EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021

EURL-PT-DPB_2105-DCP

FEED

Report

PBDEs and HBCDDs

(Version 1.1)

Changes to the previous version 1.0: LC 79 was modified to LC 79B

06 December 2022

EURL POPs

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Summary

Test sample	**FEED:** Fortified dried citrus pulp [2105-DCP]
Analytes of interest	**PBDEs** (BDE-28, -47, -49, -99, -100, -153, -154, -183 and BDE-209) **HBCDDs** (α-HBCDD, β-HBCDD, γ-HBCDD)
Methods	Any kind of method
Participants	NRLs, OFLs, other official laboratories, commercial laboratories performing the analysis of samples taken by feed business operators
Statistical evaluation	ISO 13528:2020, IUPAC Protocol
Report of final results	06 December 2022 (Version 1.1)
Publication	EURL POPs reserves all rights to publish and present the anonymised results of the interlaboratory study in scientific journals and/or during conferences.

1. Structure of the ILS, test material and analytes

This proficiency test (PT) on the determination of **PCDD/Fs, PCBs, PBDEs** and **HBCDDs** in **dried citrus pulp** was organized by the European Union Reference Laboratory (EURL) for halogenated persistent organic pollutants (POPs) in Feed and Food to be performed between September and November 2021. The objective was to assess analytical performance of laboratories and the interlaboratory comparability of results from analyses of PCDD/Fs, PCBs, PBDEs and HBCDDs in one sample of **dried citrus pulp.**

National Reference Laboratories (NRLs) for halogenated POPs in Feed and Food from EU member states were requested to participate as part of their work programme for 2021. NRLs were invited to encourage the participation of Official Laboratories (OFLs) from their member states as part of their duties following Article 101 of regulation (EU) 2017/625 of the European Parliament and of the Council of 15 March 2017. Furthermore, participation of OFLs allowed the extension of the data basis for calculation of assigned values and evaluation of results.

Other official laboratories and **commercial laboratories** performing the analysis of samples taken by feed business operators were invited to participate in this proficiency test. The evaluated results were discussed by representatives of European Commission, NRLs and the EURL at the COM/EURL/NRL workshop on 23 and 24 November 2021.

1.1. Samples and coding

The test sample was prepared from commercially available feed and with PCDD/Fs naturally contaminated material. Additionally it was fortified with analytes of interest using standards and technical mixtures of PCBs, PBDEs and HBCDDs.

Dried citrus pulp	**Sample no. 2105-DCP-xxx**

Each participant received about **80 g** of the test sample in a HDPE bottle.

1.2. Analytes of interest

Participants were requested to determine the following parameters:

Polybrominated diphenyl ethers (PBDEs)

- Individual congeners: BDE-28, -47, -49, -99, -100, -153, -154, -183, -209
- Sum of 8 PBDEs (without BDE-209)
- Sum of 9 PBDEs (with BDE-209)

Hexabromocyclododecanes (HBCDDs)

- α-HBCDD, β-HBCDD, γ-HBCDD stereoisomers
- Sum of α-, β-, γ-HBCDD (using HPLC methods)
- Total HBCDD (using GC methods)

1.3. Methods

All kinds of detection and quantification methods could be applied.

1.4. Coding of laboratories and confidentiality

The laboratory code of the participating laboratories will be kept confidential and will not be revealed to other participants.
For NRLs, the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with Community reference laboratories (CRLs) activities" will be observed. The confidentiality of NRLs will be kept according to this protocol.
The confidentiality between NRLs and their OFLs will be kept unless a Member State initiated a cooperation between the NRL, OFLs and the EURL.

1.5. Results of PBDEs and HBCDDs

Laboratories should:

- use their own reference standards for identification and quantification,
- report results for each analyte,
- report the limit of quantification (LOQ), at least for each non-quantified analyte,
- give method information and
- give information about the accreditation of the laboratory according to ISO/IEC 17025 *(for metrological traceability of consensus values of participants used as assigned values).*

Results had to be reported in **µg/kg, relative to a feed with a moisture content of 12 %**, for PBDEs and HBCDDs.

2. Participating laboratories

This proficiency test was open for participation of:

- National Reference Laboratories (NRLs) of EU member states
- National Reference Laboratories of other European countries
- Official laboratories
- Commercial laboratories

83 laboratories registered for this proficiency test. For PBDE and HBCDD, 26 and 18 sets of results were reported, respectively.

Table 1: Participating laboratories

Participating laboratories	Region	No. of participants
National Reference Laboratories	European Union Other Countries	16 1
Official Laboratories	European Union Other European Countries Africa Americas Asia Oceania	7 1 0 0 0 1
Commercial Laboratories	European Union Other European Countries Africa Americas Asia Oceania	1 0 0 0 0 0
	Total	**27**

2.1. Number of reported results

Table 2: Reported results for PBDEs and moisture content for dried citrus pulp (2105-DCP)

Reported results (2105-DCP)	All laboratories	NRLs
BDE-28	26	15
BDE-47	26	15
BDE-49	22	13
BDE-99	26	15
BDE-100	26	15
BDE-153	26	14
BDE-154	26	15
BDE-183	26	13
BDE-209	21	9
Sum of 8 PBDEs (without BDE-209) (ub)	26	15
Sum of 8 PBDEs (without BDE-209) (lb)	26	15
Sum of 9 PBDEs (with BDE-209) (ub)	21	10
Sum of 9 PBDEs (with BDE-209) (lb)	21	10
Moisture content	23	14

Table 3: Reported results for HBCDDs for dried citrus pulp (2105-DCP)

Reported results (2105-DCP)	All laboratories	NRLs
α-HBCDD	16	11
β-HBCDD	16	11
γ-HBCDD	16	11
Sum of α-, β-, γ-HBCDD (ub)	16	11
Sum of α-, β-, γ-HBCDD (lb)	16	11
Total HBCDD (using GC methods)	2	2

2.2. Accreditation

Table 4: Reported accreditation according to ISO/IEC 17025 by participants for PBDEs and HBCDDs

Dried Citrus Pulp	PBDEs	HBCDDs
Accreditation	17	5
No accreditation	8	12

2.3. Detection methods

The following detection methods were applied:

- GC-HRMS-, GC-MS/MS-methods for PBDEs
- GC-HRMS-, GC-MS/MS-, LC-MS/MS-, LC-HRMS-methods for HBCDDs

Table 5: Overview of chromatographic separation and detection methods for the determination of PBDEs and HBCDDs in dried citrus pulp (2105-DCP)

Detection methods	PBDEs	HBCDDs
GC-HRMS	18	2
GC-MS/MS	6	-
GC-LRMS	-	-
LC-MS/MS	-	14
LC-HRMS	-	2

3. Homogeneity and stability of the test material

The test for sufficient homogeneity was performed according to DIN ISO 13528:2020 [2] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [1].

Therefore, 10 portions of the test samples 2105-DCP were analysed in duplicate for PBDEs. The test for sufficient homogeneity was performed for the individual congeners. The test materials showed sufficient homogeneity for PBDEs in this proficiency test.

The stability check of the analytes of interest applying room temperature storage was performed according to DIN ISO 13528:2020 [2] for PBDEs. The test material showed sufficient stability for PBDEs. Homogeneity and stability can be concluded also for HBCDDs due to similar physico-chemical properties for this proficiency test.

4. Determination of the assigned value

Statistical evaluation of the PT results was performed by the EURL for halogenated POPs in feed and food according to ISO 13528:2020 [2] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [1].

The determination of the assigned value was performed according [1] by estimating of the assigned value as the consensus of participants' results (using only results of physico-chemical methods). The Huber robust mean was taken as assigned value after excluding extreme outliers (outside the range of ± 50% of the median of all reported results) and examination of the distribution of the remaining results using histogram and Kernel density estimation, if necessary.

Assigned values were calculated for individual PBDE congeners, sum of 8 (without BDE-209) and sum of 9 (with BDE-209) PBDEs, for individual HBCDD diastereomers, sum of α-, β- and γ-HBCDD and total HBCDD (including limits of quantification (LOQs)), if possible. Additionally the median of all values was calculated.
For individual congeners (including LOQs) assigned values were only calculated according to the above mentioned procedure, if more than 2/3 of all results are above the LOQ and less than 1/3 of all results (including LOQs) are outside the range of ± 50 % of the median of all reported results. Levels for individual congeners are only taken for evaluation and calculation if these levels are equal to or above the LOQ; otherwise the LOQ will be taken instead.

Due to high variation of participants' results in the range of the respective LOQ or too few results, no assigned values could be calculated for:

- (+/–)-α- HBCDD
- (+/–)-β - HBCDD
- Total HBCDD (using GC-methods)

Since there are no traceable reference values available, the assigned values in this PT were calculated based on the Huber robust mean of the participants' results. Therefore, the assigned values are only traceable to the results of the participants. Additionally the results of all participants reporting results and the results of participants having accreditation according to ISO/IEC 17025 were compared for PBDE sum parameters. Only 17 of 25 participating laboratories were accredited according to ISO/IEC 17025 for PBDEs. After eliminating outliers, 13 to 16 results contributed to the calculation of the assigned values from the ISO/IEC 17025 group. No significant differences (3 %) between the assigned values calculated for both data sets for PBDEs were observed. For HBCDDs only 5 out of 17 participating laboratories were accredited according to ISO/IEC 17025. Therefore, no assigned values for HBCDDs could be calculated for this group of participants (Table 6).

Table 6: Comparison of assigned values for all participants and participants with reported accreditation according to ISO/IEC 17025 for PBDE and HBCDD sum parameters

Sum parameters	Assigned value All participants	Assigned value ISO/IEC 17025 accreditation	Deviation
	µg/kg product (12 % moisture content)		%
Sum of PBDE without BDE-209 (ub)	0.358	0.348	3
Sum of PBDE without BDE-209 (lb)	0.356	0.344	3
Sum of PBDE including BDE-209 (ub)	1.03	1.06	3
Sum of PBDE including BDE-209 (lb)	1.05	1.08	3
γ -HBCDD	0.917	-*	-
Sum of α-, β-, γ-HBCDD (ub)	1.03	-*	-
Sum of α-, β-, γ-HBCDD (lb)	0.959	-*	-

*calculation of assigned values was not possible, due to few results

4.1. PBDEs – individual congeners and sum parameter

The assigned values for the test sample 2105-DCP were calculated as consensus of participants' results for individual PBDEs and sum parameters, taking into account the calculation criteria described above (Table 7 ; tabular summary see annex 1; Figure 1).

Table 7: Assigned values for PBDEs (rounded to three significant figures)

Dried Citrus Pulp (2105-DCP)	Assigned value µg/kg product (12 % moisture content)
BDE-28	0.00918
BDE-47	0.115
BDE-49	0.0120
BDE-99	0.150
BDE-100	0.0323
BDE-153	0.0149
BDE-154	0.0129
BDE-183	0.00719
BDE-209	0.675
Sum of 8 PBDEs (without BDE-209) (ub)	0.358
Sum of 8 PBDEs (without BDE-209) (lb)	0.356
Sum of 9 PBDEs (with BDE-209) (ub)	1.03
Sum of 9 PBDEs (with BDE-209) (lb)	1.05

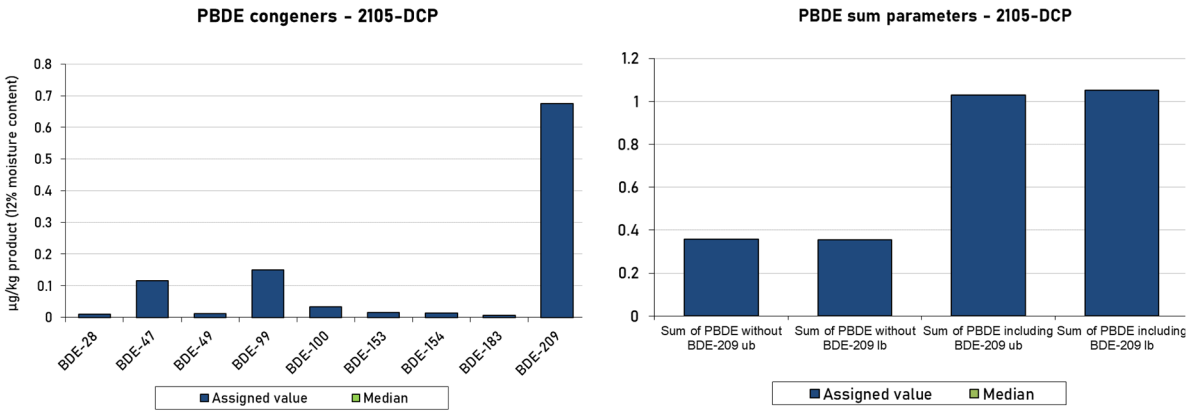

Figure 1: Assigned values (blue) and median values (green) for PBDE individual congeners and sum parameters for dried citrus pulp (2105-DCP) [µg/kg product (12% moisture content)]

4.2. HBCDDs – individual stereoisomers and sum parameter

The assigned values for the test sample 2105-DCP were calculated as consensus of participants' results for individual HBCDDs and sum parameters, taking into account the calculation criteria described above (Table 9 ; tabular summary see annex 1; Figure 2).

Table 8: Assigned values for HBCDDs (rounded to three significant figures)

Dried Citrus Pulp (2105-DCP)	Assigned value µg/kg product (12 % moisture content)
(+/–)-γ- HBCDD	0.917
Sum of α-, β-, γ-HBCDD (ub)	1.03
Sum of α-, β-, γ-HBCDD (lb)	0.959

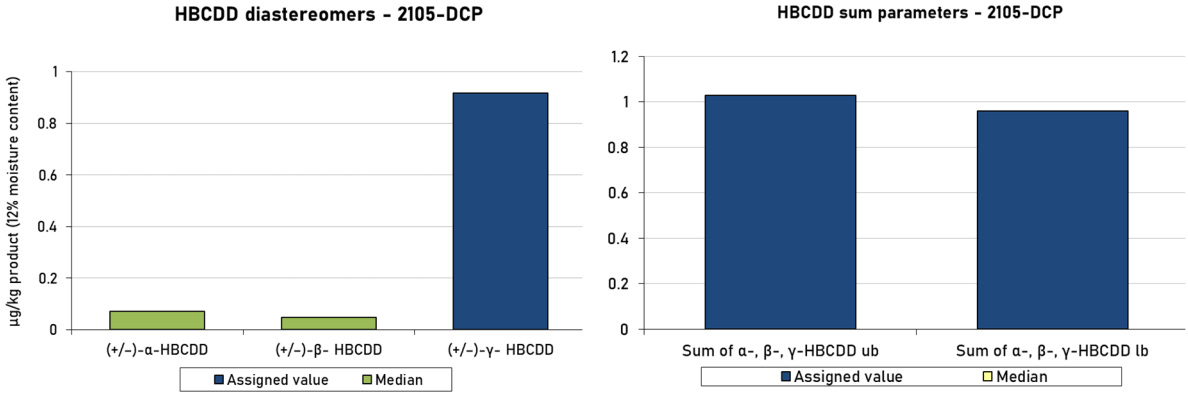

Figure 2: Assigned values (blue) and median values (green) for HBCDD individual congeners and sum parameters for dried citrus pulp (2105-DCP) [µg/kg product (12% moisture content)]

4.3. Moisture content

For the moisture content an assigned value of 8.80 % for the test sample 2105-DCP was calculated as a consensus of the participants' results, taking into account the calculation criteria described above. One lab reported values for **dry matter** instead of **moisture content.**

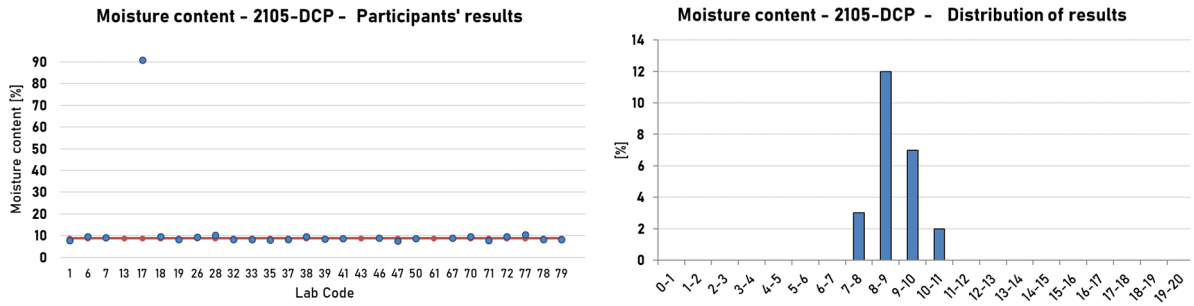

Figure 3: Participant's results (red line assigned value) and distribution of participant's results of the moisture content in % for dried citrus pulp (2105-DCP)

4.4. Comparison of assigned values with recommended LOQs

The limits of quantification are currently based on the values specified in Commission Recommendation of 3 March 2014, on the monitoring of trace levels of brominated flame retardants in food (2014/118/EU). For PBDEs the recommended LOQ value is 0.01 µg/kg w.w. for individual congeners. However, it was discussed in the meetings of the core working group "Brominated Contaminants and PCNs" of the EURL/NRL network that for feed an LOQ value of 0.01 µg/kg product, compared to a feed with a moisture content of 12%, is preferable for all congeners and given that some feeds show concentrations below this an even lower targeted LOQ of 0.001 µg/kg product (12% moisture content), except for BDE-209 was recommended (Table 9). Valid data on the background contamination of feedstuffs with BFRs is particularly important for a reliable risk assessment. For HBCDDs the recommended LOQ value is at 0.01 µg/kg product, compared to a feed with a moisture content of 12% for α-, β- and γ-stereoisomers (Table 9). For total HBCDD measured by GC-MS, the corresponding LOQ value is 0.003 µg/kg product (12% moisture content), as cumulative response of all possible HBCDD diastereomers (Table 9).

Table 9: Analytical recommendations from "Guidance document on analytical parameters for the determination of organobromine contaminants in food and feed" (CWG "BCons and PCNs")

Undesirable Substances in Feed	Limit of quantification per congener/stereoisomer µg/kg product (12 % moisture content)
PBDEs	0.01 and 0.001 (all congeners except BDE-209)
HBCDDs	0.01 (sum of HBCDDs) and 0.003 (total HBCDD)

PBDEs:

The calculated assigned values for BDE-28 (0.00918 µg/kg) and BDE-183 (0.00719 µg/kg) were in the range between the targeted and recommended LOQs for the test sample dried citrus pulp (2105-DCP). For the calculation of the BDE-28 assigned value, 25 out of 26 results were above the LOQs of the laboratories and for BDE-49 20 out of 26 results, showing that most participating laboratories are able to reliably achieve the recommended LOQ of 0.01 µg/kg product for feed.

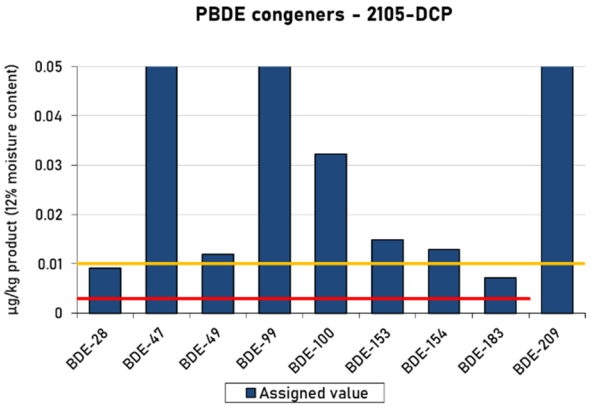

Figure 4: Comparison of assigned values for PBDE congeners with recommended LOQs (yellow line at 0.01 µg/kg product and red line at 0.001 µg/kg product) in dried citrus pulp (2105-DCP)

HBCDDs:

For α- and β-HBCDD no assigned values could be calculated, because less than 2/3 of all 16 reported results were above the LOQs (see calculation criteria section 4). Therefore, the median values were taken for comparison with the recommended LOQs. For α-HBCDD (0.0716 µg/kg) and β-HBCDD (0.0485 µg/kg) both median values were 5- to 7-times above the recommended LOQs of 0.01 µg/kg product, showing that the majority of the laboratories in this PT could not reliably report results for HBCDDs in feed in this low concentration range.

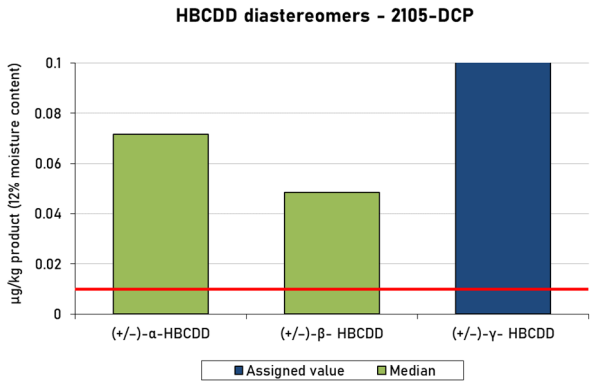

Figure 4: Comparison of assigned values for HBCDD stereoisomers with recommended LOQs (red line at 0.01 µg/kg product) in dried citrus pulp (2105-DCP)

5. Evaluation of results

5.1. Z-scores calculation

Criteria for successful participation of laboratories were based on the evaluation of the results of individual congeners and sum parameters. For evaluation of results of physico-chemical methods the z-scores were calculated according to the following formula:

$$z = \frac{(x - x_a)}{\sigma_p}$$

x: *participant's result*

x_a: *assigned value*

σ_p: *fitness-for-purpose-based standard deviation for proficiency assessment*

For individual PBDE congeners, individual HBCDD diastereomers and PBDE and HBCDD sum parameters, the standard deviation for proficiency assessment σ_p is defined as 20 %.

Z-scores for individual congeners / substances and diastereomers are only calculated and reported if levels for these congeners are equal to or above the LOQ. Otherwise, no z-scores will be given.

Interpretation of z-scores:

$\lvert z\text{-score} \rvert \leq 2$	*satisfactory performance*
$2 < \lvert z\text{-score} \rvert < 3$	*questionable performance (warning signal)*
$\lvert z\text{-score} \rvert \geq 3$	*unsatisfactory performance (action signal)*

5.2. PBDEs - Participants' z-scores

Table 10: Distribution of participants' z-scores for PBDEs for dried citrus pulp (2105-DCP)

Percentage of participants' results	|z-score| ≤ 2	2 < |z-score| < 3	|z-score| ≥ 3
BDE-28	92%	4%	4%
BDE-47	88%	8%	4%
BDE-49	95%	5%	-
BDE-99	96%	-	4%
BDE-100	96%	4%	-
BDE-153	88%	4%	8%
BDE-154	96%	-	4%
BDE-183	86%	-	14%
BDE-209	80%	-	20%
Sum of 8 PBDEs without BDE-209 (ub)	96%	-	4%
Sum of 8 PBDE including BDE-209 (lb)	96%	-	4%
Sum of 9 PBDE including BDE-209 (ub)	81%	5%	14%
Sum of 9 PBDE including BDE-209 (lb)	76%	5%	19%

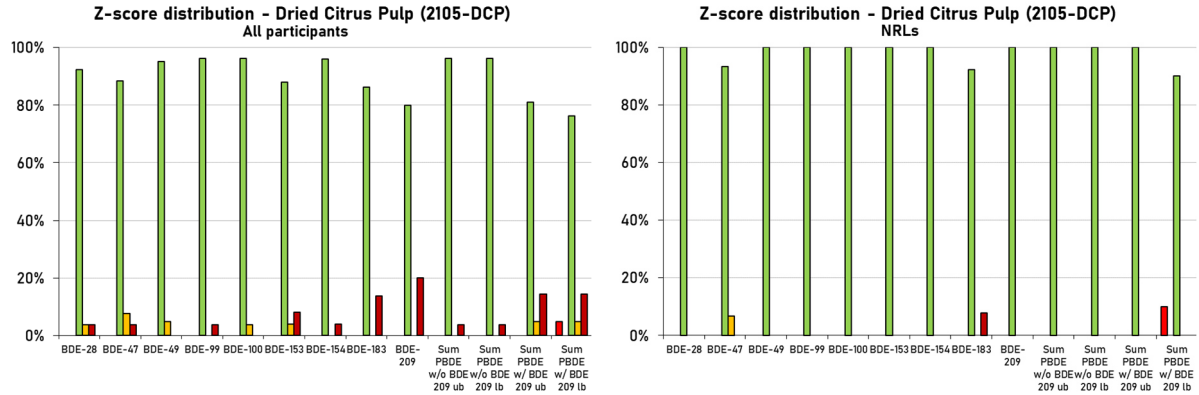

Figure 7: Distribution of participants' z-scores and NRLs only for PBDE congeners / sum parameters for dried citrus pulp (2105-DCP) [Green bars: -2 ≤ z-score ≤ 2, orange bars: -3 < z-score < -2, 2 < z-score < 3, red bars: z-score ≤ -3, z-score ≥ 3]

5.3. HBCDDs - Participants' z-scores

HBCDD stereoisomers undergo thermal isomerization at temperatures above 160 °C. With GC elution temperature of these compounds of normally above 160 °C a separation of HBCDD stereoisomers using GC analysis is not possible. Only one unresolved peak is obtained. Additional thermal decomposition of HBCDDs is reported for temperatures above 240 °C. Therefore, in case of applying GC-MS methods for HBCDD analysis determination of total HBCDD (as sum of all originally present HBCDD diastereomers) is possible only.

Due to the low numbers of results for total HBCDD the sum of α-, β-, γ-HBCDD (using LC separation) was taken for comparison.

Table 11: Distribution of participants' z-scores for HBCDD for dried citrus pulp (2105-DCP)

Percentage of participants' results	|z-score| ≤ 2	2 < |z-score| < 3	|z-score| ≥ 3
γ - HBCDD	75%	12.5%	12.5%
Sum of α-, β-, γ-HBCDD (lb)	81%	6%	13%
Sum of α-, β-, γ-HBCDD (ub)	75%	12.5%	12.5%
Total HBCDD*	100%	-	-

*Comparison of participants' results for total HBCDD with assigned value for sum of α-, β-, γ-HBCDD

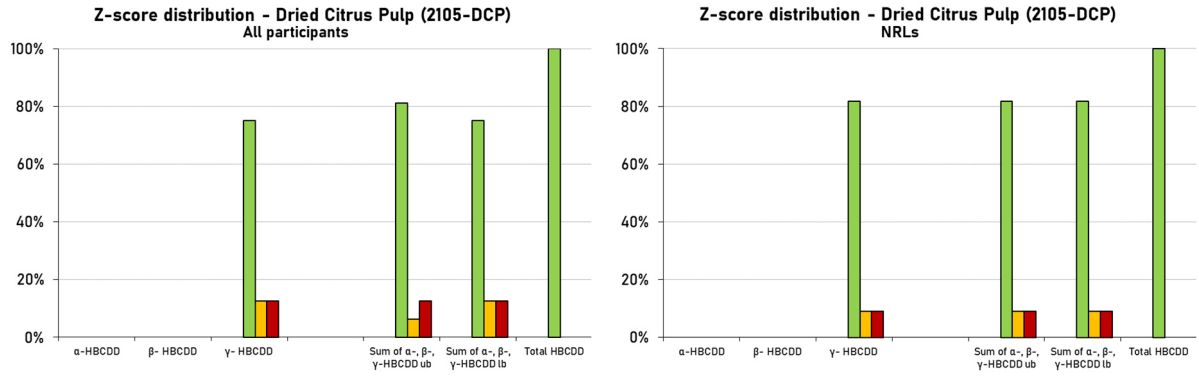

Figure 8: Distribution of participants' z-scores and NRLs only for HBCDD stereoisomers / sum parameters for dried citrus pulp (2105-DCP) [Green bars: -2 ≤ z-score ≤ 2, orange bars: -3 < z-score <-2, 2 < z-score < 3, red bars: z-score ≤ -3, z-score ≥ 3]

6. Participants' feedback

A questionnaire for feedback from participants of this EURL proficiency test was available as online survey between 03 December 2021 and 21 January 2022. The survey was anonymous, but participants could also give their laboratory name. The identity of the laboratories is kept confidential. The survey included several questions related to different topics (participants' information, organization of the proficiency test, PT test samples and evaluation of results and summary of data) and a possibility to include comments and further suggestions.

In total, 12 laboratories (15 % of all PT participants) replied to this survey.

Table 12: Participating laboratories in the feedback survey

Type of laboratory	Answers
National Reference Laboratory (NRL)	6
Official Laboratory (OFL)	3
Commercial laboratory	3
Other (e.g. research and development)	0
No Answer	0

General aspect

How satisfied are you with the organization of this proficiency test in general? Please rate the parts below according to your experience, with 0 stars meaning "no opinion" and 5 stars meaning "full satisfaction".

Did the proficiency test meet expectations?

Specific aspects of this proficiency test

We would like to know a bit more about specific aspects of this proficiency test. Please rate the aspects below according to your experience, with 0 stars meaning "no opinion" and 5 stars meaning "full satisfaction".

Was all necessary information for participation and performance of the PT provided in an understandable way?	
Was the time frame acceptable?	
Was the handling of EUSurvey as webtool for reporting and source of instructions manageable?	
Was the evaluation of participant's results and the information in the preliminary report clear and comprehensible?	

Was the selected sample adequate for the goal to assess analytical performance of laboratories in relevant matrices?

Choice of matrix	
Level of contamination	

The following comments or suggestions for improvements were submitted:
"The matrix did not correspond to the routinely tested samples. It was the first citrus pulp sample past 10 years."

7. Quality control

The Deutsche Akkreditierungsstelle GmbH attests that the provider of proficiency testing Chemisches und Veterinäruntersuchungsamt Freiburg, EU Reference Laboratory (EURL) for halogenated persistent organic pollutants (POPs) in feed and food is competent under the terms of DIN EN ISO/IEC 17043:2010 to carry out proficiency testing in the testing field of determination of halogenated persistent organic pollutants (POPs) in food and feed (Accreditation number: D-EP-18625-01-00).

8. Results of participants

An overview of the PBDE and HBCDD results for the PT test sample dried citrus pulp (2105-DCP) is given in the following annexes. Laboratories are coded according to the laboratory codes sent after registration.

9. References

[1] M. Thompson, S.L.R. Ellison, R. Wood: The International Harmonized Protocol For The Proficiency Testing Of Analytical Chemistry Laboratories, Pure Appl. Chem., Vol. 78, No. 1, pp. 145-196, 2006.

[2] DIN ISO 13528:2020, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization

10. Annex

Dried Citrus Pulp – 2105-DCP	
Annex 1	Assigned values – PBDEs, HBCDDs
Annex 2	Participants' results – Tables – PBDEs, HBCDDs
Annex 3	Participants' z-scores – Tables – PBDEs, HBCDDs
Annex 4	Participants' z-scores – Charts – PBDEs, HBCDDs
Annex 5	Homogeneity and stability test – PBDE
Annex 6	Participants' methods – PBDE, HBCDD

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EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
06 December 2022

Annex 1: Assigned values of PBDEs and HBCDDs

Test sample - Dried Citrus Pulp (2105-DCP)

Assigned values of sum parameters and individual congeners

Estimation of the assigned value as the consensus of participants' results
Assigned value = Huber robust mean after exlusion of extreme outliers

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
PBDE - Assigned values

Analyte		Result µg/kg product (12 % moisture content)	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
BDE-28	2,2′,4-tribromodiphenyl ether		0.00918	0.0012	0.00030	25	0.00942
BDE-47	2,2′,4,4′-tetrabromodiphenyl ether		0.115	0.017	0.0043	24	0.114
BDE-49	2,2′,4,5′-tetrabromodiphenyl ether		0.0120	0.0023	0.00064	21	0.0120
BDE-99	2,2′,4,4′,5-pentabromodiphenyl ether		0.150	0.014	0.0036	25	0.152
BDE-100	2,2′,4,4′,6-pentabromodiphenyl ether		0.0323	0.0045	0.0011	25	0.0326
BDE-153	2,2′,4,4′,5,5′-hexabromodiphenyl ether		0.0149	0.0018	0.00046	24	0.0154
BDE-154	2,2′,4,4′,5,6′-hexabromodiphenyl ether		0.0129	0.0020	0.00051	25	0.0129
BDE-183	2,2′,3,4,4′,5′,6-heptabromodiphenyl ether		0.00719	0.0015	0.00042	20	0.00776
BDE-209	2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether		0.675	0.14	0.042	16	0.722
Sum of 8 PBDE	without BDE-209 (ub)		0.358	0.047	0.012	25	0.350
Sum of 8 PBDE	without BDE-209 (lb)		0.356	0.047	0.012	25	0.347
Sum of 9 PBDE	including BDE-209 (ub)		1.03	0.18	0.053	18	1.10
Sum of 9 PBDE	including BDE-209 (lb)		1.05	0.17	0.051	17	1.10

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Baby Food 2021 [EURL-PT-DPB-2101-BF]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
HBCDD - Assigned values

Analyte		Result µg/kg product (12 % moisture content)	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
(+/–)-α-HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane)						0.0716
(+/–)-β- HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane)						0.0485
(+/–)-γ- HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane)		0.917	0.20	0.066	14	0.937
Sum of α-, β-, γ-HBCDD	(ub)		1.03	0.22	0.073	14	1.04
Sum of α-, β-, γ-HBCDD	(lb)		0.959	0.18	0.063	13	1.01
Total HBCDD	(using GC-methods)						0.893

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Moisture content (BFR) - Assigned value

Analyte	Result %	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
Moisture content		8.80	0.85	0.22	24	8.80

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
06 December 2022

Annex 2: Participants' results of PBDEs and HBCDDs

Test sample - Dried Citrus Pulp (2105-DCP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)

PBDE - Results

LC	Sample	Result µg/kg product (12 % moisture content)	2,2',4-tribromodiphenyl ether **BDE-28**	2,2',4,4'-tetrabromodiphenyl ether **BDE-47**	2,2',4,5'-tetrabromodiphenyl ether **BDE-49**	2,2',4,4',5-pentabromodiphenyl ether **BDE-99**	2,2',4,4',6-pentabromodiphenyl ether **BDE-100**	2,2',4,4',5,5'-hexabromodiphenyl ether **BDE-153**	2,2',4,4',5,6'-hexabromodiphenyl ether **BDE-154**	2,2',3,4,4',5',6-heptabromodiphenyl ether **BDE-183**	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether **BDE-209**		**Sum of 8 PBDE** without BDE-209 (ub)	**Sum of 8 PBDE** without BDE-209 (lb)	**Sum of 9 PBDE** including BDE-209 (ub)	**Sum of 9 PBDE** without BDE-209 (lb)
1	2105-DCP		0.00955	0.12		0.149	0.0314	0.0158	0.0131	0.00781			0.347	0.347		
6	2105-DCP		0.00802	0.113	0.0152	0.144	0.0369	0.0165	0.00973	< 0.00195			0.346	0.344		
7	2105-DCP		0.00832	0.0983	< 0.045	0.123	0.0283	0.0148	0.0126	0.00656	0.793		0.303	0.303	1.1	1.1
13	2105-DCP		0.0121	0.135	0.0118	0.179	0.0374	0.0178	0.0152	0.0077			0.416	0.416		
17	2105-DCP		0.01	0.12	0.013	0.17	0.037	0.015	0.0135	0.0083	0.6		0.387	0.387	0.987	0.987
18	2105-DCP		0.0083	0.16	0.012	0.16	0.043	0.016	0.015	0.01			0.42	0.42		
19	2105-DCP		0.00824	0.0965	0.0134	0.136	0.0267	0.0148	0.0133	0.00656	0.807		0.316	0.316	1.12	1.12
26	2105-DCP		0.00968	0.18	0.0163	0.21	0.0358	0.0104	0.0109	0.0133	0.74		0.486	0.486	1.23	1.23
28	2105-DCP		0.0098	0.108	0.0106	0.155	0.0371	0.025	0.0154	0.0387	0.54		0.399	0.399	0.939	0.939
32	2105-DCP		0.007	0.103	0.00908	0.132	0.0274	0.0136	0.0118	0.00608	0.546		0.31	0.31	0.856	0.856
33	2105-DCP		0.00925	0.125	0.00931	0.162	0.0334	0.0156	0.0123	0.00507	0.695		0.372	0.372	1.07	1.07
35	2105-DCP		0.0101	0.115	0.0121	0.156	0.0333	0.016	0.0131	0.00744			0.364	0.364		
37	2105-DCP		0.007	0.091	0.01	0.134	0.027	0.012	0.009	0.005	0.501		0.29	0.29	0.8	0.8
38	2105-DCP		0.0105	0.109	0.00931	0.151	0.0301	0.0154	0.0127	0.00793	0.556		0.347	0.347	0.903	0.903
39	2105-DCP		0.014	0.185	0.017	0.247	0.051	0.027	0.021	0.012	1.28		0.576	0.576	1.85	1.85
41	2105-DCP		0.0071	0.101	0.0119	0.133	0.0268	0.0122	0.0107	0.0055	0.496		0.308	0.308	0.805	0.805
43	2105-DCP		0.0102	0.112	0.0103	0.139	0.0295	0.0133	0.0114	0.00652	1.28		0.332	0.332	1.61	1.61
46	2105-DCP		0.00876	0.113		0.153	0.0321	0.0165	0.0135	0.00811	0.722		0.344	0.344	1.07	1.07
47	2105-DCP		0.0088	0.108		0.132	0.028	0.0139	0.0108	0.0098	2.28		0.311	0.311	2.59	2.59
50	2105-DCP		0.00928	0.149	0.0137	0.149	0.0343	0.0153	0.0126	0.006	0.859		0.397	0.393	1.26	1.25
61	2105-DCP		0.0197	0.165	0.0146	0.16	0.038	0.023	< 0.019	< 0.019	2.09		0.458	0.42	2.55	2.51
67	2105-DCP		0.0084	0.14	0.012	0.16	0.035	0.015	0.018	0.0079	0.67		0.4	0.4	1.1	1.1
70	2105-DCP		0.01	0.115	0.012	0.147	0.031	0.016	0.014	0.007	0.76		0.352	0.352	1.11	1.11
71	2105-DCP															
72	2105-DCP		0.00856	0.103	0.00948	0.146	0.0297	0.0143	0.0119	0.00652	0.803		0.329	0.329	1.13	1.13
77	2105-DCP		0.0096	0.102		0.156	0.0299	0.0154	0.0122	< 0.02	0.716		0.344	0.324	1.06	1.04
78	2105-DCP															
79B	2105-DCP		0.01	0.119	0.011	0.152	0.033	< 0.008	0.015	< 0.009	< 0.354		0.357	0.34	0.711	0.34
39*	2105-DCP		0.007	0.0925	0.0085	0.1235	0.0255	0.0135	0.0105	0.006	0.6385		0.288	0.288	0.9265	0.9265

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
HBCDD - Results

LC	Sample	Result µg/kg product (12 % moisture content)	(+/–)-α-HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane	(+/–)-β- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane	(+/–)-γ- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane		Sum of α-, β-, γ-HBCDD (ub)	Sum of α-, β-, γ-HBCDD (lb)	Total HBCDD (using GC-methods)
1	2105-DCP		0.13	0.26	4.6		4.99	4.99	
6	2105-DCP								
7	2105-DCP		0.0692	0.027	0.739		0.835	0.835	
13	2105-DCP		0.0731	0.0705	0.673		0.817	0.817	
17	2105-DCP								
18	2105-DCP								
19	2105-DCP		< 0.048	< 0.048	0.736		0.832	0.736	
26	2105-DCP		0.0945	0.065	0.817		0.976	0.976	
28	2105-DCP								
32	2105-DCP								0.736
33	2105-DCP								
35	2105-DCP		0.0462	0.0252	0.984		1.06	1.06	
37	2105-DCP		0.037	0.027	0.938		1	1	
38	2105-DCP								1.05
39	2105-DCP		0.048	0.032	0.936		1.02	1.02	
41	2105-DCP		0.125	0.049	1.35		1.52	1.52	
43	2105-DCP								
46	2105-DCP		0.929	0.399	3.57		4.9	4.9	
47	2105-DCP								
50	2105-DCP		< 0.1	< 0.1	0.895		1.1	0.895	
61	2105-DCP								
67	2105-DCP								
70	2105-DCP		0.08	0.05	1.31		1.44	1.44	
71	2105-DCP		< 0.038	< 0.019	0.723		0.78	0.723	
72	2105-DCP								
77	2105-DCP		0.116	0.054	1.15		1.32	1.32	
78	2105-DCP		0.07	0.03	0.94		1.05	1.05	
79B	2105-DCP		< 0.04	0.0157	0.896		0.952	0.912	

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Moisture content - Results

LC	Sample	Result %	Moisture content PBDE	Moisture content HBCDD	Moisture content Mean
1	2105-DCP		7.8	7.8	7.8
6	2105-DCP		9.6		9.6
7	2105-DCP		9.1	9.1	9.1
13	2105-DCP				
17	2105-DCP		91.0		91.0
18	2105-DCP		9.6		9.6
19	2105-DCP		8.3	8.3	8.3
26	2105-DCP		9.3	9.3	9.3
28	2105-DCP		10.3		10.3
32	2105-DCP		8.4	8.0	8.2
33	2105-DCP		8.2		8.2
35	2105-DCP		8.0	8.0	8.0
37	2105-DCP		8.2	8.2	8.2
38	2105-DCP		9.7	9.7	9.7
39	2105-DCP		8.4	8.6	8.5
41	2105-DCP		8.8	8.8	8.8
43	2105-DCP				
46	2105-DCP		9.0	9.0	9.0
47	2105-DCP		7.6		7.6
50	2105-DCP		8.8	8.8	8.8
61	2105-DCP				
67	2105-DCP		9.0		9.0
70	2105-DCP		9.6	9.6	9.6
71	2105-DCP			7.7	7.7
72	2105-DCP		9.6		9.6
77	2105-DCP		10.6	10.6	10.6
78	2105-DCP			8.3	8.3
79B	2105-DCP		8.3	8.3	8.3

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
06 December 2022

Annex 3: Participants' z-scores of PBDEs and HBCDDs - Tables

Test sample - Dried Citrus Pulp (2105-DCP)

Z-scores of sum parameters and individual results

Calculation of z-score on basis of assigned value

$z = (x - x_a) / \sigma_p$

x_a: assigned value
x: participant's result
σ_p: fitness-for-purpose-based standard deviation for proficiency assessment
20%: Evaluated individual PBDE congeners and HBCDD diastereomers and sum

* Modified/additional results reported after distribution of preliminary results to all participating laboratories

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
PBDE - Z-scores

LC	Sample	Z-score [σ_p = 20 %]	2,2',4-tribromodiphenyl ether **BDE-28**	2,2',4,4'-tetrabromodiphenyl ether **BDE-47**	2,2',4,5'-tetrabromodiphenyl ether **BDE-49**	2,2',4,4',5-pentabromodiphenyl ether **BDE-99**	2,2',4,4',6-pentabromodiphenyl ether **BDE-100**	2,2',4,4',5,5'-hexabromodiphenyl ether **BDE-153**	2,2',4,4',5,6'-hexabromodiphenyl ether **BDE-154**	2,2',3,4,4',5',6-heptabromodiphenyl ether **BDE-183**	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether **BDE-209**	**Sum of 8 PBDE** without BDE-209 (ub)	**Sum of 8 PBDE** without BDE-209 (lb)	**Sum of 9 PBDE** including BDE-209 (ub)	**Sum of 9 PBDE** without BDE-209 (lb)
1	2105-DCP		0.2	0.2		0.0	-0.1	0.3	0.1	0.4		-0.2	-0.1		
6	2105-DCP		-0.6	-0.1	1.3	-0.2	0.7	0.5	-1.2			-0.2	-0.2		
7	2105-DCP		-0.5	-0.7		-0.9	-0.6	0.0	-0.1	-0.4	0.9	-0.8	-0.7	0.3	0.2
13	2105-DCP		1.6	0.9	-0.1	1.0	0.8	1.0	0.9	0.4		0.8	0.8		
17	2105-DCP		0.4	0.2	0.4	0.7	0.7	0.0	0.2	0.8	-0.6	0.4	0.4	-0.2	-0.3
18	2105-DCP		-0.5	2.0	0.0	0.3	1.7	0.4	0.8	2.0		0.9	0.9		
19	2105-DCP		-0.5	-0.8	0.6	-0.5	-0.9	0.0	0.2	-0.4	1.0	-0.6	-0.6	0.4	0.3
26	2105-DCP		0.3	2.8	1.8	2.0	0.5	-1.5	-0.8	4.2	0.5	1.8	1.8	1.0	0.9
28	2105-DCP		0.3	-0.3	-0.6	0.2	0.7	3.4	1.0	21.9	-1.0	0.6	0.6	-0.4	-0.5
32	2105-DCP		-1.2	-0.5	-1.2	-0.6	-0.8	-0.4	-0.4	-0.8	-1.0	-0.7	-0.6	-0.8	-0.9
33	2105-DCP		0.0	0.4	-1.1	0.4	0.2	0.2	-0.2	-1.5	0.1	0.2	0.2	0.2	0.1
35	2105-DCP		0.5	0.0	0.0	0.2	0.2	0.4	0.1	0.2		0.1	0.1		
37	2105-DCP		-1.2	-1.0	-0.8	-0.5	-0.8	-1.0	-1.5	-1.5	-1.3	-0.9	-0.9	-1.1	-1.2
38	2105-DCP		0.7	-0.3	-1.1	0.0	-0.3	0.2	-0.1	0.5	-0.9	-0.2	-0.1	-0.6	-0.7
39	2105-DCP		2.6	3.0	2.1	3.2	2.9	4.1	3.1	3.3	4.5	3.0	3.1	4.0	3.8
41	2105-DCP		-1.1	-0.6	0.0	-0.6	-0.9	-0.9	-0.9	-1.2	-1.3	-0.7	-0.7	-1.1	-1.2
43	2105-DCP		0.6	-0.1	-0.7	-0.4	-0.4	-0.5	-0.6	-0.5	4.5	-0.4	-0.3	2.8	2.7
46	2105-DCP		-0.2	-0.1		0.1	0.0	0.5	0.2	0.6	0.3	-0.2	-0.2	0.2	0.1
47	2105-DCP		-0.2	-0.3		-0.6	-0.7	-0.3	-0.8	1.8	11.9	-0.7	-0.6	7.6	7.3
50	2105-DCP		0.1	1.5	0.7	0.0	0.3	0.1	-0.1	-0.8	1.4	0.5	0.5	1.1	1.0
61	2105-DCP		5.7	2.2	1.1	0.3	0.9	2.7			10.5	1.4	0.9	7.4	7.0
67	2105-DCP		-0.4	1.1	0.0	0.3	0.4	0.0	2.0	0.5	0.0	0.6	0.6	0.3	0.2
70	2105-DCP		0.4	0.0	0.0	-0.1	-0.2	0.4	0.4	-0.1	0.6	-0.1	-0.1	0.4	0.3
71	2105-DCP														
72	2105-DCP		-0.3	-0.5	-1.1	-0.1	-0.4	-0.2	-0.4	-0.5	0.9	-0.4	-0.4	0.5	0.4
77	2105-DCP		0.2	-0.6		0.2	-0.4	0.2	-0.3		0.3	-0.2	-0.4	0.1	0.0
78	2105-DCP														
79B	2105-DCP		0.4	0.2	-0.4	0.1	0.1		0.8			0.0	-0.2	-1.5	-3.4
39*	2105-DCP		-1.2	-1.0	-1.5	-0.9	-1.1	-0.5	-0.9	-0.8	-0.3	-1.0	-1.0	-0.5	-0.6

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
HBCDD - Z-scores

LC	Sample	Z-score [σ_p = 20 %]	**(+/–)-α-HBCDD** 1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane	**(+/–)-β- HBCDD** 1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane	**(+/–)-γ- HBCDD** 1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane		**Sum of α-, β-, γ-HBCDD** (ub)	**Sum of α-, β-, γ-HBCDD** (lb)	**Total HBCDD*** (using GC-methods)
1	2105-DCP				20.1		19.2	21.0	
6	2105-DCP								
7	2105-DCP				-1.0		-0.9	-0.6	
13	2105-DCP				-1.3		-1.0	-0.7	
17	2105-DCP								
18	2105-DCP								
19	2105-DCP				-1.0		-1.0	-1.2	
26	2105-DCP				-0.5		-0.3	0.1	
28	2105-DCP								
32	2105-DCP								-1.2
33	2105-DCP								
35	2105-DCP				0.4		0.1	0.5	
37	2105-DCP				0.1		-0.1	0.2	
38	2105-DCP								0.5
39	2105-DCP				0.1		0.0	0.3	
41	2105-DCP				2.4		2.4	2.9	
43	2105-DCP								
46	2105-DCP				14.5		18.8	20.5	
47	2105-DCP								
50	2105-DCP				-0.1		0.3	-0.3	
61	2105-DCP								
67	2105-DCP								
70	2105-DCP				2.1		2.0	2.5	
71	2105-DCP				-1.1		-1.2	-1.2	
72	2105-DCP								
77	2105-DCP				1.3		1.4	1.9	
78	2105-DCP				0.1		0.1	0.5	
79B	2105-DCP				-0.1		-0.4	-0.2	

* Z-scores for information only; calculation based on assigned value for sum of α-, β-, γ-HBCDD (lb)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Moisture content - Results

LC	Sample	Z-score [σ_p = 10 %]	Moisture content	Moisture content	Moisture content
			PBDE	HBCDD	Mean
1	2105-DCP		-1.1	-1.1	-1.1
6	2105-DCP		0.9		0.9
7	2105-DCP		0.3	0.3	0.3
13	2105-DCP				
17	2105-DCP		93.4		93.4
18	2105-DCP		0.9		0.9
19	2105-DCP		-0.5	-0.5	-0.5
26	2105-DCP		0.6	0.6	0.6
28	2105-DCP		1.7		1.7
32	2105-DCP		-0.5	-0.9	-0.7
33	2105-DCP		-0.7		-0.7
35	2105-DCP		-0.9	-0.9	-0.9
37	2105-DCP		-0.7	-0.7	-0.7
38	2105-DCP		1.0	1.0	1.0
39	2105-DCP		-0.5	-0.2	-0.3
41	2105-DCP		0.0	0.0	0.0
43	2105-DCP				
46	2105-DCP		0.2	0.2	0.2
47	2105-DCP		-1.4		-1.4
50	2105-DCP		0.0	0.0	0.0
61	2105-DCP				
67	2105-DCP		0.2		0.2
70	2105-DCP		0.9	0.9	0.9
71	2105-DCP			-1.3	-1.3
72	2105-DCP		0.9		0.9
77	2105-DCP		2.0	2.0	2.0
78	2105-DCP			-0.6	-0.6
79B	2105-DCP		-0.6	-0.6	-0.6

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
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Annex 4: Participants' z-scores of PBDEs and HBCDDs - Charts

Test sample - Dried Citrus Pulp (2105-DCP)

Z-scores of sum parameters and individual results

Calculation of z-score on basis of assigned value

$z = (x - x_a) / \sigma_p$

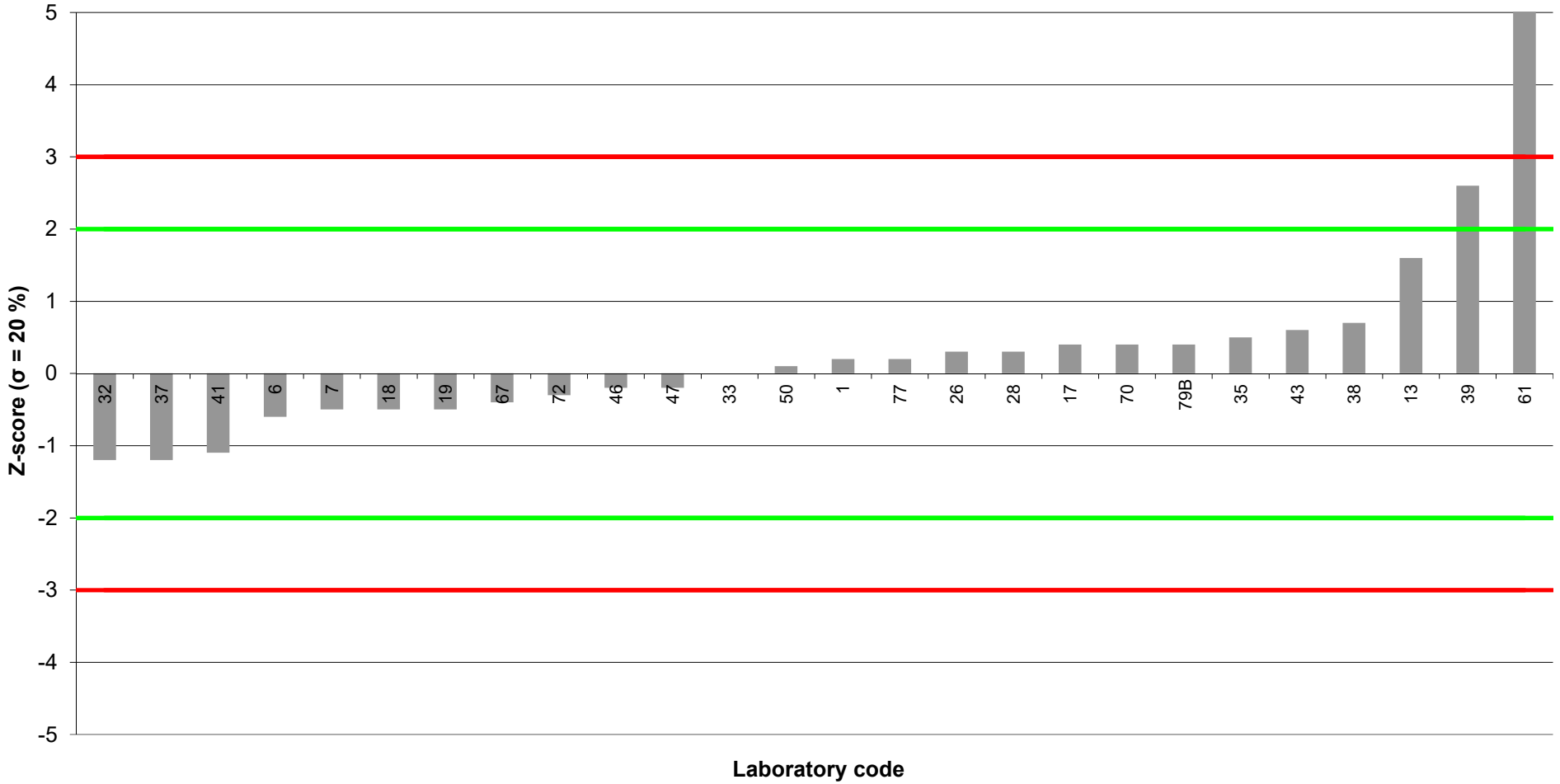
x_a: assigned value
x: participant's result
σ_p: fitness-for-purpose-based standard deviation for proficiency assessment
20%: Evaluated individual PBDE congeners and HBCDD diastereomers and sum

± 2 z-scores:
± 3 z-scores:

Dried Citrus Pulp (2105-DCP)

BDE-28

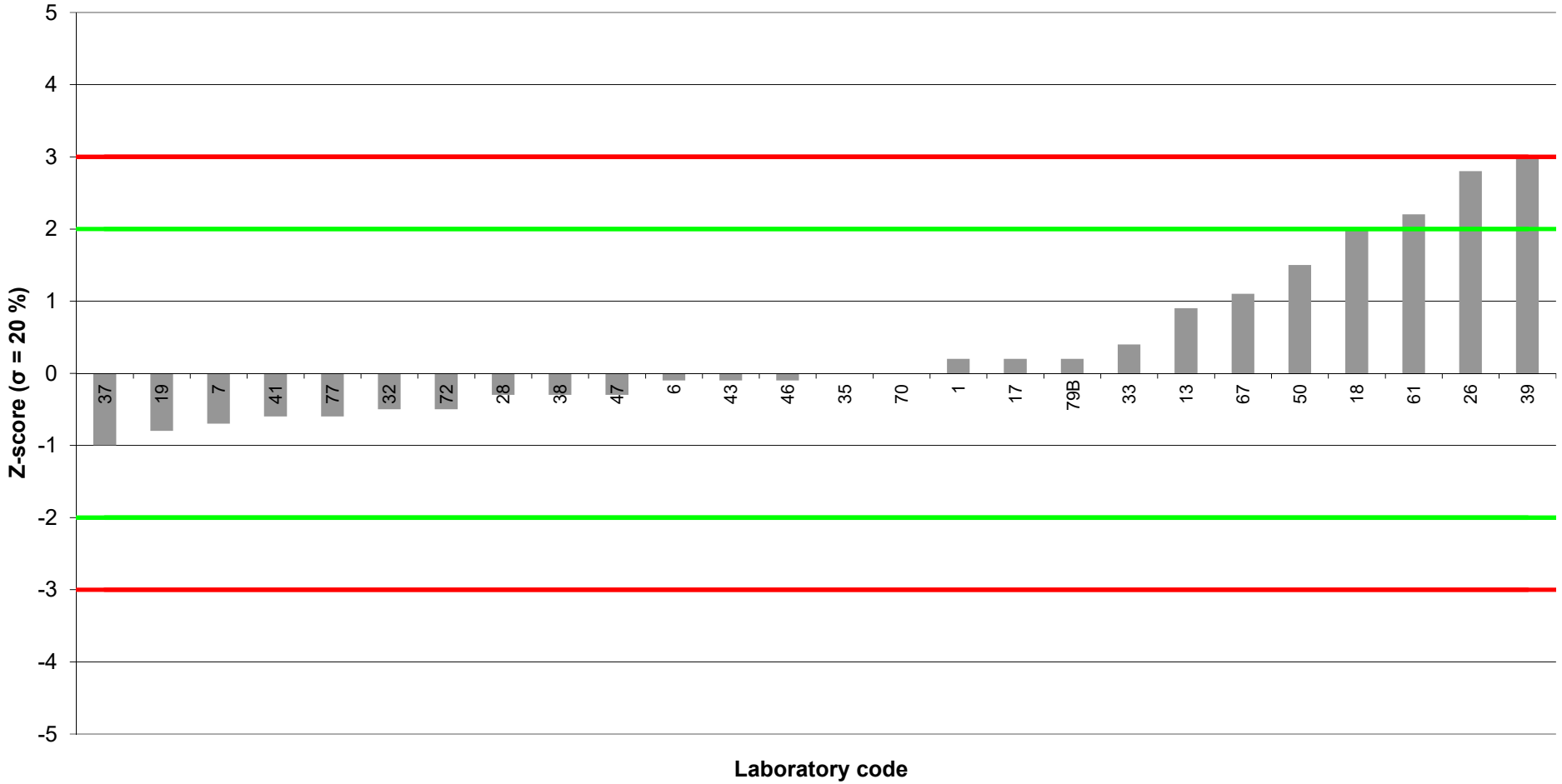
Assigned value: 0.00918 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-47

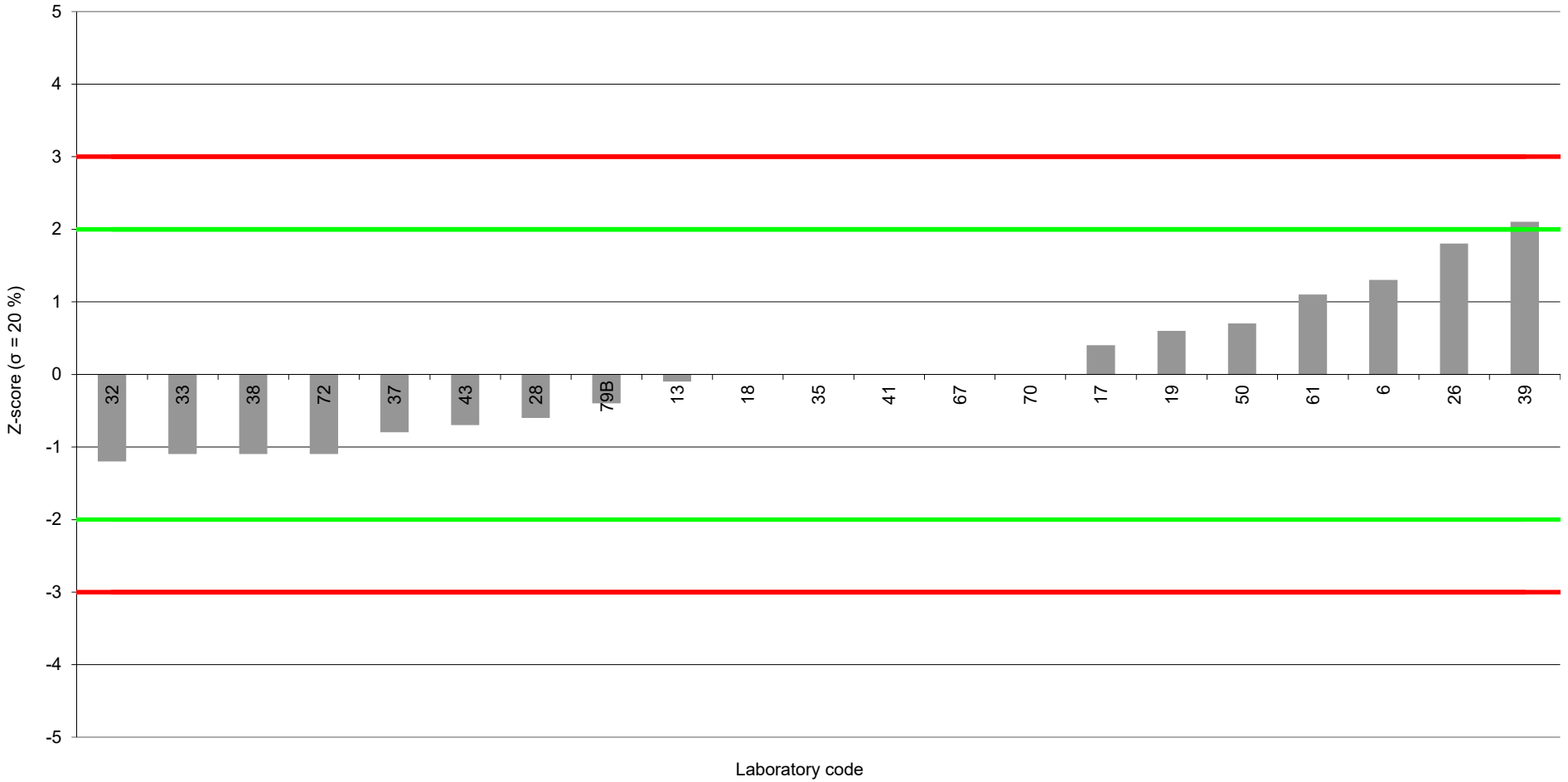
Assigned value: 0.115 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-49

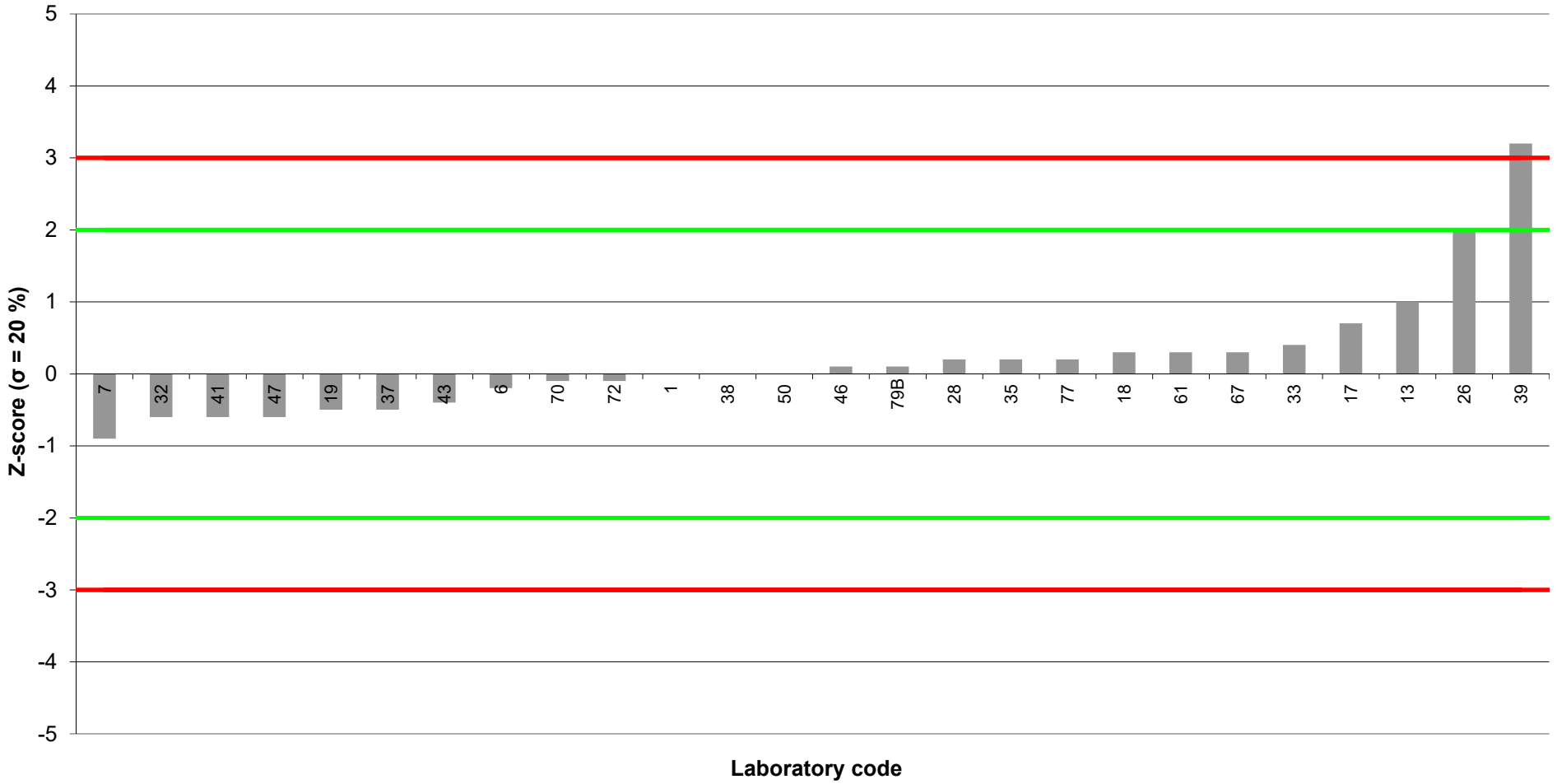
Assigned value: 0.012 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-99

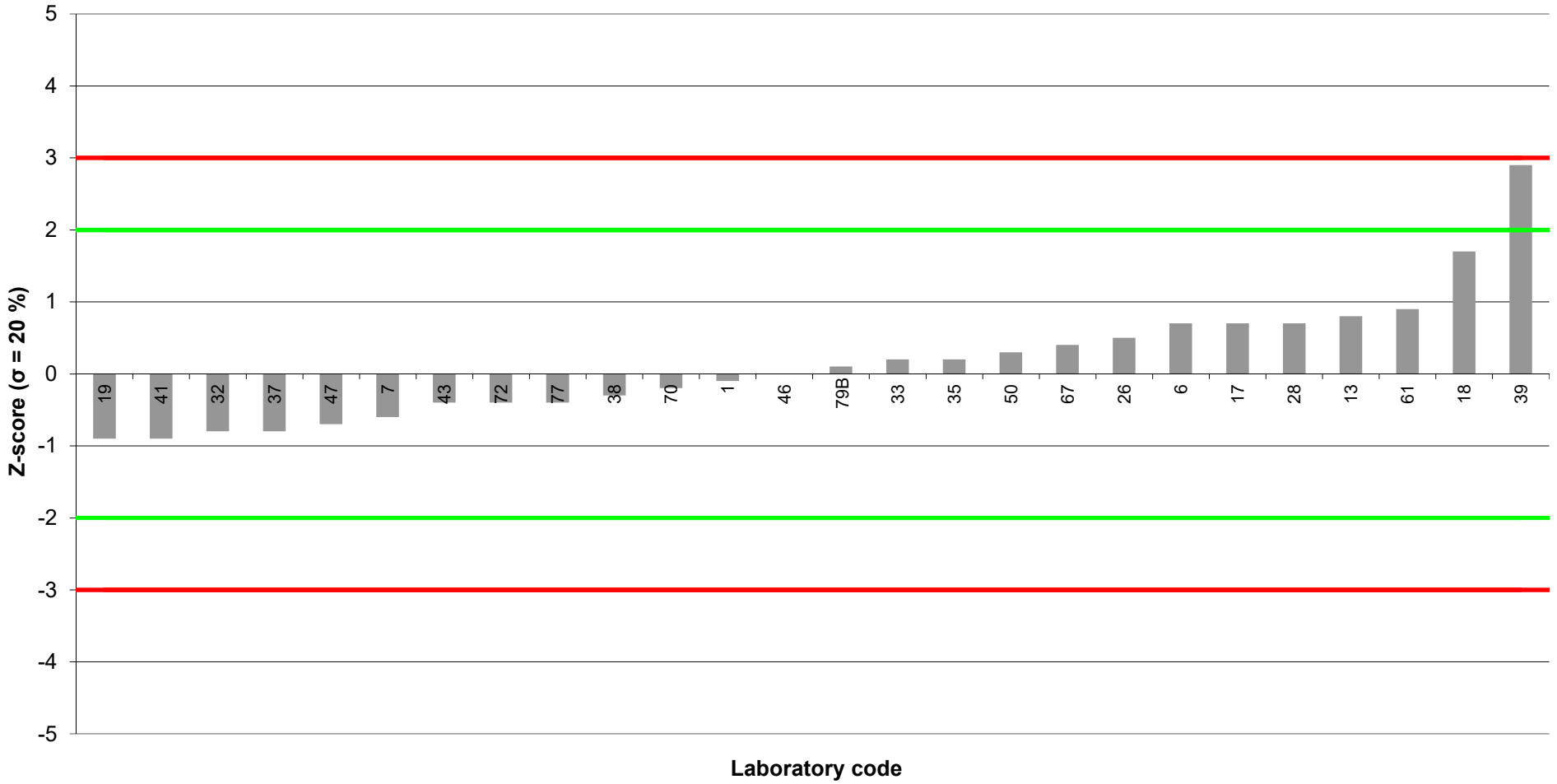
Assigned value: 0.15 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-100

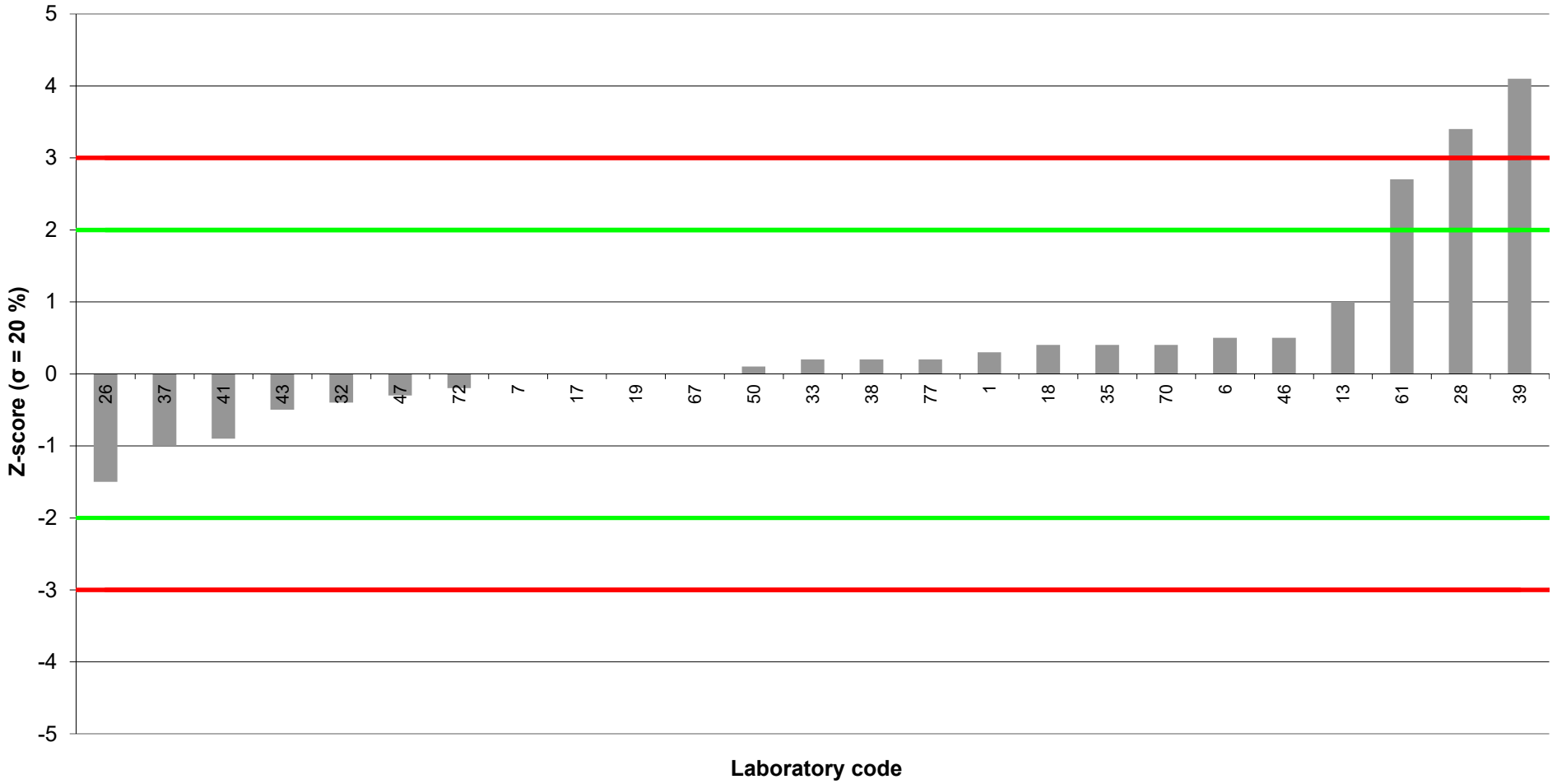
Assigned value: 0.0323 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-153

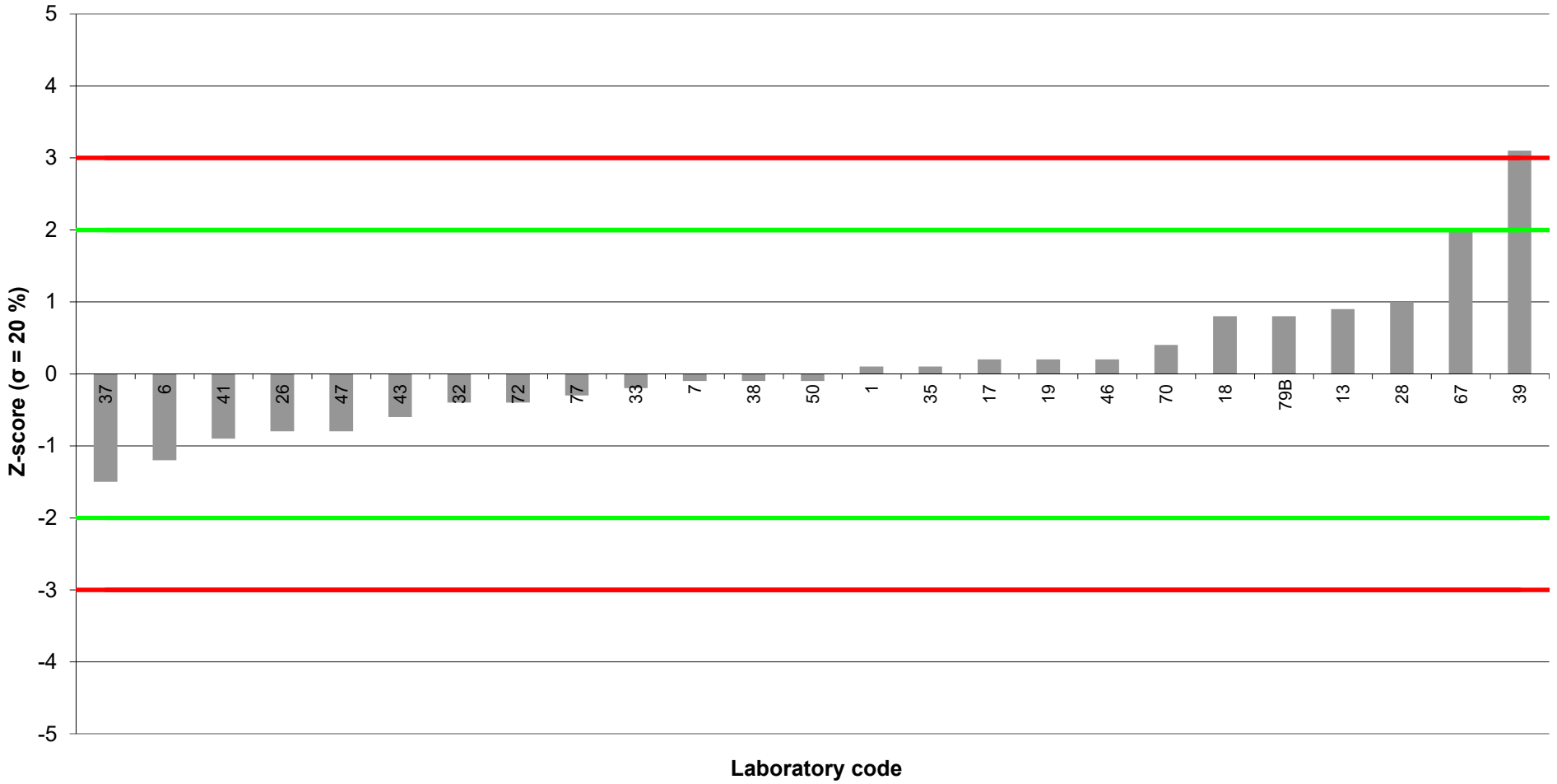
Assigned value: 0.0149 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-154

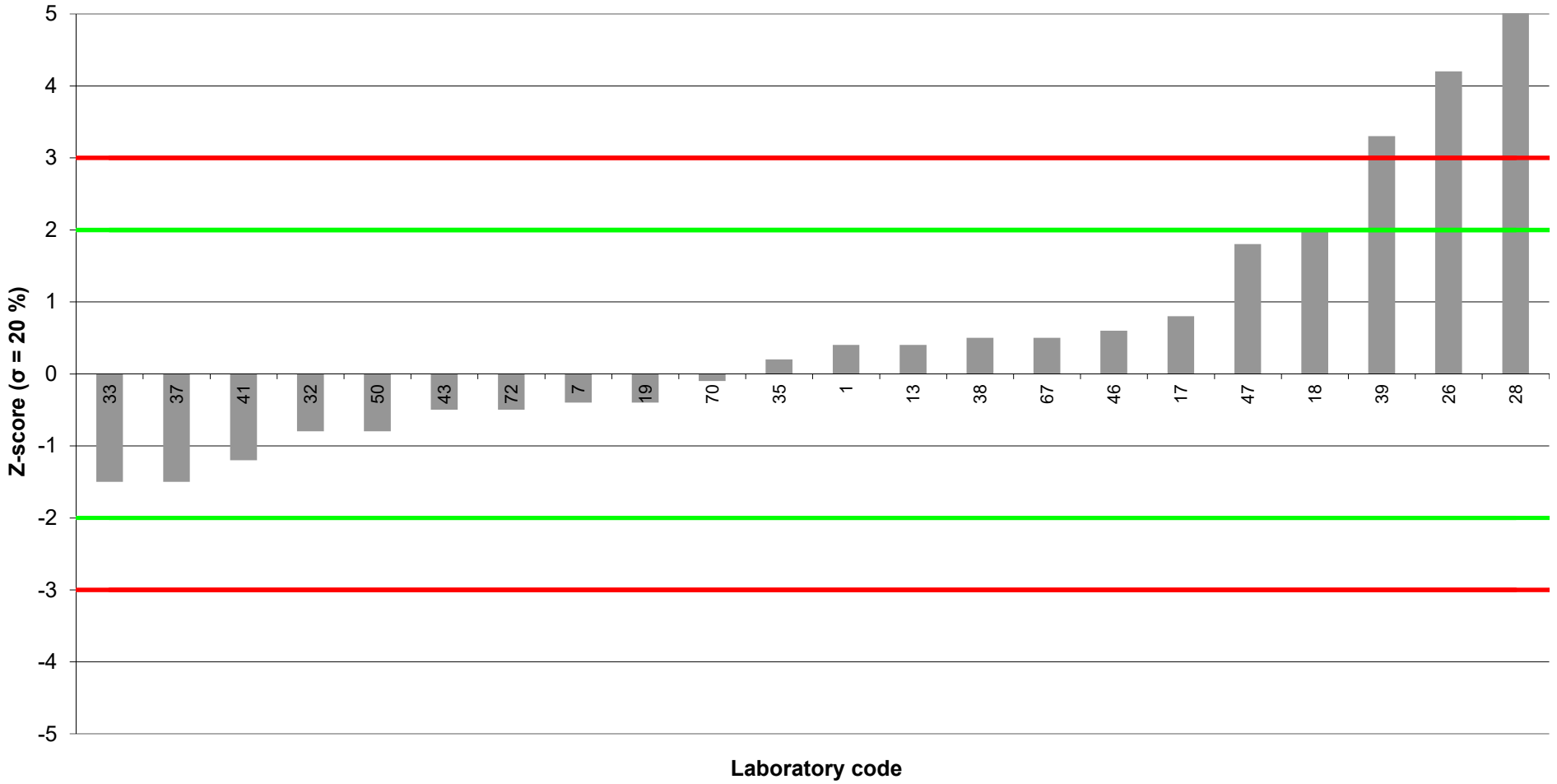
Assigned value: 0.0129 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-183

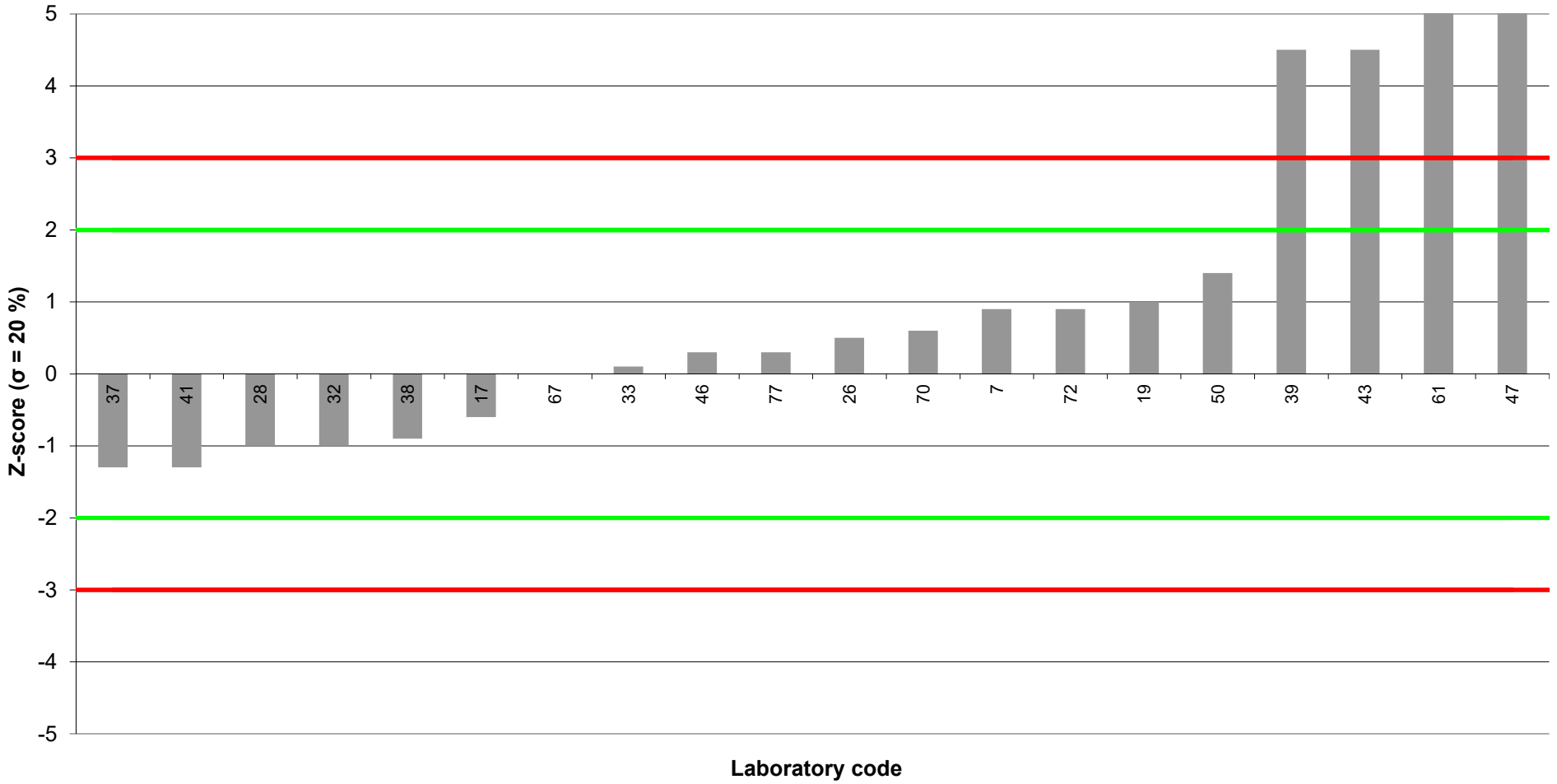
Assigned value: 0.00719 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

BDE-209

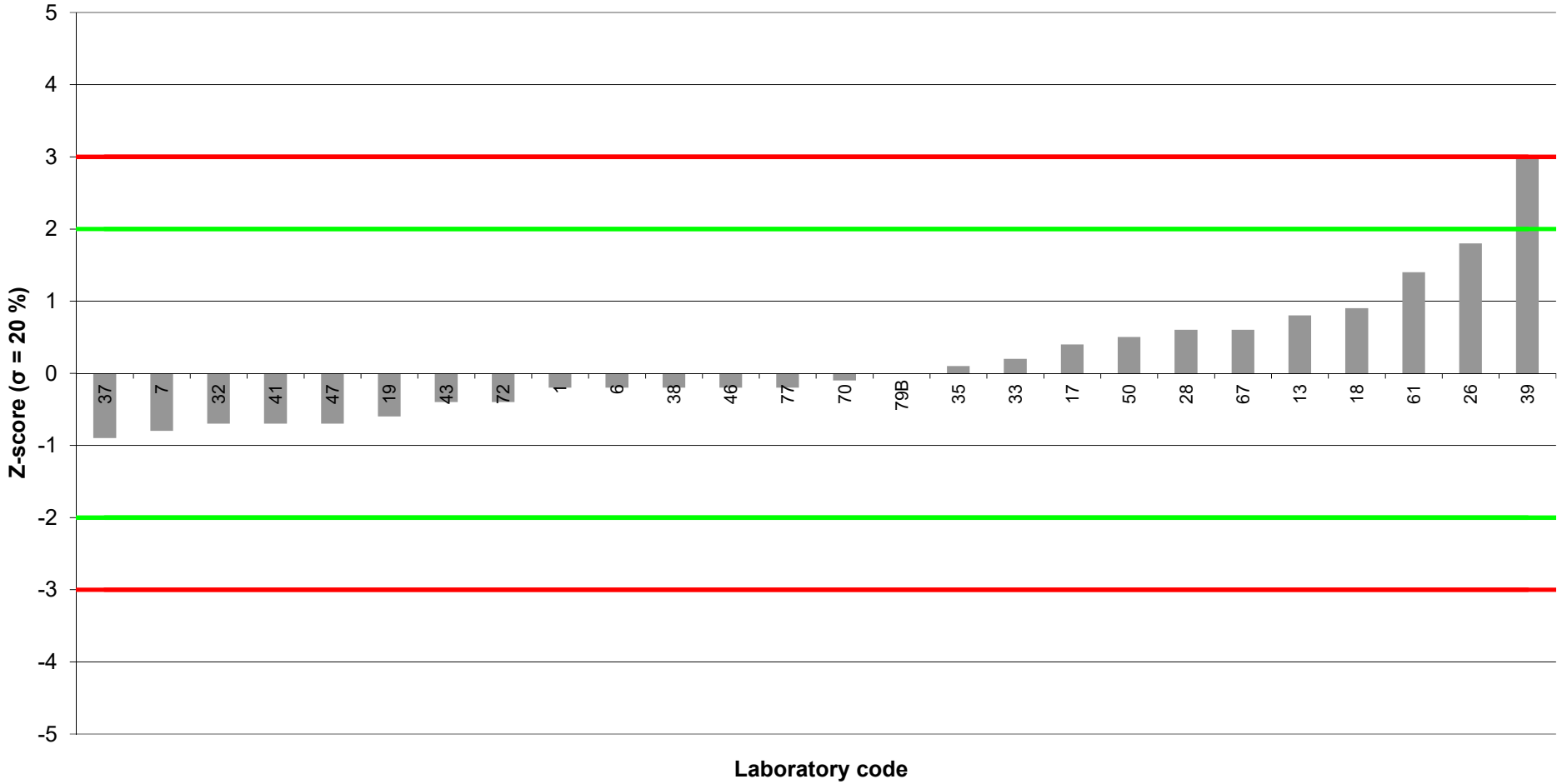
Assigned value: 0.675 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

Sum of PBDE without BDE-209 ub

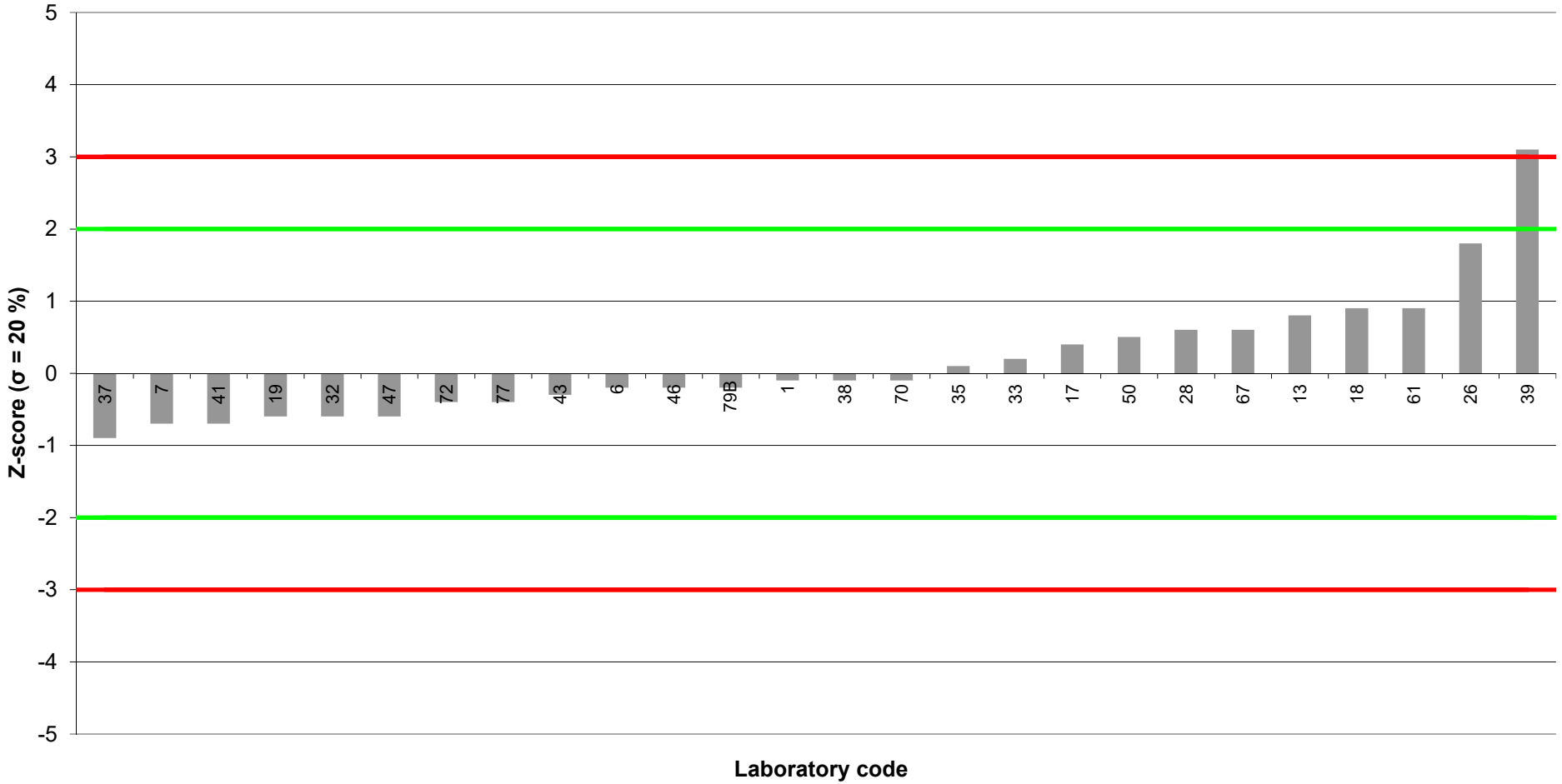
Assigned value: 0.358 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

Sum of PBDE without BDE-209 lb

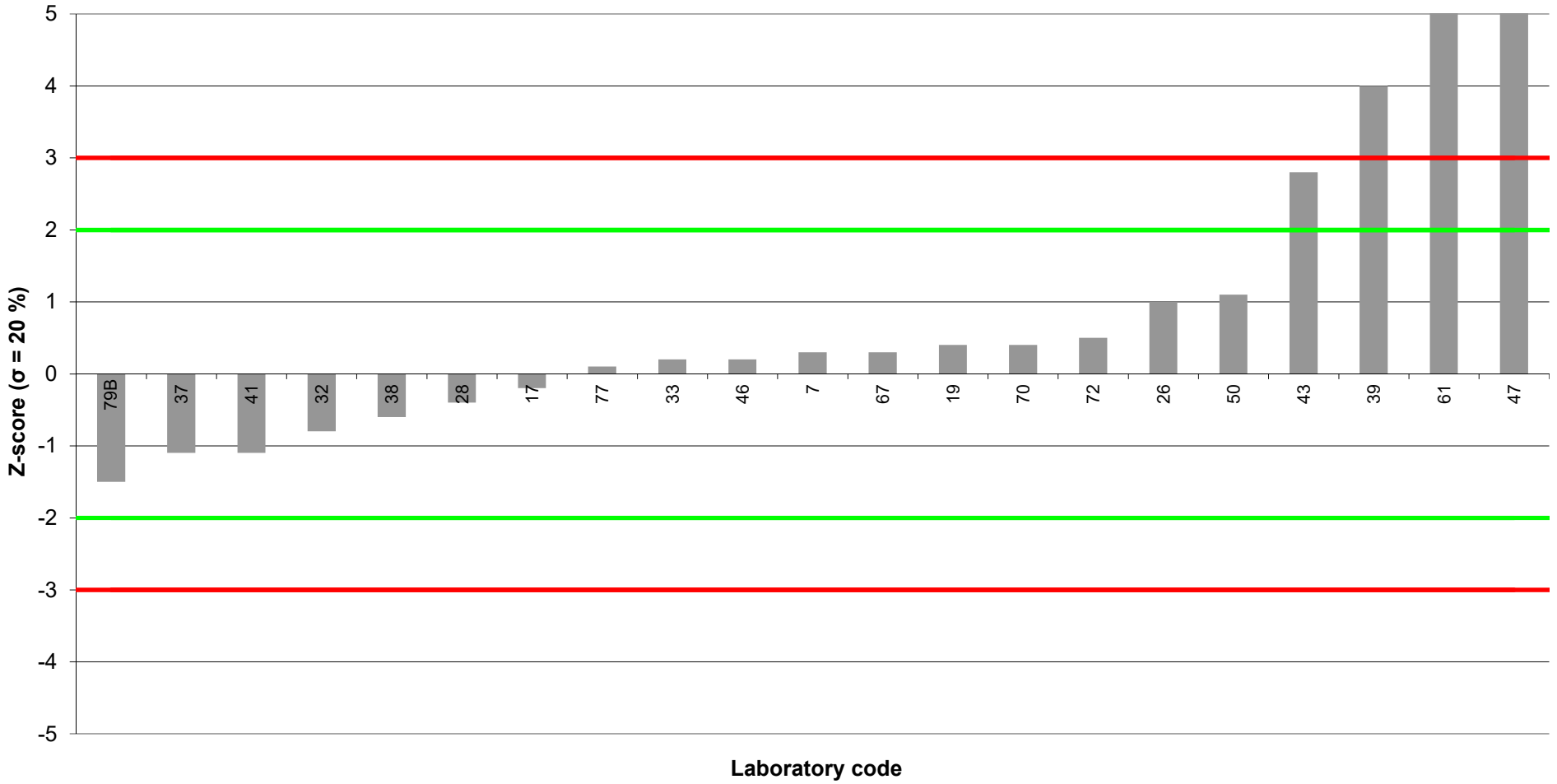
Assigned value: 0.356 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

Sum of PBDE including BDE-209 ub

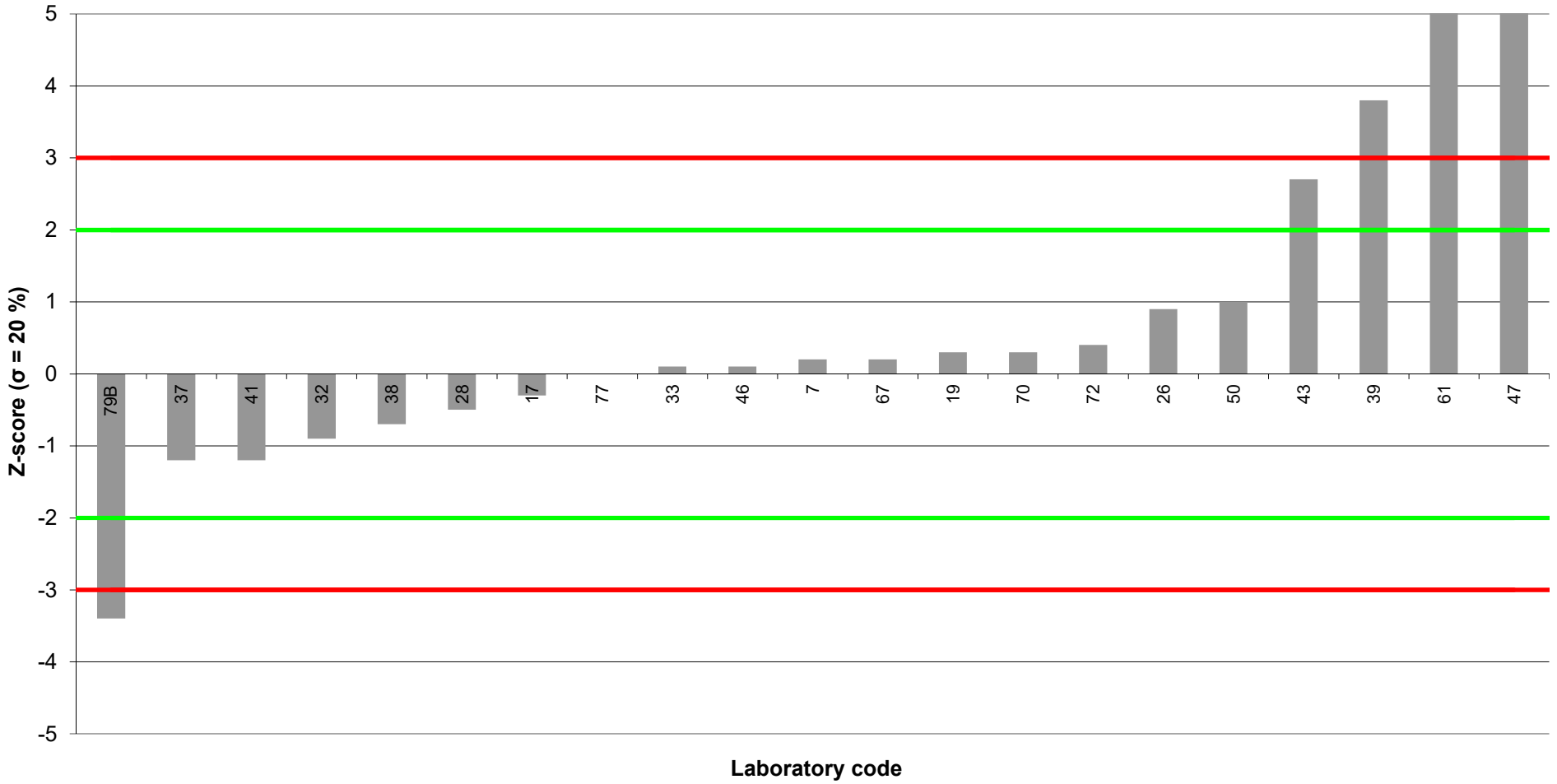
Assigned value: 1.03 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

Sum of PBDE including BDE-209 lb

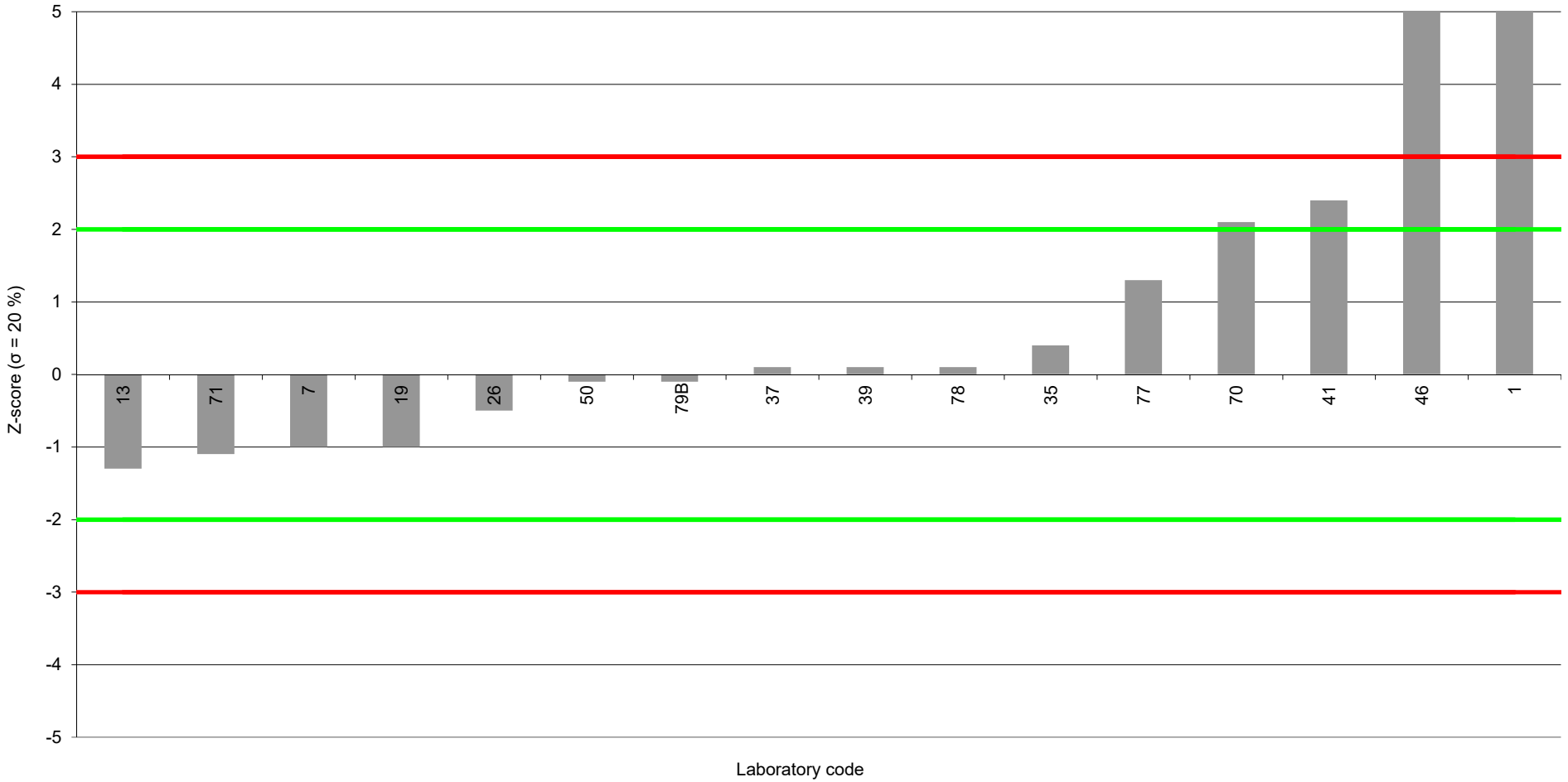
Assigned value: 1.05 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

(+/–)-γ- HBCDD

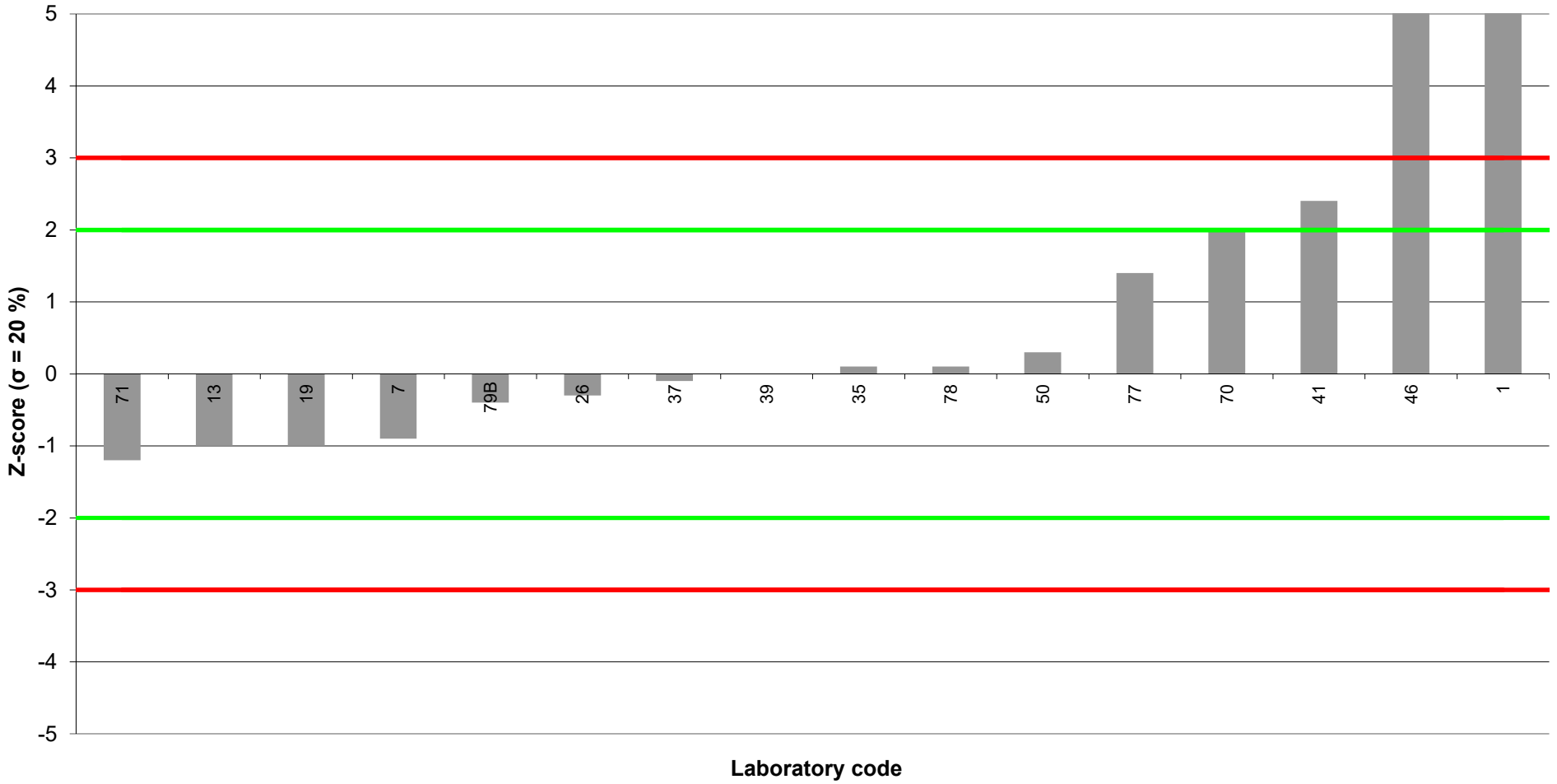
Assigned value: 0.917 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

Sum of α-, β-, γ-HBCDD ub

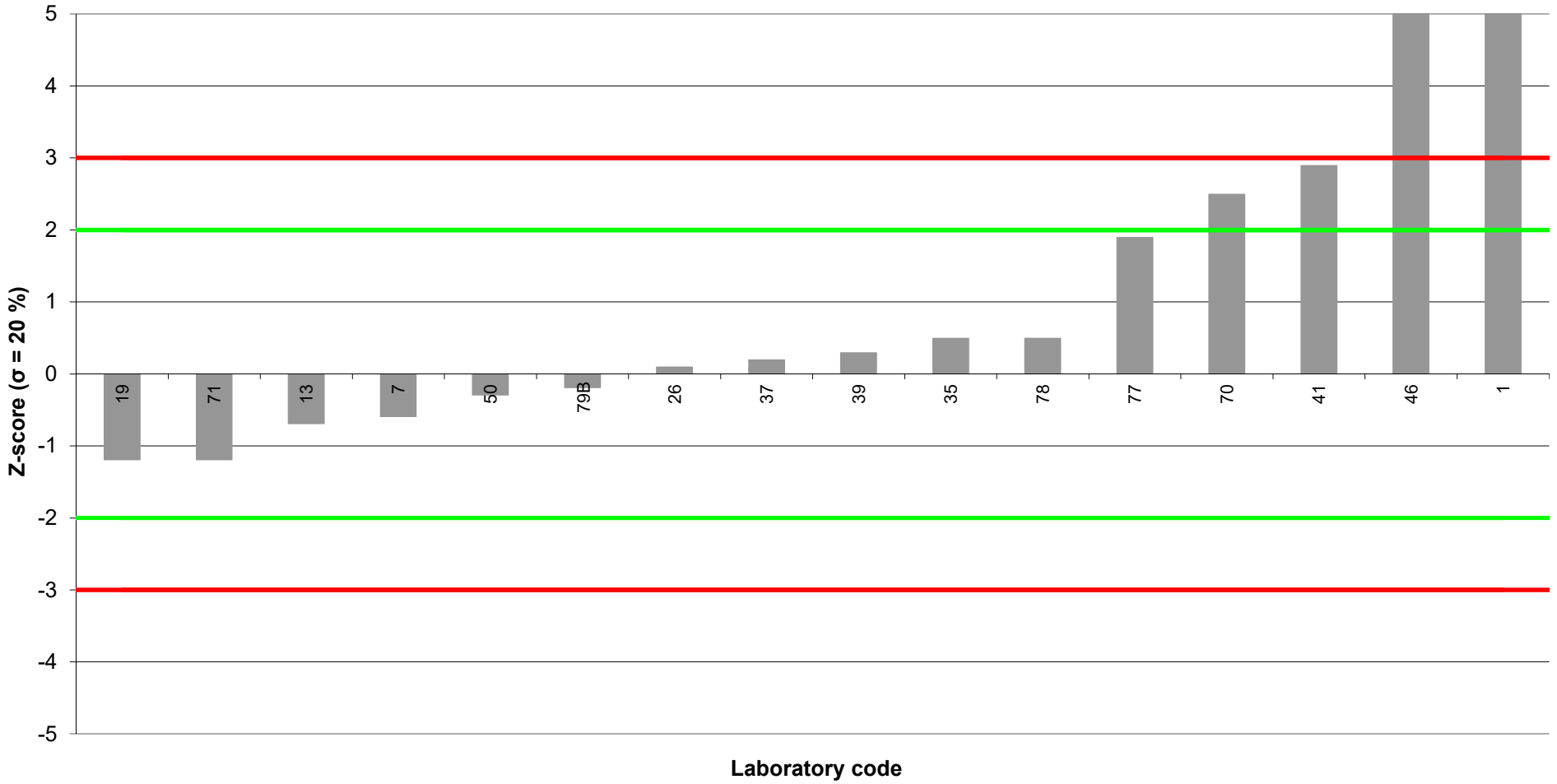
Assigned value: 1.03 µg/kg product (12 % moisture content)



Dried Citrus Pulp (2105-DCP)

Sum of α-, β-, γ-HBCDD lb

Assigned value: 0.959 µg/kg product (12 % moisture content)



EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
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Annex 5: Test for sufficient homogeneity and stability for PBDEs

Test sample - Dried Citrus Pulp (2105-DCP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
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Dried Citrus Pulp (2105-DCP)
PBDE - Homogeneity test - Data

Analyte	Result µg/kg product (12% moisture content)	**Mean** (n = 10, duplicate analysis)	**Median** (n = 10, duplicate analysis)	**Relative standard deviation** [%]
Sum of PBDE without BDE-209 ub		0.366	0.368	3%
Sum of PBDE including BDE-209 ub		1.12	1.13	13%
BDE-28		0.00975	0.00989	5%
BDE-47		0.115	0.116	3%
BDE-49		0.0118	0.0117	6%
BDE-99		0.160	0.160	4%
BDE-100		0.0331	0.0331	5%
BDE-153		0.0151	0.0151	7%
BDE-154		0.0144	0.0147	7%
BDE-183		0.00683	0.00687	6%
BDE-209		0.753	0.758	20%

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DC
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Selected PBDE congeners - Homogeneity test - Data

Sample	Replicate	Result µg/kg product (12% moisture content)	**BDE-153**
5	1		0.0150
	2		0.0153
8	1		0.0153
	2		0.0170
66	1		0.0146
	2		0.0161
79	1		0.0138
	2		0.0162
103	1		0.0143
	2		0.0148
116	1		0.0134
	2		0.0157
120	1		0.0156
	2		0.0136
146	1		0.0142
	2		0.0136
202	1		0.0156
	2		0.0147
210	1		0.0173
	2		0.0150
Cochran's C-test			
C			0.211
$C_{critical}$ (α = 0.05, m = 2, n = 10)			0.602
$C_{critical}$ (α = 0.01, m = 2, n = 10)			0.718
$C < C_{critical}$			yes
Outliers			no evidence for analytical outliers
Homogeneity test			
General average $\bar{x}$			0.0151
Standard deviation of sample averages s_x			0.00070
Wthin-sample standard deviation s_w			0.00116
Between-sample standard deviation s_s			0.00000
Standard deviation for proficiency assessment σ_{PT}			0.0030
s_s / σ_{PT}			0
Test for homogeneity ($s_s \leq 0.3\ \sigma_{PT}$)			passed

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Selected congeners - Stability test - Data

Sample	Replicate	Result µg/kg product (12% moisture content)	**BDE-153**
5	1		0.0141
	2		0.0144
120	1		0.0153
	2		0.0151
210	1		0.0156
	2		0.0151
Stability test			
General average (stability test) $\bar{y}$			0.015
General average (homogeneity test) $\bar{x}$			0.015
Standard deviation for proficiency assessment σPT			0.0030
$\lvert \bar{y} - \bar{x} \rvert$			0.00012
Test for stability ($\lvert \bar{y} - \bar{x} \rvert \leq 0.3$ σPT)			passed

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp 2021 [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
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Annex 6: Participants' methods for PBDEs and HBCDDs

Test sample - Dried Citrus Pulp (2105-DCP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)

Physico-chemical Methods PBDEs - Internal standards

LC	Sample	**Weighed sample** [g]	**Use of isotope-labelled internal standards for …** PBDE congeners (yes/no)	**Other internal standards** for PBDEs	
1	2105-DCP	20	yes		
6	2105-DCP	4.5	Yes		
7	2105-DCP	10.0	yes		
13	2105-DCP	15.0	yes		
17	2105-DCP	10	yes		
18	2105-DCP	9.0	yes (except for BDE-49)		
19	2105-DCP	20.0	Yes		
26	2105-DCP	2.0	YES		
28	2105-DCP	6.1	YES		
32	2105-DCP	11.4	yes		
33	2105-DCP	30.7	yes		
35	2105-DCP	10.00	yes		
37	2105-DCP	5	yes		
38	2105-DCP	20.0	yes		
39	2105-DCP	20 g	yes		
41	2105-DCP	5.544	yes		
43	2105-DCP	15.1	YES		
46	2105-DCP	30	YES		
47	2105-DCP	7.07	yes		
50	2105-DCP	10	yes		
61	2105-DCP	2.5	no		
67	2105-DCP	2.5	yes		
70	2105-DCP	25.1	yes		
71	2105-DCP				
72	2105-DCP	10	yes		
77	2105-DCP	50.217	yes		
78	2105-DCP				
79B	2105-DCP	5	yes		

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Physico-chemical Methods PBDEs - Pre-treatment and extraction

		Pre-treatment and extraction					
LC	Sample	Sample preparation/pre-treatment	Extraction technique	Extraction solvent	Extraction time [h]	Extraction temperature [ºC]	Extraction pressure [MPa]
1	2105-DCP	thorough homogenization	Soxhlet (ultrasonic bath, agitate)	dichloromethane:acetone 3:1	21	thorough homogenization	0.1
6	2105-DCP	Mixing with sodium sulfate	Soxhlet	Toluene	18	Mixing with sodium sulfate	
7	2105-DCP	Mixed with sodium sulphate	ASE	Hexane/Acetone (70:30)	1	Mixed with sodium sulphate	10.3
13	2105-DCP	drying	soxhlet	DCM:hexane 1:1	8	drying	normal
17	2105-DCP		Soxhlet	toluen/acetone 7/3	5		
18	2105-DCP	sample mixed with sodium sulphate before extraction	Soxhlet	DCM:Hexane (50:50)	24 h	sample mixed with sodium sulphate before extraction	
19	2105-DCP		Soxhlet aparattus	Hexane/DCM (1/1)	12 h		*
26	2105-DCP	drying	PLE	Toluene/Acetone		drying	
28	2105-DCP		SOXHLET	HEXANE/DCM (1/1)	24H		
32	2105-DCP	Drying for 24 hours in 80°C	Accelerated Solvent Extraction (ASE)	acetone:toluene (3:7)	3 x 5 min	Drying for 24 hours in 80°C	10
33	2105-DCP		Soxhlet	Toluene / Ethanol (30/70)	12		
35	2105-DCP		ASE	Toluol (1 cycle), Toluol/Ethanol, 9+1 (2 cycles)	Heat: 0.083 h, Static: 0.25 h		10
37	2105-DCP	no	no	no	no	no	no
38	2105-DCP	no (only drying of the sample used for moisture content determination)	Soxhlet	1.method: n-hexane:acetone (1:1), 2.method: toluene	16	no (only drying of the sample used for moisture content determination)	ambient
39	2105-DCP		Twisselmann	Ethanol/Toluol (70/30)	6		
41	2105-DCP	none	Quechers	EtAc	10 minutes	none	-
43	2105-DCP	None	ASE	Toluene	0.5	None	11.7
46	2105-DCP	drying	ASE	HEXANE/ACETONE 50/50	0.33	drying	10.13
47	2105-DCP	no	ASE	Toluen/Ethanol; 90/10	1	no	13,79
50	2105-DCP	no	ASE	15% ethanol/85% toluene v/v	0.4	no	10.3
61	2105-DCP	no	ASE	toluene	0,75	no	10,342
67	2105-DCP		Soxhlet	toluene	12		
70	2105-DCP	ULTRA TURRAXING WITH HEXANE	SILICA GEL /SOLVENT EXTRACT- MANUAL	40:60 DCM:HEXANE	2-4HRS	ULTRA TURRAXING WITH HEXANE	GRAVITY
71	2105-DCP						
72	2105-DCP	-	ASE	(1) Toluene - (2) Toluene:Ethanol 90:10	0.25	-	10.3
77	2105-DCP	Homogenisation	Soxhlet	Toluene/ethanol 50/50	24	Homogenisation	atmospheric
78	2105-DCP						
79B	2105-DCP	drying, homogenization	cold extraction	hexane		drying, homogenization	

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Physico-chemical Methods PBDEs - Clean-up

LC	Sample		Clean-up						Final volume [µl]: PBDE
			Gelchromatography	Silica/sulfuric acid column	Florisil column	Alumina column	Carbon column	Others	
1	2105-DCP		no	yes	no	yes	yes	basic silica, silver nitrate silica	20
6	2105-DCP		No	Yes	No	Yes	No		50
7	2105-DCP		no	yes	no	yes	no	acid hydrolysis with sulphuric acid	80
13	2105-DCP		yes	yes	no	no	yes		20
17	2105-DCP		no	yes	no	yes	yes		100
18	2105-DCP		no	yes	no			basic set of "power-prep system" columns	40
19	2105-DCP		Yes	Yes	Yes	No	Yes	No	50
26	2105-DCP		YES	YES	YES	NO	YES		50
28	2105-DCP		NO	YES	NO	YES	NO	NO	20
32	2105-DCP		no	yes	yes	yes	no	no	50
33	2105-DCP		no	yes	yes	yes	no	acidic treatment	50
35	2105-DCP		no	yes	no	yes	yes	Silver nitrate	50
37	2105-DCP		yes	yes	no	no	no	no	250
38	2105-DCP		no	yes	yes	yes	yes	PowerPrep FMS columns (basic-neutral silica, alumina, carbon)	20
39	2105-DCP		yes	yes	yes	no	no		100
41	2105-DCP		no	yes	no	no	no		250 µl
43	2105-DCP		No	Yes	No	Yes	Yes	None	30
46	2105-DCP		NO	YES	YES	YES	YES		100
47	2105-DCP		no	yes	no	yes	yes		200
50	2105-DCP		no	yes	no	yes	yes		500
61	2105-DCP		no	yes	no	yes	no	no	50
67	2105-DCP		no	yes	no	yes	yes	Silica/AgNO3	100
70	2105-DCP		YES	YES	NO	YES	YES		25
71	2105-DCP								
72	2105-DCP		yes	yes	no	yes	yes	-	100
77	2105-DCP		no	yes	no	yes	no		25
78	2105-DCP								
79B	2105-DCP		no	yes	no	yes	no		100

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Physico-chemical Methods PBDEs - Chromatographic separation and detection method

		Chromatographic separation and detection method					
LC	Sample	GC injection	Injected volume [µl]	Chromatographic separation: Stationary phase	Detector	Additional information1	Additional information2
1	2105-DCP	pulsed splitless	1	DB-5MS (60m x 0,25mm x 0,10 µm)	HRMS (R>10000)		
6	2105-DCP	Splitless	1.5	DB-5MS	HRMS, DFS		
7	2105-DCP	splitless	1	Rtx-1614 30m x 0.25mm x 0.1µm	HRMS		
13	2105-DCP	cold splitless	2	DB 5MS	MSMS		
17	2105-DCP	splittless	2	DB 5 MS	HRMS		
18	2105-DCP	Splitless	1	DB-5MS (30 m, 0.25 mm id, 0,25 mm film)	HRMS (Mat-95 XP)		
19	2105-DCP	PTV	1	Rtx-1614 (25 m x 0.25 mm x 0.1 um)	Autospec Premier HRMS (SIR)		
26	2105-DCP	Splitless	2	HT8PCB	GC-HRMS		
28	2105-DCP	SPLITLESS	1	DB5	HRMS		
32	2105-DCP	PTV Splitless	1	60m DB-5ms; 15 m RTX 1614	HRMS		
33	2105-DCP	splitless	2.0	DB-5HT	HRMS (Autospec Ultima Waters)		
35	2105-DCP	splitless	2	DB-5MS (15 m x 0,2 5mm x 0,1 µm) + 2 m retention cap (uncoated)	MS/MS		
37	2105-DCP	PTV	10	RTX1614 15 m x 0.25 mm; 0.1 um	MS/MS		
38	2105-DCP	splitless	2	DB-5ht (15m)	HRMS	Extract after Soxhlet and clean-up by PowerPrep contains small amount of waxes which has deformed the shape of peaks for PBDE congeners. Therefore, after analysis	it was cleaned-up on florisil column. The shape of peaks was after clean-up still not ideal, but the manual integration of peaks was finaly possible.
39	2105-DCP	PTV	5	Rtx-1614 - 30m	HRMS		
41	2105-DCP	PTV	10	Rtx-ClPesticides 30 m x 0.25 mm x 0.25 µm	GC-HRMS		
43	2105-DCP	Splitless	1	5%-Phenyl-Arylene-95% DimethylPolysiloxane (ZB5-MS) column 30m×0.1mm×0.1µm	Waters Micromass AutoSpec Premier HRMS (>10,000 Mass resolution)		
46	2105-DCP	PTV	1	100% dimethylpolysiloxane	HRMS		
47	2105-DCP	Splitless	2	5 % phenyl 95% dimethylpolysiloxane	APGC-MS/MS		
50	2105-DCP	splitless	5	DB5-MS	MSMS		
61	2105-DCP	MMI	3	DB5	GC-MS/MS-NCI		
67	2105-DCP	PTV	1	ZB - Semi Volatiles, 20m, 0.18 mm, 0.18µm	MS/MS		
70	2105-DCP	PTV	10	Rtx-1614	GC-HRMS	lysis performed by an ISO 17025 accr	
71	2105-DCP						
72	2105-DCP	PTV	5	RTX-1614	HRMS	Method not validated for feed	
77	2105-DCP	splitless	1	Rtx-1614	HRMS		
78	2105-DCP						
79B	2105-DCP	pulsed splitless	2	Diphenyl-/dimethylpolysiloxan (5%/95%)	MS/MS		

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)

Physico-chemical Methods HBCDDs - Internal standards

LC	Sample	**Weighed sample** GC injection	**Use of isotope-labelled internal standards for …** HBCDD diastereomers (yes/no)	**Other internal standards** for HBCDDs	
1	2105-DCP	5	yes		
6	2105-DCP				
7	2105-DCP	10	yes		
13	2105-DCP	15	yes		
17	2105-DCP				
18	2105-DCP				
19	2105-DCP	1-1.5	Yes		
26	2105-DCP	2.0	YES		
28	2105-DCP				
32	2105-DCP	10	yes		
33	2105-DCP				
35	2105-DCP	3.00	yes		
37	2105-DCP	5	yes		
38	2105-DCP	20.0	yes		
39	2105-DCP	10 g	yes		
41	2105-DCP	9.295	yes		
43	2105-DCP				
46	2105-DCP	17	YES		
47	2105-DCP				
50	2105-DCP	10	yes		
61	2105-DCP				
67	2105-DCP				
70	2105-DCP	4.25	yes		
71	2105-DCP	5	yes		
72	2105-DCP				
77	2105-DCP	50.217	yes		
78	2105-DCP	10	yes		
79B	2105-DCP	10	yes		

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EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Physico-chemical Methods HBCDDs - Pre-treatment and extraction

LC	Sample	Pre-treatment and extraction Sample preparation/pre-treatment	Extraction technique	Extraction solvent	Extraction time [h]	Extraction temperature [ºC]	Extraction pressure [MPa]
1	2105-DCP	drying by Na2SO4	Soxhlet	petroleum ether	4	160	0.1
6	2105-DCP						
7	2105-DCP	Mixed with sodium sulfate	ASE	Hexane/Acetone (70:30)	1	125	10.3
13	2105-DCP	drying	soxhlet	DCM:hexane	8	room	normal
17	2105-DCP						
18	2105-DCP						
19	2105-DCP	-	Ultrasound assisted extraction + mechanical mixing	DCM:n-Hex (1:1, v/v)	1h	Room temperature	
26	2105-DCP	drying	PLE	Toluene/Acetone			
28	2105-DCP						
32	2105-DCP	Oven drying 24 hours in 80°C	ASE 350	acetone:toluene (3:7)	3 x 5 min	80	10
33	2105-DCP						
35	2105-DCP		cold extraction	Hexan/DCM 1/1	roughly 2-3 hours	ambient	ambient
37	2105-DCP	no	no	no	no	no	no
38	2105-DCP	no	Soxhlet	1.method: n-hexane:acetone (1:1), 2.method: toluene	16	T by Soxhlet extraction dependent on boiling T of used organic solvents and mixtures	ambient
39	2105-DCP		Twisselmann	Ethanol/Toluol (70/30)	6	boiling point	
41	2105-DCP	Sodium Sulfate	ASE	Hexane/Acetone 1:1	30 minutes	100	1500 psi
43	2105-DCP						
46	2105-DCP	drying	ASE	HEXANE/ACETONE 50/50	0.33	100	10.13
47	2105-DCP						
50	2105-DCP	no	ASE	15% ethanol/85% toluene v/v	0.4	120	10.3
61	2105-DCP						
67	2105-DCP						
70	2105-DCP	none	acidified silica homogenisation	40/60 DCM/hexane	0.2	ambient	n/a
71	2105-DCP	no	solid / liquid	Hexane / dichloromethane (1/1)	0.33	ambiente	ambiente
72	2105-DCP						
77	2105-DCP	Homogenisation	Soxhlet	Toluene/ethanol 50/50	24		atmospheric
78	2105-DCP		Soxhlet	Acetone/hexane 1:1	6	boiling	atmospheric
79B	2105-DCP	no	Quecher	Acetonitrile/water (1:1)	0,25	ambient	ambient

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Physico-chemical Methods HBCDDs - Clean-up

LC	Sample		Clean-up Gelchromatography	Silica/sulfuric acid column	Florisil column	Alumina column	Carbon column	Others	Final volume [µl]: HBCDD
1	2105-DCP		yes	no	no	no	no	silica/1% H2O	500
6	2105-DCP								
7	2105-DCP		no	yes	no	no	no		100
13	2105-DCP		yes	yes	no	no	yes		200
17	2105-DCP								
18	2105-DCP								
19	2105-DCP		No	Yes	Yes	No	No	Direct H2SO4 treatment prior column clean-up	50
26	2105-DCP		YES	YES	NO	NO	NO	liquid liquid extraction	50
28	2105-DCP								
32	2105-DCP		no	yes	no	no	no	NaOH	20
33	2105-DCP								
35	2105-DCP		no	yes	no	no	no	no	400
37	2105-DCP		yes	yes	no	no	no	no	250
38	2105-DCP		no	yes	no	no	no	elution of silica/sulfuric acid column with 10% and 50% n-hexane:DCM after elution of PCDDF, PCB, PBDE	20
39	2105-DCP		no	yes	yes	no	no	no	100
41	2105-DCP		no	yes	no	no	no		500 µl
43	2105-DCP								
46	2105-DCP		NO	YES	NO	NO	NO		100
47	2105-DCP								
50	2105-DCP		no	yes	no	no	no		500
61	2105-DCP								
67	2105-DCP								
70	2105-DCP		no	no	no	no	no	clean-up combined in extraction	150
71	2105-DCP		no	yes	no	no	no	no	200
72	2105-DCP								
77	2105-DCP		no	yes	no	no	no		25
78	2105-DCP							sulphuric acid , concentrated	
79B	2105-DCP		no	yes	no	no	no	no	1000

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs and HBCDDs in Dried Citrus Pulp [EURL-PT-DPB-2105-DCP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Dried Citrus Pulp (2105-DCP)
Physico-chemical Methods HBCDDs - Chromatographic separation and detection method

LC	Sample	Chromatographic separation and detection method: Injection	Injected volume [µl]	Chromatographic separation: Stationary phase	Detector	Additional information1
1	2105-DCP	normal	5	RP-C18	MS/MS	
6	2105-DCP					
7	2105-DCP		5	BEH C18 (100 mm x 2.1 µm; 1.7 µm)	HRMS	
13	2105-DCP		70	Luna PFP	MSMS	
17	2105-DCP					
18	2105-DCP					
19	2105-DCP	HPLC	4	C18	HRMS (Orbitrap)	
26	2105-DCP		15	Hypersil Gold	MS/MS	
28	2105-DCP					
32	2105-DCP	PTV solvent split	5	DB-5MS (30m x 0.25 mm x 0.1 µm)	HRMS (DFS), R=10 000	
33	2105-DCP					
35	2105-DCP		15	C18	MS/MS	
37	2105-DCP	prtial loop	20	kinetex XB C18 2.7 um, 100 x 2.1 mm	MS/MS	
38	2105-DCP	splitless	3	DB-5ht (15m)	HRMS	After analysis of 3 extracts they were combined, evaporated to 20ul and analysed as one extract for better response of HBCDD fragments.
39	2105-DCP	HPLC	2	C18	MS/MS	Column: Zorbax Eclipse Plus C18, 2.1x50mm, 1,8 µm
41	2105-DCP		10	C18 (Waters symmetry), 150 mm x 2.1 mm x 3.5 µm	LCMSMS	
43	2105-DCP					
46	2105-DCP	HPLC	10	C18	MS/MS	
47	2105-DCP					
50	2105-DCP	Needle	5	C18(50x2,1mm,3.5µm)	MS/MS	
61	2105-DCP					
67	2105-DCP					
70	2105-DCP	Liquid	5	Agilent Zorbax RRHD Eclipse Plus C18 1.8 µm (150 x 2.1 mm)	LC-MS/MS	Moisture content analysis performed by an ISO 17025 accredited sub-contractor
71	2105-DCP	LC	5	RRHD Eclipse Plus C18	MS/MS	
72	2105-DCP					
77	2105-DCP	LC		Acquity BEH C18 150 mm	LC/MS/MS	
78	2105-DCP	LC	5	Acquity UPLC BEHC18	MS/MS	
79B	2105-DCP	standard	10	C18	MS/MS	