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Potential chlorinated and brominated interferences on the polybrominated diphenyl ether determinations by gas chromatography–mass spectrometry

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Abstract

The analysis of polybrominated diphenyl ether (PBDE) congeners by GC–MS was studied in terms of potential interferences. Different MS approaches were normally used for the PBDE analyses: negative ion chemical ionization (NICI-MS) and electron ionization (EI-MS). This paper studied the presence of potential interferences in each instrumental technique approach, principally those corresponding to different chlorinated compounds (PCBs, PCNs, etc.) as well as brominated compounds (PBBs, MeO-PBDEs, TBBPA, etc.). The two ionization modes are subjected to different types of interferences. In general, EI-MS is affected by chlorinated interferences, especially PCBs. NICI-MS eliminated chlorinated interferences but presented different brominated interferences, well resolved with the EI-MS approach.

Keywords: Interference; Electron ionization; Negative ion chemical ionization; Polybrominated diphenyl ethers; Polychlorinated biphenyls

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used in large quantities for several applications including electrical appliances such as televisions and computers, building materials, and textiles due to their fire retarding properties [1]. The similarity in molecular structure of PBDEs with that of environmental toxic pollutants such as PCBs, PBBs, dioxins, etc., and their resistance to degradative processes, gives rise to concern that they may lead to similar environmental problems. PBDEs are suspected to cause endocrine dysfunction by interfering with the thyroid hormone metabolism [2,3]. Moreover, for many countries, decreasing levels of organochlorine compounds have been reported recently in human milk [4] while levels for PBDEs increased continuously since 1972 [5]. Due to these findings, there is a growing tendency to analyze PBDEs in various environmental and biotic matrices.

Analytical methodologies for persistent organic pollutant (POP) determinations are especially difficult due to the complexity of the mixtures of congeners (210 PCDDs/Fs, 209 PCBs, 75 PCNs, 209 PBDEs, etc.) and to the low detection limits required (ppb to ppq). Moreover, time consuming

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sample preparation steps are needed due to the presence of a large number of interfering compounds. Overcoming these analytical problems has only been possible with the application of rigorous clean-up schemes and by using GC coupled to MS. The clean-up steps provide a suitable removal of the bulk matrix and some interfering compounds; the GC allows an appropriate separation between the different congeners, and MS affords a sensitive and selective method of detection. Finally, an isotopic dilution technique based on the use of labelled standards provides a reliable quantification needed to accurately determine such analytes.

PBDEs and PCBs are structurally similar and have been shown to have similar chemical behaviour during sample preparation steps (extraction and clean-up). Several sample preparation methods for analysis of PBDEs have been developed [6], based on the application of similar schemes used for the PCB determinations. Regarding the instrumental analysis, qualitative and quantitative methods have been developed involving GC–negative chemical ionization (NICI)-MS [7,8] or GC–electron ionization (EI)-MS [9,10]. Generally, NICI presents higher sensitivity than EI but is less selective since only bromine can be monitored. Furthermore, it does not allow the quantification by isotopic dilution technique whereas EI does, making the analysis more reliable at trace levels. On the other hand, a dioxin-like GC–high resolution (HR)-MS based analytical method was developed for the determination of congener-specific PBDE compounds [11]. GC–HRMS in EI mode provided the most selective method and reasonable sensitivity for the determination of PBDEs. However, sophisticated and expensive instruments which require trained personnel and frequent maintenance are needed for HRMS. Therefore, the use of low resolution (LR)-MS is often preferred.

Environmental and biotic samples are usually polluted with a variety of compounds. The general problem in analysis of complex samples is that the extract obtained by exhaustive extraction techniques typically contains a large number of matrix components, which may co-elute with the analytes and disturb the quantitative analysis. The presence of interfering substances demands either a very selective detection or tedious extraction clean-up or even both. In this paper, potential interferences, principally those corresponding to chlorinated and brominated compounds, in each instrumental technique were studied.

2. Materials and methods

2.1. Standards and reagents

The Polybrominated Diphenyl Ether Analytical Standard Solution EO-5099 was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The components of EO-5099 solution were: three mono-BDEs (BDE-1, BDE-2 and BDE-3), seven di-BDEs (BDE-7, BDE-8, BDE-10, BDE-11, BDE-12, BDE-13 and BDE-15), eight tri-BDEs (BDE-17, BDE-25, BDE-28, BDE-30, BDE-32, BDE-33, BDE-35 and BDE-37), six tetra-BDEs (BDE-47, BDE-49, BDE-66, BDE-71, BDE-75 and BDE-77), seven penta-BDEs (BDE-85, BDE-99, BDE-100, BDE-116, BDE-118, BDE-119 and BDE-126), five hexa-BDEs (BDE-138, BDE-153, BDE-154, BDE-155 and BDE-166) and three hepta-BDEs (BDE-181, BDE-183 and BDE-190). Moreover, the mixture also contains 11 ^{13}C-labeled BDE congeners. The decachlorinated biphenyl (PCB-209) was purchased from Lab. Dr. Ehrenstorfer (Augsburg, Germany).

Solvents (dichloromethane and hexane) for organic trace analysis were purchased from Merck (Darmstadt, Germany). Neutral alumina (0.063–0.200 mm) and copper ($<$63 μm) were obtained from Merck, and Hydromatrix from Varian (Palo Alto, USA).

2.2. Sample preparation

It is well known that pressurized liquid extraction (PLE) allows a reduction of the extraction time. However, in most of the applications, an exhaustive clean-up of the extracts prior to injection in the chromatographic system is necessary. A selective PLE (SPLE) without further clean-up step was recently optimized for PBDE analysis. SPLE was carried out using a fully automated ASE 200 system (Dionex, Sunnyvale, CA, USA). In this method, a

22-ml extraction cell was loaded by inserting two cellulose filters into the cell outlet, followed by 6 g of alumina. Sediment samples were ground with alumina and copper (1:2:2). The mixture was loaded into the extraction cell on top of the alumina. The dead volume was filled with Hydromatrix, and the cell was sealed with the top cell cap. The extraction cell was heated to 100 °C and filled with *n*-hexane–dichloromethane (1:1) mixture until the pressure reached 1500 p.s.i. After an oven heat-up time of 5 min under these conditions, two static extractions of 10 min at constant pressure and temperature were developed. After this static period, fresh solvent was introduced to flush the lines and cell, and the extract was collected in the vial. The flush volume amounted to 100% of the extraction cell. The extraction was cycled twice. The volume of the resulting extract was about 35 ml. Extracts were finally concentrated to incipient dryness and re-dissolved with 10 μl of the recovery standard (PCB-209, 100 pg/μl) and 40 μl of isooctane prior to the analysis by GC–MS.

2.3. Chromatographic separation

GC–MS analyses were performed on an Agilent 6890 gas chromatograph connected to an Agilent 5973 Network mass spectrometer (Agilent Technologies, Madrid, Spain). A HP-5ms (30 m×0.25 mm I.D., 0.25 μm film thickness) containing 5% phenyl methyl siloxane (model HP 19091S-433) capillary column was used for the determination of congeners from mono- to hepta-BDEs. 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 to 240 °C (held for 5 min) at 2 °C/min, and then from 240 to 265 °C (held for 6 min) at 2 °C/min, using the splitless injection mode during 1 min. Using these chromatographic conditions, different time windows were performed in selected ion monitoring (SIM) (Fig. 1).

Additional experiments were carried out using a HP-5ms (60 m×0.25 mm I.D., 0.25 μm film thickness). The temperature program used for these experiments was from 110 °C (held for 1 min) to 180 °C (held for 1 min) at 8 °C/min, then from 180 to 240 °C (held for 5 min) at 2 °C/min, and then from 240 to 310 °C (held for 20 min) at 2 °C/min.

2.4. Mass spectrometric detection

Table 1 shows the settings of the GC–EI-MS system. The two most abundant isotope peaks for each level of bromination, corresponding to molecular cluster for mono- to tri-BDEs and $[M-Br_2]^+$ for tetra- to hepta-BDEs, were monitored. When quantification is done using the isotopic dilution method, the labelled masses must be added to the experiment. Moreover, the detection was divided into different groups according to the chromatographic windows previously defined (Fig. 1). The GC–EI-MS operating conditions were as follows: ion source temperature, 250 °C; interface temperature, 270 °C; ionization energy, 35 eV. These conditions were previously optimised in order to obtain maximum sensitivity [12].

Table 2 presents the settings of the GC–NICI-MS system. In this case, the two most abundant isotope peaks from the mass spectra were also monitored, corresponding to *m*/*z* 79 and 81 ($[Br]^-$) for all degrees of bromination. Additional masses, corresponding to deca-CB, were monitored in both experiments. In the literature, PCB-209 was normally used as an internal standard in PBDE determinations. The GC–NICI-MS operating conditions were as follows: ion source temperature, 250 °C; ammonia as chemical ionization moderating gas at an ion source pressure of 1.9×10^{-4} Torr.

3. Results and discussion

On a HP-5ms chromatographic column, PBDEs are eluted in order of increasing bromine number. Fig. 1 show a GC–EI-MS chromatogram obtained following the injection of a standard mixture containing 40 from mono- to hepta-BDE congeners. Different ion traces were monitored in the SIM mode, corresponding to each degree of bromination: *m*/*z* 248, 328, 406, 326, 406, 484 and 564. As it can be seen, the latest mono-BDE congener (BDE-3) eluted before the first di-BDE congener (BDE-10), and the latest di-BDE congener (BDE-15) eluted before the first tri-BDE congener (BDE-30), etc. However, some coelution between penta- and hexa-congeners was observed, i.e. hexa-BDE-155 was eluted before penta-BDE-105.

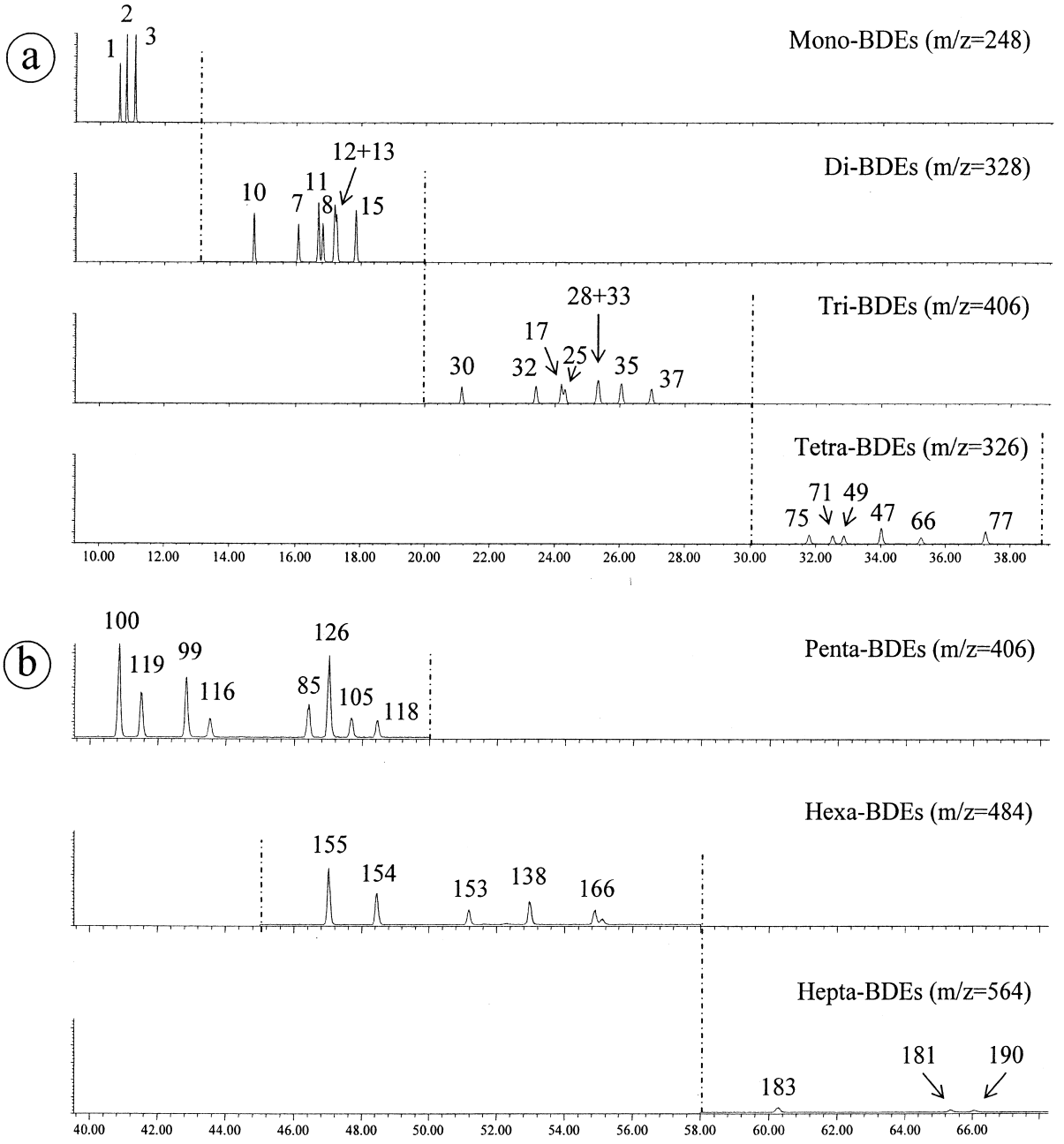

Fig. 1. Chromatogram of a standard solution containing 40 PBDE congeners at 100 pg/μl, by GC–EI-MS (SIM) using a HP-5ms (30 m) chromatographic column: (a) mono- through tetra-BDE congeners (10–40 min), and (b) penta- through hepta-BDE congeners (40–68 min).

For some halogenated contaminants (PCDDs, PCDFs, PCBs), chromatographic separation of different congeners requires the use of at least two columns with different composition and polarity. Isomer-specific elution patterns of these compounds are well established for widely used columns [13–15]. A few studies were published regarding the PBDE elution pattern [16]. De Boer et al. [6]

Table 1
Selected ions for the GC–EI-MS-SIM experiments

Compound	Window (min)	Ions monitored from molecular cluster			
MonoBDEs	4:00 to 13:00	248	$[M]^+$	250	$[M+2]^+$
^{13}C-MonoBDEs		260	$[M]^{+a}$	262	$[M+2]^{+a}$
DiBDEs	13:00 to 20:00	326	$[M]^+$	328	$[M+2]^+$
^{13}C-DiBDEs		338	$[M]^{+a}$	340	$[M+2]^{+a}$
TriBDEs	20:00 to 30:00	406	$[M+2]^+$	408	$[M+4]^+$
^{13}C-TriBDEs		418	$[M+2]^{+a}$	420	$[M+4]^{+a}$
TetraBDEs	30:00 to 39:00	326	$[M+2-Br_2]^+$	328	$[M+4-Br_2]^+$
^{13}C-TetraBDEs		338	$[M+2-Br_2]^{+a}$	340	$[M+4-Br_2]^{+a}$
PentaBDEs	39:00 to 45:00	406	$[M+4-Br_2]^+$	408	$[M+6-Br_2]^+$
^{13}C-PentaBDEs		418	$[M+4-Br_2]^{+a}$	420	$[M+6-Br_2]^{+a}$
PentaBDEs	45:00 to 50:00	406	$[M+4-Br_2]^+$	408	$[M+6-Br_2]^+$
^{13}C-PentaBDEs		418	$[M+4-Br_2]^{+a}$	420	$[M+6-Br_2]^{+a}$
HexaBDEs		484	$[M+4-Br_2]^+$	486	$[M+6-Br_2]^+$
^{13}C-HexaBDEs		496	$[M+4-Br_2]^{+a}$	498	$[M+6-Br_2]^{+a}$
DecaCB		498	$[M+4]^+$	500	$[M+6]^+$
HexaBDEs	50:00 to 58:00	484	$[M+4-Br_2]^+$	486	$[M+6-Br_2]^+$
^{13}C-HexaBDEs		496	$[M+4-Br_2]^{+a}$	498	$[M+6-Br_2]^{+a}$
HeptaBDEs	58:00 to 67:00	564	$[M+4-Br_2]^+$	566	$[M+6-Br_2]^+$
^{13}C-HeptaBDEs		576	$[M+4-Br_2]^{+a}$	578	$[M+6-Br_2]^{+a}$

[a] Labeled with ^{13}C.

reported that a good separation can be obtained for most PBDE congeners using 50-m columns. However, more studies are required in order to determine potential coelutions between PBDE congeners.

Developed methods for PBDE determinations included GC coupled with either NICI- or EI-MS. A previous study comparing the capabilities of both approaches for PBDE determination has been published [12]. Using NICI, the mass spectra of all PBDEs were dominated by the $[Br]^-$ ion and did not show the molecular ions. However, EI provided better structural information, giving the molecular ions and the sequential losses of bromine atoms (Fig. 2). On the other hand, NICI showed better sensitivity, with lower detection limits (between 30 fg and 2 pg). Since some PBDE ^{13}C-labeled standards are readily available, use of these standards is preferred over external or internal calibration techniques. However, the quantification by isotopic dilution method could only be used with GC–EI-MS.

3.1. Interferences on the EI-MS approach

The detection and measurement of the molecular

Table 2
Selected ions for the GC–NICI-MS-SIM experiments

Compound	Window (min)	Ions monitored from molecular cluster			
MonoBDEs	4:00 to 45:00	79	$[^{79}Br]^-$	81	$[^{81}Br]^-$
DiBDEs					
TriBDEs					
TetraBDEs					
PentaBDEs					
PentaBDEs	45:00 to 50:00	79	$[^{79}Br]^-$	81	$[^{81}Br]^-$
HexaBDEs					
DecaCB		498	$[M+4]^-$	500	$[M+6]^-$
HexaBDEs	50:00 to 67:00	79	$[^{79}Br]^-$	81	$[^{81}Br]^-$
HeptaBDEs					

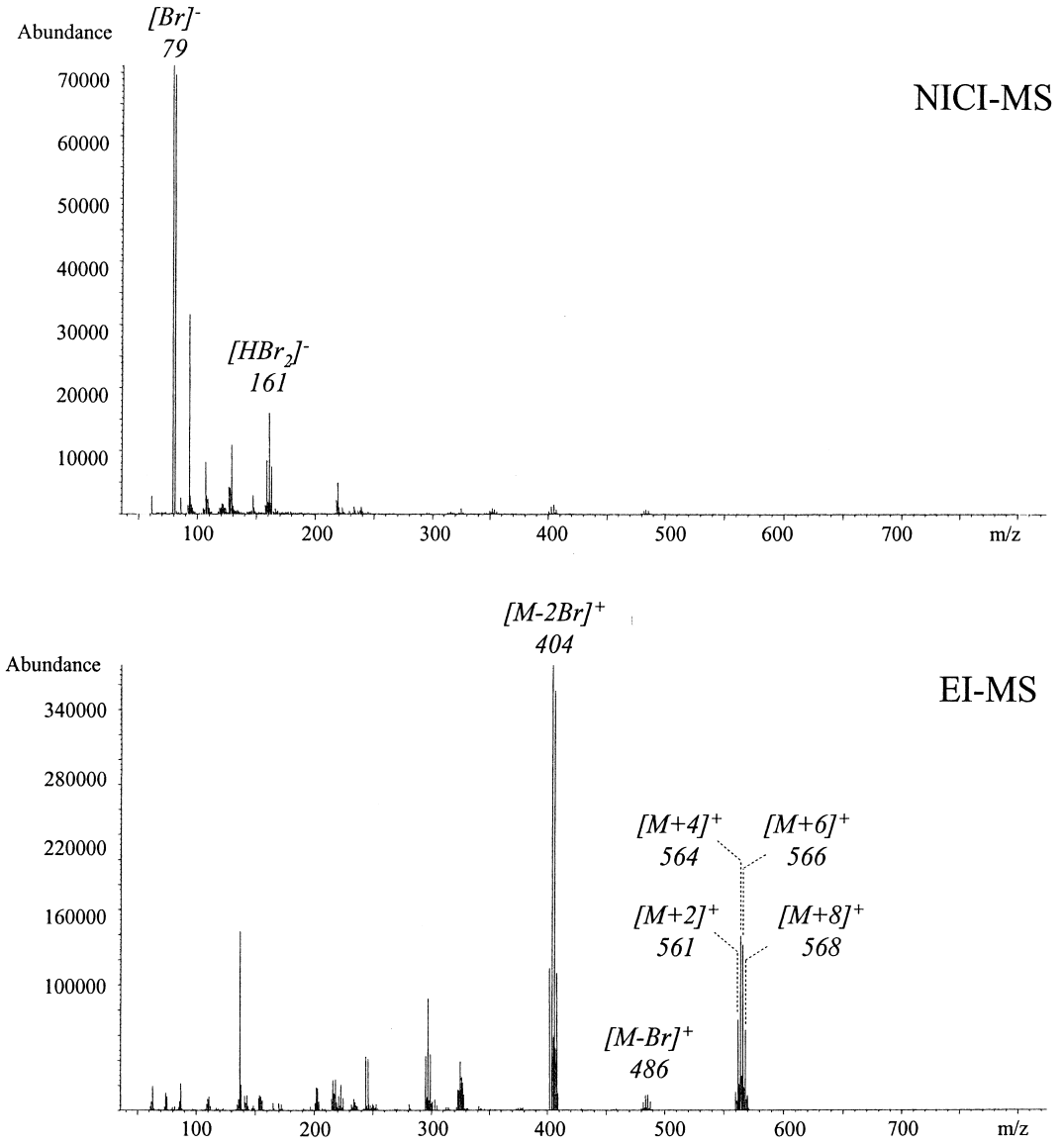

Fig. 2. Mass spectra of BDE-99 using NICI-MS and EI-MS approaches.

ions produced by a member of a given isomer group may be interfered with the $[M-2Br]^{+\bullet}$ fragment ions of homologues with two additional bromine atoms. However, the chromatographic separation obtained allows work without the risk of internal contribution. As mentioned before, different chromatographic windows could be defined according to each degree of bromination.

3.1.1. Potential PCB interferences

Environmental and biotic samples are frequently contaminated with both PBDEs and PCBs. Moreover, the analytical procedures for PBDE analyses available today are mainly based on already available analytical methods for PCB quantification. Thus, purified extracts contained both PCBs and PBDEs, and the GC–EI-MS analysis could be affected by

Table 3
Potential interferences and theoretical resolution needed to resolve the different coelutions

Homologue	Fragment	m/z	Homologue	Fragment	m/z	Resolution
PBDEs			PCBs			
Di-BDEs	M	325.8942	Penta-CBs	M+2	325.8804	24 000
Tetra-BDEs	M−2Br	323.8785	Hepta-CBs	M−2Cl	323.8647	23 500
PBDEs			PCTs			
Penta-BDEs	M−2Br	403.7870	Penta-CTs	M+4	403.9088	3300
PBDEs			PCNs			
Penta-BDEs	M−2Br	403.7870	Octa-CN	M+4	403.7450	9600
PBDEs			PCDFs			
Penta-BDEs	M−2Br	405.7849	Hepta-CDFs	M	405.7847	2 030 000
PBDEs			MeO-PBDEs			
^{13}C-Penta-BDEs	M+4	417.8253	MeO-Tetra-BDEs	M−CH_3Br	417.7840	10 100

PCB interferences. Few of the ions commonly used for the determination of di-, tetra- and penta-BDE homologue groups are isobaric with penta- and hepta-CB homologue groups (Table 3). For example, the nominal masses corresponding to ions monitored for di-BDEs and penta-CBs are the same (m/z = 326). Their exact masses are different being 325.8942 for di-BDEs and 325.8804 for penta-CBs. An RP of 24 000 is needed to separate the two ions. However, it is not recommended to work at such elevated resolutions due to the significant loss of sensitivity.

Fig. 3 shows an example of the above mentioned PCB interference on a sediment sample analysis. Identification of PBDEs was based on the following restrictive criteria: (i) retention times of chromatographic peaks must be within the appropriate chromatographic windows; (ii) simultaneous responses for the two masses monitored must be obtained; and (iii) relative isotopic peak ratios must be within ±15% of the theoretical values. In our EI chromatogram example, (i) and (ii) were accomplished, and two different peaks at retention time (t_R) 11.39 and 14.54 were detected. However, calculated isotopic ratios were 1.59 and 0.74, respectively, whereas the theoretical value of compounds with two bromine atoms is 0.51. The first eluting peak (t_R = 11.39) could be a penta-CB interference: the theoretical value of the isotopic ratio between penta-CB (M+2, m/z 326) and penta-CB (M+4, m/z 328) is 1.53,

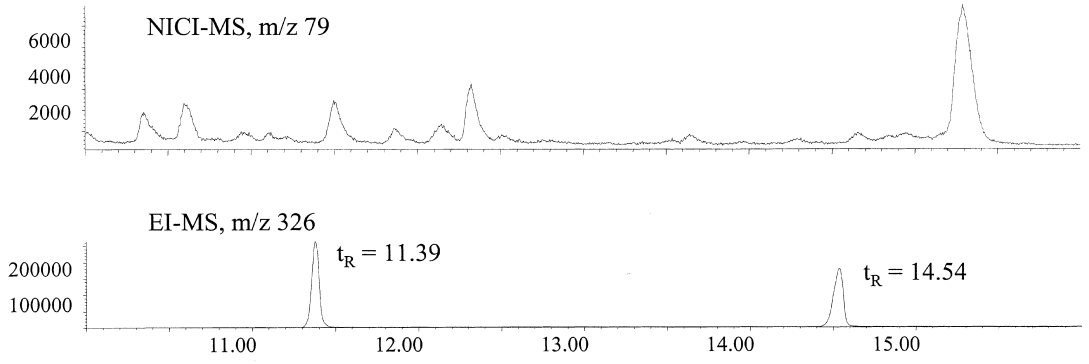

Fig. 3. Di-BDE chromatograms obtained by both NICI-MS and EI-MS approaches for a sediment sample. The two major peaks observed in EI are interferences, which were solved using NICI.

matching reasonably well with our experimental value (1.59). The second chromatographic peak has an isotopic ratio very different from 1.53 (0.74); however, it should be noted that the peak shape indicated that some coelution occurred, distorting the isotopic ratio.

To solve this PCB interference, NICI mode could be applied. In the NICI system, m/z 79 and 81 corresponding to bromine ions were monitored and thus chlorinated interferences were eliminated. Fig. 3 also shows the NICI chromatogram for the same sediment sample. Interferences detected using the EI approach at t_R 11.39 and 14.54 were not present in the NICI chromatogram. Moreover, using the NICI approach, different di-BDEs were detected at low levels. The interferences observed using EI were detected at high levels, and that because they masked potential di-BDEs present in the sample. However, it should be noted that the use of NICI provided less structural information than EI.

On the other hand, hepta-CBs interfered with tetra-BDEs. The monitored mass selected for tetra-BDE detection, corresponding to M−2Br, has the same nominal mass as that corresponding to hepta-CBs when losing two chlorine atoms (Fig. 4). In this case, high RP is also required to solve this interference (RP 23 500). Moreover, under the chromatographic conditions used, hepta-CBs eluted in the same chromatographic window as tetra-BDEs. Fig. 5 shows the chromatograms obtained following the

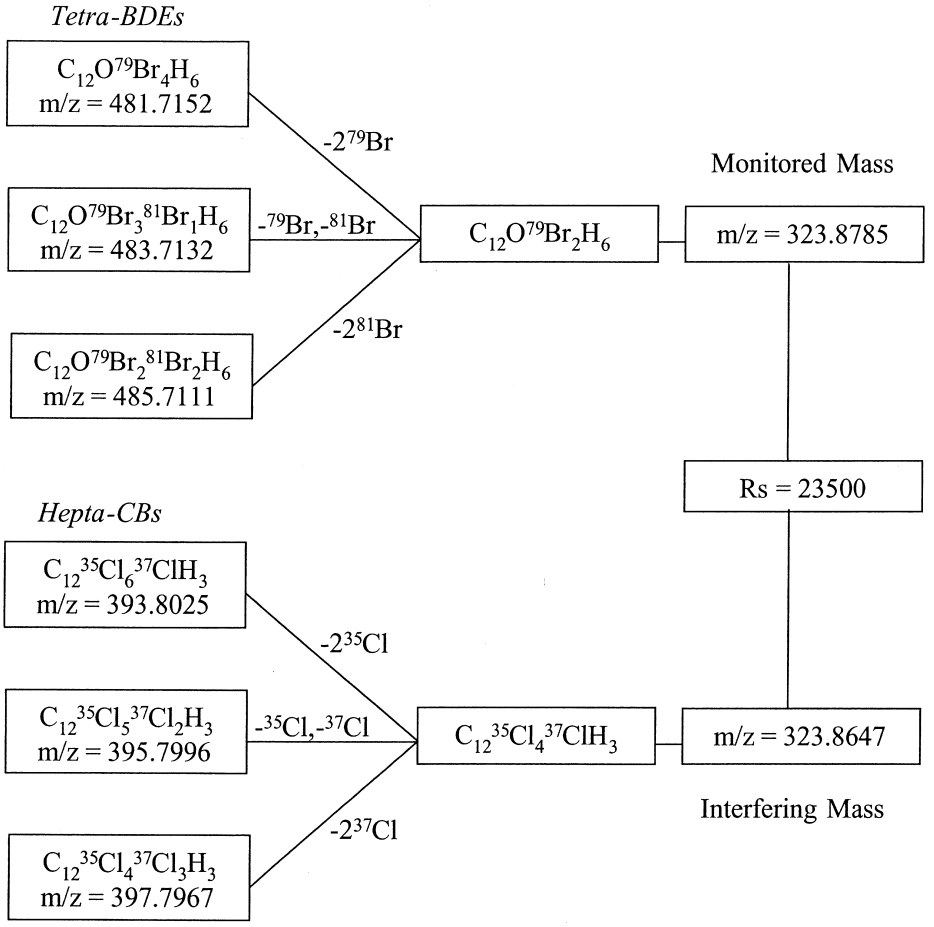

Fig. 4. Interferences between tetra-BDEs and hepta-CBs. An RP of 23 500 is needed to resolve the ions obtained by losses of two bromine and two chlorine atoms, respectively.

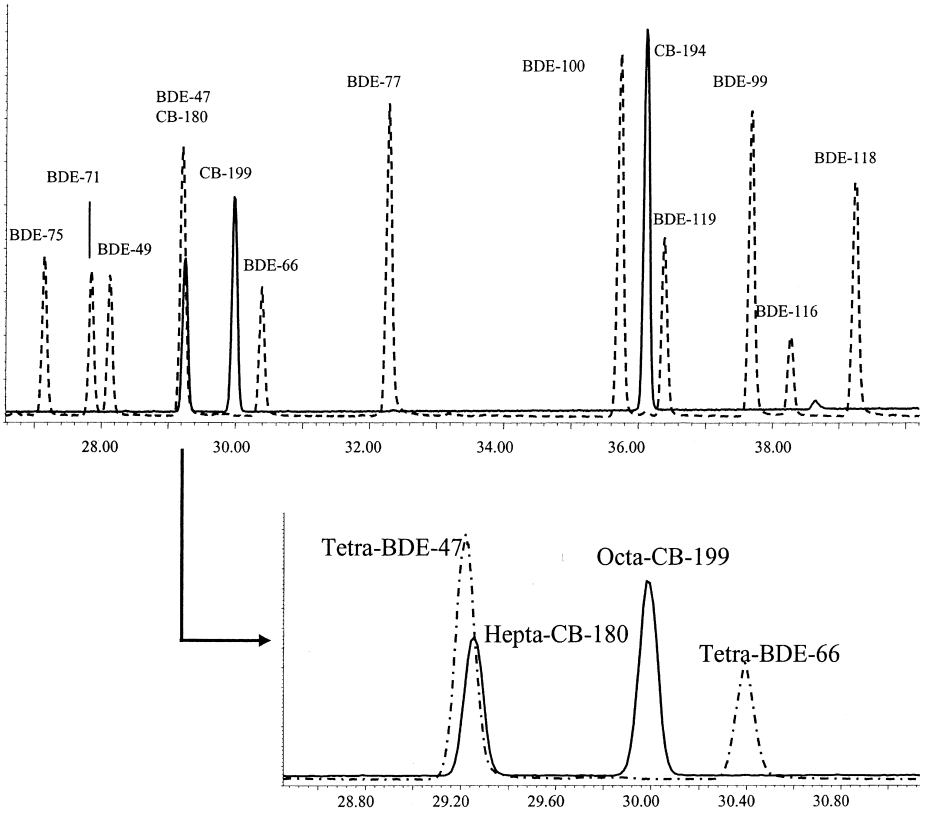

Fig. 5. TIC obtained following the co-injection of PBDE and PCB standard mixtures. Hepta- and octa-CBs eluted within the chromatographic window defined for tetra- and penta-BDEs. BDE-47 and CB-180 eluted at the same retention time.

injection of a PBDE as well as PCB standard mixtures. As can be seen, some hepta- (CB-180) and octa-CBs (CB-199) eluted with tetra-BDEs. Moreover, some octa-CBs (CB-194) eluted with penta-BDEs. Special attention must be paid to the coelution of tetra-BDE-47 and hepta-CB-180; both contaminants eluted at t_R 29.20. This coelution was previously reported by other authors [17,18]. Manchester et al. [18] reported a successful separation of BDE-47 from CB-180 with the same chromatographic column used in our study. However, their time run was 150 min whereas our chromatographic program was accomplished in 70 min.

Another option to solve the hepta-CB interferences could be applied, using the EI-MS approach. Monitoring ions from the molecular peak, i.e. m/z 484 (M+2) and 486 (M+4), instead of the selected ions in our experiment (M−2Br), produces a less sensitive response but without hepta-CB contributions. The m/z 486 ion gives approximately a two times lower response than that obtained monitoring the m/z 326 ion.

3.1.2. Other theoretical chlorinated interferences

Table 3 shows other potential chlorinated interferences on the PBDE determinations. PCN is another contaminant group present in environmental and biotic samples, and with similar properties to PBDEs or PCBs. Different PCN congeners could also interfere in the GC–EI-MS analysis of PBDEs. Using the sample preparation methods applied for PCBs or PBDEs, purified extracts will contain also potential PCNs. Penta-BDEs could be interfered with the octa-CN congener. An RP of 9600 is required to distinguish between the monitored mass (m/z 403.7870, M−2Br) and the interfering mass (m/z 403.7450, M+4). Polychlorinated terphenyls (PCTs) could also be a potential interference on the penta-BDE analy-

sis. In this case, an RP of 3300 allowed a satisfactory detection of the monitored mass for penta-BDEs. These two examples showed the advantages of the HRMS methods developed for PBDE determinations. The usual RP applied (RP 10 000) is sufficient to eliminate PCN or PCT interferences.

Finally, Table 3 shows an example of a possible interference between penta-BDEs and hepta-CDFs. In this case, exact masses of two compounds are not the same, but they are very close: 405.7849 for penta-BDEs and 405.7847 for hepta-CDFs. The theoretical RP value was calculated, with RP$>2\times 10^6$ as a minimum requirement to discriminate between two compounds. However, different sample preparation methods were developed collecting PCBs, or PBDEs, and PCDDs/Fs in different fractions.

3.1.3. Brominated interferences published in the literature

Although chlorinated compounds constitute the principal group of potential interferences in the EI-MS system, some brominated compounds could also interfere with the PBDE determinations. Methoxy-polybrominated diphenylethers (MeO-PBDEs) have been identified and quantified in various biotic samples [19]. They have been reported as natural products most frequently found in marine sponges, as well as metabolites of PBDEs. One MeO-tetra-BDE congener and one MeO-monochloro-tetra-BDE were found to coelute with BDE-100 and BDE-99, respectively, using a DB-5 column [20]. Moreover, fragmentation of MeO-PBDEs giving a mass fragment of 418 was detected [19]. This fragment corresponded to CH_3Br loss. The same fragmentation is well documented for *ortho* methoxy polychlorinated and polybrominated biphenyls [21,22]. The m/z 418 fragment could interfere with the mass ion selected to monitor ^{13}C-penta-BDEs, used as internal standard in the isotopic dilution methodologies (Table 3). It should be noted that ^{13}C-BDE-100 is normally present in commercial surrogate spiking solutions (Cambridge Isotope Laboratories, MA, USA; Wellington Laboratories, Guelph, ON, Canada). The application of high resolution (RP 10 000) may resolve the masses of coeluting compounds, and thus the quantification by isotopic dilution technique could be applied.

3.2. Interferences on the NICI-MS approach

Potential coelutions between BDE congeners with different degree of bromination represented a possible interference in the NICI-MS method. As an example, Fig. 6 shows the coelution between penta-BDE-126 and hexa-BDE-155. Since all the PBDE congener spectra were dominated by the same mass fragment $[Br]^-$ (m/z 79, 81) in the NICI-MS-SIM experiments, this system was not able to resolve this coelution, and could not differentiate between the two compounds. A successful separation of BDE-126 from BDE-155 could be obtained using a 60-m chromatographic column. However, t_R of these BDE congeners increased with respect to those obtained with a 30-m column: from 41.81 min to 59.38 and 59.54 min, respectively.

The same interferences observed in the EI-MS approach due to losses of bromine atoms are present in the NICI-MS system. However, as mentioned before, an experiment divided on different chromatographic windows eliminated the risk of these contributions.

Other bromine interferences in the NICI method solved by the use of the EI approach are the following two critical chromatographic pairs: BDE-154 and PBB-153, and BDE-153 and tetrabromobisphenol-A (TBBPA), which coelute in many cases [6]. EI-MS normally offers enough selectivity for the identification and quantification of TBBPA (m/z 540) and BDE-153 (m/z 484) even when they coelute. The same occurs with the pair formed by BDE-154 (m/z 484) and PBB-153 (m/z 622). However, using NICI-MS, the simultaneous presence of PBDEs, PBBs and TBBPA in the same extract could result in erroneous PBDE quantifications.

The presence of MeO-PBDEs interfered with the penta-BDE determinations by NICI. The same interference was observed in EI-LRMS experiments, as explained above. However, the isotopic ratio calculation in EI indicated that some interference is present. This isotopic ratio is different for a tetra- and for a penta-brominated compound, being 0.51 and 1.03, respectively. In contrast, the isotopic ratio in NICI is 1.03 for all the brominated compounds. Thus, the presence of MeO-PBDEs coeluting with PBDEs resulted in an overestimation of some of the PBDE concentrations.

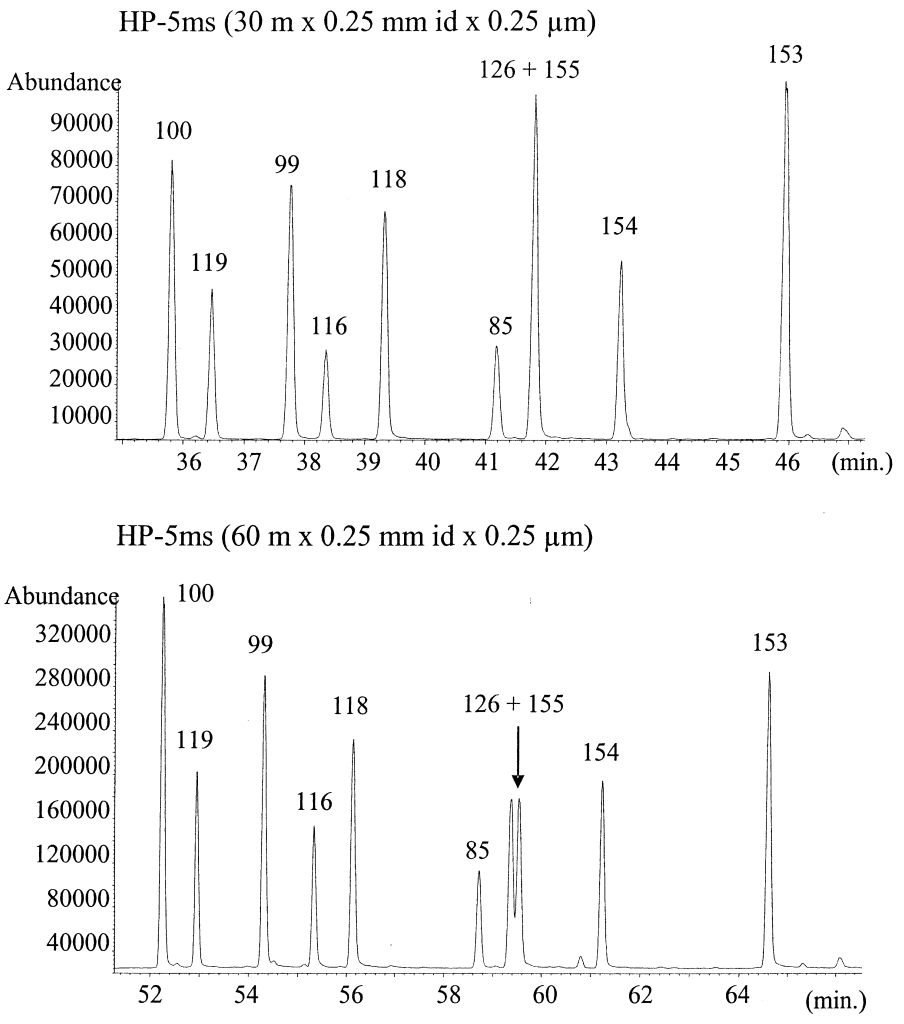

Fig. 6. Chromatogram of a standard solution containing different PBDE congeners at 10 pg/μl, by GC–NICI-MS (m/z 79) using HP-5ms (30 m) and HP-5ms (60 m) chromatographic columns.

4. Conclusions

In general, GC–EI-MS provided better structural information, giving the molecular ions and the sequential losses of bromine atoms. However, this technique is affected by different chlorinated interferences. Few of the ions commonly used for the PBDE determinations are isobaric with some chlorinated contaminants normally present in environmental and biotic samples. GC–NICI-MS eliminated chlorinated interferences and also showed better sensitivity, but the use of NICI provided less structural information than that provided by EI. The NICI approach was not able to resolve potential coelutions between BDE congeners with different degrees of bromination, and also presented different brominated interferences. These bromine interferences well resolved with the EI-MS approach, could lead to erroneous PBDE quantifications in the NICI mode. For example, PBB-153 coeluted with BDE-154, TBBPA with BDE-153, one MeO-tetra-BDE congener with BDE-100, or one MeO-monochloro-tetra-BDE with BDE-99. Moreover, isotopic ratio criteria cannot be applied in the NICI approach: all the

brominated compounds give the same isotopic ratio. The identification criteria were thus reduced to the retention time.

PCBs constitute one of the principal group of potential interferences in the EI-MS system. Environmental and biotic samples are frequently polluted with both PBDEs and PCBs. Moreover, due to similar chemical properties, it is very difficult to develop protocols in which PCBs and PBDEs were collected in two separate fractions. The application of HRMS did not solve the PCB interferences. A very high RP must be applied (more than 20 000), with the consequent loss of sensitivity. Other chlorinated interferences, like PCNs or PCTs, were well resolved applying the established HRMS methodologies (working at RP 10 000). To eliminate PCB interferences, longer chromatographic programmes could be developed in order to avoid coelutions between PBDE and PCB congeners. On the other hand, additional research is needed to develop sample preparation methodologies in which PCBs and PBDEs were collected in two different extract fractions, avoiding potential instrumental interferences.

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