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Determination of phthalates in food simulant A solution

FCM-19/02 Proficiency Testing Report

F. Cordeiro, L. Karasek, A. Cizek-Stroh,
J. Charoud-Got, P. Robouch and E. Hoekstra

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268-PT Accredited by the
Belgian Accreditation Body (BELAC)

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Executive summary

The European Union Reference Laboratory for Food Contact Materials (EURL-FCM) organised a proficiency testing round (FCM-19/02) for the determination of four selected phthalates in a food simulant A solution (ethanol/water 10 % v/v) to support Regulation 10/2011 on plastic materials and articles intended to come into contact with food. This proficiency testing round was open to National Reference Laboratories (NRLs) and Official Control Laboratories (OCLs).

A food simulant A solution, spiked with bis(2-ethylhexyl) ester (DEHP), dibutyl ester (DnBP), diallyl ester (DAP) and benzyl butyl ester (BBP), was used as test item. The homogeneity and stability of the test item was evaluated and the assigned values were derived from the results reported by the EURL-FCM. Unfortunately three of the phthalates investigated proved to be unstable after ampouling, while the content of DEHP was shown to be adequately homogeneous and stable.

Twenty three NRLs from 23 EU Member States and nine OCLs (from four EU Member States plus Switzerland) registered to the exercise. Three laboratories did not report their results.

Results reported for DEHP (only) were rated using z and zeta (ζ) scores in accordance with ISO 13528:2015. A relative standard deviation for proficiency assessment (σ_{pt}) of 15 % of the respective assigned value was set based on the perception of experts.

The overall performance of the participants (63 % satisfactory performance) may indicate that some improvements are needed in the determination of this substance in order to demonstrate the measurement capability of NRLs in monitoring the selected phthalate in the frame of Regulation (EC) 10/2011.

The majority of the laboratories (62 %) reported realistic measurement uncertainty evaluations.

List of abbreviations and symbols

BBP	Benzyl butyl phthalate
DG SANTE	Directorate General for Health and Food Safety
DAP	Diallyl phthalate
DEHP	Bis(2-ethylhexyl) ester
DnBP	Di-n-butyl phthalate
EURL-FCM	European Union Reference Laboratory for Food Contact Materials
GUM	Guide for the Expression of Uncertainty in Measurement
HPLC-DAD	High Performance Liquid Chromatography coupled with Diode Array Detection
ISO	International Organization for Standardization
ID-GC/MS	Isotope dilution gas chromatography coupled with mass spectrometry
JRC	Joint Research Centre
LC-MS/MS	Liquid Chromatography-tandem mass spectrometry
NRL	National Reference Laboratory
OCL	Official Control Laboratory
PT	Proficiency Testing
SML	Specific migration limit

k	coverage factor
σ_{pt}	standard deviation for proficiency assessment
$u(x_i)$	calculated standard measurement uncertainty (of participant "i")
$u(x_{pt})$	standard measurement uncertainty of the assigned value
u_{char}	(standard) measurement uncertainty contribution due to characterisation
u_{hom}	(standard) measurement uncertainty contribution due to inhomogeneity
u_{st}	(standard) measurement uncertainty contribution due to instability
$U(x_i)$	reported expanded uncertainty by participant "i"
$U(x_{pt})$	expanded uncertainty of the assigned value
x_i	reported mean value by participant "i"
x_{pt}	assigned value
z	z score
ζ	zeta score

1 Introduction

The European Union Reference Laboratory for Food Contact Materials (EURL-FCM), hosted by the Joint Research Centre (JRC) of the European Commission, organised a proficiency testing round (PT) for the determination of four phthalates in a food simulant A solution to support Commission Regulation (EC) No 10/2011 [1].

This PT was agreed with the Directorate General for Health and Food Safety (DG SANTE) as part of the EURL-FCM annual work programme 2019, thus complying with the mandate set in Regulation (EU) 2017/625 [2]. The PT was open to National Reference Laboratories (NRLs) and to Official Control Laboratories (OCLs) willing to participate.

This report summarises the outcome of the PT.

2 Scope

The present PT aims to assess the performance of NRLs and OCLs in the determination of the mass fractions of di-*n*-butyl phthalate (DnBP), diallyl phthalate (DAP), benzyl butyl phthalate (BBP) and bis(2-ethylhexyl) phthalate (DEHP) in a food simulant A (10 % v/v ethanol/water) solution.

Unfortunately three of the phthalates investigated proved to be unstable after ampouling, while the content of DEHP was shown to be adequately homogeneous and stable. Hence only the results reported for DEHP were evaluated.

This PT, organised in line with ISO 17043:2010 [3], is identified as "**FCM-19/02**".

3 Set up of the exercise

3.1 Quality assurance

The JRC Unit hosting the EURL-FCM is accredited according to:

- ISO/IEC 17025:2005 (certificate number: BELAC 268-TEST); and
- ISO/IEC 17043:2010 (certificate number: BELAC 268-PT, proficiency test provider)

The reported results were evaluated following the relevant administrative and logistic procedures.

3.2 Confidentiality

The procedures used for the organisation of PTs guarantee that the identity of the participants and the information provided by them is treated as confidential. The participants in this PT received a unique laboratory code used throughout this report. However, the laboratory codes of NRLs appointed in line with Regulation (EU) 2017/625 [2] may be disclosed to DG SANTE upon request for the purpose of an assessment of their (long-term) performance. Similarly laboratory codes of appointed OCLs may be disclosed to their respective NRL upon request.

3.3 Time frame

The organisation of the FCM-19/02 PT round was announced by invitation letters to NRLs and OCLs on April 05, 2019 (Annex 1). The registration deadline was set to April 30, 2019. Samples were sent to participants on May 20, 2019. The deadline for reporting of results was set to July 26, 2019.

3.4 Distribution

Each participant received:

- One sealed ampoule in amber glass containing 20 ml of food simulant A solution spiked with the four selected phthalates;
- The "Test item accompanying letter" (Annex 2); and
- The "Confirmation of receipt form" to be sent back to the PT coordinator after receipt of the test item (Annex 3).

The ampules were inserted into plastic containers and dispatched in cardboard boxes under ambient conditions.

3.5 Instructions to participants

Detailed instructions were given to participants in the "Test item accompanying letter" mentioned above (Annex 2).

The measurands were defined as

- "The mass fraction (mg kg^{-1}) of each of the four selected phthalates as described above in the food simulant A solution",
- "The concentration (mg L^{-1}) of each of the selected phthalates in the food simulant A solution".

Participants were asked to check whether the test item was undamaged after transport, and to report the "Confirmation of receipt form" (Annex 3).

Participants were asked to perform two or three independent measurements and to report their calculated mean (x_i) and the associated expanded measurement uncertainty ($U(x_i)$) together with the coverage factor (k) and the analytical technique used for analysis.

Results had to be reported in the same format (e.g. number of significant figures) as normally reported to customers. Since the homogeneity study was performed with intakes of 10 g (gravimetrically prepared) of the test item, this amount was recommended as the minimum sample intake.

Participants were informed that the procedure used for the analysis should resemble as closely as possible their routine procedures for this type of matrix/analytes and mass fraction or concentration levels.

Participants received an individual code to access the on-line reporting interface, to report their measurement results and to complete the related questionnaire. The latter was designed to gather additional information related to measurements and laboratories (Annex 4).

Random laboratory codes were attributed and communicated to participants by e-mail.

4 Test item

4.1 Preparation

The test material was prepared gravimetrically by spiking 5 L of food simulant A solution (10 % v/v ethanol/water) with a phthalate standard solution containing the four selected analytes at the relevant concentration levels. These concentration levels were selected to be around their respective specific migration limit (SML) as set in the European legislation [1]. The standard solution was prepared from neat reference materials purchased from Sigma - Aldrich (St. Louis, MO, USA). Single standard stock solutions of

each analyte were produced by weighing of neat substances on an analytical balance followed by dissolution in gravimetrically added ethanol. A mixed standard solution in ethanol was prepared gravimetrically from these standard stock solutions containing the individual analytes.

After spiking, the test material was homogenised by intensive stirring. Aliquots of about 20 mL of the test material were flame sealed under inert atmosphere in 25 mL amber glass ampoules.

The EURL-FCM and the Reference Material Unit of the JRC prepared the test items. In order to avoid contamination of the test material by phthalates (present in solvents and in the laboratory environment), all solvents including hexane, ethanol and water were treated prior to their use with 20 g/L of aluminium oxide, which was previously activated in an oven for at least 6 hours at 400 °C. All amber glass ampoules were kept for at least 12 hours in an oven at 400 °C prior to their use, and consequently stored in desiccators over activated aluminium oxide.

4.2 Analytical method used for characterisation

The mass fractions of the four selected phthalates were determined by formulation (gravimetrically) and confirmed by the EURL-FCM using a single-laboratory validated method based on isotope dilution gas chromatography coupled with mass spectrometry (ID-GC-MS).

In brief, a sample aliquot (10 g) was placed in a 50 mL centrifuge tube, 50 µL of the isotope labelled internal standard solution in ethanol was added to each sample. The mixture was shaken vigorously for 30 min in order to equilibrate the internal standard with the test sample. Afterwards, 6 mL of ethanol and 10 mL of hexane were added and shaken vigorously (vortex) for 15 min. The mixture was then left in an ultrasonic bath for 30 min and centrifuged for 5 min at 4000 rpm to accelerate phase separation. An aliquot was taken from the organic phase and transferred into a 10 mL test tube. The solvent was evaporated under a stream of nitrogen at 35 °C until about one mL of final extract was left. Evaporation to dryness was avoided as well as exceeding a temperature of 40 °C. The pre-concentrated sample extract was then transferred into an autosampler vial, and analysed by GC-MS with electron ionisation in selected ion monitoring mode. A procedural blank sample was prepared and analysed in each sample batch for the proper evaluation of possible contamination.

4.3 Homogeneity and stability

Measurements for the homogeneity and stability studies and the statistical treatment of data were performed by the EURL-FCM.

The assessment of homogeneity was performed after the preparation of the test item and before distribution to participants. Ten units (sealed ampoules) were randomly selected and analysed in duplicate.

Results were evaluated according to ISO 13528:2015 [4]. The test item proved to be adequately homogeneous for bis(2-ethylhexyl)phthalate (DEHP, Annex 5). The contribution from homogeneity (u_{hom}) to the standard uncertainty of the assigned value ($u(x_{pt})$) was calculated using SoftCRM [5].

Three additional samples of the test item were analysed for DEHP (only) in duplicate after the reporting deadline. Results were then compared to those obtained from the homogeneity study. This stability study confirmed that the test item was adequately stable for the content of DEHP (i) at 20 °C, over the whole period of time of the PT (9 weeks, from the value assignment till the deadline for reporting results, Annex 5), (ii) for 1 week at 40 °C (simulating extreme conditions which may occur during transport,

results not shown). Hence, the uncertainty contribution due to instability was set to zero (u_{st} = 0) for the investigated analyte (Annex 5).

A significant chemical instability was observed for BBP within two weeks after sealing the test material in the amber glass ampoules. At a later stage of the study an instability was also detected for the two other phthalates (DnBP and DAP). Therefore no value could be assigned for the content of these substances.

5 Assigned value and corresponding measurement uncertainty

5.1 Assigned value

Table 1 presents the assigned value (x_{pt}) of the mass fraction of DEHP (expressed in mg kg^{-1}) determined by the EURL-FCM together with the relevant parameters needed for scoring: namely, its associated expanded uncertainty ($U(x_{pt})$ calculated with a coverage factor k=2), and the standard deviation for the PT assessment (σ_{pt}).

5.2 Associated measurement uncertainty

The associated standard uncertainty of the assigned value ($u(x_{pt})$) was calculated following the law of uncertainty propagation, combining the standard measurement uncertainty of the characterization (u_{char}, estimated by formulation) with the standard uncertainty contributions from homogeneity (u_{hom}, s_s in Annex 5) and stability (u_{st}), in compliance with ISO 13528:2015 [4]:

$$u(x_{pt}) = \sqrt{u_{char}^2 + u_{hom}^2 + u_{st}^2} \qquad \text{Eq. 1}$$

where u_{char} was derived combining the uncertainty contributions of weighing with the standard uncertainty associated with the certified purity of the substance [DEHP].

5.3 Standard deviation for proficiency assessment, σ_{pt}

A relative standard deviation for PT assessment (σ_{pt}) of 15 % of the respective assigned value for DEHP was selected based on expert judgment [4].

Table 1: Assigned range related to the determination of the selected phthalate in food simulant solution A.

Phthalate	$x_{pt} \pm U(x_{pt})$, $k=2$ in mg kg^{-1}	σ_{pt} in mg kg^{-1}	$u(x_{pt})/\sigma_{pt}$
DEHP	0.943 ± 0.028	0.141	0.10

6 Evaluation of results

6.1 Scores and evaluation criteria

Since the standard uncertainty of the assigned value $u(x_{pt})$ was smaller than the acceptance criterion of $0.3\sigma_{pt}$ set by ISO 13238:2015 [4], the individual laboratory performances were expressed in terms of z and ζ performance scores [4]:

$$z = \frac{x_i - x_{pt}}{\sigma_{pt}} \qquad \text{Eq. 2}$$

$$\zeta = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}} \qquad \text{Eq. 3}$$

where: $u(x_i)$ is the standard measurement uncertainty reported by a participant;

$u(x_{pt})$ is the standard measurement uncertainty of the assigned value;

σ_{pt} is the standard deviation for proficiency assessment.

The interpretation of the z and ζ performance scores is done according to ISO 13528:2015 [4]:

|score| ≤ 2	satisfactory performance	(green in Annexe 6)
2 < |score| < 3	questionable performance	(yellow in Annexe 6)
|score| ≥ 3	unsatisfactory performance	(red in Annexe 6)

The z scores compare the participant's deviation from the assigned value with the standard deviation for proficiency test assessment (σ_{pt}) used as common quality criterion.

The ζ scores state whether the laboratory's result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value $u(x_{pt})$ and the measurement uncertainty as stated by the laboratory $u(x_i)$. The ζ score includes all parts of a measurement result, namely the expected value (assigned value), its measurement uncertainty in the unit of the result as well as the uncertainty of the reported values. An unsatisfactory ζ score can either be caused by an inappropriate estimation of the concentration, or of its measurement uncertainty, or both.

The standard measurement uncertainty of the laboratory $u(x_i)$ was obtained by dividing the reported expanded measurement uncertainty by the reported coverage factor, k. When no uncertainty was reported, it was set to zero ($u(x_i) = 0$) by the PT coordinator. When k was not specified, the reported expanded measurement uncertainty was considered by the PT coordinator as the half-width of a rectangular distribution; $u(x_i)$ was then calculated by dividing this half-width by √3, as recommended by Eurachem [6].

Uncertainty estimation is not trivial, therefore an additional assessment was provided to each laboratory reporting measurement uncertainty, indicating how reasonable has been their measurement uncertainty estimation. Relative standard measurement uncertainty was calculated based on the absolute values for either the assigned values [$u_{rel}(x_{pt}) = (u(x_{pt})/ x_{pt}) \times 100$] and of the reported values [$u_{rel}(x_i) = (u(x_i)/ x_i) \times 100$] respectively.

The relative standard measurement uncertainty from the laboratory $u_{rel}(x_i)$ is most likely to fall in a range between a minimum and a maximum allowed uncertainty (case "a": $u_{rel\ min} \leq u_{rel}(x_i) \leq u_{rel\ max}$). $u_{rel\ min}$ is set to the relative standard measurement uncertainties of the assigned values $u_{rel}(x_{pt})$.

It is unlikely that a laboratory carrying out the analysis on a routine basis would determine the measurand with a smaller measurement uncertainty than the uncertainty of the assigned value established by expert laboratories (ISO 13528:2015 §7.6) or, if applicable, by formulation (ISO 13528:2015 §7.3) or than the certified measurement uncertainty associated with a certified reference material property value (ISO 13528:2015 §7.4). $u_{rel\ max}$ is set to the standard deviation accepted for the PT assessment, σ_{pt}. Consequently, case "a" becomes: $u_{rel}(x_{pt}) \leq u_{rel}(x_i) \leq \sigma_{pt}$ (the later expressed as a percentage of the assigned value).

If $u_{rel}(x_i)$ is smaller than $u_{rel}(x_{pt})$ (case "b") the laboratory may have underestimated its measurement uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the measurement uncertainty associated with the assigned value also includes contributions for homogeneity and stability of the test item. If those are large, relative measurement uncertainties smaller than $u_{rel}(x_{pt})$ are possible and plausible.

If $u_{rel}(x_i)$ is larger than σ_{pt} (case "c") the laboratory may have overestimated its measurement uncertainty. An evaluation of this statement can be made when looking at the difference between the reported value and the assigned value: if the difference is smaller than the expanded uncertainty $U(x_{pt})$ then overestimation is likely. If the difference is larger but x_i agrees with x_{pt} within their respective expanded measurement uncertainties, then the measurement uncertainty is properly assessed resulting in a satisfactory performance expressed as a ζ score, though the corresponding performance, expressed as a z score, may be questionable or unsatisfactory.

It should be pointed out that $u_{rel\ max}$ is a normative criterion when set by legislation.

6.2 General observations

Twenty three NRLs from 23 EU Member States and nine OCLs (from four EU Member States plus Switzerland) registered to the exercise. Three NRLs and two OCL did not report results for DEHP.

The following instrumental techniques were applied by participants for the determination of the selected phthalate (DEHP): gas chromatography coupled with mass spectrometry (GC-MS, 61 %) or coupled with flame-ionisation detection (GC-FID, 9 %); and high performance liquid chromatography coupled with diode array detection, ultra violet spectrometry (HPLC-DAD, HPLC-UV, 17 %) or mass spectrometry (LC-MS, 13 %).

Three participants reported results not specifying their method of analysis.

Due to the instability observed after ampouling for three of the phthalates investigated, only the results reported for DEHP were further evaluated.

6.3 Laboratory results and scorings

6.3.1 Performances

Annex 6 presents the reported results for DEHP. National Reference Laboratories and Official Control Laboratories are denoted as N-xx and O-xx, respectively. Annex 7 presents the results reported for the other phthalates.

The Kernel density plot in Annex 6 was obtained by using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [7].

Figure 1 presents the laboratory performances for the mass fraction of DEHP in food simulant A. Additionally, participants were requested to report their values in mg L^{-1}

(thus taken into account the density of the food simulant A solution). Density values used by the participants were ranging from 0.981 to 1.019, with 6 laboratories using the value of 1.000 g mL^{-1}.

Most of the participants reported results with led to satisfactory performance ($|z| \leq 2$). Laboratory performance, expressed as ζ scores, was significantly lower compared to z scores.

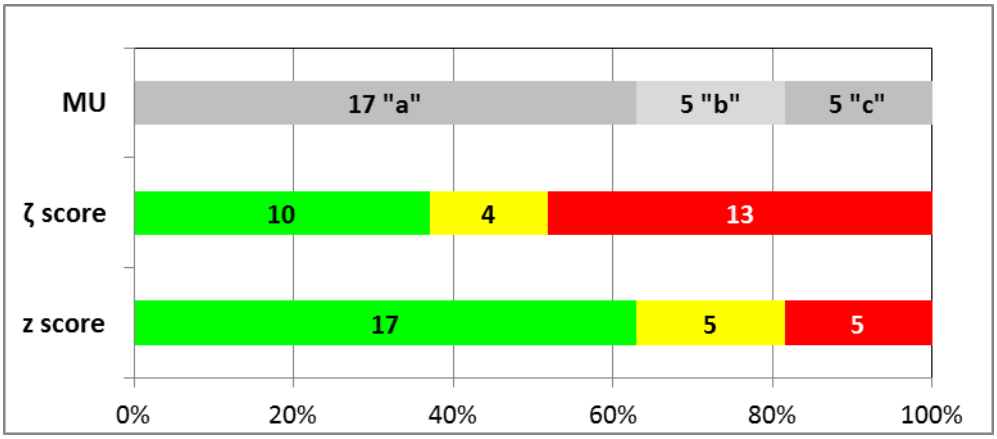


Figure 1: Overview of laboratory performance according to *z* and ζ scores and with measurement uncertainty (MU) evaluation (see 6.3.2). Corresponding number of laboratories included in the graph. Satisfactory, questionable and unsatisfactory performances indicated in green, yellow and red, respectively.

6.3.2 Measurement uncertainties

Most of the participants (21 out of 29) routinely report uncertainties for this type of analysis to their customers. Several approaches were used to estimate measurement uncertainties. Most of the laboratories derived their uncertainty estimates from in-house (single-laboratory) validation studies (9 out of 25) or using replicates (under repeatability conditions, 8 out of 25).

The majority of laboratories having reported quantitative results provided expanded measurement uncertainties and coverage factors. Figure 1 presents the measurement uncertainty evaluation. The percentage of the participants having reported realistic measurement uncertainty evaluations (Case "a": $u_{rel}(x_{pt}) \leq u_{rel}(x_i) \leq \sigma_{pt}$ (the later expressed as a % of x_{pt}) was 62 %. The remaining participants reported either a potentially overestimated measurement uncertainty (19 %) or a potentially underestimated measurement uncertainty (19 %).

6.3.3 Additional information extracted from the questionnaire

The questionnaire was answered by the large majority of the participants giving valuable information on the laboratories, their way of working and their analytical methods.

All participants, except one, stated that they have an ISO/IEC 17025 accreditation.

The slight majority of the participants (54 %) stated having a limited experience with the analysis of the determination of DEHP in food simulant A solution (0-50 analysis per year of similar test items), while 15 % of them reported that they have a slightly higher experience (51-250 analysis per year of similar test items). The remaining 31 % of participant laboratories stated having no experience in this type of analysis.

6.3.4 Compliance assessment

The majority of the participants reported a compliance assessment. The large majority stated, correctly, that the test item should be considered in compliance with the relevant EU legislation regarding the specific migration limit of DEHP (1.5 mg kg^{-1}). Thus, the percentage of participants which reported a correct compliance statement reached 86 %. Laboratories which concluded for the test item was not compliant based their decision on the fact that they could detect diallyl ester (DAP). This compliance statement should also be considered correct as the test item was designed to have a mass fraction of this phthalate above the detection limit of the official method of analysis (> 0.010 mg kg^{-1}). It might be that chemical instability, observed as significant for the tested sealed glass ampoules at the JRC laboratories was not uniform for all the glass ampoules. Hence the percentage of participants reporting a correct compliance statement sums up to 97 %.

7 Conclusions

The present proficiency testing round FCM-19/02 was organised to assess the analytical capabilities of EU NRLs and OCLs to determine the mass fraction of four phthalates in a food simulant A solution. Due to the instability of three phthalates only the results related to DEHP could be evaluated.

A majority of laboratories (63 %) reported results which led to satisfactory performance. The improvement of the analytical capabilities of such official control laboratories on the determination of the selected phthalate is deemed necessary to guarantee the correct enforcement of Commission Regulation (EC) No 10/2011.

Similarly, only 62 % of the participants reported a realistic measurement uncertainty evaluation while the remaining 38 % reported measurement uncertainties which could be considered either underestimated or overestimated.

Acknowledgements

The twenty nine laboratories (who reported for the different phthalates) listed hereafter are kindly acknowledged for their participation in the PT.

Organisation	Country
Sciensano	BELGIUM
National Center of Public Health and Analyses	BULGARIA
Croatian Institute of Public Health	CROATIA
State General Laboratory	CYPRUS
National Institute for Public Health	CZECH REPUBLIC
National Food Institute, Technical University of Denmark	DENMARK
Health Board	ESTONIA
Finnish Customs Laboratory	FINLAND
Service Commun des Laboratoires - L33	FRANCE
LNE	FRANCE
German Federal Institute for Risk Assessment	GERMANY
Hessisches Landeslabor	GERMANY
Thueringer Landesamt fuer Verbraucherschutz	GERMANY
General Chemical State Laboratory	GREECE
Dublin Public Analyst's Laboratory	IRELAND
Istituto zooprofilattico sperimentale lombardia emilia romagna	ITALY
ARPA LAZIO	ITALY
ARPA PUGLIA	ITALY
ARPA FVG	ITALY
National Public Health Surveillance Laboratory	LITHUANIA
Laboratoire National de Santé	LUXEMBOURG
National Institute of Public Health - National Institute of Hygiene	POLAND
Escola Superior de Biotecnologia - Universidade Católica Portuguesa	PORTUGAL
Centro Nacional de Embalagem	PORTUGAL
Regional public health authority	SLOVAKIA
National Laboratory of Health, Environment and Food	SLOVENIA
Centro Nacional Alimentacion(CNA)-AESAN	SPAIN
University of Zaragoza	SPAIN
Amt für Verbraucherschutz und Veterinärwesen St. Gallen	SWITZERLAND

References

[1] Commission Regulation (EC) No 10/2011 of the European on plastic materials and articles intended to come into contact with food, Off. J. Eur. Communities L12/1, 2011.

[2] Commission Regulation, (EU) No 2017/625 of The European Parliament and of The Council of 15 march 2017 on official controls and other official activities performed to ensure the application of food and feed law, rules on animal health and welfare, plant health and plant protection products, Off. J. Eur. Communities. L 95/1, 2017.

[3] ISO/IEC 17043 *"Conformity assessment – General requirements for proficiency testing"*, issued by ISO-Geneva (CH), International Organisation for Standardization, 2010.

[4] ISO 13528:2015 *"Statistical methods for use in proficiency testing by interlaboratory comparisons"*, issued by ISO-Geneva (CH), International Organisation for Standardization, 2015.

[5] SoftCRM, (n.d.). http://www.eie.gr/iopc/softcrm/index.html.

[6] Eurachem/Citac, *"Quantifying Uncertainty in Analytical Measurement"*, 2012. http://www.eurachem.org.

[7] Analytical Methods Committee, *"Representing data distributions with kernel density estimates"*, AMC Tech. Br. 4 (2006) 2. http://www.rsc.org/images/brief4_tcm18-25925.pdf.

Annex 1: Invitation letter

EUROPEAN COMMISSION
Joint Research Centre
Directorate F – Health, Consumers & Reference Materials
European Union Reference Laboratory for Food Contact Materials

Ref. Ares(2019)2429853 - 05/04/2019

Ispra, 5 April 2019

(sent by e-mail)

Subject: Invitation to participate in Proficiency Testing round "FCM-19/02"

Dear National Reference Laboratory representative,

On behalf of the EURL for Food Contact Materials (EURL-FCM), we would like to invite you to participate in the Proficiency Testing round FCM-19/02 "Determination of phthalates in food simulant A solution".

The PT fulfils the EURL-FCM mandate under Regulation (EU) 2017/625.

According to Regulation (EU) 2017/625 it is your duty as NRL to participate in PTs organised by the EURL-FCM.

Your participation is free of charge.

Please register electronically by using the link below and following the instructions on screen.

http://apps.jrc.cec.eu.int/ILCAdmin/comparison/comparison.do?comparisonId=2261

Once you have submitted your registration electronically, you will have to:

- Print your registration form, as indicated on screen
- Sign it, date it and send it to us by e-mail (JRC-EURL-FCM@ec.europa.eu)

Please register by Monday the 30th of April 2019.

Please forward this invitation to the Official Control Laboratories (OCLs) in your network that would be interested in participating. They should also register electronically by using the same link above.

Samples will be dispatched on the 13th of May 2019.

The deadline for submission of results is the 26th of July 2019.

Do not hesitate to contact us if you have any further questions.

Kind regards,

/signed electronically in Ares/
Dr. F. Cordeiro
FCM-19/02 PT Coordinator

/signed electronically in Ares/
Dr. E.J. Hoekstra
Operating Manager EURL-FCM

Cc: Prof. Dr. H. Emons (Head of Unit, Food & Feed Compliance, F.5)

Annex 2: Test item accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Directorate F - Health, Consumers & Reference Materials (Geel/Ispra)
Food & Feed Compliance

EURL
European Union Reference Laboratory
for Food Contact Materials

Ispra, 20th May 2019
JRC.F.5/FCR/AS/Ares(2019)3453705

Attn.: «Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address2»
«Zip» «Town»
«Country»

Subject: **Participation in FCM-19/02 – "Determination of phthalates in food simulant A solution"**

Dear «Title» «Surname»,

Thank you for participating in the FCM-19/02 proficiency test (PT) for the **"Determination of phthalates in food simulant A solution".** This PT is organised in support to *Regulation (EU) 10/2011* on plastic materials and articles intended to come into contact with food.

The measurands are mass fractions (mg kg^{-1}) of dibutyl phthalate (DnBP), diallyl phthalate (DAP), benzyl butyl phthalate (BBP) and bis (2-ethylhexyl) phthalate (DEHP) in food simulant A solution.

Please keep this letter. You will need it to report your results.

The parcel you received contains,

- one sealed ampule (25 ml) containing the food simulant A solution.

Upon arrival of this parcel, please check whether the ampules are undamaged after transport.

May I kindly ask you to send us or email the "**Confirmation of receipt**" form within 3 days after receipt of the samples.

The procedure used for the analyses should resemble as closely as possible the one you use in routine analyses.

Please report the following:

- the **mean** of your two or three measurements results (in mg kg^{-1} and in mg l^{-1});

European Commission, Via Enrico Fermi 2749, I-21027 Ispra (Varese) - Italy. Telephone: (39)0332-78-9111
e-mail: jrc-eurl-fcm@ec.europa.eu
URL: https://ec.europa.eu/jrc/en/eurl/food-contact-materials

- the associated expanded **uncertainty** (in mg kg^{-1});
- the **coverage factor;** and
- the analytical technique used.

(Only results reported in mg kg^{-1} will be used to assess participant performance)

The results should be reported in the same format (e.g. number of significant figures) as you normally report to customers.

The reporting website is https://web.jrc.ec.europa.eu/ilcReportingWeb

To access the webpage you need the following personal password key: «Partkey».

The system will guide you through the reporting procedure. Then complete the corresponding questionnaire. **Do not forget to submit and confirm when required.**

Directly after submitting your results and the questionnaire online, you will be requested to print the completed report form. Please check carefully this report form. In the case mistakes are detected contact the PT coordinator as soon as possible before the reporting deadline.

The deadline for submission of results is **26/07/2019**.

The procedures used for the organisation of PTs are accredited according to ISO/IEC 17043:2010 and guarantee that the identity of the participants and the information provided by them is treated as confidential. However, lab codes of National Reference Laboratories appointed in line with Regulation (EU) 2017/625, will be disclosed to DG SANTE upon request for (long-term) performance assessment. Lab codes of appointed Official Control Laboratories may be disclosed to their National Reference Laboratory upon request.

Remember that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Your participation in this project is greatly appreciated.

Do not hesitate to contact me for further information.

With kind regards,

/signed electronically in Ares/

Dr. Fernando Cordeiro
FCM-19/02 PT Coordinator

Cc: H. Emons (Head of Unit, Food & Feed Compliance, F.5),
E. Hoekstra (Operating Manager EURL-FCM)
L. Karasek (FCM-19/02 Deputy PT Coordinator)

European Commission, Via Enrico Fermi 2749, I-21027 Ispra (Varese) - Italy. Telephone: (39)0332-78-9111
e-mail: jrc-eurl-fcm@ec.europa.eu, URL: https://ec.europa.eu/jrc/en/eurl/food-contact-materials

Annex 3: Confirmation of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Directorate F – Health, Consumers and Reference Materials
European Union Reference Laboratory for Food Contact Materials

EURL
European Union Reference Laboratory
for Food Contact Materials

Ispra, 27 May 2019
JRC.F.5/FCR/AS/Ares(2019)3453705

Attn.: «Title» «Firstname» «Surname»
«Organisation»
«Country»

Subject: "Confirmation receipt" form - FCM-19/02 - Determination of phthalates in food simulant A solution

Please return this form at your earliest convenience, to confirm that the package arrived well to your laboratory. If samples are damaged, please mention it below and contact us as soon as possible.

Date of package arrival _____

Were the samples damaged? ☐ YES ☐ NO

Remarks _____
_____

Signature

Thank you for returning this form by email to:

/signed electronically in Ares/

Dr. F. Cordeiro
FCM-19/02 Coordinator
e-mail : jrc-eurl-fcm@ec.europa.eu

European Commission, Via Enrico Fermi 2749, I-21027 Ispra (Varese) - Italy. Telephone: (39)0332-78-9111.
e-mail: jrc-eurl-fcm@ec.europa.eu. URL: https://ec.europa.eu/jrc/en/eurl/food-contact-materials

Annex 4: Questionnaire

Mile questionnaire

Comparison for FCM-19/02

This questionnaire is meant to collect additional information about your laboratory and experimental details about your analytical method. Your answers will be used in the evaluation of the proficiency test FCM-19/02. Please enter the information related to the method used for the determination of the mass fraction of phthalates in food simulant A. Please do so comprehensively, in order to allow appropriate evaluation and relevant discussion of the results.

Submission Form

1. **Please identify yourself. You are ....**

- ○ National Reference Laboratory (NRL)
- ○ Official Control Laboratory (OCL)

1.1. Does your laboratory have a quality management system?

- ○ No
- ○ Yes

1.1.1. If "Yes" based on which standards?

- ○ ISO 17025
- ○ ISO 9001
- ○ Other

2. **Is the PT test item in compliance with the relevant European legislation?**

- ○ No
- ○ Yes

Questions/ Response table	From in-house validation study	From interlaboratory comparison	From replicatio (repeatabil conditions	ISO GUI	Knowr from standar metho (ISO 21748)	Other	based or (expert) judgmen	Info
Benzyl butyl ester (BBP)	☐	☐	☐	☐	☐	☐	☐	
Bis(2-ethylhexyl) ester	☐	☐	☐	☐	☐	☐	☐	

7. **Do you participate in other PTs for this type of analysis?**

○ No

○ Yes

8. **Which type of method did you follow?**

Questions/ Response table	Accredited method	Fully validated method	Standard method	Info
Dibutyl ester (DnBP)	☐	☐	☐	
Diallyl ester (DAP)	☐	☐	☐	
Benzylo butyl ester (BBP)	☐	☐	☐	
Bis(2-ethylhexyl) ester (DEHP)	☐	☐	☐	

Annex 5: Homogeneity and stability results for DEHP in food simulant A solution

Homogeneity study

Bottle ID	DEHP [mg kg^{-1}]	
	R_1	R_2
1	0.980	0.920
2	0.911	0.960
3	0.907	0.892
4	0.902	0.914
5	0.963	0.922
6	0.952	0.970
7	0.884	0.915
8	0.922	0.872
9	0.913	0.934
10	0.934	0.899
Mean	0.923	
s_x	0.023	
s_w	0.026	
s_s	0.013	
σ_{pt} (15 %)	0.139	
0.3 σ_{pt}	0.041	
$s_s \leq 0.3 * \sigma_{pt}$	passed	
Assessment	Homogeneous	

Where: σ_{pt} is the standard deviation for the PT assessment,
s_x is the standard deviation of the sample averages,
s_w is the within-sample standard deviation,
s_s is the between-sample standard deviation.
All values expressed in mg kg^{-1}

Stability study (at 20 °C, time in weeks, w)

	Bottle ID	0 weeks	9 weeks	Stability criteria [a]	Assessment
DEHP	1	0.911	0.937	Passed	Stable
	2	0.902	0.897		
	3	0.952	0.912		

[a] Stability criteria according to ISO 13528:2015 § B.5 (values presented are average values for each bottle and under each time conditions.
All values expressed in mg kg^{-1}

Annex 6: Results for DEHP in food simulant A solution

Assigned range: x_{pt} = 0.943 ± 0.028 (k = 2); σ_{pt} = 0.141 (all values in mg kg^{-1})

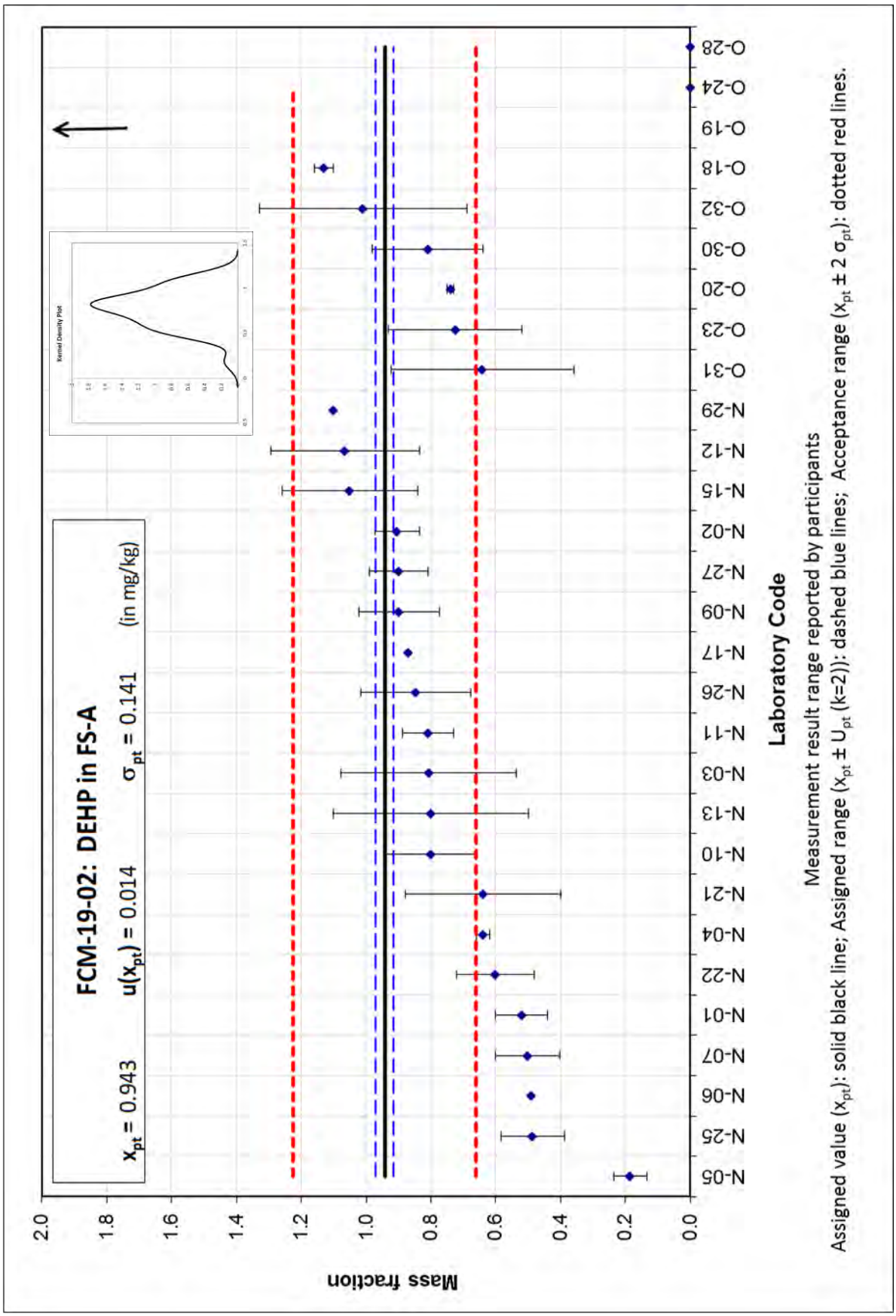
Lab Code	x_i	$U(x_i)$	k [a]	Technique	$u(x_i)$	z [b]	ζ [b]	unc. [c]
N-01	0.52	0.08	2	HPLC-DAD	0.040	-3.0	-10.0	a
N-02	0.904	0.068	2		0.034	-0.3	-1.1	a
N-03	0.807	0.271	2	LC-MS/MS	0.136	-1.0	-1.0	c
N-04	0.64	0.02	2	GC-MS	0.010	-2.1	-17.3	a
N-05	0.185	0.05	2	GC-MS	0.025	-5.4	-26.3	a
N-06	0.49	0	2	GC-FID	0.000	-3.2	-31.6	b
N-07	0.502	0.1	2	LC-MS/MS	0.050	-3.1	-8.5	a
N-09	0.898	0.124	2	UPLC-UV	0.062	-0.3	-0.7	a
N-10	0.8	0.14	2	HPLC/DAD	0.070	-1.0	-2.0	a
N-11	0.809	0.08	2	GC-MS/MS	0.040	-0.9	-3.2	a
N-12	1.065	0.23	√3	GC-MS	0.133	0.9	0.9	a
N-13	0.8	0.3	2	GC-MS	0.150	-1.0	-0.9	c
N-15	1.05	0.21	2	LLE	0.105	0.8	1.0	a
N-17	0.87			GC-MS	0.000	-0.5	-5.1	b
N-21	0.64	0.24	2	GC-MS	0.120	-2.1	-2.5	c
N-22	0.60	0.12	2	GC-MS	0.060	-2.4	-5.6	a
N-25	0.486	0.097	2	GC-MS	0.049	-3.2	-9.0	a
N-26	0.846	0.17	2	GC/MS-MS	0.085	-0.7	-1.1	a
N-27	0.9	0.09	2	GC-MS	0.045	-0.3	-0.9	a
N-29	1.1				0.000	1.1	10.9	b
O-18	1.13	0.03	2	GC-FID	0.015	1.3	9.0	b
O-19	347.76 [d]	31 [d]	2	GC-MS/MS	15.50 [d]	2451.9	22.4	a
O-20	0.739	0.01	2	HPLC/DAD	0.005	-1.4	-13.4	b
O-23	0.725	0.205	2		0.103	-1.5	-2.1	a
O-24								
O-28								
O-30	0.81	0.17	2	GC-MS	0.085	-0.9	-1.5	a
O-31	0.641	0.282	2	GC MS/MS	0.141	-2.1	-2.1	c
O-32	1.01	0.32	2	LC-MS	0.160	0.5	0.4	c

[a] √3 is set by the PT coordinator when no coverage factor k is reported. The reported measurement uncertainty was assumed to have a rectangular distribution with k = √3,

[b] Performance: satisfactory, questionable, unsatisfactory,

[c] a: $u_{rel\ min}(u_{rel}(x_{pt})) \leq u_{rel}(x_i) \leq u_{rel\ max}(\sigma_{pt})$; b: $u_{rel}(x_i) < u_{rel}(x_{pt})$; and c: $u_{rel}(x_i) > \sigma_{pt}$ (σ_{pt} expressed as a % of x_{pt})

[d] Results reported with a gross error (multiplied by a factor of 1000). This information was provided (by the participant) after the deadline for submission of results.


FCM-19-02: DEHP in FS-A
x_{pt} = 0.943 $u(x_{pt})$ = 0.014 σ_{pt} = 0.141 (in mg/kg)
Kernel Density Plot
Mass fraction
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
N-05
N-25
N-06
N-07
N-01
N-22
N-04
N-21
N-10
N-13
N-03
N-11
N-26
N-17
N-09
N-27
N-02
N-15
N-12
N-29
O-31
O-23
O-20
O-30
O-32
O-18
O-19
O-24
O-28
Laboratory Code
Measurement result range reported by participants
Assigned value (x_{pt}): solid black line; Assigned range ($x_{pt} \pm U_{pt}$ (k=2)): dashed blue lines; Acceptance range ($x_{pt} \pm 2\ \sigma_{pt}$): dotted red lines.

Annex 7: Results for BBP, DAP and DnBP (all values in mg kg^{-1})

Lab code	BBP	DAP	DnBP
N-01	0.19	0.46	0.06
N-02	< 1	< 0.8	0.031
N-03	0.271	< 0.006	0.081
N-04	0.19	1.51	< 0.005
N-05	0.297	< 0.002	0.063
N-06	0.29	-	0
N-07	< 0.01	< 0.01	0.017
N-09	0.0311	< 0.01	0.0383
N-10	< 0.04	< 0.01	0.12
N-11	0.03	< 0.01	0.042
N-12	0.163	< 0.0019	0.053
N-13	0.2	< 0.05	< 0.1
N-15	0.047	< 0.008	0.078
N-17	0.066	< 0.015	0.043
N-21	< 0.1	< 0.1	0.18
N-22	0.013	0.002	0.045
N-25	< 0.01	< 0.01	0.06
N-26	0.067	< 0.004	0.045
N-27	< 0.3	< 0.01	0.056
N-29	< 0.04	< 0.01	< 0.02
O-18	0.0356	< 0.0000929	0.0486
O-19	59.76	< 3.2	50.82
O-20	0.238	0.505	0.056
O-23	0.324	< 0.05	0.16
O-24			
O-28	0	0	0
O-30	0.51	-	< 0.1
O-31	0.044	< 0.03	0.037
O-32	0.15	0	0.26

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