# Improved identification of organic markers in ambient particulate matter (PM2.5) for reliable source attribution

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## Introduction

Airborne particulate matter with diameters <2.5 µm (so-called PM2.5) is a concern when it comes to urban air quality, as long-term exposure has been shown to have a major impact on public health.
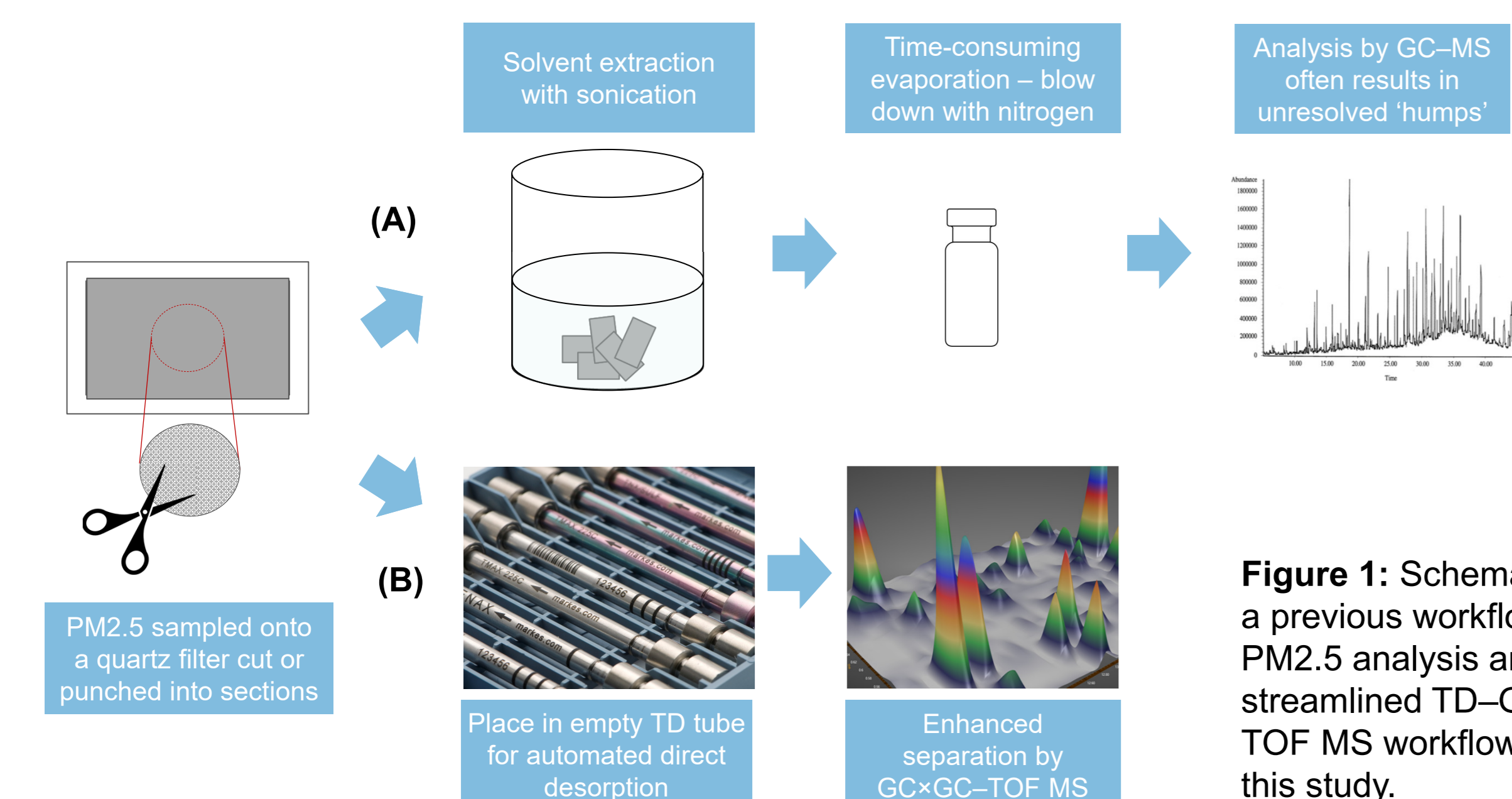
PM2.5 consists of wide-ranging compounds from both primary emissions and secondary reactions, meaning that accurate chemical fingerprinting and reliable source attribution is essential.

However, chemical fingerprinting of PM2.5 is a challenge due to time-consuming sample preparation and sample complexity.

Here, we demonstrate how direct thermal desorption (TD) of PM2.5 filters offers a streamlined solution to sample preparation, while enhanced separation and sensitive detection by comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOF MS) offers improved sample characterisation for organic components.

This study highlights the improved performance of TD–GC×GC–TOF MS by analysis of a number of real-world samples, including PM2.5 and tyre emission profiles.

## Experimental



**Figure 1:** Schematic of (A) a previous workflow used for PM2.5 analysis and (B) the streamlined TD–GC×GC–TOF MS workflow used in this study.

**Sample preparation:** A quartz filter was obtained from sampling PM2.5 in an urban area in Europe. Circular sections 6 mm in diameter were taken from the filter using a punch and placed in an empty TD tube (Markes International) for direct desorption (Figure 1).

**TD:** Instrument: TD100-xr™ (Markes International); Desorption: 10 min at 310°C.

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

**TOF MS:** Instrument: BenchTOF2™; Mass range: m/z 45–500; Acquisition rate: 100 Hz.

**Software:** Full instrument control and data processing by ChromSpace®.

## Results and discussion

### Analysis of PM2.5 by TD–GC×GC–TOF MS

The TD–GC×GC–TOF MS colour plot for direct desorption of a PM2.5 filter is displayed in Figure 2, alongside the equivalent TD–GC–FID chromatogram analysed using the same 1D column and oven temperature program.
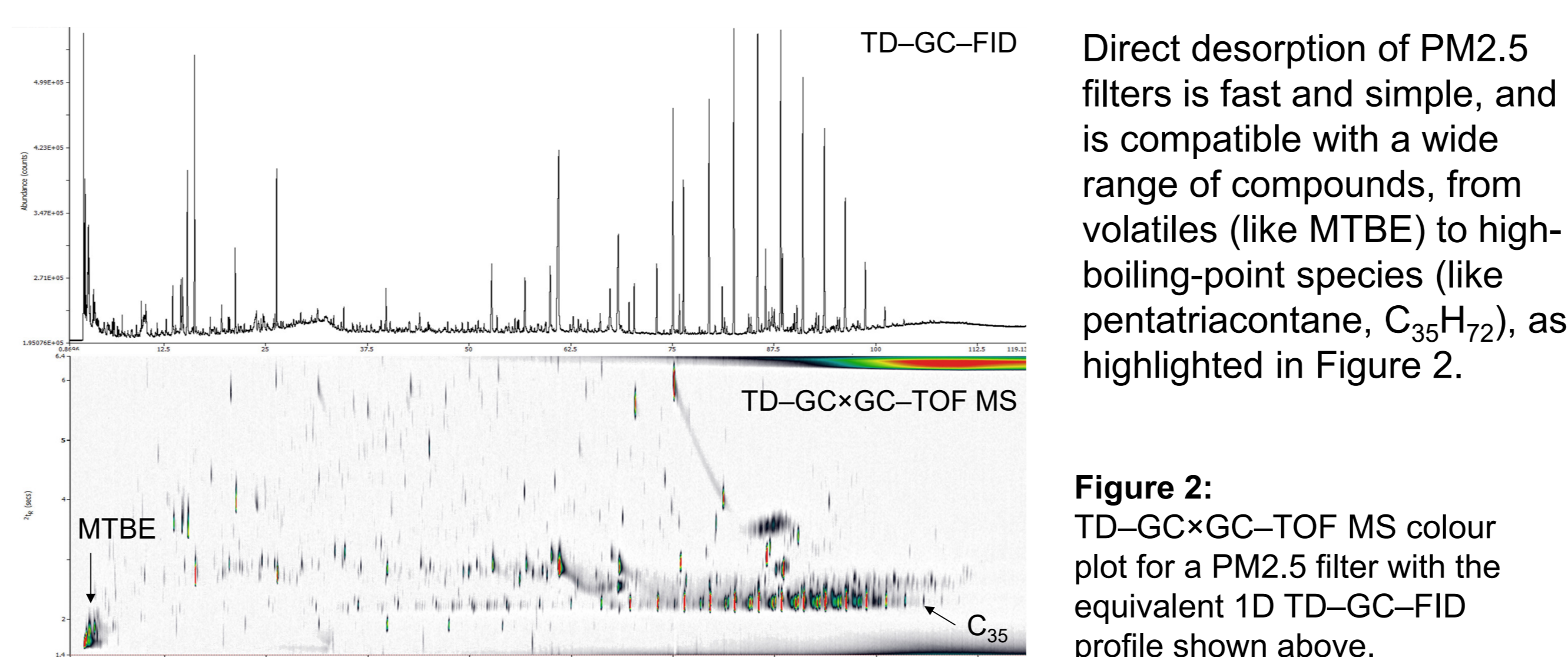


Direct desorption of PM2.5 filters is fast and simple, and is compatible with a wide range of compounds, from volatiles (like MTBE) to high-boiling-point species (like pentatriacontane, $C_{35}H_{72}$), as highlighted in Figure 2.

**Figure 2:** TD–GC×GC–TOF MS colour plot for a PM2.5 filter with the equivalent 1D TD–GC–FID profile shown above.

The benefit of GC×GC is immediately obvious, with numerous co-elutions resolved, resulting in cleaner spectra for more confident identification and quantitation, as highlighted in the analysis of a second filter in Figure 3.
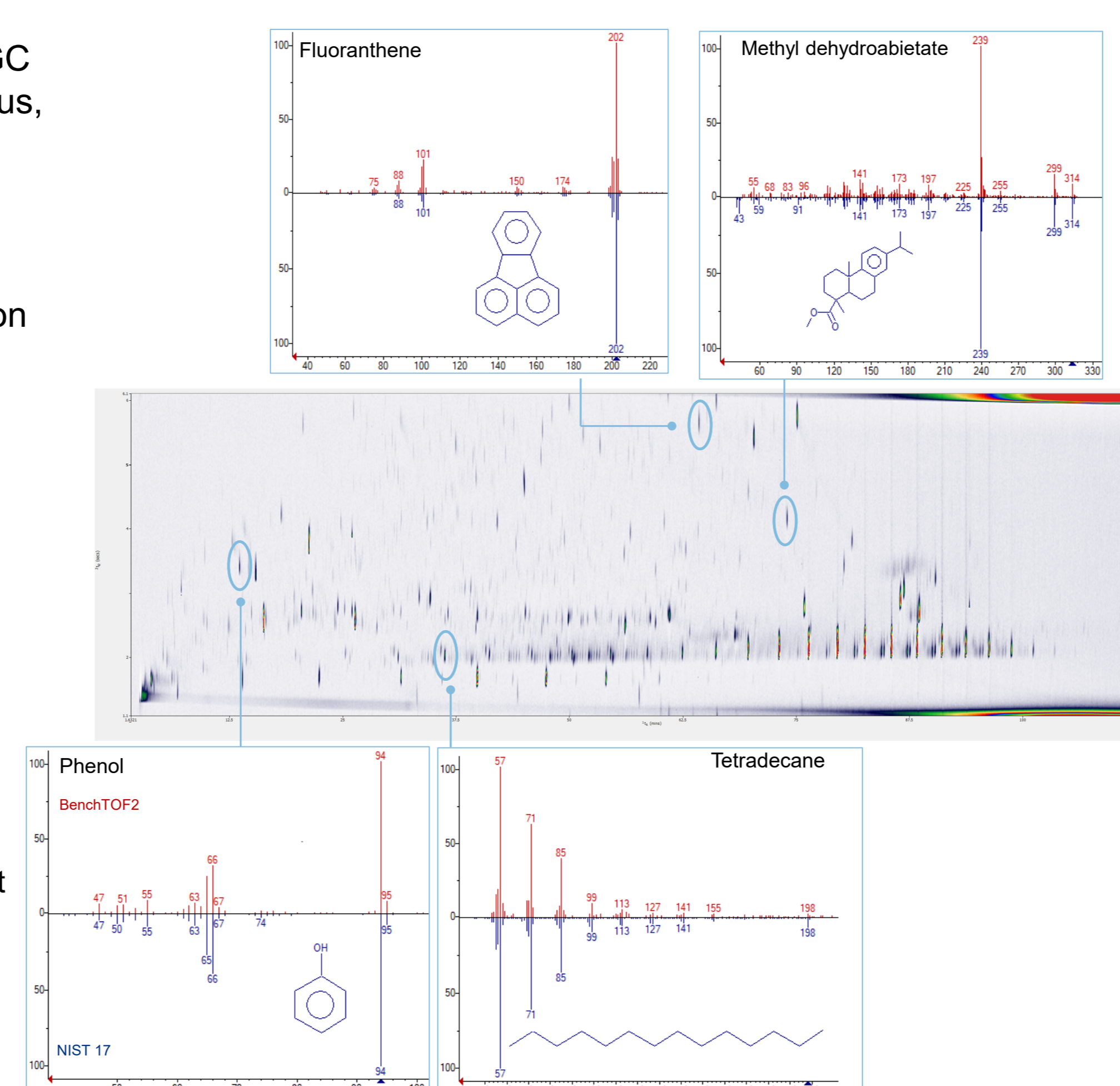


**Figure 3:** TD–GC×GC–TOF MS colour plot for PM2.5, highlighting the excellent separation and spectral quality of BenchTOF2 for confident identification of wide-ranging analytes.

### Analysis of tyre emissions

Due to an increase in the uptake of electric vehicles, the focus of research into vehicle contributions to urban particulate matter has begun to shift towards tyre emissions. We analysed a section of tyre using the TD–GC×GC–TOF MS system, resulting in a diverse chromatogram with over 600 peaks (Figure 4).
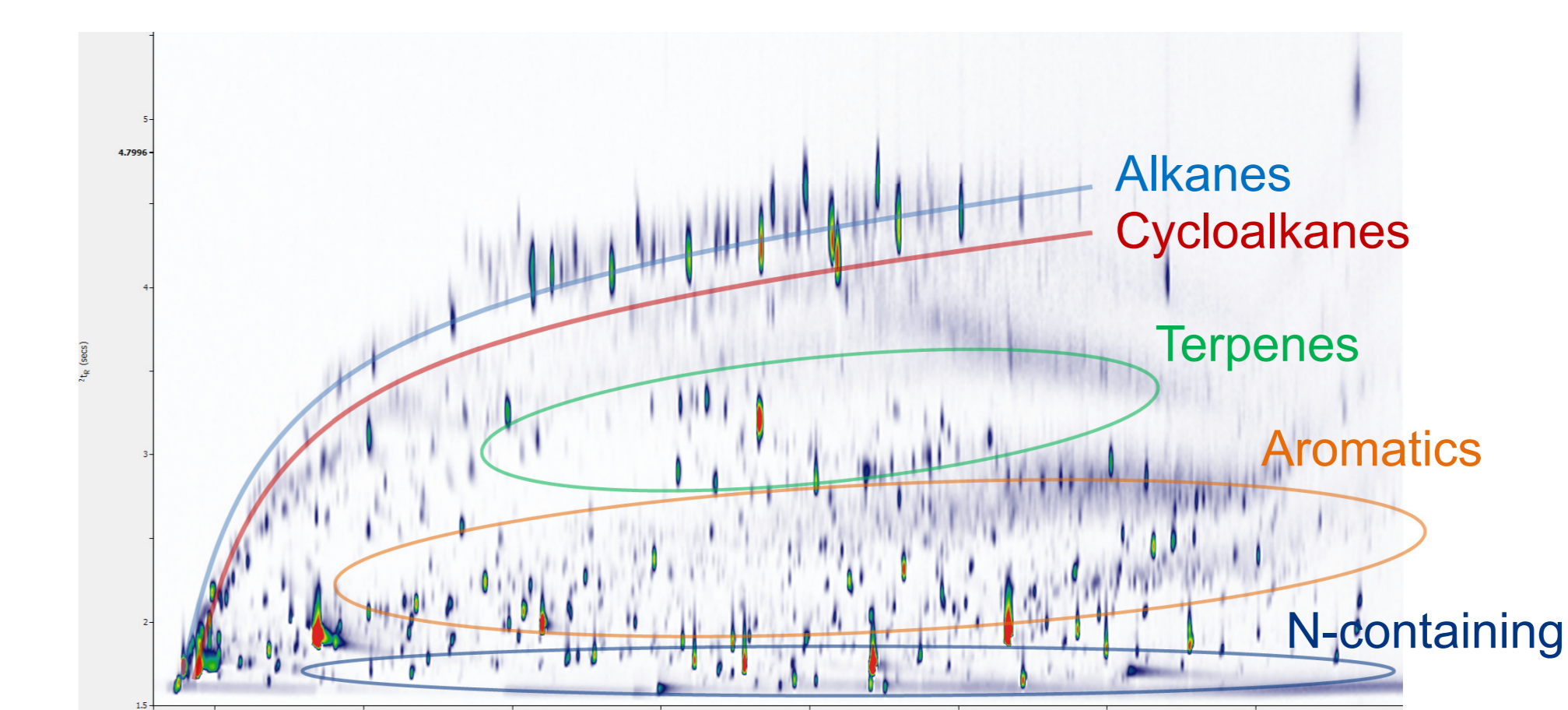


**Figure 4:** TD–GC×GC–TOF MS colour plot for a section of tyre, illustrating the wide range of chemical classes in tyre emissions.

GC×GC separation was essential in this case, and provided a structured chromatogram with chemical classes eluting in distinct bands for simpler identification.

Among these were over 70 nitrogen-containing compounds that were identified by screening against the NIST database. Figure 5 shows a close-up region of the 3D surface plot, highlighting some of these nitrogen compounds, many of which would have co-eluted with high-loading peaks in a 1D separation and may have been overlooked.
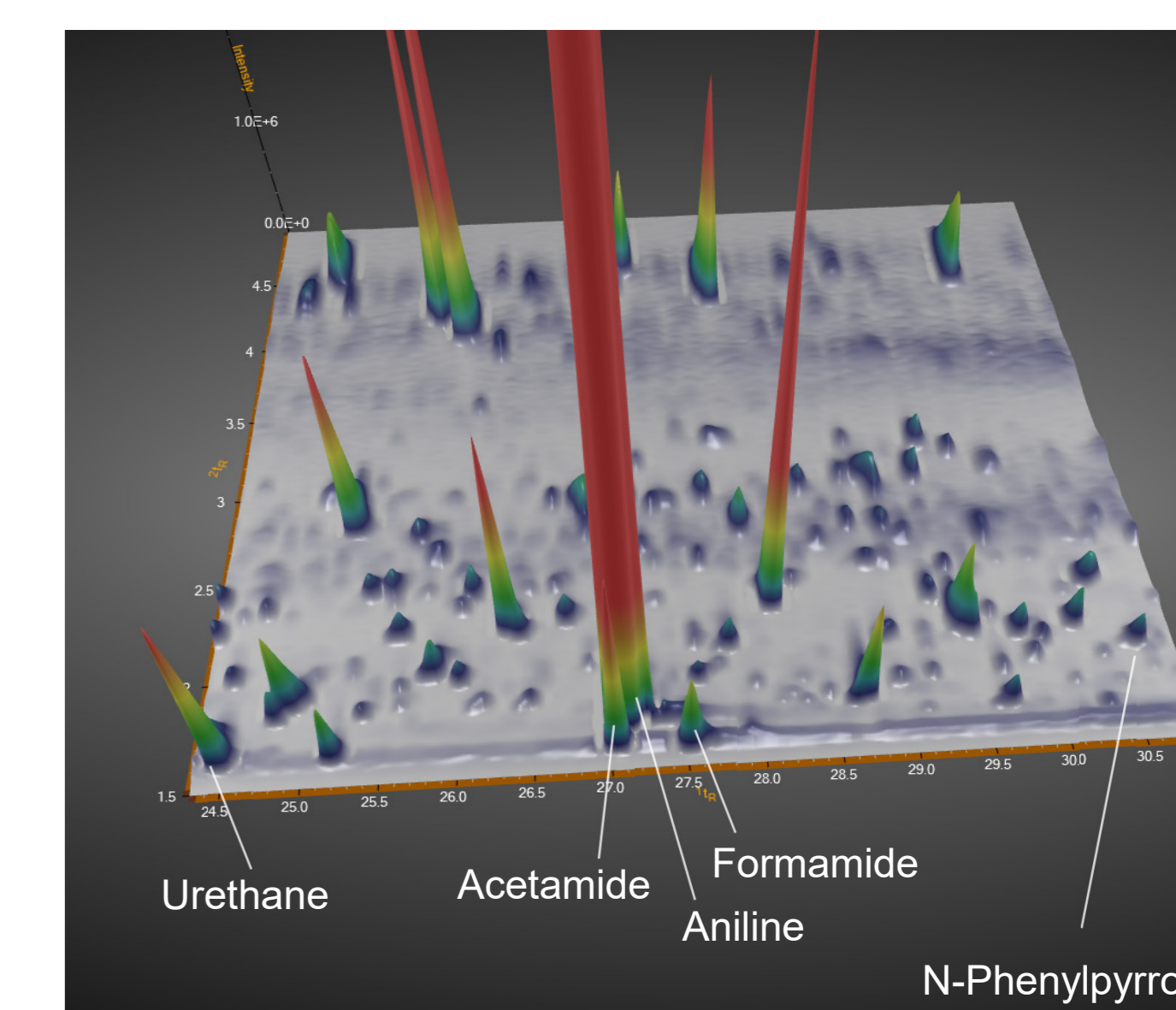


**Figure 5:** TD–GC×GC–TOF MS surface chart for a section of tyre, showing the identification of numerous nitrogen-containing species.

## Conclusions

► There is a wealth of information available with the chemical fingerprinting of PM2.5.

► Thermal desorption can simplify sample preparation for analysis of PM2.5 and provide re-collection capabilities for repeat analysis.

► GC×GC allows you to discover more about sample composition for enhanced separation of a wide range of analytes.

► BenchTOF2 mass spectrometers are fast-acquiring, sensitive detectors for confident identification of targets and non-targets, such as potentially harmful compounds in PM2.5.