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A Pyrolysis-GC/MS Screening System for Analysis of Phthalate Esters and Brominated Flame Retardants

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Introduction

Restriction of Hazardous Substances (RoHS) Directive, short for directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment, restricts the use of six hazardous substances commonly used in electronic and electrical equipment. Two of the substances are brominated flame retardants - polybrominated biphenyls (PBB), and polybrominated diphenyl ethers (PBDE), which are known to cause series of health concerns due to the high halogenated content. Furthermore, four types of phthalate esters are expected to be regulated in 2019 in Europe, which add phthalate esters to the list of substances restricted under RoHS. To quantitate these substance in polymer matrix, traditional method involves identifying matrix material using FTIR for solvent determination and extraction of PBBs, PBDEs and phthalate esters from sample matrix, followed by gas chromatography. This method is time consuming and also poses the risk to expose to multiple toxic solvents.

To quantitate these substances in a polymer matrix, the traditional approach involves solvent extraction of PBBs, PBDEs and phthalate esters from the sample matrix, followed by detection and quantitation by gas chromatography/mass spectrometry (GC/MS). This method is time consuming and poses the risk of exposure to multiple toxic solvents.

Pyrolysis followed by GC/MS has been well established for detection of volatile and semi-volatile compounds in both natural and synthetic polymers. Using the pyrolysis technique described here, a temperature programed micro-furnace provides thermal desorption processes at two temperature ranges, releasing the PBBs, PBDEs and phthalate esters from the polymer matrix for subsequent analysis by GC/MS.

In this poster, a PY-GC/MS method has been used to screen for seven phthalate esters and 11 brominated flame retardants. A commercially available method package was used, which includes phthalate ester and PBDE standards, pre-registered instrument methods with acquisition and data processing parameters, and calibration curves for semi-quantitative calculation of compound concentration. Quantitation results were generated with minimal sample preparation, requiring no organic solvents. A software program for efficient multi-analyte data confirmation and QAQC review is also discussed.

Figure 1. Frontier Multi-Shot EGA/PY-3030D pyrolyzer and AS-1020E Auto-Shot sampler installed on the Shimadzu GCMS-QP2010 Ultra

Experimental

This study was conducted using the Shimadzu GCMS-QP2010 Ultra, Frontier Multi-Shot EGA/PY-3030D pyrolyzer, and AS-1020E Auto-Shot sampler, as shown in Figure 1. Method details for the method package Py-Screener and a complete compound list can be found in tables 1 and 2.

Analytical standards used for this project were included with the Py-Screener package. The phthalate standards were comprised of three thin polymer films, which contain seven phthalates at 0, 100 ppm, and 1000 ppm, and one flame retardant standard containing 11 PBBs and PBDEs. All standards and samples were prepared by slicing off small pieces of the polymer using the knife from the sampling tool kit. Approximately 0.5 mg of standards and samples were weighed using an electronic balance with accuracy of 0.01 mg before loading into the sample cups.

A simultaneous selected ion monitoring (SIM) and full scan acquisition method (Scan/SIM) was used on the GCMS-QP2010 Ultra. Using a Scan/SIM method provides enhanced sensitivity of the target compounds by monitoring their signature fragments, while simultaneously screening for the unknown analytes in the full mass range at the same time.

Table 1: Experimental conditions for the instrument acquisition method

Gas Chromatograph	**: CG-2010 Plus**
Column	: UA-PBDE, 15 m x 0.25 mm x 0.05 µm (Shimadzu PN 220-94824-20)
Oven Program	: 80 °C, no hold 20 °C/minute to 300 °C, hold 5 minutes
Injector	: Split mode, split ratio 50:1 300 °C Split Liner w/ wool (Shimadzu PN 220-90784-00)
Carrier Gas	: Helium
Carrier Gas Flow	: Constant linear velocity mode, 52.1 cm/second Total Flow 54 mL/minute, Column Flow = 1.00 mL/minute Purge Flow 3.0 mL/minute
Interface Temperature	: 320 °C
Mass Spectrometer	**: GCMS-QP2010 Ultra**
Ion Source Temperature	: 230 °C
Solvent Cut Time	: 0.5 minutes
Detector Voltage	: Relative to tune + 0.1 kV
MS Operating Mode	: Acquisition mode: Scan/SIM Total loop time 0.45 second Scan event time 0.15 second — SIM event time 0.3 second Mass range: 50-1000 amu — SIM method details listed in table 2
Pyrolyzer	**: PY-3030D (Frontier Labs)**
Sample amount	: 0.5 mg
Furnace Temp	: TD1 200 °C to 300 °C @ 20 °C/minute, total 5 minutes TD2 300 °C to 340 °C @ 5 °C/minute, total 9 minutes
PY-GC Interface Temperature	: Furnace temperature plus 100 °C, up to 300 °C
Analysis Time	
PY program	: 14 minutes
GC/MS program	: 16 minutes
Total Cycle Time per sample	: 30 minutes

Table 2. Compound list and selected ions for SIM method.

Compound Name	Abbreviation / Congeners	Selected Ions for the SIM Mode Quantitation		
		Quantitation	Reference #1	Reference
Diisobutyl phthalate	DIBP	223.0	205.0	149.0
Dibutyl phthalate	DBP	223.0	205.0	149.0
Butyl benzyl phthalate	BBP	206.0	91.0	149.0
Di(2-ethylhexyl) phthalate	DEHP	279.0	167.0	149.0
Di(n-octyl) phthalate	DnOP	279.0	167.0	149.0
Diisononyl phthalate	DINP	293.0	167.0	149.0
Diisodecyl phthalate	DIDP	307.0	167.0	149.0
Hexabromocyclododecane	HBCDD	238.9	560.6	
2,2',4,4'-tetrabromodiphenyl ether	BDE-47	325.8	483.6	
2,2',3,4,4'-pentabromodiphenyl ether	BDE-99	403.8	561.6	
2,2',4,4',6-pentabromodiphenyl ether	BDE-100	403.8	561.6	
2,2',4,4',5,5'-hexabromodiphenyl ether	BDE-153	483.6	643.5	
2,2',4,4',5,6'-hexabromodiphenyl ether	BDE-154	483.6	643.5	
2,2',3,4,4',5,6'-heptabromodiphenyl ether	BDE-183	561.6	721.4	
2,2',3,3',4,4',6,6'-Octabromodiphenyl ether + 2,2',3,4,4',5,6,6'-Octabromodiphenyl ether	BDE-197+204	641.5	643.5	
Nonabromodiphenyl ethers	BDE-206+207+208	719.4	879.2	
Decabromodiphenyl ether	BDE-209	799.3	959.1	
Decabrominated biphenyl	BB-209	783.3	785.3	

Results and Discussion

Calibration Standards

Four standards were analyzed using the Scan/SIM method, which include three standards with phthalates at 0 ppm, 100 ppm and 1000 ppm, and one with PBDEs at various concentration between 26 ppm and 780 ppm. Figure 2 shows the SIM chromatographic profiles for the individual target compounds. DIBP, DBP, BBP, DEHP, and DnOP present as narrow sharp chromatographic peaks, while the profiles for DINP and DIDP present as a broad cluster of chromatographic peaks due to their multiple isomeric components. The area count of mass chromatogram in SIM mode for each compound was determined, and applied to the calibration curve in the quantitation method.

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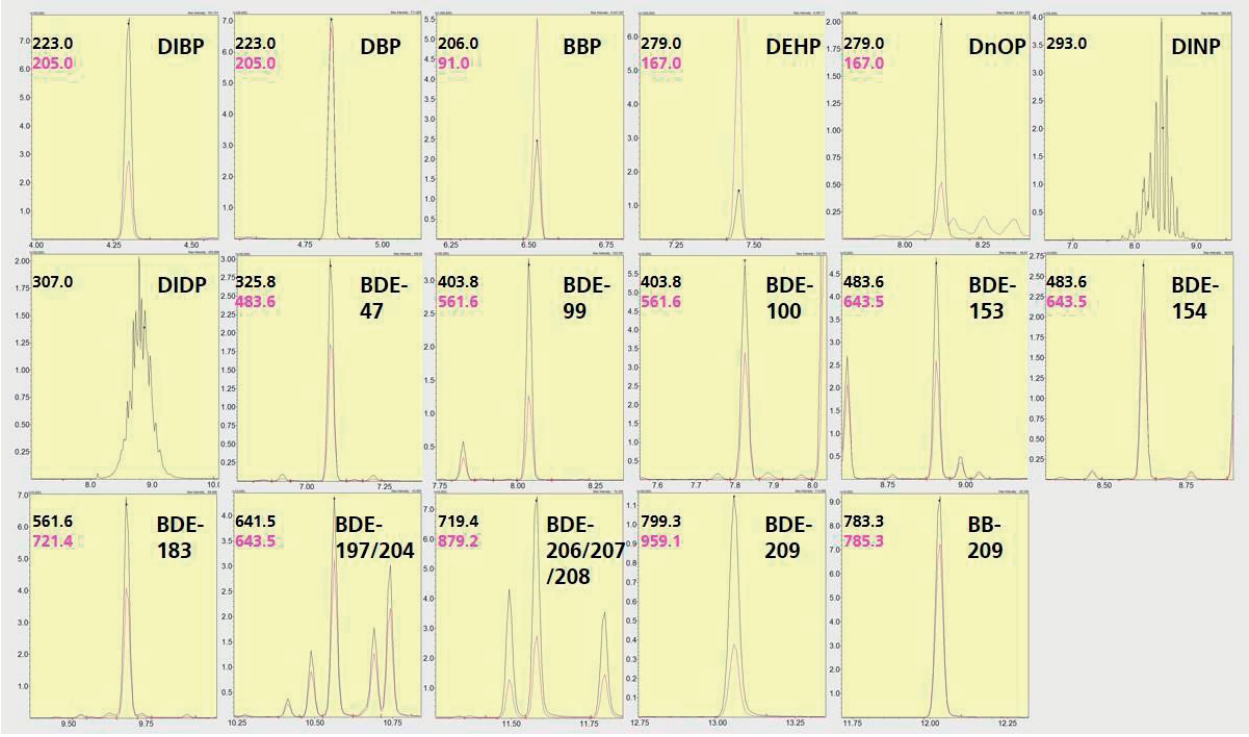

Figure 2. Chromatographic profile of the target compounds extracted from SIM chromatogram of the phthalate and PBDE standards. The primary SIM ions are shown in black, and the secondary reference ions are shown in pink.

LabSolution Insight

For this project three polymer samples were analyzed using the PY-GC/MS method described above; they are labeled Blue Conveyor, White Conveyor, and Gasket. A blank sample cup was also analyzed using the same method for quality control purposes. The pre-registered calibration curve from the Py-Screener package was used for quantitation. The calibration is based on a one-point calibration from analysis of the highest phthalate standard at 1000 ppm, and the PBDE standard. The quantitation results are categorized into three groups to comply with multiple regulations: below 500 ppm, between 500 and 1500 ppm, and beyond 1500 ppm. All 7 target phthalate compounds from one standard and the three samples are displayed side-by-side in LabSolution Insight, and the outliers with concentration above 1500 ppm are labeled with flags, as shown in Figure 3.

The two samples labeled Blue Conveyor and White Conveyor have similar chromatographic profiles, which both show significant phthalate content compared to the Gasket sample. Quantitative analysis results on the blank and the three polymer samples are shown in table 3. DINP and DIDP were detected at around 3% and 0.7% in both Blue Conveyor and White Conveyor samples, which exceed the 0.1% limit in several regulations. The Gasket sample shows only low content of DINP and DIDP at about 0.03% and 0.02%. All the other types of phthalates and PBDEs are either negligible or non-detected in all the three samples.

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Table 3: Quantitative analysis result of three polymer samples

Compound Name	Blank (ppm)	Blue Conveyor (ppm)	White Conveyor (ppm)	Gasket (ppm)
DIBP	ND	ND	ND	23
DBP	1	ND	ND	11
BBP	< 1	9	ND	ND
DEHP	< 1	12	11	81
DNOP	ND	ND	ND	ND
DINP	ND	31489	31722	297
DIDP	ND	7149	7860	192

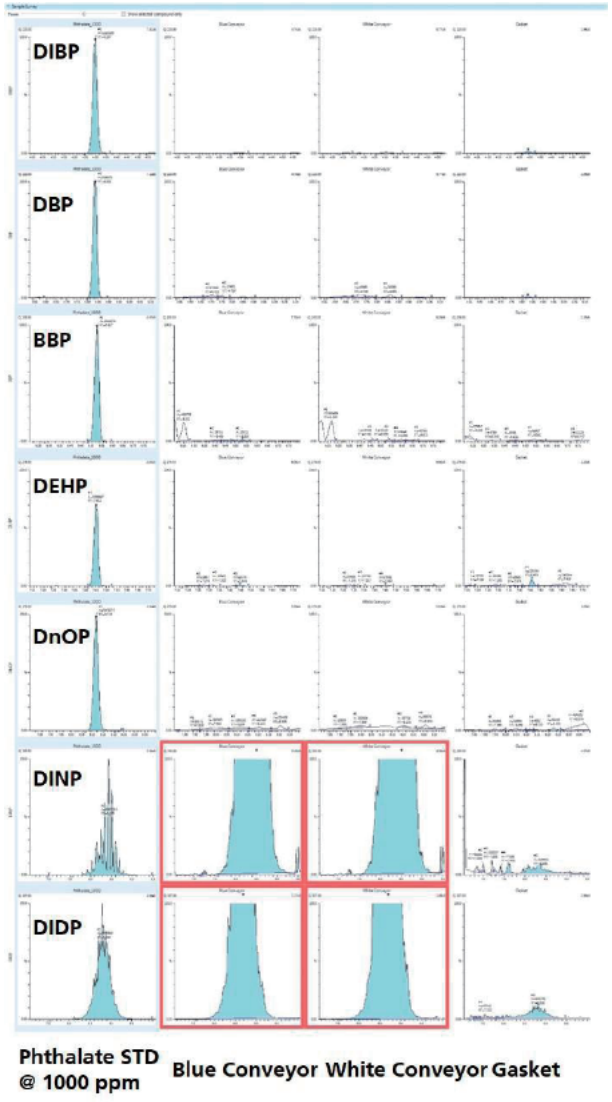

Figure 3. Quantitative analysis of the seven phthalate analytes in one standard and three polymer samples using the LabSolution Insight QAQC software. All the phthalate target compounds from three samples with unknown phthalate concentration are displayed with intensity scaled at the same level as phthalate standard at 1000 ppm. Phthalate content higher than 1500 ppm have been automatically flagged with a red box by the LabSolution Insight software

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Summary and Conclusions

The Py-Screener method package was used to investigate the phthalates and PBDEs content in three polymer samples. Experimental conditions and data processing method are described in detail. The LabSolution Insight program was used to review multiple data and flag outliers based on defined QAQC parameters. This system and software works well as a Semi-Quantitative method for investigating phthalates and PBDEs in different polymers.

References

1. A Pyrolysis-GC/MS Screening System for Analysis of Phthalate Esters and Brominated Flame Retardants, Application News No. GCMS-1504

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