

Proficiency - testing scheme for dioxins in food

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INTRODUCTION

Dioxins are persistent organic pollutants that can appear during natural phenomena such as forest fires or volcanic eruptions, but their spread and high presence in the environment is mainly due to industrialization. Dioxin presence in the environment is a cause for concern in terms of public health because they

tend to accumulate in the food chain, which can lead to harmful effects on human health. For this reason, regulations aim to limit their presence in food and feed. In order to comply with regulations and ensure food safety, laboratories have developed methods for the detection and quantification of dioxins in food. Laboratory performance assessment is achieved by participating in interlaboratory

Proficiency Testing Scheme (PTS) according to requirements of the ISO/CEI 17025 standard [1]. Since 2001, BIPEA (Bureau Interprofessionnel d'Études Analytiques) has offered a proficiency testing scheme for the determination of dioxins in the agri-food domain. The statistical treatment of laboratory results is performed according to ISO 13528 standard [2], assigned values are calculated

from the participants' results and the performances of laboratories can then be evaluated according to ISO/CEI 17043 standard [3]. This Proficiency Testing Scheme enables the participating laboratories to have an overview of different methods used, draw up a general inventory of their analytical skills and improve their performances for the detection and quantification of dioxins in food.

BIPEA

LABORATORIES

BIPEA

LABORATORIES



Fig. 1 - Organisation of the PTS by BIPEA

SAMPLES PRODUCTION

In November 2023, a trial was conducted on a "fish oil" matrix, more precisely a salmon oil naturally contaminated with dioxins. The whole batch of oil (10 L) was homogenized for 30 minutes by using a homogenization vat with a mixer and then divided into series of samples of 100mL. The principle of a quick successive production which involves a quasi-simultaneous filling, ensures the homogeneity of the product between all the samples. Thus, the samples were stored in a cool dark place at $(5 \pm 3)^\circ\text{C}$ and sent to participants for analysis. Twenty-six laboratories took part in this test.



Fig. 2 - Homogenization tun with mixer

HOMOGENEITY and STABILITY CHECK

For this trial, the homogeneity between samples was checked during the step of statistical treatment of laboratories' data by comparison between the robust standard deviation of the laboratory results of the studied trial compared with previous ones on similar samples, produced according to the same procedure.

The stability of the samples was checked during the statistical treatment through the follow-up of the robust standard deviation and the examination of participants' results consistency with previous trials on similar products demonstrated to be sufficiently stable for the duration of the test.

STATISTICAL TREATMENT

The participants were required to return their results through an online reply form after a period of six weeks. The list of analytical criteria requested in the reply form is shown in Table 1. Statistical treatment was conducted according to ISO 13528 [2]. Assigned values (x_{pt}) was estimated using the robust means of the results from application of robust algorithm A. Performances of each laboratory were evaluated using a tolerance value (VT) of 50% of x_{pt} . This value is used to identify an interval around the assigned value. Results in this range are considered as satisfactory. Moreover, laboratory results (x_i) were also evaluated through z-scores (z). The z-score for a result x_i is calculated as :

$$z_i = \frac{(x_i - x_{pt})}{\sigma_{pt}}$$

Where σ_{pt} is the standard deviation for proficiency assessment (VT/2). The results can then be classified as follows:

- $z_i \leq |2|$: satisfactory
- $|2| < z_i \leq |3|$: questionable
- $z_i > |3|$: unsatisfactory

RESULTS and DISCUSSION

ANALYTICAL CRITERIA		unit
DIBENZO-p-DIOXINES		
TCDD	2,3,7,8-TCDD	PEE
PeCDD	1,2,3,7,8-PeCDD	PEE
4HxCDD	1,2,3,4,7,8-HxCDD	PEE
6HxCDD	1,2,3,6,7,8-HxCDD	PEE
7HxCDD	1,2,3,7,8,9-HxCDD	PEE
HpCDD	1,2,3,4,6,7,8-HpCDD	PEE
OCDD	OCDD (Octa-chlorodibenzodioxin)	PEE
DIBENZOFURANES		
TCDF	2,3,7,8-TCDF	PEE
1PxCDF	1,2,3,7,8-PxCDF	PEE
2PxCDF	2,3,4,7,8-PxCDF	PEE
4HxCDF	1,2,3,4,7,8-HxCDF	PEE
6HxCDF	1,2,3,6,7,8-HxCDF	PEE
7HxCDF	1,2,3,7,8,9-HxCDF	PEE
2HxCDF	2,3,4,6,7,8-HxCDF	PEE
6HxCDF	1,2,3,4,6,7,8-HxCDF	PEE
7HxCDF	1,2,3,4,7,8,9-HxCDF	PEE
OCDF	OCDF (Octa-chlorodibenzofuran)	PEE
PCDFnp	SOMME DES PCDD / PCDF (Higher concentrations)	TEQ
PCDFinf	SOMME DES PCDD / PCDF (Lower concentrations)	TEQ
DIOXIN-LIKE PCBs		
PCBD77	PCB 77	PEE
PCBD81	PCB 81	PEE
PCBD126	PCB 126	PEE
PCBD169	PCB 169	PEE
PCBD105	PCB 105	PEE
PCBD114	PCB 114	PEE
PCBD118	PCB 118	PEE
PCBD123	PCB 123	PEE
PCBD156	PCB 156	PEE
PCBD157	PCB 157	PEE
PCBD167	PCB 167	PEE
PCBD189	PCB 189	PEE
PCBDnp	SUM OF PCBd (Higher concentrations)	TEQ
PCBDinf	SUM OF PCBd (Lower concentrations)	TEQ
TOTALnp	SUM OF PCDD / PCDF and PCBd (Higher concentrations)	TEQ
TOTALinf	SUM OF PCDD / PCDF and PCBd (Lower concentrations)	TEQ

Table 1 – List of analytical criteria

	x_{pt}	$u(x_{pt})$	$s(x_{pt})$	$p(x_{pt})$	$CV(x_{pt})\%$	σ_{pt}	VT
PCB 105 (pg/g)	775.40	35.48	106.21	14	14	193.85	387.70
2,3,7,8-TCDF (pg/g)	2.26	0.09	0.25	13	11	0.57	1.13

x_{pt} : assigned value
 $u(x_{pt})$: Standard uncertainty of the assigned value
 $s(x_{pt})$: Robust standard deviation of the results
 $p(x_{pt})$: Number of results considered for the estimation of the assigned value
 $CV(x_{pt})$: Coefficient of variation
 σ_{pt} : Standard deviation for proficiency assessment
 VT : Tolerance value (50% of x_{pt})

Table 2 - Statistical summary of the results for PCB 105 and 2,3,7,8-TCDF criteria

Laboratory	Result of PCB 105 (pg/g)		2,3,7,8-TCDF (pg/g)	
	x_i	Z-score	x_i	Z-score
1	765.70	-0.05	<49,70	
2	715.00	-0.31	2,33	0,12
3	869.20	0.48	2,30	0,07
4	753.00	-0.12	2,57	0,55
5	860.00	0.44	2,00	-0,46
6	807.66	0.17	2,17	-0,16
7	689.63	-0.44	2,14	0,21
8	893.00	0.61	2,30	0,07
9	106.00	-3.45	0,28	-3,50
10	761.70	-0.07	2,61	0,62
11	933.00	0.81	2,17	-0,16
12	653.00	-0.63	1,83	-0,76
13	713.84	-0.32	2,47	0,37
14	824.80	0.25	2,38	0,21
15	588.01	-0.97	2,00	-0,46

Table 3 – Laboratories data for PCB 105 and 2,3,7,8-TCDF criteria

For this trial, 15 laboratories out of 26 communicated their results for the interpretation of the data. Assigned values (x_{pt}) of 775,40 pg/g and 2,26 pg/g were calculated for PCB 105 and 2,3,7,8-TCDF respectively, both from the robust mean of all results except incoherent ones. A summary of the statistical results obtained from the data collected is shown in Table 2. Table 3 shows results and z-scores of laboratories for these two analytical criteria. These results are also presented as histograms in Fig. 3 and in Fig. 4, and also as "laboratory z-scores" graphs in Fig. 5 and in Fig. 6. Laboratory results obtained are consistent, with only one laboratory with an unsatisfactory result which shows that most laboratories are experienced and familiar with these analyses.

CONCLUSION

This interlaboratory test was part of an annual proficiency testing program. It has been implemented successfully and the results obtained were good for most of the laboratories. Taking part in interlaboratory Proficiency Testing Scheme enables laboratories to monitor punctually and/or continuously through time the reliability of their results, and also have a global overview of their analytical strengths and weaknesses, which is the first step before the implementation of corrective/curative actions.

REFERENCES

- [1] ISO 17025 - General requirements for the competence of testing and calibration laboratories
- [2] ISO 13528 - Statistical methods for use in proficiency testing by interlaboratory comparison
- [3] ISO 17043 - Conformity assessment - General requirements for proficiency testing.

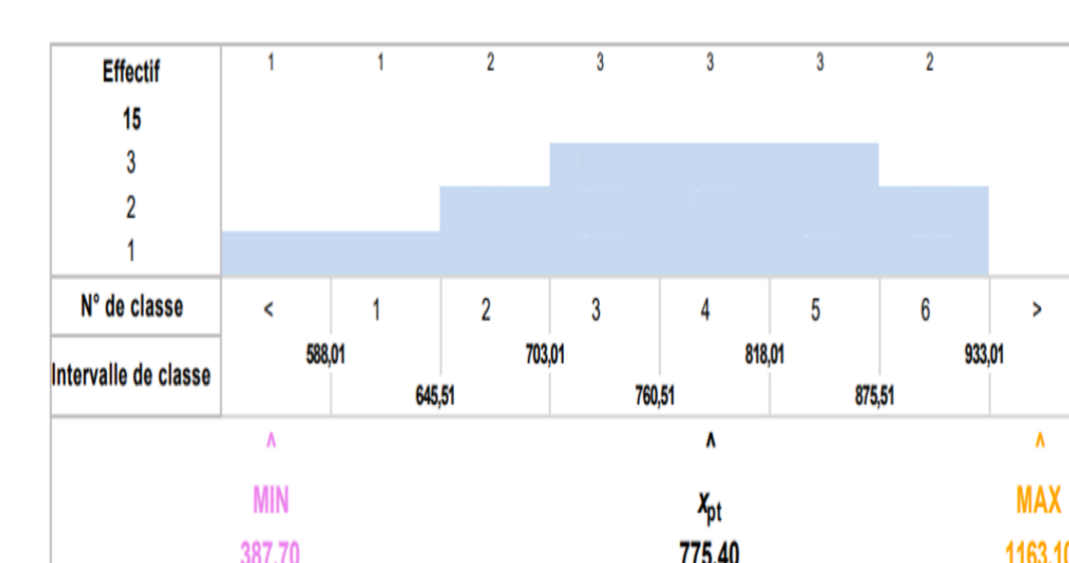


Fig. 3 – Results for PCB 105 represented as a histogram

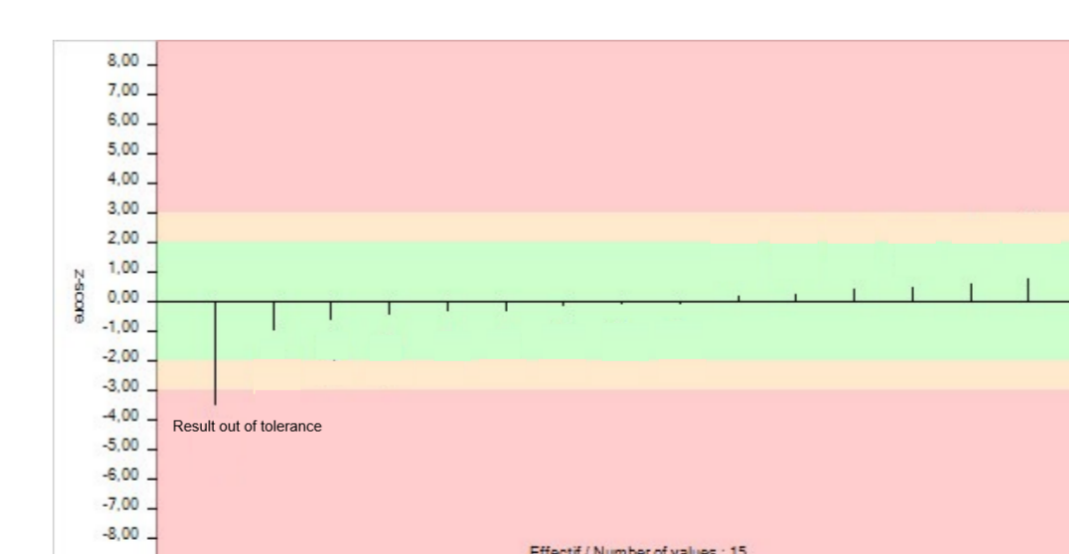


Fig. 5 - Laboratory z-scores graph - PCB 105

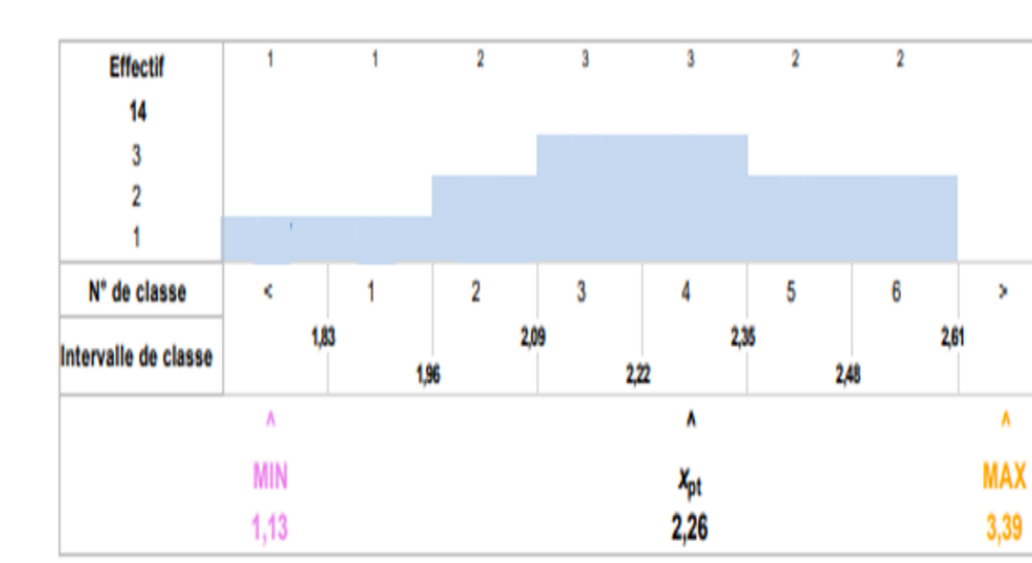


Fig. 4 – Results for 2,3,7,8-TCDF represented as a histogram

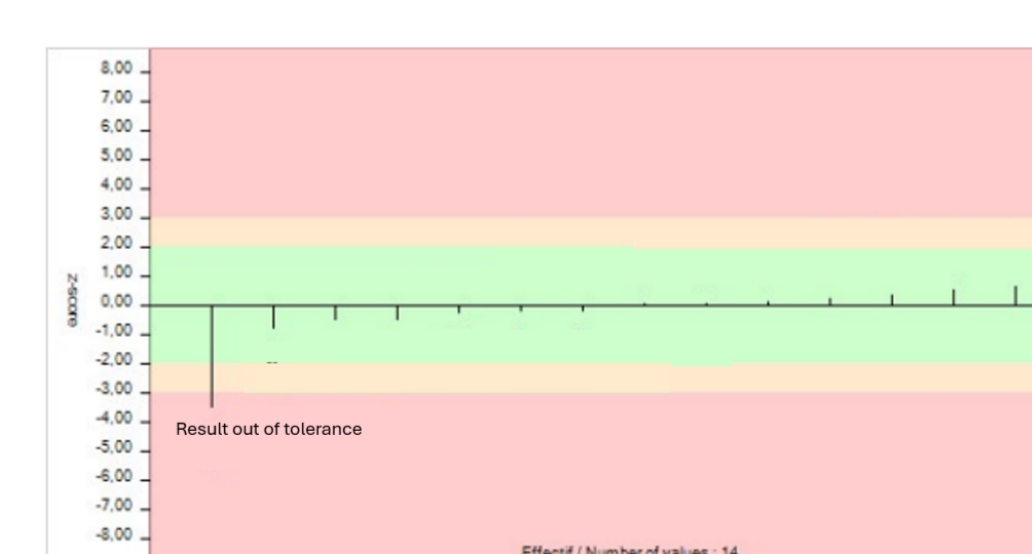


Fig. 6 - Laboratory z-scores graph - 2,3,7,8-TCDF