



GC-MS

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

LAAN-J-MS-E048

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/ $\mu$ L. Solid standard samples were prepared by adding 5  $\mu$ L 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.	Analy	/tical	Conditions
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Pyrolysis Instrument	EGA/PY-3030D Multi-Shot Pyrolyzer			
GC-MS	:GCMS-QP2010 Ultra			
Column	:Ultra ALLOY-PBDE [15 m length, 0.25 mm l.D. , df = 0.05 μm]			
[Pyrolyzer]				
Pyrolysis Furnace Tem	p. :200 °C $\rightarrow$ (20 °C/min) $\rightarrow$ 300 °C $\rightarrow$ (5 °C	/min) $\rightarrow$ 340 °C ( 1 min)		
Interface Temp.	:Manual (300 °C)	[MS]		
[GC]		Interface Temp.	:320 °C	
Injection Temp.	:320 °C	Ion Source Temp.	:230 °C	
Column Oven Temp.	:80 °C $\rightarrow$ (20 °C/min) $\rightarrow$ 300 °C (5 min)	Solvent Cut Time	:0.5 min	
Injection Mode	:Split	Tuning Mode	:Normal	
Carrier Gas	:Helium	Measurement Mode	:FASST (simultaneous Scan/SIM measurements)	
Flow Control Mode	:Constant linear velocity (52.1 cm/sec)	Scan Mass Range	: <i>m/z</i> 50 - 1000	
Purge Flow Rate	:3.0 mL/min	Scan Event Time	:0.15 sec	
Split Ratio	:50	Scan Speed	:10,000 <i>u</i> /sec	
		SIM Monitoring m/z	:See Fig. 2.	
		SIM Event Time	:0.3 sec	
		SIM Micro-Scan Width	:0.5 <i>u</i>	

1 I	min Group 1 (No. of <i>m/z</i> channels: 21)	10 min Group 2   I (No. of <i>m/z</i> channels: 11)	16 min
	Tetra-BDE ( <i>m</i> /z 325.9, 483.7)	Hexa-BDE ( <i>m/z</i> 483.7, 641.5)	
	Penta-BDE ( <i>m/z</i> 403.8, 563.6)	Hepta-BDE ( <i>m</i> /z 563.6, 721.4)	
Hexa-BDE ( <i>m</i> / <i>z</i> 483.7, 641.5)		Octa-BDE ( <i>m/z</i> 641.5, 801.3)	
	Hepta-BDE ( <i>m/z</i> 563.6, 721.4)	Nona-BDE ( <i>m/z</i> 719.4, 721.4)	
	Tetrabromobisphenol A [TBBPA] ( <i>m/z</i> 528.7, 543.7)	Deca-BDE ( <i>m/z</i> 799.3, 801.3)	
	Hexabromocyclododecane [HBCDD] (m/z 319.1, 560.6)	Deca-BB ( <i>m/z</i> 941.3, 943.3)	
	Diisobutyl phthalate [DIBP] ( <i>m</i> /z 149.0, 205.1, 223.1)	Bis(pentabromophenyl)ethane (m/z 484.5, 969.2	)
	Di- <i>n</i> -butyl phthalate [DIBP] ( <i>m</i> / <i>z</i> 149.0, 205.1, 223.1)		
	Benzylbutyl phthalate [BBP] ( <i>m/z</i> 91.0, 149.0, 206.1)		
	Bis(2-ehtylhexyl) phthalate [DEHP] (m/z 149.0, 167.0, 279.1)		
	Di- <i>n</i> -octyll phthalate [DOP] ( <i>m</i> / <i>z</i> 149.0, 261.1, 279.1)		
	Di-isononyl phthalate [DINP] (m/z 149.0, 167.0, 293.1)		
	Di-isodecyl phthalate [DIDP] ( <i>m</i> /z 149.0, 167.0, 307.1)		

## 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.





Table 2: Linearity of Calibration Curve for Seven Phthalate Esters						
	(concentration range: 5 to 500 ng)					
	Compound Namo	Correlation				
	Compound Name	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.



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