± 0.3% DEHP: 99.5% ± 0.3%	Purity was determined by mass-balance method	The capability is underpinned by participating in CCQM-K55 series.
INMETRO	NIST Solution CRM	NIST 3074 DBP: (51.2 ± 1.2) mg/kg BBP: (52.2 ± 1.4) mg/kg DEHP: (58.6 ± 1.3) mg/kg	N/A	N/A
NIM	Sigma Aldrich DR.E neat	DBP:99.7% ± 0.4% BBP: 98.7% ± 1.5% DEHP: 99.5% ±0 .7%	Purity was assayed using mass-balance	CCQM-K55a,b,c,d used similar techniques
EXHM	Sigma-Aldrich neat	DBP: (988.5 ± 2.5) mg/g BBP: (977.2 ± 2.5) mg/g DEHP: (993.8 ± 2.5) mg/g	Purity was determined by EXHM using qNMR with traceability to NMIJ 4601a	CCQM-K55c/P117c, CCQM-P150, CCQM-K131
NMISA	NIM Solution CRM	DBP: GBW (E) 100224 (164.0 ± 4.9) μg/mL BBP: GBW (E) 100226 (160.0 ± 4.0) μg/mL DEHP: GBW (E) 100223 (202 ± 8.0) μg/mL	N/A	N/A
UME	Dr.Ehrenstorfer neat	DBP:99.22% ± 0.32% BBP: 97.12% ± 0.38% DEHP: 99.71% ± 0.29%	Purity was determined by UME using qNMR	Participation in CCQM-K55b-d underpins claimed uncertainties
NMIJ	NMIJ neat	DBP:NMIJ CRM4023-a 0.9996±0.0001 BBP: NMIJ CRM4029-a 0.998±0.00075 DEHP: NMIJ CRM4024-b 0.9994±0.0001	N/A	N/A

KEBS	Results not submitted	

Solution CRMs of PAEs are available from NIST and NIM China. Pure CRMs are available from NMIJ. Pure PAEs are also commercially available from different suppliers as neat reagents (e.g. Sigma-Aldrich, Dr. Ehrenstorfer, TCI) and as solutions (e.g. Sigma-Aldrich, Accustandard, Wellington Laboratories, CIL).

Most of the participating laboratories (6 out of 9) used pure PAEs as the source of traceability, and all of them assessed the purity of the pure PAEs using in house methods (e.g. qNMR, GC-FID, HPLC-DAD, mass-balance method). NMIJ used its own pure CRM (not commercially distributed). Two laboratories (GLHK and NMISA) used the NIM solution CRMs which were assessed by the OAWG to meet the CIPM traceability requirements. NIST had acknowledged at the OAWG meeting where the CCQM-K133 protocol was finalised that their solution CRM was not certified in a way that met the CIPM requirements and thus it could not be used and was not listed in the protocol. INMETRO used the NIST solution without any further assessment and thus their result would not be deemed to meet the CIPM traceability requirements.

Methods Used by Participants

The methods for extraction, clean-up, instrumental techniques, the internal standards as well as the calibration type used by the participants in CCQM-K133 are listed in Table 5. The full details on the analytical methods as reported by each participant, are given in appendix E.

Different dissolution or extraction methods were used among the participants. All nine participants used tetrahydrofuran (THF) as extraction solvent, and five of them used ultrasonic method for dissolution. Other four did not use any equipment for dissolution.

For clean-up procedures, All nine participants applied precipitation by adding different solvents (methanol, hexane or ethanol).

Regarding the instrumental analysis, various techniques were applied in the comparison. Most of participants (8 out of 9) used GC technique for chromatographic separation. Most of participants used MS technique for detection. KRISS used GC-IDHRMS. GLHK used LC-IDMS/MS. NMISA used GC-IDTOFMS. Three labs (VNIIM, EXHM, NMIJ) used GC-IDMS. NIM and UME used GC-IDMS/MS. INMETRO used GC-MS.

Most of the labs (8 out of 9) used IDMS methods and they used the corresponding deuterated (Ring-D4) compounds as internal standards for calibration and most applied bracketing or single point calibration. INMETRO only used GC-MS, not IDMS, and used Benzyl benzoate as internal standard.

Table 5. Summary of analytical methods used by the participants

Participant	Sample intake / bottle number(s)	(Pre-treatment) Extraction	Clean-up	Instrumental technique	Internal standard(s)	Calibration
KRISS	(0.1~0.2) g / (58,379),(155,277)	Dissolution with Tetrahydrofuran (THF) 5 mL for LCPVC, 8 mL for HCPVC	Precipitation with methanol 15 mL for LCPVC, 25ml for HCPVC	GC-IDHRMS	CIL, D4-BBP,DEHP; ISOTECH, D4-DBP	IDMS Single-point exact matching
GLHK	0.1 g / (256,178),(173,117)	Dissolution with THF, 10 mL	Precipitation with methanol, 20 mL	LC-IDMS/MS	CIL, D4-DBP,BBP,DEHP	IDMS, Bracketing method
VNIIM	0.1 g / (27,185),(164,36)	Dissolution with THF, 10 mL, ultrasonic extraction:15min	Take 0.5 mL extraction solution, Precipitation with 1 mL of hexane	GC-IDMS	CIL, D4-DBP,BBP,DEHP 100 µg/mL in nonane	IDMS, Bracketing method
INMETRO	0.3 g / (64,328),(28,180)	Dissolution with THF, 5 mL, ultrasound	Precipitation with hexane, 10 mL	GC-MS	Benzyl benzoate	Internal standard calibration
NIM	0.1 g / (96,133),(18,162)	Dissolution with THF, 5 mL Ultrasound-assisted Extr. 30 min	Precipitation with methanol, 10 mL	GC-IDMS/MS	CIL, D4-DBP,BBP,DEHP,neat	IDMS Single-point exact matching
EXHM	0.5 g / (72,217),(11,156)	Dissolution with THF, 10 mL	Precipitation with n-hexane, 40 mL	GC-IDMS	D4-DBP,BBP,DEHP	Single point calibration at exact matching concentrations - IDMS
NMISA	(0.1-0.15) g / (163,009),(047,107)	Dissolution with THF, 3 mL, Sonication	Precipitation with methanol, 7 mL	GC-IDTOFMS	D4-DBP,BBP,DEHP	IDMS bracketing
UME	0.2 g / (391,203),(55,185)	Dissolution with THF, 10 mL, ultrasonic	Precipitation with ethanol, 30 mL	GC-IDMS/MS	D4-DBP,BBP,DEHP	IDMS, Single point,
NMIJ	0.1 g / (197,386),(073,150)	Dissolution with THF, 10 mL	Precipitation with hexane, 40 mL	GC-IDMS	D4-DBP,BBP,DEHP	IDMS
KEBS	Results not submitted					

Participants Results

The measurement results officially submitted for BBP (low level), BBP (high level), DBP and DEHP in CCQM-K133 are summarised in Tables 6, 7, 8 and 9, respectively.

Table 6. Results for BBP in LCPVC

Participant	Mass fraction (mg/kg)	Combined standard uncertainty u (mg/kg)	Coverage factor, k	Expanded uncertainty U (mg/kg)
EXHM	90.7	3.39	2	6.78
UME	92.2	5.5	2	11.0
GLHK	92.42	2.87	2	5.73
KRISS	94.0	1.8	2.31	4.2
NIM	94.9	0.9	2	1.8
NMIJ	101	2	2	4
NMISA	103.1	3.55	2	7.1
VNIIM	105.2	2.2	2	4.4
INMETRO	114	4.4	2	9
KEBS	Result not submitted			

Table 7. Results for DBP in HCPVC

Participant	Mass fraction (mg/kg)	Combined standard uncertainty u (mg/kg)	Coverage factor, k	Expanded uncertainty U (mg/kg)
GLHK	430.57	11.55	2	23.10
NMISA	434.3	11.2	2	22.4
NIM	437	3	2	6
NMIJ	450	27	2	54
KRISS	456	6.5	2.45	16
VNIIM	456	12	2	24
EXHM	453.44	10.84	2	21.68
INMETRO	460	12	2	24
UME	479.8	24.8	2	49.6
KEBS	Result not submitted			

Table 8. Results for BBP in HCPVC

Participant	Mass fraction (mg/kg)	Combined standard uncertainty u (mg/kg)	Coverage factor, k	Expanded uncertainty U (mg/kg)
NMISA	418.5	11.2	2	22.3
GLHK	418.87	9.85	2	19.7
KRISS	453	9.0	2.31	21
NIM	454	5	2	10
EXHM	456.59	10.18	2	20.36
UME	465.6	27.8	2	55.5
VNIIM	488	10	2	20
NMIJ	499	14	2	28
INMETRO	529	24.6	2	49
KEBS	Result not submitted			

Table 9. Results for DEHP in HCPVC

Participant	Mass fraction (mg/kg)	Combined standard uncertainty u (mg/kg)	Coverage factor, k	Expanded uncertainty U (mg/kg)
NMISA	834.6	20	2	40
NIM	849	7	2	14
GLHK	859.61	21.53	2	43.06
KRISS	884	17	2.45	42
EXHM	905.29	16.78	2	33.56
UME	908.5	52.8	2	105.6
NMIJ	943	31	2	62
VNIIM	968	42	2	84
INMETRO	976	17	2	34
KEBS	Result not submitted			

Approaches to Uncertainty Estimation

The major contributions to the uncertainty budgets are summarised in Table 10. The full details of the uncertainty evaluation reported by the laboratories are given in appendix F.

Table 10 Summary of Participants' Uncertainty Estimation Approaches

Participant	source of the major contributions to uncertainty budget estimation
KRISS	(i) area ratio of native/istd for the calibration standard mixture observed by GC-MS. (ii) purity of primary standard. (iii) gravimetric preparation for standard solution. (iv) gravimetric mixing for calibration isotope standard mixtures.
GLHK	(i) preparation of calibration standard solution. (ii) weighing of standards/internal standard in sample blends and calibration blends. (iii) method precision. (iv) recovery. (v) method bias.
VNIIM	(i) the Response Factor (RF). (ii) the mass fraction of analyte in the sample. (iii) the recovery of analyte from reference material.
INMETRO	(i) Mass fraction of the analyte in diluted solution. (ii) Dilution Factor. (iii) measurement (interpolation uncertainty and repeatability).
NIM	(i) Repeatability of PVC analysis in GC-MS. (ii) purity of analyte. (iii) weighing of stock solution/calibration solution/sample.
EXHM	(i) method precision. (ii) weighing of stock solution/calibration solution/sample. (iii) mass fraction of analyte in the calibration solution. (iv) recovery. (v) measured peak area ratio of the selected ions in the sample blend. (vi) measured peak area ratio of the selected ions in the calibration blend.
NMISA	(i) traceability transfer/value assignment of Restek calibrant from NIM CRM calibrant (ii) balance certificate uncertainty (iii) ESDM of the ratio (iv) repeat measurements
UME	(i) mass of sample intake+IS. (ii) native stock solution. (iii) calibration. (iv) recovery. (v) repeatability.
NMIJ	(i) the mass ratio of standard solutions.

	(ii) the mass ratio of sample and phthalates-d4. (iii) analysis of standard solutions (repeatability). (iv) analysis of sample solutions (repeatability). (v) purity of the CRM of phthalates.
KEBS	**Did not report**

Discussion of Results

From table 6 to 9, the results of each measurand are consistent, but their uncertainties are quite different. The main reason for the results with the large uncertainty is that the participants specifically considered the contribution of recovery in their uncertainty estimates. NIM had a much smaller uncertainty than others as they did not include any factors for biases such as recovery. They relied on the fact that they were using IDMS to not include anything like recovery but this is potentially dangerous when the matrix is a solid such as a plastic and the internal standard is simply added as a solution. INMETRO also had no components for extraction, in that case there were not using IDMS so it would be expected that an uncertainty factor to account for such effects would be needed.

After the Italy OAWG meeting in October 2019, EXHM provided further information on their approach to the assessment of recovery in their uncertainty. The NMIJ's CRM 8152-a was used as mentioned in the section 15 of the results reporting form. In more details, low and high blank materials were spiked with appropriate (according to samples amount) amounts of the CRM and the quantification was performed against matrix matched calibrants (low and high blank materials spiked with EXHM’s calibration solutions). The recovery did not differ statistically from 100%, however, the variation of the above experiments (standard deviation of the mean) was used as the uncertainty of the recovery. EXHM found that the uncertainty of NMIJ's CRM 8152-a was not taken into account in the calculation of the uncertainty of the recovery, which lead their uncertainty to be low.

KEY COMPARISON REFERENCE VALUE (KCRV) CALCULATION

According to the results reported by participants, 8 sets data of CCQM-K133 were used for the KCRV calculation for all measurands, this excluded INMETRO's values because they don't meet the CIPM traceability requirements.

Table 11 summarises provisional KCRVs and their related standard uncertainty *u*(KCRV) using three different statistical approaches, i.e. arithmetic mean (standard deviation), median (MADe) and Bayes.

Table 11. Provisional KCRVs and *u*(KCRV)

Statistical Method	Measurand	LCPVC	HCPVC		
		BBP	DBP	BBP	DEHP
	No. of data	8	8	8	8
Arithmetic	Mean **(mg/kg)**	96.7	449.6	456.7	894.0
	SD **(mg/kg)**	5.6	15.9	28.7	46.4
	Standard uncertainty (=SD/$\sqrt{n}, mg/kg$)	2.0	5.6	10.1	16.4
Median	Median **(mg/kg)**	94.5	451.7	455.3	894.7
	MADe (mg/kg)	4.5	14.1	31.9	59.8
	Standard uncertainty (=1.25×MADe/$\sqrt{n}, mg/kg$)	2.0	6.2	14.1	26.4
Bayes[a] (Consensus values)	Consensus estimate (**mg/kg**)	97.0	445.3	455.8	884.6
	Standard uncertainty**(mg/kg)**	2.2	5.5	11.8	18.0
Note: [a] estimated using NICOB[12].					

From Table 11, there was no significant difference amongst calculated KCRV estimates from the three different methods (arthmetic mean, median and Bayes). However, the standard uncertainty of the arithmetic mean and the standard uncertainty of the median do not take into account the uncertainties of the participants' results[13].The Hierarchical Bayes approach was considered more appropriate given that it accounts for the relatively large *dark uncertainty* (excess variance) amongst these small datasets, as well as the participant's reported uncertainties. The working group agreed that the Hierarchical Bayesian procedure implemented in the NIST Consensus Builder (NICOB) [12] be used for calculating the KCRV values and associated uncertainty. This method is based on a Gaussian random effects model:

$$X_i = \mu + \lambda_i + E_i$$

Where i indexes the participating laboratories, X_i are the lab-reported means, μ is the consensus value, λ_i are the laboratory effects distributed as Gaussian with mean 0 and variance σ_λ^2, and E_i are the lab-specific measurement errors distributed as Gaussian with mean 0 and variance $u(X_i)^2$. The parameter σ_λ^2 directly estimates the excess variance and the estimate of μ is close to the weighted mean.

The model is estimated via Markov Chain Monte Carlo (MCMC) resampling, which produces large numbers of realisations (draws) of the parameters of the random effects model. This allows the value, standard uncertainty, and 95% credible interval of a parameter to be estimated, respectively, as the arithmetic mean, standard deviation, and 95% credible interval between the 2.5th percentile and 97.5th percentile of a sufficiently large number (typically several tens of thousands) of draws.

BBP in LCPVC, BBP in HCPVC and DEHP in HCPVC are not clear that random effects model alone can explain the dispersion in this dataset (APPENDIX H). These results are indicated as non-equivalent. If the Bayes estimator is to be used for this dataset, it would be better to calculate and to add the degrees of equivalence (including uncertainties) with respect to the same model determined. The consensus values in Table 11 were calculated by this method.

The participants' results with their standard uncertainties and the KCRV and its associated standard uncertainty are plotted in Figures 1-4 for BBP in LCPVC, DBP in HCPVC, BBP in HCPVC, and DEHP in HCPVC.

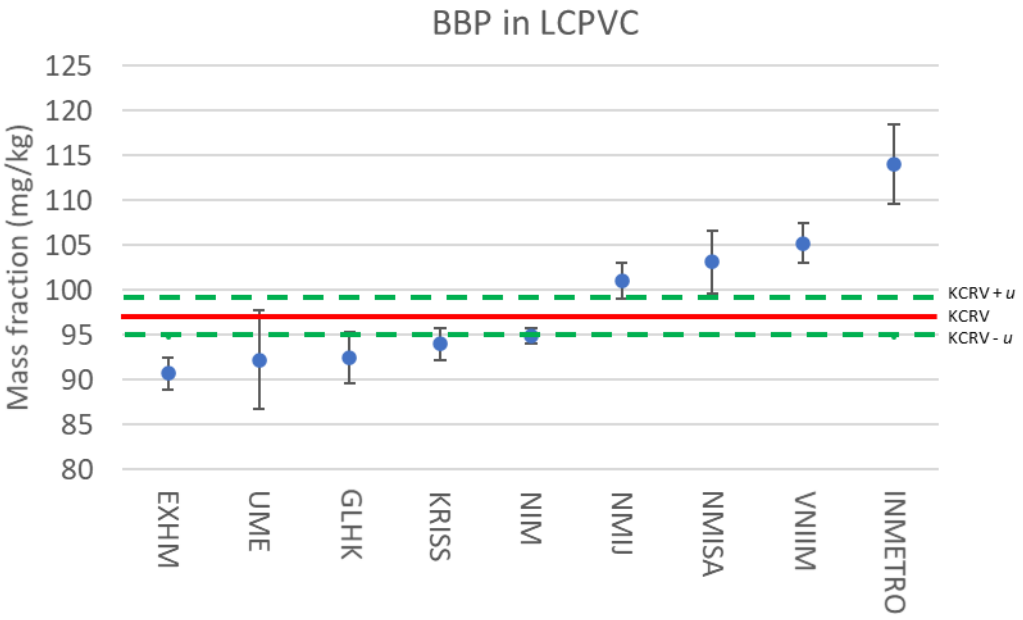


Figure 1. KCRV and participants' results for BBP in LCPVC

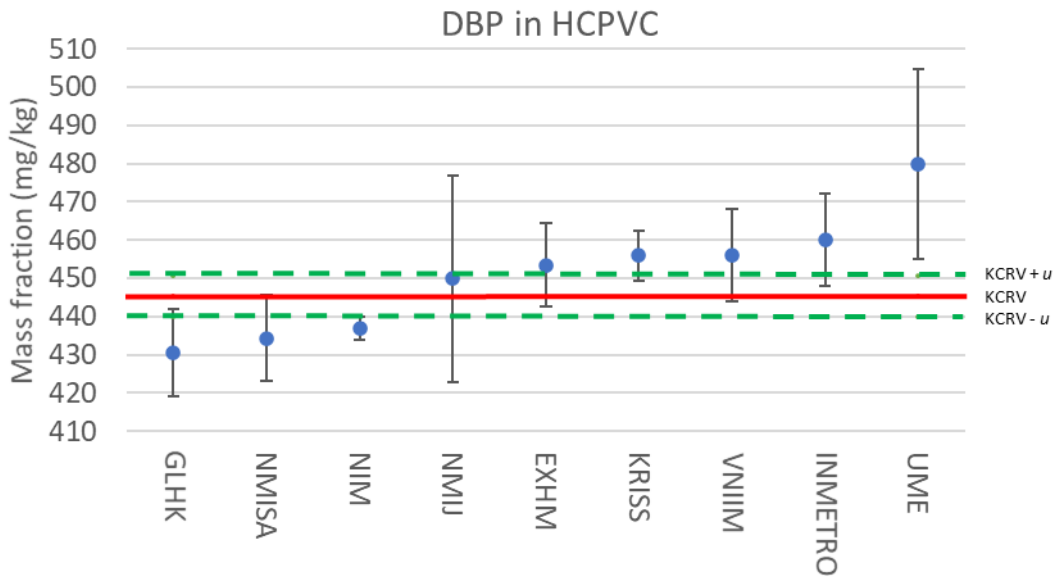


Figure 2. KCRV and participants' results for DBP in HCPVC

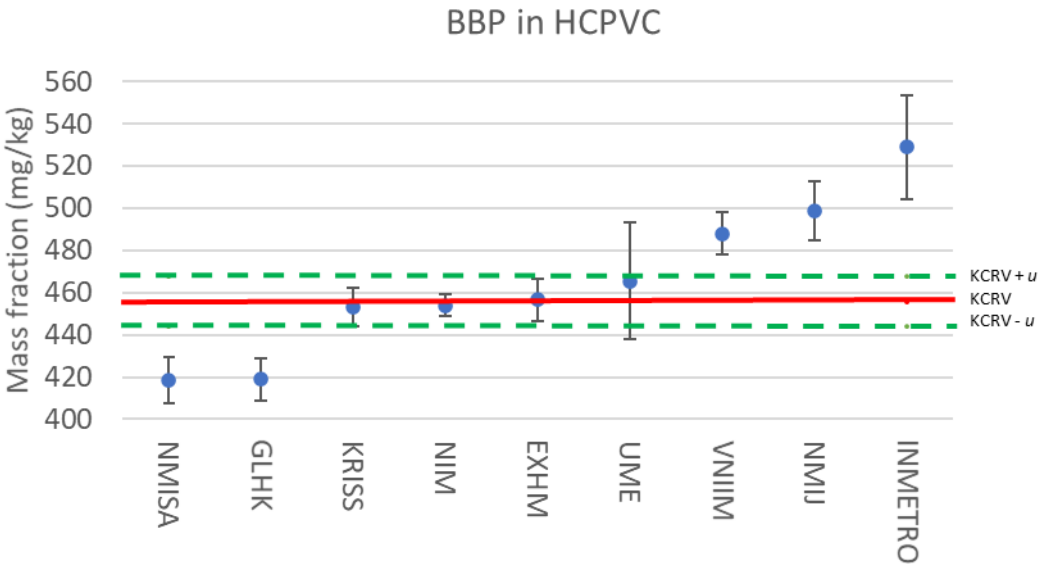


Figure 3. KCRV and participants' results for BBP in HCPVC

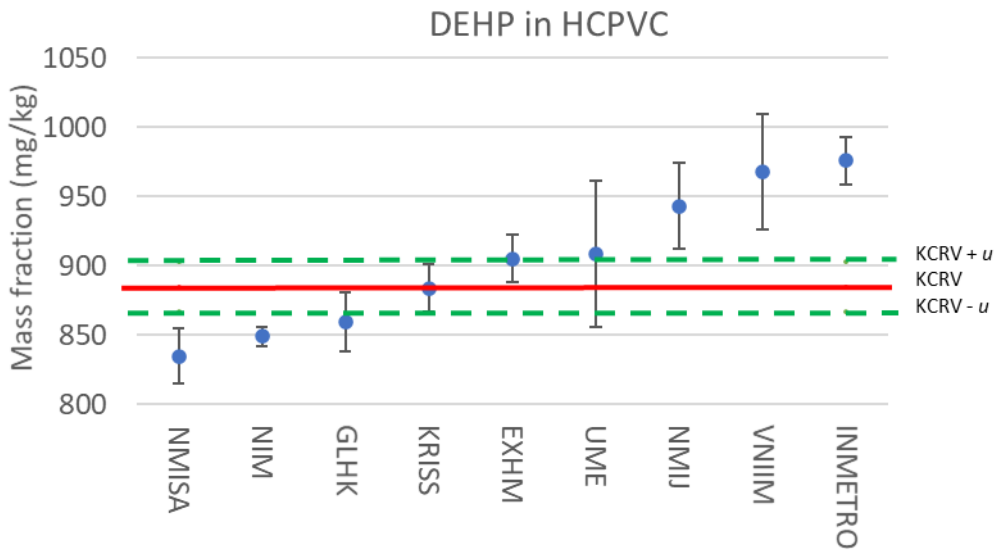


Figure 4. KCRV and participants' results for DEHP in HCPVC

DEGREES OF EQUIVALENCE (DoE) CALCULATION

The Degrees of Equivalence (DoE), D_i, for participants of CCQM-K133 except for INMETRO are estimated by NICOB. DoE for INMETRO are estimated for the following formula (1).

$$D_i = (X_i - X_{KCRV}) \qquad (1)$$

Where X_i is the result reported by participant i and X_{KCRV} is the KCRV. Using a Monte Carlo (MC) technique, the D_i and their uncertainties at the 95% level of confidence, $U(D_i)$, can be estimated along with the KCRV. This was accomplished for this report using the NICOB Hierarchical Bayes procedure. The distributions of the D_i were determined to be essentially symmetric, allowing the $U(D_i)$, to be estimated as the half-width of the interval between the 2.5th and 97.5th percentiles of the MC draws.

The absolute and relative [$\%D_i$ = 100·D_i/KCRV and $\%U(D_i)$ = 100·$U(D_i)$/KCRV] degree of equivalence and associated expanded uncertainty of each result with the KCRV for four measurands in CCQM-K133 are listed in Tables 12-15.

Figures 5-12 display the absolute $D_i \pm U(D_i)$ and the relative $\%D_i \pm \%U(D_i)$ for the four measurands in CCQM-K133.

Table 12 Degree of Equivalence (DoE) and their uncertainties for BBP in LCPVC

Lab	D_i	$U(D_i)$	Lower limit	Upper limit
EXHM	-6.3	13.6	-20.0	7.2
UME	-4.8	15.9	-20.6	11.2
GLHK	-4.6	13.1	-17.3	9.1
KRISS	-3.0	12.3	-15.1	9.5
NIM	-2.1	12.0	-14.1	9.8
NMIJ	4.0	12.3	-8.2	16.3
NMISA	6.1	13.4	-7.2	19.7
VNIIM	8.2	12.6	-4.5	20.6
INMETRO	17.0	15.0	2.0	32.0

KCRV: 97.0 mg/kg, u=2.2, 95% coverage interval [92.6, 101.3]

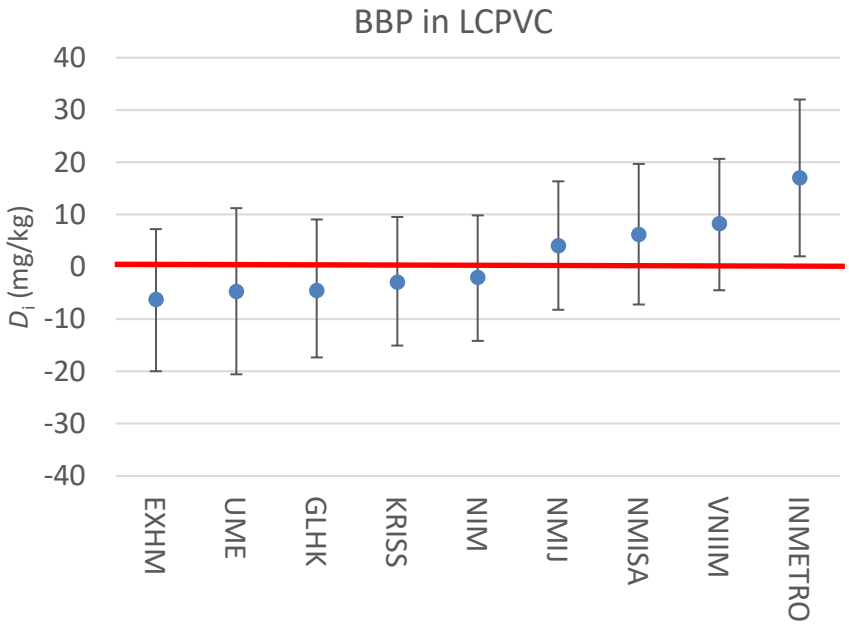


Figure 5. Absolute Degrees of Equivalence, $D_i \pm \boldsymbol{U(D_i)}$ for BBP in LCPVC

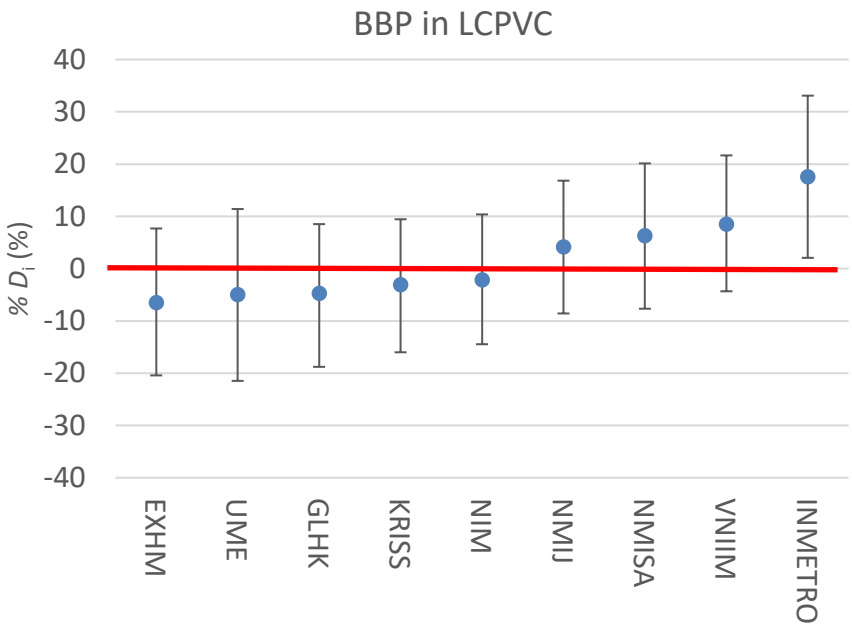


Figure 6. Relative Degrees of Equivalence, %D_i ± %$\boldsymbol{U(D_i)}$ for BBP in LCPVC

Table 13 DoEs and their uncertainties for DBP in HCPVC

Lab	D_i	$U(D_i)$	Lower limit	Upper limit
GLHK	-14.8	33.9	-49.3	18.1
NMISA	-11.0	33	-44.8	21.3
NIM	-8.3	25.3	-34	16.7
NMIJ	4.7	58.5	-55	62
EXHM	8.1	32.1	-24.9	39.4
KRISS	10.7	27.9	-18.7	36.9
VNIIM	10.7	33.7	-23.7	43.6
INMETRO	14.7	33.6	-19.7	47.7
UME	34.5	54.4	-20.4	88.3

KCRV: 445.3, u=5.5, 95% coverage interval [435.4, 457.3]

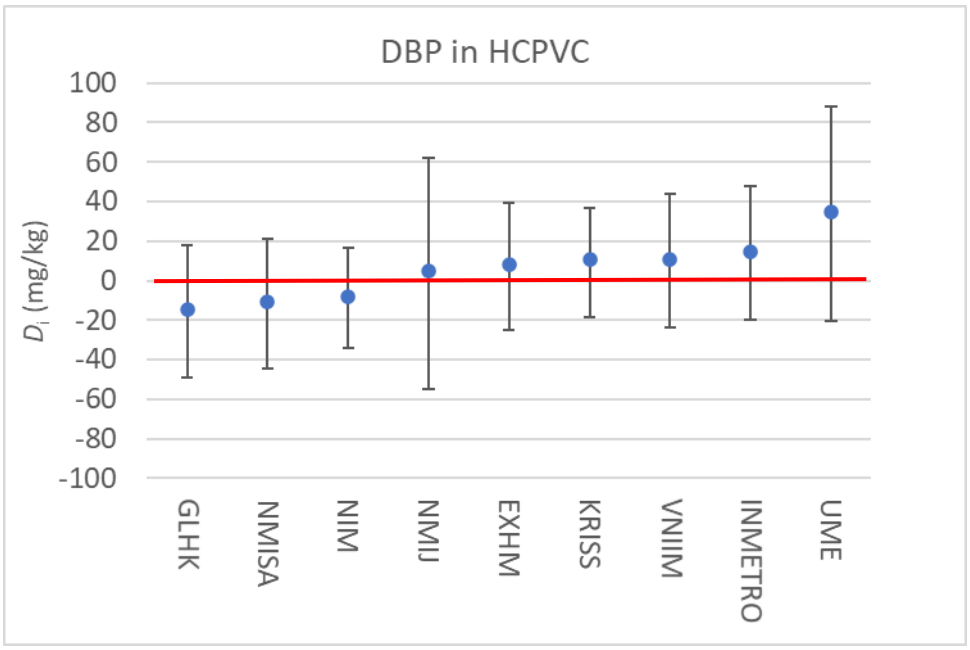


Figure 7. Absolute Degrees of Equivalence, $D_i \pm \boldsymbol{U(D_i)}$ for DBP in HCPVC

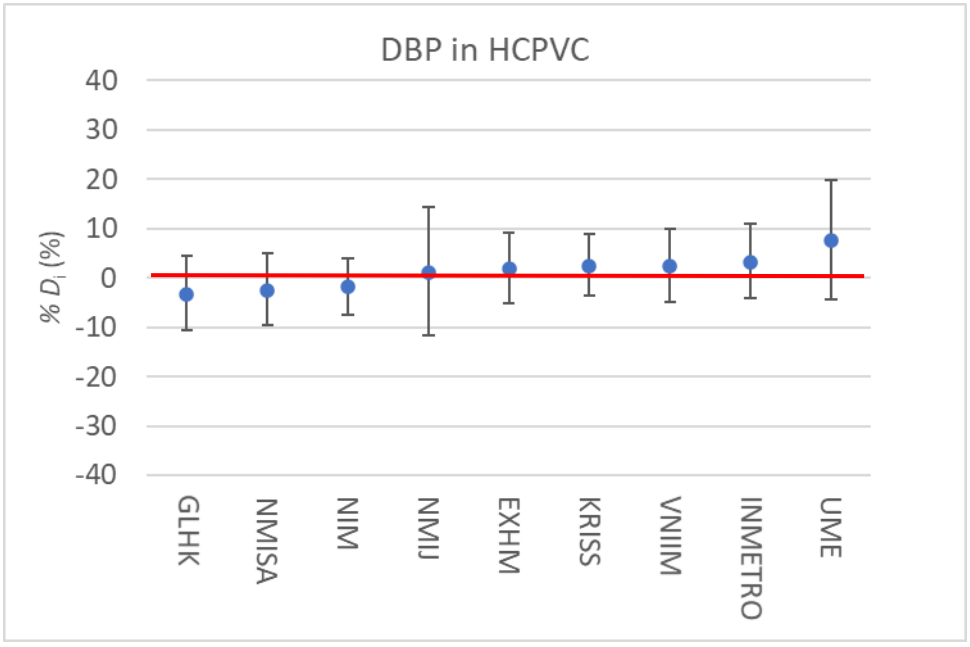


Figure 8. Relative Degrees of Equivalence, $\%D_i \pm \%\boldsymbol{U(D_i)}$ for DBP in HCPVC

Table 14 DoEs and their uncertainties for BBP in HCPVC

Lab	D_i	$U(D_i)$	Lower limit	Upper limit
NMISA	-37.2	70.6	-107.0	34.0
GLHK	-36.8	69.5	-106.0	32.9
KRISS	-2.7	69.6	-73.6	65.6
NIM	-1.7	68.3	-69.5	67.2
EXHM	0.9	70.4	-70.3	70.5
UME	9.9	86.8	-78.8	94.9
VNIIM	32.3	69.4	-36.8	102.0
NMIJ	43.3	71.1	-29.3	113.0
INMETRO	73.3	81.9	-10.1	153.0

KCRV: 455.8, u=11.8, 95% coverage interval [432.3, 479.7]

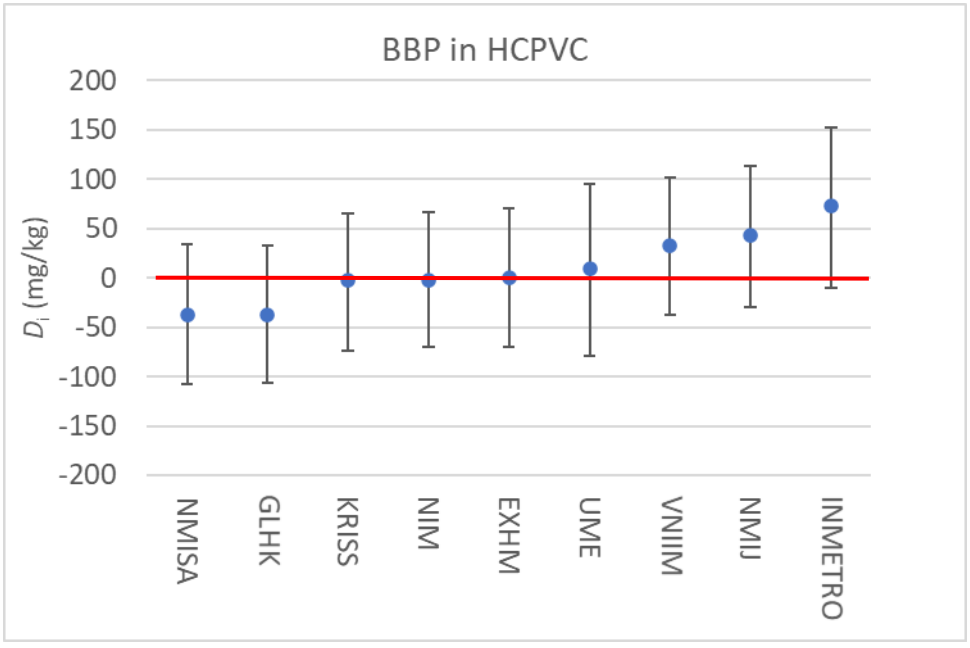


Figure 9. Absolute Degrees of Equivalence, $D_i \pm \boldsymbol{U(D_i)}$ for BBP in HCPVC

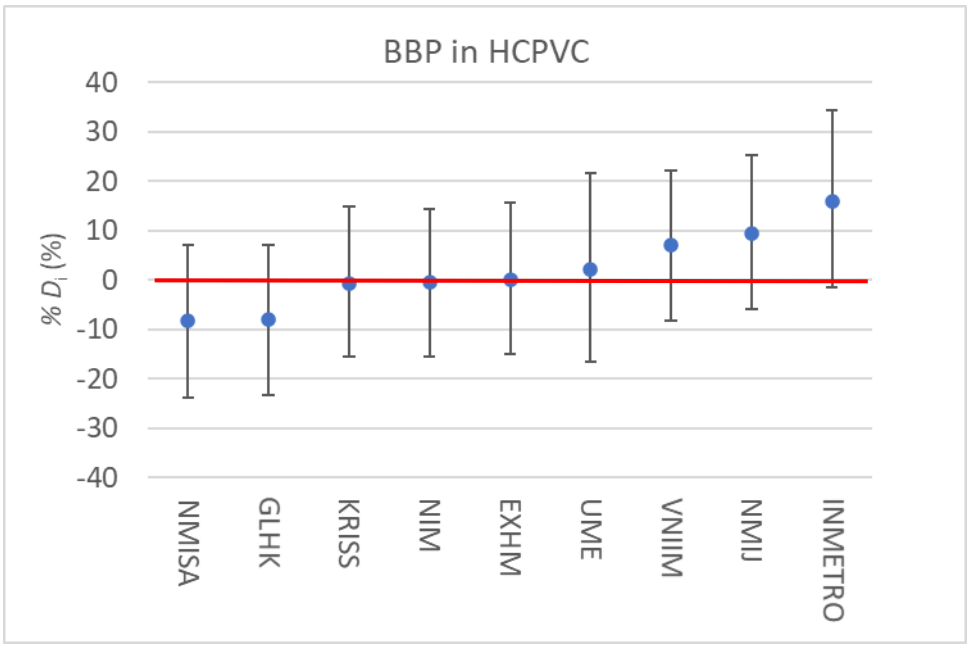


Figure 10. Relative Degrees of Equivalence, $\%D_i \pm \%\boldsymbol{U(D_i)}$ for BBP in HCPVC

Table 15 DoEs and their uncertainties for DEHP in HCPVC

Lab	D_i	$U(D_i)$	Lower limit	upper limit
NMISA	-50.0	103.0	-156.0	51.1
NIM	-35.6	96.4	-137.0	55.0
GLHK	-25.0	104.0	-133.0	75.9
KRISS	-0.6	99.8	-102.0	97.1
EXHM	20.7	101.0	-83.8	117.0
UME	23.9	137.0	-116.0	157.0
NMIJ	58.4	112.0	-56.6	168.0
VNIIM	83.4	125.0	-41.7	207.0
INMETRO	91.4	99.7	-10.8	189.0

KCRV: 884.6, u=18.0, 95% coverage interval [851.8, 923.4]

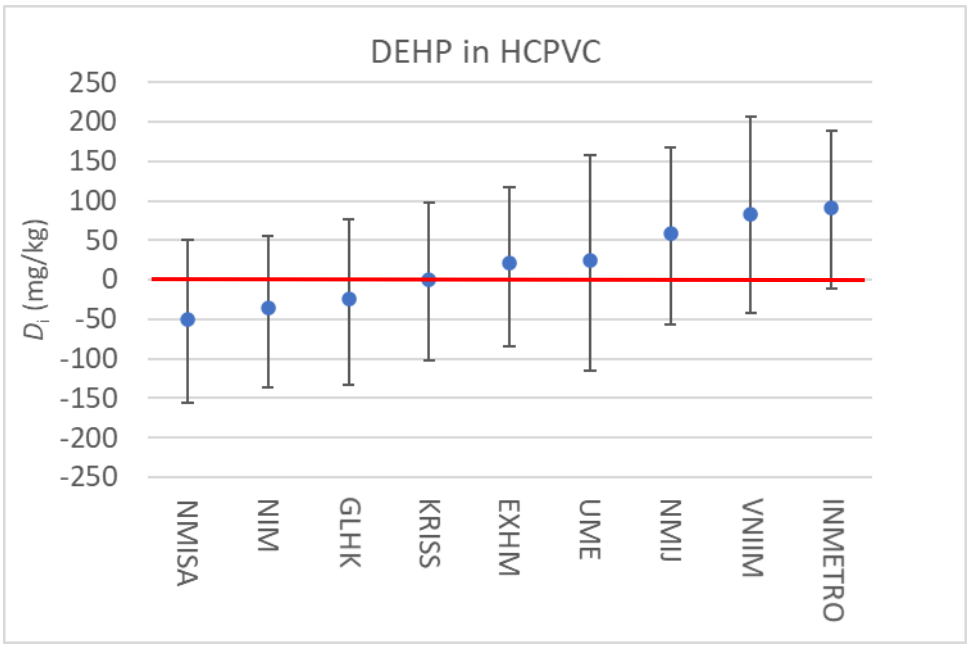


Figure 11. Absolute Degrees of Equivalence, $D_i \pm \boldsymbol{U(D_i)}$ for DEHP in HCPVC

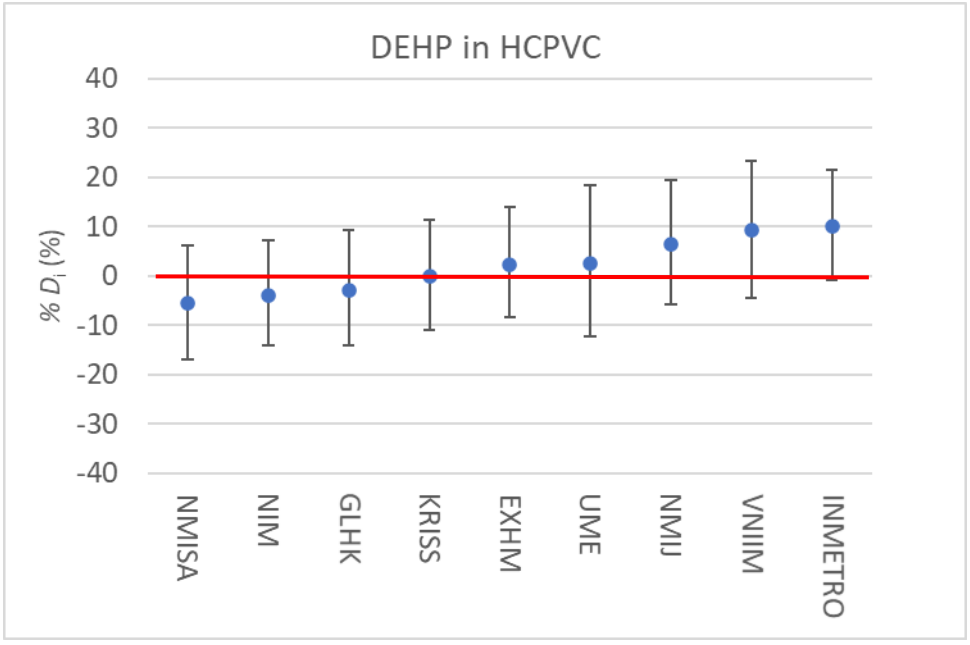


Figure 12. Relative Degrees of Equivalence, $\%D_i \pm \%\boldsymbol{U(D_i)}$ for DEHP in HCPVC

Most of the participants showed good performance for most analytes except for BBP in the LCPVC from INMETRO. INMETRO's result was high for BBP in the LCPVC. INMETRO was the only participant who do not use IDMS and this may have been the one reason for their biased results.

INMETRO attributed its high result for BBP to the internal standard used during extraction and GC analysis. Because INMETRO did not have labelled phthalates to be used as internal standards and to perform IDMS, benzyl benzoate was used instead, in both samples and calibrants. Benzyl benzoate polarity (log Kow = 3.97) is slightly closer to

DBP (4.50) than to the other phthalates (4.73 for BBP and 8.70 for DEHP). This may have influenced the good result that INMETRO achieved for DBP in contrast to the positively biased results for BBP and DEHP, besides other potential differences in MS detection between measurands and internal standard. Moreover, INMETRO used NIST SRM 3074 for calibration. Even though this CRM was mentioned in the protocol, its recommendation was later withdrawn for traceability issues but this was the only CRM for phthalates available at INMETRO during the time of the key comparison.

CORE COMPETENCIES AND HOW FAR DOES THE LIGHT SHINE

This Track C comparison (CCQM-K133) was intended to provide the means for the assessment of the measurement capability of analysing "low-polarity organic analytes in plastics".

In general, it demonstrates the participants' capabilities of determining the polar and non-polar analytes with molecular mass range from 100 g/mol to 800 g/mol at levels of 10 mg/kg to 5000 mg/kg in plastics.

This measurement capabilities include: (i) value assignment of primary reference standards; (ii) value assignment of calibration solutions; (iii) extraction of analyte of interest from the matrix; (iv) clean-up and separation of analyte of interest from other interfering matrix or extract components; (v) separation and quantification using techniques such as GC-IDMS, GC-IDHRMS, HPLC-DAD or LC-IDMS/MS.

The Core Competencies claimed by the participants in CCQM-K133 are given in appendix G. The details of the specific approaches/techniques used by each participant underpinning their competencies are included in appendix E.

CONCLUSIONS

Most of the participants in CCQM-K133 successfully determined BBP, DBP and DEHP in the LCPVC and HCPVC samples. They were able to demonstrate their capabilities in determining low-polar organic molecules in plastics through the key comparison, though some participants have room for further improvement, particularly INMETRO who did not use an IDMS approach. The measurement of PAEs in plastic involves not only extraction, clean-up, separation and selective detection of the analytes, but also the pre-treatment procedures of the material and interference removal.

In view of the complexity of the matrix, the complexity of the potential interferences and the complexity of the analytical procedure, the relative standard deviations for the eight sets of data included in the KCRV calculation were all less than 7% which were satisfactory.

ACKNOWLEDGEMENTS

The comparison coordinator thank all participating laboratories for their contribution and would like to give special thanks to Dr. Lindsey Mackay, the chair of OAWG, Li Hongmei and Ma Liandi from NIM for providing their guidance throughout the course of this comparison. We thank a lot for Dr. Michael A. Nelson from NIM who calculated DoE analysis.

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Appendix A: Protocol

CCQM-K133/P170 polar and non-polar analytes in plastic:
Phthalate esters in Polyvinyl Chloride (PVC)

Key Comparison/Pilot Study
Track C

Coordinating Laboratory: NMIJ and NIM
Study Protocol
January 2018

1. Introduction

Phthalate esters (phthalates) are widely used as plasticizer for Polyvinyl Chloride (PVC). On the other hand, some research articles have reported the effect of the phthalates on wild animals and human beings. Recently, many countries have restricted to use phthalates for toys and children articles. Especially, European Union (EU) directive on "the reduction of certain hazardous substances in electrical and electronic equipment" (RoHS II) will restrict four phthalates in 2019. Di-*n*-butyl Phthalate (DBP), Di-*iso*-butyl Phthalate (DiBP), Benzyl Butyl Phthalate (BBP) and Bis (2-ethylhexyl) Phthalate (DEHP) will be prohibited from being used in electronic and electrical equipment.

At the CCQM Organic Working Group meeting held in Tsukuba in October 2014, possibilities for new studies in the organic field were discussed, including selected phthalates in PVC. NMIJ and NIM offered the provision of a suitable study material and were requested to review possibilities for coordinating a study in that field.

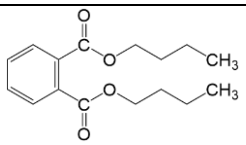
2. Measurands

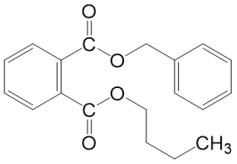
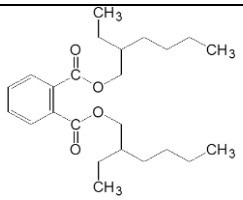
Minimum reporting requirements for participants to CCQM-K133/P170 are the mass fractions of DBP, BBP and DEHP in the high concentration sample and BBP in the low concentration sample.

DBP, BBP and DEHP are the restricted materials in RoHS directive in EU. Although DiBP is also restricted material and its molar mass is same as DBP, DBP is more popular plasticizer for PVC.

DEHP has enantiomers. Because it is difficult to separate the enantiomers with versatile GC columns, the reported mass fraction of DEHP shall include all enantiomers.

Table 1, Selected phthalates as study measurands for CCQM K133/P170

Congener	Structural Formula	Measurand	
		Low Concentration sample from NMIJ	High Concentration sample from NIM
Di-n-butyl Phthalate (DBP)		No (Included, but unnecessary to report)	Yes

Benzyl Butyl Phthalate (BBP)		Yes	Yes
Bis (2-ethylhexyl) Phthalate (DEHP)		No (Included, but unnecessary to report)	Yes

3. Description of the material

Two types of PVC pellets in the glass bottle will be provided for CCQM-K133/170. Two bottles for each of low and high concentration samples will be shipped together from NMIJ (NIM send high level sample to NMIJ in advance). The PVC pellets were prepared by mixing and molding the available PVC, phthalates and other polymer additives.

Concentration range of low level sample (from NMIJ) is from 30 mg/kg to 200 mg/kg, and the ones of high level sample (from NIM) are from 300 mg/kg to 1200 mg/kg.

The PVC pellets from NIM (high concentration) should keep under freezing point. PVC pellets from NMIJ (low concentration) keeps under 30 °C.

3.1. Homogeneity

Homogeneity of BBP in low level sample was assessed by three subsamples on 10 units (0.1 g sample intake) measured. Homogeneity of phthalates in high level sample were assessed by three subsamples on 11 units (0.1 g sample intake) measured.

Figure 1 to figure 4 show the homogeneity results of the samples. Table 2 to table 5 show the results of ANOVA for each measurands. *F*-values for all measurands are smaller than the F_{crit} in table 2 to table 5, therefore it is expected that all study materials are homogenous. Estimation of potential between-unit inhomogeneity u_{bb} were accomplished by ANOVA. The summarized results of the homogeneity are shown in table 6.

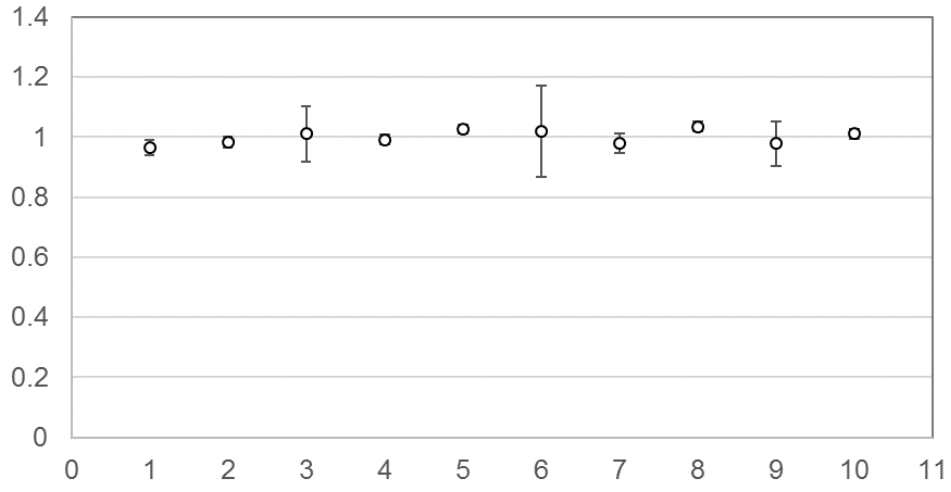


Figure 1 Homogeneity of BBP in Low Level PVC

Table 2. Summary of ANOVA for homogeneity test of BBP in the low level PVC.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}
Between Groups	0.0148	9	0.0016	0.41	0.914	2.39
Within Groups	0.0800	20	0.0040			

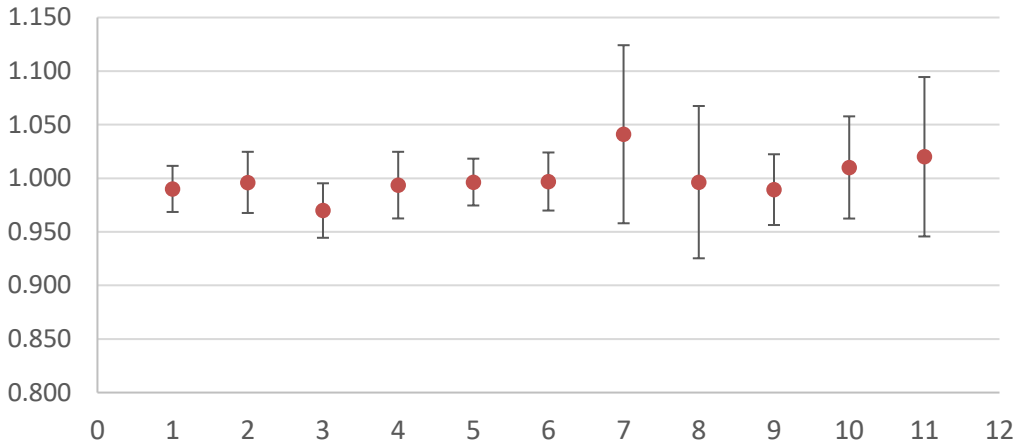


Figure 2 Homogeneity of DBP in the high level PVC

Table 3. Summary of ANOVA for homogeneity test of DBP in the highlow level sample.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}
Between Groups	0.0102	10	0.00102	2.11	0.95	2.30
Within Groups	0.0106	22	0.000483			

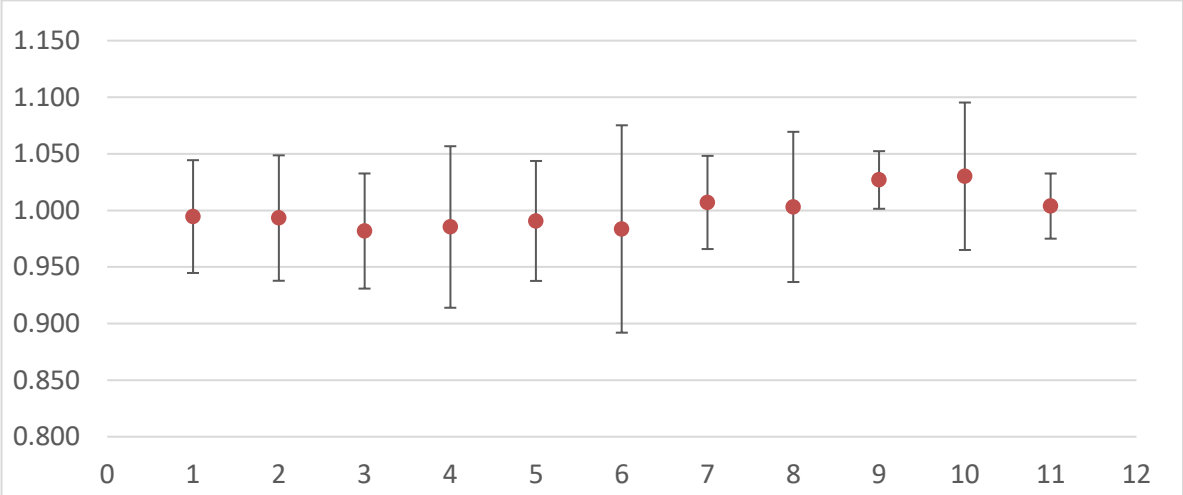


Figure 3 Homogeneity of BBP in the high level PVC

Table 4. Summary of ANOVA for homogeneity test of BBP in the high level sample.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}
Between Groups	0.00806	10	0.000806	1.16	0.95	2.30
Within Groups	0.0153	22	0.000697			

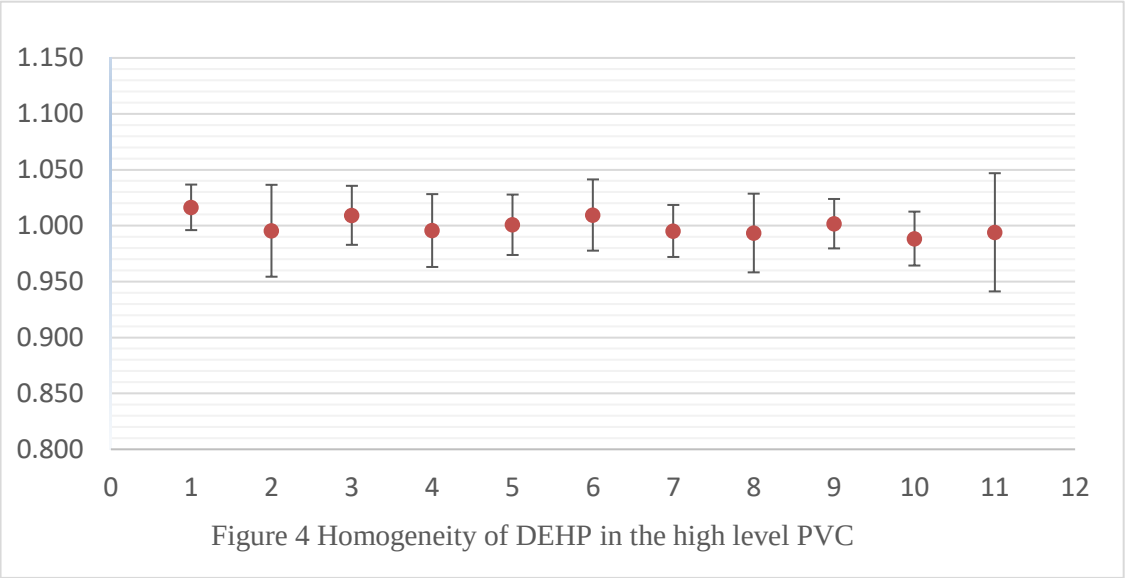


Figure 4 Homogeneity of DEHP in the high level PVC

Table 5. Summary of ANOVA for homogeneity test of DEHP in the high level sample.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}
Between Groups	0.00217	10	0.000217	1.40	0.95	2.30
Within Groups	0.00340	22	0.000155			

Table 6. Homogeneity of the samples

Congener	u_{bb} (%)	
	Low Concentration sample from NMIJ	High Concentration sample from NIM
DBP		0.70
BBP	1.2	0.84
DEHP		0.40

3.2 Long-term stability monitoring

The long-term stabilities were studied for more than one year. The results of the long-term stability monitoring for the measurands are shown in figure 5 to figure 8. Regression analyses were done for all measurands, and their results were listed in table 7 to table 10. From the regression analyses, *P*-values of DBP and BBP in high level PVC were larger than the usual critical 0.05 confidence level that means the measurands were stable in the monitoring term. On the other hand, *P*-values of BBP in low level PVC and of DEHP in high level PVC were lower than the 0.05 confidence level. Until August 2018, the regression lines of BBP in low level PVC and DEHP in high level PVC did not over twice the standard deviations calculates from the long-term monitoring (table 11). Therefore all measurands will be stable in the period of this CCQM comparison.

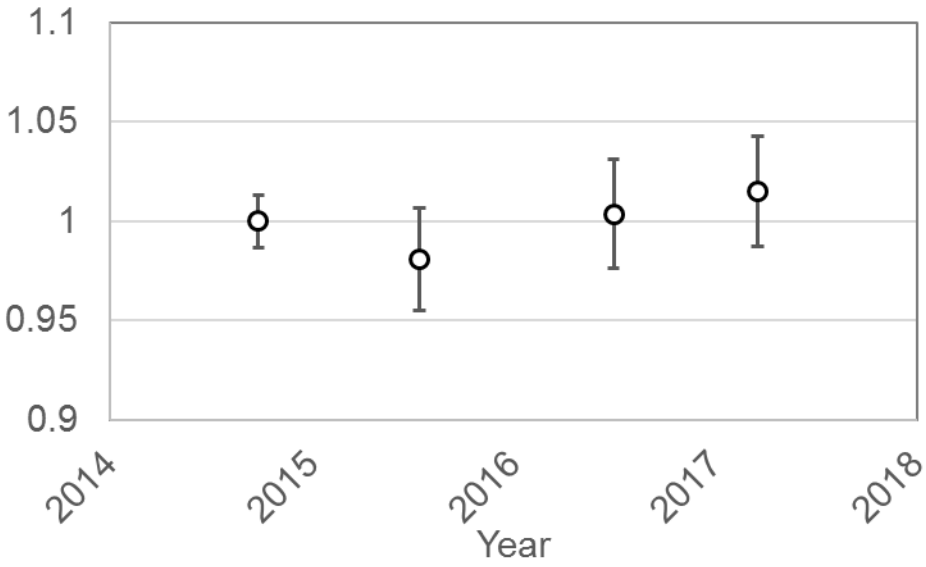


Figure 5 Long term stability of BBP in the low level PVC.

Table 7 Summary of regression analysis for the long-term stability study of BBP in the low level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.00071	0.00071	5.118	0.047
Residual	10	0.00139	0.00014		
Total	11	0.00211			

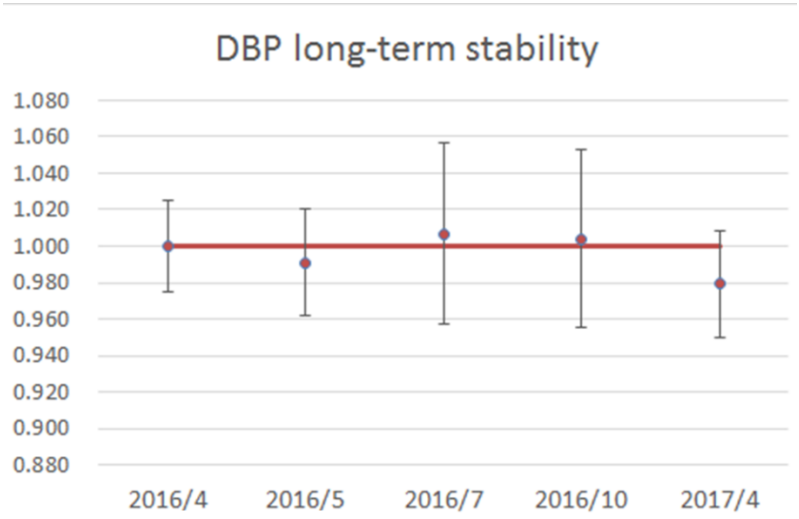


Figure 6 Long term stability of DBP in the high level PVC.

Table 8 Summary of regression analysis for the long-term stability study of DBP in the high level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.00055	0.00055	3.161	0.099
Residual	13	0.00227	0.00017		
Total	14	0.00282			

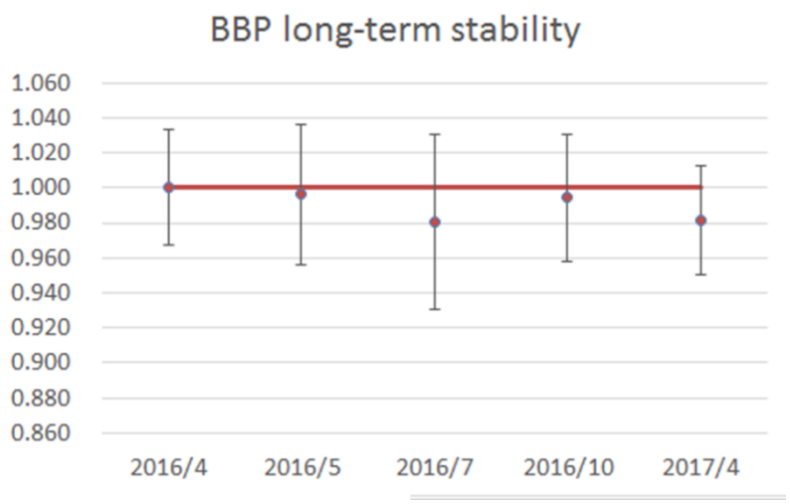


Figure 7 Long term stability of BBP in the high level PVC

Table 9 Summary of regression analysis for the long-term stability study of BBP in the high level PVC.

	Df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.000403	0.000403	2.311	0.152
Residual	13	0.00227	0.00017		
Total	14	0.00267			

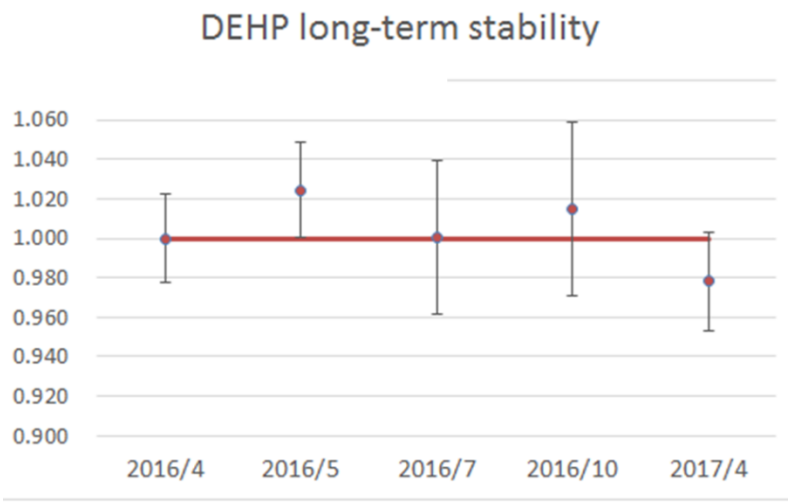


Figure 8 Long term stability of DEHP in the high level PVC.

Table 10 Summary of regression analysis for the long-term stability study of DEHP in the high level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.00164	0.00164	7.091	0.0195
Residual	13	0.00300	0.000231		
Total	14	0.00464			

Table 11 Standard deviations calculated from ANOVA for long-term monitoring

Measurands	Time (year)	number	RSD (%)	u_{bb} (%)
BBP in the low level PVC	2.5	4	1.4	1.4
DBP in the high level PVC	1	5	1.1	1.5
BBP in the high level PVC	1	5	0.9	1.1
DEHP in the high level PVC	1	5	1.7	1.7

3.3 Short-term stability monitoring

A four weeks isochronous short-term stability study was performed at 40 °C. The results of the short-term stability monitoring for the measurands are shown in figure 9 to figure 12. Regression analyses were done for all measurands, and their results were listed in table 12 to table 15. All measurands except for DBP in high level PVC were stable, because *P*-values of them were larger than the usual critical 0.05 confidence level. Though *P*-values of DBP in high level PVC was lower than 0.05, DBP in high level was stable in 3 weeks. Short-term stability monitoring is to ensure the quality of the CRM during the shipping. The concentrations of phthalates in PVC during shipping will be stable within 3 weeks.

No significant changes have been found in the concentrations for the all phthalates.

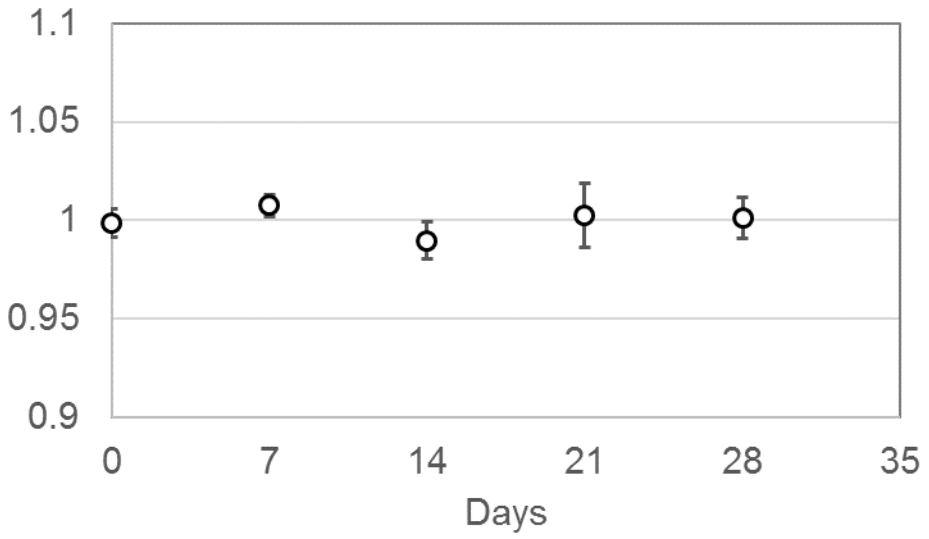


Figure 9. Short term stability of BBP in the low level PVC

Table 12 Summary of regression analysis for the short-term stability study of BBP in the low level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	1.01×10^{-7}	1.01×10^{-7}	0.0013	0.982
Residual	23	0.0031	0.0014		
Total	24	0.0031			

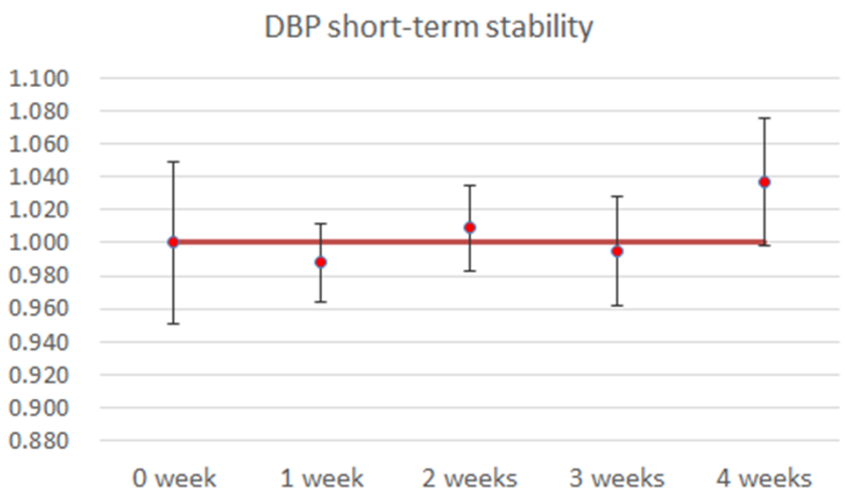


Figure 10. Short term stability of DBP in the high level PVC

Table 13 Summary of regression analysis for the short-term stability study of DBP in the high level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.00194	0.00194	7.681	0.0159
Residual	13	0.00328	0.000252		
Total	14	0.00521			

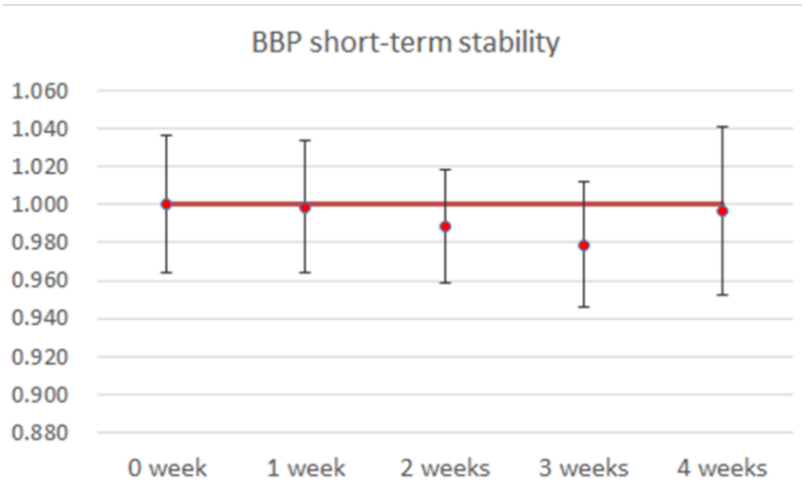


Figure 11. Short term stability of BBP in the high level PVC

Table 14 Summary of regression analysis for the short-term stability study of BBP in high level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.000207	0.000207	1.936	0.187
Residual	13	0.00139	0.000107		
Total	14	0.00160			

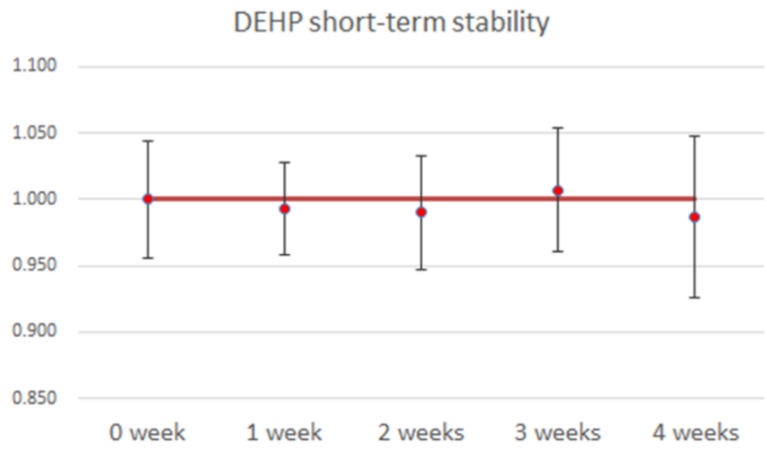


Figure 12. Short term stability of DEHP in the high level PVC

Table 15 Summary of regression analysis for the short-term stability study of DEHP in the high level PVC.

	df	*SS*	*MS*	*F*	*P-value*
Regression	1	0.0000506	0.0000506	0.309	0.588
Residual	13	0.00213	0.000164		
Total	14	0.00218			

4. Contamination

As phthalates are widely used in the world and existing in laboratories, the contamination of phthalates to the glass apparatus is sometimes occurred. [9-10] In addition, some rubber materials, such as septum in GC, and some plastics, such as the cap of screw glass bottles, contain phthalates. IEC 62321-8 [11] recommends that non-volumetric glassware (e.g. beakers, round/flat bottom flasks, vials) should be kept under 400 °C to 500 °C for four hours or overnight to remove possible contaminations. We strongly recommend that the blank test should be performed during analyzing the samples.

5. Study guidelines

Each participant will receive 2 bottles of low concentration sample from NMIJ and 2 bottles of high concentration sample from NIM. Additional bottles are available upon request to NMIJ or NIM. Each bottle (both high and low levels) contains approximately 10 g of PVC pellets.

The samples will be dispatched together with a receipt form (to be completed upon sample reception and sent back by e-mail to “s.matsuyama@aist.go.jp”). At the same time, the reporting sheet for the results will be sent to each participant via e-mail.

Though two level samples will be dispatched at room temperature, it is better to keep the high level sample under freezing point until usage.

The minimum sample intake must be at least 0.1 g.

Participants are required to report the mass fractions (mg/kg) of DBP (in the high level sample), BBP (in the low level and high level samples) and DEHP (in the high level sample). All bottles at each level can be used for reporting Participating laboratories shall report results obtained from each bottle, and may use their preferred analytical methodology. We strongly recommend

that three subsamples are prepared and analyzed for each bottles. If you prepare subsamples, each results of all subsamples must be reported in the reporting form.

CRMs for calibration (standard solutions) are available from

NIM (China)

GBW(E)100223	DEHP in Methanol (186 mg/kg)
GBW(E)100224	DBP in Methanol (195 mg/kg)
GBW(E)100226	BBP in Methanol (165 mg/kg)

NIST (USA)

NIST SRM 3074	6 Phthalates in Methanol (45 – 60 mg/kg)

Native and isotopically labelled phthalate esters are commercially available from different commercial suppliers (Sigma-Aldrich, Wako Pure Chemical Industries, Kanto Chemical, C/D/N isotopes, Cambridge isotope laboratories, etc.) as neat reagents or solutions. If commercial neat reagents are used as calibrants, purity assessment with appropriate metrological traceability will be the responsibility of individual participants.

6. Time schedule

Call for participation	January 19, 2018
Deadline for registration	February 2, 2018
Dispatch of samples	March 2018
Deadline for submission of results	July 2018
Preliminary discussion of results Meeting	October 2018, CCQM-OAWG

7. Submission of results

Each participant must indicate in the reporting form and Core competency table if he/she participates in the CCQM-K133 or CCQM-P170 study.

The results shall be entered in the provided reporting sheet and sent back via e-mail together with the Core competency table to “s.matsuyama@aist.go.jp” before the deadline for submission. Participants should be aware that submitted results are considered final and no correction or adjustment of analytical data will be accepted.

They shall include

 Mass fractions (mg/kg) of each individual measurand in the study samples.

 Standard and expanded measurement uncertainties, with a detailed description/breakdown of the full uncertainty budget

Description of the analytical procedure employed (extraction, clean-up, separation/detection and quantification) as well as details concerning the calibration and internal standards used

(purity statement or verifications done at the laboratory's premises etc…) should be supplied through the Core competency table, and participants are encouraged in providing exhaustive and complete information.

8. How Far Does the Light Shine?

The participation in the Track C "polar and non-polar analytes" CCQM-K133 study, phthalates in PVC provides the means for assessing measurement capabilities for the determination of using procedures requiring extraction from the matrix, clean-up from interfering substances, analytical separation, selective detection and final quantification by analytical methods.

This Key Comparison will demonstrate the capabilities of participants for assigning mass concentration of analytes with molecular mass range from 100 g/mol to 1000 g/mol in plastic at the 10 mg/kg to 5000 mg/kg mass concentration levels.

9. Coordinating laboratories and contact person

Coordinating laboratory 1:

National Metrology Institute of Japan (NMIJ)

National Institute of Advanced Industrial Science and Technology (AIST)

Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

Study coordinator contact details:

Shigetomo Matsuyama (s.matsuyama@aist.go.jp)

Phone: +81-29-861-9377

Fax: +81-29-861-4618

Coordinating laboratory 2:

National Institute of Metrology (NIM)

No.18, Bei San Huan Dong Lu, Chaoyang Dist, Beijing, 100029, P.R.China

Study coordinator contact details:

Shao Mingwu (shaomw@nim.ac.cn)

Phone: + 86-010-64524788

Fax: + 86-010-64271639

Please complete and return the attached registration forms to the above contact persons for the participation no later than December 1, 2017.

Appendix B: Registration Form

Registration form

CCQM-K133/P170

Phthalate esters in Polyvinyl Chloride (PVC)

"Track C" – polar and non-polar analytes in plastics

Participation to:

□ CCQM-K133

□ CCQM-P170

ORGANISATION / DEPARTMENT / LABORATORY

_____/_____/_____/

FULL ADDRESS (no PO box)

_____/_____/

CONTACT PERSON

_____/

TELEPHONE, FAX, E-MAIL

TEL : _____.

FAX : _____,

E-mail : _____.

Date ____/____/____.

Please complete the form and send it back to s.matsuyama@aist.go.jp and shaomw@nim.ac.cn **before 5 March 2018**.

Appendix C: Reporting Form

The original was distributed as an Excel workbook. The following are pictures of the relevant portions of the workbook's three worksheets.

"Participant Details" worksheet

CCQM-K133/P170

Phthalate esters in Polyvinyl Chloride (PVC)

"Track C" – polar and non-polar analytes in plastic

Data Submission Form

Please complete all pages of this reporting form and submit it before **31/July/2018** to s.matsuyama@aist.go.jp

- ☐ CCQM-K133
- ☐ CCQM-P170

Reporting Date	
Institute	
Department	
Address	
Postal Code	
Contact Person: (Given name Family name)	
Co-workers: (Given name Family name)	
Email	
Tel	
Fax	

"Results" worksheet

CCQM Key Comparison/Pilot Study
CCQM-K133/P170
Phthalate esters in Polyvinyl Chloride (PVC)
Results Reporting Form

Please use this excel sheet for reporting.
Please submitted this report electronically to s.matsuyama@aist.go.jp
Please fill in all blanks and use the requested units.
Please provide any extra information in the comments section or on a separate sheet if necessary.

Participant's Information

Laboratory Name:	
Submitted by:	
Reporting Date: (dd/mm/yy)	
Programme Participated: (CCQM-K133, CCQM-P170)	

Results of low level sample

	from	to
Analysis date		~

	Bottle Number		Mass fraction of each compounds (mg/kg) DBP	BBP	DEHP
Bottle 1		Subsample 1			
		Subsample 2			
		Subsample 3			
		Mean			
Bottle 2		Subsample 1			
		Subsample 2			
		Subsample 3			
		Mean			
Overall Mean of Results (mg/kg)					
Combined Standard Uncertainty (mg/kg)					
Coverage Factor, *k* (95% confidence level)					
Expanded Uncertainty (mg/kg)					

Results of high level asmple

	from	to
Analysis date		~

	Bottle Number		Mass fraction of each compounds (mg/kg) DBP	BBP	DEHP
Bottle 1		Subsample 1			
		Subsample 2			
		Subsample 3			
		Mean			
Bottle 2		Subsample 1			
		Subsample 2			
		Subsample 3			
		Mean			
Overall Mean of Results (mg/kg)					
Combined Standard Uncertainty (mg/kg)					
Coverage Factor, *k* (95% confidence level)					
Expanded Uncertainty (mg/kg)					

"Analytical information" worksheet

Analytical Information for low level pellets

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

2. Sample intake used for analysis: g

3. Sample pre-treatment
   - Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....
   - Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL
   - Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL
   - Other specific treatment

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

6. GC or LC settings
   - Injection method Split (split ratio or split less), on-col, temp, injection volume
   - Column details (brand, length, inner diameter, film thickness, etc.)
   - Flow rate
   - Temperature programing
   - Temperature settings for interface ...
   - Detection

7. MS settings
   - MS mode: SIM or Scan
   - Ionization mode: e.g. EI 70 eV
   - Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"
   - Electron multiplier voltage
   - Carrier gas
   - Selected ion. (m/z)

8. Calibration type / details
   (e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

9. Calibration standards (e.g., source, purity, uncertainty)

10. Internal standards used (Please specify the compounds, and at which stage were added)

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

14. Concentrations of other phthalate esters in the low level pellets (if applicable)
(e.g. compound's name, mass fraction, uncertainty)

15. Additional information, observations or comments

Analytical Information for high level pellets

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

2. Sample intake used for analysis: g

3. Sample pre-treatment
- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....
- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL
- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL
- Other specific treatment

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

6. GC or LC settings
- Injection method Split (split ratio or split less), on-col, temp, injection volume
- Column details (brand, length, inner diameter, film thickness, etc.)
- Flow rate
- Temperature programing
-Temperature settings for interface ...
- Detection

7. MS settings
- MS mode: SIM or Scan
- Ionization mode: e.g. EI 70 eV
- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"
- Electron multiplier voltage
- Carrier gas
- Selected ion. (m/z)

8. Calibration type / details
(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

9. Calibration standards (e.g., source, purity, uncertainty)
10. Internal standards used (Please specify the compounds, and at which stage were added)
11. Purity assessment of the calibrant (if applicable) (e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)
12. The measurement equations used to calculate the mass fraction of each analyte. Please provide details of all the factors listed in the equations and indicate how these values were determined.
13. Estimation of uncertainties for each factor. Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Appendix D: Core Competency Form

CCQM OAWG: Core Competency Template for Analyte(s) in Matrix

CCQM-K133	***NMI***	**polar and non-polar analytes in plastics - Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Participation in this study would provide the opportunity to demonstrate measurement capabilities including: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) cleanup and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC/MS, GC-HRMS, HPLC-FLD or LC-MS. The study will test the capabilities of participants for assigning the polar and non-polar analytes with molecular mass range from 100 g/mol to 1000 g/mol at levels of 10 mg/kg to 5000 mg/kg in plastics.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		<Identity of supplier & CRM>
Identity verification of analyte in calibration material. #		<Methods used to confirm structure>
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #		<Specify>
For calibrants which are a calibration solution: Value-assignment method(s). #		<Specify>
Sample Analysis Competencies		
Identification of analyte(s) in sample		<Methods used to identify the analyte>
Extraction of analyte(s) of interest from matrix		<Specify>
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)		<Specify>
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)		<Specify>
Analytical system		<Specify>
Calibration approach for value-assignment of analyte(s) in matrix		<Specify>
Verification method(s) for value-assignment of analyte(s) in sample (if used)		<Specify>
Other		

- In the middle column place a tick, cross or say the entry is not applicable for each of the competencies listed (the first row does not require a response)
- Fill in the right hand column with the information requested in blue in each row

Enter the details of the calibrant in the top row, then for materials which would not meet the CIPM traceability requirements the three rows with a # require entries.

Appendix E:Full Details of the Analytical Methods Employed by Participants

NIM

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

the whole bottle content is ground, and sub-samples are taken as starting material

2. Sample intake used for analysis: g

0.1g

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Ultrasound-assisted Extr.30min, THF and precipitated by adding Methanol

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

THF 5mL, Methanol 10mL

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

centrifuge the solution at 15000r/min at 4℃ for 10min

- Other specific treatment

/

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

GC/IDMSMS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Agilent 7890A-Agilent 7000, GC/MSMS

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

split(25:1), 250℃，1μL

- Column details (brand, length, inner diameter, film thickness, etc.)

Agilent，DB-5HT，15m×0.25mm×0.1μm

- Flow rate

1.0mL/min

- Temperature programing

50℃(1min)-8℃/min-220℃-20℃/min-280℃(5min)

-Temperature settings for interface ...

280℃

- Detection

/

7. MS settings

- MS mode: SIM or Scan

MRM

- Ionization mode: e.g. EI 70 eV

EI

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

ion source:300℃, Q-pole:180℃

- Electron multiplier voltage

- Carrier gas

He

- Selected ion. (m/z)

	Precursor ion	Product ion	CE
DBP	223	149	10eV
d4-DBP	227	153	15eV
BBP	206	149	10eV
d4-BBP	210	153	10eV
DEHP	279	149	11eV
d4-DEHP	283	153	12eV

8. Calibration type / details
(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

single-point

9. Calibration standards (e.g., source, purity, uncertainty)

DBP, sigma，99.7%，relative standard uncertainty:0.4%(k=2)
BBP,aldrich，98.7%， relative standard uncertainty:1.5%(*k*=2)
DEHP,Dr.E， 99.5%，relative standard uncertainty:0.7%(k=2)

10. Internal standards used (Please specify the compounds, and at which stage were added)

d4-DBP(CIL,purity≥98%),d4-BBP(CIL,purity≥98%), d4-DEHP(CIL,purity≥98%)，dissolved in Methanol and added while precipitation

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

GC/FID，HPLC/DAD

12. The measurement equations used to calculate the mass fraction of each analyte. Please provide details of all the factors listed in the equations and indicate how these values were determined.

$C_{sample} = \frac{m_{is(sample)}}{m_{is(std)}} \times \frac{A_{is(std)}}{A_{std}} \times \frac{A_{sample}}{A_{is(sample)}} \times m_{std} \times P \times \frac{1}{m_{sample}}$
$m_{is(sample)}$: Mass of d4-phthalate solution added to PVC;
$m_{is(std)}$: Mass of d4-phthalate solution added to stardard solution;
$A_{is(std)}$: Area of d4-phthalate in standard solution;
A_{std}: Area of phthalate in standard solution;
A_{sample}: Area of phthalate in sample;
$A_{is(sample)}$: Area of d4-phthalate in sample;
m_{std}: Mass of phthalate in standard solution
P： Purity of the pure material;
m_{sample}: Mass of PVC sample

NMIJ

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

pellets were weighted

2. Sample intake used for analysis: g

0.1

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Samples were dissoluted into THF and precepitated by hexane.

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

THF/Hexane (1/4, v/v) 50 mL

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

Centrifugation

- Other specific treatment

-

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

GC-EI-MS, ID/MS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Agilent 6890-Agilent 5985B

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

splitles,

- Column details (brand, length, inner diameter, film thickness, etc.)

Frontier Lab. Ltd., UA-phthalate (0.25 mm i.d. * 0.05 μm thickness * 30 m length

- Flow rate

1.2 mL/min

- Temperature programing

80 ℃ → (10 ℃ /min) → 200 ℃ → (5 ℃ /min) → 300 ℃ (4 min)

-Temperature settings for interface ...

300 ℃

- Detection

GC-EI-MS

7. MS settings

- MS mode: SIM or Scan

SIM

- Ionization mode: e.g. EI 70 eV

EI 70 eV

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

ion source : 230 ℃, Q-pole: 150 ℃

- Electron multiplier voltage

753

- Carrier gas

He

- Selected ion. (m/z)

149, 153

8. Calibration type / details
(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

IDMS

9. Calibration standards (e.g., source, purity, uncertainty)

DBP: NMIJ CRM 4023-a, 0.9996, U=0.0001
BBP: NMIJ CRM 4029-a, 0.998, U=0.00075
DEHP: NMIJ CRM 4024-b, 0.9994, 0.0001

10. Internal standards used (Please specify the compounds, and at which stage were added)

DBP-d4, BBP-d4, DEHP-d4 (from Wako Chemical co.Ltd.), spiked ISTD solution (d4-BBP) to weighed PVC sample

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

-

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

$$C_{sample} = \phi_{phthalate} \frac{M_{is-sol,spiked} AR_{sample} M_{s-sol,std-mix} C_{s-sol}}{M_{sample} AR_{std.mix} M_{is-sol,std.mix}}$$

$\phi_{ohthalate}$: is the purity of the pure phthalates.
C_{samole}: is the concentration of analytes in the sample;
$C_{s\text{-}sol}$: is the concentration of the analytes standard solution;
Msample: is the mass of the sample taken for analysis;
$M_{is\text{-}sol.\ soiked}$: is the mass of the isotope standard solution added to the sample aliquot;
$M_{is\text{-}sol.\ std.\ mix}$: is the mass of the isotope standard solution added to the isotope ratio standard solution;
$M_{s\text{-}sol.\ std.\ mix.}$: is the mass of the standard solution added to the isotope ratio standard solution;
AR_{samole}: is the area ratio of analyte/isotope for sample extract, observed by GC/MS;
$AR_{std.\ mix.}$: is the area ratio of analyte/isotope for the isotope ratio standard solution, observed by GC/MS.

VNIIM

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

no pretreatment

2. Sample intake used for analysis: g

0.1

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation….

Sample was solved into 10 ml of THF and ultrasonic extraction was performed (15 min); the aliquot 1 (2 ml) was diluted by 8 mL of THF and ultrasonic extraction was performed (15 min); the aliquot 2 (0,5 ml) was taken from aliquot 1;1 ml Hexane was added into aliquot 2 for matrix precipitation

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

THF, 50 mL

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

no clean-up

- Other specific treatment

supernatant was filtered through nylon syringe filter (0,22um) after matrix precipitation

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

ID/MS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Agilent GC/MS 7890A/7000D

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

Split - 50:1, Inlet Temp. - 280°C, Inj. volume - 1 µL

- Column details (brand, length, inner diameter, film thickness, etc.)

Restek, Rtx-Dioxin2, 60 meter×0,25 mmID×0,25µm

- Flow rate

1 mL/min

- Temperature programing

50°C (1 min) -> 20°C/min -> 250°C (1 min) -> 2°C/min -> 300°C (15 min)

-Temperature settings for interface ...

280°C

- Detection

MS

7. MS settings

- MS mode: SIM or Scan

SIM

- Ionization mode: e.g. EI 70 eV

EI 70 eV

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

Ion Source Temp. - 230°C, Quad Temp. - 150°C

- Electron multiplier voltage

1541 V

- Carrier gas

He

- Selected ion. (m/z)

DBPh,BBPh, DEHPh - m/z149; DBPh-D4, BBPh-D4, DEHPh-D4 - m/z 153

8. Calibration type / details

(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

bracketing IDMS

9. Calibration standards (e.g., source, purity, uncertainty)

Pure materials: Di-n-Butyl Phthalate (99,6±0,3)%; Benzyl Butyl Phthalate (98,3±0,3)%; Bis(2-EthylHexyl)Phthalate (99,5±0,3)%

10. Internal standards used (Please specify the compounds, and at which stage were added)

Di-n-Butyl Phthalate (Ring-D4, 98%) 100 ug/mL in Nonane, CIL Cat.# DLM-1367-S; Benzyl Butyl Phthalate (Ring-D4, 98%) 100 ug/mL in Nonane, CIL Cat.# DLM-1369-S, Bis(2-EthylHexyl)Phthalate (Ring-D4, 98%) 100 ug/mL in Nonane, CIL Cat.# DLM-1368-S. The Internal Standards ware added into aliquot 2 before Hexane adding.

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

The purity of commercially available highly-pure substances (Sigma-Aldrich #524980, #308501, #D201154) was determined in-house by mass balance approach.
(KF titration; ICP/MS/MS; Vacuum evaporation, GC/MS; GC-FID, LC/UV). Successful participation in CCQM-K55 series.

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

$$w_{an} = \frac{A_{an} \times m_{IS} \times m_{sol_1} \times m_{sol_2}}{A_{IS} \times m_{al_1} \times m_{al_2} \times RF \times m_s}$$

$$RF = \frac{A_{an} \times m_{IS}}{A_{IS} \times m_{an}}$$

w_{an}	– the mass fraction of the analyte in the sample, mg/kg;
A_{an}	– the area of the analyte in the sample;
A_{IS}	– the area of the Internal Standard in the sample;
m_{IS}	– the mass of Internal Standard added to sample, mg;
m_{sol_1}	– the mass of solution after dissolution PVC in THF, g;
m_{sol_2}	– the mass of solution after dissolution aliquot 1 in THF, g;
m_{al_1}	– the mass of aliquot of solution after dissolution PVC in THF, g;
m_{al_2}	– the mass of aliquot of solution after dissolution aliquot 1 in THF, g;
m_s	– the mass of sample, kg;
RF	– the response factor.
A_{an}	– the area of the analyte in the calibration solution;
A_{IS}	– the area of the Internal Standard in the calibration solution;
m_{an}	– the mass of the analyte in the calibration solution, mkg
m_{IS}	– the mass of Internal Standard in the calibration solution, mkg;

GLHK

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

The sample is cut into 2mm x 2mm and sub-sample is weighed out for extraction

2. Sample intake used for analysis: g

about 0.1 g

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Dissolution and precipitation

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

Dissolution: THF, 10 mL & Precipitation: MeOH, 20 mL

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

Nil

- Other specific treatment

Solvent exchange - 1 mL sample solution was taken out and evaporated to just dryness under gentle stream of nitrogen and was reconstituted in 1 mL MeOH

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

LC-MS/MS, IDMS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Agilent 1200 HPLC with AB Sciex 3200

6. ~~GC or~~ LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

Injection volume: 10 uL

- Column details (brand, length, inner diameter, film thickness, etc.)

Phenomenex Synergi 4µ Polar-RP 80A 250 x 3.0mm (Part no.: 00G-4336-Y0)

- Flow rate

0.45 mL/min

- ~~Temperature programing~~ LC Program

Step	Total Time(min)	A(%)	B(%)
0	0.00	25.0	75.0
1	12.00	25.0	75.0
2	15.00	15.0	85.0
3	32.00	15.0	85.0
4	32.50	0.0	100.0
5	36.50	0.0	100.0
6	37.00	25.0	75.0
7	45.00	25.0	75.0

A = 0.1% Formic Acid
B = MeOH
Column Temperature: 25°C

-Temperature settings for interface ...

n/a

- Detection

Tandem mass spectrometry (MS/MS)

7. MS settings

- MS mode: SIM or Scan

Multiple reaction monitoring (MRM)

- Ionization mode: e.g. EI 70 eV

Positive ESI

- ~~Temperature of "ion source" and "separator (e.g., temperature of Q pole)"~~ MS Parameters

Source Temperature (TEM): 450°C
Curtain Gas (CUR): 20.00
Gas 1 (GS1): 60.00
Gas 2 (GS2): 60.00
CAD Gas (CAD): 7.00
Ion Spray Voltage (IS): 5500.00

- Electron multiplier voltage

n/a

- Carrier gas

n/a

- Selected ion. (m/z)

Analyte	Q1 Mass (Da)	Q3 Mass (Da)
BBP	313.20	148.90
BBP	313.20	205.00
BBP	313.20	239.30
BBP-d4	317.20	153.00
BBP-d4	317.20	209.20
BBP-d4	317.20	243.20
DBP	279.10	149.00
DBP	279.10	205.10
DBP	279.10	121.00
DBP-d4	283.20	153.00
DBP-d4	283.20	209.10
DBP-d4	283.20	125.00
DEHP	391.30	148.90
DEHP	391.30	167.00
DEHP	391.30	113.00
DEHP-d4	395.30	152.80
DEHP-d4	395.30	171.10
DEHP-d4	395.30	113.00

8. Calibration type / details

(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

Bracketing method, IDMS

9. Calibration standards (e.g., source, purity, uncertainty)

DBP: GBW (E) 100224 (16001) - 164 ug/mL (3.0%)
BBP: GBW (E) 100226 (17001) - 160 ug/mL (2.5%)
DEHP: GBW (E) 100223 (17001) - 202 ug/mL (4.0%)

10. Internal standards used (Please specify the compounds, and at which stage were added)

DBP-d4: Cambridge Isotope Laboratories, Inc., DLM-1367-0
BBP-d4: Cambridge Isotope Laboratories, Inc., DLM-1369-0
DEHP-d4: Cambridge Isotope Laboratories, Inc., DLM-1368-0

11. Purity assessment of the calibrant (if applicable)

(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

n/a

12. The measurement equations used to calculate the mass fraction of each analyte.

Please provide details of all the factors listed in the equations and indicate how these values were determined.

$$C_X = C_Z \cdot \frac{M_Y}{M_X} \cdot \frac{M_{Zc}}{M_{Yc}} \cdot \frac{R_B}{R_{Bc}} \cdot DF_x$$

C_X = mass fraction of analyte in sample
C_Z = mass fraction of reference analyte in reference standard solution
M_Y = mass of internal standard solution added to sample blend
M_X = mass of sample added to sample blend
M_{Zc} = mass of reference standard solution added to calibration blend
M_{Yc} = mass of internal standard solution added to calibration blend
R_B = peak area ratio of selected ions of analyte to internal standard in sample blend solution
R_{Bc} = peak area ratio of selected ions of analyte to internal standard in calibration blend solution
DF_x = dilution factors, if any

UME

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

The whole bottle was ground cryogenically with Fritsch Pulverisette 14 grinder

to 1 mm fineness and sub-samples are taken from the starting material

2. Sample intake used for analysis: g

0.2

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Extraction was performed by dissolution and precipitation technique.

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

10 mL of THF was used for dissolution, 30 mL of ethanol was used for

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

- Other specific treatment

First, 0.2 g of sample and then isotopic labelled standard solution was weighed into a teflon centrifuge tube. 10 mL of THF was added and it was kept in ultrasonic bath for 30 minutes to have dissolution. After dissolution, 30 mL of ethanol was added by dripping to perform precipitation of plastic. After completion of precipitation, centrifugation was applied at 2308 g and 18 °C for 5 minutes. After centrifugation, 5 mL of supernatant was transferred to a glass vial by passing through 0.45 µm PTFE filter. The cap of vial is made from PTFE.

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

GC-MS/MS and IDMS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Thermo Scientific TSQ Quantum GC-MS/MS

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

Split, split ratio is 1-20, injection volume is 1 µL, injection temperature is 300 °C.

- Column details (brand, length, inner diameter, film thickness, etc.)

TG-5MS, 5% phenyl methylpolysiloxane, 30 mx0.25 mmx0.25 µm

- Flow rate

Constant flow, 1 mL/min

- Temperature programing

Initial temperature is 100 °C. Temperature is increased to 200 °C with 30 °C/min rate. Then temperature is increased to 280°C with 2.5 °C/min rate and hold for 5 min.

-Temperature settings for interface ...

Interface temperature is 280 °C

- Detection

7. MS settings
- MS mode: SIM or Scan
SRM (MS-MS) was applied.
- Ionization mode: e.g. EI 70 eV
EI 70 eV
- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"
Ion source temperature is 230 °C and emission current is 50 µA
- Electron multiplier voltage
10
- Carrier gas
Helium 99% purity
- Selected ion. (m/z)
Benzyl Butyl Phthalate (BBP) Parent ion: 206 Product ion: 149 Benzyl Butyl Phthalate- D4 (3,4,5,6) (BBP-D4) Parent ion: 210 Product ion: 153 Di-n-butyl Phthalate (DBP) Parent ion: 223 Product ion: 149 Di-n-butyl Phthalate- D4 (DBP-D4) Parent ion: 227 Product ion: 153 Bis (2-ethylhexyl) Phthalate (DEHP) Parent ion: 279 Product ion: 149 Bis (2-ethylhexyl) Phthalate (DEHP-D4) Parent ion: 283 Product ion: 153
8. Calibration type / details
(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)
Single point, IDMS
9. Calibration standards (e.g., source, purity, uncertainty)
Phthalic acid, benzybutyl ester (BBP), LGC/Dr. Ehrenstorfer, (97.120±0.373)% Phthalic acid, bis-butyl ester (DBP), LGC/Dr. Ehrenstorfer, (99.224±0.314)% Phthalic acid, bis-2-ethylhexyl ester (DEHP), LGC/Dr. Ehrenstorfer, (99.706± 0.284)%
10. Internal standards used (Please specify the compounds, and at which stage were added)
Phthalic acid, benzybutyl ester-D4, Dr. Ehrenstorfer, Phthalic acid, bis-butyl ester-D4, LGC/Dr. Ehrenstorfer, Phthalic acid, bis-2-ethylhexyl ester-D4, Dr. Ehrenstorfer It was added while sample was weighing, at the begining of method application
11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification)
The purity determination of BBP was performed by qNMR with using maleic acid IS in traceability chain of UME-CRM-1301. The purity determination of DBP was performed by qNMR with using maleic acid IS in traceability chain of UME-CRM-1301. The purity determination of DEHP was performed by qNMR with using maleic acid IS in traceability chain of UME-CRM-1301. >②= † d ÿFirst, 0.2 g of sample and then isotopic labelled standard solution was weighed into a teflon

12. The measurement equations used to calculate the mass fraction of each analyte. Please provide details of all the factors listed in the equations and indicate how these values were determined.

$$C_X = \frac{A_x x n_{ISx}}{A_{isx} x RF x M_{sample}}$$

C_X: Concentration of analyte in unknown sample (mg/kg)

A_X: Peak area of analyte in unknown sample

A_{ISX}: Peak area of labelled analyte

n_{ISX}: Total amount of added internal standard (µg)

Msample: Sample mass (g)

RF: Response Factor

$RF=(N_A x L_C)/(N_C x L_A)$

N_A: Area of native compound in calibration solution

L_A: Area of labelled compound in calibration solution

N_C: Concentration of native compound in calibration solution

L_C: Concentration of labelled compound in calibration solution

14. Concentrations of other phthalate esters in the high level pellets (if applicable) (e.g. compound's name, mass fraction, uncertainty)

15. Additional information, observations or comments

KRISS

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

spiked ISTD solution (d4-DBP, d4-BBP, d4-DEHP) to weighed PVC sample

2. Sample intake used for analysis: g

0.1 ~ 0.2

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

dissolution and precipitation

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

dissolution with Tetrahydrofuran (THF) 8 mL and precipitation with Methanol 25 mL

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

- Other specific treatment

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

GC-ID/HRMS (resolution = 10000)

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Agilent GC 7890 - Jeol GC/MS 800D-UF MS

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

spiltless, 1 uL

- Column details (brand, length, inner diameter, film thickness, etc.)

Rtx-5MS (60 m * 0.25 mm * 0.25 um)

- Flow rate

1 mL/min

- Temperature programing

80 C (3min) -> 30 °C/min -> 180 °C -> 10 °C/min -> 300 °C (7 min)

-Temperature settings for interface ...

300 °C

- Detection

GC-EI/MS

7. MS settings

- MS mode: SIM or Scan

SIM (High resolution, R = 10000)

- Ionization mode: e.g. EI 70 eV

EI 70 eV

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

ion source: 250 C

- Electron multiplier voltage

1.3 eV

- Carrier gas

Helium

- Selected ion. (m/z)

Native: m/z 140.0239, ISTD (d4) : 153.0490 for all compounds

8. Calibration type / details

(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

single-point

9. Calibration standards (e.g., source, purity, uncertainty)

DBP (TCI, 99.53 % ± 0.26 %), BBP, (TIC, 98.37 % ± 0.26 %), DEHP (TCI, 99.52 % ± 0.19 %) based on mass-balance method

10. Internal standards used (Please specify the compounds, and at which stage were added)

DBP (D4-DBP, ISOTECH), BBP (D4-BBP, CIL), DEHP (D4-DEHP, CIL),
spiked ISTD solution (d4-DBP, d4-BBP, d4-DEHP) to weighed PVC sample

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

Purity was assayed by KRISS with mass-balance method and verified with qNMR. With using the neat calibrant, calibration solutions were prepared gravimmetrically and verified by ID-GC/MS. KRISS capability for purity assay was proved through participation of CCQM-K55b, 55c, 55d and CCQM-P55a.

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

$$C_{\text{sample}} = f \bullet \frac{M_{\text{is-sol,spiked}} \cdot AR_{\text{sample}} \cdot M_{\text{s-sol,std. mix.}} \cdot C_{\text{s-sol}}}{M_{\text{sample}} \cdot AR_{\text{std. mix.}} \cdot M_{\text{is-sol,std.mix.}}}$$

f: dry-mass correction factor; it is not applied in this experiment.

C_{sample}: is the concentration of analytes in the sample;

$C_{s\text{-}sol}$: is the concentration of the analytes standard solution;

Msample: is the mass of the sample taken for analysis;

$M_{is\text{-}sol,\ spiked}$: is the mass of the isotope standard solution added to the sample aliquot;

$M_{is\text{-}sol,\ std.\ mix.}$: is the mass of the isotope standard solution added to the isotope ratio standard solution;

$M_{s\text{-}sol,\ std.\ mix.}$: is the mass of the standard solution added to the isotope ratio standard solution;

AR_{sample}: is the area ratio of analyte/isotope for sample extract, observed by GC/MS;

$AR_{std.\ mix}$: is the area ratio of analyte/isotope for the isotope ratio standard solution, observed by GC/MS.

EXHM

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

the material was analyzed in the form of pelets

2. Sample intake used for analysis: g

0,5 g

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Dissolution and precipitation

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

dissolution THF - 10 mL - precipitation n-hexane 40 mL

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

extraction in 50 mL hexane

- Other specific treatment

The dissolution precipitation step was repeated three times
The pellets were left to dissolve in THF for two days under continuous shaking. The internal standards were added and the mixture was left under continuous shaking for one day. Hexane was added under vigorous shaking and the material was left to precipitate. The solvent mix was decanted and the precipitated polymer was subjected twice to the same procedure

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

GC-IDMS

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Thermo Trace Ultra GC coupled to PolarisQ ion trap MS

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

PTV injector - 10 µL inj vol. - inj program: initial T 85 C, split flow 25 mL/min, inj pressure 160 kPa, flow 25 mL/min, evaporation temp 15 C/s to 85 C for 0,5 min, transfer temp: 15 min/s to 300 C, cleaning 14,5 C/s to 320, hold 28 min

- Column details (brand, length, inner diameter, film thickness, etc.)

Agilent J&W DB-35 ms (30 m x 0.25 mm ID, 0.25 µm film thickness)

- Flow rate

He carrier gas - 0-15 min: 1,5 mL/min, with 0,1 mL/min ramp to 2 mL/min - hold for 13 min

- Temperature programing

oven initial T: 80 C (hold 3 min), 50 C/min to 270 (hold 18 min), 50 C/min to 320 (hold 7 min)

-Temperature settings for interface ...

transfer line 280 C

- Detection

MS

7. MS settings

- MS mode: SIM or Scan

SRM

- Ionization mode: e.g. EI 70 eV

EI 70 eV

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

230 oC

- Electron multiplier voltage

1700

- Carrier gas

He

- Selected ion. (m/z)

149, 153

8. Calibration type / details
(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

single point calibration at exact matching concentrations - IDMS

9. Calibration standards (e.g., source, purity, uncertainty)

DBP (Sigma Aldrich, TRACERT, 988.5 ± 2.5 mg/g, determined by EXHM)
BBP (Sigma Aldrich, TRACERT, 977.2 ± 2.5 mg/g, determined by EXHM),
DEHP (Sigma Aldrich, TRACECERT, 993.8 ± 2.5 mg/g, determined by EXHM)

10. Internal standards used (Please specify the compounds, and at which stage were added)

DBP-d4, BBP-d4, DEHP-d4 all added during dissolution

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

qNMR (CCQM-K55c, CCQM-P150a, CCQM-K131)

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

please refer to separate file

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

please refer to separate file

14. Concentrations of other phthalate esters in the low level pellets (if applicable)
(e.g. compound's name, mass fraction, uncertainty)

DBP - 93.41 ± 1.82 mg/kg (k=2)
DEHP - 91.25 ± 1.92 mg/kg (k=2)
DMP (dimethyl phthalate) - 92.32 ± 5.44 mg/kg (k=2)
DEP (diethyl phthalate) - 92.82 ± 5.47 mg/kg
DIBP (diisobutyl phthalate) - 91.10 ± 5.36 mg/kg
DICP (dicyclohexyl phthalate) - 90.60 ± 5.33 mg/kg
DOP (di n-octyl phthalate) - 93.33 ± 5.47 mg/kg (k=2)

(data reported for phthalate esters that EXHM had available calibrants)

dipropyl, dipentyl, dihexyl, diheptyl phthalate esters also identified in significan amounts
but were not quantified due to lack of calibrants

15. Additional information, observations or comments

EXHM performed qNMR on SIGMA TRACERT DBP, BBP, DEHP using NMIJ CRM 4601-a as an IS and prepared in-house calibrants to verify the results obtained via NMIJ's CRM 8152-a and report the recovery

INMETRO

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

Each sub-sample was weighed and then extracted.

2. Sample intake used for analysis: g

0.3 g

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Dissolution and precipitation

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

Sample dissolution with 5 mL THF; polymer precipitation with 10 mL Hexane

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

Not applied

- Other specific treatment

After addition of THF, ultrasound was used for extraction during 2.5 h. Hexane was added and the flask was stored during one day in refrigerator (4°C ± 2°C) for complete polymer precipitation. The extract was centrifuged at 4800 rpm, 22 °C and 20 min. An aliquot of 1.5 g was diluted with 0.3 g of internal standard solution (~250 mg/kg) and 1.8 g of methanol and centrifuged again. The sobrenadant was injected in GC-MS system.

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

The analytical method was gas chromatography coupled to mass spectrometer (GC-MS). The quantification of the analyte was performed by internal standard calibration. KRISS CRM 113-03-006 was used as quality control.

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

GC - Agilent 6890N; MS - Agilent 5975B

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

Volume: 0.2 µL; Temperature: 300 °C, Split 5:1

- Column details (brand, length, inner diameter, film thickness, etc.)

DB 1701 (30 m x 0.25 mm x 0.25 µm)

- Flow rate

1.3 mL/min

- Temperature programing

160 °C (1 min), 280 °C (10 °C /min) 9 min.

-Temperature settings for interface ...

Transfer line 280 °C

- Detection

See MS settings

7. MS settings

- MS mode: SIM or Scan

SIM

- Ionization mode: e.g. EI 70 eV

EI 70 eV

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

Source temperature 230 °C, Temperature of quadrupole 150 °C

- Electron multiplier voltage

1700

- Carrier gas

He

- Selected ion. (m/z)

m/z = 206 for BBP, m/z = 149 for DBP, m/z = 279 for DEHP, m/z = 212 for internal standard

8. Calibration type / details

(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

Internal standard calibration

9. Calibration standards (e.g., source, purity, uncertainty)

MRC NIST 3074 - Phthalates in Methanol: BBP = 52.2 mg/Kg, U = 1.4 mg/Kg, DBP = 51.2 mg/Kg, U = 1.2 mg/Kg; DEHP = 58.6 mg/Kg, U = 1.3 mg/Kg.

10. Internal standards used (Please specify the compounds, and at which stage were added)

Benzyl benzoate (Sigma Aldrich): It was added after extraction and polymer precipitation

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

Not applied. It was used CRM of Phthalates solution from NIST.

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

Step 1: Mass fraction of the analyte in diluted solution

$$w_{dil} = \left(\frac{A - b_0}{b_1}\right) * \frac{m_{IS} * P}{m_{Aliq}}$$

w_{dil} = mass fraction of the analyte in diluted solution
A = area ratio of the analyte in the diluted solution
b_0 = linear coefficient of the calibration curve
m_{Aliq} = aliquot of initial PVC solution
b_1 = angular coefficient of the calibration curve
m_{IS} = mass of the internal standard solution
P = purity of the standard used in the calibration curve (It was used CRM from Nist, therefore assuming unitary value)

Step 2: Dilution Factor

$$w_{final} = w_{dil} * DF \qquad DF = \frac{m_{sol\ PVC}}{m_{PVC\ pel}}$$

DF = dilution factor
$m_{sol\ PVC}$ = mass of PVC initial solution (PVC pellet + extraction solvent)
$m_{PVC\ pel}$ = mass of PVC pellet
w_{final} = mass fraction of the analyte in PVC pallet
w_{dil} = mass fraction of the analyte in diluted solution

Step 3: Combined Result

Overall mean of bottles 028 and 180, in triplicate each one

NMISA

1. Please specify whether the whole bottle content is ground, and sub-samples are taken as starting material, or whether a sub-sample is weighed out which is ground and then extracted.

Sample was not ground before subsample taken as pellets fully dissolve during extraction

2. Sample intake used for analysis: g

0,100 g to 0,150 g

3. Sample pre-treatment

- Extraction or other methods, e.g. PLE, Soxleth extraction, dissolution and precipitation....

Dissolution (Sonication in THF for 2 hours)

- Solvents used. e.g. Toluene-THF(1:1, v/v) 10 mL

3 mL tetrahydrofuran (THF), followed by 7 mL methanol (MeOH)

- Sample clean-up methods e.g. SPE (Silica, C18... , xx mg,) elution with xx solvent xx mL

Polymer was precipitated out after sonication with the addition of methanol, followed by separation by centrifugation

- Other specific treatment

4. Specify detailed analytical method and type of quantification. e.g. GC-EI-MS, ID/MS

GC-TOFMS analysis using ID/MS bracketing quantification

5. Instrument used : e.g. Agilent GC 6890 - Jeol GC/MS 700D

Leco Pegasus 4D

6. GC or LC settings

- Injection method Split (split ratio or split less), on-col, temp, injection volume

Spilt 10:1, 1 µL injection, into a split/splitless injector set at 290°C

- Column details (brand, length, inner diameter, film thickness, etc.)

Restek Rxi-5SilMS; 30 m, 0.25 mm ID, 0.25 µm

- Flow rate

1,2 mL/min

- Temperature programing

Ramp from 150°C to 230°C at 30°C/min, followed by a ramp at 10°C/min to 260°C and finally ramped to 300° C at 20°C/min where it is held for 5 min

-Temperature settings for interface ...

Transfer line 290 °C

- Detection

TOFMS

7. MS settings

- MS mode: SIM or Scan

Scan

- Ionization mode: e.g. EI 70 eV

70 eV

- Temperature of "ion source" and "separator (e.g., temperature of Q-pole)"

Source at 250 °C

- Electron multiplier voltage

1500

- Carrier gas

Helium

- Selected ion. (m/z)

m/z 149 for native and 153 for isotope

8. Calibration type / details

(e.g., single-point, bracketing /external calibration, internal standard calibration, IDMS)

bracketing IDMS

9. Calibration standards (e.g., source, purity, uncertainty)

NIM calibrants were used to value assign ISO guide 34 Accredited calibrants:
NCS ZC 76043 (GBW 100224) dibutyl phthalate acid ester (DBP) 164 µg/mL ± 3 µg/mL
NCS ZC 76045 (GBW 100226) benzyl butyl phthalate acid (BBP) 160,0 µg/mL ± 2,5 µg/mL
NCS ZC 76042 (GBW 100223) di(2-ethylhexyl)phthalate acid ester (DEHP) 202,0 µg/mL ± 4,0 µg/mL
Value assigned calibrants used for the quantification of the samples:
DBP 2471,7 µg/g ± 102,9 µg/g
BBP 2394,8 µg/g ± 100,7 µg/g
DEHP 2409,0 µg/g ± 93,9 µg/g

10. Internal standards used (Please specify the compounds, and at which stage were added)

D4 DBP; D4 BBP and D4 DEHP isotopes were added to the 0,1 g sample before extraction/dissolution

11. Purity assessment of the calibrant (if applicable)
(e.g. methods used for value assignment/verification, ensure evidence for the demonstration of competence to carry out in house assessment is included)

N/A. The NIM CRMs were used to value assigned Restek ISO guide 34 accredited calibrants

12. The measurement equations used to calculate the mass fraction of each analyte.
Please provide details of all the factors listed in the equations and indicate how these values were determined.

Wx = mass fraction of analyte in the sample
Wz = concentration (ug/g) of calibration solution used to spike cal solutions
mz = weight of calibrant solution added to calibration blend
myc = weight of isotope solution added to calibration blend
mx = mass of sample analysed
RB = ratio of peak areas (native/labelled) in the samples
RBc = ratio of peak areas (native/labelled) in the calibration blends

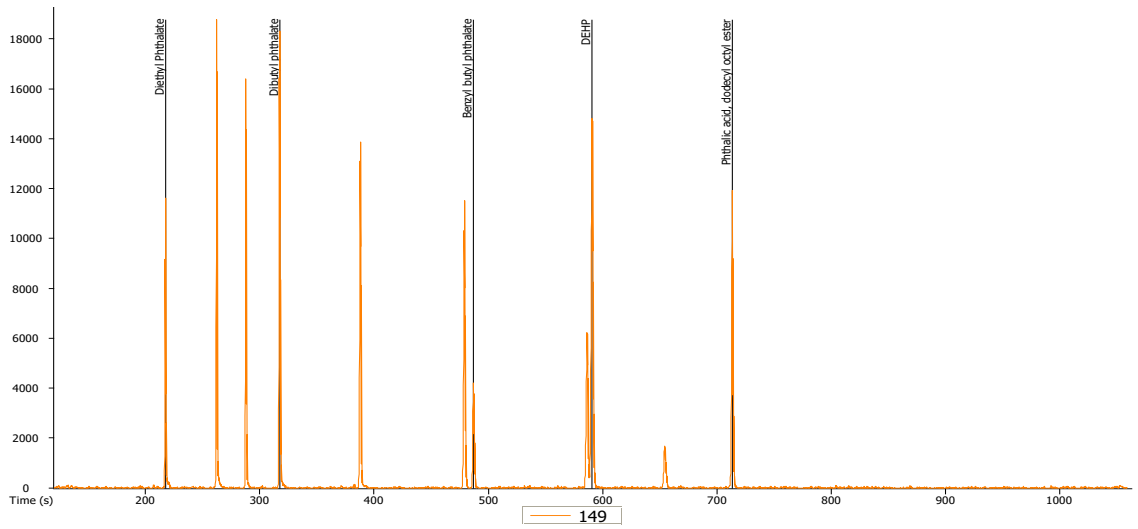
$$W_x = W_z \frac{m_z}{m_{yc}} \frac{m_y}{m_x} \frac{R_B}{R_{BC}}$$

14. Concentrations of other phthalate esters in the low level pellets (if applicable)
(e.g. compound's name, mass fraction, uncertainty)

DBP 112,3 mg/kg ± 7,7 mg/kg

The following phthalates were positively identified against a standard, however not quantified
DEP (Diethyl phthalate) CAS 84-66-2
DEHP (Bis 2 ethyl hexyl phthlate) CAS 117-81-7
Di-n-octyl phthalate CAS 117-84-0

The adjacent chromtogram is the reconstructed ion chromotogram (m/z) of the extracted 009 PVC sample. Positively identified phthalates have been labelled.



Appendix F: Full Details of the Uncertainty Budgets Estimated by Participants

NIM

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

the uncertainty of the result is mainly from method repeatability, mass uncertainty and CRM uncertainty.

	BBP(low)	DBP (high)	BBP (high)	DEHP (high)
Repeatability of PVC analysis in GC-MS	0.44%	0.56%	0.66%	0.65%
Purity relative standard uncertainty	0.75%	0.2%	0.75%	0.35%
relative standard uncertainty of $m_{is(sample)}$	0.0013%	0.0013%	0.0013%	0.0013%
relative standard uncertainty of $m_{is(std)}$	0.0022%	0.0022%	0.0022%	0.0022%
relative standard uncertainty of m_{std}（pure material weight when preparing stock solution)	0.0639%	0.0652%	0.0639%	0.0649%
relative standard uncertainty of m_{std}（solvent weight when preparing stock solution)	0.0001%	0.0001%	0.0001%	0.0001%
relative standard uncertainty of m_{std}（calibration solution preparation)	0.0939%	0.0199%	0.0207%	0.0103%
relative standard uncertainty of m_{sample}	0.0516%	0.0516%	0.0516%	0.0516%
Combined relative standard uncertainty	0.9%	0.6%	1.0%	0.8%
Combined standard uncertainty (mg/kg)	0.9	3	5	7
Expanded standard uncertainty (k=2)(mg/kg)	1.8	6	10	14

NMIJ

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

	BBP(low)		DBP(high)		BBP(high)		DEHP(high)	
	relative standard uncertaintity	standard uncertaintity (mg/kg)	relative standard uncertaintity	standard uncertaintity (mg/kg)	relative standard uncertaintity	standard uncertaintity (mg/kg)	relative standard uncertaintity	standard uncertaintity (mg/kg)
Uncertaintity from the mass ratio of standard solutions	0.001	0.1	0.001	0.46	0.001	0.51	0.001	0.97
Uncertaintity from the mass ratio of sample and phthalates-d4	0.0003	0.03	0.001	0.49	0.001	0.54	0.001	1.03
Uncertatinty from analysis of standard solutions (repeatability)	0.018	1.83	0.056	25.3	0.018	9.06	0.03	28.7
Uncertatinty from analysis of sample solutions (repeatability)	0.012	1.21	0.02	9.14	0.022	10.8	0.011	10.6
purity of the CRM of phthalates.	0.0008	0.08	0.0001	0.05	0.0008	0.37	0.0001	0.09
total	0.0183	1.85	0.06	26.9	0.028	14.1	0.032	30.6

VNIIM

LOW SAMPLE

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

$$\frac{u_{(x)}}{x} = \sqrt{\left(\frac{u_{(RF)}}{RF}\right)^2 + \left(\frac{u_{(w_{bl})}}{w_{bl}}\right)^2 + \left(\frac{u_{(w_s)}}{w_s}\right)^2 + \left(\frac{u_{(rec)}}{w_{RM}}\right)^2}$$

$$\frac{u_{(RF)}}{RF} = \sqrt{\left(\frac{u_{(m_{IS})}}{m_{IS}}\right)^2 + \sum\left(\frac{u_{(m_{nat})}}{m_{nat}}\right)^2 + \left(\frac{u_{(pur)}}{w_{pur}}\right)^2 + \left(\frac{u_{(hom)}}{w_{pur}}\right)^2 \left(\frac{u_{(stab)}}{w_{pur}}\right)^2 + \sum\left(\frac{u_{(m_{cal})}}{m_{cal}}\right)^2 + \left(\frac{u_{(RF_{av})}}{RF_{av}}\right)^2}$$

$$\frac{u_{(w_{bl})}}{w_{bl}} = \sqrt{\left(\frac{u_{(m_{IS_{bl}})}}{m_{IS_{bl}}}\right)^2 + \left(\frac{u_{(w_{av_{bl}})}}{w_{av_{bl}}}\right)^2 + \left(\frac{u_{(m_{THF_{bl}})}}{m_{THF_{bl}}}\right)^2 + \left(\frac{u_{(m_{al_{bl}})}}{m_{al_{bl}}}\right)^2}$$

$$\frac{u_{(w_s)}}{w_s} = \sqrt{\left(\frac{u_{(m_{IS_s})}}{m_{IS_s}}\right)^2 + \left(\frac{u_{(m_s)}}{m_s}\right)^2 + \left(\frac{u_{(w_{av_s})}}{w_{av_s}}\right)^2 + \left(\frac{u_{(m_{THF_s})}}{m_{THF_s}}\right)^2 + \left(\frac{u_{(m_{al_s})}}{m_{al_s}}\right)^2}$$

14. Concentrations of other phthalate esters in the low level pellets (if applicable)
(e.g. compound's name, mass fraction, uncertainty)

Di-n-Butyl Phthalate
Mass fraction (mg/kg): 92,4
Combined Standard Uncertainty (mg/kg): 2,3
Coverage Factor, k (95% confidence level): 2
Expanded Uncertainty (mg/kg): 4,6
Bis(2-ethylhexyl) Phthalate
Mass fraction (mg/kg): 63,3
Combined Standard Uncertainty (mg/kg): 2,3
Coverage Factor, k (95% confidence level): 2
Expanded Uncertainty (mg/kg): 4,6

15. Additional information, observations or comments

The results were verified by measuring using NIST SRM 3074

$u_{(RF)}$	– the standard uncertainty of the Response Factor (RF);
$u_{(w_{bl})}$	– the standard uncertainty of the mass fraction of analyte in the blank;
$u_{(w_s)}$	– the standard uncertainty of the mass fraction of analyte in the sample
$u_{(rec)}$	– the standard uncertainty of the recovery of analyte from reference material
$u_{(m_{IS})}$	– the standard uncertainty of the mass (preparation of the Internal Standard solution)
$u_{(m_{nat})}$	– the standard uncertainty of the masses (preparation of the native stock solution)
$u_{(pur)}$	– the standard uncertainty of the purity of analyte
$u_{(m_{cal})}$	– the standard uncertainty of the masses (preparation of the calibration blend)
$u_{(RF_{av})}$	– the standard uncertainty of calibration (standard deviation of the multiple IDMS results)
$u_{(hom)}$	– the standard uncertainty of homogeneity of pure substance (standard deviation of the multiple IDMS results)
$u_{(stab)}$	– the standard uncertainty of stability of pure substance (standard deviation of the multiple IDMS results)
$u_{(m_{IS_{bl}})}$	– the standard uncertainty of the mass (addition the internal standard to the blank)
$u_{(w_{av_{bl}})}$	– the standard uncertainty of mass fraction of analyte in blank (standard deviation of the multiple IDMS results)
$u_{(m_{THF_{bl}})}$	– the standard uncertainty of the mass (solution of THF)
$u_{(m_{al_{bl}})}$	– the standard uncertainty of the mass (the aliquot of solution of THF)
$u_{(m_{IS_s})}$	– the standard uncertainty of the mass (addition the internal standard to the sample)
$u_{(m_s)}$	– the standard uncertainty of the mass of the sample
$u_{(w_{av_s})}$	– the standard uncertainty of mass fraction of analyte in sample (standard deviation of the multiple IDMS results)
$u_{(m_{THF_s})}$	– the standard uncertainty of the mass (solution after dissolution PVC in THF)
$u_{(m_{al_s})}$	– the standard uncertainty of the mass (the aliquot of solution after dissolution PVC in THF)

Source of uncertainty	u, % (Di-n-Butyl Phthalate)	u, % (BenzylButyl Phthalate)	u, % (Bis(2-ethylhexyl) Phthalate)
$u_{(m_{IS})}$	0.05	0.05	0.05
$u_{(m_{nat})}$	0.12	0.12	0.12
$u_{(pur)}$	0.3	0.3	0.2
$u_{(m_{cal})}$	0.2	0.2	0.2
$u_{(RF_{av})}$	0.31	0.53	0.44
$u_{(hom)}$	0.5	0.5	0.5
$u_{(stab)}$	0.5	0.5	0.5
$u_{(RF)}$	**0.86**	**0.96**	**0.89**
$u_{(m_{IS_{bl}})}$	0.24	-	0.24
$u_{(w_{av_{bl}})}$	0.27	-	2.72
$u_{(m_{THF_{bl}})}$	0.0005	-	0.0005
$u_{(m_{al_{bl}})}$	0.01	-	0.01
$u_{(w_{bl})}$	**0.36**	-	**2.73**
$u_{(m_{IS_s})}$	0.19	0.19	0.19
$u_{(m_s)}$	0.05	0.05	0.05
$u_{(w_{av_s})}$	0.39	0.96	0.59
$u_{(m_{THF_s})}$	0.0005	0.0005	0.0005
$u_{(m_{al_s})}$	0.0085	0.0085	0.0085
$u_{(w_s)}$	**0.44**	**0.98**	**0.62**
$u_{(rec)}$	**2.2**	**1.6**	**2.1**
Relative Standard Uncertainty	**2.43**	**2.11**	**3.61**
Relative expanded uncertainty	**4,86 (4,9)**	**4,22 (4,2)**	**7,22 (7,2)**

HIGH SAMPLE

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

$$\frac{u_{(x)}}{x} = \sqrt{\left(\frac{u_{(RF)}}{RF}\right)^2 + \left(\frac{u_{(w_s)}}{w_s}\right)^2 + \left(\frac{u_{(rec)}}{w_{RM}}\right)^2}$$

$$\frac{u_{(RF)}}{RF} = \sqrt{\left(\frac{u_{(m_{IS})}}{m_{IS}}\right)^2 + \sum\left(\frac{u_{(m_{nat})}}{m_{nat}}\right)^2 + \left(\frac{u_{(pur)}}{w_{pur}}\right)^2 + \left(\frac{u_{(hom)}}{w_{pur}}\right)^2 \left(\frac{u_{(stab)}}{w_{pur}}\right)^2 + \sum\left(\frac{u_{(m_{cal})}}{m_{cal}}\right)^2 + \left(\frac{u_{(RF_{av})}}{RF_{av}}\right)^2}$$

$$\frac{u_{(w_s)}}{w_s} = \sqrt{\left(\frac{u_{(m_{IS})}}{m_{IS}}\right)^2 + \left(\frac{u_{(m_s)}}{m_s}\right)^2 + \left(\frac{u_{(w_{av})}}{w_{av}}\right)^2 + \left(\frac{u_{(m_{sol_1})}}{m_{sol_1}}\right)^2 + \left(\frac{u_{(m_{al_1})}}{m_{al_1}}\right)^2 + \left(\frac{u_{(m_{sol_2})}}{m_{sol_2}}\right)^2 + \left(\frac{u_{(m_{al_2})}}{m_{al_2}}\right)^2}$$

15. Additional information, observations or comments

The results were verified by measuring using NIST SRM 3074

$u_{(RF)}$	– the standard uncertainty of the Response Factor (RF);
$u_{(w_s)}$	– the standard uncertainty of the mass fraction of analyte in the sample
$u_{(rec)}$	– the standard uncertainty of the recovery of analyte from reference material
$u_{(m_{IS})}$	– the standard uncertainty of the mass (preparation of the Internal Standard solution)
$u_{(m_{nat})}$	– the standard uncertainty of the masses (preparation of the native stock solution)
$u_{(pur)}$	– the standard uncertainty of the purity of analyte
$u_{(m_{cal})}$	– the standard uncertainty of the masses (preparation of the calibration blend)
$u_{(RF_{av})}$	– the standard uncertainty of calibration (standard deviation of the multiple IDMS results)
$u_{(hom)}$	– the standard uncertainty of homogeneity of pure substance (standard deviation of the multiple IDMS results)
$u_{(stab)}$	– the standard uncertainty of stability of pure substance (standard deviation of the multiple IDMS results)
$u_{(m_{IS})}$	– the standard uncertainty of the mass (addition the internal standard to the sample)
$u_{(m_s)}$	– the standard uncertainty of the mass of the sample
$u_{(w_{av})}$	– the standard uncertainty of mass fraction of analyte in sample (standard deviation of the multiple IDMS results)
$u_{(m_{sol_1})}$	– the standard uncertainty of the mass (solution after dissolution PVC in THF)
$u_{(m_{al_1})}$	– the standard uncertainty of the mass (the aliquot of solution after dissolution PVC in THF)
$u_{(m_{sol_2})}$	– the standard uncertainty of the mass (solution after dissolution aliquot 1 in THF)
$u_{(m_{al_2})}$	– the standard uncertainty of the mass (the aliquot of solution after dissolution aliquot 1 in THF)

Source of uncertainty	u, % (Di-n-Butyl Phthalate)	u, % (BenzylButyl Phthalate)	u, % (Bis(2-ethylhexyl) Phthalate)
$u_{(m_{IS})}$	0.05	0.05	0.05
$u_{(m_{nat})}$	0.12	0.12	0.12
$u_{(pur)}$	0.3	0.3	0.2
$u_{(m_{cal})}$	0.19	0.19	0.19
$u_{(RF_{av})}$	0.31	0.53	0.65
$u_{(hom)}$	0.5	0.5	0.5
$u_{(stab)}$	0.5	0.5	0.5
$u_{(RF)}$	**0.86**	**0.96**	**1.0**
$u_{(m_{IS})}$	0.24	0.24	0.24
$u_{(m_s)}$	0.05	0.05	0.05
$u_{(w_{av})}$	0.98	0.67	3.6
$u_{(m_{sol_1})}$	0.0005	0.0005	0.0005
$u_{(m_{al_1})}$	0.0085	0.0085	0.0085
$u_{(m_{sol_2})}$	0.0005	0.0005	0.0005
$u_{(m_{al_2})}$	0.0085	0.0085	0.0085
$u_{(w_s)}$	**1.0**	**0.71**	**3.6**
$u_{(rec)}$	2.2	1.6	2.1
Relative Standard Uncertainty	**2.57**	**2.00**	**4.29**
Relative expanded uncertainty	**5,14 (5,2)**	**4,00 (4,0)**	**8,58 (8,6)**

GLHK

13. Estimation of uncertainties for each factor.

Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Uncertainties were estimated based on the contributions from (1) preparation of calibration standard solution, (2) weighing of standards/internal standard in sample blends and calibration blends, (3) method precision and (4) method bias. Detailed breakdowns are given in the attached table.

14. Concentrations of other phthalate esters in the high level pellets (if applicable)

(e.g. compound's name, mass fraction, uncertainty)

n/a

15. Additional information, observations or comments

Nil

BBP in low level samples

Parameters	Units	Typical Values (X)	u(x)	u(x)/X	Percent contribution to total uncertainty	Remarks
Preparation of calibration standard solution	ug/g	14.51765	0.18178	0.01252	23.63%	Standard prepared gravimetrically, density and certifiied purity from CRM were taken into account
Mass of labelled standard in sample blend	g	0.65306	0.00002	0.00003	0.06%	Calibration of balance
Mass of sample in sample blend	g	0.10259	0.00002	0.00020	0.38%	
Mass of primary standard in calibration blend	g	0.22286	0.00002	0.00009	0.18%	
Mass of labelled stadnard in calibration blend	g	0.23835	0.00002	0.00009	0.17%	
Method Precision	-	1.00	0.02131	0.02131	40.22%	Determined from sample analysis and spike
Recovery	-	1.00	0.01874	0.01874	35.36%	Determined from CRM recovery and spike
Relative Combined Uncertainty				0.03102		
Result (mg/kg)		92.42				
Standard Combined Uncertainty			2.87			
Expanded Uncertainty (k=2)			5.73			
Relative Uncertainty (%)			6.20%			
Reported Value with Expanded Uncertainty (k=2)		**92.42**	**±**	**5.73**		

BBP in high level samples

Parameters	Units	Typical Values (X)	u(x)	u(x)/X	Percent contribution to total uncertainty	Remarks
Preparation of calibration standard solution	ug/g	14.96351	0.18736	0.01252	33.48%	Standard prepared gravimetrically, density and certifiied purity from CRM were taken into account
Mass of labelled standard in sample blend	g	0.50160	0.00002	0.00004	0.11%	Calibration of balance
Mass of sample in sample blend	g	0.10141	0.00002	0.00021	0.55%	
Mass of primary standard in calibration blend	g	0.19021	0.00002	0.00011	0.29%	
Mass of labelled stadnard in calibration blend	g	0.19770	0.00002	0.00011	0.28%	
Method Precision	-	1.00	0.00520	0.00520	13.91%	Determined from sample analysis and CRM analysis
Recovery	-	1.00	0.01921	0.01921	51.37%	Determined from CRM recovery and spike recovery
Relative Combined Uncertainty				0.02352		
Result (mg/kg)		418.87				
Standard Combined Uncertainty			9.85			
Expanded Uncertainty (k=2)			19.70			
Relative Uncertainty (%)			4.70%			
Reported Value with Expanded Uncertainty (k=2)		**418.87**	**±**	**19.70**		

DBP in high level samples

Parameters	Units	Typical Values (X)	u(x)	u(x)/X	Percent contribution to	Remarks
Preparation of calibration standard solution	ug/g	15.45927	0.23217	0.01502	34.54%	Standard prepared gravimetrically, density and certifiied purity from CRM were taken into account
Mass of labelled standard in sample blend	g	0.50160	0.00002	0.00004	0.10%	Calibration of balance
Mass of sample in sample blend	g	0.10141	0.00002	0.00021	0.47%	
Mass of primary standard in calibration blend	g	0.19021	0.00002	0.00011	0.25%	
Mass of labelled stadnard in calibration blend	g	0.19770	0.00002	0.00011	0.24%	
Method Precision	-	1.00	0.00686	0.00686	15.77%	Determined from sample analysis and CRM analysis
Recovery	-	1.00	0.02115	0.02115	48.63%	Determined from CRM recovery and spike recovery
Relative Combined Uncertainty				0.02683		
Result (mg/kg)		430.57				
Standard Combined Uncertainty			11.55			
Expanded Uncertainty (k=2)			23.10			
Relative Uncertainty (%)			5.37%			
Reported Value with Expanded Uncertainty (k=2)		**430.57**	**±**	**23.10**		

DEHP in high level samples

Parameters	Units	Typical Values (X)	u(x)	u(x)/X	Percent contribution to	Remarks
Preparation of calibration standard solution	ug/g	31.01849	0.62078	0.02001	49.60%	Standard prepared gravimetrically, density and certifiied purity from CRM were taken into account
Mass of labelled standard in sample blend	g	0.50160	0.00002	0.00004	0.10%	Calibration of balance
Mass of sample in sample blend	g	0.10141	0.00002	0.00021	0.51%	
Mass of primary standard in calibration blend	g	0.19021	0.00002	0.00011	0.27%	
Mass of labelled stadnard in calibration blend	g	0.19770	0.00002	0.00011	0.26%	
Method Precision	-	1.00	0.00611	0.00611	15.14%	Determined from sample analysis and CRM analysis
Recovery	-	1.00	0.01376	0.01376	34.11%	Determined from CRM recovery and spike recovery
Relative Combined Uncertainty				0.02505		
Result (mg/kg)		859.61				
Standard Combined Uncertainty			21.53			
Expanded Uncertainty (k=2)			43.06			
Relative Uncertainty (%)			5.01%			
Reported Value with Expanded Uncertainty (k=2)		**859.61**	**±**	**43.06**		

UME

13. Estimation of uncertainties for each factor.

Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Uncertainty Calculations CCQM-K141/P178

Bottom up approach was used

Sources :
1-Mass of sample intake+IS
2-Native stock solution
3-Calibration
4-Recovery
5-Repeatability

1-Mass of sample intake+Adding of IS

		Value	Standard Measurement Uncertainty
Mass of bovine tissue sample			
	Calibration	m_{tissue} (g)	$m_{calibrationsample}$ (g)
Mass of Tare			
	Calibration	m_{tare} (g)	$um_{calibrationtare}$
Mass of IS			
	Calibration	m_{tare} (g)	$um_{calibrationtare}$

$$u(m_{SI}) = \sqrt{(u_{mcalibsample})^2 + (u_{mcalibtare})^2 + (u_{IS})^2}$$

2-Native Stock Solution

$$u(C_{stocksol}) = \sqrt{(u_{purity})^2 + (u_m)^2}$$

3-Calibration

$$u(RF) = SD$$

4-Uncertainty of Recovery

$$u(R_m) = R_m \sqrt{\left(\frac{u(C_{obs})}{C_{obs}}\right)^2 + \left(\frac{u(C_{cert})}{C_{cert}}\right)^2} \qquad R_m = \frac{\overline{C_{obs}}}{C_{cert}}$$

uC_{obs} standard measurement uncertainty of observed concentration of analyte
C_{obs} observed concentration of analyte
uC_{cert} standard measurement uncertainty of certified concentration of analyte
C_{cert} certified concentration of analyte
R_m Mean recovery

5-Uncertainty of Repeatability

$$u(r) = \frac{SD}{\sqrt{n}}$$

COMBINED STANDARD MEASUREMENT UNCERTAINTY

$$\frac{u_c(Analyte)}{C_{Analyte}} = \sqrt{\left(\frac{u(m_{SI})}{m_{SI}}\right)^2 + \left(\frac{u(C_{NSS})}{C_{NSS}}\right)^2 + \left(\frac{u(RF)}{RF}\right)^2 + \left(\frac{u(R_m)}{R_m}\right)^2 + \left(\frac{u(r)}{r}\right)^2}$$

Uncertainty Budget of BBP (Low Level)

Parameters	Unit Value (X)	u(x)	u(x)/X
Mass of sample intake(g)	0.2	0.000386247	1.93E-03
Native stock solution (mg/kg)	820	31.54	3.85E-02
Calibration	1.00	0.037	3.69E-02
Recovery	0.99	0.025	2.55E-02
Repeatability	1.00	0.01	7.92E-03

Relative Standard Measurement Uncertainty	0.060
Result (mg/kg)	92.2
Combined Standard Measurement Uncertainty	5.5
Expanded Uncertainty (mg/kg) (k=2)	11.0
Relative Mesurement Uncertainty (%)	11.9

Uncertainty Budget of DBP

Parameters	Unit Value (X)	u(x)	u(x)/X
Mass of sample intake (g)	0.2	0.000386247	1.93E-03
Native stock solution (mg/kg)	787	31.52	4.01E-02
Calibration	0.99	0.020	1.99E-02
Recovery	0.96	0.024	2.45E-02
Repeatability	1.00	0.01	8.08E-03

Relative Standard Measurement Uncertainty	0.052
Result (mg/kg)	479.8
Combined Standard Measurement Uncertainty	24.8
Expanded Uncertainty (mg/kg) (k=2)	49.6
Relative Mesurement Uncertainty (%)	10.3

Uncertainty Budget of BBP (High Level)

Parameters	Unit Value (X)	u(x)	u(x)/X
Mass of sample intake (g)	0.2	0.000386247	1.93E-03
Native stock solution (mg/kg)	820	31.54	3.85E-02
Calibration	1.00	0.037	3.69E-02
Recovery	0.99	0.025	2.55E-02
Repeatability	1.00	0.01	7.92E-03

Relative Standard Measurement Uncertainty		0.060
Result (mg/kg)	465.6	
Combined Standard Measurement Uncertainty		27.8
Expanded Uncertainty (mg/kg) (k=2)		55.5
Relative Mesurement Uncertainty (%)		11.9

Uncertainty Budget of DEHP

Parameters	Unit Value(X)	u(x)	u(x)/X
Mass of sample intake (g)	0.2	0.000386247	1.93E-03
Native stock solution (mg/kg)	838.9	31.52	3.76E-02
Calibration	1.19	0.038	3.16E-02
Recovery	1.00	0.030	3.00E-02
Repeatability	1.00	0.01	7.67E-03

Relative Standard Measurement Uncertainty		0.058
Result (mg/kg)	908.5	
Combined Standard Measurement Uncertainty		52.8
Expanded Uncertainty (mg/kg) (k=2)		105.6
Relative Mesurement Uncertainty (%)		11.6

KRISS

13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

$$u(C_{\text{mean}}) = \sqrt{u^2_{\text{s.p.,systematic}} + \frac{s^2}{n}}$$

s: Standard deviations of multiple measurement results from 6 subsamplings
Combined standard uncertainties were obtained by combining systematic uncertainties and random uncertainties as shown above equation
low sample

Systematic	U,sys (rel%)	DOF
Uncertainty of purity of primary standard	0.10%	5
Uncertainty of gravimetric preparation for standard solution	0.90%	3
Uncertainty of gravimetric mixing for calibration isotope standard mixtures.	1.25%	4
Area ratio of native/istd for the calibration standard mixture, observed by GC/MS	1.16%	2
SUM	1.93%	8

high sample

	DBP		BBP		DEHP	
Systematic	U,sys (rel%)	DOF	U,sys (rel%)	DOF	U,sys (rel%)	DOF
Uncertainty of purity of primary standard	0.09%	4	0.10%	5	0.06%	3
Uncertainty of gravimetric preparation for standard solution	0.62%	3	0.90%	3	1.15%	3
Uncertainty of gravimetric mixing for calibration isotope standard mixtures.	1.20%	4	1.25%	4	1.42%	3
Area ratio of native/istd for the calibration standard mixture, observed by GC/MS	0.35%	2	1.16%	2	0.61%	3
SUM	1.39%	6	1.93%	8	1.93%	6

EXHM

The measurement equation is:

$$w_{M,S} = w_{M,C} \times \frac{m_{is,S}}{m_{M,S}} \times \frac{m_{M,C}}{m_{is,C}} \times \frac{R_S}{R_C}$$

where
$w_{M,S}$ = phthalate ester mass fraction in the sample, (*mg/g*)
$w_{M,C}$ = phthalate ester mass fraction in the calibration solution, (mg/g)
$m_{is,S}$ = mass of internal standard solution added to the sample blend, (*g*)
$m_{M,S}$ = mass of sample in sample blend, (*g*)
$m_{M,C}$ = mass of the calibration solution in the calibration blend, (*g*)
$m_{is,C}$ = mass of internal standard solution added to the calibration blend, (*g*)
R_S = measured peak area ratio of the selected ions in the sample blend
R_C = measured peak area ratio of the selected ions in the calibration blend

The equation used to estimate standard uncertainty is:

$$u(w_{BS}) = \sqrt{\left({s_R}/{\sqrt{n}}\right)^2 + \sum \left(C_j u(m_i)\right)^2 + \left(C_j u(w_{MC})\right)^2 + \left(C_j u(R)\right)^2}$$

where s_R is the standard deviation under reproducibility conditions, n the number of determinations and C_i the sensitivity coefficients associated with each uncertainty component. The uncertainty of the peak area ratios was considered to have been included in the estimation of method precision.

Uncertainty estimation was carried out according to JCGM 100: 2008. The standard uncertainties were combined as the sum of the squares of the product of the sensitivity coefficient (obtained by partial differentiation of the measurement equation) and standard uncertainty to give the square of the combined uncertainty. The square root of this value was multiplied by a coverage factor (95% confidence interval) from the t-distribution at the total effective degrees of freedom obtained from the Welch-Satterthwaite equation to give the expanded uncertainty.

The uncertainty budgets for the two CCQM-K133 samples are shown in the pages that follow.

Low level sample, BBP

uncertainty component	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	90.70	1.00	1.02	0.0120	1.02	1.04
mass fraction of BBP in the calibration solution, (*mg/kg*)	637.10	0.14	1.60	0.0025	0.23	0.05
recovery (%)	100.00	-0.91	3.55	0.0355	-3.22	10.38
mass of BBP-d_4 solution added to sample blend, (*g*)	0.88000	103.07	0.00007	0.0001	0.01	0.00
mass of high PVC test material in sample blend, (*g*)	0.50500	-179.61	0.00003	0.0001	0.00	0.00
mass of BBP solution added to calibration blend, (*g*)	0.06970	1301.35	0.00003	0.0004	0.04	0.00
mass of BBP-d_4 solution added to calibration blend, (*g*)	0.86190	-105.24	0.00003	0.0000	0.00	0.00
measured peak area ratio of the selected ions in the sample blend	0.7850	115.55	considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	0.7770	-116.74	estimation of method precision			

result (mg/kg)	90.70
combined standard uncertainty (mg/kg)	3.39
relative standard uncertainty (%)	3.73
effective degrees of freedom	971
coverage factor	2.00
expanded uncertainty (mg/kg)	6.78

High level sample, DBP

uncertainty component	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	453,44	1,00	8,20	0,0181	8,20	67,24
mass fraction of DBP in the calibration solution, (*mg/kg*)	2888,67	0,16	7,30	0,0025	1,15	1,31
recovery (%)	100,00	-4,53	1,542	0,0154	-6,99	48,90
mass of DBP-d_4 solution added to sample blend, (*g*)	0,89000	509,48	0,00007	0,0001	0,04	0,00
mass of high PVC test material in sample blend, (*g*)	0,50000	-906,88	0,00003	0,0001	-0,02	0,00
mass of DBP solution added to calibration blend, (*g*)	0,07650	5927,34	0,00003	0,0004	0,18	0,03
mass of DBP-d_4 solution added to calibration blend, (*g*)	0,86000	-527,26	0,00003	0,0000	-0,02	0,00
measured peak area ratio of the selected ions in the sample blend	0,5750	788,59	considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	0,5800	-781,80	estimation of method precision			

result (mg/kg)	453,44
combined standard uncertainty (mg/kg)	10,84
relative standard uncertainty (%)	2,39
effective degrees of freedom	24
coverage factor	2,00
expanded uncertainty (mg/kg)	21,68

High level sample, BBP

uncertainty component	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	456,59	1,00	7,24	0,0159	7,24	52,42
mass fraction of BBP in the calibration solution, (mg/kg)	3212,41	0,14	8,60	0,0027	1,22	1,49
recovery (%)	100,00	-4,57	1,542	0,0154	-7,04	49,58
mass of BBP-d_4 solution added to sample blend, (g)	0,88000	518,85	0,00007	0,0001	0,04	0,00
mass of high PVC test material in sample blend, (g)	0,50000	-913,17	0,00003	0,0001	-0,02	0,00
mass of BBP solution added to calibration blend, (g)	0,07170	6368,02	0,00003	0,0004	0,19	0,04
mass of BBP-d_4 solution added to calibration blend, (g)	0,86000	-530,92	0,00003	0,0000	-0,02	0,00
measured peak area ratio of the selected ions in the sample blend	3,7583	121,49	considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	3,8800	-117,68	estimation of method precision			

result (mg/kg)	456,59
combined standard uncertainty (mg/kg)	10,18
relative standard uncertainty (%)	2,23
effective degrees of freedom	31
coverage factor	2,00
expanded uncertainty (mg/kg)	20,35

High level sample, DEHP

uncertainty component	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	$C_i \times u_i$	$(C_i \times u_i)^2$
method precision	905,28	1,00	9,00	0,0099	9,00	81,00
mass fraction of DEHP in the calibration solution, (mg/kg)	5219,61	0,17	13,40	0,0026	2,32	5,40
recovery (%)	100,00	-9,05	1,542	0,0154	-13,96	194,92
mass of DEHP-d_4 solution added to sample blend, (g)	0,88000	1028,72	0,00007	0,0001	0,07	0,01
mass of high PVC test material in sample blend, (g)	0,50000	-1810,56	0,00003	0,0001	-0,05	0,00
mass of DEHP solution added to calibration blend, (g)	0,08680	10429,47	0,00003	0,0003	0,31	0,10
mass of DEHP-d_4 solution added to calibration blend, (g)	0,86000	-1052,65	0,00003	0,0000	-0,03	0,00
measured peak area ratio of the selected ions in the sample blend	2,4214	373,87	considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	2,4800	-365,03	estimation of method precision			

result (mg/kg)	905,28
combined standard uncertainty (mg/kg)	16,78
relative standard uncertainty (%)	1,85
effective degrees of freedom	96
coverage factor	2,00
expanded uncertainty (mg/kg)	33,55

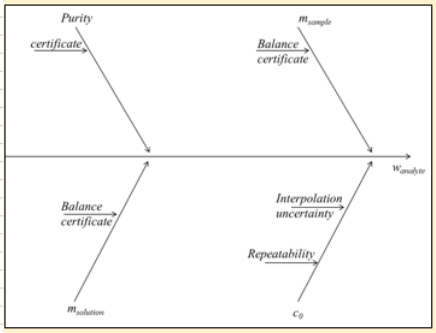
13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

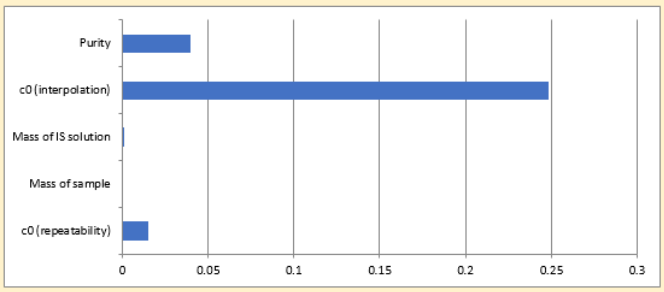
Step 1: Mass fraction of the analyte in diluted solution. Example of the first subsample for BBP

Dissociating te equation " W_{dil} "

$$w_{dil} = c_0 * \frac{m_{IS} * P}{m_{Aliq}} \longleftarrow c_0 = \left(\frac{A - b_0}{b_1}\right)$$

Ishikawa Diagram





Uncertainty sources	Value	Type	Distribution	Standard uncertainty	Sensitivity coeff.	Uncertainty comp.
c0 (repeatability)	232,0383	A	Normal	1,20E+00	1,27E-02	1,53E-02
Mass of sample	2,54214	B	Normal	1,00E-05	-1,16E+00	1,16E-05
Mass of IS solution	0,03224	B	Normal	1,00E-05	9,13E+01	9,13E-04
Angular coefficient (b1)	0,00217333	A	Normal	6,43E-05	-	
Linear coefficient (b0)	-0,048777565	A	Normal	1,93E-02	-	
c0 (interpolation)	232,0383	A	Normal	1,96E+01	1,27E-02	2,48E-01
Purity	1,00000	B	Normal	1,34E-02	2,94E+00	3,94E-02
					Combined uncertainty	0,251737759

Step 2: Dilution Factor

m_{PVC} (g)	m_{sol} (g)	DF	u_{DF}	W_{dil}	u_{dil}
0,3047	11,2030	36,7673	0,0012	2,9428	0,2517

m_{PVC} = mass of PVC pallet
m_{sol} = mass of PVC initial solution
DF = Dilution factor
u_{DF} = Combinated uncertainty of DF
W_{dil} = Mass fraction of diluted solution of PVC
u_{dil} = Combinated uncertainty of diluted solution of PVC
W_{PVC} = Mass fraction of PVC pellet
u_{PVC} = Combinated uncertainty of PVC pellet

$$u_{PVC} = W_{PVC} \cdot \sqrt{\left(\frac{u_{dil}}{W_{dil}}\right)^2 + \left(\frac{u_{DF}}{DF}\right)^2}$$

W_{PVC}	u_{PVC}
108,1975	9,2557

Step 3: Combined Result (all six subsamples)

$$d_i = x_i - \mu \longrightarrow u_c = \sqrt{\frac{\left(\sum_{j=1}^{m}(d_i)^2/m - 1\right) + \left(\sum_{j=1}^{m} u_{(y_j)}^2/m\right)}{m}}$$

d_i = difference between each measurement and the mean of all
x_i = each measurement
μ = mean of the measurements included in the combination
m = number of measurements
$u_{(yj)}$ = combined uncertainty of each measurement

Overall Mean of Results (mg/kg)	Combined Standard Uncertainty (mg/kg)	Expanded uncertainty (mg/kg)
114	4	9

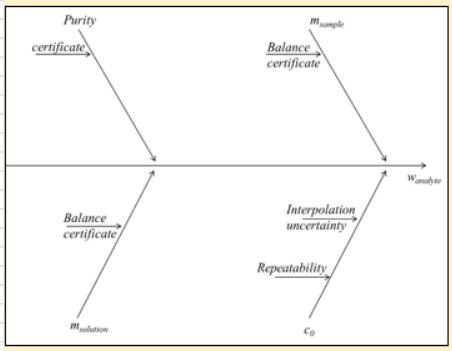
13. Estimation of uncertainties for each factor.
Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

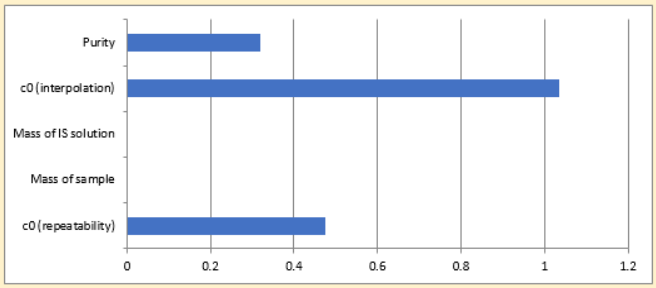
Step 1: Mass fraction of the analyte in diluted solution. Example of the first subsample for DEHP. DBP and BBP uncertainty budget follows the same approach.

Dissociating te equation " W_{dil} "

$$w_{dil} = c_0 * \frac{m_{IS} * P}{m_{Aliq}} \longleftarrow c_0 = \left(\frac{A - b_0}{b_1}\right)$$

Ishikawa Diagram





Uncertainty sources	Value	Type	Distribution	Standard uncertainty	Sensitivity coeff.	Uncertainty comp.
c0 (repeatability)	150,0135	A	Normal	2,48E+00	1,92E-01	4,75E-01
Mass of sample	1,45518	B	Normal	1,00E-05	-1,98E+01	1,98E-04
Mass of IS solution	0,27924	B	Normal	1,00E-05	1,03E+02	1,03E-03
Angular coefficient (b1)	0,000925219	A	Normal	1,68E-05	-	
Linear coefficient (b0)	-0,015317376	A	Normal	2,57E-03	-	
c0 (interpolation)	150,0135	A	Normal	5,39E+00	1,92E-01	1,03E+00
Purity	1,00000	B	Normal	1,11E-02	2,88E+01	3,19E-01
					Combined uncertainty	1,182396126

Step 2: Dilution Factor

m_{PVC} (g)	m_{sol} (g)	DF	u_{DF}	W_{dil}	u_{dil}
0,3212	11,2325	34,9704	0,0011	28,7867	1,1824

m_{PVC} = mass of PVC pallet
m_{sol} = mass of PVC initial solution
DF = Dilution factor
u_{DF} = Combinated uncertainty of DF
W_{dil} = Mass fraction of diluted solution of PVC
u_{dil} = Combinated uncertainty of diluted solution of PVC
W_{PVC} = Mass fraction of PVC pellet
u_{PVC} = Combinated uncertainty of PVC pellet

$$u_{PVC} = W_{PVC} \cdot \sqrt{\left(\frac{u_{dil}}{W_{dil}}\right)^2 + \left(\frac{u_{DF}}{DF}\right)^2}$$

W_{PVC}	u_{PVC}
1006,6818	41,3489

Step 3: Combined Result (all six subsamples)

$$d_i = x_i - \mu$$

d_i = difference between each measurement and the mean of all
x_i = each measurement
μ = mean of the measurements included in the combination
m = number of measurements
$u_{(yj)}$ = combined uncertainty of each measurement

$$u_c = \sqrt{\frac{\left(\sum_{j=1}^{m}(d_i)^2/m - 1\right) + \left(\sum_{j=1}^{m} u_{(y_j)}^2/m\right)}{m}}$$

Overall Mean of Results (mg/kg)	Combined Standard Uncertainty (mg/kg)	Expanded uncertainty (mg/kg)
976	17	34

13. Estimation of uncertainties for each factor.

Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

BBP uncertainty extimation for low sample.

BBP		x	u	u/x	u/x^2	
W_z	[native] solution added to calibration blend (ug/g) (x= ug/g of the spiking solution; u = traceability transfer/value assignment of Restek calibrant from NIM CRM calibrant)	117,8	2,4765	0,0210246	0,000442	ug/g
m_z	weight native solution added to calibration blend (g) (x= average g native added to cals; u = balance certificate uncertainty)	0,0839	0,00002	0,0002384	5,685E-08	g
m_y	weight of Isotope solution added to sample (g) (x= average g isotope added to samples; u = balance certificate uncertainty)	0,0959	0,00002	0,0002086	4,35E-08	g
m_{yo}	weight of Isotope solution added to calibration blend (g) (x= average g isotope added to calibration blends; u = balance certificate uncertainty)	0,0964	0,00002	0,0002076	4,308E-08	g
m_x	Mass of sample analysed (x= average mass of sample analysed; u = balance certificate uncertainty)	0,1111	0,00002	0,0001801	3,243E-08	g
R_B	ratio of peaks areas of native/ labelled in the samples (x= average area ratio across all samples; u = ESDM of the ratio)	1,129	0,02930	0,0259698	0,0006739	
R_{BC}	ratio of peaks areas of RM native/labelled in the calibration blend (x= average area ratio across all samples; u = ESDM of the ratio)	1,019	0,0005	0,0004765	2,27E-07	
Precision	Repeat measurements (x= average value; u = esdm across repeats)	103,1	0,8595	0,0083391	6,954E-05	ug/g
					0,0011859	
					3,5	u
					7,1	U (k= 2)
					6,9	Rel U (%)

W_z		x	u	u/x	u/x^2	
[CRM]	concentration of the Restek calibrant solution (x = calculated by value transfer from NIM CRM; u = calculated considering uncertainties as those listed in the table above)	2394,8	5,0E+01	0,0210243	0,000442	ug/g
stock	dilution (mass of aliquot)	0,19	0,000020	0,0001062	1,129E-08	
	dilution (mass of solvent)	3,83	0,000020	5,225E-06	2,73E-11	
					2,4765	ug/g

13. Estimation of uncertainties for each factor.

Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Estimation of uncertainty for DBP in the high sample, uncertainties for the BBP and DEHP analytes were estimated in the same way

DBP		x	u	u/x	u/x^2	
W_z	[native] solution added to calibration blend (ug/g) (x= ug/g of the spiking solution; u = traceability transfer/value assignment of Restek calibrant from NIM CRM calibrant)	258,21	5,38	0,020835718	0,00043413	ug/g
m_z	weight native solution added to calibration blend (g) (x= average g native added to cals; u = balance certificate uncertainty)	0,2504	0,00002	7,98743E-05	6,3799E-09	g
m_y	weight of Isotope solution added to sample (g) (x= average g isotope added to samples; u = balance certificate uncertainty)	0,154	0,00002	0,000129828	1,6855E-08	g
m_{yo}	weight of Isotope solution added to calibration blend (g) (x= average g isotope added to calibration blends; u = balance certificate uncertainty)	0,155	2,0E-05	0,000128891	1,6613E-08	g
m_x	Mass of sample analysed (x= average mass of sample analysed; u = balance certificate uncertainty)	0,125	0,00002	0,000159744	2,5518E-08	g
R_B	ratio of peaks areas of native/labelled in the samples (x= average area ratio across all samples; u = ESDM of the ratio)	1,231	0,0174	0,014120374	0,00019938	
R_{BC}	ratio of peaks areas of RM native/labelled in the calibration blend (x= average area ratio across all samples; u = ESDM of the ratio)	1,298	0,0074	0,005680766	3,2271E-05	
Precision	Repeat measurements (x= average value; u = esdm across repeats)	434,3	0,4863	0,001119722	1,2538E-06	
					0,0006671	
					11,2	u
					22,4	U (k=2)
					5,17	Rel U

W_z		x	u	u/x	u/x^2	
[CRM]	concentration of the Restek calibrant solution (x = calculated by value transfer from NIM CRM; u = calculated considering uncertainties as those listed in the table above)	2471,7	51,5	0,020835525	0,00043412	ug/g
stock	dilution (mass of aliquot)	0,22	0,000020	8,96459E-05	8,0364E-09	
	dilution (mass of solvent)	5,04	0,000020	3,96918E-06	1,5754E-11	
					5,3800	ug/g (u)

Appendix G: Core Competency Claimed by Participant

Table G-1 Core Competency claimed by NIM in CCQM-K133

CCQM-K133	***NIM***	**polar and non-polar analytes in plastics - Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		High pure material, DBP from Sigma, BBP from Aldrich, DEHP from Dr.E.
Identity verification of analyte in calibration material. #	√	GCMS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	√	GC-FID, HPLC-DAD
For calibrants which are a calibration solution: Value-assignment method(s). #	√	weighing
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	GC-MS
Extraction of analyte(s) of interest from matrix	√	Ultrasound-assisted Extr.30min, THF
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	precipitated by adding Methanol, centrifuge the solution at 15000r/min at 4℃ for 10min
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS
Calibration approach for value-assignment of analyte(s) in matrix	√	GC-IDMS/MS, single-point
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

Table G-2 Core Competency claimed by VNIIM in CCQM-K133

CCQM-K133	***VNIIM***	**polar and non-polar analytes in plastics - Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Commercially available highly-pure substances from Sigma-Aldrich:Di-n-Butyl Phthalate #524980, Benzyl Butyl Phthalate #308501, Bis(2-EthylHexyl)Phthalate #D201154
Identity verification of analyte in calibration material. #	√	GC/MS (NIST 14)
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	√	The purity of highly-pure substances was determined in-house by mass balance approach. Structurally related organics: GC/FID, GC/MS, LC/UV, LC/LS Moisture: Karl Fisher Titration VOC: GC/FID, GC/MS Non-volatiles: ICP/MS; Vacuum evaporation
For calibrants which are a calibration solution: Value-assignment method(s). #	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	GC/MS (NIST 14), RT
Extraction of analyte(s) of interest from matrix	√	Matrix dissolving in the organic solvent (TGF), ultrasonic extraction
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Matrix precipitation by adding 1 ml Hexane Filtration through nylon syringe filter (0,22um)
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	√	Bracketing IDMS
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Measuring by using Reference Material CPEX CRM PVC001 Measuring by using SRM NIST 3074
Other	N/A	

Table G-3 Core Competency claimed by GLHK in CCQM-K133

CCQM-K133	***GLHK***	**polar and non-polar analytes in plastics** **- Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		The following certified reference materials in solutions were used as the calibrants. DBP: GBW (E) 100224 (16001) BBP: GBW (E) 100226 (17001) DEHP: GBW (E) 100223 (17001)
Identity verification of analyte in calibration material. #	✓	Counter checked with NIST SRM 3074
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	N/A	Nil
For calibrants which are a calibration solution: Value-assignment method(s). #	N/A	Nil
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	The analytes in sample were identified by LC-MS/MS/ GC-MS/MS/ GC-MS (Full scan)
Extraction of analyte(s) of interest from matrix	✓	The analytes were extracted according to the CPSC method CPSC-CH-C1001-09.3 using THF until the sample was completely dissolved
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	Methanol was used to precipitate the plastics from the extract
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	Nil
Analytical system	✓	LC-QqQMS, GC-QqQMS, GC-qMS
Calibration approach for value-assignment of analyte(s) in matrix	✓	IDMS with bracketing method
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	GC-MS/MS was used for verification
Other	N/A	Nil

Table G-4 Core Competency claimed by UME in CCQM-K133

CCQM-K133	**TUBITAK UME**	**polar and non-polar analytes in plastics - Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		*Highly pure substances were used* *Phthalic acid, benzybutyl ester (BBP), LGC/Dr. Ehrenstorfer,* *Phthalic acid, bis-butyl ester (DBP), LGC/Dr. Ehrenstorfer,* *Phthalic acid, bis-2-ethylhexyl ester (DEHP), LGC/Dr. Ehrenstorfer,*
Identity verification of analyte in calibration material. #	√	*GC-MS/MS and IDMS*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	√	*The purity determination of BBP, DBP and DEHP was performed by qNMR by using maleic acid IS in traceability chain of UME-CRM-1301.* *Phthalic acid, benzybutyl ester (BBP), (97.120±0.373)%* *Phthalic acid, bis-butyl ester (DBP), (99.224±0.314)%* *Phthalic acid, bis-2-ethylhexyl ester (DEHP), (99.706±0.284)%*
For calibrants which are a calibration solution: Value-assignment method(s). #	N/A	-
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	*Retention time* *Parent/product ion*
Extraction of analyte(s) of interest from matrix	√	*Dissolution and precipitation technique*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	-
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	-
Analytical system	√	*GC-MS/MS*
Calibration approach for value-assignment of analyte(s) in matrix		*a) IDMS* *b) single-point calibration*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	-
Other	N/A	-

Table G-5 Core Competency claimed by KRISS in CCQM-K133

CCQM-K133	*KRISS*	**Low-polarity and high-polarity analytes in plastic**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Neat commercial calibrants for DBP, BBP, and DEHP were from TCI (Tokyo Chemical Industry). Purities of them were assayed by KRISS with mass-balance method and verified with qNMR.
Identity verification of analyte in calibration material.	√	ID-GC/MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).	√	The purity of the primary materials was determined following protocols maintained in KRISS. GC-FID used for the analysis of structurally related impurities, Karl-Fischer Coulometry for water content, thermogravimetric analysis for non-volatile impurities, headspace-GC/MS for reidual solvents. As a result, the purity of each was 99.53% ± 0.26% (DBP), 98.37% ± 0.26% (BBP), and 99.52 ± 0.19 % (DEHP)
For calibrants which are a calibration solution: Value-assignment method(s).	√	Calibration solutions were gravimetrically prepared in KRISS and verified by cross-checking of multiple calibration solutions.
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	GC retention time, mass spec ion ratios, comparison of GC/MS measurement results by high resolution SIM.
Extraction of analyte(s) of interest from matrix	√	dissolution with Tetrahydrofuran (THF) and precipitation with methanol
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)		None
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)		None
Analytical system		GC/MS, resolution = 10000 (HR)
Calibration approach for value-assignment of analyte(s) in matrix	√	Gravimetrically prepared calibration solution was used as a calibrant. For ID-GC/MS analysis, calibration bland was prepared by gravimetrically mixing the calibration solution and the internal standard solution. IDMS with exact matching single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	KRISS CRM 113-03-006
Other		

Table G-6 Core Competency claimed by EXHM in CCQM-K133

CCQM-K133	*EXHM*	**Low-polarity and high-polarity analytes in plastic- Phthalate esters in Polyvinyl Chloride (PVC)**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		*NMIJ CRM 4601-a* *own calibration solutions*
Identity verification of analyte(s) in calibration material.#	✓	*NMR*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*qNMR* *purities assigned against NMIJ 4601-a* *DBP, BBP, DEHP*
For calibrants which are a calibration solution: Value-assignment method(s).	✓	*gravimetrically*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*retention time, MRMs, ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*dissolution-precipitation/ centrifugation*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	*N/A*	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	*N/A*	
Analytical system	✓	*GC-IT-MS*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*single-point calibration, IDMS at exact matching*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*used HPLC-UV to verify the measurements*
Other	✓	*used NMIJ CRM 8152-a to assess recovery*

Table G-7 Core Competency claimed by INMETRO in CCQM-K133

CCQM-K133	***INMETRO***	**polar and non-polar analytes in plastics - Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		SRM NIST 3074 - Phthalates in Methanol
Identity verification of analyte in calibration material. #	✓	GC-MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	N/A	
For calibrants which are a calibration solution: Value-assignment method(s). #	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time, mass spectrum (m/z)
Extraction of analyte(s) of interest from matrix	✓	Sample dissolution with THF; polymer precipitation with Hexane
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	X	Internal standard calibration
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

The result for INMETRO for BBP in the LCPVC did not overlap with the zero line for their DoE. INMETRO did not use IDMS and this is likely to have been the cause of this deviation.

Table G-8 Core Competency claimed by NMISA in CCQM-K133

CCQM-K133	***NMISA***	**polar and non-polar analytes in plastics** **- Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		NIM CRMs were used to value assign ISO guide 34 accredited calibrants
Identity verification of analyte in calibration material. #	√	Identity was confirmed by comparing mass spectra and retention time of calibrant against NIM CRM
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	N/A	
For calibrants which are a calibration solution: Value-assignment method(s). #	√	Single point dIDMS using NIM CRM
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	The retention time and mass spectra of the target analytes was compared to the standard using GC TOFMS
Extraction of analyte(s) of interest from matrix	√	Liquid-solid extraction by dissolution (sonication)of pellets in THF
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Polymer was precipitated with the addition of methanol and separated by centrifugation
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	Leco Pegasus 4D GC-TOFMS
Calibration approach for value-assignment of analyte(s) in matrix	√	Double isotope dilution mass spectrometry bracketing
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other		

Table G-9 Core Competency claimed by NMIJ in CCQM-K133

CCQM-K133	***NMIJ***	**polar and non-polar analytes in plastics - Phthalate esters in Polyvinyl Chloride (PVC) -**
Scope of Measurement: Successful participation in CCQM-K133 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 100 g/mol to 800 g/mol, in a plastic matrix ranging in mass fraction from 10 mg/kg to 5000 mg/kg.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	Highly-pure CRMs (NMIJ CRM 4023-b, 4024-a and 4029-a)
Identity verification of analyte in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s). #	✓	Certified by mass balance approach (GC, HPLC and Karl Fischer titration)
For calibrants which are a calibration solution: Value-assignment method(s). #	N/A	-
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	GC retention time and mass spectra
Extraction of analyte(s) of interest from matrix	✓	Samples were dissolved into THF.
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	Matrix was precipitated with hexane, and the supernatant was recovered by centrifuge
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	IDMS with triple-point calibration using gravimetrically prepared calibration solutions (IS: D_4-labeled respective phthalate esters)
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

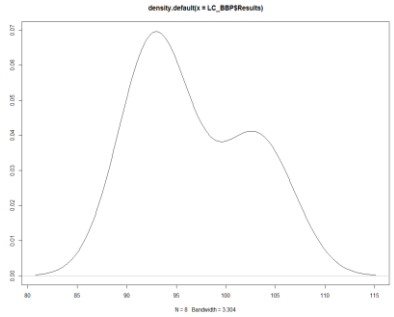
Appendix H: Analysis of Dispersions

LCPVC BBP

Chi square: 41.3

Critical: 14.1

Conclusion: Excess Dispersion

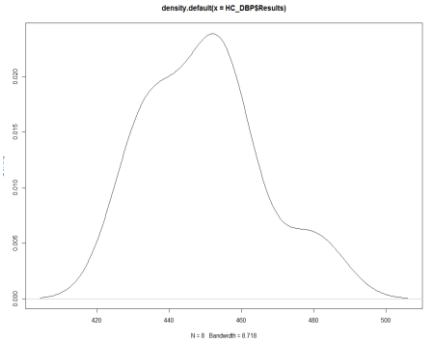


HCPVC DBP

Chi square: 13.7

Critical: 14.1

Conclusion: No excess dispersion

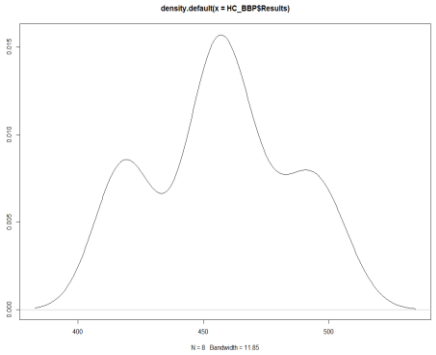


HCPVC BBP

Chi square: 44.9

Critical: 14.1

Conclusion: Excess Dispersion

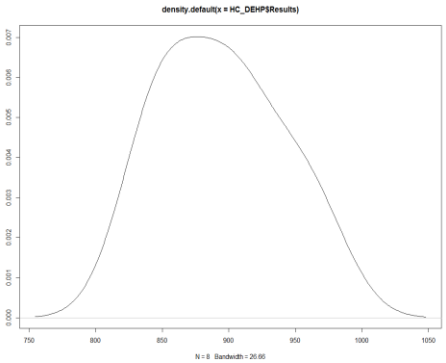


HCPVC DEHP

Chi square: 27.6

Critical: 14.1

Conclusion: Excess Dispersion



	DSL Mean, mg/kg	DSL standard Uncertainty, mg/kg	HB Mean, mg/kg	HB standard Uncertainty, mg/kg
LCPVC BBP	96.75	1.77	96.7	2.2
HCPVC DBP	445.61	4.82	445.3	5.5
HCPVC BBP	455.41	9.03	455.8	11.8
HCPVC DEHP	883.61	14.04	884.6	18.0