

# Comprehensive screening of volatile emissions from plastics



This study demonstrates the use of a discovery platform combining thermal desorption (TD) with GC×GC–TOF MS for comprehensive screening of emissions from plastics.

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## Introduction

The release of chemicals from products and materials has been the subject of various mandatory regulations and ‘green codes’ for many years. US building codes, European Construction Product Regulation (CPR) and REACH<sup>[1]</sup> are key examples of regulatory developments that increase the need for chemical emissions testing as part of product labelling.

Recently, vehicle interior air quality (VIAQ) has been the major focus for emissions testing, with new Chinese mandates dictating the worldwide response to health concerns and off-odour complaints (read more in our white paper “[New car smell: Improved identification of odours in vehicle interior air](#)”). However, more pressure has also been placed on the manufacturers of electronic products, respiratory medical devices, food packaging, children’s toys and consumer goods to report emissions of hazardous and odorous compounds.

In particular, the analysis of plastic has gained increased attention, due to the global push to reduce pollution and utilise more recycled products. Recycling of plastic requires further quality control to ensure the final products – which may be used for food and beverage packaging – will not produce volatile emissions that could be considered harmful or have a negative impact on the packaged product (i.e. malodours).

Here, we describe a discovery platform combining TD with GC×GC–TOF MS to uncover ‘hidden’ compounds which would have been overlooked using conventional GC–MS techniques.

## Experimental

**Samples:** Four different types of plastic pellets (Figure 1) were obtained for analysis as listed in Table 1.



**Figure 1**

The plastic pellets analysed in this study.

Sample	Composition
Polypropylene (PP)	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---} \\   \\ \text{H} \end{array} \right]_n$
Polyethylene (PE)	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---} \\   \\ \text{H} \end{array} \right]_n$
Acrylonitrile butadiene styrene (ABS)	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---} \\   \\ \text{H} \end{array} \right]_l \left[ \begin{array}{c} \text{H} \\   \\ \text{---} \\   \\ \text{H} \end{array} \right]_m \left[ \begin{array}{c} \text{H} \\   \\ \text{---} \\   \\ \text{H} \end{array} \right]_n$
Polyvinyl chloride (PVC)	$\left[ \begin{array}{c} \text{H} \\   \\ \text{---} \\   \\ \text{H} \end{array} \right]_n$

**Table 1**

Composition of the plastic pellets.

**Dynamic headspace:** Approximately 3 g of plastic was placed within a sealed chamber for dynamic headspace combined with subsequent focusing and TD. (Note: Relevant methods include ISO 12219-series and ISO 16000-series standards.)

**TD:** Instrument: xr-series thermal desorber (Markes International). Sorbents: Quartz, Tenax<sup>®</sup> and carbon black (per ISO 16000-6); Trapping temperature: 25°C; Desorption temperature: 280°C; Trap heating rate: Max.

**GC×GC:** Modulator: INSIGHT<sup>®</sup> (SepSolve Analytical); Modulation period ( $P_M$ ): 5 s.

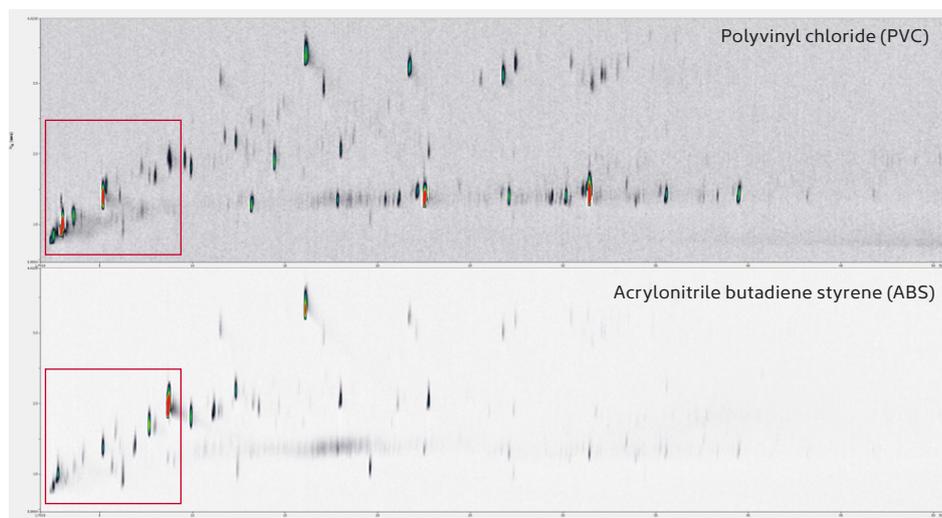
**TOF MS:** Instrument: BenchTOF-Select<sup>™</sup>; Mass range:  $m/z$  45–500; Acquisition rate: 100 Hz in Tandem Ionisation<sup>®</sup> mode at 70 eV and 14 eV.

**Software:** Instrument control and data processing by ChromSpace®.

Please contact SepSolve for full analytical parameters.

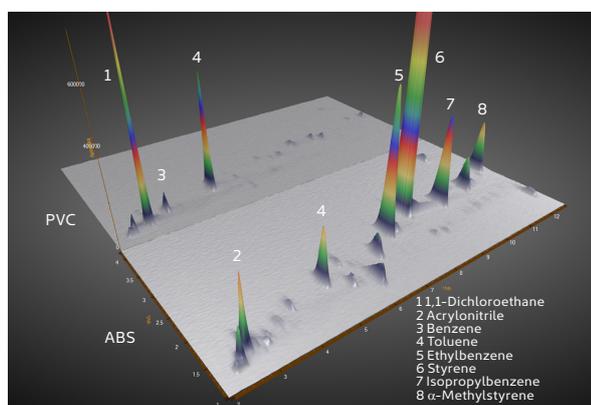
## Results

The TD–GC×GC–TOF MS colour plots for the polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS) samples are shown in Figure 2. At first glance, the compositions appear similar; however, the expanded regions – displayed as surface charts in Figure 3 – show the differences in volatile emissions from the two samples.



**Figure 2**

TD–GC×GC–TOF MS colour plots for the PVC and ABS samples.

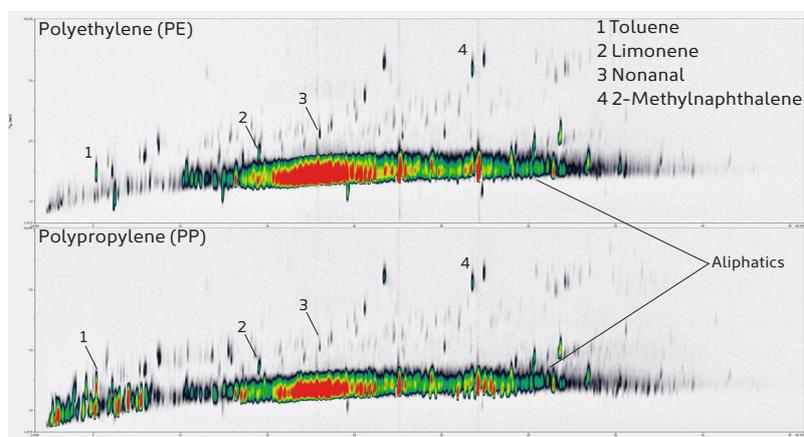


**Figure 3**

Expanded region of the TD–GC×GC–TOF MS surface charts for PVC and ABS showing compositional differences.

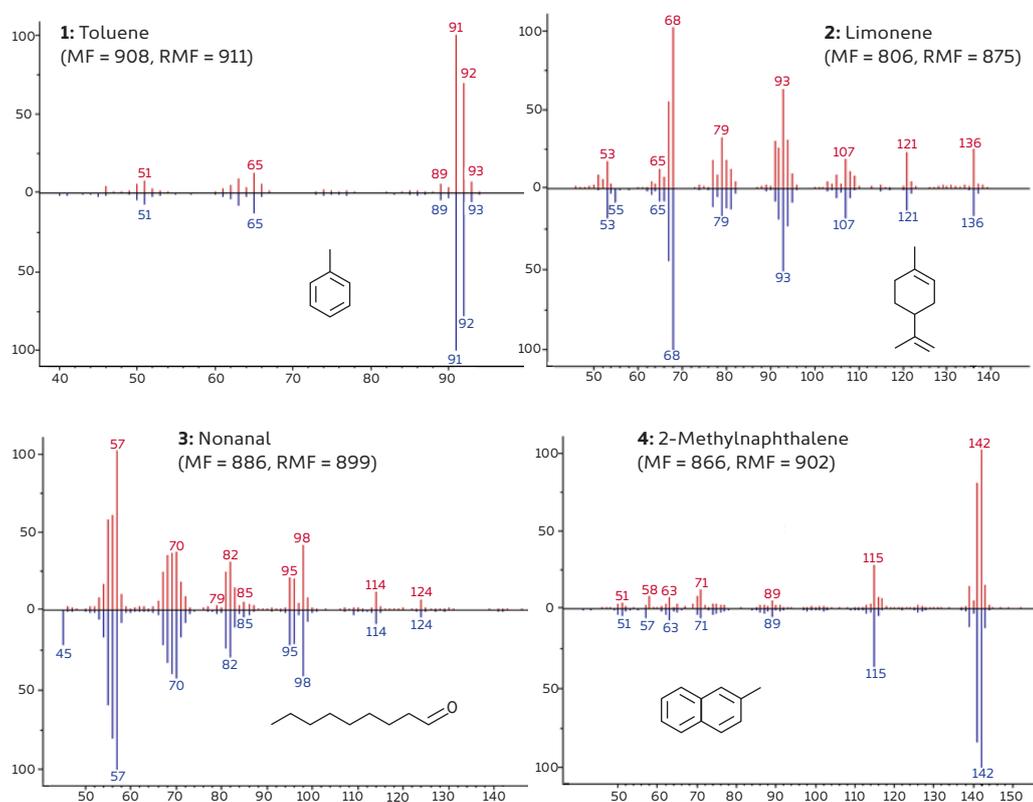
Figure 4 shows the TD–GC×GC–TOF MS colour plots for the polyethylene (PE) and polypropylene (PP) samples. The volatile emissions from both plastics are dominated by aliphatic hydrocarbons. The enhanced separation of GC×GC provides cleaner spectra for confident identification of key analytes – for example, the four compounds highlighted in Figure 4 which would have co-eluted with the high-loading aliphatics in a 1D separation.

The coupling of BenchTOF MS with GC×GC ensures that these components can be identified confidently, using simple screening against commercial libraries, such as NIST and Wiley (Figure 4).



**Figure 4**

TD-GC×GC-TOF MS colour plots for the PE and PP samples, with a selection of compounds identified by BenchTOF MS (top, red) against the NIST 17 library (bottom, blue).



Previous studies have attributed  $C_6$ – $C_{11}$  carbonyls (e.g. aldehydes and ketones) as major odour contributors from thermal oxidation of plastic.<sup>[2]</sup> In a 1D separation, these compounds would be completely masked by the high-loading aliphatics.

In fact, numerous aldehydes were identified across the four plastic samples, including octanal, nonanal and decanal. Table 2 provides a summary of key components identified in each sample.

As expected, given its molecular structure, PVC was found to release numerous chlorinated compounds, such as 1,1-dichloroethane and 1,4-dichlorobenzene – both of which are deemed environmental pollutants. Interestingly, PVC was the only sample not found to contain tetrachloroethylene – it was detected from all other plastics.

A range of odorous compounds were also detected, including octanal and styrene, as well as components that are thought to be hazardous to health, such as methyl methacrylate and benzene.

Once such target compounds are known, the method can be easily translated to simpler TD–GC×GC–FID systems for use across QC labs, while the GC×GC–TOF MS can be used in an R&D environment to troubleshoot any issues that may arise with sample batches.

Compound	<sup>1</sup> t <sub>R</sub> (min)	<sup>2</sup> t <sub>R</sub> (s)	Peak area			
			ABS	PVC	PP	PE
2-Propenenitrile	2.7295	1.4679	4.86E+06			
1,1-Dichloroethane	2.9797	1.3928		9.57E+06		
Benzene	3.5916	1.5916	4.59E+05	1.12E+06	4.36E+05	7.62E+05
Trichloroethylene	4.0406	1.5987		1.21E+05		
Methyl methacrylate	4.0825	1.7270	4.99E+05			
2-Methylbutan-1-ol	4.6014	1.7993			1.79E+06	
Toluene	5.1851	1.8720	2.65E+06	5.89E+06	9.62E+06	4.53E+06
Tetrachloroethylene	6.0833	1.9076	9.59E+04		9.69E+05	1.20E+06
Vinylcyclohexene	6.8880	1.9000	1.43E+06			
Chlorobenzene	7.2325	2.2958		1.71E+05		
Ethylbenzene	7.6859	2.1922	6.56E+06	8.21E+04	2.08E+05	3.56E+05
<i>p</i> -Xylene	7.9714	2.1607	7.59E+05	3.55E+05	8.33E+05	1.69E+06
Styrene	8.6607	2.4232	7.06E+07			1.73E+06
Butylprop-2-enoate	8.9517	2.4392	3.53E+06	8.18E+05	8.81E+05	
1,3-Dichloro-2-butene	9.6728	2.3724		3.86E+05	3.04E+05	
Isopropylbenzene	9.9191	2.3076	4.83E+06	3.82E+05		7.51E+04
<i>p</i> -Ethyltoluene	11.4666	2.4235	6.63E+05		1.42E+05	3.42E+05
Benzaldehyde	11.4963	3.5493	6.70E+05	1.98E+05		2.04E+05
Mesitylene	11.8127	2.4081			3.95E+05	1.99E+05
$\alpha$ -Methylstyrene	12.3531	2.6876	2.81E+06	3.74E+05	4.68E+04	5.37E+04
3,4-Dichlorobut-1-ene	13.1667	2.9685		5.65E+04		
Octanal	13.2818	2.4981	4.36E+05	3.49E+04	3.47E+04	1.94E+05
3-Carene	13.5756	2.1554			2.43E+05	1.09E+06
<i>sec</i> -Butylbenzene	13.6037	2.4325	7.10E+05		9.00E+03	

**Table 2**

Key components identified in the four plastic samples.

Compound	<sup>1</sup> t <sub>R</sub> (min)	<sup>2</sup> t <sub>R</sub> (s)	Peak area			
			ABS	PVC	PP	PE
1,4-Dichlorobenzene	13.8333	2.9285		5.62E+04		
2-Ethylhexan-1-ol	14.4167	2.3879		9.96E+05	1.29E+05	
Limonene	14.5000	2.1876	7.57E+04		1.16E+06	4.51E+06
Eucalyptol	14.6667	2.4676	1.40E+05			
Indane	14.6667	2.8879		4.76E+04	2.91E+04	6.01E+04
Acetophenone	16.0865	3.8098	1.31E+07	2.05E+06		
α,α-Dimethylbenzene methanol	17.0621	3.3974	1.33E+05	2.75E+05		
Terpinolene	17.0978	2.3618			3.87E+05	
Nonanal	17.9794	2.5328	2.11E+06	4.23E+05	2.62E+05	8.78E+05
Tetralin	20.606	3.1734		4.24E+04	3.77E+05	1.28E+06
Naphthalene	21.6973	3.7149	7.60E+05	1.05E+06	9.14E+05	2.08E+06
Methyl salicylate	22.0833	3.4876	1.52E+05			1.41E+05
Decanal	22.7299	2.5132	2.11E+06	1.70E+05	1.57E+05	4.41E+05
Hexylbenzene	25.1487	2.5437			3.31E+05	6.24E+05
2-Methylnaphthalene	26.7729	3.4985	5.02E+05	8.91E+05	9.26E+05	
Undecanal	27.3333	2.3676	1.33E+05			
1-Methylnaphthalene	27.4349	3.6563	2.39E+05	4.58E+05	5.07E+05	
Longifolene	31.7862	2.365	1.28E+05	2.96E+04	5.35E+06	1.01E+07
Octylbenzene	34.0833	2.6076				1.22E+05

**Table 2**

Key components identified in the four plastic samples (continued from previous page).

## Conclusions

This white paper has shown the TD–GC×GC–TOF MS system provides:

- ▶ Efficient sampling of VOCs from plastics using dynamic headspace and preconcentration by TD.
- ▶ Compatibility with wide-ranging analytes – including VOCs, SVOCs and thermally labile species.
- ▶ Enhanced separation for improved discovery of sample composition and robust quality control of sample batches.
- ▶ Cryogen-free sampling and analysis for low running costs.
- ▶ Confident identification using the reference-quality spectra of BenchTOF.
- ▶ Flexible configurations with simple translation from TD–GC×GC–TOF MS to TD–GC×GC–FID for use in QC labs.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

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## References

- [1] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/4, *Official Journal of the European Union*, 2007, 3–280.
- [2] H. Hopfer, C. Sauer, N. Haar and E. Leitner, Comparison of Different Analytical Methods for Volatile and Odour-Active Substances in Polyolefins, *Macromolecular Symposia*, 2010, 296, 176–182.

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