

Rapid determination of phthalates in polymers

Maximizing sample throughput to <10 min per sample using pyrolyzer/thermal desorption GC-MS

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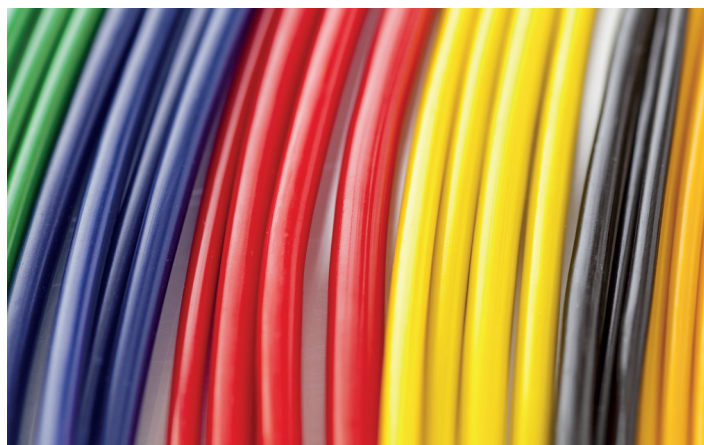
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Goal

Establish a simple and highly automated analytical method to detect and quantify phthalates in polymers with a view to providing an improved rapid screening method.

Introduction

Phthalates are esters of phthalic acid and are extensively used as plasticizers to increase flexibility, durability, and longevity. They are widely used in various industrial and consumer products including plastics, rubber, adhesives, cellulose, resins, medical devices, electronics, children's toys, paints, cosmetics, pharmaceuticals, and personal care products. These compounds are also found as leachables from plastics during the production process, as well during storage, in products such as food, pharmaceutical, and personal care products.



Many phthalates and their metabolites are classified as hazardous due to their effects on the reproductive system, suspected endocrine disruption, and increased risk of cancer.¹ Because of these health risks many phthalates are regulated as banned or restricted above specific limits.¹ In addition to this, the EU has banned specific phthalates for use in toys due to possible adverse effects on infants.

Traditional methods for the analysis of phthalates in plastic such as Soxhlet or microwave assisted solvent extraction are time consuming and use vast amounts of organic solvents. For example the conventional Soxhlet extraction method involves a lengthy 6-hour Soxhlet extraction, requiring a large amount of solvent and sample (>120 mL *n*-hexane per 500 mg sample), with a resulting extract that could contain multiple co-extracts, making the analysis even more challenging and costly.

The aim of this work was to develop an efficient method for the rapid analysis of phthalates in plastic that meets regulatory requirements, reduces cost per analysis, and increases sample throughput. The following analytical methodology is based on the International Electrotechnical Commission (IEC) method detailed in IEC 62321-8:2017: Determination of certain substances in electrotechnical products – Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatography-mass spectrometry using a pyrolyzer/thermal desorption accessory (Py/TD-GC-MS).²

Experimental

Sample preparation

A 0.50 mg sample was weighed (accurate to 0.01 mg), and then loaded onto the pyrolyzer unit ready for analysis. An example of the sampling process is shown in Figure 1. Three samples of different plastic materials were taken for analysis (Figure 2).

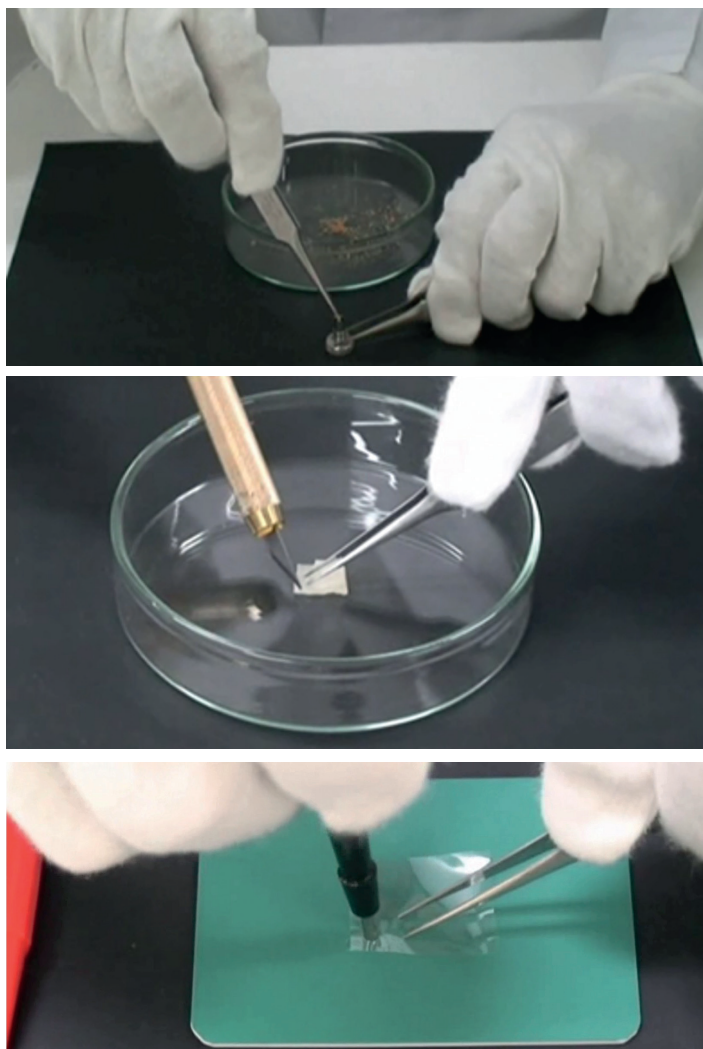


Figure 1. Sample preparation, where 0.50 mg of sample is prepared prior to loading on to the pyrolyzer unit

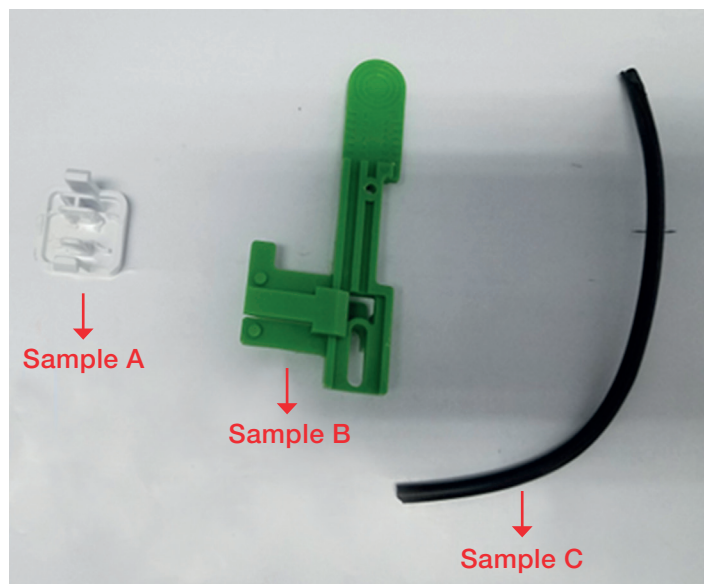


Figure 2. Examples of samples for phthalate analysis

Standard preparation

A standard PVC substrate (1,000 mg/kg) was weighed to 0.50 mg (accurate to 0.01 mg) and analyzed as detailed to produce a single-point calibration curve.

Instrument and method setup

A Thermo Scientific pyrolyzer/thermal desorption GC-MS system, composed of a Thermo Scientific[™] ISQ[™] 7000 GC-MS coupled with a Frontier EGA/PY-3030D Multi-Shot Pyrolyzer[™] system with a thermal desorption accessory, and a Thermo Scientific[™] TRACE[™] 1310 Gas Chromatograph, was used for all sample and standard evaluations (Figure 3). The unique pyrolyzer inlet interfaces perfectly with the modular inlet configuration of the ISQ 7000 GC-MS.



Figure 3. Thermo Scientific pyrolyzer/thermal desorption GC-MS system, composed of an ISQ 7000 GC-MS coupled with a Frontier EGA/PY-3030D Multi-Shot Pyrolyzer system with a thermal desorption accessory, and a TRACE 1310 Gas Chromatograph

Compound separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-5HT 15 m × 0.25 mm × 0.10 μm column (P/N 26095-0350).

System features

1. High degree of automation—the autosampler can take up to 48 samples meeting the requirements of high-throughput analysis.
2. Unique inlet interface design—the inlet is easily configured without needing to cut the carrier gas flow path. The TRACE 1310 GC can be switched freely between the pyrolyzer sampling method and other sampling methods.
3. Stable performance—the system produces less residual content after high-concentration injections, which greatly reduces the maintenance time needed and permits prolonged continuous screening.

Additional details on instrument parameters are listed in Tables 1–4. The total running time is 10.0 min, which included both the pyrolyzer and GC-MS operation times.

Data processing

GC-MS data were acquired, processed, and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), version 7.2. Chromeleon CDS allows the analyst to set up acquisition, processing, and reporting methods with simplified data review and reporting. The Chromeleon e-Workflow™ method option provides customizable instrument methods, analysis methods, and method specific report templates. The result of which is a solution that allows one click to start analysis and generate a report.

Table 1. TRACE 1310 GC and injector conditions

TRACE 1310 GC system parameters			
Liner	SSL Liner, 2 × 2.75 × 84.2 mm (P/N 45322059)		
Inlet temperature	300 °C		
Carrier gas, mode	He, 1.5 mL/min, constant flow		
Inlet module and mode	SSL, split mode		
Split ratio	100:1		
Column	TraceGOLD TG-5HT 15 m × 0.25 mm × 0.10 μm (P/N 26095-0350)		
Oven temperature program	Rate (°C/min)	Target temperature (°C)	Hold time (min)
Stage 1	-	80	0
Final	50	300	1.8

Table 2. ISQ 7000 Mass Spectrometer conditions

ISQ 7000 GC-MS system parameters	
Transfer line (°C)	280
Ionization mode	El (ExtractaBrite™)
Ion source (°C)	320
Electron energy (eV)	70
Acquisition mode	Selected ion monitoring (SIM)

Table 4. Frontier EGA/PY-3030D conditions, using double-shot thermal desorption operating mode

Initial (°C)	Initial (min)	Rate (°C/min)	Final (°C)	Final (min)	Total
200	0	50	340	1	3.8

Table 3. Phthalate compound monitoring details selected ion monitoring (SIM) quantitative and qualitative ions

Compound number	Chemical compound	Quantitative ion	Qualitative ion
1	DIBP	223	205, 149
2	DBP	223	205, 149
3	BBP	206	91, 149
4	DEHP	279	167, 149

Results and discussion

Chromatographic resolution and peak asymmetry are vital for accurate determination of peak area, and in turn accurate concentration of the target analytes. The resolution and peak shape are shown in the total ion chromatogram obtained using the method conditions described (Figure 4) for 0.5 mg of 1,000 mg/kg standard PVC substrate. The retention time details are listed in Table 5.

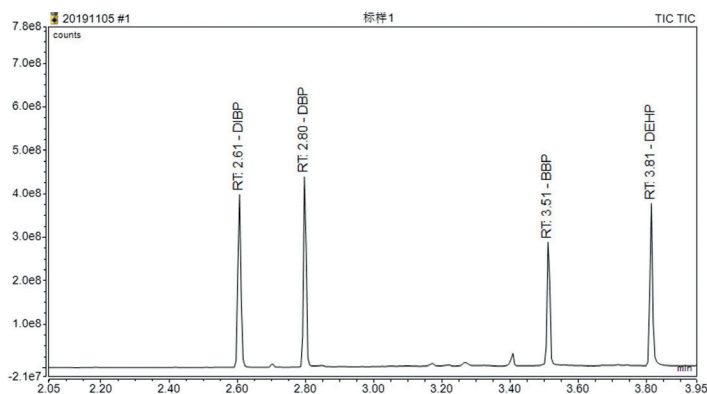


Figure 4. Total ion chromatogram (full scan, EI) of 0.5 mg of 1000 mg/kg standard PVC substrate

Table 5. Retention times of four phthalates, using the Py/TD-GC-MS method conditions detailed

Compound number	Chemical compound	Retention time (min)
1	DIBP	2.61
2	DBP	2.80
3	BBP	3.51
4	DEHP	3.81

RSD and system residue determination

0.50 mg of 1,000 mg/kg PVC standards were weighed (accurate to 0.01 mg) using the detailed method to separately analyze (n=8) samples and to analyze one sample multiple times (n=9). For the four components, % RSD of between 5.67 and 7.85 were achieved, illustrating good repeatability; also low system residue values were achieved after repeat analysis of the same sample nine times (Table 6).

Table 6. Repeat separate analysis of a PVC standard (n=8) with additional continuous injections (n=9), to give % RSD and residual amount (ng)

Compound number	Chemical compound	Retention time (min)	% RSD (n=8)	Residual amount (ng) (After 9 stitches, the theoretical value is 500 ng)
1	DIBP	2.61	7.66	21.38
2	DBP	2.80	5.67	26.61
3	BBP	3.51	7.85	ND
4	DEHP	3.81	6.55	ND

Note: ND = not detected.

Sample determination

Three samples of different plastic materials were analyzed as detailed to test for phthalates. The results and chromatograms are shown in Table 7 and Figure 5, respectively.

Table 7. Phthalate results for three plastic samples

Compound number	Chemical compound	Sample (mg/kg)		
		A	B	C
1	DIBP	1.63	1.22	46.21
2	DBP	0.48	0.87	43.14
3	BBP	4.31	3.69	ND
4	DEHP	2.11	5.12	73.62

Note: ND = not detected.

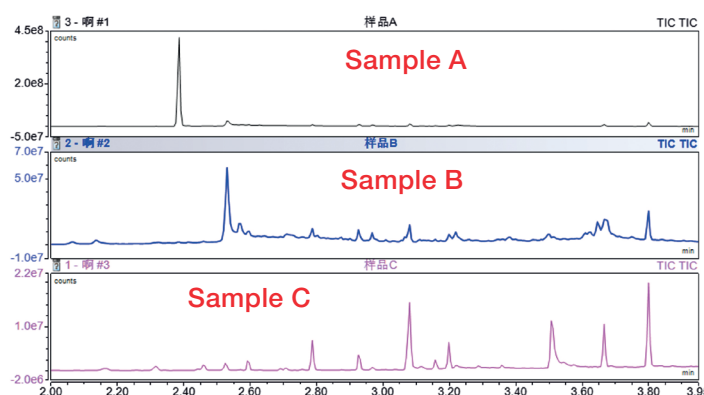


Figure 5. Total ion chromatograms (full scan, EI) achieved for the three analyzed plastic samples

Based on the generated results and overall analysis time, clear advantages to traditional methods for plastic analysis are apparent. A comparison between conventional Soxhlet extraction and pyrolyzer methods, taken from IEC 62321-8: 2017³ is shown in Table 8. The table highlights several advantages when using a pyrolyzer method which requires:

- **No solvent**, saving 170 mL of *n*-hexane per sample
- **Less sample**, 1,000-fold less sample amount
- **No extraction process**, saving ~7 hours per sample

Table 8. Comparison of Soxhlet and pyrolyzer processes (taken from IEC 62321-8: 2017)

Soxhlet extraction process	Pyrolyzer process
a) Quantitatively transfer 500 ± 10 mg of the sample to the cellulose thimble using a funnel for Soxhlet extraction. To ensure quantitative transfer the funnel should be rinsed with 10 mL of <i>n</i> -hexane.	a) Using a micro spatula or tweezers, place approximately 0.5 mg of the sample (cut or powder) into the pre-weighed sample cup.
b) Add 10 µL of pseudo standard (1,000 µg/mL).	b) Record the total weight of the sample cup to the nearest 0.01 mg and subtract the weight of the sample cup to obtain the weight of the sample.
c) Cover the thimble with glass wool to prevent the sample from floating.	c) Put an appropriate amount of deactivated glass wool into the sample cup to ensure that the sample powder will not overflow.
d) Extract the sample for at least 6 hours, with 6 to 8 cycles per hour. Shorter extraction time will reduce the recovery of the analyte.	
e) After 6 hours of reflux, the extract is concentrated to about 10 mL using rotary evaporation under vacuum (or using a comparable method), and then made up to 50 mL with <i>n</i> -hexane.	

Extraction methods such as Soxhlet or microwave assisted solvent extraction are time consuming and/or use vast amounts of organic solvents. Using the developed Py/TD-GC-MS method when compared to the conventional Soxhlet, a batch of 10 samples would take a fifth of the time, while saving 1.7 L of *n*-hexane. The Py/TD-GC-MS method, where no solvent is used for sample extraction, minimizes potential health and safety concerns of solvent storage, usage, and disposal when compared to Soxhlet extraction techniques involving high solvent usage with associated solvent disposal or recycling cost.

Conclusion

A Thermo Scientific Pyrolyzer/thermal desorption GC-MS analysis system composed of a Thermo Scientific ISQ 7000 GC-MS, coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph and a Frontier EGA/PY-3030D multi-shot Pyrolyzer system, is a suitable analytical solution for the analysis of phthalates in plastic samples.

- Using the developed Py/TD-GC-MS method for a batch of 10 samples when compared to the conventional Soxhlet extraction (considering a batch of 10 Soxhlet extraction units) and analyzed using GC-MS, the simplified sample preparation results in five times greater sample throughput while providing a green approach that uses no solvent (1.7 L of *n*-hexane saved per 10 samples).

- Excellent repeatability of results was achieved for the analysis of PVC standards (0.50 mg of 1,000 mg/kg PVC, n=8) with % RSD between 5.67 and 7.85 obtained for the four analyzed phthalates.
- The unique pyrolyzer inlet interface realizes the perfect combination of ISQ GC-MS and pyrolyzer, enabling thermal desorption to be used as a inventive sample introduction technology. The Py/TD-GC-MS method greatly simplifies the pre-treatment process by reducing the difficulties of sample preparation, while improving the efficiency of sample analysis, with good repeatability, and low compound residues.
- Chromeleon CDS software offers a customizable solution for the targeted analysis of phthalates with fully automated sample handling and data processing and reporting for high-throughput routine laboratories where time and cost of analysis are key.

References

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