

Monofluorinated analogues of polybrominated diphenylethers (F-PBDEs) - standards for analysis: retention behaviour in gas chromatography

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Introduction

Polybrominated diphenyl ethers (PBDEs) are globally distributed in the environment. Over the past two decades, they have been used as flame retardants [1]. PBDEs have been found to bioaccumulate. There is a concern about the health effects of PBDE exposure, because of their potential endocrine disrupting properties. PBDEs are structurally similar to polychlorinated biphenyls (PCBs), dibenzodioxines and dibenzofuranes.

Therefore, they have to be determined very frequently at the trace level in, *e.g.* water, food, sediment and soil. The sample preparation and final determination may well lead to systematic and non-systematic (random) errors. It is generally accepted that the accurate determination of micro contaminants in such complex mixtures requires the use of external or, preferably, internal standards (ISs). The benefit of using ISs with physico-chemical properties similar to those of the target compounds, is that both types of errors will be minimized.

While preliminary work on monofluorinated polycyclic aromatic hydrocarbons (F-PAHs) as ISs in gas chromatography (GC) was very promising [2], we recently synthesized [3] a series of monofluorinated polybrominated diphenylethers (F-PBDE). We found that they are a very promising set of internal standards for trace-level analysis of PBDEs and are alternatives to ¹³C-labelled analogues. In the present study, we focused attention on the retention behavior of F-PBDEs in GC, with the intention to use them as calibration standards for electron impact mass spectrometry (EI-MS) and GC-MS in the negative chemical ionisation mode (ECNI) GC-ECNI-MS.

Materials and Methods

Chemicals

The following F-PBDEs were synthesized [3], the numbers behind the names refer to the official numbers of the corresponding parent PBDEs: 3-Bromo-4'-fluorodiphenyl ether (2), 4-Fluoro-3,3'-di-bromodiphenyl ether (11), 4'-Fluoro-2,3',4-tribromo-diphenyl ether (25), 4'-Fluoro-2,3',6-tribromodiphenyl ether (27), 3'-Fluoro-2,4,4'-tribromodiphenyl ether (28), 6-Fluoro-2,2',4,4'-tetrabromodiphenyl ether (47), 6-Fluoro-2,3',4,4'-tetrabromodiphenyl ether (66), 4'-Fluoro-2,3',4,6-tetrabromodiphenyl ether (69), 3-Fluoro-2,2',4,4',6-pentabromodiphenyl ether (100), 3-Fluoro-2,3',4,4',6-penta-bromodiphenyl ether (119), 4'-Fluoro-2,3,3',4,5,6-hexabromodiphenyl ether (160), 3-Fluoro-2,2',4,4',5',6-hexabromodiphenyl ether (154), 3-Fluoro-2,2',4,4',5,5',6-heptabromodiphenyl ether (183), 6,4'-Difluoro-2,2',3,3',4,5,5',6'-octabromodiphenyl ether (199), 4'-Fluoro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether (208).

GC-MS

Analyses of three mixtures, PBDEs, F-PBDEs and PBDEs with the corresponding F-PBDEs, were carried out on a HP 6890 (Hewlett Packard, Palo Alto, CA, USA) gas chromatograph with MS detection. Briefly, 1- μ l volumes of the samples were injected. Separation was performed on a Restek XTI-5 capillary column (30 m \times 0.25 mm I.D., 0.25 μ m film thickness). Helium was used as the carrier gas at a column head pressure of 97 kPa. The split flow was 120 ml/min. The split less time was 1.5 min. The column temperature was programmed from 103°C (4.5 min) to 280°C at 12°C/min. The final temperature was held for 20 min.

Detection was based on the simultaneous registration, at the appropriate retention time, of the signals corresponding to the two m/z values selected for each analyte.

Results and discussion

The unusually small but administrable effect of fluorine monosubstitution on the properties of aromatic hydrocarbons, like F-PBDEs, can be qualitatively understood by considering the influence of a fluorine atom on an aromatic system. First, fluorine induces a dipole moment, though not as strong as one might expect. The small fluorine atom is too hard to retain the complete electron charge. In addition, hyperconjugation caused by overlap of the aromatic π -orbitals and the free fluorine p-orbitals, results in a partial transfer of the charge back to the aromatic system [4]. Secondly, as regards intermolecular interactions, as a result of the reduced polarisability, the London forces are less strong for F-PBDEs than for the parent PBDEs. The latter effect is antagonistic to the effect of an increased permanent dipole moment and is of similar magnitude. Consequently, the overall effect of fluorine substitution has two antagonistic effects: the creation of a permanent dipole moment and the reduction of the London forces. As a result, F-PBDEs are surprisingly similar to their corresponding parent PBDEs in terms of physico-chemical properties. A simple model of the electronic effects of fluorine substitution is shown in Fig. 1.

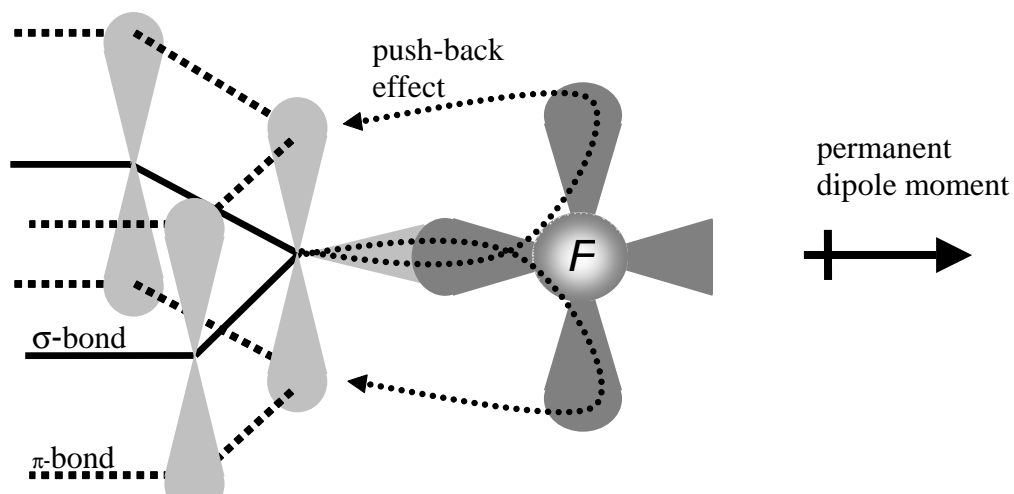


Fig. 1: Model of the electronic effects of fluorine substitution on an aromatic system

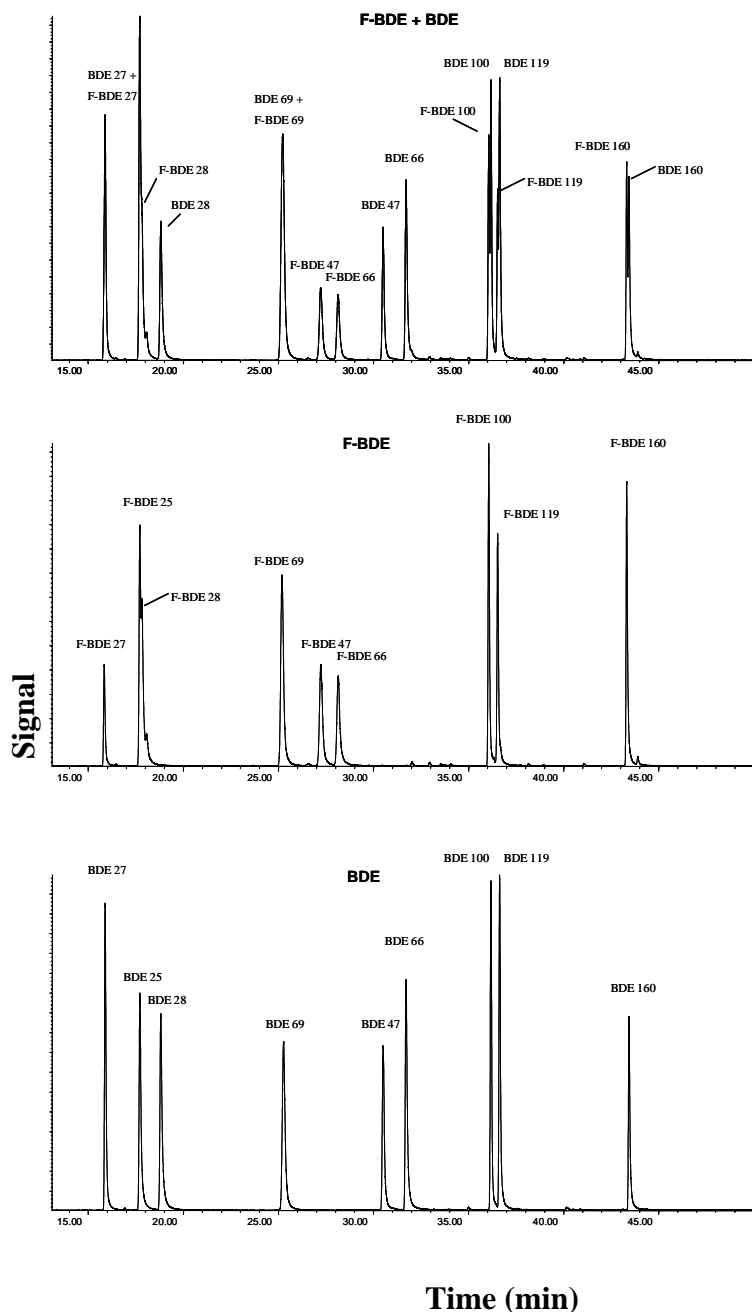


Fig. 2: GC-MS of nine F-PBDE/PBDE pairs (50 ng/ml each in *iso*-octane). Conditions: m/z 35–400; for other details, see Materials and Methods.

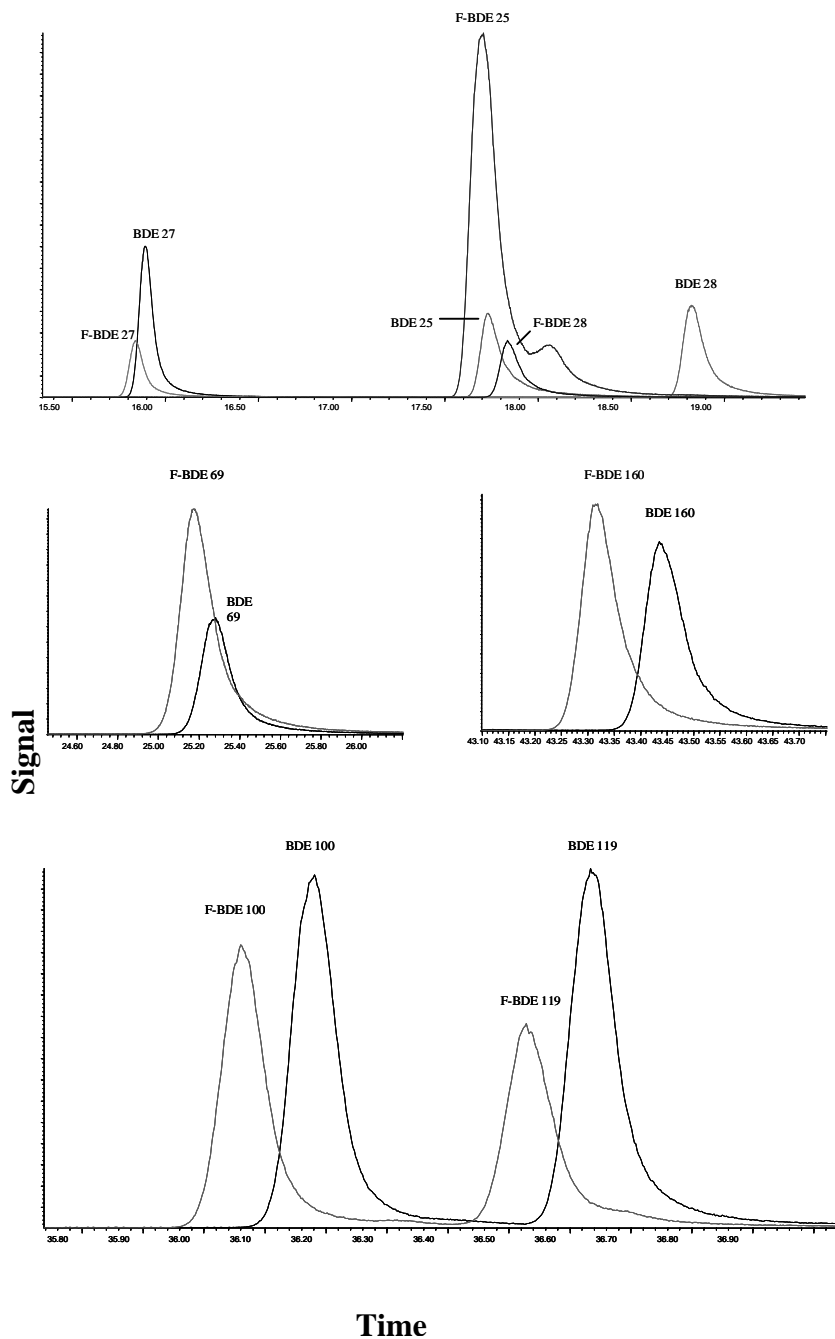


Fig. 3: Extended view of the separation of F-PBDE/PBDE pairs.

Depending on the fluorine substitution in *ortho*-, *meta*- or *para*-position, the retention behaviour compared to the corresponding parent PBDEs is different. As shown in the Fig. 2 and 3, all F-PBDEs in general have shorter or identical retention times because they are slightly more non-polar. The reduction of the London force is variable compensated by the introduction of the permanent dipole moment. This depends on the pattern of fluorine substitution. The four F-PBDEs (25), (27), (69) and (100) fluorine substituted in the *para*-positions, co-elute with their corresponding parent PBDE. Because of the higher degree of bromination and longer retention time, F-PBDE (160) can be partly separated. The permanent dipole moment caused by fluorine in the *para* position is the strongest. Here, the compensation of the reduction of the London force is almost reached. The F-PBDE congeners (28), (100) and (119) are substituted in the *meta*-positions. The monofluorinated congener (28) is well separated, (100) and (119) show a small overlap with the corresponding parent PBDEs. This last observation can be explained by the high degree of bromination of the fluorinated aromatic ring. Because of the extension of the delocalisation of the electron density, the impact of the permanent dipole moment created by fluorine is decreased. The F-PBDEs (47) and (66) are *ortho*-substituted by fluorine. They show up to three minutes shorter retention times. This has two reasons. First the impact of the permanent dipole moment is the weakest in this position. Secondly, the conformation is changed partly by steric hindrance.

In this paper, the behavior of nine F-PBDEs - which were synthesized by us - in GC-MS, is discussed for the first time. The main conclusion is that mono-substitution with fluorine causes only slight differences in retention behavior. Mainly depending on the *ortho*-, *meta*- or *para* position of fluorine substitution we observe complete or partial co-elution or separation of each F-PBDE/PBDE pair.

This opens the way to use electron capture detection ECD instead of or in addition to MS. Furthermore, the difference between the molecule ions of the F-PBDE/PBDE pairs is m/z 18, which allows a simultaneous detection without separation using MS in the electron impact (EI) mode. F-PBDEs are valuable internal standards, especially for the analysis with MS in the negative chemical ionisation mode (ECNI). In ECNI mode the dominant ions for F-PBDEs, ^{13}C -PBDEs and PBDEs are m/z 79 and 81, and a separation by retention time between the internal standards (F-PBDEs or ^{13}C -PBDEs) and PBDEs is, therefore, necessary. Only the F-PBDEs can be separated by retention time from the PBDEs, and ^{13}C -PBDEs are, therefore, not useful in ECNI-MS. The use of F-PBDEs as ISs is much more cost-consciously in comparison with ^{13}C labelled analogues.

Ongoing investigations show, that the use of F-PBDEs as ISs causes a highly desirable improved precision in PBDE analysis [4]. Additional studies with dynamic ^{19}F nuclear magnet resonance spectroscopy (^{19}F -NMR) and solid state-NMR provide us with information concerning the dynamic of planarity and can be useful for toxicological studies.

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