

POLYBROMINATED FLAMES RETARDANTS

OPTIMIZATION OF CONGENER-SPECIFIC ANALYSIS OF 40 PBDES BY GC-MS

Ethel Eljarrat, Sílvia Lacorte, Damià Barceló

Dep. of Environmental Chemistry, IIQAB, CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain.

Introduction

In order to evaluate the global distribution and fate of PBDEs in the environment, a sensitive and comprehensive analytical method is required for their determination in environmental matrices. Several methods for qualitative and quantitative analysis of PBDEs have been developed involving GC-NCI-MS¹ or GC-EI-MS². Most of the analyses have concentrated on only a few specific major PBDE congeners. However, a reliable method for the separation and ultra-trace quantification of individual congeners is required to determine the extent of environmental exposure, the risk associated with specific congeners and their fate in the environment.

Given the lack of a method for the simultaneous determination of PBDEs, the purpose of this study is to develop a methodology for the congener-specific analysis of 40 different PBDEs (table 1). The study was based on: (i) the optimization of GC-NCI-MS analyses, (ii) the optimization of different parameters for GC-EI-MS, (iii) the characterization of each PBDE and (iv) the comparison between NCI and EI in their application to PBDE analyses.

Table1. List of the 40 PBDEs involved in this optimization study

<i>MonoBDEs</i>	<i>TriBDEs</i>	BDE # 66	<i>HexaBDEs</i>
BDE # 1	BDE # 17	BDE # 71	BDE # 138
BDE # 2	BDE # 25	BDE # 75	BDE # 140
BDE # 3	BDE # 28	BDE # 77	BDE # 153
	BDE # 30		BDE # 154
<i>DiBDEs</i>	BDE # 32	<i>PentaBDEs</i>	BDE # 155
BDE # 7	BDE # 33	BDE # 85	BDE # 166
BDE # 8	BDE # 35	BDE # 99	
BDE # 10	BDE # 37	BDE # 100	<i>HeptaBDEs</i>
BDE # 11		BDE # 105	BDE # 181
BDE # 12	<i>TetraBDEs</i>	BDE # 116	BDE # 183
BDE # 13	BDE # 47	BDE # 119	BDE # 190
BDE # 15	BDE # 49	BDE # 126	

Methods and Materials

Gas chromatography/mass spectrometry

GC-NCI-MS and GC-EI-MS analyses were performed on a gas chromatograph Agilent 6890 connected to a mass spectrometer Agilent 5973 Network (Agilent). A HP-5ms (30m x 0.25 mm i.d., 0.25 µm film thickness) containing 5 % phenyl methyl siloxane (model HP 19091S-433) capillary

POLYBROMINATED FLAMES RETARDANTS

column was used with helium as the carrier gas at 10 psi. The temperature program was from 110 °C (held for 1 min.) to 180 °C (held for 1 min.) at 8 °C/min., then from 180 °C to 240 °C (held for 5 min.) at 2 °C/min., and then from 240 °C to 280 °C (held for 6 min.) at 2 °C/min., using the splitless injection mode during 1 min.

The GC-NCI-MS operating conditions were as follows: ion source temperature between 130 and 250 °C, methane and ammonia as chemical ionization moderating gas at an ion source pressure between $1.2 \cdot 10^{-4}$ torr and $2.7 \cdot 10^{-4}$ torr. Initial experiments were carried out to optimize the NCI parameters such as chemical ionization moderating gas, source temperature and system pressure.

The GC-EI-MS operating conditions were as follows: ion source temperature between 130 and 250 °C, interface temperature at 270 °C, and ionization energy between 30 and 70 eV. Initial experiments were conducted to optimize the EI parameters such as source temperature and electron energy.

Quantification

Three different methods for quantification were tested: the external standard calibration, the internal standard calibration using the PCB # 209 as internal standard and the isotopic dilution method. The quantification by isotopic dilution method technique is based on the use of five ^{13}C -labeled standards: ^{13}C -tetraBDE # 47, ^{13}C -tetraBDE # 77, ^{13}C -pentaBDE # 99, ^{13}C -pentaBDE # 100 and ^{13}C -pentaBDE # 126, and could only be used with GC-EI-MS.

Results and Discussion

Mass spectra

Mass spectra depend strongly on the type of ionization used. For all the PBDEs studied, the NCI spectra were dominated by the mass fragment $[\text{Br}]^-$ ($m/z = 79, 81$), whereas the molecular cluster was not observed or constituted a minority peak. GC-NCI-MS on SIM mode was applied in order to enhance the sensitivity. The experiments were carried out monitoring the two most abundant isotope peaks from the mass spectra corresponding to $m/z = 79$ and 81 ($[\text{Br}]^-$), as well as additional fragment ions corresponding to $[\text{M}]^-$, $[\text{M}-\text{HBr}]^-$ or $[\text{M}-\text{HBr}_2]^-$. Chromatographic windows for each group of PBDE homologues (from mono- to hepta-BDEs) were defined. Each group of bromination eluted separately, with the exception of pentaBDEs and hexaBDEs, where the hexaBDE # 155 eluted before the pentaBDE # 105. It should be pointed that under the conditions used, the pentaBDE#126 co-eluted with the hexaBDE#155. Since all the PBDE congener spectra were dominated by the same mass fragment $[\text{Br}]^-$ ($m/z = 79, 81$), and these are the ions monitored in the NCI-MS-SIM experiments for quantitative purposes, the NCI system was not able to resolve this co-elution, and could not differentiate between the two compounds (Figure 1a).

Regarding to the EI analyses, significant features of these spectra include the sequential losses of bromine atoms. The GC-EI-MS on SIM mode experiments were carried out monitoring the two most abundant isotope peaks from the molecular ion region for each level of bromination, as well as an additional intense characteristic fragment ion corresponding to $[\text{M}-\text{Br}_2]^+$. The most intense peak from the molecular cluster was used for the quantification of the mono- to tetra-BDE congeners, while the fragment $[\text{M}-\text{Br}_2]^+$ was selected for the quantification of penta- to hepta-BDE congeners. Regarding the co-elution of the pentaBDE#126 with the hexaBDE#155 observed in the NCI study, it should be pointed that the EI-MS-SIM mode allowed the separation of these two compounds by monitoring selected ions of each bromination group (Figure 1b). Therefore, the EI mode gives a better selectivity than the NCI mode. This is one of the main advantages of EI.

Optimization of analytical parameters

Different experiments were conducted to optimize the $\text{NCI}(\text{NH}_3)$ parameters such as source

POLYBROMINATED FLAMES RETARDANTS

temperature and system pressure. Maximum abundances were obtained at $1.9 \cdot 10^{-4}$ torr and 250°C for practically all BDE congeners. Similar experiments were carried out to optimize the NCI (CH_4) parameters and maximum abundances were obtained at $2.7 \cdot 10^{-4}$ torr and 250°C for all BDE congeners. The optimization of the EI analyses was undertaken modifying the source temperature and the electron energy. Maximum abundances were obtained at 250°C and 35 eV. Similar conditions were used to analyze PCDDs and PCDFs by GC-EI-MS³.

Quantitative analysis

In order to evaluate the three different quantitative approaches tested, different quality parameters such as linearity, intra- and inter-assay variation and sensitivity were studied and compared. This study showed good inter- and intra-assay variations for the NCI mode, and slight differences were observed between $\text{NCI}(\text{NH}_3)$ and $\text{NCI}(\text{CH}_4)$. For the EI mode, these variations were greatly improved with the use of an isotope dilution method. Regarding the sensitivity, the better LODs were obtained with the GC-NCI-MS experiments: the NCI-MS gave detection limits between 30 fg and 1.72 pg, whereas EI-MS gave detection limits between 0.53 and 32.09 pg. Regarding the NCI system, the LODs were similar from the di- to hepta-BDEs; however, the sensitivity decreased considerably for the mono-BDEs. For the EI mode, the LODs increased with the bromination degree.

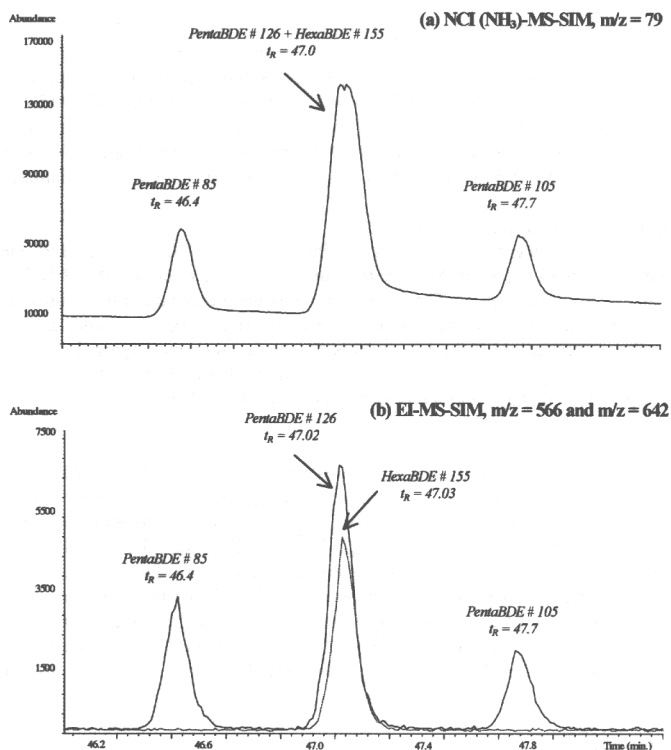


Figure 1. PentaBDE#126 and hexaBDE#155 chromatogram in (a) NCI-MS-SIM and (b) EI-MS-SIM conditions.

POLYBROMINATED FLAMES RETARDANTS

Acknowledgements

This work was financially supported by the Ministerio de Ciencia y Tecnología (PPQ2001-1805-CO3-01). R. Chaler and D. Fangul are thanked for assistance with the MS work.

References

1. de Boer J., van der Horst A. and Wester P.G. (2000) *Organohalogen Compd.* 47, 85
2. Ikonomou M.G., Fisher M., He T., Addison R.F. and Smith T. (2000) *Organohalogen Compd.* 47, 77
3. U.S.Environmental Protection Ag., EPA, Method 1613: ATetra through octa chlorinated dioxins and furans by isotopic dilution HRGC-HRMS. @, Washington DC, 1994.