IDENTIFICATION AND QUANTIFICATION METHOD FOR POLYBROMINATED DIOXINS IN STATIONARY SOURCE EMISSIONS

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Introduction

Emissions of chlorinated dioxins/furans are determined in Europe by application of the standard EN 1948. The emission limit value of chlorinated dioxins is 0.1 ng I-TEQ/Nm^3. More and more studies have shown the existence of brominated dioxins in stationary source emissions and shown that toxicity of theses molecules can be similar to chlorinated dioxins. The aim of the study, that DIOXLAB and CAE have realized with ADEME support is to develop a method for identification and quantification of polybrominated dioxins/furans (PBDD/Fs). The determination of the mass concentration of PBDD/F in flue gas includes optimization of several steps : sampling, sample preparation and analytical conditions. This paper exposes optimization of analytical parameters for detection of PBDD/Fs. Targeted molecules are 17 PBDD/Fs homologues of the 17 chlorinated toxic congeners.

Materials and methods

Mixtures

Polybrominated dioxins are less studied than polychlorinated dioxins. Then, all standard mixtures for PBDDs/Fs analyses are not available on the market. Table 1 shows the available standard of PBDD/F mixtures compared to chlorinated compounds. When no native or labeled molecule exists, quantification will be carried out by total homologue congener calculation.

The mixture used for optimization of the method is the solution CS6 of the mixture EDF-5381. This mixture contains following labeled and native analytes.

Chlorinated Native	*Native brominated dioxins*	*Labeled brominated dioxins*	*Type of standard*
2,3,7,8-TeCDD	**2,3,7,8-TeBDD**	**$^{13}C_{12}$-2,3,7,8-TeBDD**	Cleanup standard
1,2,3,7,8-PeCDD	**1,2,3,7,8-PeBDD**	**$^{13}C_{12}$-1,2,3,7,8-PeBDD**	Cleanup standard
1,2,3,4,7,8-HxCDD	**1,2,3,4,7,8-HxBDD**	**$^{13}C_{12}$-1,2,3,4,7,8-HxBDD**	Cleanup standard
1,2,3,6,7,8-HxCDD	**1,2,3,6,7,8-HxBDD**	**$^{13}C_{12}$-1,2,3,6,7,8-HxBDD**	Cleanup standard
1,2,3,7,8,9-HxCDD	**1,2,3,7,8,9-HxBDD**	**$^{13}C_{12}$-1,2,3,7,8,9-HxBDD**	Syringue Standard
1,2,3,4,6,7,8-HpCDD	No Native 1,2,3,4,6,7,8-HpBDD	No Standard 1,2,3,4,6,7,8-HpBDD	
OCDD	**OBDD**	**$^{13}C_{12}$-OBDD**	Cleanup standard
2,3,7,8-TeCDF	**2,3,7,8-TeBDF**	**$^{13}C_{12}$-2,3,7,8-TeBDF**	Cleanup standard
2,3,4,7,8-PeCDF	**2,3,4,7,8-PeBDF**	**$^{13}C_{12}$-2,3,4,7,8-PeBDF**	Cleanup standard
1,2,3,7,8-PeCDF	**1,2,3,7,8-PeBDF**	**$^{13}C_{12}$-1,2,3,7,8-PeBDF**	Syringue Standard
1,2,3,4,7,8-HxCDF	**1,2,3,4,7,8-HxBDF**	**$^{13}C_{12}$-1,2,3,4,7,8-HxBDF**	Cleanup standard
1,2,3,6,7,8-HxCDF	No Native 1,2,3,6,7,8-HxBDF	No Standard 1,2,3,6,7,8-HxBDF	
1,2,3,7,8,9-HxCDF	No Native 1,2,3,7,8,9-HxBDF	No Standard 1,2,3,7,8,9-HxBDF	
2,3,4,6,7,8-HxCDF	No Native 2,3,4,6,7,8-HxBDF	No Standard 2,3,4,6,7,8-HxBDF	
1,2,3,4,6,7,8-HpCDF	**1,2,3,4,6,7,8-HpBDF**	**$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDF**	Cleanup standard
1,2,3,4,7,8,9–HpCDF	No Native 1,2,3,4,7,8,9-HpBDF	No Standard 1,2,3,4,7,8,9-HxBDF	
OCDF	**OBDF**	**$^{13}C_{12}$-OBDF**	Cleanup standard
Chlorinated congener not analysed	**2,4,6,8-TeBDF**	**13C_{12}-2,4,6,8-TeBDF**	Sampling Standard

Table 1 : Comparison between existing chlorinated native and brominated native standards ; composition of the mixture used for optimization of GC-MS method (bold)

Sample preparation

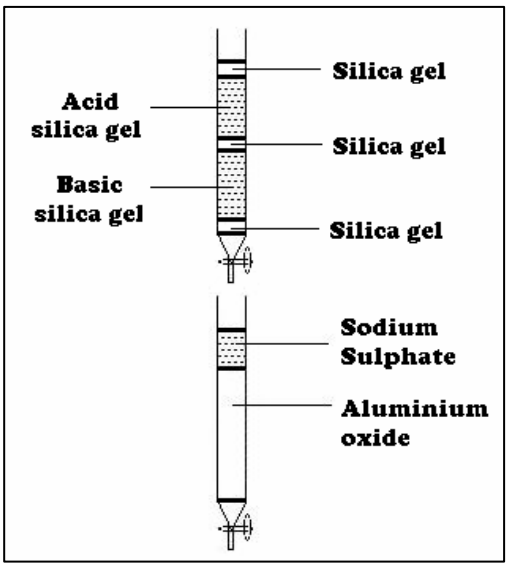


Figure 1 : Sample purification

Sampling

AMESA sample from an Energy for Waste plant (EfW) is used to test the method. Sampling period of the AMESA sample is one month. This type of sample allows to trap many organics pollutants on the adsorbent (due to a long sampling period) and permits to obtain some extract more concentrated. Then, identification and quantification of PBDD/Fs will be easier.

Extraction and purification

Extraction and purification method used for sample preparation to analyze PBDD/Fs is the same as sample preparation for PCDD/Fs analysis (standard EN 1948-2).

Extraction of the adsorbent is carried out by high temperature extraction in soxhlet (solvent : toluene).

Purification : two successive multilayer columns as shown in figure 1. Solvent elution : Hexane/dichloromethane (v/v, 80/20)

Analytical conditions

The analyser used for PBDD/Fs identification and quantification is a Gas Chromatograph (Agilent technologies) coupled with a High Resolution Mass Spectrometer (Autospec, Micromass).

Analytical conditions (GC) for PBDD/F identification were determined and optimized through injection of CS6 solution. Characteristics of the capillary column are : DB5 MS, length 60m, internal diameter 0.25mm, thick film 0.25µm.

Table 2 represents the oven temperature programme :

Temperature	*Rate*	*Hold*	*Run time*
160 °C	0 °C/min	1 min	1 min
200 °C	20 °C/min	0 min	3 min
290 °C	5 °C/min	10 min	31 min
300 °C	10 °C/min	5 min	37 min
330 °C	5 °C/min	6 min	49 min
340 °C	10 °C/min	10 min	60 min

Table 2 : GC Oven Temperature Programme

Mass detection is based on the two most abundant ions for each molecule :

	TeBDD		PeBDD		HxBDD		HpBDD		OBDD	
Abundance (%)	100	67,8	100	98,5	76,3	100	100	98,4	81,4	100
^{12}C	497,6923	499,6903	577,6008	579,5988	655,5113	657,5093	735,4198	737,4178	813,3302	815,3282
^{13}C	509,7326	511,7306	589,6411	591,6391	667,5515	669,5495	747,46	749,458	825,3705	827,3685

Table 3 : Monitoring of PBDDs ions mass for MS method

	TeBDD		PeBDD		HxBDD		HpBDD		OBDD	
Abundance (%)	100	67,8	100	98,5	76,3	100	100	98,4	81,4	100
^{12}C	497,6923	499,6903	577,6008	579,5988	655,5113	657,5093	735,4198	737,4178	813,3302	815,3282
^{13}C	509,7326	511,7306	589,6411	591,6391	667,5515	669,5495	747,46	749,458	825,3705	827,3685

Table 4 : Monitoring of PBDDs ions mass for MS method

Results and Discussion

After analytical conditions optimization, the injection of standard mixture allowed to identify and determine retention time of each molecule.

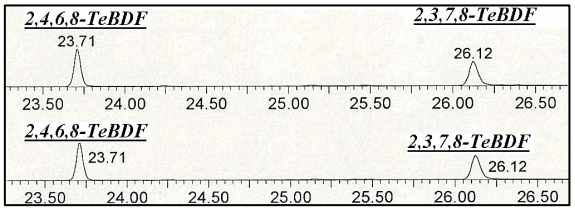
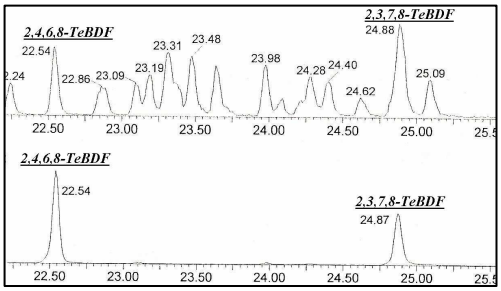
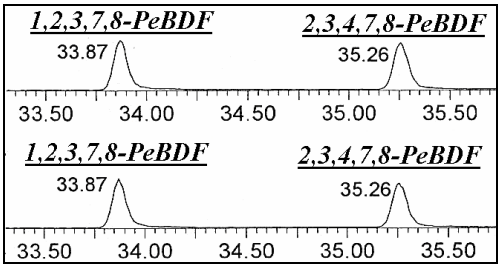
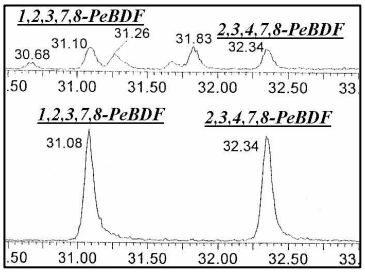
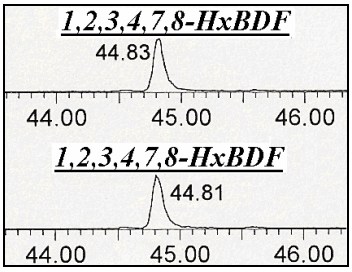
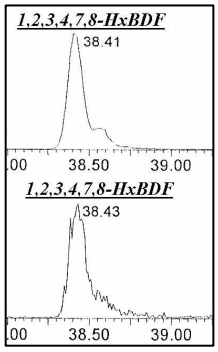
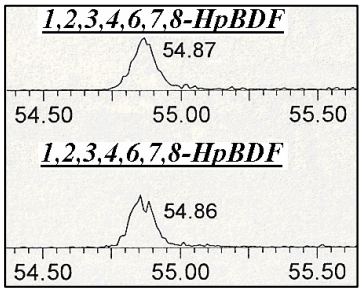
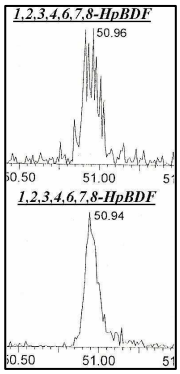
Standard (native and labeled)	Sample (native and labeled)	Ion (m/z)
		483.6954 (native) 495.7357 (labeled)
		561.6059 (native) 573.6462 (labeled)
		641.5144 (native) 653.5546 (labeled)
		719.4248 (native) 731.4651 (labeled)
OBDF not detected	OBDF not detected	

Table 5 : PBDFs in Standard and AMESA sample

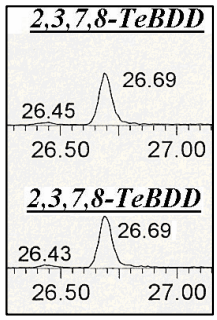
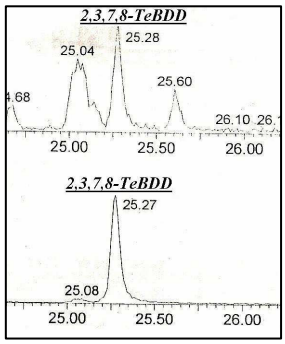
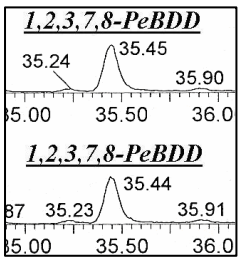
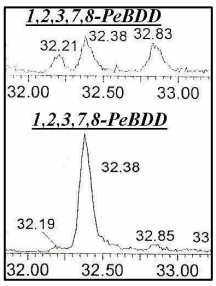
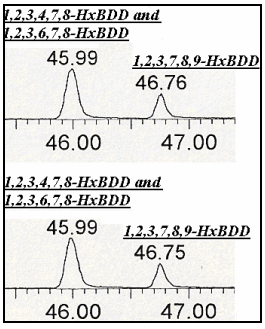
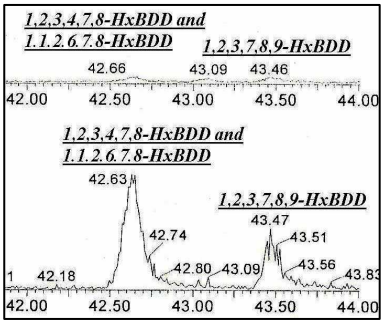
Standard (native and labeled)	Sample (native and labeled)	Ion (m/z)
		499.6903 (native) 511.7306 (labeled)
		577.6008 (native) 589.6411 (labeled)
		735.4198 (native) 747.4600 (labeled)
OBDD not detected	OBDD not detected	

Table 6 : PBDDs in Standard and AMESA sample

It can be noted that OBDD and OBDF are not detected. Indeed, theses molecules do not appear on the chromatogram. Theses molecules are very heavy and the column very long. It is possible that for heavy molecules retention on the column is too strong and, so, very long time is necessary to elute the molecules.
Tables 5 and 6 represent chromatogram of standards and flue gas sample.

Preparation and analyse of the flue gas sample confirm that PBDDs and PBDFs are present in flue gas of Energy for Waste plant. The presented method does not allow to detect the 17 targeted compounds, but it is forecasted to change the column to improve the detection of OBDD and OBDF. Then the next step of the study will be to determine the level of concentration of the PBDD/Fs in AMESA samples, and punctual sampling (sampling according to the standard EN 1948-1).

Acknowledgements

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