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Report on the inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

MCPD esters and glycidyl esters in food

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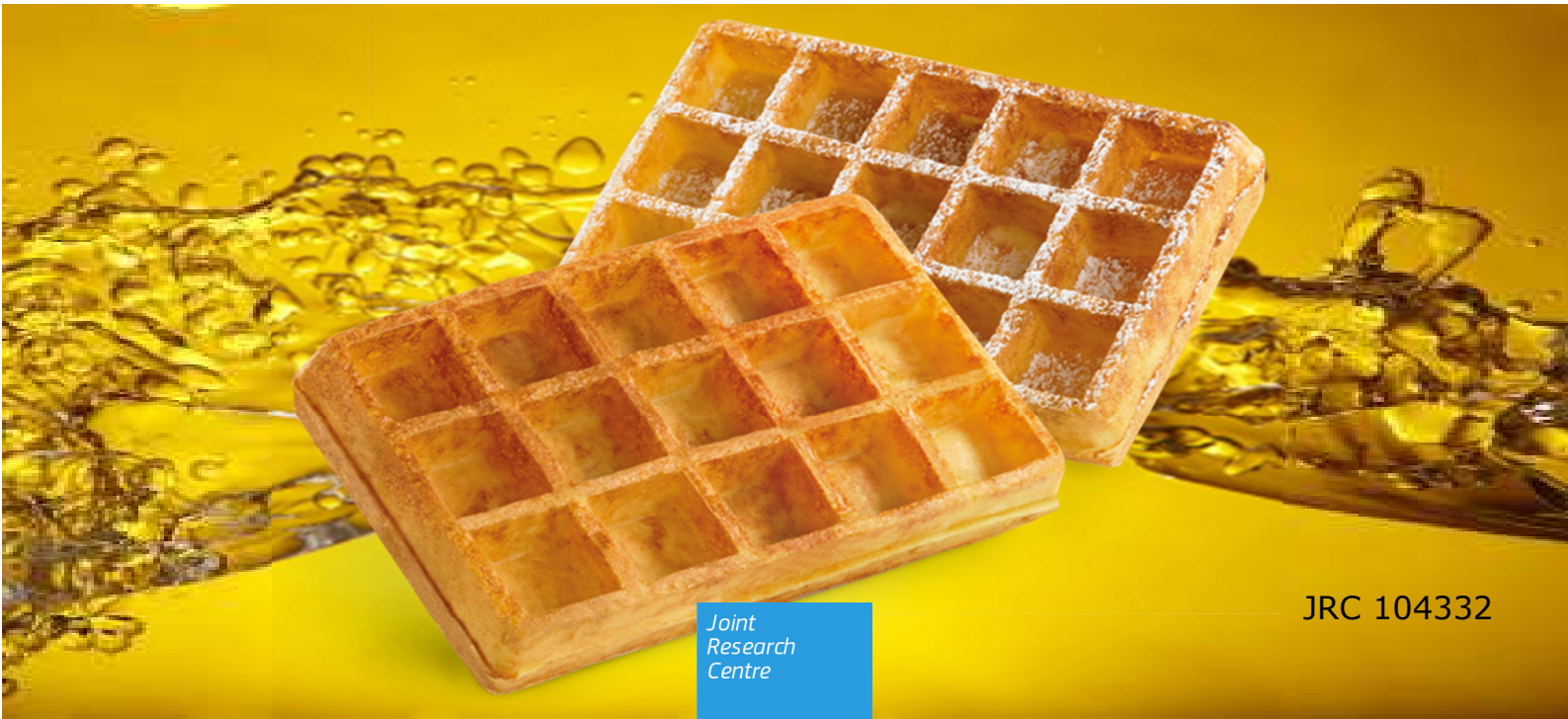

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Abstract

This report presents the results of the inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAH) under its extended scope to process contaminants. The aim of the ILC is to evaluate the readiness of the European official control laboratories to reliably analyse MCPD esters and glycidyl esters in food. Hence the ILC is a proficiency test on the determination of the 3-MCPD esters, 2-MCPD-esters and glycidyl esters in fatty food. Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States participated. Twenty one laboratories registered for participation while only 16 reported results.

On request by DG SANTE and in agreement with National Reference Laboratories, the test materials used in this exercise were waffles and edible oil. Participants also received a solution of native and labelled target compounds with known content to be used for instrument calibration in case of necessity. EURL provided as well standard operation procedure for the participants without previous experience.

The participants were free to choose the method of analysis. Reference values were used to benchmark the results reported by participants. The performance of the participating laboratories in the determination of the target analyte was expressed by z-scores. The target standard deviation for proficiency assessment was set to truncated Horwitz equation. Satisfactory performance with regard to z-scores was assigned to about 78 % of the reported results.

EURL-PAHs is an ISO/IEC 17043 accredited provider of proficiency testing schemes and the respective rules were applied during all phases of this PT.

1. Introduction

One of the core tasks of the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL-PAH) is to organize interlaboratory comparisons (ILCs) and to assess the performance of National Reference Laboratories (NRLs) of the EU Member States. Proficiency tests (PTs) are organized for that purpose.

Fatty acid esters of 3-monochloropropanediol (3-MCPDEs), of 2-monochloropropanediol (2-MCPDEs) and of glycidol (GEs) are substances that are generated during the refining of edible fats and oils (1). They were detected in a variety of different foodstuffs, especially in products containing higher amounts of vegetable oils (2). Recently, the monitoring of MCPD esters (MCPDEs) and GEs in a broad set of food products revealed significant variability in their concentration levels. The highest values were found in margarines, potato crisps, puff pastries and other fat-rich products, whereas bread and cereal-based snacks contained significantly lower levels (3). Given the outcome of the assessment by the European Food Safety Authority (EFSA) of the risks to human health related to the intake of MCPDEs and GEs, the continuous monitoring of these compounds is regarded important (4, 5).

This study fell under the extended scope of the EURL-PAHs, which now is PAHs and other process contaminants. It aimed to evaluate the preparedness of European control laboratories for the coming regulatory measures concerning the content of the MCPDEs and GEs in food by organising a PT to determine the contents of MCPDEs and GEs in two food commodities - Belgium waffles and edible oil. The participants were asked to determine the MCPDEs and GEs content by application of their in-house analysis methods.

2. Scope

As specified in Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules [6], one of the core duties of EURLs is to organise PTs. The PT is organised to support measuring capability of the laboratories in MS. It aimed to evaluate the comparability of results reported by NRLs and EU official food control laboratories (OCLs) for the content of the MCPD esters (MCPDEs) and glycedyl esters (GEs) in two food commodities.

The PT was designed and evaluated under the umbrella of accreditation according to ISO/IEC Standard 17043:2010 [7].

3. Setup of the exercise

3.1 Time frame

The PT was announced on the EURL-PAH web page (see ANNEX 1) and invitation letters were sent to the laboratories on 13th April 2016 (see ANNEX 2) with deadline for registration via EUSurvey webpage (see ANNEX 3) until 4th May 2016. Test samples were dispatched (see ANNEX 4) on 06th June 2016 and the deadline for reporting of results was set to 29th July 2016. The documents sent to the participants are presented in ANNEX 5.

3.2 Participating Laboratories

In contrary to the PTs on the determination of PAHs in food, participation of NRLs for PAHs was not mandatory in this study. This was agreed with the NRLs on the 2015 WS as it could not be expected that NRLs for PAHs in food will automatically cover this analysis task.

However, if NRLs for PAHs do not work in this area, or if the distribution of competences within their country does not allow them to become active in this area, they were requested to identify laboratories in their country that would be more suitable/interested in participation.

At the beginning of 2016 a survey was conducted amongst NRLs for PAHs. According to the answers to the survey, 14 NRLs expressed interest in participation in a PT on MCPDEs and GEs in food. Hands-on training has been organized for the interested NRLs. Ten NRLs reported results

Table 1: List of laboratories, registered for participation

Institute	*Country*
Institut für Lebensmittelsicherheit, Linz	Austria
CART-ULg	Belgium
Danish Veterinary and Food Administration	Denmark
National Food Institute, Technical University of Denmark	Denmark
Spanish Consumer Food Safety and Nutrition Agency	Spain
Finnish Food Safety Authority Evira	Finland
General Chemical State Laboratory (GCSL)	Greece
"National Food Chain Safety Office Food and Feed Safety Directorate"	Hungary
Dublin Public Analysts Laboratory	Ireland
Laboratoire National de Santé	Luxembourg
National Institute of Public Health - National Institute of Hygiene	Poland
Veterinary and Food Institute Bratislava	Slovak Republic
Fera Science Ltd.	UK
Landesuntersuchungsamt, Institut für Lebensmittelchemie Trier	Germany
Eurofins WEJ Contaminants GmbH	Germany
CVUA Rheinland	Germany
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit	Germany
SCL	France
ARPA PUGLIA	Italy
Edinburgh Scientific Services	UK
Lancashire County Scientific Services	UK

From the 21 registered labs, 5 did not report results.

3.3 Confidentiality

The laboratory codes of participants are disclosed only to the participants, unless they were enrolled in the study by a third party, covering the participation fee. In this case the codes of the respective laboratories will be also disclosed to the enrolling third party. In all other cases codes will only be disclosed on a request and upon the written consent of the participant.

3.4 Design of the proficiency test

Detailed instructions were given to participants in the *Outline and Reporting Instructions* (Annex 5), sent to the participants together with the test samples and electronically via mail.

The design of the PT foresaw triplicate analysis of the test items and reporting on product basis of the individual results of replicate analyses. Additionally a "final value for proficiency assessment", in the following denoted as "final value", was requested, expressed as mass/mass test sample and mass/mass extracted fat for waffle sample. All results had to be reported corrected for recovery; the "final value" had also to be accompanied by the respective expanded measurement uncertainty and the coverage factor. Only final values were used for performance assessment.

Participants were asked to report besides analysis results also details of the performance of the applied analytical method (see ANNEX 9).

Each participant received also stock standard solutions of the native and labelled compounds with disclosed content. Some of the participants used the provided standard solutions for calibration of their instruments.

4. Test materials

4.1 Preparation

The test items of this proficiency test were naturally contaminated waffles and spiked olive oil..

The naturally contaminated waffles test item was prepared in house starting from 2.5 kg of Belgium waffles, acquired in a local supermarket. The material was ground and homogenized, giving a fine powder. Aliquots of about 25 g were packed in amber glass screw cap vials and stored in a freezer at about -18 °C.

The edible oil test material was purchased in a local supermarket. An aliquot of 100 ml was spiked with the standard solution of native MCPDEs and GEs to relevant concentrations. After spiking, the test sample was homogenized over night by intensive stirring. Aliquots of about 2-3 ml were ampouled under inert atmosphere and flame sealed in 5 ml amber glass ampoules.

The standard solutions were prepared from neat reference materials (Toronto Research Chemicals Inc., TRC®, Canada). Single standard stock solutions of each analyte were produced by weighing of neat substances on a microbalance and dissolution in toluene. Mixed standards were prepared gravimetrically from the single standard stock solutions in toluene. Technical specifications of the standard solutions are provided in ANNEX 6. The standard solutions were ampouled under inert atmosphere and flame sealed in 5 ml amber glass ampoules.

4.2 Homogeneity and stability

The waffles and oil test samples were tested for significant inhomogeneity, according to the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [11], and for sufficient homogeneity according to ISO 13528:2005 [8].

Homogeneity experiments included duplicate analysis of 10 samples, randomly selected along the filling sequence, among the amber glass vials prepared for dispatch. The duplicate analyses were performed in random order. The test material was rated sufficiently homogenous and no trend was observed. Details of the homogeneity tests are given in ANNEX 7.

The stability of the test materials was evaluated following requirements of ISO13528:2015. Randomly selected samples were stored at two different conditions over the period from the dispatch of the material to the end of the submission of the results.

The first set of three edible oil samples was stored in a refrigerator at recommended conditions (~ 4 °C). The second set of three edible oil samples was stored for the whole period of the study in a deep freezer at the reference conditions - (~ -18°C). After the deadline for reporting of results had expired, all six samples were analysed in duplicate under repeatability conditions.

The first set of waffles samples (2x3 samples each) was stored in a freezer at recommended conditions (~ -18°C, 4°C). The second set of waffles samples was stored for the whole period of the study in a deep freezer at the reference conditions - (~ -80°C). After the deadline for reporting of results had expired, all nine samples were analysed in duplicate under repeatability conditions

No significant difference of the analyte contents among the test samples was found. Hence stability of the samples over the whole period can be assumed under the recommended conditions (ANNEX 8)

4.3 Assigned values and standard deviations for proficiency assessment

The assigned values were determined in-house applying an analytical method based on isotope dilution mass spectrometry with bracketing calibration [9]. The analytical method was validated in-house and tested in a PT against methods of 5 others expert laboratories. The respective associated uncertainties of the assigned values were calculated based on GUM approach [12].

The standard deviation for proficiency assessment, σ_P, was calculated using the Horwitz equation, modified by Thompson [7] for analyte concentrations < 120 µg/kg:

- for analyte concentration < 120 µg/kg

$$\sigma_p = 0.22 \cdot c \qquad \text{Equation 1}$$

- for analyte concentration ≥ 120 µg/kg

$$\sigma_p = 0.02 \cdot c^{0.8495} \qquad \text{Equation 2}$$

where:
c = concentration of the measurand (assigned value, $X_{ref,}$) expressed as a dimensionless mass ratio, e.g. 1 µg/kg = 10^{-9}, 1 mg/kg = 10^{-6}

The assigned values and their uncertainties for the waffle test item were expressed on mass/mass test sample as well as on mass/mass extracted fat in µg/kg (Table 2 and 3)

Table 2: Assigned values and their associated expanded uncertainties (k=2) for the test items, expressed as mass/mass test.sample

Analyte short name	Assigned value	U	σ_P	
	µg/kg	µg/kg	µg/kg	%
Naturally contaminated waffles test sample				
3-MCPD (for 3-MCPDEs)	**266**	**23**	51.9	19.5
2-MCPD (for 2-MCPDEs)	**135**	**12**	29.2	21.6
3-MBPD (for GEs)	**78**	**13**	17.2	22.0
Spiked oil test sample				
3-MCPD (for 3-MCPDEs)	**963**	**16.2**	154.9	16.1
2-MCPD (for 2-MCPDEs)	**626**	**8.0**	107.5	17.2
3-MBPD (for GEs)	**1062**	**21**	168.4	15.9

Table 3: Assigned values and their associated expanded uncertainties (k=2) for the waffles test items, **expressed on** mass/mass extracted fat**.**

Analyte short name	Assigned value	U	σ_P	
	µg/kg	µg/kg	µg/kg	%
Naturally contaminated waffles test sample, fat bases				
3-MCPD (for 3-MCPDEs)	**981**	**84**	157.4	16.0
2-MCPD (for 2-MCPDEs)	**498**	**45**	88.5	17.8
3-MBPD (for GEs)	**286**	**47**	55.2	19.3

σ_p standard deviation for proficiency assessment.

U expanded uncertainty of the assigned value (k=2).

5. Evaluation of laboratories

5.1 General

The most important evaluation parameter was the performance of the laboratories in the determination of the target analytes in the test materials, which was expressed by z-scores [8]. zeta-Scores were calculated in addition considering the uncertainty of the test results as estimated by each participant.

The results as reported by participants are listed in ANNEX 11. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed.

5.2 Evaluation criteria

z-Scores

z-Scores were calculated based on the final values. Equation 2 presents the formula for calculation of z-scores.

Equation 3 $$z = \frac{\left(x_{lab} - X_{assigned}\right)}{\sigma_P} \quad [8]$$

where z refers to the z-score, x_{lab} to the reported "final value", $X_{assigned}$ to the assigned value, and σ_P to the standard deviation for proficiency testing.

zeta-Scores

In addition to z-scores, zeta-scores were calculated. In contrast to z-scores, zeta-scores describe the agreement of the reported result with the assigned value within the respective uncertainties. zeta-Scores were calculated according to Equation 3.

Equation 4 $$zeta = \frac{x_{lab} - X_{assigned}}{\sqrt{u_{lab}^2 + u_{assigned}^2}} \quad [8]$$

where zeta refers to the zeta-score, x_{lab} to the reported "final value", $X_{assigned}$ to the assigned value, u_{lab} to the standard measurement uncertainty of the reported result, and $u_{assigned}$ to the standard uncertainty of the assigned value.

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [7]. The following scheme is applied for the interpretation of z-scores:

|score| ≤ 2.0 = satisfactory performance
2.0<|score| < 3.0 = questionable performance
|score| ≥ 3.0 = unsatisfactory performance

zeta-Scores are presented for information only informatively as still the analytical method itself represents a challenge to the laboratories.

5.3 Evaluation of results

z-Scores were attributed only to the "final values". The individual results of replicate analyses were not rated.

Twenty one laboratories registered for participation in the PT, but only 16 reported results, despite on extended deadline. The results, reported by participants are presented in ANNEX 11.

Statistical evaluation of the results was performed using PROLab software [10]. Robust mean values and robust standard deviations were calculated according to Algorithm A+S of ISO 13528:2005 [8]. However having in mind the low number of the submitted results especially for GEs (only 12), 1/3 of which were only positive outliers, the robustness of the algorithms was questioned and other robust algorithms were applied (Hample and Hubert) [10] as well for comparison. As expected, some significant differences were noticed in robust RSD estimation in those cases; however the trend that the robust RSD for 2-MCPDEs and GEs in waffle samples were much higher than the target RSD was obvious (Fig. 1). For 3-MCPDEs in both samples and for 2-MCPDEs and GEs in spiked oil robust standard deviations of the results of participants were comparable with the target standard deviations, which were lower than 20% due to the higher analyte content.

Figure 1 Comparison between relative standard deviation of the PT for proficiency assessment (tr-Horwitz) and the robust relative standard deviation of the participants' results, calculated according to algorithm A+S from ISO 13528:20015.

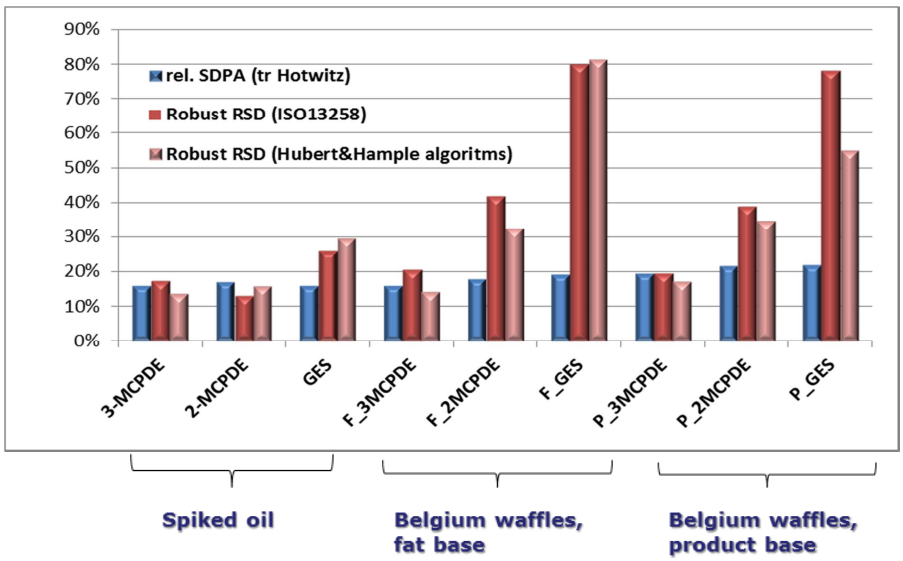
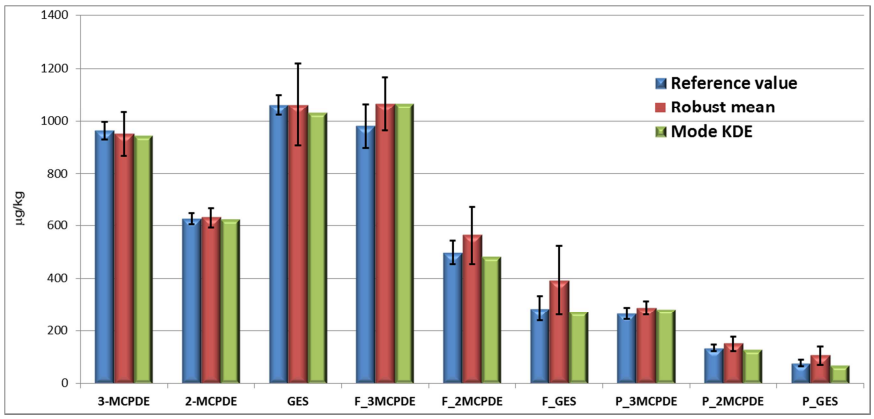


Figure 2 Comparison between independently assigned (reference) value and robust mean from the participants' results.



It should be noted however, that the confidence intervals of the robust means calculated from the participants' results (ANNEX 11) overlap in all cases with the confidence intervals of the assigned (reference) value and the Kernel density mode as well (Fig. 2).

Figure 3 presents the overall laboratory performance expressed as histograms of z-scores

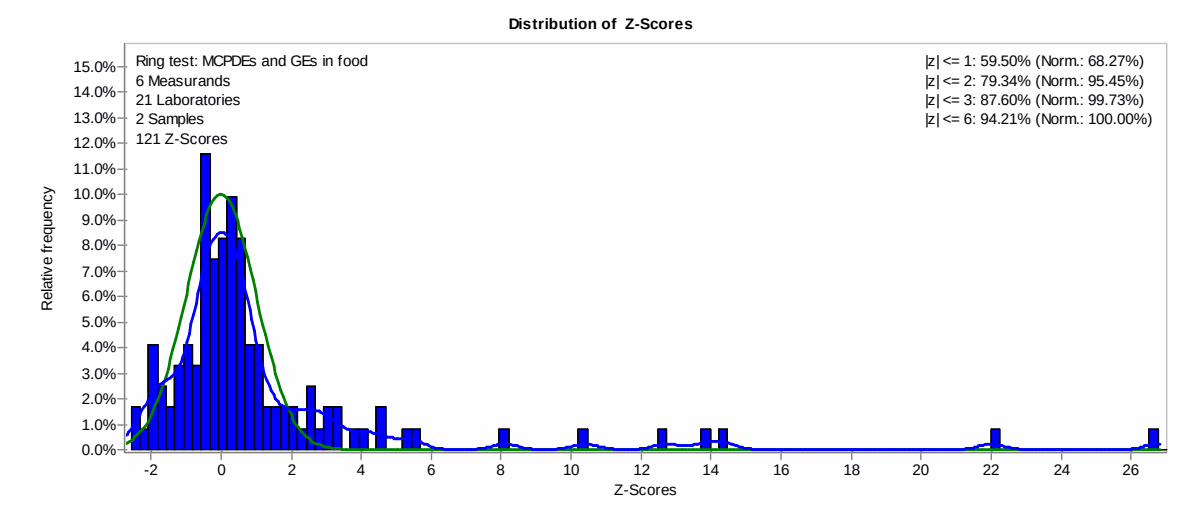
79.3% of the results reported by the participants obtained satisfactory z-scores ≤ I2I. 12.4% of the results fall into the unsatisfactory performance range with z-scores > |3|.

Figure 4 presents the performance of the participants, expressed as z- and zeta-scores, grouped by analyte/matrix combinations.

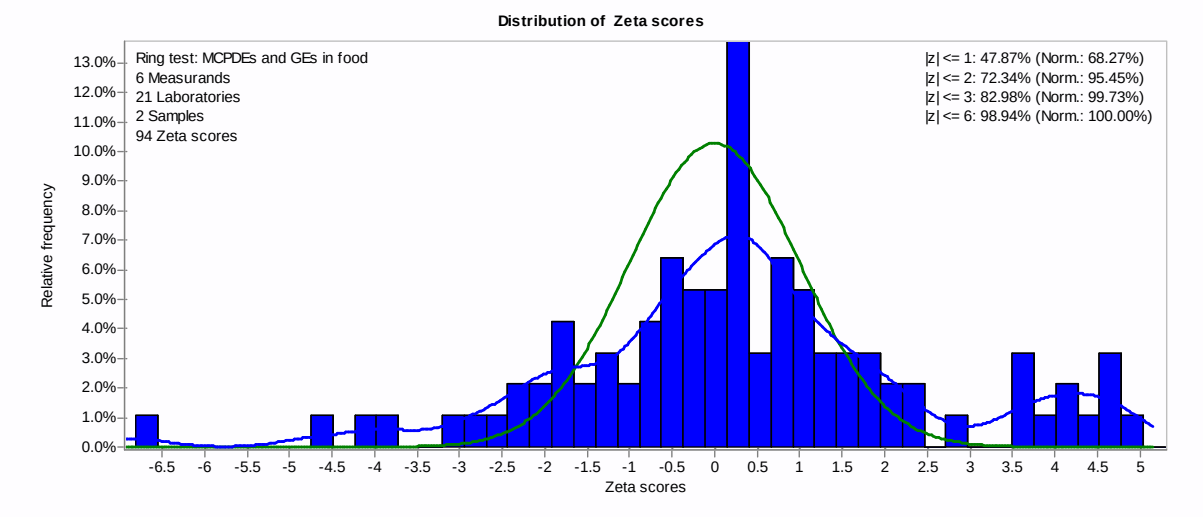
Analyses of the laboratories performance by target analytes and matrices confirmed the general expectation of higher level of superior proficiency in determination of 3-MCPDEs in edible oil which might be result of longer experience in this type of analysis and the availability of standardised analytical methods for that analyte/matrix combination.

Figure 3: Histogram of z- and zeta-scores for the contents of 3-MCPDEs, 2-MCPDEs and GEs in waffles and oil test samples

a) z-scores



b) zeta-scores



Hundred percent satisfactory scores received participants for the determination of 3-MCPDEs in waffles, expressed as mass/mass test sample. However unexplained remains the inferior performance of the results expressed as mass/mass extracted fat, as the first step of the analytical procedure is the fat extraction from the matrix, following by aliquotation and respective determination of the analyte in the fat.

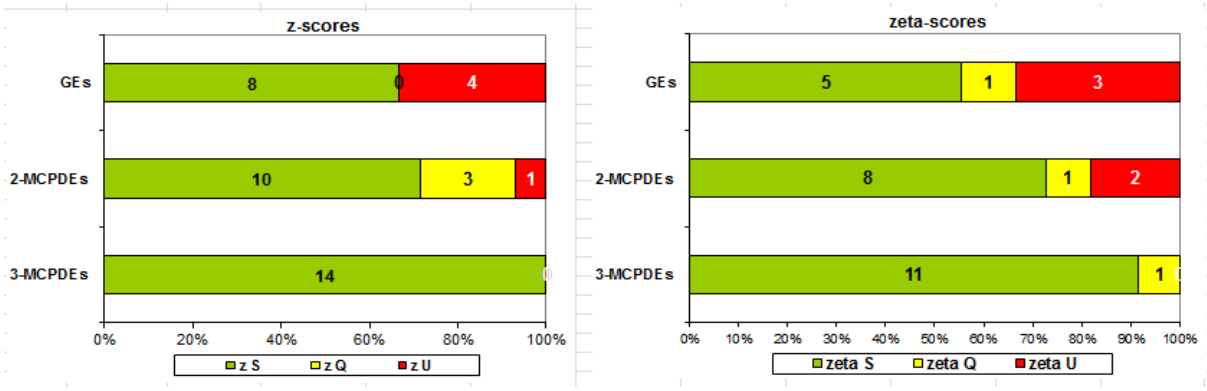
In general the overall performance of the participants could be summarised as satisfactory.

Figure 5 provides overviews of the individual z- and zeta-scores assigned to the results from the participants. The larger the triangles, the larger were the differences to the assigned values. Blue triangles correspond to the satisfactory results, yellow triangles represent z-scores in the questionable and red triangle in the non-satisfactory performance range. The corresponding scores are presented next to the triangles.

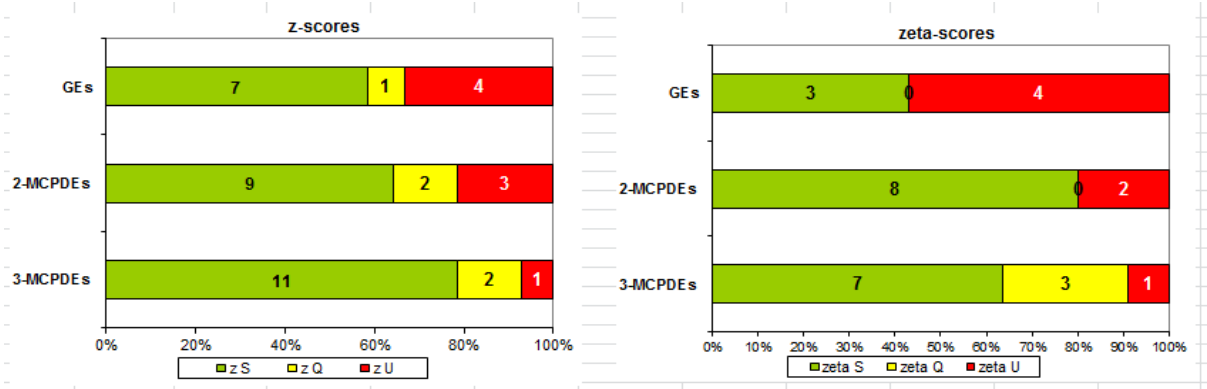
Half of the participants (*8*) obtained more than 100 % satisfactory z-scores (*9*).

Figure 4 Overview of laboratory performance per measurand according to z- and zeta-scores. Corresponding number of laboratories indicated in the graph. Satisfactory (green); Questionable (yellow); Unsatisfactory (red)

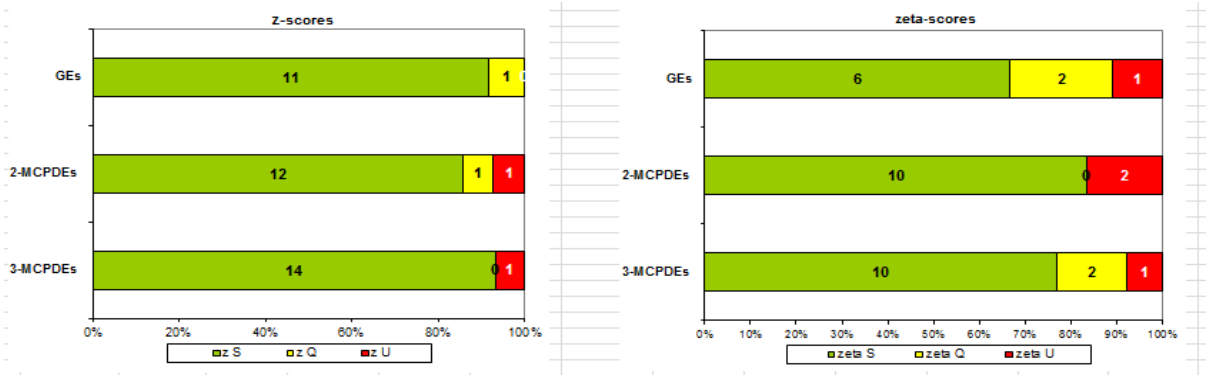
Waffles, product base



Waffles, fat base



Edible oil



The numerical values of the calculated z- and zeta-scores are reported together with the repeated results reported by the laboratories in the tables of Annex 11. In green are highlighted satisfactory results. All z- and zeta-scores in the questionable performance range are highlighted in yellow, while z- and zeta-scores indicating unsatisfactory performance are presented on red background. This mode of presentation allows easy distinction between the two performance ranges even on black-and-white prints.

The graphical representations of the distribution of results for the individual analytes are given in ANNEX 11 together with respective Kernel density plot.

For each analyte the figures in the Annex show the individual analysis results of the three replicate determinations.

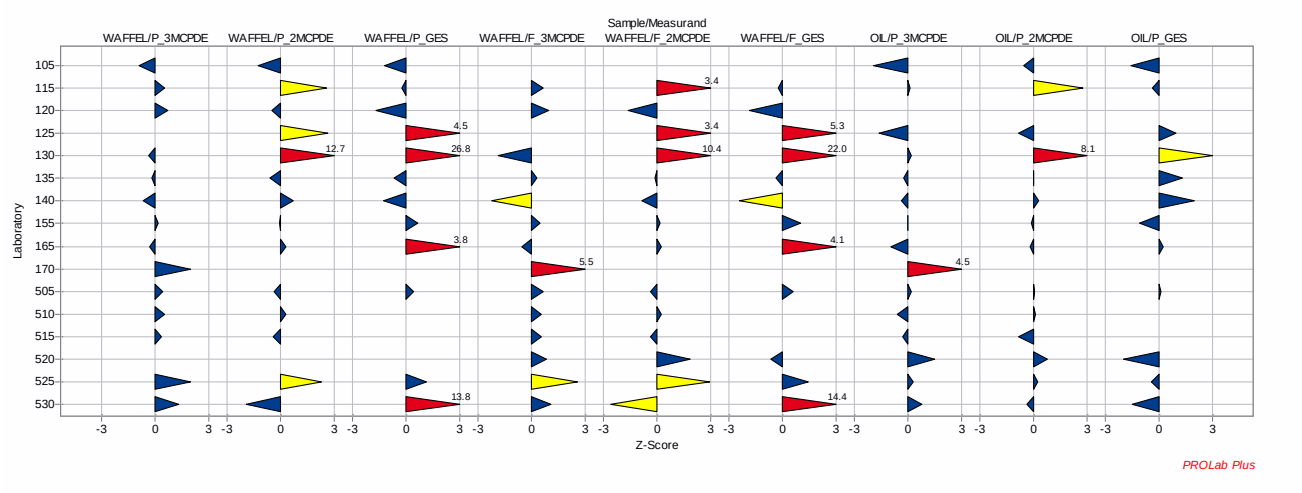
As could be seen from the Kernel density plots the distributions of results are close to a Gaussian distribution. The major modes are close to the assigned (reference) value and the robust mean calculated from the results of the participants. This supports the conclusion that the measurement of MCPDEs and GEs in waffles and edible oils test samples is from the statistical point of view under control.

zeta-Scores are presented only for information and not considered as significant for evaluation of the laboratory performance.

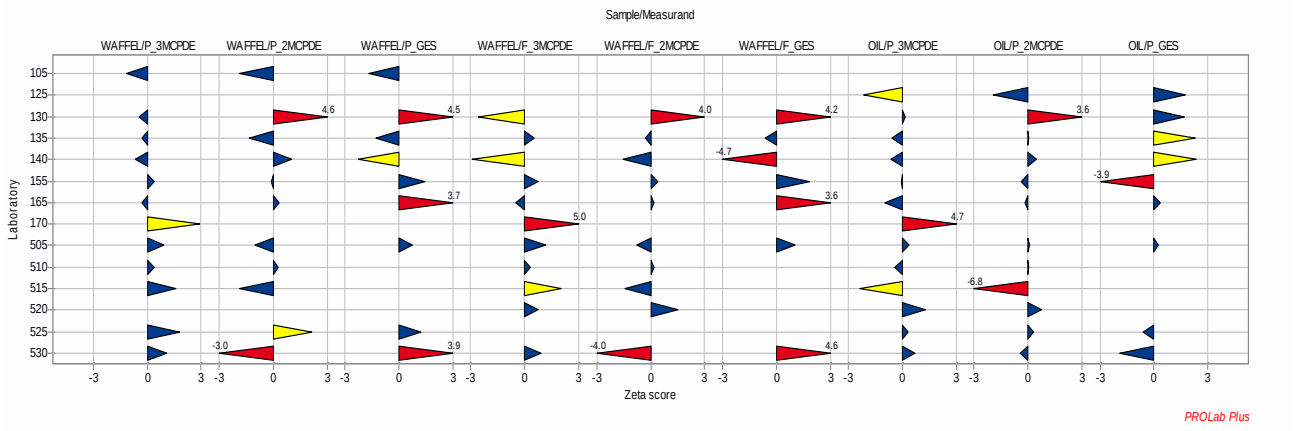
PT's in that fields were very limited and mainly targeted to determination of MCPD esters in oils. For simultaneous determination of GEs together with MCPDEs, to our knowledge this is the first PT covering the scope.

Figure 5: Graphical presentation of z- and zeta- scores corresponding to the "final values for proficiency assessment" reported by the NRLs for the contents of 3-MCPD esters, 2-MCPD-esters and glycidyl esters in edible oil and waffles test samples on product and fat base.

a) z-scores



b) zeta-scores



The plausibility of the uncertainty statements classifying them into three groups (Annex 11) according to the following rules was performed:

The standard measurement uncertainty from a laboratory (u_{lab}) is most likely to fall in a range between a minimum and a maximum uncertainty (case "a": $u_{min} \leq u_{lab} \leq u_{max}$). The minimum uncertainty (u_{min}) is set for the respective analyte to the standard uncertainty of the assigned value (u_{ref}). This is based on the assumption that it is unlikely that a laboratory carrying out the analysis on a routine basis would determine the measurand with a smaller measurement uncertainty than that achieved in the experiments for the characterisation of the test material, which were based on isotope dilution mass spectrometry applying bracketing calibration. The maximum uncertainty is set to the standard deviation accepted for the assessment of results (σ), in this PT set to the maximum threshold given by the "fitness-for-purpose" function U_f. Consequently, case "a" becomes: $u_{ref} \leq u_{lab} \leq \sigma$.

If u_{lab} is smaller than u_{ref} (case "b": $u_{lab} < u_{ref}$) the laboratory might have underestimated its measurement uncertainty.

If u_{lab} is larger than σ (case "c": $u_{lab} > \sigma$) the laboratory might have overestimated its measurement uncertainty, or applied an analytical method that was not fit-for-purpose. Both cases require corrective action!

5.4 Additional information extracted from the questionnaire

Additional information was collected from the questionnaire filled in by the participants (ANNEX 9). Data are presented as reported.

As MCPDEs and GEs are not yet regulated and there is no standardised method for their determination in other food commodities than oil, the number of experienced laboratories for such kind of analysis is low. This was reflected in the total number of participants - 21 laboratories registered for participation, while only 16 reported results (12 for glycidyl esters). Seven laboratories, reporting results, did not have previous experience in analysing the MCPDEs and GEs in food at all (Fig. 6). The SOP is provided for all interested participants and eight of the participants applied it for performing analysis (Fig.7). Standard solutions of native and labelled compounds were provided as well and six laboratories used them for calibration of their instruments while 10 used their own.

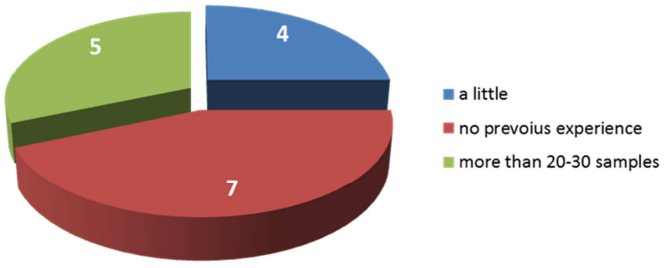


Figure 6.

Experience of the laboratories for analysis of MCPDEs and GEs in food samples

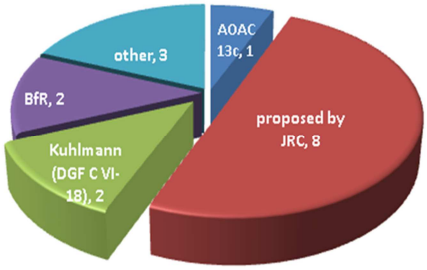


Figure 7.

Method applied for analysis of MCPDEs and GEs in food samples

After detailed analysis of the responses to the questionnaire (Annex 8) it can be concluded that the performance of the laboratories is depended mostly on the previous experience of the participants.

LODs/LOQs reported by the participants fell in very wide range (Annex 10).

6. Follow-up actions for underperforming laboratories

Participants, whose data are outside the satisfactory performance area, will be send a form for root cause analysis to report to the EURL PAH

However no other direct follow up measures are scheduled. The repetition of the study in the future is strongly recommended.

Conclusion

Participation rate was not very high, but reflects the current situation amongst European control laboratory in a time when still legislative regulation is not adopted.

Twenty one participants registered but 16 reported analysis results. Participants showed good measuring capability (78.5% successful rate) as far as the 3-MCPDEs was concerned even in waffles. Challenging remains determination of GE in food, due to the intercross reactivity. Repetition of the study is strongly recommended.

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6 EU, Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Official Journal of the European Communities, 2004. **L191**: p. 1-52. Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2004:191:0001:0052:en:pdf
7 ISO/IEC 17043:2010. "Conformity assessment - General requirements for proficiency testing providers". Geneva, Switzerland
8 ISO 13528:2005 "Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons", issued by International Organisation for Standardisation, Geneva, Switzerland
9 EUR 27288 EN - Development and validation of analytical methods for the analysis of 3-MCPD (both in free and ester form) and glycidyl esters in various food matrices and performance of an ad-hoc survey on specific food groups in support to a scientific opinion on comprehensive risk assessment on the presence of 3-MCPD and glycidyl esters in food, Thomas Wenzl, Vasilios Samaras, Anupam Giri, Gerhard Buttinger, Lubomir Karasek, Zuzana Zelinkova, Luxembourg Publications Office of the European Union, 2015.
10 Software for PT programs and collaborative studies, PROLab; http://quodata.de/en/software/for-interlaboratory-tests.html
11 IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories http://www.iupac.org/publications/pac/2006/pdf/7801x0145.pdf
12 Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections)

List of abbreviations and definitions

3-MCPDEs	3-monochloropropanediol (3-MCPD) fatty acid esters
2-MCPDEs	2-monochloropropanediol (2-MCPD) fatty acid esters
GEs	glycidyl fatty acid esters
EC -	European Commission
EFSA -	European Food Safety Authority
EU –	European Union
EURL PAHs -	European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons and other process contaminants
ILC –	inter-laboratory comparison
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC -	Joint Research Centre
LOD -	Limit of Detection
LOQ -	Limit of Quantitation
ML -	maximum level
NIST	National Institute of Standards and Technology
NRL -	National Reference Laboratory
OCL -	Official food control laboratory
PT -	proficiency test

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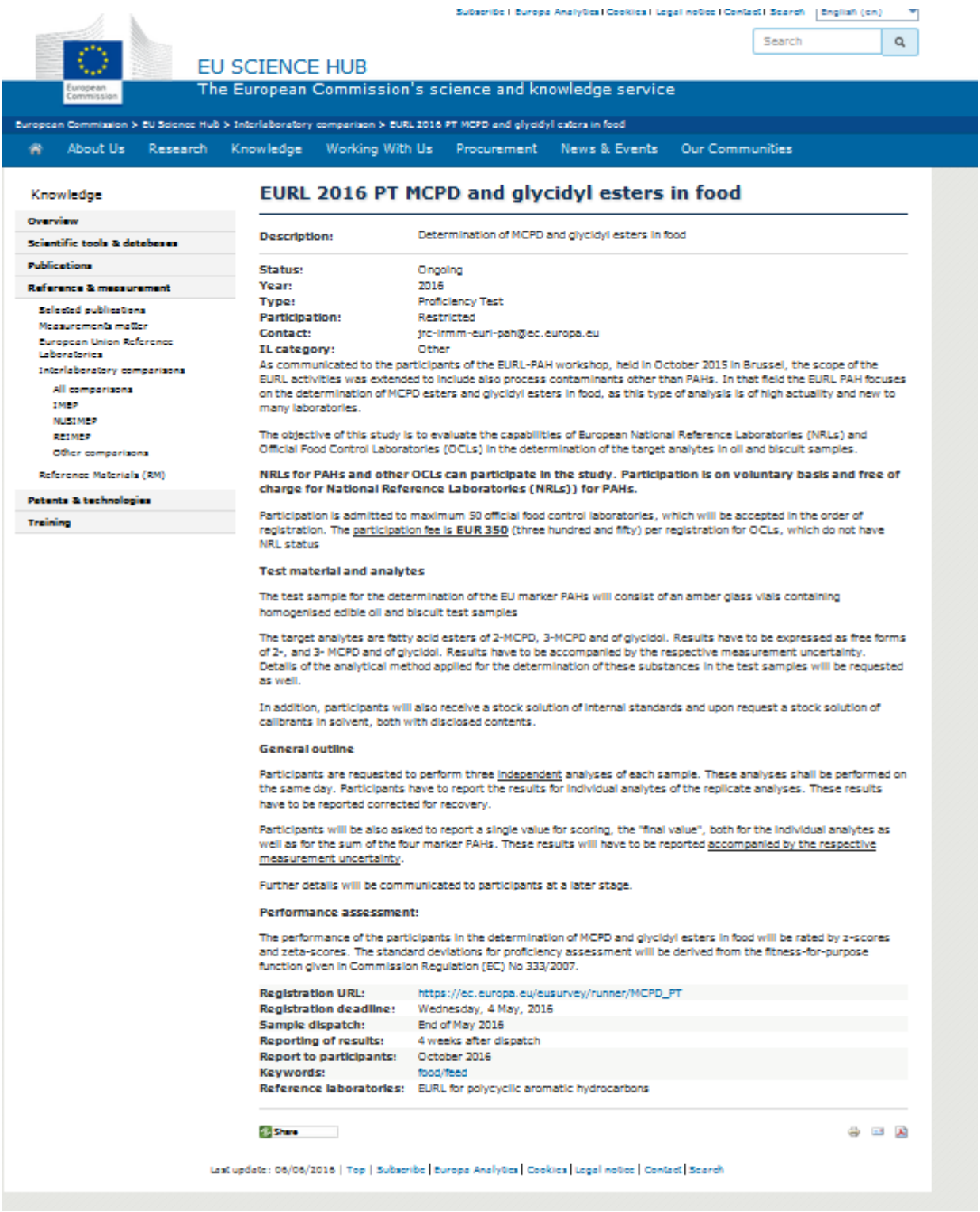
ANNEXES

ANNEX 1: Announcement of the PT on the IRMM webpage



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- Training

EURL 2016 PT MCPD and glycidyl esters in food

Description: Determination of MCPD and glycidyl esters in food

Status: Ongoing
Year: 2016
Type: Proficiency Test
Participation: Restricted
Contact: jrc-irmm-eurl-pah@ec.europa.eu
IL category: Other

As communicated to the participants of the EURL-PAH workshop, held in October 2015 in Brussel, the scope of the EURL activities was extended to include also process contaminants other than PAHs. In that field the EURL PAH focuses on the determination of MCPD esters and glycidyl esters in food, as this type of analysis is of high actuality and new to many laboratories.

The objective of this study is to evaluate the capabilities of European National Reference Laboratories (NRLs) and Official Food Control Laboratories (OCLs) in the determination of the target analytes in oil and biscuit samples.

NRLs for PAHs and other OCLs can participate in the study. Participation is on voluntary basis and free of charge for National Reference Laboratories (NRLs)) for PAHs.

Participation is admitted to maximum 50 official food control laboratories, which will be accepted in the order of registration. The participation fee is **EUR 350** (three hundred and fifty) per registration for OCLs, which do not have NRL status

Test material and analytes

The test sample for the determination of the EU marker PAHs will consist of an amber glass vials containing homogenised edible oil and biscuit test samples

The target analytes are fatty acid esters of 2-MCPD, 3-MCPD and of glycidol. Results have to be expressed as free forms of 2-, and 3- MCPD and of glycidol. Results have to be accompanied by the respective measurement uncertainty. Details of the analytical method applied for the determination of these substances in the test samples will be requested as well.

In addition, participants will also receive a stock solution of internal standards and upon request a stock solution of calibrants in solvent, both with disclosed contents.

General outline

Participants are requested to perform three independent analyses of each sample. These analyses shall be performed on the same day. Participants have to report the results for individual analytes of the replicate analyses. These results have to be reported corrected for recovery.

Participants will be also asked to report a single value for scoring, the "final value", both for the individual analytes as well as for the sum of the four marker PAHs. These results will have to be reported accompanied by the respective measurement uncertainty.

Further details will be communicated to participants at a later stage.

Performance assessment:

The performance of the participants in the determination of MCPD and glycidyl esters in food will be rated by z-scores and zeta-scores. The standard deviations for proficiency assessment will be derived from the fitness-for-purpose function given in Commission Regulation (EC) No 333/2007.

Registration URL:	https://ec.europa.eu/eusurvey/runner/MCPD_PT
Registration deadline:	Wednesday, 4 May, 2016
Sample dispatch:	End of May 2016
Reporting of results:	4 weeks after dispatch
Report to participants:	October 2016
Keywords:	food/feed
Reference laboratories:	EURL for polycyclic aromatic hydrocarbons

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ANNEX 2: Announcement of the registration via e-mail

Ref. Ares(2016)1752514 - 13/04/2016

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 14/04/2016

Inter-laboratory comparison on the determination of MCPD esters and glycidyl esters in food

Dear Madam/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EURL PAH on the determination of MCPD esters and glycidyl esters in food is **open until 4 May 2016.**

Participation is on voluntary basis and free of charge for National Reference Laboratories (NRLs) for PAHs. **The participation fee for official food control laboratories is 350 Euro per participation.** Confidentiality of data is granted.

The target analytes are fatty acid esters of 2-MCPD, 3-MCPD and of glycidol. Results have to be expressed as free forms of 2-, and 3- MCPD and of glycidol. Results have to be accompanied by the respective measurement uncertainty. Details of the analytical method applied for the determination of these substances in the test samples will be requested as well.

Reporting of results has to be accomplished within 4 weeks after sample dispatch, due to potential issues with sample stability. An extension of the reporting deadline will not be possible!

Each participant will be provided with two amber glass vials containing
a) a (spiked) edible oil and
b) a biscuits test sample with naturally incurred analytes.
Participants will also receive a stock solution of internal standards and upon request a stock solution of calibrants in solvent, both with disclosed contents.

This inter-laboratory comparison is organised under accreditation to ISO 17043.

Detailed information will soon be available on the EURL website:
http://irmm.jrc.ec.europa.eu/EURLs/EURL_PAHs/interlaboratory_comparisons/Pages/index.aspx

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-eurl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Timing:

- **Deadline for registration:** 4 May 2016
- Dispatch of samples: end-May. A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser
- Deadline for reporting of results: 4 weeks after the dispatch of the samples.

Registration procedure:

You are invited to register via following link:
https://ec.europa.eu/eusurvey/runner/MCPD_PT

PT coordinator	Second contact
Thomas Wenzl	Stefanka Bratinova
Fax: 0032-14-571783 e-mail: jrc-irmm-eurl-pah@ec.europa.eu	

Participants are invited to indicate any justified requests.

Distribution of information:
The NRLs are kindly requested to distribute as soon as possible this information and the link to the Registration form to the interested OCLs, and to assist the EURL in identifying other laboratories that are eligible to participate in the study.

Access of NRLs to performance data of official food control laboratories:
Two options:

1) *NRL enrols OCLs and covers participation fee.*
The NRL submits to the EURL a list of participants including name and address of laboratory, and details of the contact person (name, address - no post box! - email and telephone number). The coverage of the participation fees must be confirmed and details for invoicing (e.g. order number) have to be provided. It shall be made clear, that the full participation fee is payable upon dispatch of the test samples. In return, the performance data of the respective official food control laboratories will be disclosed to the NRL.

2) The *OCL (identified as such by the respective NRL) enrols itself* in the inter-laboratory comparison *and covers the participation fee.*
The NRL will get access to performance data of the OCL only upon providing to the EU-RL for PAHs a letter of consent.

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Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-eurl-pah@ec.europa.eu

Web site: http://irmm.jrc.ec.europa.eu

Should you require further clarification, please do not hesitate to contact the EURL team via: JRC-IRMM-EURL-PAH@ec.europa.eu

With kind regards,
Stefanka Bratinova

Cc: Thomas Wenzl, Beatriz de la Calle, Franz Ulberth

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-eurl-pah@ec.europa.eu

Web site: http://irmm.jrc.ec.europa.eu

ANNEX 3: Registration form

2016 Proficiency Test on the determination of MCPD esters and glycidyl esters in food

Fields marked with * are mandatory.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

2016 PT - MCPD esters and glycidyl esters in food - Registration

This inter-laboratory comparison targets the analysis of MCPD esters and glycidyl esters in food. The set of test samples will be distributed in the second half of May after the Workshop and will consisting of amber glass vials containing commercial edible oil and biscuit samples.

Results have to be reported for the individual PAHs as well as for the sum of the four PAHs within 4 weeks from sample dispatch.

In addition, a solution of internal standards in solvent will be supplied to all participants. Upon request we could provide as well a calibrant with disclosed concentration of the analytes, in order to allow participants to verify their instrument calibration. Therefore, results have not to be reported for this material.

This interlaboratory comparison is organised under accreditation to ISO 17043.

Participation is on a voluntary basis, and free of charge for National Reference Laboratories.

The PARTICIPATION FEE is 450 Euro for Official Food Control Laboratories per participation

*
Organisation

1

Department

*
Address (for DHL shipment)

*
City

*
Postal code

*
Country

*
Name of the contact person

*Email

*
Telephone (DHL requirement)

2

*
NRL or OCL

- NRL
- OCL

Who is the enrolling laboratory (respectively to whom the invoce should be sent)

- enrolled by OCL itself (invoice sent to the abovementioned address)
- enrolled by the respective NRL (invoice sent to the respective NRL)

Any comment or request (not more than 100 characters)

3

ANNEX 4: Announcement of material dispatch

ANNEX 5: Documents sent to participants - OUTLINE and REPORTING INSTRUCTIONS

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 24 May 2016

I

EURL-PAH 2016 PT- MCPDEs and GEs in food

Dear Madame/Sir,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of MCPDEs and GEs in food starts with the dispatch of the samples.

The target analytes are 2-MCPD and 3-MCPD from MCPD ester; 3-MBPD from glycidyl ester. The participants are requested to report results on all of them.

Each participant is provided with about 20 g of bakery products test sample, 2.5 ml spiked oil test sample; 4 ml blank oil, 1 ml labelled standard mix to be used as internal standard and 1 ml unlabeled standard mix with disclosed concentration to be used for calibration check.

Outline of the study.

The participating laboratories shall apply for the analyses a method of their choice.

The laboratories shall report the results by 29th July 2016 at the latest following the instructions provided further on in this document.

The participants are requested to report the results obtained from three replicate analyses. They also have to report a final value for proficiency assessment. Results have to be reported corrected for recovery and the results for proficiency assessment ("final values") have to be accompanied by the respective measurement uncertainty.

Participants are also requested to report together with the results details of the applied analysis method and some method performance characteristics.

Test material and analytes

1. One 60 ml amber glass vial, labelled as *"EU-RL PAHs PT 2016 interlaboratory comparison 440, MCPDEs and GEs in WAFFLES"* containing 25-30 g of a naturally contaminated homogenised waffles. The analytes content shall be determined in triplicate and expressed on product base. For waffle sample the analyte content expressed on fat base should be reported as well, however it will be not mandatory and benchmarked. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value".

   If not analysed immediately after receiving, please store the waffle test sample in the freezer (-18°C).

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E-mail: jrc-irmm-crl-pah@ec.europa.eu

2. One 5 ml amber glass ampule, labelled *EU-RL PAHs PT 2016 Interlaboratory comparison 440, MCPDEs and GEs in olive oil*, containing 1 ml spiked with MCPDEs and GEs extra virgin olive oil test sample and
3. One 5 ml amber glass ampule, labelled *EU-RL PAHs PT 2016 Interlaboratory comparison 440, MCPDEs and GEs in blank oil*, containing 4 ml blank olive oil.

   If not analysed immediately after receiving, please store the olive oil samples in the refrigerator (4°C).

4. One 5 ml amber glass ampules containing 2 ml labelled standard mix to be used as internal standard;
5. One 5 ml amber glass ampules containing 2 ml native standard mix with disclosed concentration; the analytes concentrations are given in the attached document. The solution may be used by the participants to check their instrument calibration against an independent reference. Participants do not have to report results for this solution.

Reporting the results

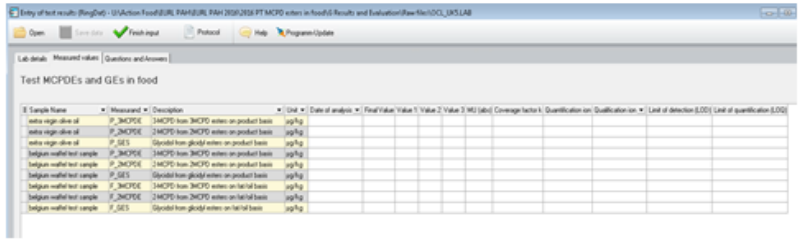
Data generated by the participants will be collected by using software RingDat, supplementary to ProLab software, used until now for professional data handling and statistical analyses of interlaboratory tests results.
You will receive by mail some files for reporting results. You should follow the following instructions:

1. If not available already, please download the data entry program RingDat free from the QuoData web page using following link: http://quodata.de/ringdat_en.php
User: *ringdat*
Password: *prolabdata*

2. Save to the same folder the two lab specific files with the extension **"*.LAB"** and **"*.LAZ"**, generated by the ProLab software and provided to each laboratory individually (personal files) by mail.

3. Start the RingDat.exe program and open **"*.LAB"** file for reporting the results. A table will appear with cells for every measurand/sample combination
   - the name of each laboratory is codified by the software,
   - The **"*.LAZ"** file contains information about the participant – laboratory name and laboratory code;
   - The **"*.LAB"** file is unique to each laboratory (personal) and contains information about the samples and measurands, that have to be analysed and reported.
   - First tab contains the detailed information for the laboratory
   - Second tab contains table for entering the results. You could filter the entries by sample or by measurand. The cells marked with red are mandatory to be filled
   - Third tab contains a general questionnaire.

4. Fill in the result table with your data.



5. Afterwards, please fill in the questionnaire on the next tab.

6. After finishing the input, save the file using the button on the top menu of the window. You could change the inputs after saving the file as long as you haven't pushed "Finish input" button. At the end finalise the data entry by pushing the "Finish input" button.

7. Send both the "*.LAB" and "*.LA" files back to us by e-mail on our functional mail box - jrc-irmm-eurl-pah@ec.europa.eu

8. If you want to correct some of your entries after finishing the input, you should use the original *.LAB file downloaded from the mail.

In case of questions, please do not hesitate to contact us.

With kind regards,

Stefanka Bratinova
EURL-PAH

SAMPLE RECEIPT

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

PROFICIENCY TESTING MATERIAL RECEIPT FORM

2016 PT- MCPDEs and GEs in food

Contact person	
Affiliation	
City, Country	

Content of the parcel

1. One 60 ml amber glass vial containing about 25-30 g of bakery products test sample;
2. One 5 ml amber glass ampules containing 1 ml spiked oil test sample;
3. One 5 ml amber glass ampules containing 4 ml blank oil;
4. One 5 ml amber glass ampules containing 2 ml labelled standard mix to be used as internal standard;
5. One 5 ml amber glass ampules containing 2 ml native standard mix to be used for calibration check;
6. Standard solution mixtures specification sheets;
7. Solvent safety data sheet;
8. One sample receipt form (= this form), which is e-mailed as well to be filed and send electronically

IF NOT ANALYSED IMMEDIATLY AFTER RECEIVING THE PARCEL, PLEASE PUTTHE TEST SAMPLES IN THE FRIZER (at -18°C).

Please ensure that the items listed below have been received undamaged, and then describe the relevant statement:

Date of the receipt of the test materials	
All items have been received undamaged	YES ☐ / NO ☐
If NO, please list damaged items	

Please return the completed form by mail to

Stefanka Bratinova

ANNEX 6: Technical specifications of the calibration solutions

LABLED STANDARD SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
European Union - Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 16.06.2015

Standard solution specification sheet	**Product ID: Labelled compounds**
Date of production: 20/05/2016	Total volume: 2.5 mL
Expiry date: *November 2016*	**MCPDEs & GEs**

Labelled standard solution composition:

	Product name	CAS	Conc.*	Conc.*	U**
			(µg/g)	(µg/ml)	± %
1	Rac-1,2-Distearoyl-3chloropropanediol-d5	124681	6.38	5.50	1.15
2	1,3-Dipalmitoyl-2-chloropropanediol-d5	N/A	6.33	5.46	1.15
3	Glycidyl oleate -d5	N/A	6.38	5.50	1.15

* *The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the density of toluene 0.8621 g/ml at 25ºC.*

** *U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Toluene

Ratio of mol masses (R_M) of labelled free forms of 3-MCPD, 2-MCPD respectively glycidol and the corresponding esters used to prepare calibration standards

	Product name	M.W.	M.W. free form	R_M
		(g/mol)	(g/mol)	
2	3-MCPD-d5 ester	648.49	115.57	0.1782
4	2-MCPD-d5 ester	592.39	115.57	0.1951
6	Gly-O-d5	343.56	74.08	0.2156

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E-mail: jrc-irmm-crl-pah@ec.europa.eu

NATIVE STANDARD SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
European Union - Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 16.06.2015

Standard solution specification sheet	**Product ID: Native compounds**
Date of production: 20/05/2016	Total volume: 2.5 mL
Expiry date: *November 2016*	**MCPDEs & GEs**

Native standard solution composition:

	Product name	CAS	Conc.*	Conc.*	U**
			(µg/g)	(µg/ml)	± %
1	Rac-1,2-Distearoyl-3-chloropropanediol	72468-92-9	6.37	5.49	1.15
2	1,3-Dipalmitoyl-2-chloropropanediol	169471-41-4	6.39	5.51	1.15
3	Glycidyl palmitate	7501-44-2	6.41	5.52	1.15

* *The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in µg/mL is based on the gravimetrical preparation data and the density of toluene 0.8621 g/ml at 25ºC.*

** *U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Toluene

Ratio of mol masses (R_M) of native (labelled) free forms of 3-MCPD, 2-MCPD respectively glycidol and the corresponding esters used to prepare calibration standards.

	Product name	M.W. ester	M.W. free form	R_M
		(g/mol)	(g/mol)	
1	3-MCPD ester	643.46	110.54	0.1718
2	2-MCPD ester	587.36	110.54	0.1882
3	Gly-P	312.49	74.08	0.2371

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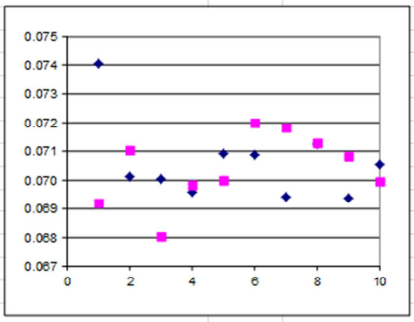
E-mail: jrc-irmm-crl-pah@ec.europa.eu

ANNEX 7: Homogeneity of the test materials

a) waffles

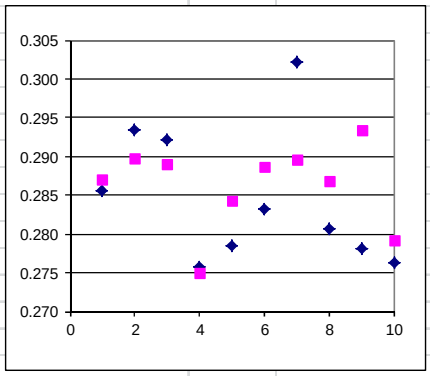
	n =	10				
	mean =	0.07049	22%	= **σ-trg(%)**		
6.3E-07	**s_x =**	0.00079	0.01551	= **σ-trg**		**3-MBPD for GEs**
√MSW =	**s_w =**	0.00139				
u_{∞} =	**s_s =**	0.00058	0.00465	= **0,3*σ**		
	ISO-13528	passed				
	F =	0.64782	3.02038	= Fcrit		
		passed				
	IUPAC					
	(MSB-MSW)/2	-3E-07	4.3E-05	= F1*(0,3*σ)²+F2*MSW		
		passed				

Bottle	Result a	Result b	diff	sum	avg
Vial 10	0.074	0.069	0.00	0.14	0.07
Vial 19	0.070	0.071	0.00	0.14	0.07
Vial 28	0.070	0.068	0.00	0.14	0.07
Vial 3	0.070	0.070	0.00	0.14	0.07
Vial 35	0.071	0.070	0.00	0.14	0.07
Vial 42	0.071	0.072	0.00	0.14	0.07
Vial 48	0.069	0.072	0.00	0.14	0.07
Vial 76	0.071	0.071	0.00	0.14	0.07
Vial 80	0.069	0.071	0.00	0.14	0.07
Vial 89	0.071	0.070	0.00	0.14	0.07
		Σ(diff)² =	3.9E-05		
		var(sum)/2 =		1.25692E-06	=MSB



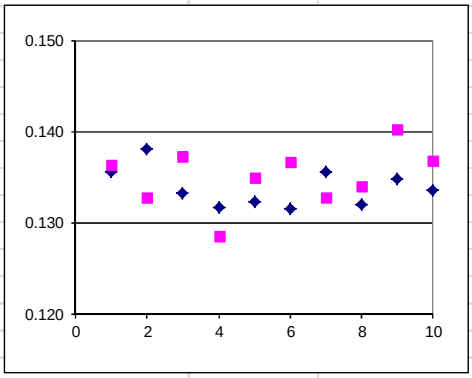
	n =	10				
	mean =	0.28546	22%	= **σ-trg(%)**		
3.9E-05	**s_x =**	0.00627	0.0628	= **σ-trg**		
√MSW =	**s_w =**	0.00512				
u_{bb} =	**s_s =**	0.00512	0.01884	= **0,3*σ**		**3-MCPDEs**
	ISO-13528	passed				
	F =	2.9984	3.02038	= Fcrit		
		passed				
	IUPAC					
	(MSB-MSW)/2	2.6E-05	0.00069	= F1*(0,3*σ)²+F2*MSW		
		passed				

Bottle	Result a	Result b	diff	sum	avg
Vial 10	0.286	0.287	0.00	0.57	0.29
Vial 19	0.293	0.290	0.00	0.58	0.29
Vial 28	0.292	0.289	0.00	0.58	0.29
Vial 3	0.276	0.275	0.00	0.55	0.28
Vial 35	0.279	0.284	-0.01	0.56	0.28
Vial 42	0.283	0.289	-0.01	0.57	0.29
Vial 48	0.302	0.290	0.01	0.59	0.30
Vial 76	0.281	0.287	-0.01	0.57	0.28
Vial 80	0.278	0.293	-0.02	0.57	0.29
Vial 89	0.276	0.279	0.00	0.56	0.28
		Σ(diff)² =	0.00052		
		var(sum)/2 =		7.85576E-05	=MSB



	n =	10							
	mean =	0.13441	22%	**= σ-trg(%)**					
4E-06	**s_x =**	0.002	0.02957	**= σ-trg**					
√MSW =	**s_w =**	0.00268						**2-MCPDEs**	
u_{bb} =	**s_s =**	0.00064	0.00887	**= 0,3*σ**					
	ISO-13528	passed							
	F =	1.11258	3.02038	= Fcrit					
		passed							
	IUPAC								
(MSB-MSW)/2		4E-07	0.00016	= F1*(0,3*σ)^2+F2*MSW					
		passed							

Bottle	Result a	Result b	diff	sum	avg
Vial 10	0.136	0.136	0.00	0.27	0.14
Vial 19	0.138	0.133	0.01	0.27	0.14
Vial 28	0.133	0.137	0.00	0.27	0.14
Vial 3	0.132	0.128	0.00	0.26	0.13
Vial 35	0.132	0.135	0.00	0.27	0.13
Vial 42	0.132	0.137	-0.01	0.27	0.13
Vial 48	0.136	0.133	0.00	0.27	0.13
Vial 76	0.132	0.134	0.00	0.27	0.13
Vial 80	0.135	0.140	-0.01	0.27	0.14
Vial 89	0.133	0.137	0.00	0.27	0.14

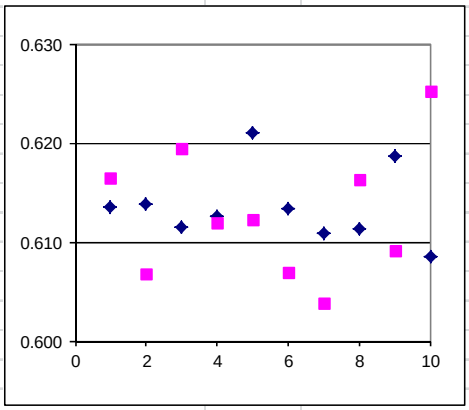


Σ(diff)^2 =	0.00014		
var(sum)/2 =		7.97148E-06	=MSB

a) spiked olive oil

	n =	10							
	mean =	0.61317	22%	**= σ-trg(%)**					
9.7E-06	**s_x =**	0.00312	0.1349	**= σ-trg**					
√MSW =	**s_w =**	0.00584						**2-MCPDEs**	
	s_s =	0.0027	0.04047	**= 0,3*σ**					
	ISO-13528	passed							
	F =	0.57179	3.02038	= Fcrit					
		passed							
	IUPAC								
(MSB-MSW)/2		-7E-06	0.00311	= F1*(0,3*σ)^2+F2*MSW					
		passed							

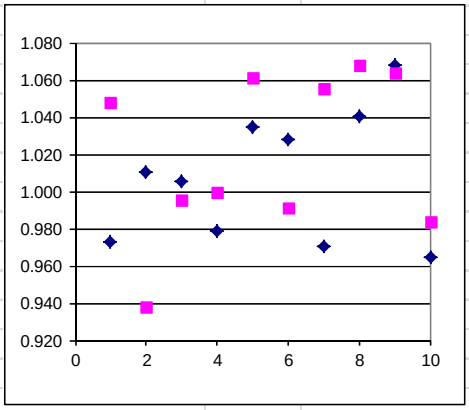
Bottle	Result a	Result b	diff	sum	avg
Ampoule 11	0.613	0.616	0.00	1.23	0.61
Ampoule 12	0.614	0.607	0.01	1.22	0.61
Ampoule 32	0.611	0.620	-0.01	1.23	0.62
Ampoule 33	0.613	0.612	0.00	1.22	0.61
Ampoule 46	0.621	0.612	0.01	1.23	0.62
Ampoule 49	0.613	0.607	0.01	1.22	0.61
Ampoule 51	0.611	0.604	0.01	1.21	0.61
Ampoule 55	0.611	0.616	-0.01	1.23	0.61
Ampoule 62	0.619	0.609	0.01	1.23	0.61
Ampoule 64	0.609	0.625	-0.02	1.23	0.62



Σ(diff)^2 =	0.00068		
var(sum)/2 =		1.9E-05	=MSB

	n =	10			
	mean =	1.01383	22%	**= σ-trg(%)**	
0.00105	**s_x =**	0.03234	0.22304	**= σ-trg**	**3-MBPD for GEs**
√MSW =	**s_w =**	0.033			
	s_s =	0.02239	0.06691	**= 0,3*σ**	
	ISO-13528	passed			
	F =	1.92085	3.02038	= Fcrit	
		passed			
	IUPAC				
	(MSB-MSW)/2	0.0005	0.00952	= F1*(0,3*σ)^2+F2*MSW	
		passed			

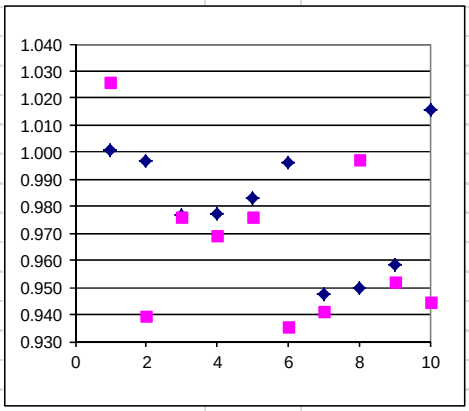
Bottle	Result a	Result b	diff	sum	avg
Ampoule 11	0.973	1.048	-0.08	2.02	1.01
Ampoule 12	1.011	0.938	0.07	1.95	0.97
Ampoule 32	1.005	0.995	0.01	2.00	1.00
Ampoule 33	0.979	1.000	-0.02	1.98	0.99
Ampoule 46	1.034	1.061	-0.03	2.10	1.05
Ampoule 49	1.028	0.992	0.04	2.02	1.01
Ampoule 51	0.970	1.055	-0.08	2.03	1.01
Ampoule 55	1.040	1.068	-0.03	2.11	1.05
Ampoule 62	1.068	1.064	0.00	2.13	1.07
Ampoule 64	0.965	0.984	-0.02	1.95	0.97



Σ(diff)^2 =	0.02178		
var(sum)/2 =		0.00209	=MSB

	n =	10			
	mean =	0.973	22%	**= σ-trg(%)**	
0.00033	**s_x =**	0.01805	0.21406	**= σ-trg**	
√MSW =	**s_w =**	0.02738			**3-MCPDEs**
	s_s =	0.00699	0.06422	**= 0,3*σ**	
	ISO-13528	passed			
	F =	0.86946	3.02038	= Fcrit	
		passed			
	IUPAC				
	(MSB-MSW)/2	-5E-05	0.00851	= F1*(0,3*σ)^2+F2*MSW	
		passed			

Bottle	Result a	Result b	diff	sum	avg
Ampoule 11	1.001	1.026	-0.03	2.03	1.01
Ampoule 12	0.997	0.939	0.06	1.94	0.97
Ampoule 32	0.977	0.976	0.00	1.95	0.98
Ampoule 33	0.977	0.969	0.01	1.95	0.97
Ampoule 46	0.983	0.976	0.01	1.96	0.98
Ampoule 49	0.996	0.936	0.06	1.93	0.97
Ampoule 51	0.948	0.941	0.01	1.89	0.94
Ampoule 55	0.950	0.997	-0.05	1.95	0.97
Ampoule 62	0.958	0.952	0.01	1.91	0.96
Ampoule 64	1.016	0.945	0.07	1.96	0.98



Σ(diff)^2 =	0.01499		
var(sum)/2 =		0.00065	=MSB

ANNEX 8. Stability of the test materials for the period of the study

a) waffles

3-MCPD

	Waffles	Time Weeks at test temerature	3-MCPD µg/kg product
-78	Replicate 1	0	0.271
	Replicate 2	0	0.264
	Replicate 3	0	0.279
(-78 to -18)	Replicate 1	6	0.279
	Replicate 2	6	0.288
	Replicate 3	6	0.271
-18	Replicate 1	12	0.274
	Replicate 2	12	0.283
	Replicate 3	12	0.274

Regression	y=ax+b		
a	0.00048	0.27292	b
SEa	0.00049	0.00378	SEb
r2	0.12248	0.00717	SEy
F	0.97705	7	df
ss(reg)	0.00005	0.00036	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.365
U_a	0.00115

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

	Waffles	Time Weeks at test temerature	3-MCPD µg/kg product
-78	Replicate 1	0	0.271
	Replicate 2	0	0.264
	Replicate 3	0	0.279
(-78 to -4)	Replicate 1	6	0.271
	Replicate 2	6	0.271
	Replicate 3	6	0.271
-4	Replicate 1	12	0.266
	Replicate 2	12	0.288
	Replicate 3	12	0.259

Regression	y=ax+b		
a	-0.00036	0.27180	b
SEa	0.00043	0.00258	SEb
r2	0.12520	0.00477	SEy
F	0.71557	5	df
ss(reg)	0.00002	0.00011	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.571
U_a	0.00110

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

2-MCPD

	Waffles	Time Weeks at test temerature	2-MCPD µg/kg product
-78	Replicate 1	0	0.1313
	Replicate 2	0	0.1306
	Replicate 3	0	0.1307
(-78 to -18)	Replicate 1	6	0.1297
	Replicate 2	6	0.1346
	Replicate 3	6	0.1314
-18	Replicate 1	12	0.1308
	Replicate 2	12	0.1317
	Replicate 3	12	0.1285

Regression	y=ax+b		
a	-0.00005	0.13132	b
SEa	0.00012	0.00093	SEb
r2	0.02280	0.00176	SEy
F	0.16335	7	df
ss(reg)	0.00000	0.00002	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.365
U_a	0.00028

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

	Waffles	Time Weeks at test temerature	2-MCPD µg/kg product
-78	Replicate 1	0	0.1313
	Replicate 2	0	0.1306
	Replicate 3	0	0.1307
(-78 to -4)	Replicate 1	6	0.1293
	Replicate 2	6	0.1304
	Replicate 3	6	0.1297
-4	Replicate 1	12	0.1304
	Replicate 2	12	0.1320
	Replicate 3	12	0.129212424

Regression	y=ax+b		
a	0.00001	0.13050	b
SEa	0.00007	0.00049	SEb
r2	0.00317	0.00092	SEy
F	0.01907	6	df
ss(reg)	0.00000	0.00001	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.447
U_a	0.00017

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

3-MBPD

	Waffles	Time Weeks at test temerature	3-MBPD µg/kg product
-78	Replicate 1	0	0.0801
	Replicate 2	0	0.0863
	Replicate 3	0	0.0816
(-78 to -18)	Replicate 1	6	0.0785
	Replicate 2	6	0.0775
	Replicate 3	6	0.0819
-18	Replicate 1	12	0.0881
	Replicate 2	12	0.0778
	Replicate 3	12	0.0786

Regression	y=ax+b		
a	-0.00010	0.08172	b
SEa	0.00027	0.00210	SEb
r2	0.01729	0.00398	SEy
F	0.12317	7	df
ss(reg)	0.00000	0.00011	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.365
U_a	0.00064

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

	Waffles	Time Weeks at test temerature	3-MBPD µg/kg product
-78	Replicate 1	0	0.0801
	Replicate 2	0	0.0863
	Replicate 3	0	0.0816
(-78 to -4)	Replicate 1	6	0.0710
	Replicate 2	6	0.0794
	Replicate 3	6	0.0743
-4	Replicate 1	12	0.0764
	Replicate 2	12	0.0938
	Replicate 3	12	0.0713

Regression	y=ax+b		
a	0.00009	0.07988	b
SEa	0.00058	0.00410	SEb
r2	0.00426	0.00772	SEy
F	0.02565	6	df
ss(reg)	0.00000	0.00036	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.447
U_a	0.00143

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

a) spiked olive oil

3-MCPD

	Olive oil	Time Weeks at test temerature	3-MCPD µg/kg product
-18	Replicate 1	0	0.939
	Replicate 2	0	0.913
	Replicate 3	0	0.946
(-18 to 4)	Replicate 1	6	0.948
	Replicate 2	6	0.960
	Replicate 3	6	0.942
4	Replicate 1	12	0.917
	Replicate 2	12	0.945
	Replicate 3	12	0.967

Regression y=ax+b

a	0.00085	0.93681	b
SEa	0.00124	0.00959	SEb
r2	0.06308	0.01820	SEy
F	0.47125	7	df
ss(reg)	0.00016	0.00232	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.365
U_a	0.00293

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

3-MBPD

	Olive oil	Time Weeks at test temerature	3-MBPD µg/kg product
-18	Replicate 1	0	1.085
	Replicate 2	0	1.097
	Replicate 3	0	1.096
(-18 to 4)	Replicate 1	6	1.078
	Replicate 2	6	1.093
	Replicate 3	6	1.045
4	Replicate 1	12	1.075
	Replicate 2	12	1.105
	Replicate 3	12	1.090

Regression y=ax+b

a	-0.00023	1.08604	b
SEa	0.00128	0.00995	SEb
r2	0.00452	0.01889	SEy
F	0.03177	7	df
ss(reg)	0.00001	0.00250	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

$t_{\alpha,df}$	2.365
U_a	0.00304

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

2-MCPD

	Olive oil	Time Weeks at test temerature	2-MCPD µg/kg product
-18	Replicate 1	0	0.625
	Replicate 2	0	0.617
	Replicate 3	0	0.611
(-18 to 4)	Replicate 1	6	0.623
	Replicate 2	6	0.625
	Replicate 3	6	0.617
4	Replicate 1	12	0.615
	Replicate 2	12	0.622
	Replicate 3	12	0.613

Regression y=ax+b

a	-0.00008	0.61901	b
SEa	0.00037	0.00284	SEb
r2	0.00693	0.00539	SEy
F	0.04883	7	df
ss(reg)	0.00000	0.00020	(ss(resid)

Uncertainty of "a" $U_a = t_{\alpha,df} \times SE_a$

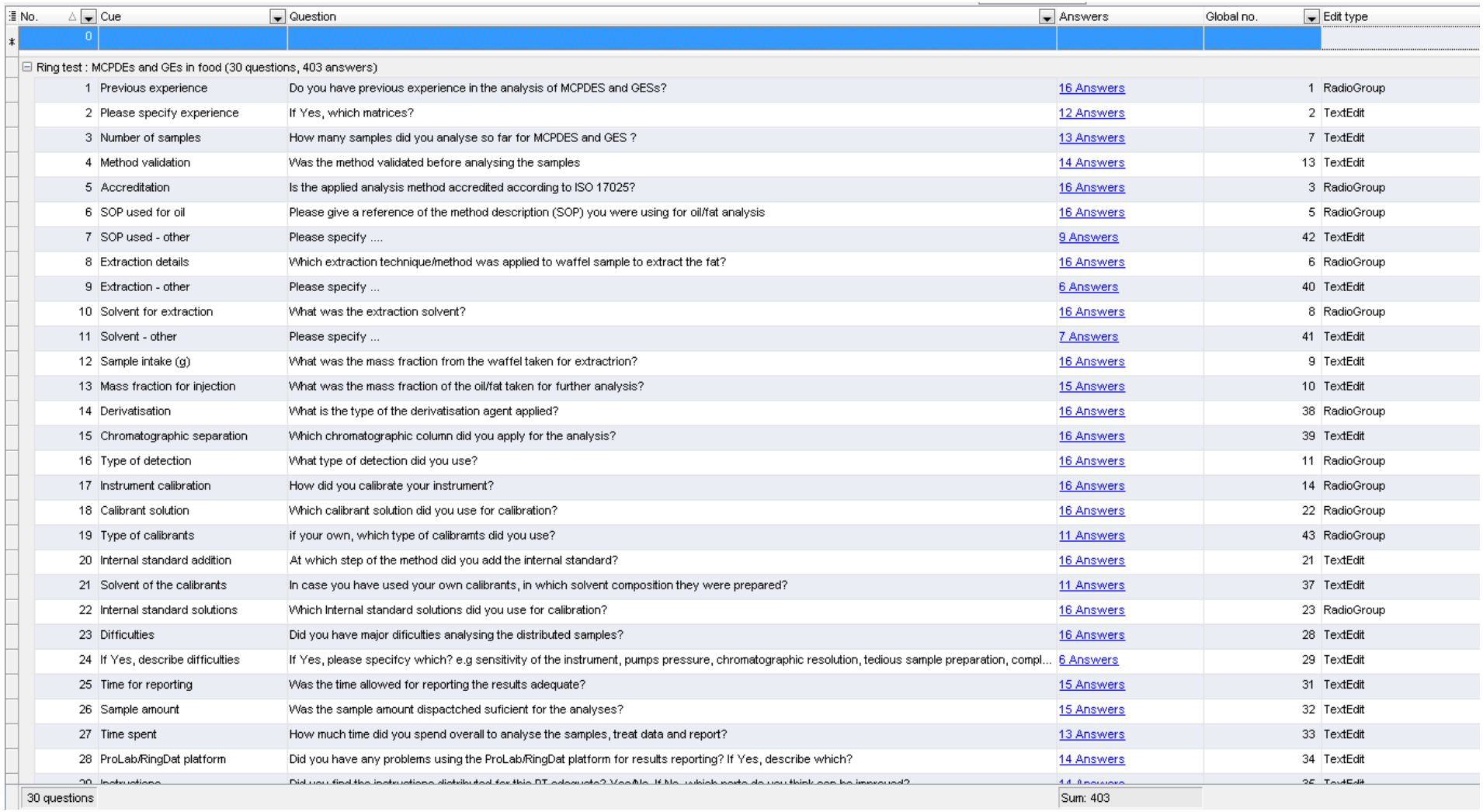
$t_{\alpha,df}$	2.365
U_a	0.00087

Decision Sample is homogeneous if: $|a| < U_a$

STABLE

ANNEX 9. Questionnaire and answers from the participants

Ring test : 2015 PT PAH in smoked fish, herring (13 questions, 487 answers)				
1	Compliance with the ML	Is the test sample compliant with the CURRENT legislative maximum levels (MLs)?	38 Answers	ComboBox
2	Level of confidence	What is the level of confidence, e.g. the coverage factore (k) given by your results?	35 Answers	TextEdit
3	Uncertainty estimate	What is the basis of your uncertainty estimation? (multiple answers are possible)	40 Answers	CheckGroup
4	Uncertainty dependance	Does the reported uncertainty depend on the analyte/matrix combination?	39 Answers	RadioGroup
5	Reporting uncertainty	Do you usually provide an uncertainty statment to your customers for this type of analysis?	39 Answers	RadioGroup
6	Basis for LOD/LOQ	What are the basis of the reported LOD/LOQs?	40 Answers	CheckGroup
7	Calibration	What type of calibration did you use?	39 Answers	RadioGroup
8	Recovery rate	Do you report your results corrected for recovery ?	40 Answers	RadioGroup
9	Laboratory accredeted	Is your laboratory accredeted for analysis of PAHs in smoked fish?	40 Answers	RadioGroup
10	Previous experience	How many smoked fish samples/year do you analyse usually?	39 Answers	TextEdit
11	Problems analysis	Did you experience problems during analysis?	37 Answers	TextEdit
12	Problems reporting	Did you experience problems during reporting?	36 Answers	TextEdit
13	Comment	Do you have any comments? Please let us know ...	25 Answers	TextEdit



No.	Cue	Question	Answers	Global no.	Edit type
0					
Ring test : MCPDEs and GEs in food (30 questions, 403 answers)					
1	Previous experience	Do you have previous experience in the analysis of MCPDES and GESs?	16 Answers	1	RadioGroup
2	Please specify experience	If Yes, which matrices?	12 Answers	2	TextEdit
3	Number of samples	How many samples did you analyse so far for MCPDES and GES ?	13 Answers	7	TextEdit
4	Method validation	Was the method validated before analysing the samples	14 Answers	13	TextEdit
5	Accreditation	Is the applied analysis method accredited according to ISO 17025?	16 Answers	3	RadioGroup
6	SOP used for oil	Please give a reference of the method description (SOP) you were using for oil/fat analysis	16 Answers	5	RadioGroup
7	SOP used - other	Please specify	9 Answers	42	TextEdit
8	Extraction details	Which extraction technique/method was applied to waffel sample to extract the fat?	16 Answers	6	RadioGroup
9	Extraction - other	Please specify ...	6 Answers	40	TextEdit
10	Solvent for extraction	What was the extraction solvent?	16 Answers	8	RadioGroup
11	Solvent - other	Please specify ...	7 Answers	41	TextEdit
12	Sample intake (g)	What was the mass fraction from the waffel taken for extractrion?	16 Answers	9	TextEdit
13	Mass fraction for injection	What was the mass fraction of the oil/fat taken for further analysis?	15 Answers	10	TextEdit
14	Derivatisation	What is the type of the derivatisation agent applied?	16 Answers	38	RadioGroup
15	Chromatographic separation	Which chromatographic column did you apply for the analysis?	16 Answers	39	TextEdit
16	Type of detection	What type of detection did you use?	16 Answers	11	RadioGroup
17	Instrument calibration	How did you calibrate your instrument?	16 Answers	14	RadioGroup
18	Calibrant solution	Which calibrant solution did you use for calibration?	16 Answers	22	RadioGroup
19	Type of calibrants	if your own, which type of calibramts did you use?	11 Answers	43	RadioGroup
20	Internal standard addition	At which step of the method did you add the internal standard?	16 Answers	21	TextEdit
21	Solvent of the calibrants	In case you have used your own calibrants, in which solvent composition they were prepared?	11 Answers	37	TextEdit
22	Internal standard solutions	Which Internal standard solutions did you use for calibration?	16 Answers	23	RadioGroup
23	Difficulties	Did you have major dificulties analysing the distributed samples?	16 Answers	28	TextEdit
24	If Yes, describe difficulties	If Yes, please specifcy which? e.g sensitivity of the instrument, pumps pressure, chromatographic resolution, tedious sample preparation, compl...	6 Answers	29	TextEdit
25	Time for reporting	Was the time allowed for reporting the results adequate?	15 Answers	31	TextEdit
26	Sample amount	Was the sample amount dispactched suficient for the analyses?	15 Answers	32	TextEdit
27	Time spent	How much time did you spend overall to analyse the samples, treat data and report?	13 Answers	33	TextEdit
28	ProLab/RingDat platform	Did you have any problems using the ProLab/RingDat platform for results reporting? If Yes, describe which?	14 Answers	34	TextEdit
29	Instructions	Did you find the instructions distributed for this PT adequate? Yes/No. If No, which parts do you think can be improved?	14 Answers	35	TextEdit
30 questions			Sum: 403		

Lab details | Measured values | Questions and Answers

Nr	Cue	Question	Answer
1	Previous experience	Do you have previous experience in the analysis of MCPDES and GESs?	○ No ○ Yes
2	Please specify experience	If Yes, which matrices?	
3	Number of samples	How many samples did you analyse so far for MCPDES and GES ?	
4	Method validation	Was the method validated before analysing the samples	
5	Accreditation	Is the applied analysis method accredeted according to ISO 17025?	○ No ○ Yes
6	Reference of the SOP used	Please give a reference of the method description (SOP) you were using.	○ AOAC 13a ○ AOAC 13b ○ AOAC 13c ○ JRC ○ other
7	SOP used - other	Please specify	
8	Extraction details	Which extraction technique/method was applied to waffel sample to extract the fat?	○ Pressurised Lquid Extraction (PLE) ○ Sonication ○ Soxhlet ectraction ○ Rose-Gottlieb ○ Other
9	Extraction - other	Please specify ...	
10	Solvent for extraction	What was the extraction solvent?	○ TBME ○ acetone ○ n-hexane ○ other
11	Solvent - other	Please specify ...	
12	Sample intake (g)	What was the mass fraction from the waffel taken for extractrion?	
13	Mass fraction for injection	What was the mass fraction of the oil/fat taken for further analysis?	
14	Derivatisation	What is the type of the derivatisation agent applied?	○ PBA ○ HFBI ○ other
15	Chromatographic separation	Which chromatographic column did you apply for the analysis?	
16	Type of detection	What type of detection did you use?	○ GC-MS ○ GC-MS/MS ○ GC-HRMS
17	Instrument calibration	How did you calibrate your instrument?	○ Internal standartisatyion ○ External calibration
18	Calibrant solution	Which calibrant solution did you use for calibration?	○ provided by JRC native compounds solution ○ laboratory own standard solutions of native compounds
19	Type of calibrants	if your own, which type of calibramts did you use?	○ free form of analytes ○ esters of analytes
20	Internal standard addition	At which step of the method did you add the internal standard?	
21	Solvent of the calibrants	In case you have used your own calibrants, in which solvent composition they were prepared?	
22	Internal standard solutions	Which Internal standard solutions did you use for calibration?	○ provided by JRC ○ laboratory own standards
23	Difficulties	Did you have major dificulties analysing the distributed samples?	
24	If Yes, describe difficulties	If Yes, please specifcy which? e.g sensitivity of the instrument, pumps pressure, chromatographic resolution, tedious sample preparation, complex matrix, purchase of standards, purchase of isotope labelled internal standards, other	
25	Time for reporting	Was the time allowed for reporting the results adequate?	
26	Sample amount	Was the sample amount dispactched suficient for the analyses?	
27	Time spent	How much time did you spend overall to analyse the samples, treat data and report?	
28	ProLab/RingDat platform	Did you have any problems using the ProLab/RingDat platform for results reporting? If Yes, describe which?	
29	Instructions	Did you find the instructions distributed for this PT adequate? Yes/No. If No, which parts do you think can be improved?	
30	Any other comments	Any other comments you wish to address?	

Lab Code	1. Previous experience	2. Please specify experience	3. Number of samples	4. Method validation	5. Accreditation
105	Yes	oil, margarine, deep-frying fat, baby food, breadsticks, chips, soy sauce	300	yes	Yes
110					
115	Yes	vegetable oil	30	yes	Yes
120	No			No	No
125	Yes	Aceites	En proceso de validaciyn	No	Yes
130	Yes		0		Yes
135	Yes	Palm Oil	1	Yes	No
140	No		0	No	No
155	Yes	Oils and fats	~50	No	Yes
160					
165	Yes	vegetable oils and fats	20-30	partially	No
170	Yes	edible oil only 3-MCPDEs	few	only 3-MCPDEs	Yes
175					
505	Yes	oil	20	no	No
510	Yes	We participated in two method testing ring trials of German BfR resulting in the method BfR_82_FC-009-01. Since then we are analysing all kinds of fats and oils used as food as well as food, rich in fat like mayonnaise, hazelnut spread or fried bakery products. We analysed infant formula as well, but encountered problems with the fat extraction with some special kinds of	Our method is validated for 2- and 3-mcpd-esters only. We have analysed about 400 samples up to now.	yes	Yes
515	Yes	vegetable oils, broaded fish, hazelnut cocoa spread, milk powder, strawberry cream, chocolate cream, onion lard,	244	Yes, except 2-MCPDE	Yes
520	Yes	oils and fatty food		yes	Yes
525	Yes	oil, chips, crisps, infant formula	200	yes, accreditation in progress	No
530	No				No
535					
540					

Lab Code	6. SOP used for oil	7. SOP used - other	8. Extraction details	9. Extraction - other	10. Solvent for extraction
105	Other	Equivalent to JRC with following modifications: Using GC/MS-MS, using Heptafluorobutylrilation for derivatization, using interlal standard addition from the beginning (to the sample weight), fat extraction integrated in the procedure (in one step	Other	sample mixed with internal standards, aeqeous sodiumsulfate solution and n-hexane, a aliqout of the n-hexane extract is used for	n-hexane
110					
115	AOAC 13c		Pressurised Liquid Extraction		n-hexane
120	JRC		Other	Both PLE and Soxhlet	other
125	JRC	JRC	Soxhlet		n-hexane
130	JRC		Pressurised Liquid Extraction		TBME
135	JRC		Other	Liquid/Liquid partition and	TBME
140	JRC		Other	Extraction recommended by JRC: 0,5g waffel +2ml water, extracted 3 times with 2 ml TBME	TBME
155	JRC		Pressurised Liquid Extraction		TBME
160					
165	JRC	with minor modification for GC method	Soxhlet		TBME
170	Other	DGF Standard Method C III 18 (2009) by difference	Sonication		TBME
175					
505	AOAC 13a		Pressurised Liquid Extraction		TBME
510	Other	BfR_82_FC-009-01 (BfR-Methode 9 + ASE-Extraktion, BfR-Methode 22)	Pressurised Liquid Extraction		other
515	Other	BfR Method 9 from "Ringversuch zur Bestimmung von 3-MCPD-Fettsдureester in Speisefetten und -цlen (2. Ringversuch	Soxhlet Extraction		other
520	Other	DGF C-VI-18 [10], modified - Kuhlmann method	Other	fat-extraction	other
525	Other	Determination of 3-Monochloropropane-1,2-diol and 2-Monochloropropane-1,3-diol (MCPD) Esters and Glycidyl Esters by Microwave Extraction in Different Foodstuffs, J. Agric. Food Chem., 2016, 64 (21), pp 4353-4361, DOI: 10.1021/acs.jafc.6b00770 microwave extraction + Kulhmann	Sonication	microwave extraction	other
530	Other	Determination of bound 2,3-epoxy-1-propanol (glycidol) and bound monochloropropanediol (MCPD) in refined oils - Jan Kuhlmann, SGS Germany GmbH, Hamburg, Germany.	Rose-Gottlieb		other
535					
540					

Lab Code	11. Solvent - other	12. Sample intake (g)	13. Mass fraction for injection	14. Derivati-sation	15. Chromatographic separation	16. Type of detection	17. Instrument calibration
105		4g	0.1g	HFBI	DB-35 MS	GS-MS	External calibration
110							
115	acetone/hexane 50/50	5 gram	0.1 gram	PBA	DB5-MS	GS-MS/MS	Internal standartisation
120	PLE: TBME SOxhlet: Pentan-acetone	PLE: 5 gram Soxhlet 10	0.1 gram	PBA	DB-5ms	GS-MS/MS	Internal standartisation
125		5	0.1 g	PBA	HP-5MS 30 Agilent	GS-MS/MS	Internal standartisation
130		5 g	100 mg	PBA	DB-5ms	GS-MS	Internal standartisation
135		1 g	100 mg	PBA	DB-5MS	GS-MS/MS	Internal standartisation
140		0,5 g	100 mg	PBA	DB-5MS 30 m x 0,25mm ID, 0,25 µm d.f.	GS-MS/MS	Internal standartisation
155		5 g	100 mg	PBA	30m x 0.25 x 0.25 5MS	GS-MS/MS	Internal standartisation
160							
165		10 g	0.100 g	PBA	VF-5ms 30 m, 0.25 mm, df=0.25 um	GS-MS/MS	Internal standartisation
170		5	0,1	PBA	DB5-MS	GS-MS/MS	Internal standartisation
175							
505		5	0,1 g	PBA	30m ZB 5 MS 0.25 mm x 0.25 µm	GS-MS/MS	Internal standartisation
510	petrol ether/ isohexane/acetone (2/2/1. v/v)	2.5 g		PBA	Restek Rxi-5ms 30 m x 0,25 mm ID 0,25 µm film	GS-MS	Internal standartisation
515	petroleum benzine	5 g	100 mg	PBA	DB-5 MS 30m*0,25 mm ID*0,25 mm FD	GS-MS/MS	Internal standartisation
520	n-Hexan/ tBME	30 g	0,3 g	PBA	VF-5	GS-MS/MS	Internal standartisation
525	ethyl acetate	0.45 g	0.1 g	PBA	HP 5 MS, 30m, 0.25 mm, 0.25 µm	GS-MS/MS	Internal standartisation
530	ethanol, diethyl ether, petroleum ether	2	0.1g	PBA	5% Penyl Polysilphenylene-siloxane 30m X 0.25mm ID X 0.25um film	GS-MS/MS	Internal standartisation
535							
540							

Lab Code	18. Calibrant solution	19. Type of calibrants	20. Internal standard addition	21. Solvent of the calibrants	22. Internal standard solutions	23. Diffi-culties	24. If Yes, describe difficulties
105	laboratory own standard solutions of native compounds	esters of analytes	right at the beginning, at the same step we add the sodiumsulfate solution and n-hexane	isooctane	Laboratory own standards	No	
110							
115	laboratory own standard solutions of native compounds	free form of analytes	oil analysis	ethylacetate	Laboratory own standards	No	
120	provided by JRC native compouds solution	esters of analytes	fat	toluene / tetrahydrofuran	Provided by JRC	no	
125	provided by JRC native compouds solution	esters of analytes	After the fat extraction		Provided by JRC	Yes	Bad extraction of fat and extraneous peaks (artifacts ?)
130	provided by JRC native compouds solution		Waffel: after PLE extraction, Oil: at the beginning before glycidyl ester conversion		Provided by JRC	Yes	chromatographic resolution (3-MBPD), extra phases during sample prepartion, evaporation of standards during the srorage.
135	provided by JRC native compouds solution		in fat (after fat extraction)		Provided by JRC	Yes	The recommended target ion of 146 m/z for MBPD could not be used due to high interference (matrix). Instead the qualifier ion
140	provided by JRC native compouds solution		We added the IS to the 100 mg fat sụolved in 2 ml THF (after we have exrtacted the fat content and weighed 100 mg of it)		Provided by JRC	Yes	Yes. On the first trial run we had a lot of background, on the second run the situation was better, but the shape of the Q1 peaks was still bad. So we used Q2 ions to quantitate. The purchase of standards is difficult and expensive.
155	laboratory own standard solutions of native compounds		To the oil or extracted oil for >5% fat matrix, to food for <5% fat matrix	Toluene	Provided by JRC	Yes	We had instrumental problems while setting up for this determination.
160							
165	provided by JRC native compouds solution		to fat sample (before GE conversion)		Provided by JRC	No	
170	laboratory own standard solutions of native compounds	free form of analytes	at beginning - after weighing fat	ethyl acetate	Laboratory own standards	Yes	purchase of standards, missing method for determination MCPDES and GES in waffels
175							
505	laboratory own standard solutions of native compounds	esters of analytes	after extraction	toluene	Laboratory own standards	No	
510	laboratory own standard solutions of native compounds	free form of analytes	Before hydrolysis of fat	in ethyl alcohole	Laboratory own standards	No	
515	laboratory own standard solutions of native compounds	free form of analytes	after fat extraction, before further analysis (alkaline hydroylsis, derivatisation)	in ethyl acetate	Laboratory own standards	No	
520	laboratory own standard solutions of native compounds	esters of analytes	after sample weighting	Toluene	Laboratory own standards	No	
525	laboratory own standard solutions of native compounds	esters of analytes	at the beginning	toluene	Laboratory own standards	No	
530	laboratory own standard solutions of native compounds	free form of analytes	at the beginning	toluene	Laboratory own standards	No	
535							
540							

Lab Code	25. Time for reporting	26. Sample amount	27. Time spent	28. ProLab/RingDat platform	29. Instructions	30. Any other comments
105	yes	mostly yes, more oil sample would be appreciated	12 hours	no	yes	
110						
115	yes	yes	1 week	no	yes	
120	yes (long)	More would have be nice	one week			
125		No		No	Yes	Insufficient time due to illness and holidays
130	No, new compounds and new matrices so there was not enough time to test the method properly	Yes	1,5 week	yes		I used both GC-MS and GC-MS/MS for analysis
135	Yes	Yes	2 weeks	No	Yes	An alternative for fat extraction has to be elaborated. The target range of expected values has to be clear.
140	Yes	Yes	2 weeks	No	No. The SOP has errors on several points. (eg. points 9.3 and 4, and Table 4)	
155	No	Yes		No	Yes	
160						
165	yes	yes	3 days	no	yes	
170	No	Yes	three weeks	No	Yes	more information before starting PT for better preparation PT in lab
175						
505	yes	yes	4 days	no	yes	
510	Yes	Yes	about four working days	No	Instructions were adequate	
515	Yes	Yes	2 weeks	Yes, could not enter additionally MU in µg/kg	Yes	
520	yes	yes			yes	
525	1 h	Yes	one week	no	yes	
530	Yes		one week	No	Yes	
535						
540						

Annex 10. Method performance LOD and LOQ as reported

Limit of detection (LOD) and Limit of quantitation (LOQ), μg/kg

Lab. Code	3-MCPDEs oil			3-MCPDEs waffles			GEs in oil			GEs in waffles	
	LOD	LOQ		LOD	LOQ		LOD	LOQ		LOD	LOQ
105											
110											
115	45	90									
120											
125											
130	50	150		50	150		100	300		100	300
135	5	18		1	4		4	14		1	3
140	58	174		30	90		20	60		6	18
155	50	100		50	100		50	100		50	100
160											
165	4	8		4	8		4	8		4	8
170	30	110		30	110						
175											
505	15	30		3	80					15	30
510	60	220					50	150			
515	11.3	300		15	30		15	30			
520	50	150		17	61						
525	30	100		7	20		30	100		7	20
530		50						50			
535											
540											

ANNEX 11: Data reported by participants

The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores. "Mean values" and "Rel. reproducibility s.d." represent the robust mean values and the robust standard deviations of the participants data, calculated according to the ISO 13528 algorithm. Very slight differences in the mean values on both graphs are possible as on the Kernel density plot mean values are calculated based on the "final values" reported by the participants while on the Distribution graphs they are calculated based on the three replicate results.

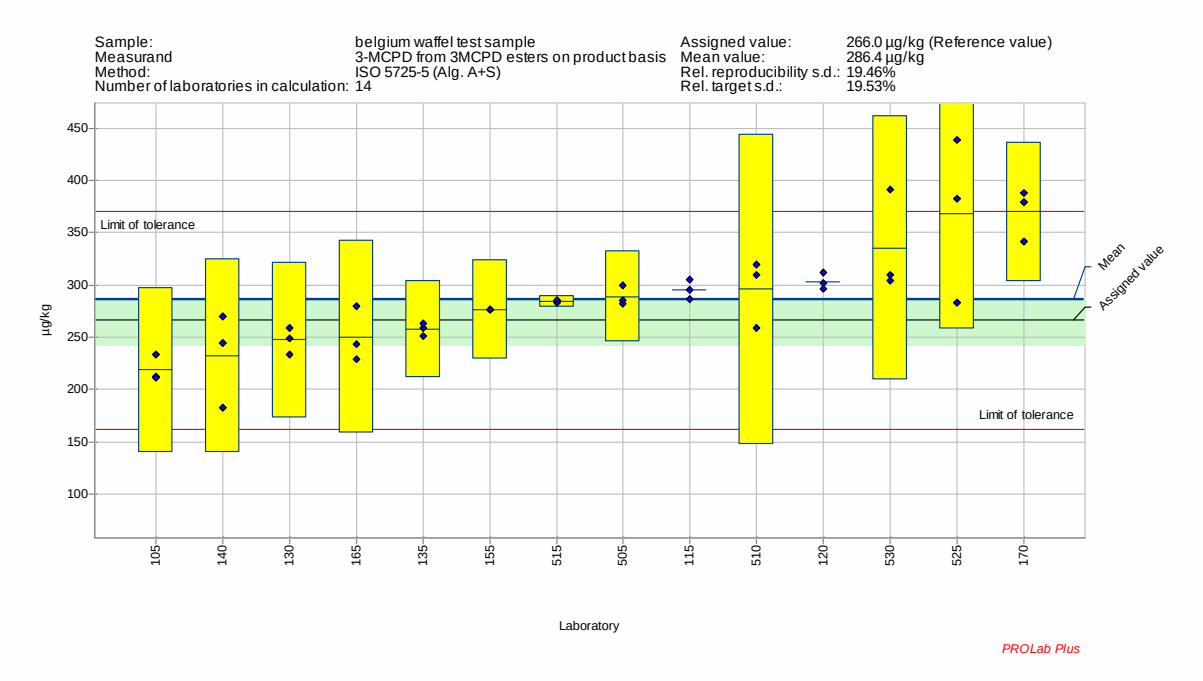
A. Results, as reported by the participants and scoring, for the content of 3-MCPD from 3-MCPDEs expressed as mass/mass waffles test sample.
Assigned value - 266 µg/kg.

Table 1: 3-MCPDEs in waffles test sample - Summary results of measured values

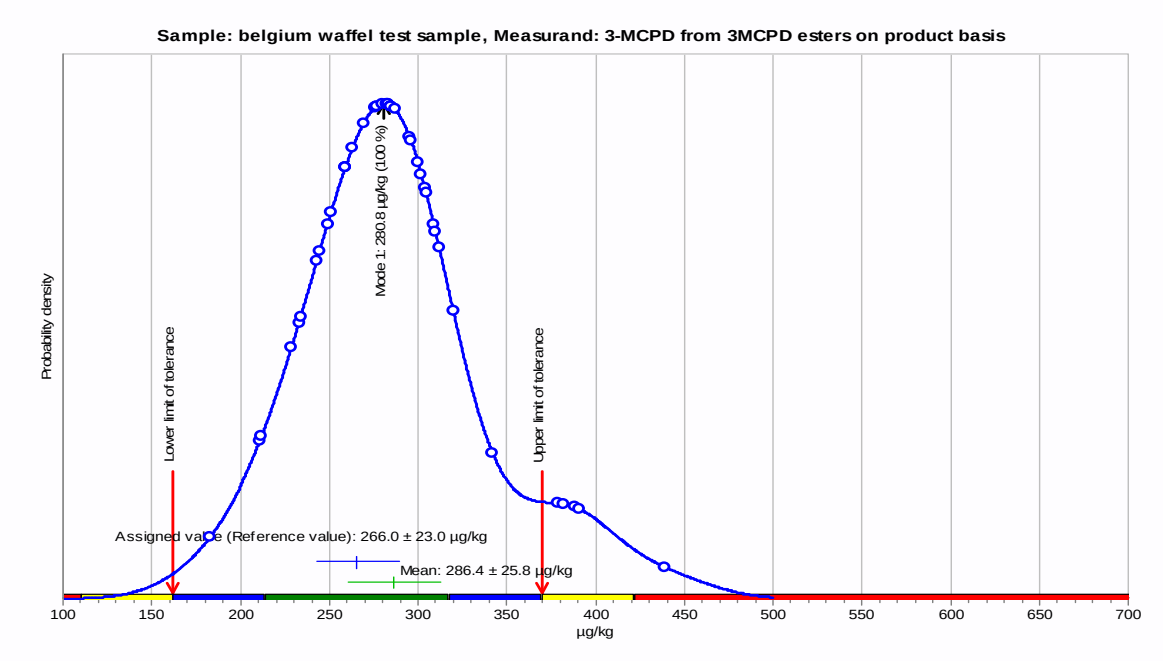
Lab code	M1 (as reported)	M2 (as reported)	M3 (as reported)	X lab	U lab	k	u lab	z-Score	zeta score	Classification
105	212	211	233	218.7	78.7	2	39.4	-0.9	-1.2	a
110										
115	286.79	304.64	295.12	295.5		2		0.6		
120	312	302	296	303.3		2		0.7		
125										
130	259	234	249	247.3	74.2	2	37.1	-0.4	-0.5	a
135	251	259	263	257.7	46.4	2	23.2	-0.2	-0.3	a
140	183,1	269,4	244,7	232.4	93.0	2	46.5	-0.6	-0.7	a
155	277	276	277	276.7	47.2	2	23.6	0.2	0.4	a
160										
165	243.1	279.7	228.8	250.5	92.0	2	46.0	-0.3	-0.3	a
170	342	388	379	369.7	66.5	2	33.3	2.0	2.9	a
175										
505	282	285	300	289.0	43.4	2	21.7	0.4	0.9	a
510	320	309	259	296.0	148.0	2	74.0	0.6	0.4	c
515	283	285	285	284.3	5.4	2	2.7	0.4	1.6	b
520										
525	283	439	382	368.0	110.4	2	55.2	2.0	1.8	c
530	304	391	310	335.0	126.3	2	63.1	1.3	1.1	c
535										
540										

Distribution of individual results of replicate determinations reported for of 3-MCPD from 3-MCPDEs in waffles test samples expressed as mass/mass test sample.

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



Kernel density plot of the reported values for proficiency assessment for 3-MCPD from 3-MCPDEs in waffles test samples expressed as mass/mass test sample



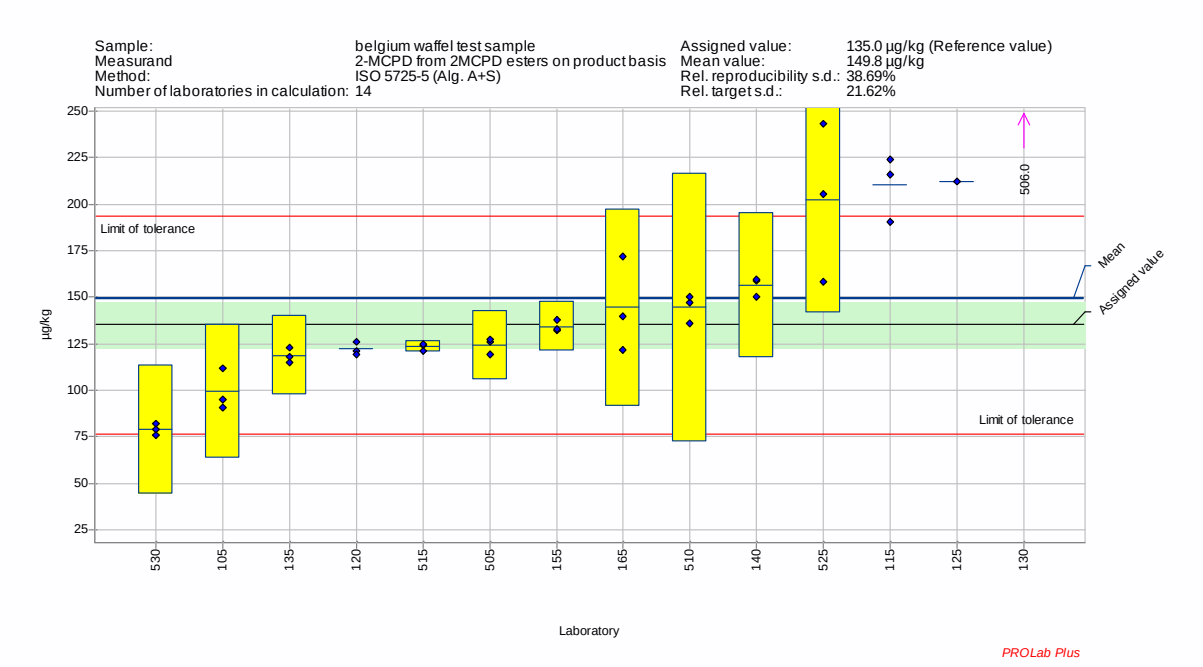
B. Results, as reported by the participants, for the content of 2-MCPD from 2-MCPDEs in waffle, expressed as mass/mass test sample.
Assigned value is 135 µg/kg**.**

Table 2: 2-MCPDEs in waffles - Summary results of measured values

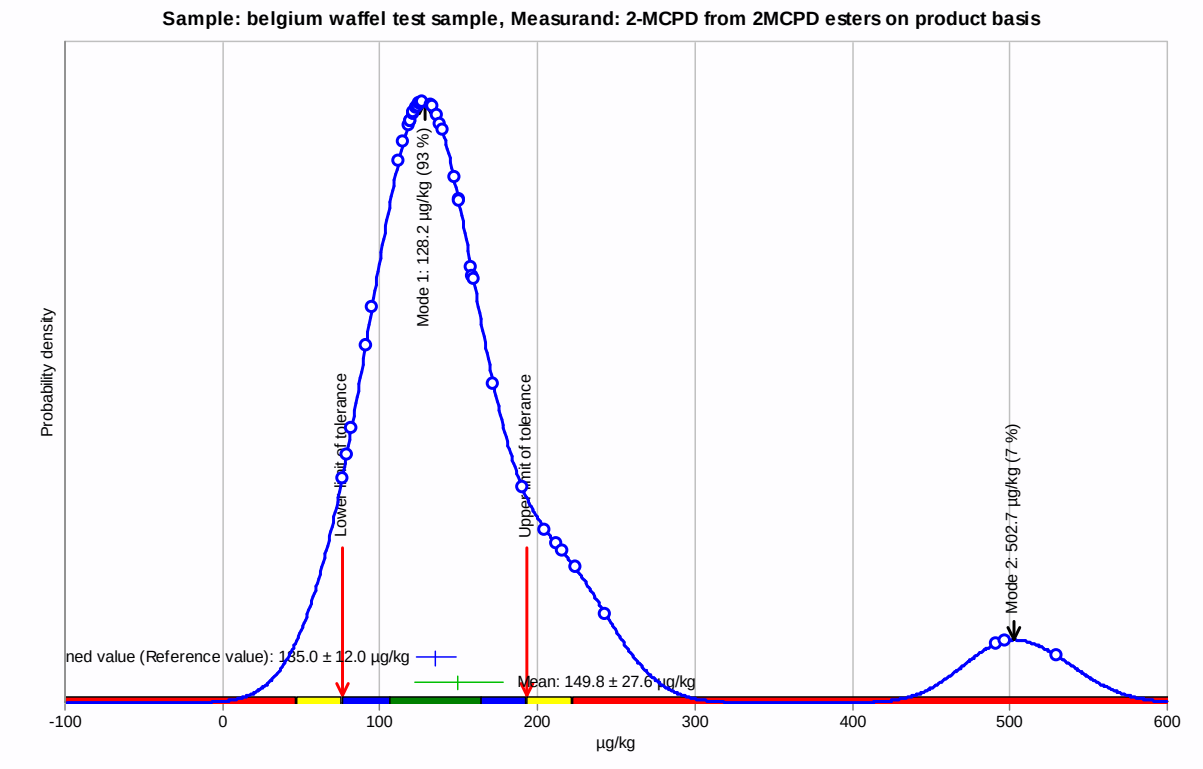
Lab code	M1 (as reported)	M2 (as reported)	M3 (as reported)	X lab	U lab	k	u lab	z-Score	zeta score	Classification
105	91	95	112	99.3	35.8	2	17.9	-1.2	-1.9	a
110										
115	190.20	223.88	215.83	210.0				2.6		
120	126	121	119	122.0				-0.4		
125	212			212.0				2.6		
130	491	530	497	506.0	161.9	2	81.0	12.7	4.6	c
135	123	118	115	118.7	21.4	2	10.7	-0.6	-1.3	a
140	150,1	159	159,3	156.1	39.0	2	19.5	0.7	1.0	a
155	132	138	133	134.3	13.2	2	6.6	0.0	-0.1	a
160										
165	121.5	172.0	139.5	144.3	53.0	2	26.5	0.3	0.3	a
170										
175										
505	119	126	127	124.0	18.6	2	9.3	-0.4	-1.0	a
510	136	147	150	144.3	72.2	2	36.1	0.3	0.3	c
515	124	125	121	123.3	3.1	2	1.5	-0.4	-1.9	b
520										
525	158	243	205	202.0	60.6	2	30.3	2.3	2.2	c
530	82	79	76	79.0	34.8	2	17.4	-1.9	-3.0	a
535										
540										

Distribution of individual results of replicate determinations reported for of 2-MCPD from 2-MCPDEs in waffle, expressed as mass/mass test sample

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



Kernel density plot of the reported values for proficiency assessment for of 2-MCPD from 2-MCPDEs in waffle, expressed as mass/mass test sample

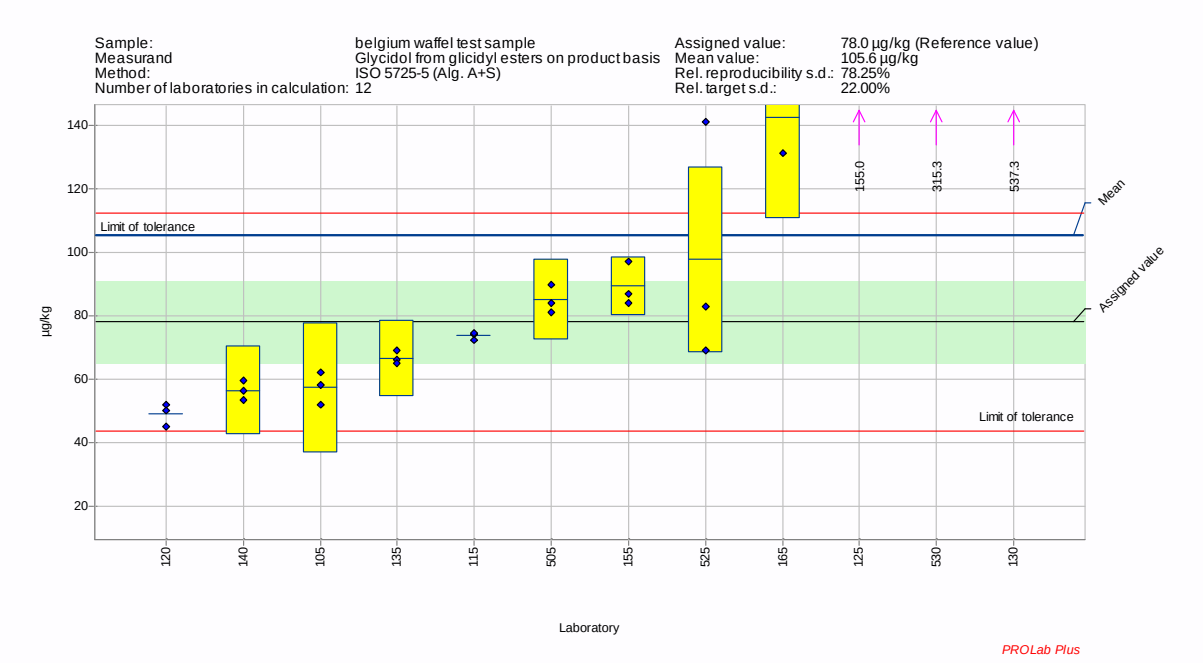


C. Results, as reported by the participants, for the content of 3-MBPD for the GEs in waffles test samples expressed as mass/mass test sample.
Assigned value is 78 µg/kg**.**

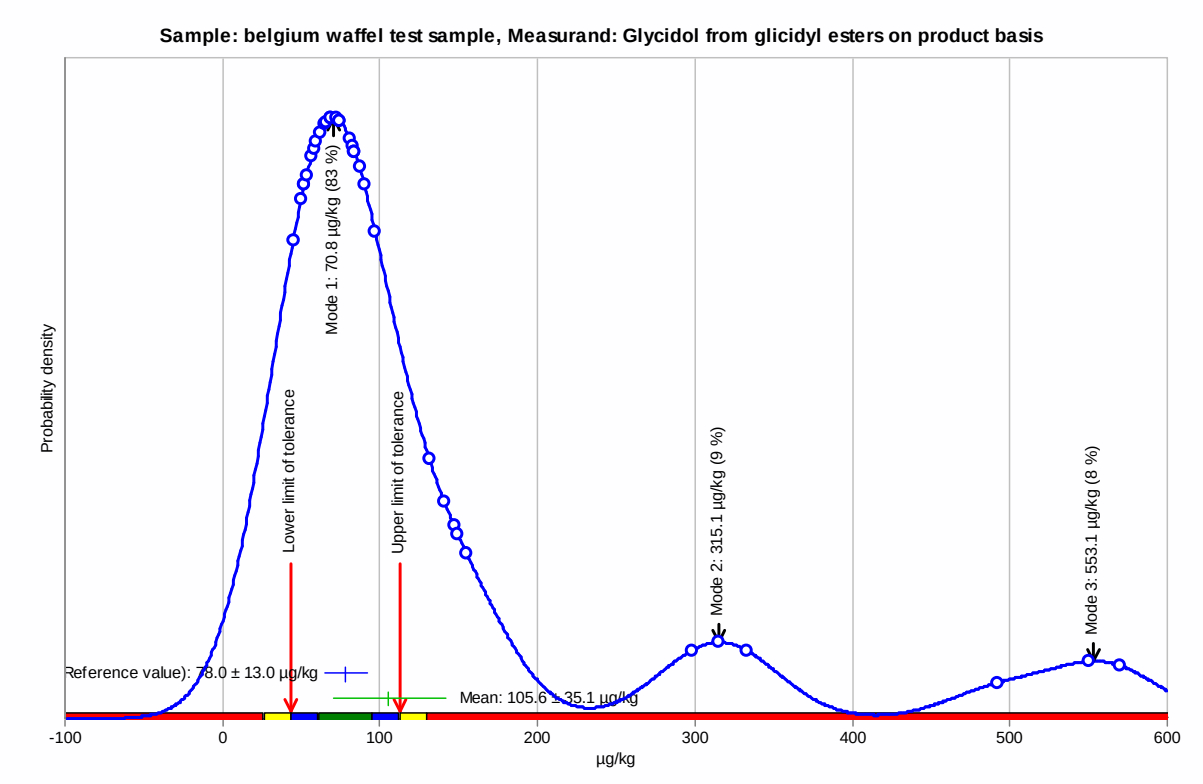
Table 3: GEs in waffles - Summary results of measured values										
Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	Z-Score	Zeta score	Classification
105	52	62	58	57.3	20.6	2	10.3	-1.2	-1.7	a
110										
115	72.42	74.21	74.66	73.8				-0.2		
120	45	52	50	49.0				-1.7		
125	155			155.0				4.5		
130	550	492	570	537.3	204.2	2	102.1	26.8	4.5	c
135	69	66	65	66.7	12.0	2	6.0	-0.7	-1.3	b
140	56,5	59,5	53,5	56.5	14.1	2	7.1	-1.3	-2.2	a
155	97	87	84	89.3	9.2	2	4.6	0.7	1.4	b
160										
165	131.4	149.5	147.2	142.7	32.0	2	16.0	3.8	3.7	a
170										
175										
505	84	81	90	85.0	12.8	2	6.4	0.4	0.8	b
510										
515										
520										
525	69	141	83	97.7	29.3	2	14.7	1.1	1.2	a
530	298	333	315	315.3	120.1	2	60.1	13.8	3.9	c
535										
540										

Distribution of individual results of replicate determinations reported for 3-MBPD for the GEs in waffles test samples expressed as mass/mass test sample.

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



Kernel density plot of the reported values for proficiency assessment for 3-MBPD for the GEs in waffles test samples expressed as mass/mass test sample.



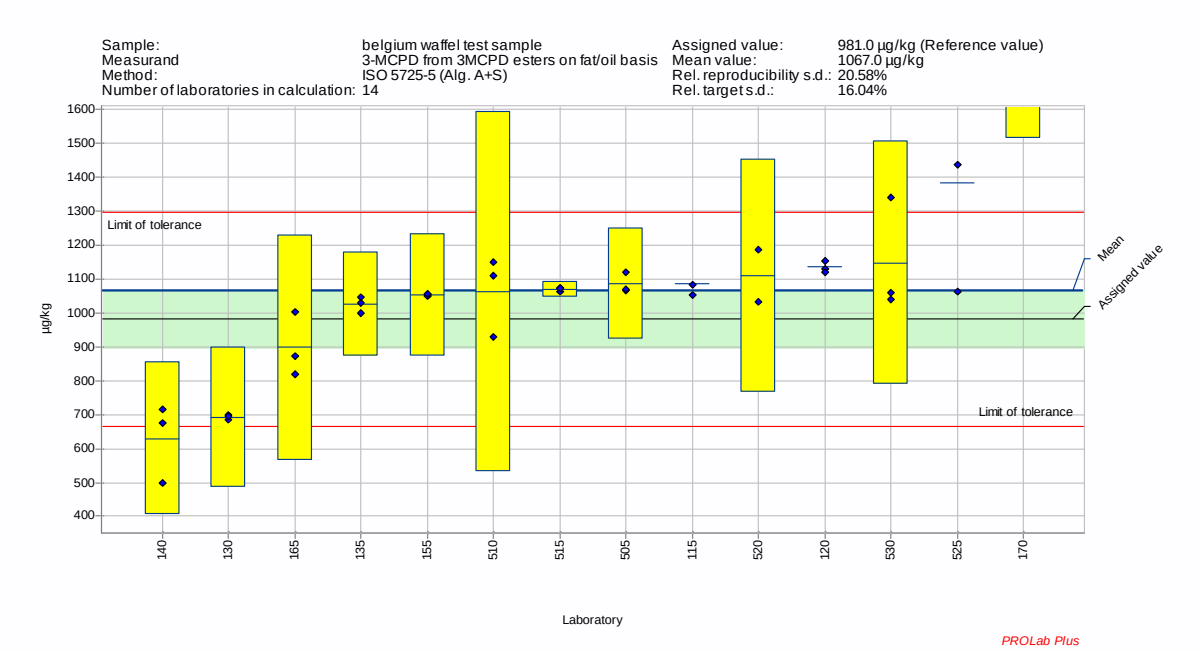
D. Results, as reported by the participants, for the content of 3-MCPD for the 3-MCPDEs in waffles test samples expressed as mass/mass extracted fat.
Assigned value is 981 µg/kg.

Table 4: 3-MCPDEs in extracted fat from waffle test sample - Summary results of measured values

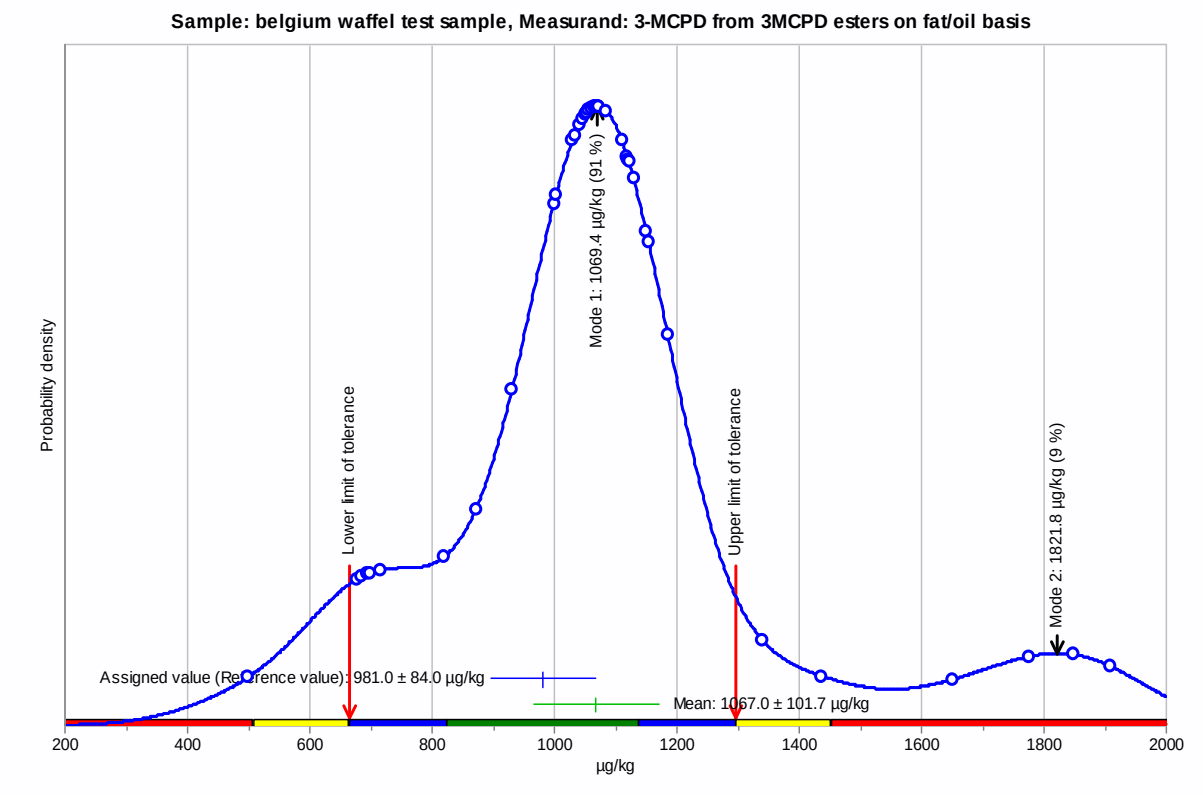
Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	Z-Score	Zeta score	Classifi-cation
105										
110										
115	1052.36	11121.73	1084.20	1086.1				0.7		
120	1154	1129	1121	1134.7				1.0		
125										
130	698	684	694	692.0	207.6	2	103.8	-1.8	-2.6	a
135	999	1030	1046	1025.0	153.8	2	76.9	0.3	0.5	a
140	498,5	716,1	676,1	630.2	226.9	2	113.4	-2.2	-2.9	a
155	1052	1050	1056	1052.7	179.6	2	89.8	0.5	0.7	a
160										
165	871.5	1002.4	820.1	898.0	332.0	2	166.0	-0.5	-0.5	c
170	1908	1848	1777	1844.3	332.0	2	166.0	5.5	5.0	c
175										
505	1067	1071	1119	1085.7	162.8	2	81.4	0.7	1.1	a
510	930	1110	1150	1063.3	531.7	2	265.8	0.5	0.3	c
515	1064	1072	1072	1069.3	23.5	2	11.8	0.6	2.0	b
520	1185	1033		1109.0	343.8	2	171.9	0.8	0.7	c
525	1064	1650	1437	1383.7				2.6		
530	1040	1340	1060	1146.7	358.9	2	179.5	1.1	0.9	c
535										
540										

Distribution of individual results of replicate determinations reported for 3-MCPD for the 3-MCPDEs in waffles test samples expressed as mass/mass extracted fat.

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



Kernel density plot of the reported values for proficiency assessment for 3-MCPD for the 3-MCPDEs in waffles test samples expressed as mass/mass extracted fat.

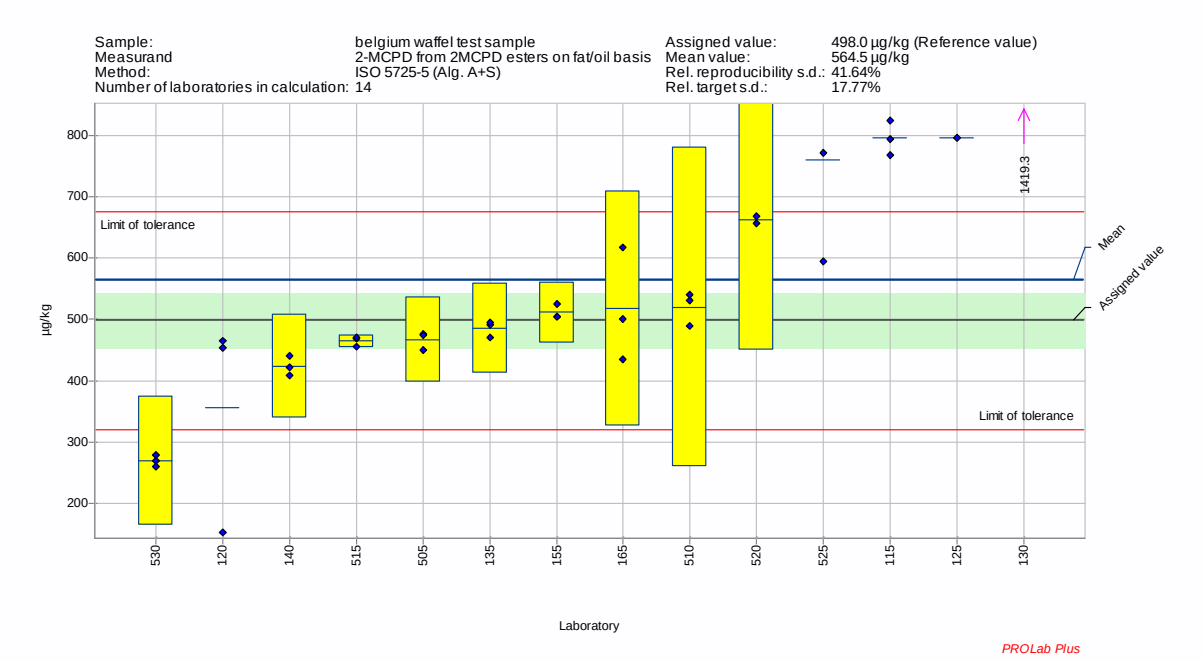


E. Results, as reported by the participants, for 2-MCPD for the 2-MCPDEs in waffles test samples expressed on fat base.
Assigned value is 498 µg/kg.

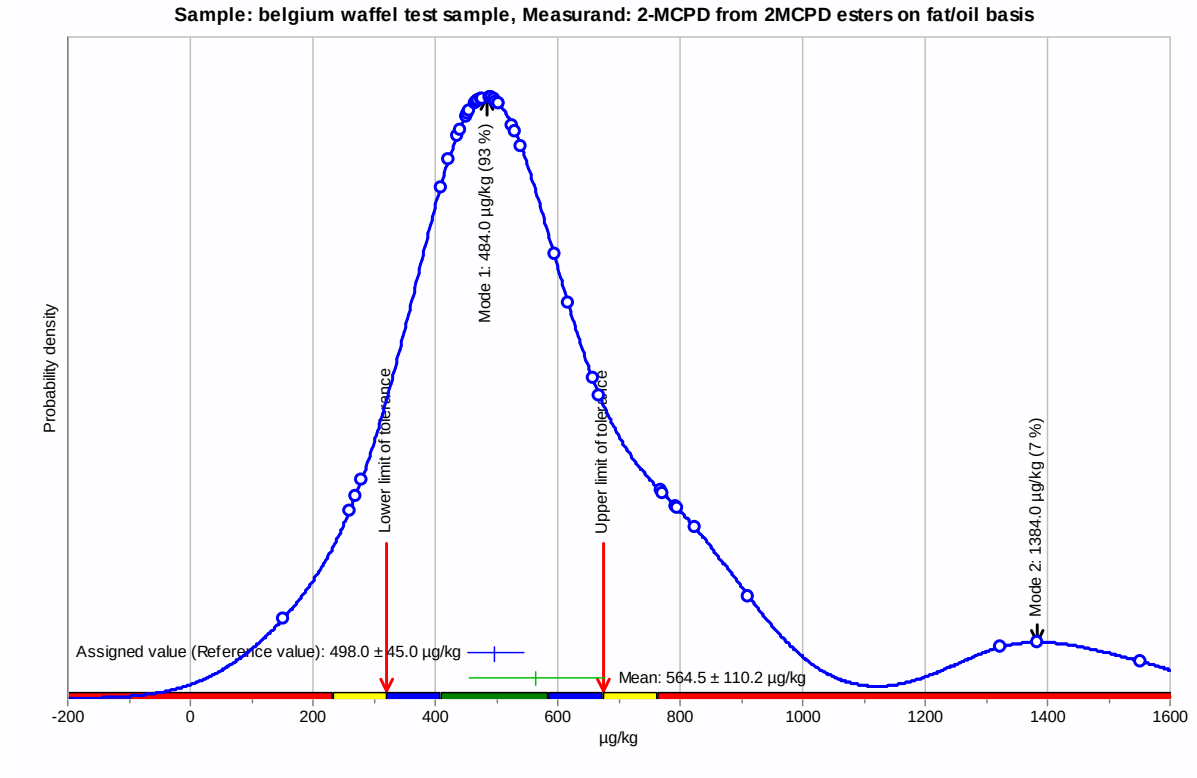
Table 5: 2-MCPDEs in extracted fat from waffle test sample - Summary results of measured values										
Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	Z-Score	Zeta score	Classifi-cation
105										
110										
115	767.49	824.34	792.93	794.9				3.4		
120	465	453	153	357.0				-1.6		
125	795			795.0				3.4		
130	1323	1551	1384	1419.3	454.2	2	227.1	10.4	4.0	c
135	491	470	496	485.7	72.8	2	36.4	-0.1	-0.3	a
140	408,7	422,6	440,3	423.9	84.8	2	42.4	-0.8	-1.5	a
155	504	526	504	511.3	50.4	2	25.2	0.2	0.4	a
160										
165	435.6	616.7	499.9	517.4	191.0	2	95.5	0.2	0.2	c
170										
175										
505	450	476	474	466.7	70.0	2	35.0	-0.4	-0.8	a
510	490	530	540	520.0	260.0	2	130.0	0.2	0.2	c
515	468	470	456	464.7	10.2	2	5.1	-0.4	-1.4	b
520	657	668		662.5	212.0	2	106.0	1.9	1.5	c
525	594	912	771	759.0				2.9		
530	280	270	260	270.0	105.3	2	52.6	-2.6	-4.0	a
535										
540										

Distribution of individual results of replicate determinations reported for 2-MCPD for the 2-MCPDEs in waffles test samples expressed on fat base.

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



Kernel density plot of the reported values for proficiency assessment for 2-MCPD for the 2-MCPDEs in waffles test samples expressed on fat base.

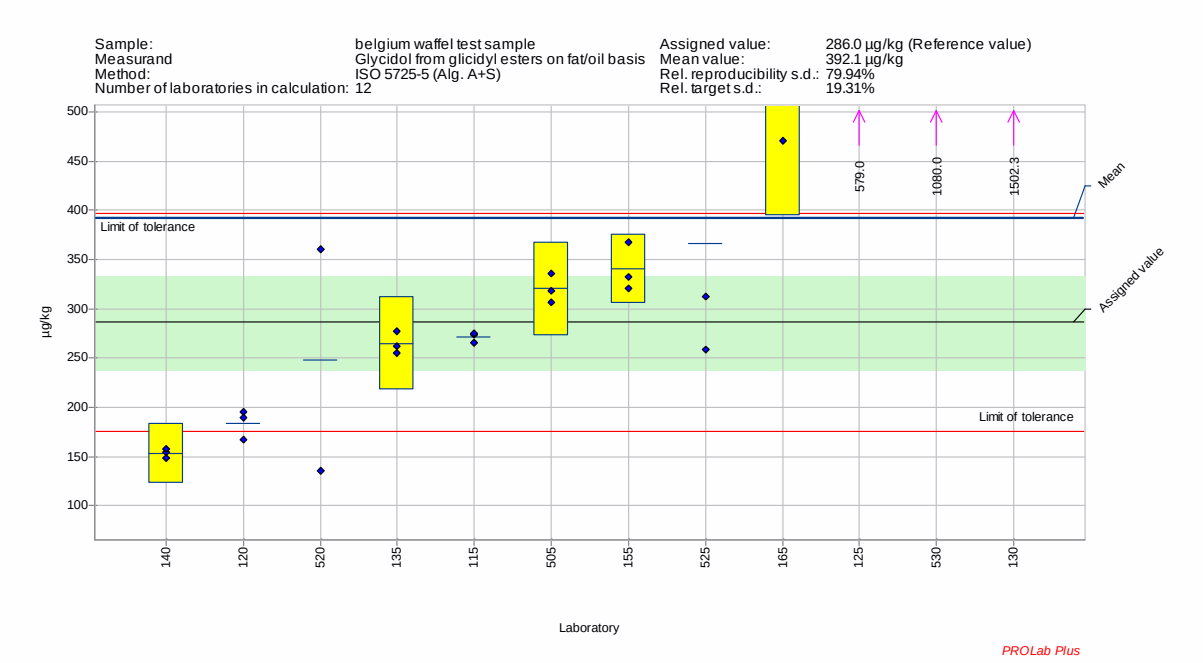


F. Results, as reported by the participants, for 3-MBPD for the GEs in waffles test samples expressed as mass/mass extracted fat.
Assigned value is 286 µg/kg.

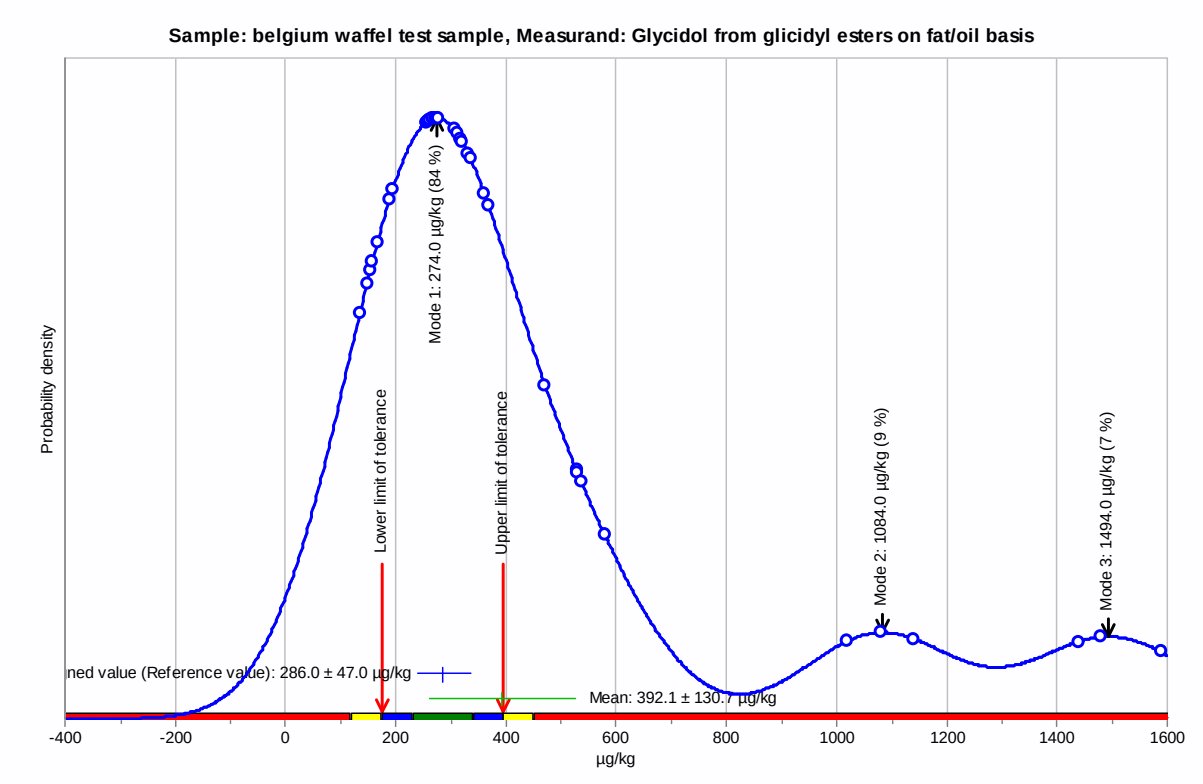
Table 6: GEs in extracted fat from waffle test sample - Summary results of measured values										
Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	Z-Score	Zeta score	Classifi-cation
105										
110										
115	265.75	273.26	274.30	271.1				-0.3		
120	167	195	189	183.7				-1.9		
125	579			579.0				5.3		
130	1480	1439	1588	1502.3	570.9	2	285.4	22.0	4.2	c
135	277	262	255	264.7	47.6	2	23.8	-0.4	-0.6	a
140	153,7	158,1	147,9	153.2	30.6	2	15.3	-2.4	-4.7	b
155	368	332	321	340.3	35.2	2	17.6	1.0	1.9	b
160										
165	471.0	535.8	527.8	511.5	117.0	2	58.5	4.1	3.6	c
170										
175										
505	318	306	336	320.0	48.0	2	24.0	0.6	1.0	a
510										
515										
520	135	361		248.0		2		-0.7		
525	258	530	312	366.7		2		1.5		
530	1020	1140	1080	1080.0	344.5	2	172.3	14.4	4.6	c
535										
540										

Distribution of individual results of replicate determinations reported for 3-MBPD for the GEs in waffles test samples expressed on fat base

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



Kernel density plot of the reported values for proficiency assessment for 3-MBPD for the GEs in waffles test samples expressed on fat base.



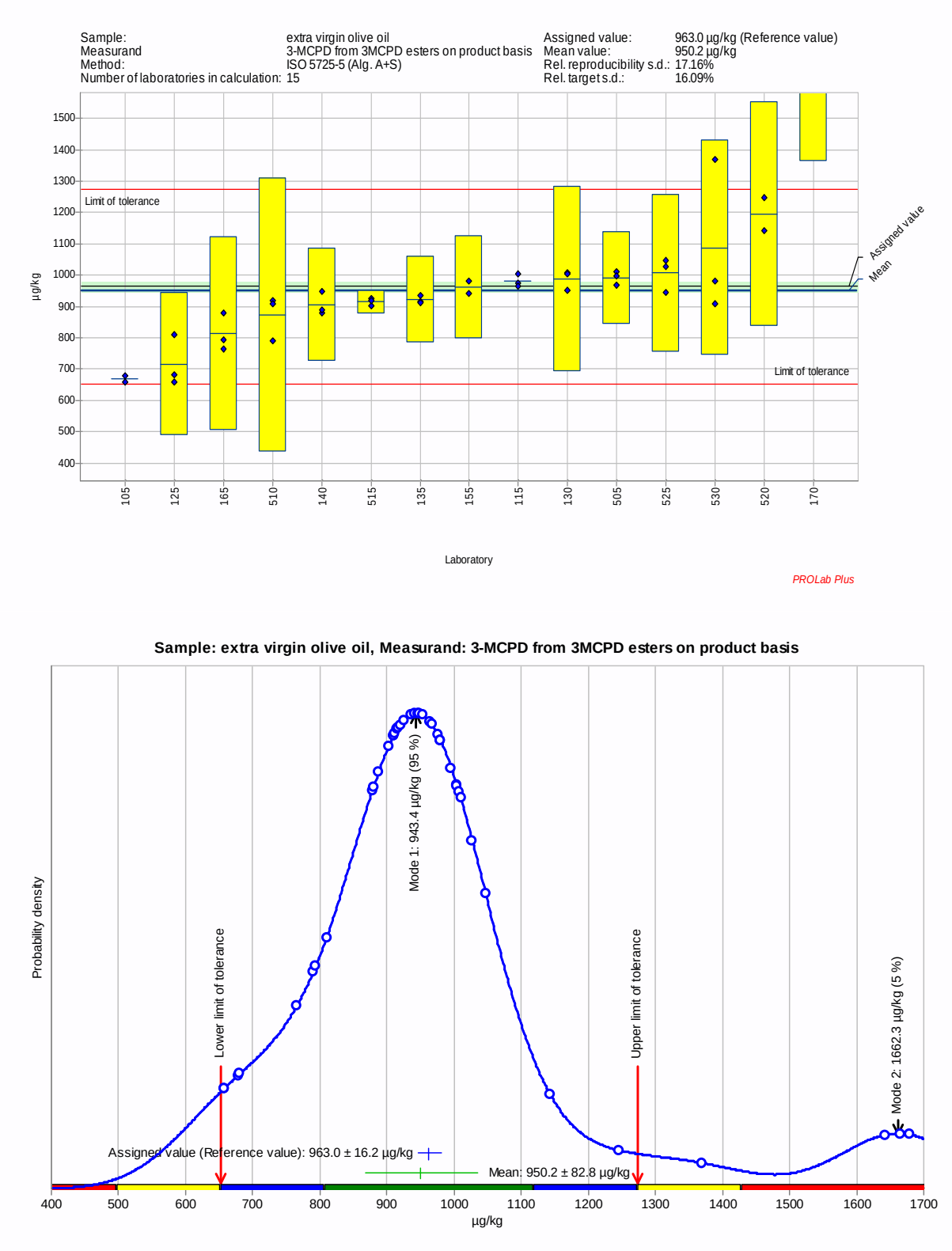
G. Results, as reported by the participants, for 3-MCPD for the 3-MCPD esters in oil test sample.
Assigned value is 963 µg/kg.

Table 7: 3-MCPDEs in oil - Summary results of measured values

Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	z-Score	zeta score	Classifi-cation
105	678	658		668.0				-1.9		
110										
115	1004.66	976.01	964.50	981.7				0.1		
120										
125	658	681	810	716.3	227.4	2	113.7	-1.6	-2.2	a
130	953	1007	1004	988.0	296.4	2	148.2	0.2	0.2	a
135	936	916	912	921.3	138.2	2	69.1	-0.3	-0.6	a
140	879,8	948,0	887,7	905.2	181.0	2	90.5	-0.4	-0.6	a
155	941	980		960.5	163.9	2	81.9	0.0	0.0	a
160										
165	793.9	765.7	878.5	812.7	309.0	2	154.5	-1.0	-1.0	a
170	1679	1665	1643	1662.3	299.2	2	149.6	4.5	4.7	a
175										
505	967	1010	996	991.0	148.7	2	74.3	0.2	0.4	a
510	920	910	790	873.3	436.7	2	218.3	-0.6	-0.4	c
515	925	903	917	915.0	37.5	2	18.8	-0.3	-2.3	a
520	1143	1246		1194.5	358.3	2	179.2	1.5	1.3	c
525	946	1047	1027	1006.7	251.7	2	125.8	0.3	0.3	a
530	980	1370	910	1086.7	343.4	2	171.7	0.8	0.7	c
535										
540										

Distribution of individual results of replicate determinations reported for 3-MCPD for the 3-MCPD esters in oil test samples

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.

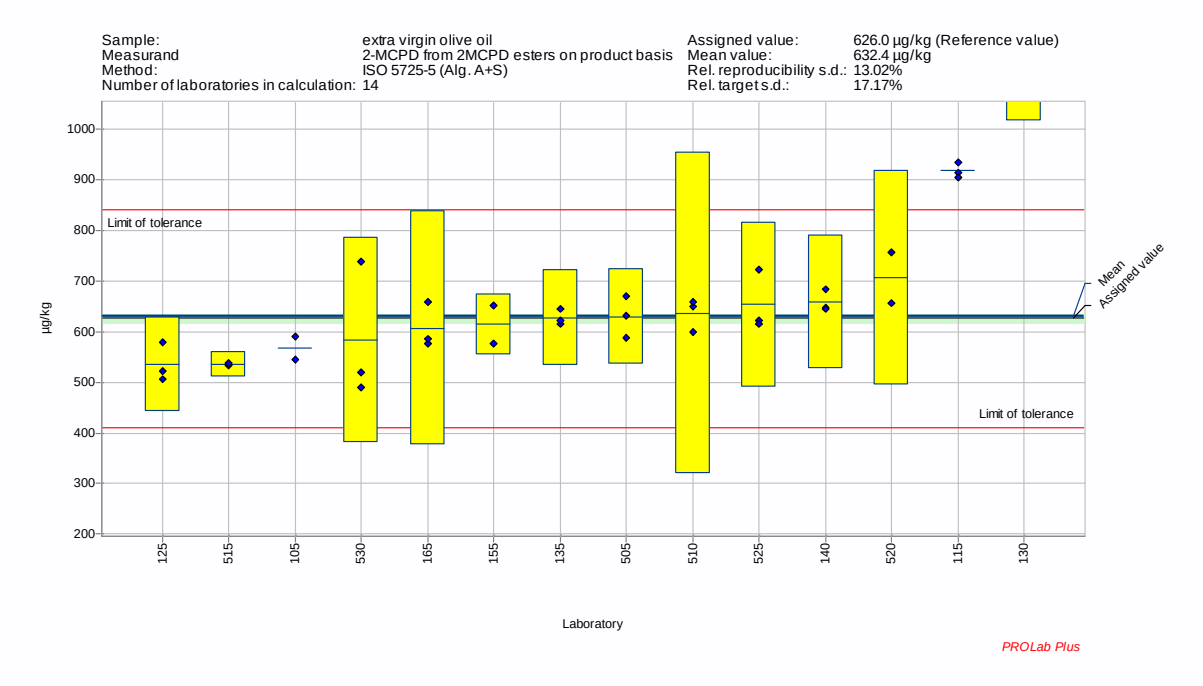


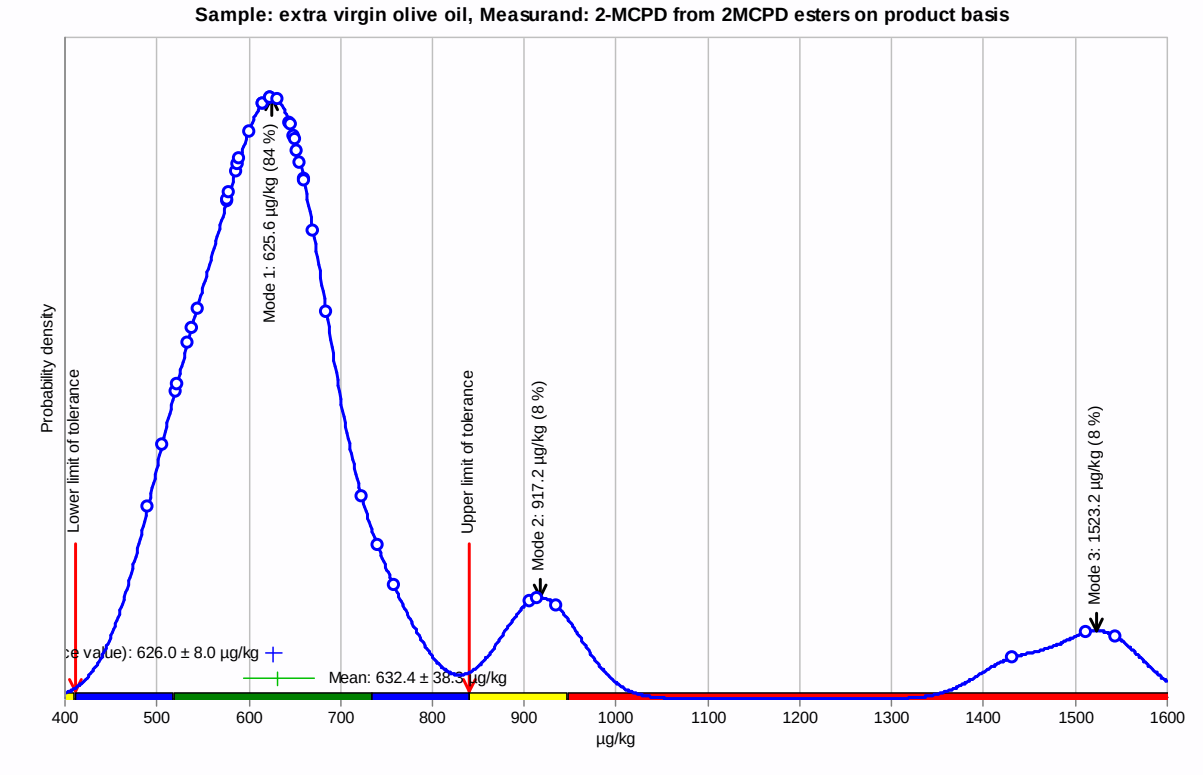
G. Results, as reported by the participants, for 2-MCPD for the 2-MCPD esters in oil test sample.
Assigned value is 626 µg/kg.

Table 8: 2-MCPDEs in oil - Summary results of measured values										
Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	Z-Score	Zeta score	Classifi-cation
105	544	590		567.0				-0.5		
110										
115	934.90	913.72	905.50	918.0				2.7		
120										
125	506	522	579	535.7	93.6	2	46.8	-0.8	-1.9	a
130	1432	1544	1512	1496.0	478.7	2	239.4	8.1	3.6	c
135	615	623	645	627.7	94.1	2	47.1	0.0	0.0	a
140	648,8	684,2	644,6	659.2	131.8	2	65.9	0.3	0.5	a
155	653	577		615.0	60.6	2	30.3	-0.1	-0.4	a
160										
165	576.2	585.7	659.7	607.2	231.0	2	115.5	-0.2	-0.2	c
170										
175										
505	588	631	670	629.7	94.4	2	47.2	0.0	0.1	a
510	650	660	600	636.7	318.3	2	159.2	0.1	0.1	c
515	534	538		536.0	25.2	2	12.6	-0.8	-6.8	a
520	758	656		707.0	212.1	2	106.0	0.8	0.8	a
525	723	623	615	653.7	163.4	2	81.7	0.3	0.3	a
530	520	740	490	583.3	202.4	2	101.2	-0.4	-0.4	a
535										
540										

Distribution of individual results of replicate determinations reported for 2-MCPD for the 2-MCPD esters in oil test samples

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.



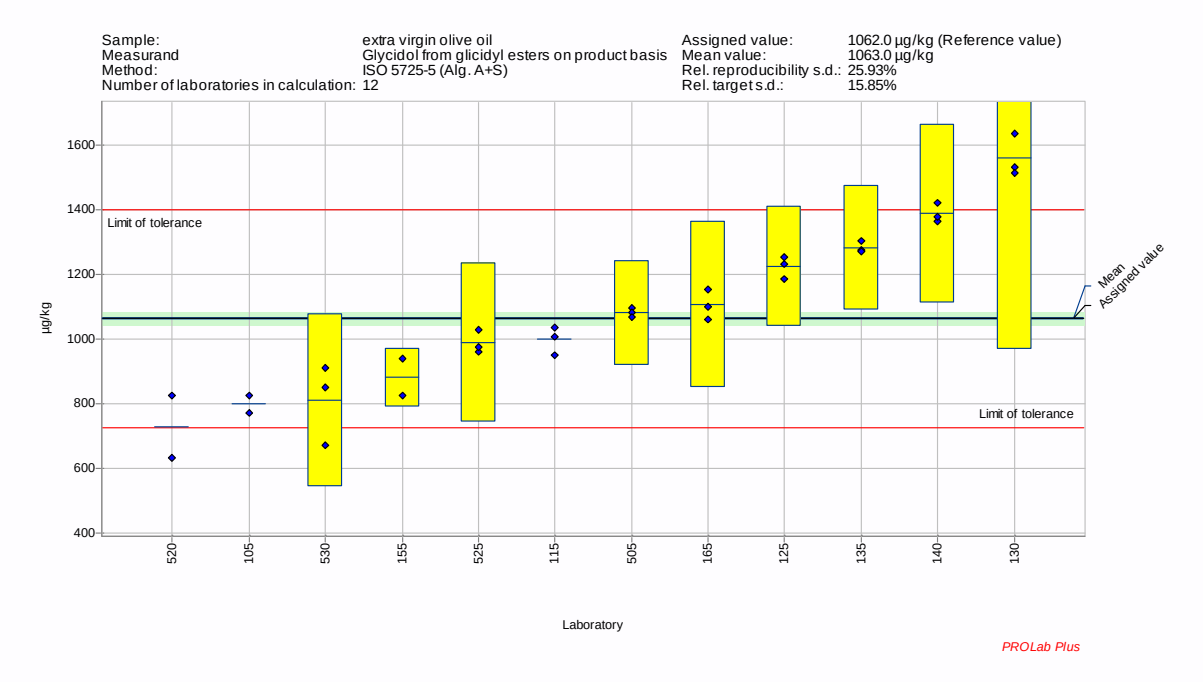


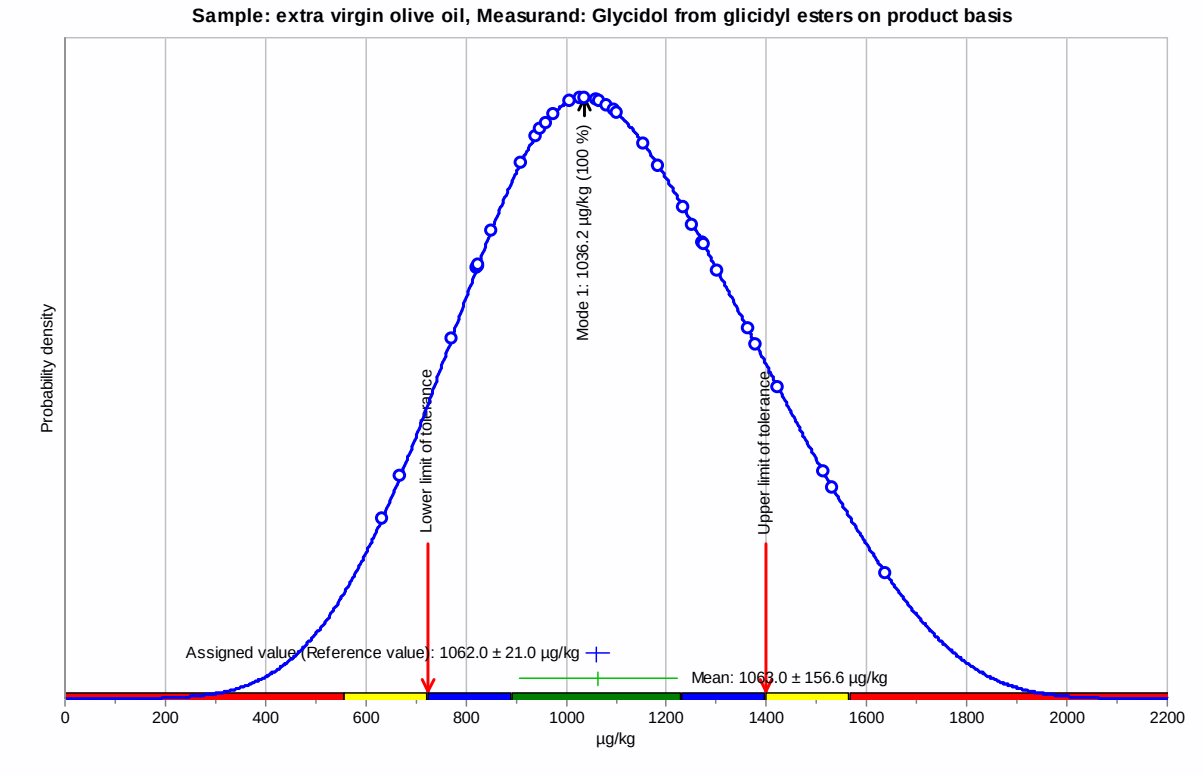
H. Results, as reported by the participants, for 3-MBPD for the glycidyl esters in oil test sample.
Assigned value is 1062 µg/kg.

Table 9: GEs in oil - Summary results of measured values										
Lab code	M 1 (as reported)	M 2 (as reported)	M 3 (as reported)	X lab	U lab	k	u lab	Z-Score	Zeta score	Classifi-cation
105	772	825		798.5				-1.6		
110										
115	1036.62	1007.89	948.89	997.8				-0.4		
120										
125	1233	1184	1253	1223.3	185.5	2	92.7	1.0	1.7	a
130	1532	1513	1637	1560.7	593.1	2	296.5	3.0	1.7	c
135	1274	1303	1272	1283.0	192.4	2	96.2	1.3	2.3	a
140	1362,8	1422,5	1378,6	1388.0	277.6	2	138.8	1.9	2.3	a
155	939	824		881.5	91.1	2	45.5	-1.1	-3.9	a
160										
165	1100.9	1154.7	1059.8	1105.1	257.0	2	128.5	0.3	0.3	a
170										
175										
505	1095	1081	1066	1080.7	162.1	2	81.0	0.1	0.2	a
510										
515										
520	823	633		728.0				-2.0		
525	959	1029	974	987.3	246.8	2	123.4	-0.4	-0.6	a
530	670	850	910	810.0	267.3	2	133.7	-1.5	-1.9	a
535										
540										

Distribution of individual results of replicate determinations reported for 3-MBPD for the GEs in oil test samples

blue rhombus: individual results of replicate determinations; yellow box: reported expanded measurement uncertainty (k=2); blue horizontal line in yellow box: average of replicate determinations; green line: assigned value; red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value.





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