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Application Data Sheet

No.48

GC-MS
Gas Chromatograph - Mass Spectrometer

Analysis of Brominated Flame Retardants and Phthalate Esters In Ploymers Under the Same Conditions Using a Pyrolysis GC-MS System (2) - Phthalate Esters -

In recent years, an analysis method is 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, and bis(pentabromophenyl)ethane). Diisobutyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), benzyl butyl phthalate (BBP), and bis(2-ehtylhexyl) phthalate (DEHP) are specified in the REACH SVHC (Substance of Very High Concern) list. This Application Data Sheet shows the results from analyzing seven phthalate esters in polymers under the same analytical conditions as those in Application Data Sheet 47 using EGA/PY-3030D Multi-Shot Pyrolyzer and GCMS-QP2020 Ultra systems.

Analytical Conditions

Standard mixture solutions were prepared by dissolving and diluting standard samples of the seven phthalate esters with acetone to concentrations of 1, 10, 50, and 100 ng/μL. Solid standard samples were prepared by adding 5 μL of the standard mixtures to an Eco-Cup LF (disposable sample cup) and evaporating the solvent to dryness. Evaluating sample was prepared by shaving cable jacket material (polyvinyl chloride) and weighing 0.5 mg. 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 analysis 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	:FASST (simultaneous Scan/SIM measurements)
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*

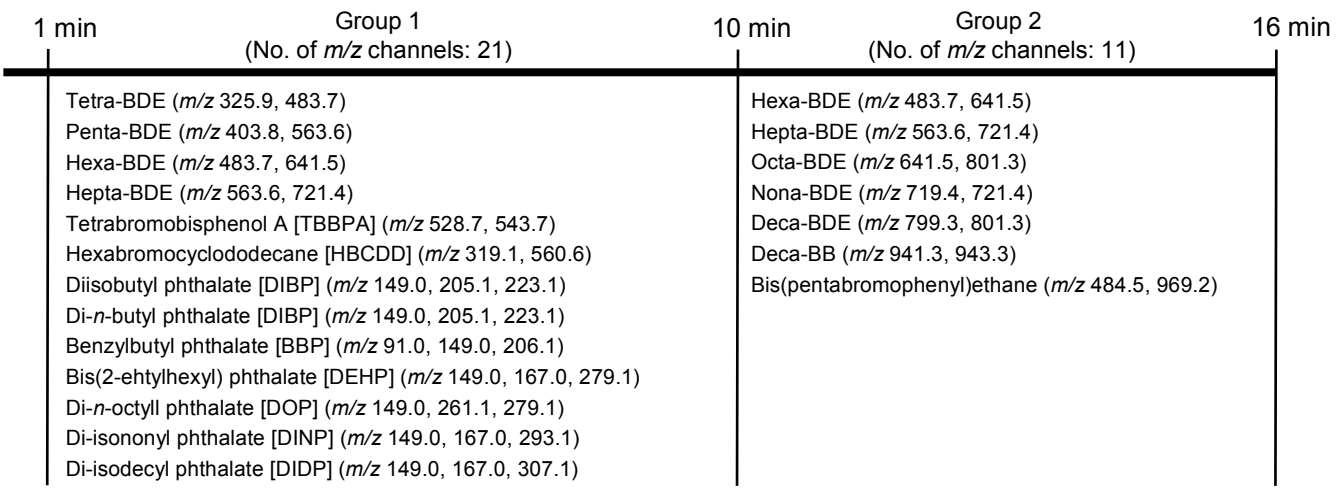

Fig. 1: SIM Measurement Program

Results

A total ion current chromatogram (TIC) for 250 ng of the seven phthalate esters is shown in Fig. 2. DOP, DINP, and DIDP could not be separated in the TIC; however, they were successfully separated in the mass chromatogram. The SIM mass chromatogram for 5 ng of DINP is shown in Fig. 3. The calibration curve coefficient of correlation for concentrations from 5 ng to 500 ng is shown in Table 2.

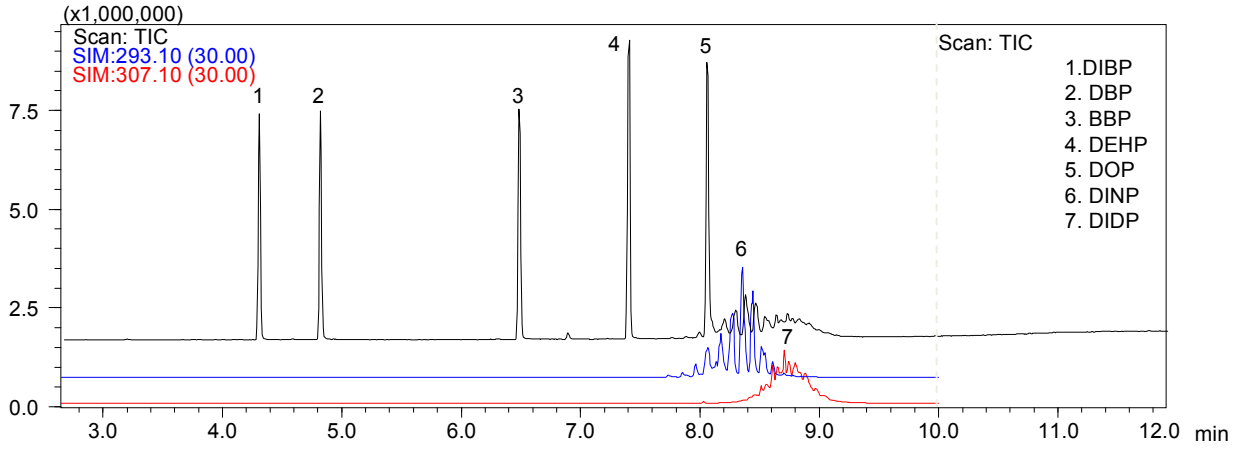

Fig. 2: Total Ion Current Chromatogram and Mass Chromatograms for 7 Phthalate Esters (250 ng)

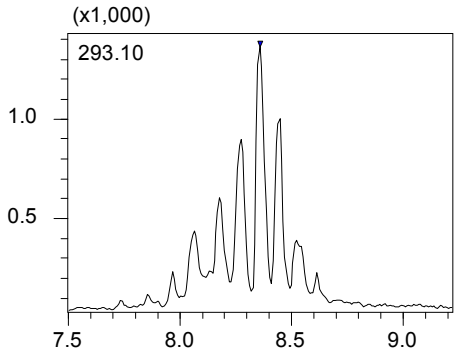

Fig. 3: SIM Mass Chromatogram of DINP (5 ng)

Table 2: Linearity of Calibration Curve for Seven Phthalate Esters (concentration range: 5 to 500 ng)

Compound Name	Correlation Coefficient (R)
DIBP	0.9995
DBP	0.9999
BBP	0.9999
DEHP	0.9999
DOP	0.9999
DINP	0.9999
DIDP	0.9997

The chromatogram from measuring the cable jacket material (polyvinyl chloride) is shown in Fig. 4. The presence of DEHP, DINP, and DIDP was confirmed in the SIM chromatogram. Also, the scan mass spectrum shows that Peak A is bis(2-ethylhexyl)adipate and Peak B is tris(2-ethylhexyl)trimellitate. A FASST measurement enabled quantitating the phthalate esters from the SIM data and identifying unregulated plasticizers from the scan data.

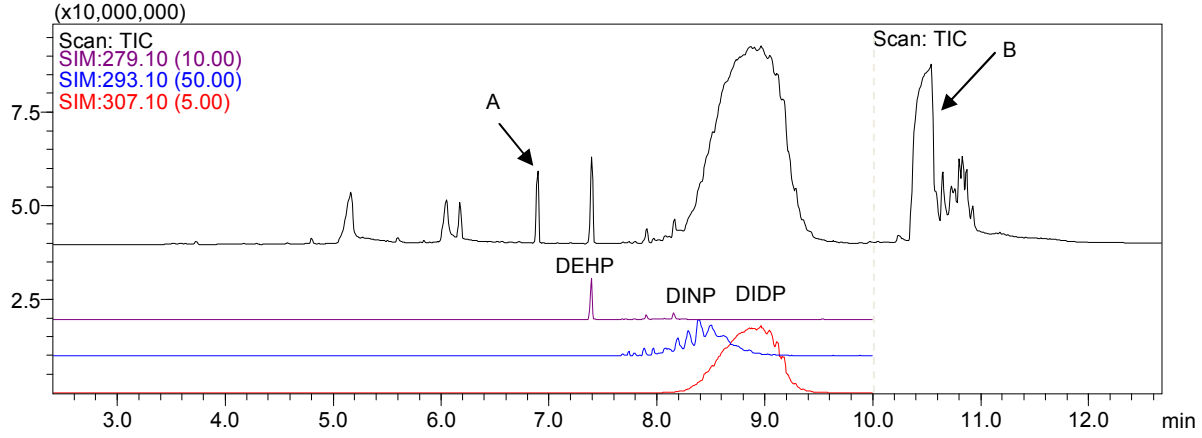

Fig. 4: Chromatogram of Cable Jacket Material

First Edition: June, 2012

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