# Application of low-pressure gas chromatography-MS/MS to the determination of polybrominated diphenylethers

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## Introduction

In recent years, the occurrence of brominated flame retardants (BFR) in the environment has raised growing concern and thus become a target of intense research. The chemical analysis of BFRs in trace concentrations remains however challenging. Modern methods using different injection techniques[1], single quadrupole[2] and tandem mass spectrometry using either ion trap[3] or triple quadrupole instrument[4] have been published. Polybrominated diphenylethers (PBDE) are high molecular weight compounds (MWs up to m/z 960) and they are relatively non-volatile. Therefore high injector and column oven temperatures are needed during analysis. This subjects the analytes to some extent to thermal degradation. The purpose of this study was to minimize the time of high temperature exposure by combining programmable temperature vaporizing injection and low-pressure gas chromatography (LP-GC). For detection of PBDEs a triple quadrupole mass spectrometer was used either in single-MS or MS/MS mode.

## Materials and Methods

All analyses were performed using Varian CP-3800 GC coupled to Varian 1200L triple quadrupole mass spectrometer. The mass spectrometer was operated in positive EI mode in all analyses. The low-pressure gas chromatography was carried out by applying short restriction capillary at the front of the wide bore analytical column (10m x 0.53mm). The vacuum pumps of the MS instrument provided the diminished pressure to the column.

### *GC method*

Temperature programmed pressure pulsed splitless injection was used. The inlet pressure was set to deliver helium flow of approximately 1 ml min$^{-1}$ through the restrictor. Varian Factor Four Rapid-MS$^{TM}$ column CP-Sil8 (a short deactivated restrictor column connected to 10m x 0.53mm id x 0.25um df) was used with the following temperature program: 100$^{o}$C // hold 2.0min // 15$^{o}$C/min to 320$^{o}$C // hold 3.33min; for total run time of 20 min.

### *EI//MS/MS method*

Positive EI with –70eV ionization energy was used. Specific fragmentation reactions were monitored ($[M]^+$-$Br_2$, $[M\text{-}Br_2]^+$-$Br_2$ and $[M\text{-}Br_2]^+$-$COBr_{(1\text{-}2)}$). MS/MS conditions were optimized and programmed for each compound to create multiple reaction monitoring (MRM) method.

In this study, a standard solution of fifteen PBDE congeners were used for evaluation of the chromatographic separation and the sensitivity of detection. An eight point calibration curve in the range of 0.12 pmol ml$^{-1}$ to 2500 pmol ml$^{-1}$ (0.05 ng ml$^{-1}$ – 1000 ng ml$^{-1}$ of BDE28 to 0.125 ng ml$^{-1}$ – 2500 ng m$^{-1}$ of BDE209) was analyzed.

## Results and Discussion

When the gas chromatographic separation of PBDEs was done at low pressure with a Rapid-MS$^{TM}$ capillary column, the total analysis time was 20 minutes. The method used did shorten the exposure time of the analytes to high temperatures significantly. At the same time peak shapes and baseline resolution of the compounds were maintained.

The fifteen PBDE congeners used were first identified by a full scan LP-GC-MS analysis. The most intensive ion clusters in their spectra were composed of $[M]^+$ and $[M\text{-}Br_2]^+$. The most abundant ions of specific ion cluster were used as precursor ions by increasing the mass resolution to 2 amu - 4 amu. The prevalent collision induced dissociation (CID) reactions were a loss of 2 Br atoms or a loss of $COBr_{(1-2)}$. The product ion cluster of these dissociation reactions were detected with the same mass resolution as precursor ion cluster. The MRM parameters are shown at Table 1.

**Table 1.** Optimized MS/MS method parameters

PBDE // Precursor ion // Product ion // Collision energy
tri bromo (#17, #28) // 405.9 $[M]^+$ // 246.1 $[- Br_2]$ // -20
tri bromo (#17, #28) // 246.1 $[M-Br_2]^+$ // 139.2 [- COBr] // -30
tetra bromo (#47, #66) // 485.8 $[M]^+$ // 326.0 $[- Br_2]$ // -25
tetra bromo (#47, #66) // 326.0 $[M-Br_2]^+$ // 138.2 $[- COBr_2]$ // -50
penta bromo (#85, #99, #100) // 563.8 $[M]^+$ // 403.9 $[- Br_2]$ // -20
penta bromo (#85, #99, #100) // 403.9 $[M-Br_2]^+$ // 297 $[- COBr_1]$ // -45
hexa bromo (#138, #153, #154) // 643.7 $[M]^+$ // 483.8 $[- Br_2]$ // -20
hexa bromo (#138, #153, #154) // 483.8 $[M-Br_2]^+$ // 376.9 [- COBr] // -45
hepta bromo (#183, #190) // 721.6 $[M]^+$ // 561.7 $[- Br_2]$ // -25
hepta bromo (#183, #190) // 561.7 $[M-Br_2]^+$ // 454.8 [-COBr] // -45
octa bromo (#203) // 801.5 $[M]^+$ // 641.6 $[- Br_2]$ // -20
octa bromo (#203) // 641.6 $[M-Br_2]^+$ // 534.7 [-COBr] // -45
nona bromo (#206) // 879.4 $[M]^+$ // 719.6 $[- Br_2]$ // -30
nona bromo (#206) // 719.6 $[M-Br_2]^+$ // 612.6 [-COBr] // -45
deca bromo (#209) // 959.3 $[M]^+$ // 799.5 $[- Br_2]$ // -25
deca bromo (#209) // 799.5 $[M-Br_2]^+$ // 639.5 $[- Br_2]$ // -40

The limits of detection were calculated from the calibration curves. The limits of quantitation were set to two - three times LODs. Sensitivity of the method varied depending on the degree of bromination from 0.2 fmol (0.08 pg) of triBDE to 1.4 fmol (1.3 pg) of decaBDE injected. The determined LODs are presented at the table 2.

**Table 2**. The determined LODs of the studied fifteen PBDEs

PBDE congener // LOD (pg injected / fmol injected)
tri bromo (#17, #28) // 0.08 / 0.20
tetra bromo (#47, #66) // 0.12 / 0.23
penta bromo (#85, #99, #100) // 0.13 / 0.23
hexa bromo (#138, #153, #154) // 0.33 / 0.50
hepta bromo (#183, #190) // 0.33 / 0.47
octa bromo (#203) // 0.37 / 0.43
nona bromo (#206) // 1.2 / 1.4
deca bromo (#209) // 1.3 / 1.4

With the low-pressure gas chromatography a sensitive high-speed method for analysis of polybrominated diphenyl ethers was developed. The GC-triple quadrupole instrument operated in multiple reaction mode provided a highly selective method to perform reliable analysis of PBDEs. Furthermore, reduced sample pretreatment is needed when environmental samples are analyzed with the MS/MS technique.

## References

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