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Application Data Sheet

No.63

GC-MS
Gas Chromatograph Mass Spectrometer

Analysis of PBDEs in Sediment Using GC-MS/MS

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) widely used in plastics. Due to their toxicity and persistence, their industrial production is to be eliminated under the Stockholm Convention. Contamination from PBDEs is widespread in the environment, including in sediments. In order to determine PBDEs in sediments, they need to be separated from a large amount interferences co-extracted during sample preparation. GC-MS and GC-MS/MS were evaluated for this purpose.

Experimental

Method 1614 Native PAR Stock Solution and Method 1614 Labeled Surrogate Stock Solution (Cambridge Isotope Laboratories) were used as target compound and surrogate standards, respectively. Calibration solutions were prepared at concentrations of 10, 20, 50, 100, 500 ng/mL (10 times higher concentrations of deca-BDE). After the addition of surrogate, sediment samples were extracted using Soxhlet extractions. The extract solution was cleaned-up by sulfuric-acid treatment, removal of sulfur using copper, and Florisil treatments.

Analytical Conditions

SIM and MRM modes were used for GC-MS and GC-MS/MS, respectively. The analytical conditions are shown in Table 1.

Table 1: Analytical Conditions

GC-MS :GCMS-QP2010 Ultra
GC-MS/MS :GCMS-TQ8030
Column :Rtx-1614 (Length 30m, 0.25mm I.D., df=0.1 µm)

[GC]
Injection Temp. :320 °C
Column Oven Temp. :140 °C (3 min)→(5 °C /min)→320 °C (5min)
Injection Mode :Splitless
Sampling Time :1 min
Flow Control Mode :Linear velocity (47.9 cm/sec)
High Pressure Injection :150 kPa (1.2 min)
Injection Volume :1 µL

[MS]
Interface Temp. :300 °C
Ion Source Temp. :230 °C
Tuning Mode :High Sensitivity

GC-MS
Acquisition Mode :SIM
SIM Event Time :0.5 sec
Micro Scan Width :0.6 *u*

GC-MS/MS
Acquisition Mode :MRM

SIM Monitoring *m/z*

Compound name	Qualitative	Quantitative
Tri-BDE	405.8	245.9
Tetra-BDE	485.7	325.9
Penta-BDE	563.6	403.8
Hexa-BDE	483.7	643.6
Hepta-BDE	561.6	721.5
Deca-BDE	799.4	959.4
13C Tri-BDE	417.8	257.9
13C Tetra-BDE	497.7	337.9
13C Penta-BDE	575.6	417.8
13C Hexa-BDE	495.7	655.6
13C Hepta-BDE	573.6	733.5
13C Deca-BDE	811.4	971.4

MRM Monitoring *m/z*

Compound name	Quantitative Transition Precursor>Product	CE (V)	Qualitative Transition Precursor>Product	CE (V)
Tri-BDE	405.8>245.9	20	405.8>247.9	20
Tetra-BDE	485.7>325.7	24	485.7>327.7	24
Penta-BDE	563.6>403.7	26	563.6>405.7	26
Hexa-BDE	643.6>483.7	26	643.6>485.7	26
Hepta-BDE	721.4>561.6	30	721.4>563.6	30
Deca-BDE	959.4>799.3	32	959.4>801.3	32
13C Tri-BDE	417.8>257.9	20	417.8>259.9	20
13C Tetra-BDE	497.7>337.7	24	497.7>339.7	24
13C Penta-BDE	575.6>415.7	26	575.6>417.7	26
13C Hexa-BDE	655.6>495.7	26	655.6>497.7	26
13C Hepta-BDE	733.4>573.6	30	733.4>575.6	30
13C Deca-BDE	971.4>811.3	32	971.4>813.3	32

Results

Fig 1. shows the MRM chromatogram of hepta-BDE (BDE-183) at 10 ng/mL. For eight PBDE congeners, calibration curves show linearity from 10 to 500 ng/mL (from 100 to 5000 ng/mL of deca-BDE) with a correlation coefficient of 0.9999 (Table 2).

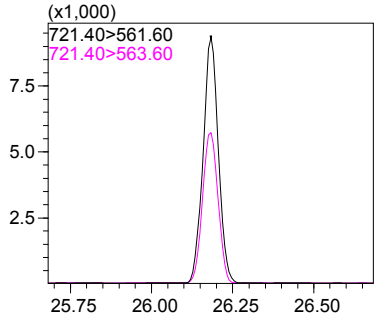

Fig. 1: MRM Chromatogram of hepta BDE (BDE-183)

Table 2: Correlation Coefficients of Calibration Curves for 8 PBDEs Congeners

Compound Name	R
Tri-BDE (BDE-028)	0.9999
Tetra-BDE (BDE-47)	0.9999
Penta-BDE (BDE-100)	0.9999
Penta-BDE (BDE-99)	0.9999
Hexa-BDE (BDE-154)	0.9999
Hexa-BDE (BDE-153)	0.9999
Hepta-BDE (BDE-183)	0.9999
Deca-BDE (BDE-209)	0.9999

Fig. 2 shows GC-MS SIM and GC-MS/MS MRM chromatograms. Several PBDEs could not be determined due to matrix interference in the SIM chromatogram, whereas those PBDEs were clearly detected in the MRM chromatogram. This demonstrates that the MRM mode allows the selective detection of target compounds even in the presence of large amounts of co-extracted interferences.

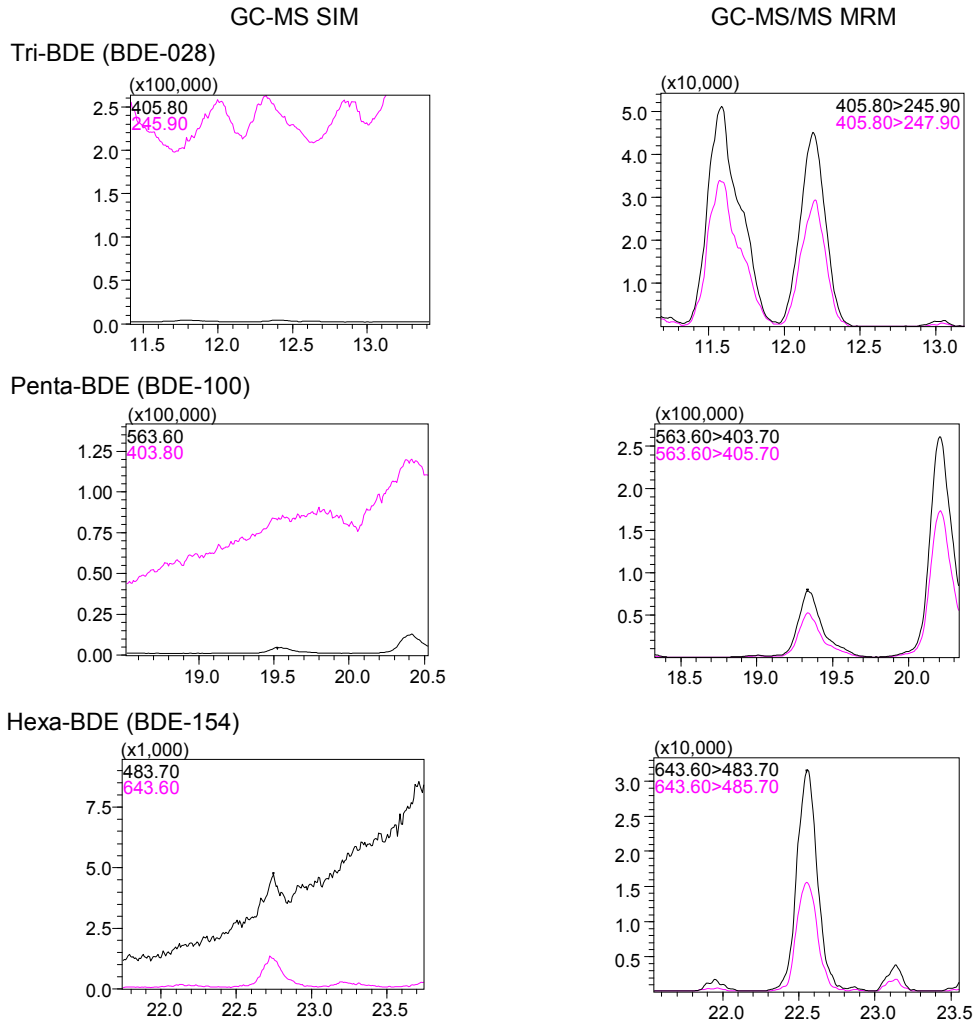

Fig. 2: SIM and MRM Chromatograms of Sediment Sample

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