



European Union Reference Laboratory
for Halogenated POPs in Feed and Food



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**EURL Proficiency Test on the Determination of
PCDD/Fs, PCBs, BFRs, PFASs and CPs
in Fish fillet
2020**

EURL-PT-POP_2001-FI

FOOD

Final report

Other brominated contaminants and CPs

05 November 2020



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Summary

Test sample (feed)	Fish fillet (fresh water fish) - 2001-FI
Analytes of interest	<u>Optional for NRLs:</u> <ul style="list-style-type: none">- CPs (SCCPs, MCCPs, total CP)- Other brominated contaminants
Methods	Any kind of method
Participants	NRLs, OFLs, other official laboratories, commercial laboratories performing the analysis of samples taken by food business operators
Statistical evaluation	ISO 13528:2015, IUPAC Protocol, combined z-scores
Report of preliminary results	24 September 2020
Final report	05 November 2020



1. Structure of the PT, test material and analytes

This proficiency test (PT) on the determination of PCDD/Fs, PCBs, BFRs, PFASs and CPs in fish fillet (fresh water fish) was organized by the EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food to be performed between February and September 2020. The objective was to assess analytical performance of laboratories and the interlaboratory comparability of results from analyses of PCDD/Fs, PCBs, BFRs, PFASs and CPs in one sample of fish fillet.

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 2020. 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 will allow the extension of the data basis for calculation of assigned values and evaluation of results.

This PT was also open for other official laboratories and commercial laboratories performing the analysis of samples taken by food business operators in order to check the comparability of results not only within the EURL/NRL/OFL network, but also with official and private laboratories performing official control or self-control of food business operators.

The evaluated results will be discussed by representatives of EU Commission, NRLs and the EURL at the COM/EURL/NRL workshop in November 2020.

1.1 Samples and coding

The fish fillet test sample was prepared of regular market food. The test sample was not fortified with analytes of interest.

Fish fillet (fresh water fish)

Sample no. 2001-FI-xxx

Each participant received about 125 g of the test sample.



1.2 Analytes of interest

Participants were requested to determine at least one of the following parameters:

Chlorinated paraffins (CPs)

- Short chained chlorinated paraffins (SCCPs)
- Medium chained chlorinated paraffins (MCCPs)
- Sum of CPs / total CPs

Other brominated contaminants

- Tetrabromobisphenol A (TBBPA)
- Decabromodiphenyl ethane (DBDPE)
- 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)
- Bromophenols (2,4,6-tribromophenol (2,4,6-TBP), 2,4-dibromophenol (2,4-DBP), 4- bromophenol (4-BP), 2,6-dibromophenol (2,6-DBP))
- Pentabromoethylbenzene (PBEB)
- Hexabromobenzene (HBB)
- Pentabromotoluene (PBT)
- Pentabromobenzene (PBBz)

1.3 Methods

One or more of the following detection methods could be applied:

- Any kind of method for other brominated contaminants and CPs

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 identity of OFLs will be kept confidential, unless a Member State initiated a co-operation between the NRL, OFLs and the EURL.



1.5 Results of other brominated contaminants and CPs

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,
- report at least results for SCCP and MCCP sum parameters (except for laboratories using only screening methods; in that case report total CP)
- report homologue patterns for SCCPs and MCCPs, if possible,
- 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 ng/g wet weight for both analyte groups.

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

Eleven laboratories reported results for at least one of the requested parameters for CPs and two laboratories for other brominated contaminants.

3. Test for sufficient homogeneity

The test for sufficient homogeneity was performed according to ISO 13528:2015 [2] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [1].

Therefore, twelve portions of the test sample 2001-FI were analyzed for CPs, with five of them being duplicates. The test for sufficient homogeneity was performed for chain length concentrations. Three samples were excluded due to process contamination caused by the extraction method. Based on the remaining samples, the test materials showed sufficient homogeneity for this proficiency test.



4. Determination of the assigned value

Statistical evaluation of the PT results is performed by the EURL for Halogenated POPs in Feed and Food according to ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization, and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories (IUPAC Technical Report 2006, *Pure Appl. Chem* 78 (1), 145-196).

The determination of the assigned value is performed according to "The international harmonized protocol for the proficiency testing of analytical chemistry laboratories" (IUPAC Technical Report, *Pure Appl. Chem*, Vol. 78, No. 1, pp-145-196, 2006) by estimating of the assigned value as the consensus of participants' results. The Huber robust mean is taken as assigned value after excluding extreme outliers (outside the range of $\pm 50\%$ of the median of all reported results) and examination of the distribution of the remaining results using histogram and kernel density estimation, if necessary.

The assigned value is calculated for sum of SCCPs, sum of MCCPs and sum of CPs (excluding limits of quantification (LOQs)), if possible. Additionally the median of all values is calculated. Due to only two results being eligible for the Huber robust mean for sum of SCCPs, z-scores and further evaluations for this parameter were calculated excluding the highest and lowest result only and are therefore seen as provisional.

Assigned values could not be calculated for other brominated contaminants, as only two laboratories reported results, many of them below LOQ.

5. Scoring of results

5.1 Participants' results

5.1.1 Z-scores

For evaluation of results the z-scores are calculated according to the following formula:

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

x_a : assigned value

x : participants result

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

For CP sum parameters, the standard deviation for proficiency assessment σ_p is defined as 25 %.

Interpretation of z-scores:

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



5.1.2 Combined z-score AZ^2

For evaluation of the overall performance of laboratories concerning the determination of chlorinated paraffins, the average of the squared z-score (AZ^2) is being used [4]. The AZ^2 is calculated as follows:

$$AZ^2 = \frac{\sum_{i=1}^n z_i^2}{n}$$

Where n is the number of z-scores to be considered in the calculation.

For the purpose of calculating the AZ^2 , z-scores higher than |5| will be classified as |5|. Z-scores derived based on reported LOQs will not be included. Based on the AZ^2 achieved, the overall performance of the laboratories will be considered as follows:

$AZ^2 \leq 2$	satisfactory overall performance
$2 < AZ^2 < 3$	questionable overall performance (warning signal)
$AZ^2 \geq 3$	unsatisfactory overall performance (action signal)

Combined z-scores are considered to be of lesser importance than the individual z-scores. To account for multiple sets of results reported by some participants, combined z-scores will be assigned for each set of results per lab and once for all results from each lab.

6. 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).

7. Results of participants

An overview of the other brominated contaminants and CP results for the PT test sample fish fillet (2001-FI) are given in the following annexes. Laboratories are coded according to the laboratory codes sent after registration.










8. 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] ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization
- [3] M. van den Berg et al., The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Toxicological Sciences 93(2), 223-241 (2006)
- [4] EU Reference Laboratories for Residues of Pesticides, General Protocol for EU Proficiency Tests on Pesticide Residues in Food and Feed, 9th Edition, Released on 15 November 2019

9. Annex

(Please double click on the pdf-icons to open the annexes.)

Fish fillet (2001-FI)		
1	Assigned values – CPs	
2	Participants' results – Tables – CPs, other brominated contaminants	
3	Participants' z-scores – Tables – CPs	
4	Participants' z-scores – Charts – CPs	
5	Participants' results – CP homologue patterns	
6	Test for sufficient homogeneity – CPs	
7	Participants' methods – Tables – CPs	

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