

# **CLEANUP AND DETERMINATION OF ORGANOCHLORINE AND ORGANOBRONINE COMPOUNDS**

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## **Introduction**

Polybrominated chemicals used as flame retardant are a cause of increasing concern, especially polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBPA). Level of PBDEs in environment have dramatically raised in the past 20 years over the world<sup>1,2</sup> and monitoring of this class of chemicals has not to be ignored. Therefore, a rapid and reliable analyse method is needed, in a cost effective way. We present here a strategy for screening a broad range of organohalogen compounds, including PBDEs, but also chlorinated compounds such as polychlorobiphenyls (PCBs), polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs). The seductive aspect of this strategy lies in the fact that the purification and the separation of all target compounds are both a single performed automated step with the Power-Prep System<sup>TM</sup> (FMS), and that the analyses are carried out with only one device, a GC PolarisQ ion trap mass spectrometer.

## **Methods and Materials**

Samples were purified using the Power-Prep System<sup>TM</sup> (Fluid Management Systems, Waltham, MA, USA). This automated system was used with disposable multilayer silica, alumina and PX21 carbon columns in order to separate analytes of interest from matrix interferences<sup>3</sup>. Analysis were conducted on a ThermoQuest Trace GC PolarisQ ion trap mass spectrometer (Austin, Tx, USA) equipped with a Rtx 5-MS (30m x 0.25 mm x 0.25  $\mu$ m) capillary column (Restek, Evry, France). The PBDEs Analytical Standard Solution EO-4980 was purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and contains 40 native congeners from mono- to heptabrominated Diphenylethers and 5 <sup>13</sup>C-labelled PBDEs (47,77,99,100 and 126). The MBDE-MXC <sup>13</sup>C-labelled internal standard solution was from Wellington Laboratories (Ontario, Canada) and contains mono- (3), di- (15), tri- (28), tetra- (47), penta- (99), hexa- (153 and 154) and heptabrominated DE (183).

## **Results and Discussion**

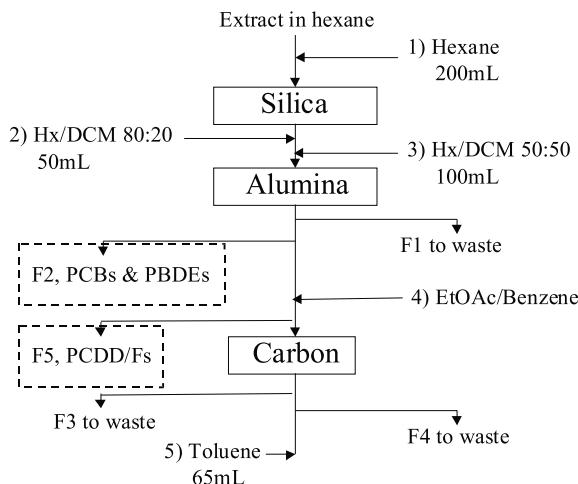
### *Sample preparation*

Recently, an automated multi-analyte cleanup procedure has been developed in our lab to allow the separation and the analyses of the 17 dioxins and furans, the 12 non- and mono-*ortho* PCBs and the 7 PCBs of the Aroclor 1260<sup>4</sup>. The drawback of this strategy was the quite high volume of solvent used for PCBs purification, yielding to high limits of quantification values (LOQs). The present study has tried to reduce solvent used and therefore decrease the LOQs but also enlarge this cleanup to brominated compounds as PBDEs.

The clean-up scheme on the automated system is depicted in Fig. 1.

Mixtures of solvent were optimised in order to separate PCBs and PBDEs from dioxins on the alumina column and then avoid the spread out of PCBs on the carbon column. This was this step that

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**Figure 1.** Scheme for fraction collection.

required large volume of solvent in our previous study. A 80:20 hexane-dichloromethane mixture has been chosen because it was able to carry quantitatively PCBs and PBDEs through the alumina column without desorbed dioxins and furans. Afterwards a 50:50 mixture eluted dioxins and furans in the forward direction through the carbon column where they are adsorbed and after additional cleanup, toluene eluted these ones in back-flush.

Table 1 shows recoveries for all target analytes. PBDEs of interest were tetra- (75,71,49 and 47BDE), penta- (100,119,99,126BDE) and hexabrominated congeners (154,153,140 and 138BDE) and were collected with satisfactory recoveries, excepted BDE126 and BDE138. None of the di- and tribrominated congeners were found in these two fractions but they were eluted from alumina with pure dichloromethane. Heptabrominated diphenylethers had poor recoveries whatever solvent or mixture of solvent used. Recoveries of dioxins ranged between 53 and 98% excepted for the second PeCDF, for three HxCDFs and 2 HxCDDs which have recoveries about 35 %. These congeners began to elute with the 80/ 20 mixture.

## Analysis

All target compounds were analysed by gas chromatography coupled to tandem in time mass spectrometry. The ion trap was set at 250 °C, with the transfer line at 280 °C. Electronic impact (EI) was used as ionisation mode, with an energy of 70eV. Analysis of PCDD/Fs, PCBs and PBDEs were carried out separately.

### a) Dioxins and furans

Determination of dioxins in GC/MSMS were already optimised using Programmable Temperature Vaporization-Large Volume (PTV-LV) injections in order to increase sensibility and decrease limits of quantification. Details are described elsewhere<sup>5</sup>.

### b) PCBs

Tandem in time mass spectrometry has been widely used for analysis of PCBs and its suitability have been already demonstrated<sup>6,7</sup>.

### c) PBDEs

	Congeners	Recovery %	LODs pg/g	RRF	Congeners	Recovery %	LODs ng/g	RRF
TB r	75	75.09	1.00	1.091	M	123 PeCB	85.99	0.00
	71	58.18	4.14	0.864	on	118 PeCB	67.43	0.16
	49	44.74	1.00	0.793	o-	114 PeCB	66.88	0.00
	47	72.55	128.22	1.395	ort	105 PeCB	61.29	0.03
Pe Br	100	67.92	28.34	1.012	ho	167 HxCB	66.29	0.00
	119	78.06	1.00	0.570	PC	156 HxCB	68.20	0.02
	99	72.56	97.94	1.096	Rs	157 HxCB	73.13	0.00
	126	11.84	1.00	1.349		189 HpCB	63.91	2.73
Hx Br	154	67.57	8.25	0.793	28	TriCB	71.37	2.38
	153	58.67	7.82	0.670	52	TCB	75.70	1.78
	140	45.43	0.83	0.905	A1	101 PeCB	72.15	0.83
	138	25.91	1.51	0.649	26	153 HxCB	64.66	0.25
<b>PCBs</b>								
c-	77 TCB	58.51	203.00	0.915		138 HxCB	59.75	0.41
	81 TCB	46.42	22.50	0.913		180 HpCB	64.88	0.22
PC	126 PeCB	86.10	6.26	0.959				
	169 HxCB	82.31	0.30	1.01				

Table 1 . LODs, RRF and recoveries for PBDEs and PCBs

	Congeners	Parent ions (m/z)	CID	Daughter (m/z)
DiBDEs	C <sub>12</sub>	325.89	3.00	168
	C <sub>13</sub>	337.89	3.00	
TriBDEs	C <sub>12</sub>	403.8	3.50	246/248
	C <sub>13</sub>	415.8	3.50	
TBDEs	C <sub>12</sub>	481.72	3.75	324/326
	C <sub>13</sub>	493.72	3.75	
PeBDEs	C <sub>12</sub>	559.63	4.00	404/406
	C <sub>13</sub>	571.63	4.00	
HxBDEs	C <sub>12</sub>	637.54	4.75	482/484/486
	C <sub>13</sub>	649.54	4.75	
HpBDEs	C <sub>12</sub>	715.45	5.50	562/564
	C <sub>13</sub>	724.45	5.50	

Tab 2. CID voltage in function of number or

### Ionisation

Negative Chemical Ionisation (NCI) is the most often used ionisation mode for determination of brominated compounds. This technique presents a higher sensitivity than Electronic Impact (EI) but is less selective since only bromine can be monitored. Furthermore, it doesn't allow the quantification by internal standard (<sup>13</sup>C- labelled PBDEs) whereas EI does, making the quantification more accurate <sup>8,9</sup>. In order to also increase selectivity, tandem in time mass spectrometry (MS/MS) was chosen as detector. To our knowledge, there's no data about analysis of PBDEs by MS/MS. Having a highly selective method allows the determination of target analytes in solutions holding other organohalogen compounds. Purification step can be therefore less rigorous.

As preliminary experiment, default parameter for energy of electronic impact was 70eV. Afterwards, since that Eljarrat<sup>10</sup> had found an optimal electron energy of 35eV on a Agilent mass spectrometer, we have compared TIC of all congeners using full scan mode for 35 and 70eV. Ionisation at 70eV seemed to be more efficient (TIC nearly twice greater than with 35eV).

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## *Optimisation of CID voltage*

Excitation step yielding the daughter ions is the most important step in MS/MS. CID voltage were optimised, excitation time and energy of excitation were default parameters. CID voltage for each congeners are presented in table 2.

In the ion trap when CID was applied, PBDEs behave as PCBs and breakdown with loss of Br<sub>2</sub> (PCBs lose Cl<sub>2</sub>) excepted for some congeners for which loss of COBr occurs. This is similar with behaviour of dioxins and furans. Amazingly, all these exceptions are the ortho-substituted congeners and for these compounds, daughter ions monitored was M-Br<sub>2</sub> and M-COBr

## *Linearity*

Calibration curves were determined for the 40 PBDEs of the solution EO-4980. Linearity was observed for a range of between 1 and 75pg for di-, tri- and tetrabrominated congeners, between 1.5 and 112pg for pentabrominated, between 2 and 150pg for hexabrominated and between 5 and 190pg for heptabrominated ones. RRF values ranged between 0.38 and 1.395 depending on the congener.

## *LODs*

For congeners not found in blank procedural method, the limit of detection (LODs) was determinate for a signal-to-noise ratio greater than 3. LODs of these one are 1 or 2pg/g depending on the congener. For congeners present in blank, LOD values was calculated as the average blank value plus three times the standard deviation (SD) of the blank. LOD values ranged between 1.51 and 128 pg/g. Details of each LODs are presented in table1.

## **Conclusions**

This simple strategy allows to analyse 7 dioxins, 10 furans, 12 non- and mono-*ortho* PCBs, 7 PCBs of Aroclor 1260, 13 PBDEs from tetra- to hexa-substituted ones, on biological samples with a single automated purification step and with a single ion trap mass spectrometer. With this strategy, determination of PBDEs and PCBs could be realised in less than four ours, evaporation step and final analyse included.

## **Acknowledgements**

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