Improved characterisation of malodours in recycled plastics using TD–GC×GC with BenchTOF2 MS

Thermal desorption (TD) with GC×GC–TOF MS can be used for comprehensive characterisation of volatiles from recycled plastics, and the method is simple to translate to routine screening in QC labs.

Introduction

The analysis of plastic has gained increased attention in recent years, due to the global push to move to a circular economy (the increased use of recycled materials to reduce waste). Manufacturers are being urged to produce or use more post-consumer recycled (PCR) plastics, especially for food and beverage packaging.

PCR plastics require more rigorous quality control (QC) measures to ensure that they will not produce volatile emissions that could be considered harmful or have a negative impact on the packaged product (e.g., malodours).

However, there are several limitations with the existing methods used for the detection of odours from plastics.

► A **human sensory panel** is a sensitive approach, but it is also subjective, time-consuming and requires skilled individuals. In addition, it is restricted to sensory information: no chemical identities are provided, so sensory panels cannot identify a possible source or clean-up process to eliminate the malodour.

► The **electronic nose** (**eNose**) is faster and simpler to use as it is a handheld device with sensor technology. However, the technique is not specific, meaning that samples that fail QC testing must undergo further analytical investigation.

► **Gas chromatography coupled with mass spectrometry** (**GC–MS**) can provide a more quantitative approach but may struggle to fully resolve all the volatile organic compounds (VOCs). Typically, the odour profiles are dominated by aliphatics from the polymer itself, which easily mask the trace-level odorants (e.g., oxygenated species). Traditional quadrupole MS

must operate in scan mode to find these non-target components, but this limits the sensitivity of the instrument. Additionally, common sample introduction techniques, such as headspace injection and solid-phase microextraction (SPME), may lack the necessary sensitivity to capture the trace odorants.

With these approaches, it is often not possible to identify the precise compounds responsible for high odour in recycled plastics, which means that the recycling process cannot be improved and QC failures continue to occur. Trace odours can cause the end users' products to fail QC further down the production chain, which passes further cost onto the customers and can cause losses in returned product or compensation claims.

Thermal desorption coupled with comprehensive two-dimensional gas chromatography and time-of-flight mass spectrometry (TD–GC×GC–TOF MS) can address these challenges by providing high sensitivity and improved separation of the odour profiles prior to confident identification of the individual analytes.

Firstly, the VOCs are sampled using direct desorption in which a small number of plastic pellets are placed directly into an empty TD tube, which is heated to release the VOCs. Using the TD100-xr™ thermal desorber from Markes International, optimal sensitivity is achieved by preconcentrating the analytes on an electrically cooled focusing trap before they are sent to the GC in a narrow band of vapour. The TD100-xr enables automated analysis of up to 100 tubes and its operation is solvent-free and cryogen-free, making it ideal for high-throughput screening of plastics.

Next, GC×GC using the consumable-free INSIGHT® flow modulator provides the enhanced separation necessary to resolve such complex odour profiles, for clean spectra and confident identification of analytes by the BenchTOF2™ mass spectrometer. BenchTOF2 provides the fast acquisition speeds necessary to cope with the narrow peak widths generated by GC×GC, as well as improved sensitivity and selectivity compared to single quadrupole MS, making it the ideal technique for untargeted 'discovery' applications.

Finally, ChromCompare+ software compares the resulting chromatograms, enabling the important differences between high- and low-odour plastics to be identified. This automated, untargeted workflow uses all the raw data to minimise the risk of missing any compounds of importance.

Here, we demonstrate how TD–GC×GC–TOF MS can provide confident characterisation of complex odour profiles from recycled plastics, for fast and simple identification of the compounds causing QC failures. Once the key odorants are known, methods can be easily translated to TD–GC×GC–FID for routine screening in QC labs at production sites.

Experimental

Samples: An empty TD tube (Markes International) was filled with 0.3 g of plastic pellets.

TD: Instrument: TD100-xr (Markes International); Focusing trap: Materials/ Emissions; Trap low: -20°C; Desorption temperature: 100°C.

GC×GC: INSIGHT flow modulator (SepSolve Analytical); Modulation period (P_M) = 2.5 s.

TOF MS: BenchTOF2 time-of-flight mass spectrometer (SepSolve Analytical); Mass range: m/z 30–600.

Software: ChromSpace® software (SepSolve Analytical) for full instrument control and data processing, with chemometric comparisons by ChromCompare+ (SepSolve Analytical).

Please contact SepSolve for full analytical parameters.

Results and discussion

In 1D GC separations, the trace odorants in plastics are often masked by the high-loading aliphatics and may be overlooked entirely. Figure 1 provides the TD–GC×GC–TOF MS chromatogram for the direct desorption of plastic pellets. Here, the aliphatics are retained longer in the second-dimension column, thus eluting in a band of intense peaks along the top of the colour plot (as annotated below). On the other hand, the odour-active compounds (such as oxygenated species) elute earlier in the second dimension, separating these compounds from the aliphatics.
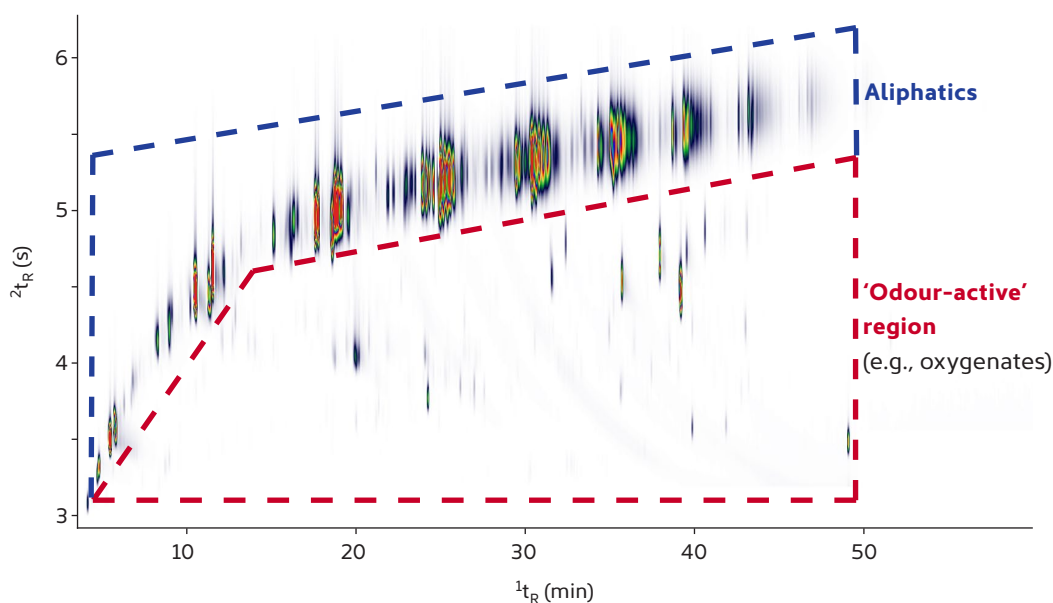

Figure 1

TD–GC×GC–TOF MS colour plot for the direct desorption of plastic pellets.

For example, Figure 2 shows a zoomed region of the chromatogram in which a trace peak is physically separated from the high-loading aliphatics and could be confidently identified as nonanal, which is known to impart a waxy, aldehydic odour.[1]
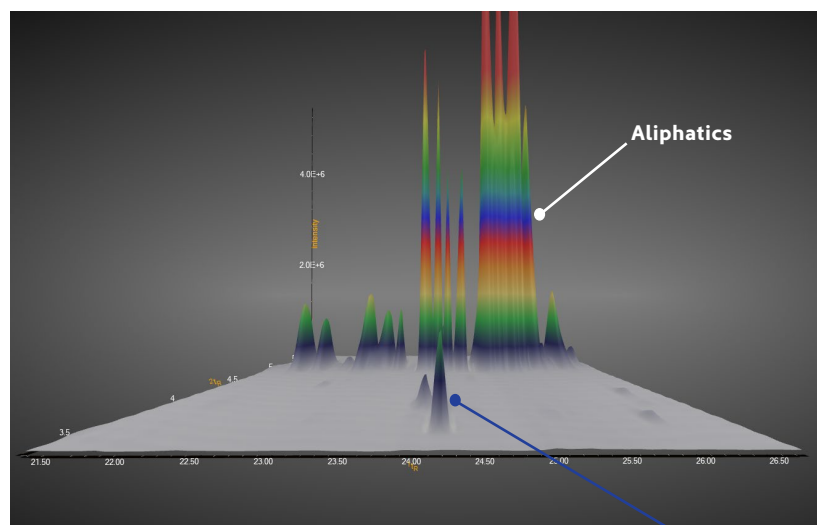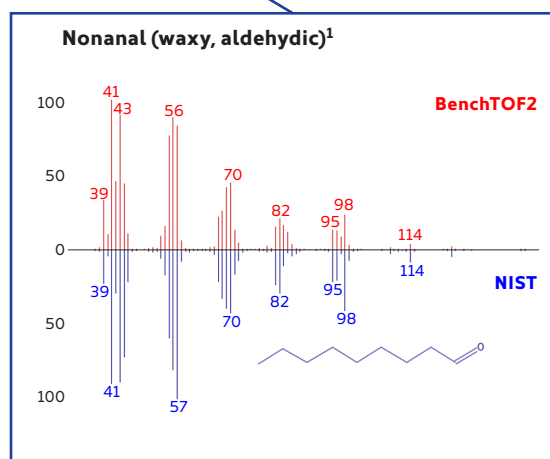
Figure 2

Zoomed region of the TD–GC×GC–TOF MS surface chart showing the separation and identification of a trace odour-active compound.

It is important to note that the rapid secondary separations in GC×GC frequently result in peak widths less than 100 ms, so detector speeds of 100 Hz are essential to maintain at least 10 datapoints across a peak. BenchTOF2 is inherently well-suited to handling such narrow GC peaks, since TOF mass spectrometers are dispersive (not scanning) instruments, and so effectively monitor all masses at once with fast acquisition rates. The ability to record full-range mass spectral information to extremely high densities enables BenchTOF2 to handle the narrowest peaks encountered in well-optimised GC×GC couplings.

To prove the performance of the TD–GC×GC–TOF MS to identify differences between plastics that have passed and failed QC tests, a selection of 'high'-odour and 'low'-odour plastics were analysed. It is clear from the example chromatograms in Figure 3 that there are additional peaks in the odour-active region of the high-odour plastic. However, for such high-throughput applications, automated comparison of samples is essential to deliver fast results.
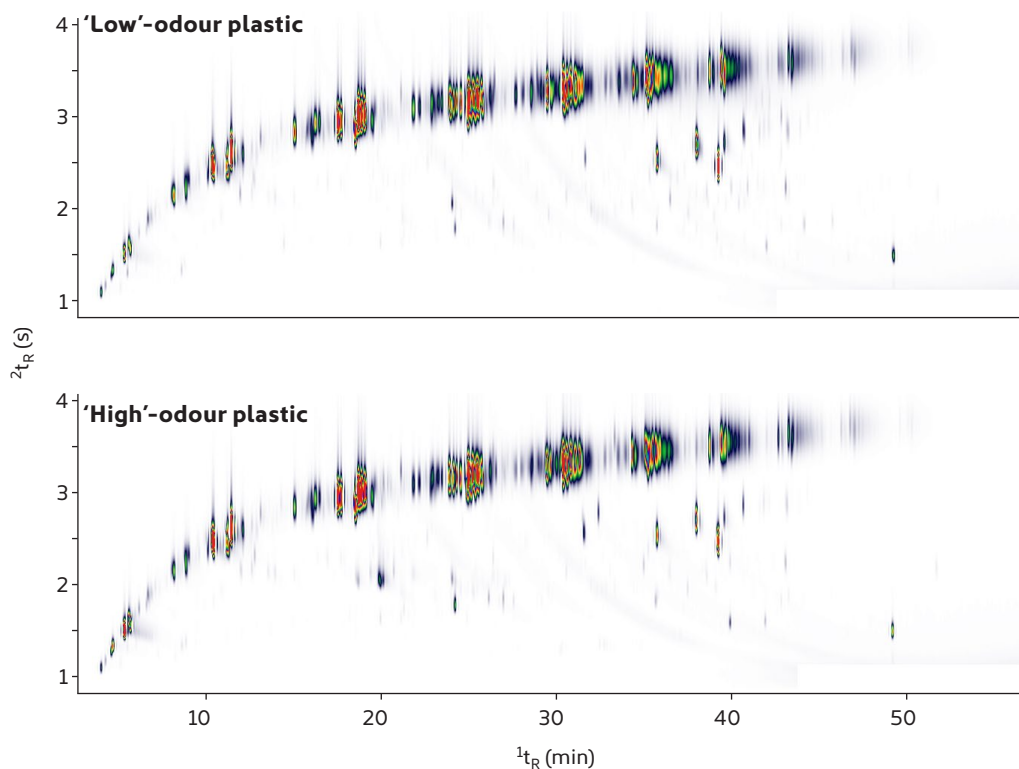
‘Low’-odour plastic

‘High’-odour plastic

Here, ChromCompare+ software was used to automatically compare all the raw TD−GC×GC−TOF MS data for three high-odour plastics and three low-odour plastics to identify the key odorants responsible. The resulting principal components analysis (PCA) score plot (Figure 4) shows the clustering of the low- and high-odour plastics, indicating there are compositional differences between their odour profiles.

‘Low’-odour plastic

‘High’-odour plastic

The Feature Discovery tool in ChromCompare+ can be used to quickly identify the components found in increased amounts in the high-odour pellets. For example, Figure 5 shows one of the top differentiators, which was identified as n-octanol. It was found to increase in the high-odour pellets and is known to impart a waxy odour.[1]
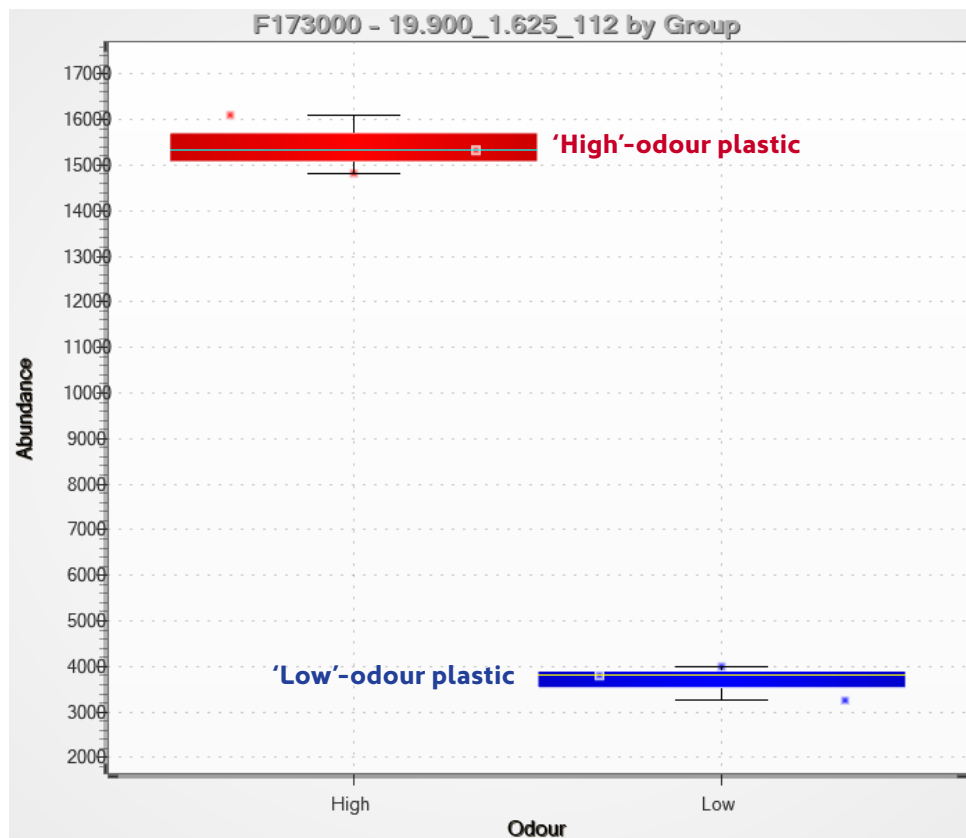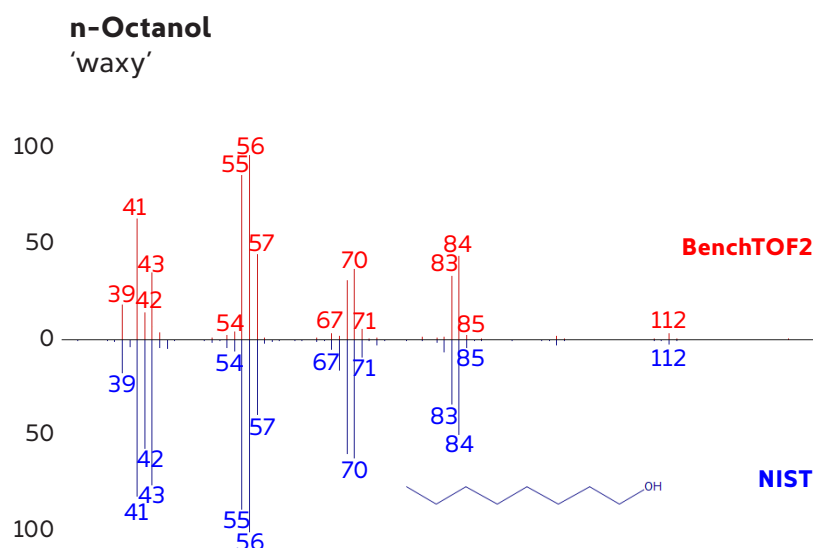

Figure 5

Box and whisker plot in ChromCompare+ showing increased levels of n-octanol in the high-odour pellets compared to those of low odour.

n-Octanol
'waxy'

Importantly, once the key odorants are identified, a class prediction model can be developed in ChromCompare+ to instantly classify future unknown samples. This is a key aspect for QC labs, where instrumentation and workflows must be as simple and cost-effective as possible. With this in mind, TD–GC×GC methods can also be easily translated to flame ionisation detection (FID), for routine use in quality control labs.

Conclusions

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

► Automated cryogen-free sampling of VOCs from plastics using direct desorption in TD tubes.

► Improved detection of trace odorants through a combination of TD preconcentration and high-sensitivity BenchTOF2 MS.

► Enhanced separation for improved discovery of odorants, using GC×GC with the INSIGHT flow modulator, that could not be identified using 1D GC–MS techniques.

► Reference-quality spectra generated by BenchTOF2 mass spectrometers enable key odorants to be confidently identified.

► Streamlined workflows using ChromSpace software for full instrument control and data processing, with powerful chemometrics in ChromCompare+ to automatically find differences between complex chromatograms.

► 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.

References

[1] The Good Scents Company Information System (search facility), www. thegoodscentscompany.com/search2.html (accessed on 2nd August 2021).

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