

PROFICIENCY TEST ON DETERMINATION OF BROMINATED FLAME RETARDANTS IN COD LIVER AND FISH LIVER OIL

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Introduction

According to Commission Recommendation of 3 March 2014 on the monitoring of traces of brominated flame retardants in food (2014/118/EU) EU Member States should perform monitoring on the presence of brominated flame retardants (BFRs) in food during the years 2014 and 2015¹. Therefore, Member States should carry out analyses of the following different classes of brominated flame retardants in order to detect the presence of the individual substances in various food commodities:

- polybrominated diphenylethers (PBDEs),
- hexabromocyclododecanes (HBCDDs),
- tetrabromobisphenol A and its derivatives,
- brominated phenols and derivatives,
- emerging and novel brominated flame retardants.

Since 2006, the EU-RL for Dioxins and PCBs in Feed and Food has performed 17 proficiency tests (PTs) on determination of PCDD/Fs and PCBs in feed or food samples for its network with National Reference Laboratories (NRLs) and Official Laboratories (OFLs). In the 2nd PT in 214, determination of PCDD/Fs and PCBs in cod liver and fish liver oil was combined with optional determination of brominated flame retardants. The objective was to assess analytical performance of laboratories and interlaboratory comparability of results from analyses of brominated flame retardants.

Materials and methods: Proficiency test

Test samples: The cod liver and the fish liver oil sample were prepared from regular market food and were not fortified with analytes of interest. The same test samples as for the determination of PCDD/Fs and PCBs were used. The test for sufficient homogeneity was performed for PCDD/Fs and PCBs, only.

Participants: The PT was open for NRLs, OFLs and other laboratories. Whereas the participation in PTs of the EURL with determination of PCDD/Fs and PCBs is mandatory for NRLs with competence in this area, the determination of BFRs was purely voluntary.

Analytes of interest: Participants could report results for the following parameters:

- Class of polybrominated diphenyl ethers (PBDEs): BDE-28, BDE 47, BDE 49, BDE 99, BDE 100, BDE 138, BDE 153, BDE 154, BDE 183, BDE 209
- Class of hexabromocyclododecanes (HBCDDs): (+/-)- α -HBCDD, (+/-)- β -HBCDD, (+/-)- γ -HBCDD
- Class of tetrabromobisphenol A and its derivatives: Tetrabromobisphenol A (TBBPA), TBBPA bismethyl ether (TBBPA-bME), TBBPA bis(2-hydroxyethyl) ether (TBBPA-boHEE), TBBPA bisallyl ether (TBBPA-bAE), Tetrabromobisphenol A bis(glycidyl ether) (TBBPA-bGE), TBBPA bis(2,3-dibromopropyl)ether (TBBPA-bDiBPrE)
- Class of brominated phenols and their derivatives: 2,4,6-tribromophenol (2,4,6-TBP), 2,4-dibromophenol (2,4-DBP), 4-bromophenol (4-BP), 2,6-dibromophenol (2,6-DBP), Tetrabrominated bisphenol S (TBBPS), Tetrabromobisphenol S bismethyl ether (TBBPS-BME)

Methods: Any kind of methods for the determination of the brominated flame retardants could be applied. According to Commission Recommendation 2014/118/EU the following limits of quantification should be reached:

Brominated flame retardants	Limit of quantification (LOQ)
PBDEs	≤ 0.01 ng/g wet weight
HBCDDs	≤ 0.01 ng/g wet weight
TBBPA and derivatives	≤ 0.1 ng/g wet weight
Brominated phenols and derivatives	≤ 0.1 ng/g wet weight

Reporting: Laboratories should:

- use their own reference standards for identification and quantification,
- report results for analytes of interest,
- report the limit of quantification (LOQ), at least for each non-quantified analyte,
- report the lipid content [%],
- give method information.

Statistical evaluation of results: Statistical evaluation of the PT results is performed by the EU-RL for Dioxins and PCBs in Feed and Food according to ISO 13528:2005 (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, Pure Appl. Chem, Vol. 78, No. 1, pp-145-196, 2006).

The determination of the assigned value is performed according to “The international harmonized protocol for the proficiency testing of analytical chemistry laboratories” 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.

Z-scores: For evaluation of results 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

The standard deviation for proficiency assessment σ_p is defined as 20 %.

Acceptable z-scores are between - 2 and + 2. Not acceptable are z-scores outside the range of - 3 to + 3.

Quality control, accreditation: The Deutsche Akkreditierungsstelle GmbH (DAkkS) attests that the EU-Reference Laboratory (EU-RL) for Dioxins and PCBs in Feed and Food at Chemisches und Veterinäruntersuchungsamt Freiburg (State Institute for Chemical and Veterinary Analysis of Food Freiburg) as provider of this proficiency test is competent under the terms of DIN EN ISO/IEC 17043:2010 to carry out proficiency testing/ interlaboratory comparisons in the testing field of chemical analysis and bioanalytical methods for determination of PCDD/Fs and PCBs in food and feed (Accreditation number: D-EP-18625-01-00).

Results and discussion:

30 laboratories (15 NRLs, 15 others) from 18 EU Member States participated in this study. The following table summarizes the number of laboratories which reported individual parameters.

Cod Liver (1402-CLA)

Parameter	No of labs	Parameter	No of labs	Parameter	No of labs	Parameter	No of labs
BDE-28	27	(+/-)- α -HBCDD	11	TBBPA	6	2,4,6-TBP	1
BDE-47	27	(+/-)- β -HBCDD	11	TBBPA-bME	0	2,4-DBP	0
BDE-49	10	(+/-)- γ -HBCDD	11	TBBPA-bOHEE	0	4-BP	0
BDE-99	27			TBBPA-bAE	0	2,6-DBP	0
BDE-100	27			TBBPA-bGE	0	TBBPS	0
BDE-138	13			TBBPA-bDiBPrE	0	TBBPS-BME	0
BDE-153	27						
BDE-154	27						
BDE-183	27						
BDE-209	14						

Fish Liver Oil (1402-CLB)

Parameter	No of labs	Parameter	No of labs	Parameter	No of labs	Parameter	No of labs
BDE-28	26	(+/-)- α -HBCDD	11	TBBPA	6	2,4,6-TBP	1
BDE-47	26	(+/-)- β -HBCDD	11	TBBPA-bME	0	2,4-DBP	0
BDE-49	10	(+/-)- γ -HBCDD	11	TBBPA-bOHEE	0	4-BP	0
BDE-99	26			TBBPA-bAE	0	2,6-DBP	0
BDE-100	26			TBBPA-bGE	0	TBBPS	0
BDE-138	13			TBBPA-bDiBPrE	0	TBBPS-BME	0
BDE-153	26						
BDE-154	26						
BDE-183	26						
BDE-209	16						

As summary:

- Results were reported for mainly PBDEs (90 %) and HBCDDs (37 %), few for TBBPA (20 %) and only one for brominated phenols (3 %).
- Assigned values were derived for PBDE and α -HBCDD.
- β -HBCDD, γ -HBCDD, TBBPA and 2,4,6-TBP were < LOQ. This raises the question of bioaccumulation of these analytes and their practical relevance for food of animal origin.
- Most results for evaluated congeners were within range of +/- 2 z-scores.
- PBDE results were well comparable even if determined with different detection methods.
- When the achievable LOQs are compared with LOQs as defined in Commission Recommendation 2014/118/EU, the defined LOQs are achievable in many cases, but not by all participants and all methods.

Acknowledgements:

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References:

1. COMMISSION RECOMMENDATION of 3 March 2014 on the monitoring of traces of brominated flame retardants in food (2014/118/EU), Official Journal of the European Union, L 65/39