INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are common flame-retardants that are considered to pose a significant environmental threat. PBDEs appear to bioaccumulate in fatty deposits, and have been detected in human breast milk. They are thought to be endocrine disruptors and interfere with brain development. Other polybrominated aromatic compounds arising from the incineration of PBDEs, from agrochemical residues or created for other purposes are also considered for their toxic threat. There are 209 possible PBDE congeners that can be represented by the general molecular weights (Br10 congener has average M 960) for GC applications. The separation and selectivity in the GC analysis of PBDEs and other polyhalogenated bis-aromatics. A schematic representation of the factors influencing separation and selectivity in the GC analysis.

RESULTS AND DISCUSSION

The importance of phase selectivity for large analytes, such as PBDEs, is demonstrated by the relative separation of octa-, nona and deca-BDEs on both BP1 (Figure 4) and BPX5 (Figure 5) columns. The only significant difference between phases is seen in the absolute retention times and is related to phase dimensions and relative PBDE solubility in each phase. For the more highly substituted analytes, steric hindrance between phase and analyte prevents the aromatic portion of the phase contributing to selectivity leaving phase robustness as the determinant in selecting BPX5 over BP1 and other 5% phenyl phases. The hindrance effect is also observed on highly aromatic non-planar phases such as BPX50 and is increased by the bulk of the substituent halogens (hindrance effects increase in the order F < Cl < Br < I).

While some similarities are drawn between brominated aromatics and their chlorine substituted counterparts, analysis of PBDEs is complicated by their thermal lability, including their propensity for debromination (Figure 2), and the need to separate some or all of the 209 possible congeners (Figure 3). Mass spectral techniques offer distinct advantages in speciation of congener groups where mass assignments give a simple halogen count that is not possible using other detectors. However, within isomer groups, simple mass spectral techniques do not allow unequivocal assignment of individual isomers. This limitation is not overcome by the use of tandem techniques where, for thermodynamic reasons, few unique data are obtained. Definitive identification of the compounds requires chromatographic resolution of all isomers within each congener grouping.

Liquid chromatographic solutions have been proposed to overcome decomposition, but they have not achieved the levels of congener resolution necessary for confirmatory analysis in a regulatory environment. GC-MS is the preferred method for PBDE analysis and separation can be enhanced by altering conditions such as phase composition, film thickness and temperature. Appropriate column selection is the most important determinant in a successful chromatographic method.

CONCLUSION

The GC analysis of polybrominated pollutants is limited by chromatographic resolution of many similar compounds as well as their individual thermal instabilities which lead to debromination and cyclisation. Simple distillation chromatography can be complemented by the speciation made possible by selective phase – analyte chemistries including debromination and cyclisation. Simple distillation chromatography can be complemented by the separation made possible by selective phase – analyte chemistries including e-π bonding on bis(cyanopropyl) like phases such as BPX70 or “BPX90”, and e-carbogel bonding on the HTB phase.

Ultimately, the effective separation of all PBDE congeners is achieved by an on- or off-line multidimensional approach that uses capillary columns with complementary selectivities. The selection of appropriate column sets for multidimensional separations requires a prior understanding of the orthogonality of the phases selected.

SGE offers a range of thermally-robust columns suitable for PBDE analyses that include non-polar BPX1 and BPX5, aromatic BPX5, very polar bis(cyanopropyl)-poly(phenylene-siloxane) based BPX70 and BPX90 and the highly selective carbogel-containing HTS and HTB columns. The diversity of phase chemistries and polarities allows for the design of column sets for resolution of PBDEs and similar analyses both from each other and from matrix-related materials.

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