

Simultaneous Analysis of TBBPA, Phthalate Esters, and Brominated Flame Retardants by PY/TD-GC-MS

Product used : Mass Spectrometer (MS)

1. Introduction

Tetrabromobisphenol A (TBBPA) is used as a flame retardant in a wide range of plastic products, such as ABS resin, phenolic resins, and adhesives. However, due to concerns about human bioaccumulation, the regulation of its use is being considered in various countries under the law such as the REACH regulation (EU), TSCA (USA), and the Chemical Substances Control Law (Japan). As a screening analysis for judgment of containing/not containing on the same kind regulation target such as Phthalate esters and PBDE, there is an analysis method using Thermal Desorption(TD)-GC-MS in the IEC62321-8.

This method allows direct analysis without sample pretreatment as shown in [MSTips No.298](#).

In this study, we tried to simultaneously analyze TBBPA, Phthalate esters and DecaBDE by TD-GC-MS method using the JMS-Q1600GC UltraQuad™ SQ-Zeta.



Gas chromatograph mass spectrometer
JMS-Q1600GC UltraQuad™ SQ-Zeta

2. Experiment

TBBPA standard reagent, NMIJ CRM 8152-a and ERM®-EC591 were used as samples. NMIJ CRM 8152-a is PVC resin that contains 9 types of phthalate esters, each at about 1000 ppm. ERM®-EC591 is PP resin that contains 10 types of brominated flame retardants, each at about 1000 ppm. In an eco-cup, about 0.5 mg of each resin was placed and 2 μ L of TBBPA at a concentration of 0.05 μ g/ μ L in THF solution was added (100 ppm for about 1.0 mg of resin). The measurement condition is shown in Table 1. In this report, the target compounds for analysis were selected as four phthalate esters (DIBP, DBP, BBP, and DEHP) and one brominated flame retardant (DecaBDE).

Table 1 Measurement Condition

Thermal Desorption (EGA/PY-3030D, FRONTIER LAB)		MS	
Furnace temp.	200 °C-20 °C/min-300 °C-5 °C/min-340 °C(1 min)	Interface temp.	300 °C
Interface temp.	300 °C	Ion source temp.	250 °C
GC		Ionization	EI (70 eV, 50 μ A)
Column	UA-PBDE(Frontier Laboratories Ltd.), 15 m \times 0.25 mm id, 0.05 μ m film thickness	Acquisition mode	SIM/Scan
Column flow	1.0 mL/min, He	SIM monitoring ion	DIBP, DBP:223, 205, 149
Oven temp.	300 °C		BBP :206, 91, 149
Inlet temp.	300 °C		DEHP:279, 167, 149
Injection mode	split (1/50)		TBBPA:528.8, 543.8, 526.7
		Scan range	DecaBDE:799.3, 797.3, 959.1
			m/z 50-1000

3. Results

3.1 The verification of the thermal desorption temperature of TBBPA using the EGA-MS method.

Using the EGA-MS method, we verified whether the extraction of TBBPA is possible at the thermal desorption temperature condition of 200 °C-20 °C/min-300 °C-5 °C/min-340 °C(1 min), in accordance with IEC 62321-8. The EIC(m/z 529) of the EGA-MS measurement (80 °C-20 °C/min-600 °C) is shown in Figure 1. The peak area within the 200-340 °C range accounted for more than 90% of the total peak area (grey), which indicates that TBBPA can be effectively extracted under these conditions.

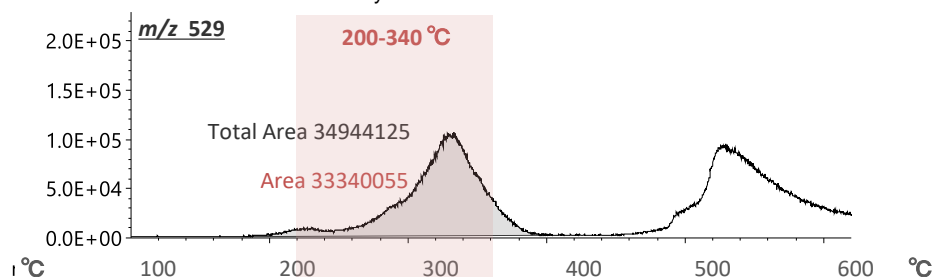


Figure 1. EIC(m/z 529) of EGA-MS(scan) measurement ※ m/z 529:Base peak of TBBPA mass spectrum

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3.2 SIM chromatogram

The SIM chromatograms of the target compounds obtained from SIM/Scan measurement are shown in Figure 2. It can be confirmed that all chromatograms show good peak separation.

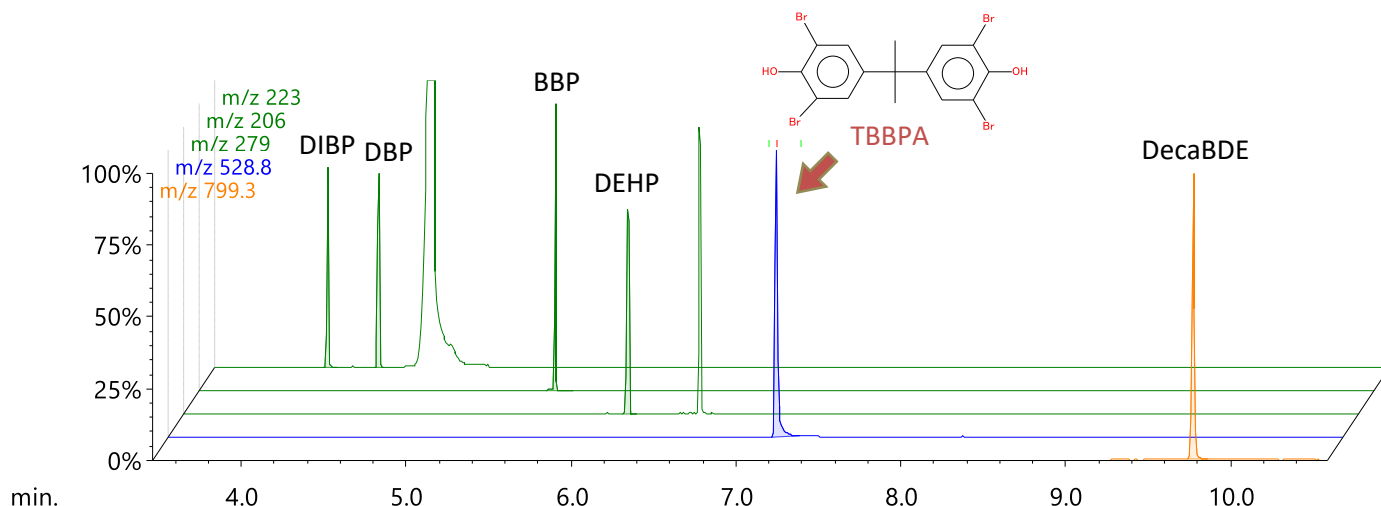


Figure 2. SIM chromatograms of each component

3.3 Sensitivity and Repeatability

Figure 3 shows each SIM chromatogram of TBBPA when SIM/Scan measurements were performed with n=3 trials. Table 2 shows the coefficient of variation (C.V.) in the weight area ratio* of the target compounds. The TBBPA peak was detected with sufficient intensity, and the C.V. was less than 10% for all target compounds.

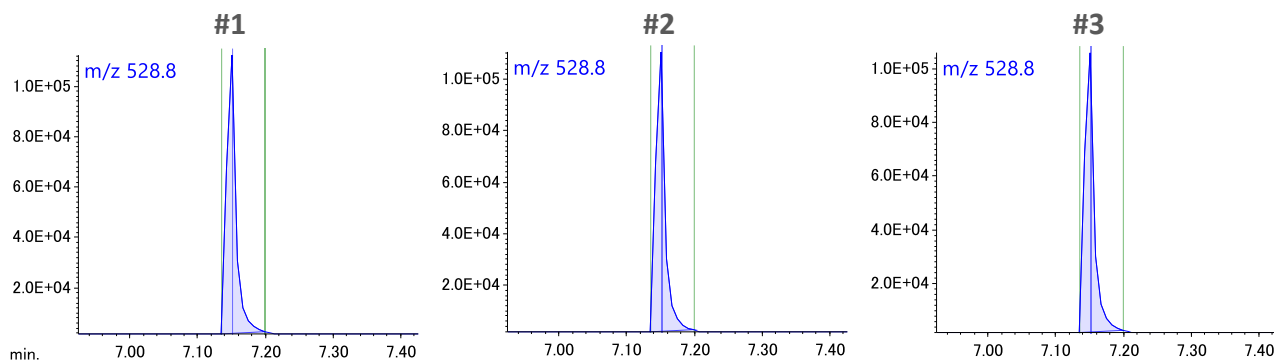


Figure 3. SIM chromatograms of TBBPA (n=3)

Table 2. Weight area ratio and C.V. of each component

Compound name	Weight area ratio			C.V.
	#1	#2	#3	
DIBP	623811	617668	617858	0.5
DBP	543706	531217	534302	1.0
BBP	1276263	1293680	1262182	1.0
DEHP	636690	620154	612234	1.6
TBBPA	228580	226292	222957	1.0
DecaBDE	126182	141878	118888	7.4

*The ratio of peak area value to resin weight value, TBBPA is not converted due to constant amount addition.

Conclusion

We tried to simultaneously analyze the resin additive TBBPA, which has recently become a concern due to its harmfulness to the human body, together with phthalate esters and brominated flame retardants by TD-GC-MS method using a JMS-Q1600GC UltraQuad™ SQ-Zeta. The results showed good sensitivity and repeatability, which indicates that this method is suitable for screening analysis.

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