SHIMADZU

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Simplifying dioxins analysis in foods and feeds using GC-MS/MS in compliant with the EU Commission Regulation

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Overview

- To enable analysis of dioxins in food and animal feed products, a versatile and sensitive GC-MS/MS equipment is required.
- Shimadzu GCMS-TQ8050 NX system (**Fig. 1**) equipped with AOC-30i + 20sU and Boost Efficiency Ion Source (BEIS) demonstrated to achieve low femtogram levels by SPL injector at 1µL for the analysis of dioxins in accordance with EU Commission Regulation 589/204 and 644/2017.
- Eurofins Special Tests, one of the most important laboratories for dioxins analysis in Brazil, collaborated with this work.

Fig. 1 Shimadzu GCMS-TQ8050 NX.

1. Introduction

- Dioxins in food and animal feed products are one of the most important Persistent Organic Pollutants (POPs) to evaluate. Quantitative analysis of dioxins in low concentration levels is necessary due to their high toxicity. Regarding to the analysis, EU Commission Regulations stablish analysis methods using GC-MS/MS as official test methods with the same positioning as methods using GC-HRMS.
- In addition to the importance to monitor them, analysis of dioxins by GC-MS/MS has attracted interest. Due to the complexity of matrix and low limits, it is common to use a PTV injector by Large Volume Injection technique to reach femtogram levels. Therefore, a robust and sensitive method that uses minimal injection volume is desirable.

2. Methods

- For the various food samples, pretreatment was performed using Eurofins Special Tests internal procedure.
- For the analytical parameters, the conditions registered in the Shimadzu's method package named EU Regulation Compliant GC-MS/MS Method Package for Dioxins in Foods (**Fig. 2**) were used. Some changes were performed to be in accordance with Eurofins internal requirement.

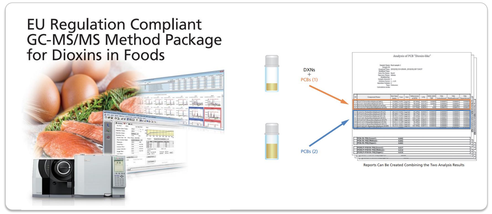

Fig. 2 Shimadzu's EU Regulation Compliant GC-MS/MS method package for dioxins in foods.

- The retention times for all dioxins and furans congeners were done automatically using the Automatic Adjustment of Retention Time (AART) function.
- Also, the use of hydrogen as alternative gas was evaluated in direct comparison with results already obtained using another instrument.

3. Result

- All calibration curve data for each congeners were obtained from 25-100000fg/µL, as shown in **Table 1**.
- Considering the maximum permitted concentrations (ML), the ML for pig's fat and meat were the lowest at 1pg/g of fat (sum of dioxins, WHO-PCDD/F-TEF). The limit of quantification (LOQ) was considered 1/5 of ML.
- The precision and accuracy parameters were conducted spiking blank samples at LOQ and ML levels. For all injections, the recovery results were obtained within range of 60-120%. The %RSD at 0.2pg/g was 6.6 and at 1.0pg/g was 8.2. The validation procedures were conducted considering replicates (n=20).

Table 1 Calibration curve data for each congeners

Compound	25fg/µL	50fg/µL	100fg/µL	500fg/µL	2000fg/µL	10000fg/µL	R^2
2,3,7,8-TCDD	23.726	47.068	98.992	611.919	2132.035	9968.025	0.99972
1,2,3,7,8-PeCDD	31.398	49.623	109.694	546.798	2079.636	9981.622	0.99993
1,2,3,4,7,8-HxCDD	32.870	54.467	107.803	511.173	2202.076	9958.906	0.99955
1,2,3,6,7,8-HxCDD	28.251	69.423	98.808	527.952	2136.168	9971.275	0.99980
1,2,3,7,8,9-HxCDD	26.323	63.742	137.118	593.647	2218.754	9951.124	0.99950
1,2,3,4,6,7,8-HpCDD	22.205	53.492	99.745	526.244	2059.510	9986.778	0.99996
OCDD	47.728	106.675	231.714	1197.367	4429.895	19903.808	0.99947
2,3,7,8-TCDF	33.147	66.368	109.577	647.276	2220.264	9948.385	0.99940
1,2,3,7,8-PeCDF	38.081	51.477	91.500	529.228	2144.940	9969.596	0.99977
2,3,4,7,8-PeCDF	36.565	60.270	106.934	608.053	2161.619	9962.124	0.99968
1,2,3,4,7,8-HxCDF	33.063	70.965	112.130	569.740	2198.799	9956.507	0.99959
1,2,3,6,7,8-HxCDF	36.116	62.819	126.985	575.487	2233.598	9949.144	0.99944
2,3,4,6,7,8-HxCDF	34.946	59.856	101.504	526.507	2184.400	9961.705	0.99964
1,2,3,7,8,9-HxCDF	35.712	51.610	109.066	589.710	2191.344	9957.120	0.99959
1,2,3,4,6,7,8-HpCDF	36.548	64.110	106.874	525.396	2183.628	9961.836	0.99965
1,2,3,4,7,8,9-HpCDF	38.228	47.944	109.585	533.886	2291.373	9939.912	0.99906
OCDF	59.825	122.586	208.172	1142.006	4566.173	19879.446	0.99912

- To evaluate accuracy by proficiency tests, one assay was conducted in pork liver achieving a Z-score at 0.4.
- **Fig. 3 and Fig. 4** represent chromatograms for some congeners.

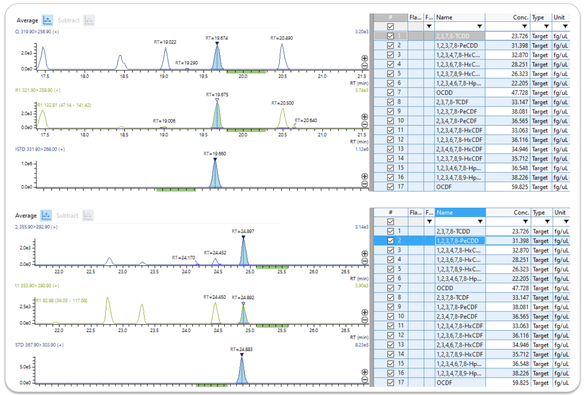

Fig. 3 Chromatograms for 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD at 25fg/µL.

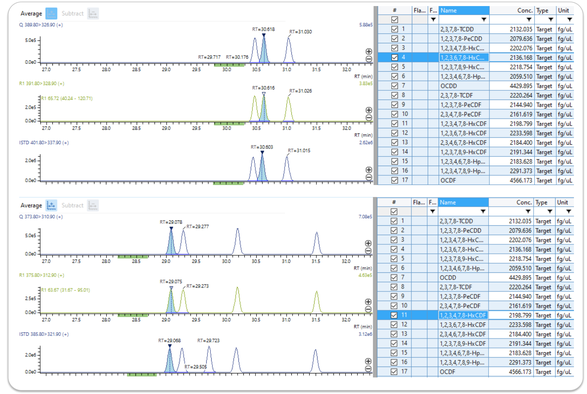

Fig. 4 Chromatograms for 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDF at 2000fg/µL.

- Table 2 represents summary of sensitivity (LOQ) for congeners groups by He and H_2.

Table 2 Sensitivity assessment for LOQ comparing data obtained by He and H_2.

Compound Group	Concentration (fg/µL)	
	LOQ (He)	LOQ (H_2)
TCDD/F	25	25
PeCDD/F	25	25
HxCDD/F	25	250
HpCDD/F	25	500
OCDD/F	25	500

4. Conclusion

- ✓ Regarding the robustness of instrument using low injection volume, more than 6900 injections were done maintaining sensitivity, showing durability of the instrument..
- ✓ The groups TCDD/F and PeCDD/F were the aim of this study, since they have the highest TEF (TEF=1). Until penta congeners, it was possible to achieve the same LOQ by helium as carrier gas. The other congeners had higher LOQ. An important result was the reduction of analysis in 23.4%.