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Application Data Sheet

No.66

GC-MS
Gas Chromatograph Mass Spectrometer

Analysis of Brominated Flame Retardants and Phthalate Esters Under the Same Conditions Using a Pyrolysis GC-MS System (3) - HBCDD -

In recent years, an analysis method has been required to determine not only polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs), which are regulated under the RoHS Directive, but also phthalate esters and other brominated flame retardants not governed by the directive (such as tetrabromobisphenol-A, hexabromocyclododecane (HBCDD), and bis(pentabromophenyl)ethane). In particular, HBCDD has been identified as a substance of very high concern (SVHC) in the REACH regulation. This Application Data Sheet shows the results from analyzing HBCDD in polymers under the same analytical conditions as those in Application Data Sheet 47 using the EGA/PY-3030D Multi-Shot Pyrolyzer and GCMS-QP2020 Ultra.

Experimental

HBCDD was dissolved with toluene at a concentration of 100 µg/mL. Polystyrene was dissolved in a mixture of 9:1 (v/v) dichloromethane and xylene at a concentration of 25 mg/mL. 20µL of polystyrene solution (0.5 mg) and 5 µL of HBCDD (0.5 µg) were added to Eco-Cup LF of the pyrolyzer and the solvent was evaporated to dryness at room temperature. The concentration of HBCDD was 1000 ppm in polystyrene.FASST (Fast Automated Scan/SIM Type), which is capable of simultaneous Scan and SIM measurements, was used as the measurement mode. Table 1 shows the analytical conditions and Fig. 1 shows the SIM measurement program.

Table 1: Analytical Conditions

Pyrolysis Instrument	:EGA/PY-3030D Multi-Shot Pyrolyzer
GC-MS	:GCMS-QP2010 Ultra
Column	:Ultra ALLOY-PBDE [15 m length, 0.25 mm I.D. , df = 0.05 µm]
[Pyrolyzer]	
Pyrolysis Furnace Temp.	:200 °C → (20 °C/min) → 300 °C → (5 °C /min) → 340 °C (1 min)
Interface Temp.	:Manual (300 °C)
[GC]	
Injection Temp.	:320 °C
Column Oven Temp.	:80 °C → (20 °C/min) →300 °C (5 min)
Injection Mode	:Split
Carrier Gas	:Helium
Flow Control Mode	:Constant linear velocity (52.1 cm/sec)
Purge Flow Rate	:3.0 mL/min
Split Ratio	:50

[MS]	
Interface Temp.	:320 °C
Ion Source Temp.	:230 °C
Solvent Cut Time	:0.5 min
Tuning Mode	:Normal
Measurement Mode	:Scan/SIM
Scan Mass Range	:*m/z* 50 - 1000
Scan Event Time	:0.15 sec
Scan Speed	:10,000 *u*/sec
SIM Monitoring m/z:	See Fig. 2.
SIM Event Time	:0.3 sec
SIM Micro-Scan Width	:0.5 *u*

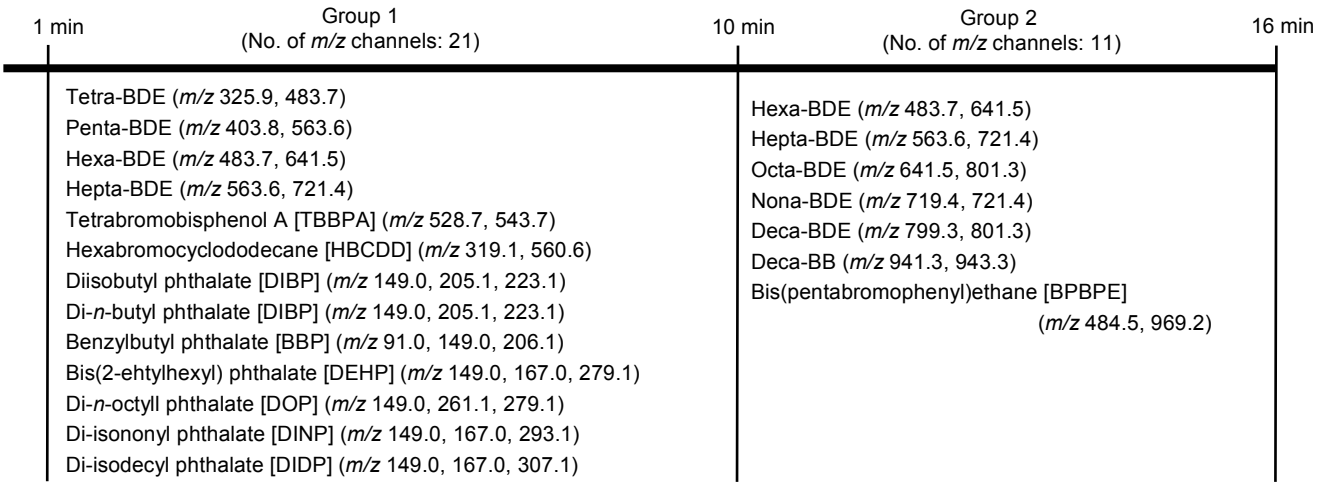

Fig. 1: SIM Measurement Program

Results

The chemical structure and mass spectrum of HBCDD are shown in Fig. 2 and 3. Fig. 4 shows the total ion current chromatogram of HBCDD in polystyrene (1000 ppm).
These analytical conditions can be applied to analyses of PBBs, PBDEs ,and phthalate esters. Moreover, using the scan/ SIM mode (FASST) enable accurate determination of target compounds from the SIM data and identification of unknown compounds from the full-scan data.

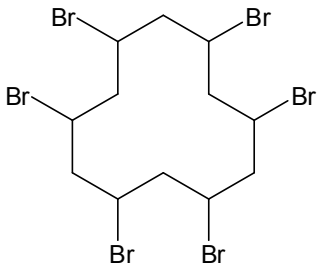

Fig. 2: Compound Structure of HBCDD

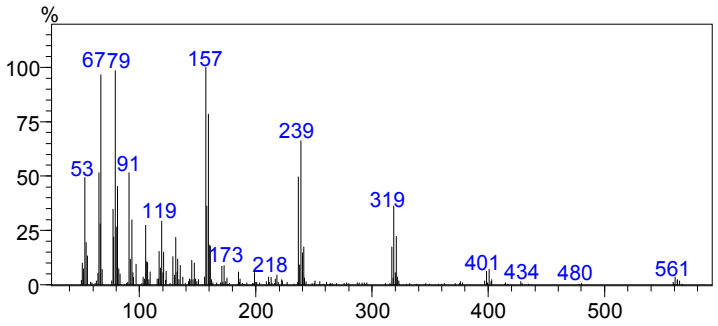

Fig. 3: Mass Spectrum of HBCDD

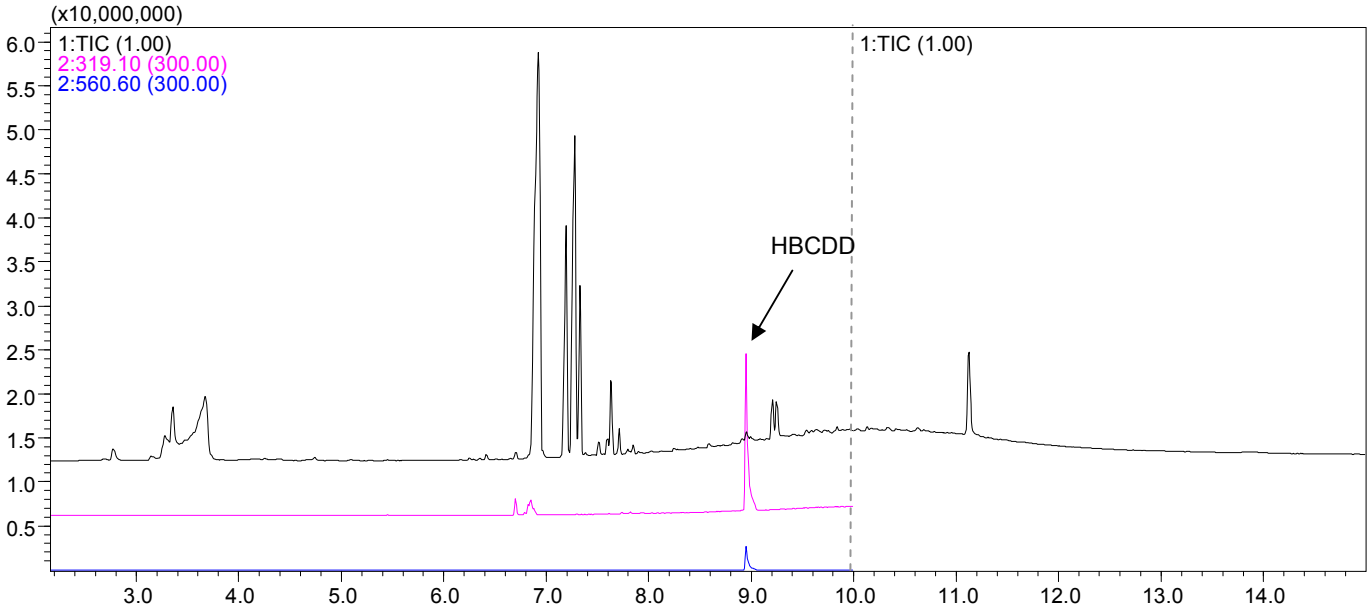

Fig. 4: Total Ion Current Chromatogram of Polystyrene Spiked HBCDD

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Shimadzu Corporation
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