Analysis of Brominated Flame Retardants by GCxGC-TOFMS

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1. Introduction

Brominated flame retardants (BFRs) such as poly-brominated diphenylethers (PBDE), hexabromocyclo-dodecane (HBCD), and tetrabromo bisphenol A (TBBPA) are persistent environmental contaminants that are being extensively studied by environmental researchers worldwide. Their potential for toxicological impacts on humans and wildlife has made these contaminants a focal point of regulatory agencies worldwide. The widespread use of these materials in electronics, household furniture, and many other building materials has lead to many different sample matrices that need to be analyzed, including very complex environmental samples.

The increasing need for a method which can chromatographically resolve several trace level PBDE congeners from complex sample matrices lends itself nicely to comprehensive two-dimensional gas chromatography (GCxGC) coupled to a time-of-flight mass spectrometer (TOFMS). GCxGC dramatically increases the separation power of the chromatographic system while increasing the detectability of analytes through the "cryo-focussing" effects of thermal modulation. The TOFMS detector offers the required acquisition speed (even at full mass range) necessary to define ultra-narrow two-dimensional chromatographic peaks. The sensitivity of the TOFMS at full-mass range also gives it a valuable advantage for characterization of new and emerging non-target BFRs. The ChromaTOF® software allows the ability to generate highly structured two-dimensional chromatograms with classification regions defining the specific congener types.

2. Experimental Conditions

GCxGC-TOFMS:
LECO Pegasus® 4D with Agilent 6890 GC and LN_2 Modulator
Column 1:
Rxi-5ms, 30 m x 0.25 mm x 0.25 µm
Primary Oven:
120°C hold 2 minutes, 12°C/minute to 295°C, hold 60 minutes
Column 2:
RTX-200, 1.5 m x 0.18 mm x 0.2 µm
Secondary Oven:
+30°C offset from main oven
Injection:
1 µL, split 10:1 at 220°C
Carrier Gas:
Helium at 3.0 ml/minute, constant flow
Modulator Temperature Offset: 45°C
Modulation Frequency:
5 seconds with a 0.8 second hot pulse time

MS:	LECO Pegasus
Acquired Mass Range:	45 to 1000 m/z
Acquisition Rate:	100 spectra/second
Source Temperature:	250°C

Samples

A gasoline sample was spiked with a forty-six component BFR mixture (BFR-PAR, available from Wellington Laboratories, Guelph, Ontario, Canada) containing various isomers ranging from monobrominated diphenyl ethers through decabromodiphenyl ethane. The spiked gasoline sample was analyzed using the Pegasus 4D instrument and experimental conditions described above. Gasoline was chosen to display the instrument's ability to detect and successfully identify BFRs in even the most complex sample matrices.

3. Results

Over 700 peaks were detected at a S/N of 100 in the spiked gasoline sample including all forty-six of the BFR congeners. A mass spectral library was created using the ChromaTOF software and analytes in the BFR standard mixture. This user-created library was used to identify all congeners found in the gasoline sample. The total ion two-dimensional contour plot is shown below in Figure 1 with a classification region drawn around the BFR congeners.

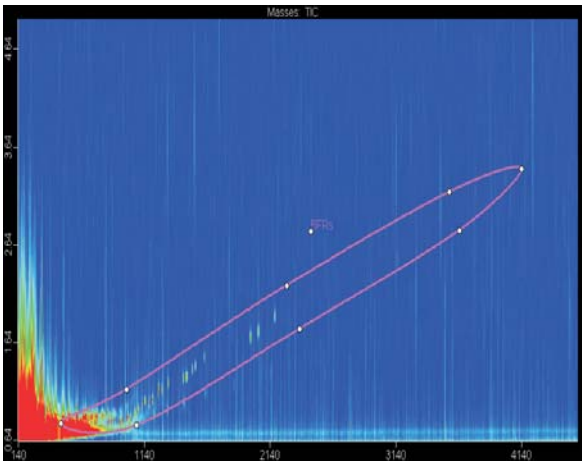

Figure 1. Two-dimensional total ion contour plot showing the BFR region.

The contour plot in Figure 2 shows the ChromaTOF software's ability to further classify the sample chromatogram by allowing classification regions to be drawn for various groups of PBDE congeners. In this figure, 14 different types of congeners have been classified.

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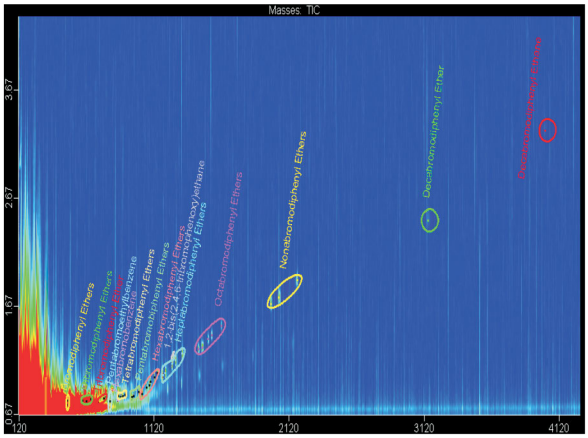

Figure 2. Two-dimensional contour plot showing detailed classification regions for BFR congeners.

A 3D view of an expanded region of the contour plot is shown in Figure 3 displaying the ability of the GCxGC separation to successfully resolve six hexabromodiphenyl ether (HBDE) isomers.

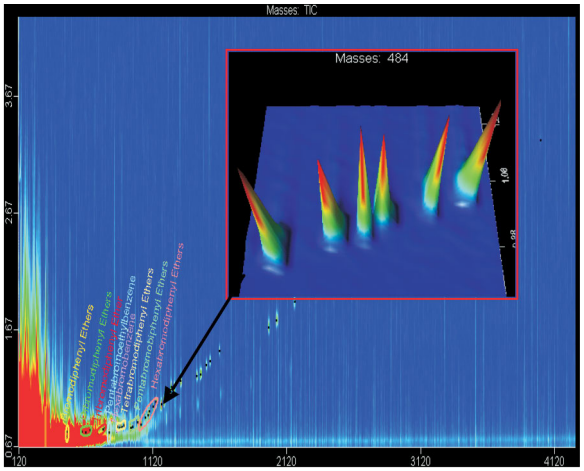

Figure 3. Expanded 3D display of HBDE isomers.

In addition to the enhanced chromatographic resolution offered by the orthogonal GCxGC separation, the detectability is significantly increased due to the "cryo-focusing" effects of thermal modulation. The limit of quantitation (LOQ) for each group of congeners by GCx GC-TOFMS is compared to the LOQ typical of a one-dimensional GC-TOFMS analysis. Based on these results, a significant increase in detectability is evident for all congener classes using GCx GC-TOFMS.

Table 1. Comparison of LOQ for PBDE congeners analyzed by one-dimensional (GC-TOFMS) vs two-dimensional (GCxGC-TOFMS) analysis.

Component I.D.	1D LOQ (ppb)	2D LOQ (ppb)
Bromodiphenyl Ethers	0.7	0.04
Dibromodiphenyl Ethers	0.5	0.02
Tribromodiphenyl Ethers	1.9	0.05
Pentabromoethylbenzene	8.7	0.13
Tetrabromodiphenyl Ethers	4.9	0.07
Hexabromobenzene	4.1	0.03
Pentabromodiphenyl Ethers	10.8	0.12
2,2',4,4',5,5'-hexabromobiphenyl	8.2	0.34
Hexabromodiphenyl Ethers	21.3	0.19
Heptabromodiphenyl Ethers	41.8	0.31
1,2-bis(2,4,6-tribromophenoxy)ethane	25.3	0.23
Octabromodiphenyl Ethers	84.7	0.75
Nonabromodiphenyl Ethers	287.0	2.05
Decabromodiphenyl Ether	684.4	13.00
Decabromodiphenyl Ethane	n.d.	12.92

5. Conclusions

The use of GCxGC-TOFMS offers many significant advantages for the analysis of BFRs. The ability of the thermally modulated GCxGC system to enhance chromatographic resolution while dramatically improving detectability makes this instrument a valuable tool for analysis of trace level components in complex sample matrices. Coupling GCxGC with the sensitivity of a TOFMS detector acquiring full mass range spectra gives researchers all the tools necessary for detection of target BFRs, as well as characterization of new and emerging non-target BFRs and their metabolites.

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