

RESULTS FROM 1ST PROFICIENCY TEST ON THE DETERMINATION OF DIOXINS AND FURANS IN FISH MUSCLE PROVIDED FROM MAPA BRAZIL

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Introduction

Participation in proficiency testing (PT) is a useful strategy for assessing accuracy and quality to the laboratory's measurements. The number of laboratories in Brazil and South America which analyses dioxins (PCDD/Fs) is increasing in the recent years. A proficiency test (PT) on the determination of PCDD/Fs, in fish muscle was organized by the Laboratory of Dioxins and PCBs (LDP/Lanagro-MG), the official laboratory of Ministry of Agriculture, Livestock and Food Supply (MAPA) from Brazil for analysis of these compounds. The PT was organized in 2014/2015. Official and private laboratories registered for this PT in a total of 9 Laboratories from different countries: Chile (4), Brazil (2), Argentina (1), Mexico (1) and Canada (1). The objective was to assess analytical performance of laboratories and to gain expertise in PT organization for these contaminants in Brazil and South America.

Materials and methods

Test Material

The proficiency test items were prepared from commercial fish fillet of *Cynoscion steindachneri* species, known in Brazilian market as *pescada*. The *pescada* fillets were prepared at LDP/LANAGRO-MG. Samples were spiked with a certified standard solution containing the 17 toxicologically relevant dioxins and furans. For that, about 3 kg of fish fillet samples were thawed until a firm consistency. The samples were homogenized and crushed in a blade homogenizer. After that, samples were freeze-dried and sieved. Particles bigger than 500 µm were disposed. The standard solution was added after dilution with n-hexane in order to allow a higher volume to be in contact to with the sample. After the solvent evaporation, sample was homogenized in rotation movements for about 30 hours. The freeze-dried samples were packed in 60 mL amber vials, containing 9.1 g. Each vial was labeled with a unique code. The produced proficiency test items were stored in freezer with controlled temperature between 2 and 10 °C, and kept in these conditions until the shipment.

Statistical design

The homogeneity evaluation of the test items was performed according to the procedures as described on *The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories*¹. The stability evaluation was performed under the procedures as described in the standard ISO 13528². For this proficiency testing scheme the assigned values were assessed through an expert reference laboratory (LDP/LANAGRO-MG) in accordance to the procedures as described in the standard ISO 13528². The analyses were performed by GC-HRMS in a quantitative method using isotope dilution³. The laboratory is ISO IEC 17025:2005 accredited to perform this method. The target standard deviation values for this proficiency testing scheme were considered as 20 % for individual congeners as suggested by Kotz⁵. The same target standard deviation was adopted for TEQ value. The assigned values for each congener are shown in **Table 1**.

Table 1. Assigned values for each congener.

PCDD	Concentration (pg/g)	PCDF	Concentration (pg/g)
2378-TCDD	1.89	2378-TCDF	2.11
12378-PeCDD	9.19	12378-PeCDF	9.39
123478-HxCDD	9.38	23478-PeCDF	9.28
123678-HxCDD	9.35	123478-HxCDF	9.35
123789-HxCDD	9.61	123678-HxCDF	9.23
1234678-HpCDD	9.25	234678-HxCDF	9.20
OCDD	18.33	123789-HxCDF	9.31
		1234678-HpCDF	9.28
		1234789-HpCDF	9.35
		OCDF	20.56
Σ PCDD/F-TEQ/OMS ²⁰⁰⁵			21.20 pg TEQ/g

Results and discussion:

The main parameters of the methods used for reporting the results are summarized in **Table 2**. Most methods are validated, but only three are ISO IEC 17025:2005 accredited. Soxhlet is still the main technique used for sample extraction, followed by Pressured Liquid Extraction (PLE). One laboratory reported that the analysis was performed by MS/MS. Two laboratories performed the analyses by bioassay and were not included in z-score calculations due to the difficulty to compare TEQ and BEQ values, especially when a small number of laboratories are involved.

Table 2. Details of methods used by the participant laboratories (bioassay methods not included).

Method details	Number of Laboratories	Method details	Number of Laboratories
Validated method used	5	Accredited method used	3
Sample weight		Extraction Solvent	
≥ 2 - < 5 g	5	DCM	4
≥ 1- < 2 g	1	DCM e n-hexane	1
≥ 5 - < 10 g	1	n-hexane and toluene	1
Extraction		Cyclohexane e toluene	1
Soxhlet	3	Quantification	
PLE	2	HRMS	6
Acid digestion	1	MS/MS	1
Sonication	1		

In **Figure 1** are shown z-scores calculated for the laboratories which performed analysis by quantitative methods for each congener. Four laboratories (57 %) presented z-score considered satisfactory ($|z| < 2$) for all the congeners. Two laboratories (29 %) presented z-score considered unsatisfactory ($|z| \geq 3$) for at least one congener. When analyzing the results for TEQ values only one laboratory reported a value classified as **questionable** ($2 < |z| < 3$), all the others were considered satisfactory

Figure 1. Compilation of z-score for each laboratory and congener.

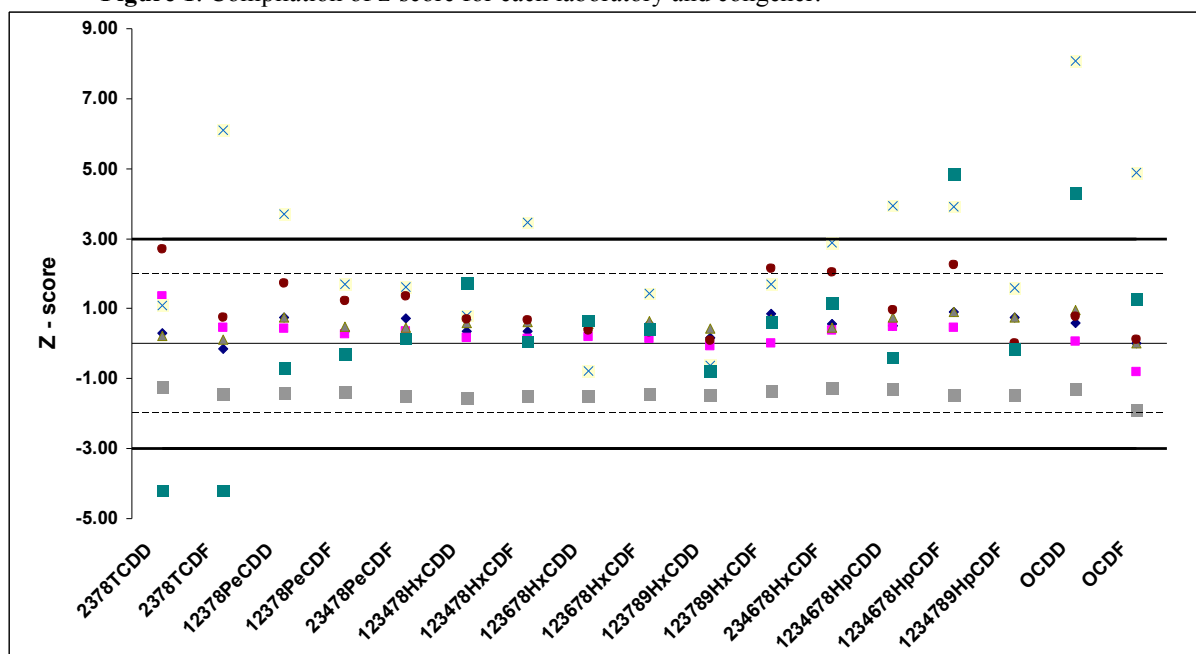
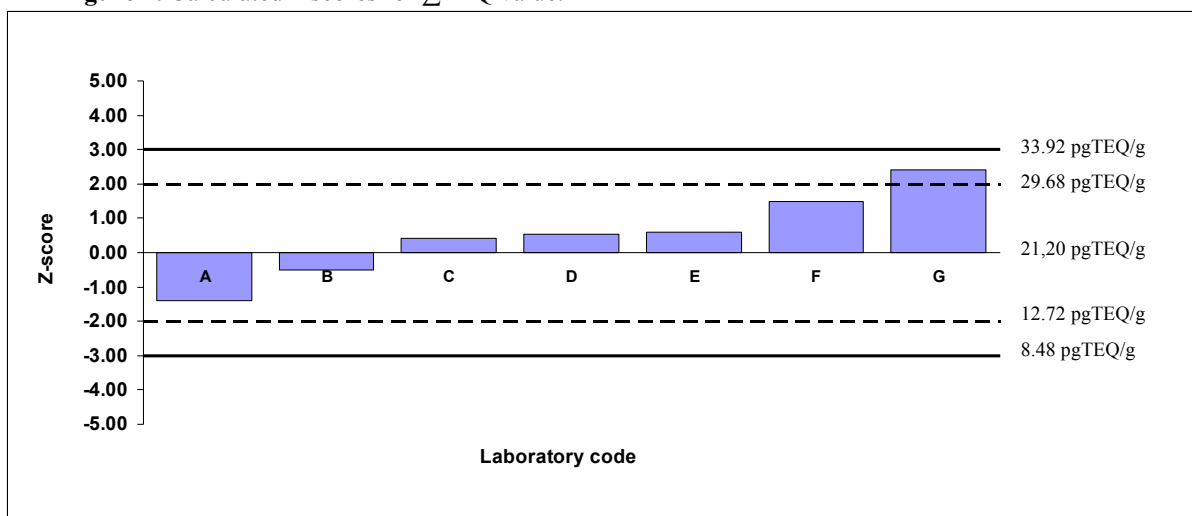


Figure 2. Calculated z-scores for Σ TEQ value.



Conclusions:

- The 1st proficiency test program was successfully organized.
- An overview of methods for dioxins analyses in food used in Brazil, South America was provided.
- Most laboratories presented satisfactory z-scores, especially for TEQ value.
- On the following programs the dl-PCBs may be included and the concentration of analytes in the PT sample can be lower.

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