

CLEANUP AND DETERMINATION OF ORGANOCHLORINE AND ORGANOCHLORINE 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^{1,2} 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 SystemTM (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 SystemTM (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 interferences³. 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 μ 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 ¹³C-labelled PBDEs (47,77,99,100 and 126). The MBDE-MXC ¹³C-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 1260⁴. 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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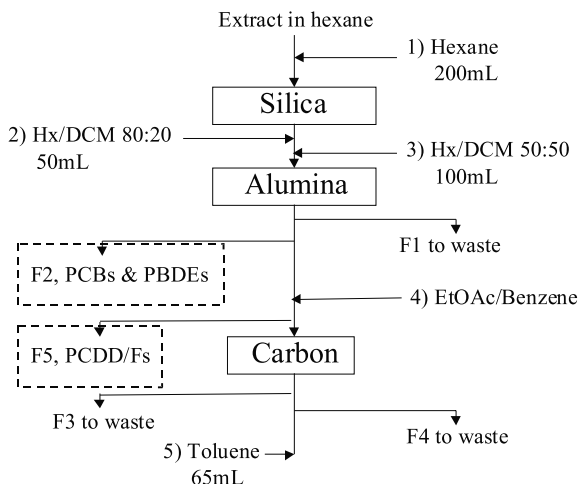


Figure 1. Scheme for fraction collection.

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 elsewhere⁵.

b) PCBs

Tandem in time mass spectrometry has been widely used for analysis of PCBs and its suitability have been already demonstrated^{6,7}.

c) PBDEs

Congeners		Recovery %	LODs pg/g	RRF	Congeners		Recovery %	LODs ng/g	RRF
TB r	75	75.09	1.00	1.091	M on o- ort ho PC Rs	123 PeCB	85.99	0.00	1.157
	71	58.18	4.14	0.864		118 PeCB	67.43	0.16	1.099
	49	44.74	1.00	0.793		114 PeCB	66.88	0.00	1.349
	47	72.55	128.22	1.395		105 PeCB	61.29	0.03	1.333
Pe Br	100	67.92	28.34	1.012	Al 26 n	167 HxCB	66.29	0.00	1.012
	119	78.06	1.00	0.570		156 HxCB	68.20	0.02	1.064
	99	72.56	97.94	1.096		157 HxCB	73.13	0.00	1.032
	126	11.84	1.00	1.349		189 HpCB	63.91	2.73	1.029
Hx Br	154	67.57	8.25	0.793		28 TriCB	71.37	2.38	0.994
	153	58.67	7.82	0.670		52 TCB	75.70	1.78	1.445
	140	45.43	0.83	0.905		101 PeCB	72.15	0.83	1.231
	138	25.91	1.51	0.649		153 HxCB	64.66	0.25	0.932
PCBs						138 HxCB	59.75	0.41	0.746
c-	77 TCB	58.51	203.00	0.915		180 HpCB	64.88	0.22	0.829
PC	81 TCB	46.42	22.50	0.913	Table 1 . LODs, RRF and recoveries for PBDEs and PCBs				
Bs	126 PeCB	86.10	6.26	0.959					
	169 HxCB	82.31	0.30	1.01					

Congeners		Parent ions (m/z)	CID	Daughter (m/z)
DiBDEs	C ₁₂	325.89	3.00	168
	C ₁₃	337.89	3.00	
TriBDEs	C ₁₂	403.8	3.50	246/248
	C ₁₃	415.8	3.50	
TBDEs	C ₁₂	481.72	3.75	324/326
	C ₁₃	493.72	3.75	
PeBDEs	C ₁₂	559.63	4.00	404/406
	C ₁₃	571.63	4.00	
HxBDEs	C ₁₂	637.54	4.75	482/484/486
	C ₁₃	649.54	4.75	
HpBDEs	C ₁₂	715.45	5.50	562/564
	C ₁₃	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 (¹³C- labelled PBDEs) whereas EI does, making the quantification more accurate ^{8,9}. 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 Eljarrat¹⁰ 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 Br₂ (PCBs lose Cl₂) 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-substitued congeners and for these compounds, daughter ions monitored was M-Br₂ 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-substitued 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.

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