

GCxGC-ECD of Polybrominated Diphenyl Ethers

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1. Introduction

The polybrominated diphenyl ethers (PBDEs) used as flame-retardants in a wide variety of household and industrial products are by now well-known environmental contaminants. PBDEs are produced commercially as mixtures containing relatively few major congeners, and these are the ones often monitored in analytical schemes, which mainly consist of gas chromatography (GC) as the separation tool.

For detection of PBDEs analyzed by GC, the electron capture detector (ECD) provides excellent sensitivity. Unfortunately it is a non-specific detector (responding to all halogenated components), including polychlorinated biphenyls (PCBs)—which are often present with PBDEs in environmental samples, even those that have been subjected to off-line cleanup methodologies (such as silica gel). When PCBs are present, GC-ECD may not provide the selectivity necessary to determine PBDEs.

A relatively new way to solve separation problems is to use comprehensive two-dimensional GC (GCxGC). GCxGC is a way to increase peak capacity by applying two independent separations to a sample in one analysis with one detector. GCxGC involves serially connected columns (differing phases) separated by a thermal modulator. A separation is performed on the first column, and then effluent from the first column is continually (and quickly) focused and "injected" onto the second column. By keeping the second column short, a series of high-speed chromatograms are generated, and the first column separation can be maintained. Separation results can be plotted as a retention plane (column 1 time x column 2 time), also known as a contour plot. By using GCxGC, the chances for coeluting interferences are reduced.

This application note introduces the possibility of determining PBDEs in an unbiased fashion with GCxGC-ECD, even in the presence of PCBs.

Standards

The PBDE standard solution was obtained from Cambridge Isotope Laboratories (Andover, Massachusetts, USA). PCBs as Aroclors were obtained from AccuStandard (New Haven, Connecticut, USA).

2. Experimental Conditions

LECO GCxGC-ECD

Agilent 6890 GC-ECD equipped with a LECO Quad Jet—Dual-Stage Thermal Modulator

Column 1:

10 m x 0.18 mm x 0.20 μ m Rtx-5 (Restek)

Column 2:

1.1 m x 0.10 mm x 0.10 μ m DB-17 (J&W Scientific)

Carrier:

Helium at 3 mL/minute, constant flow

Injection:

1 μ L split at 250°C, split ratio 20:1

Oven 1 Program:

80°C (0.2 minute), 4°/minute to 280°

Oven 2 Program:

20°C offset from oven 1

Modulation Time: 6 seconds

Detector:

ECD, 325°C, N₂ makeup gas at 147 mL/minute, 50 Hz

3. Results and Discussion

When using a non-specific detector such as an ECD, it is important to achieve good GCxGC results. Figures 1 and 2 illustrate the possibilities of GCxGC-ECD to determine PBDEs, even when PCBs are in the same extract. In a one-dimensional analysis of this same Aroclor:PBDE standard mix, coelutions would prevent accurate quantification of the early eluting PBDEs (Figure 3).

Importantly, the ECD is extremely sensitive towards PBDEs, and thermal focusing offered with GCxGC enhances this sensitivity. For example, BDE 49, a tetrabromo-compound, gave a signal-to-noise ratio of about 150:1 for 0.5 pg. Obviously, low fg levels are achievable for environmental samples if interference-free separations are accomplished.

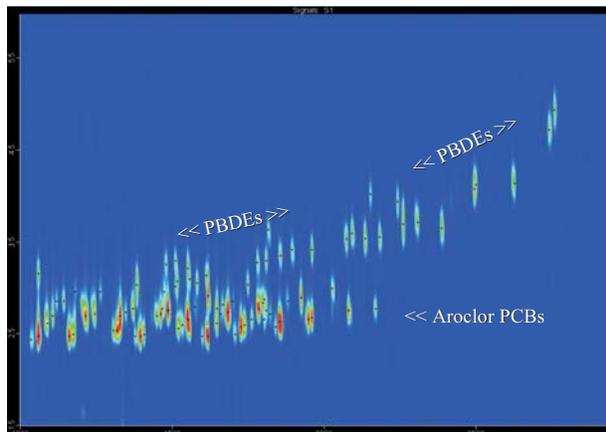


Figure 1. Contour plot showing GCxGC-ECD separation of PCBs and PBDEs. Note the separation of compounds in two dimensions with the Rtx-5 separation (and retention time) on the X-axis and the DB-17 separation occurring along the Y-axis.

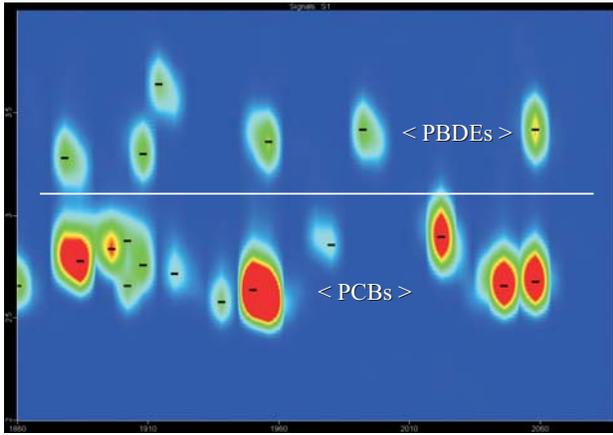


Figure 2. Zoom of Figure 1 contour plot showing distinct separation of PCBs and PBDEs in the second dimension when using GCxGC-ECD.

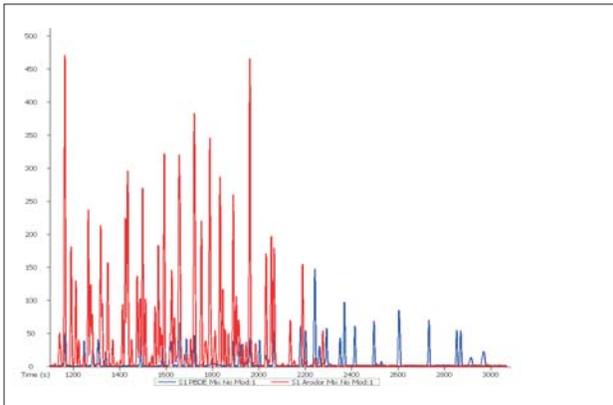


Figure 3. Overlaid one-dimensional ECD chromatograms for a PBDE standard mix (blue) and a PCB Aroclor mix (red). Numerous coelutions occur under these GC conditions.

4. Conclusions

GCxGC-ECD offers exciting possibilities for PBDE determination in environmental samples. Column combinations must be chosen that enhance the selectivity for PBDEs, to separate them from each other and from interfering matrix components. The sensitivity improvement afforded by the focusing effect of thermal modulation is valuable for improving sensitivity for PBDE congeners that often exist at very low levels in aqueous and biota samples.

5. Acknowledgment

Ben Priest at Cambridge Isotope Laboratories kindly provided the solution that contained numerous PBDE congeners from mono- to heptabromodiphenyl ether.

