

Application of TD/Py-GCxGC-TOFMS for Analysis of Microplastics and Chemical Pollutants in Ambient Particulate Matter Samples

S. Wright¹, J. Levermore¹, N. Jones², A. Griffiths²

1. Medical Research Council (MRC) Centre for Environment and Health, Environmental Research Group, School of Public Health, Imperial College London, London, UK | 2. LECO Corporation, Saint Joseph, Michigan USA

INTRODUCTION

Microplastics are a widespread and abundant environmental pollutant and there is a growing interest in understanding human exposure and subsequent impacts on health. A major knowledge gap is exposure concentrations in air.

Here, we describe the application of thermal desorption (TD) and pyrolysis (Py) coupled to Multidimensional Gas Chromatography–Time-of-Flight Mass Spectrometry (GCxGC-TOFMS) to analyse the composition of plastics and chemical pollutants in ambient particulate matter (PM), collected via aerodynamic size selective sampling (<10 µm) at various urban locations.

Specifically, a 2-step analysis of each sample was applied using firstly TD to measure, “free,” or “associated,” chemicals, and then secondly using Py to analyse and differentiate chemicals derived from microplastic particles, as strongly adsorbed or as thermal degradation species.

This methodology was also used to assess the suitability of the sample collection and sub-sampling workflows by processing the data using ChromaTOF® Tile statistical comparison software.

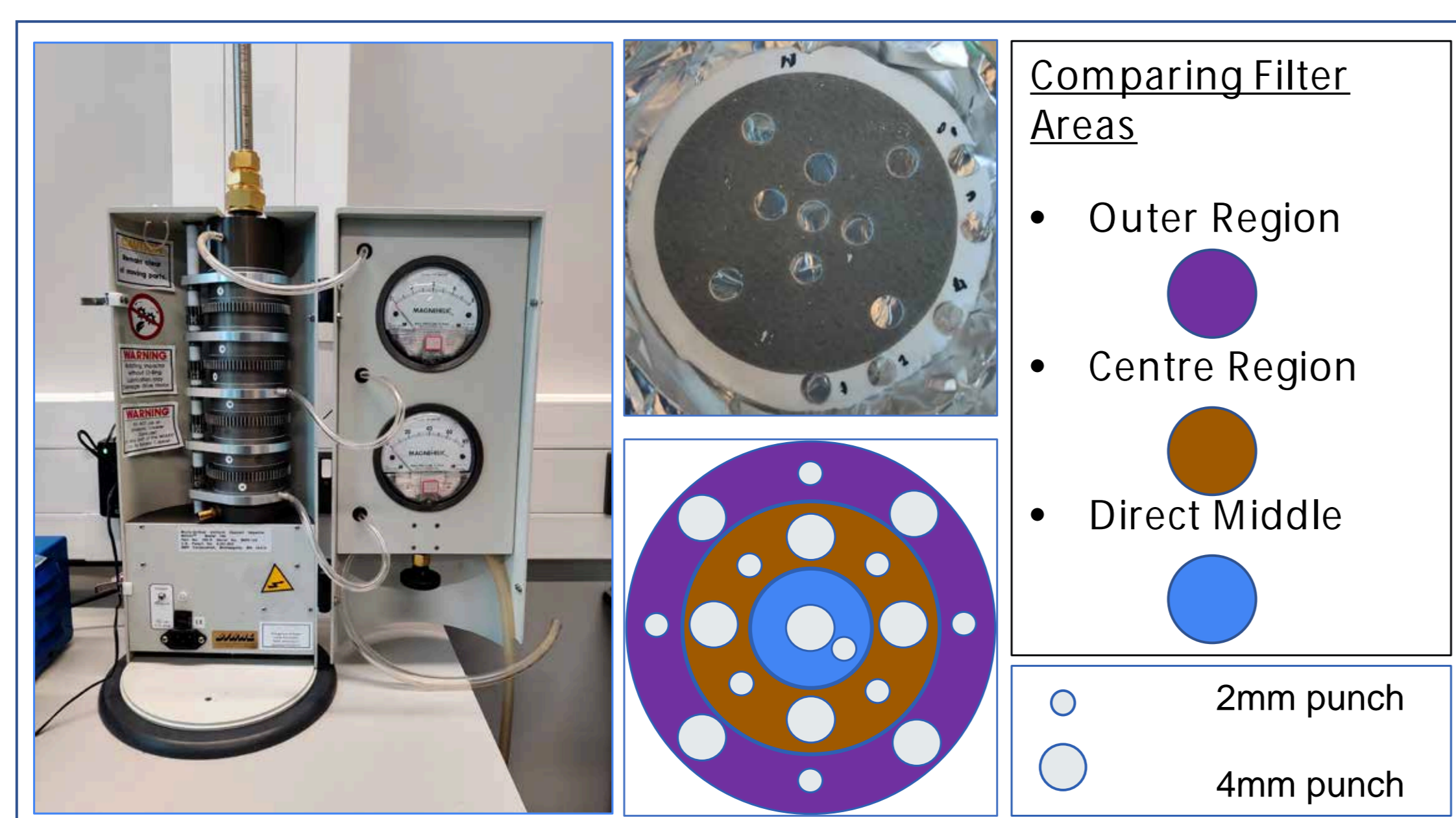


Figure 1: A PM Sampling Device, a Quartz Filter post-sub-sampling, and the sub-sampling schematic.

METHOD

“PM10, high-volume air samplers,” (Figure 1, left), sited by urban road sides in London, UK, were used to collect 24 hour samples of particulate matter (and associated chemicals) in aerosols with an aerodynamic diameter of <10 µm onto deactivated quartz filters with a diameter of 47 mm and a pore size of 0.8 µm. After sample collection, various diameter circular cross sections of the filter were obtained using biopsy punches and transferred to deactivated inlet liners and used to establish both TD and Py-GCxGC-TOFMS analysis parameters (Table 1). A number of reference polymer standards (Table 2) were used to locate target pyrolyzates.

Subsequently, a number of evenly distributed punches (both 2 mm and 4 mm sizes) were sub-sampled from different regions of a representative filter sample (Figure 1). These punches were each analysed using the 2-step approach TD and Py-GCxGC-TOFMS approach developed. An n-alkane standard (C7-C30) was analyzed for calculation of linear retention indices (RLs).

Table 1: GCxGC-TOFMS Analysis Parameters

GC	LECO GCxGC Quadjet™ Thermal Modulator
Injection Mode: Optic 4S (GL Sciences)	TD: 50 °C, ramp 60 °C/sec to 300 °C Py: 50 °C, ramp 60 °C/sec to 600 °C (60 sec hold), then 300 °C
Split Ratio	100:1 (180 s)
Columns (Restek Corporation)	¹ D: Rxi-5SilMS, 30 m x 0.25 mm i.d x 0.25 µm film ² D: Rxi-17SilMS, 0.9 m x 0.25 mm i.d x 0.25 µm film
Carrier Gas	Helium, 1.4 mL/min
Primary Oven Program	50 °C (2 min hold), Ramp 10 °C/min to 250 °C, 20 °C to 300 °C (15 min hold)
Secondary Oven	Offset + 5 °C (relative to primary oven temperature)
Modulator Temp	Offset + 10 °C (relative to primary temp temperature)
Modulation Period	3.0 s
Transfer Line	300°C
MS	LECO Pegasus® BT4D
Ion Source Temp	250 °C
Ionization	Electron ionization at 70 eV
Mass Range	40 - 600 m/z
Extraction Frequency	28 kHz
Acquisition Rate	250 spectra/s

Table 2: Polymer Standards/Pyrolyzates

Polymer Standard	Pyrolyzate
PS	Styrene Monomer
	Styrene Dimer
	Styrene Trimer
PVC	Benzene
	Biphenyl
PE	Anthracene
	Alkadienes
	Alkenes
PP	Alkanes
	2,4-Dimethyl-1-heptene
PC	2,4,6-Trimethyl-1-nonene
	Bisphenol A
PET	p-Isopropenylphenol
	Benzoic Acid
	Biphenyl
PMMA	Acetophenone
	Methylmethacrylate
N6	Caprolactam
	Caprolactam Dimer
N66	Cyclopentanone
	Hexanedinitrile
	1,8-Diacetylotetradecane-2,7-dione

RESULTS

The use of reference polymers facilitated easy identification of polymer presence via markers or patterns; in the real sample, for example, the C10-C20 series of alkane, alkene, and alkadiene triplets derived from Polyethylene (PE), (Figure 2).

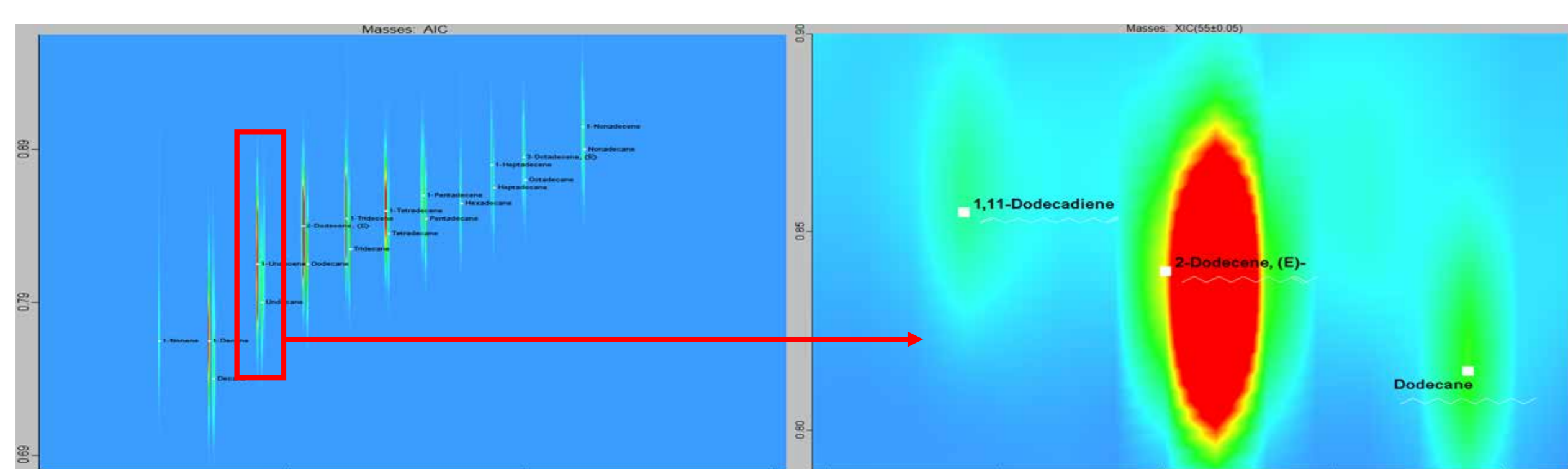


Figure 2: A series of PE pyrolyzate triplets from analysis of a real urban air filter sample.

The application of GCxGC-TOFMS facilitated high quality separation and detection of thousands of chemical features.

Furthermore, the 2-step TD/Py approach allowed differentiation of chemicals present freely in urban air or accumulated and adsorbed to particles from those produced by pyrolysis of polymer particles present in the same sample (Figure 3).

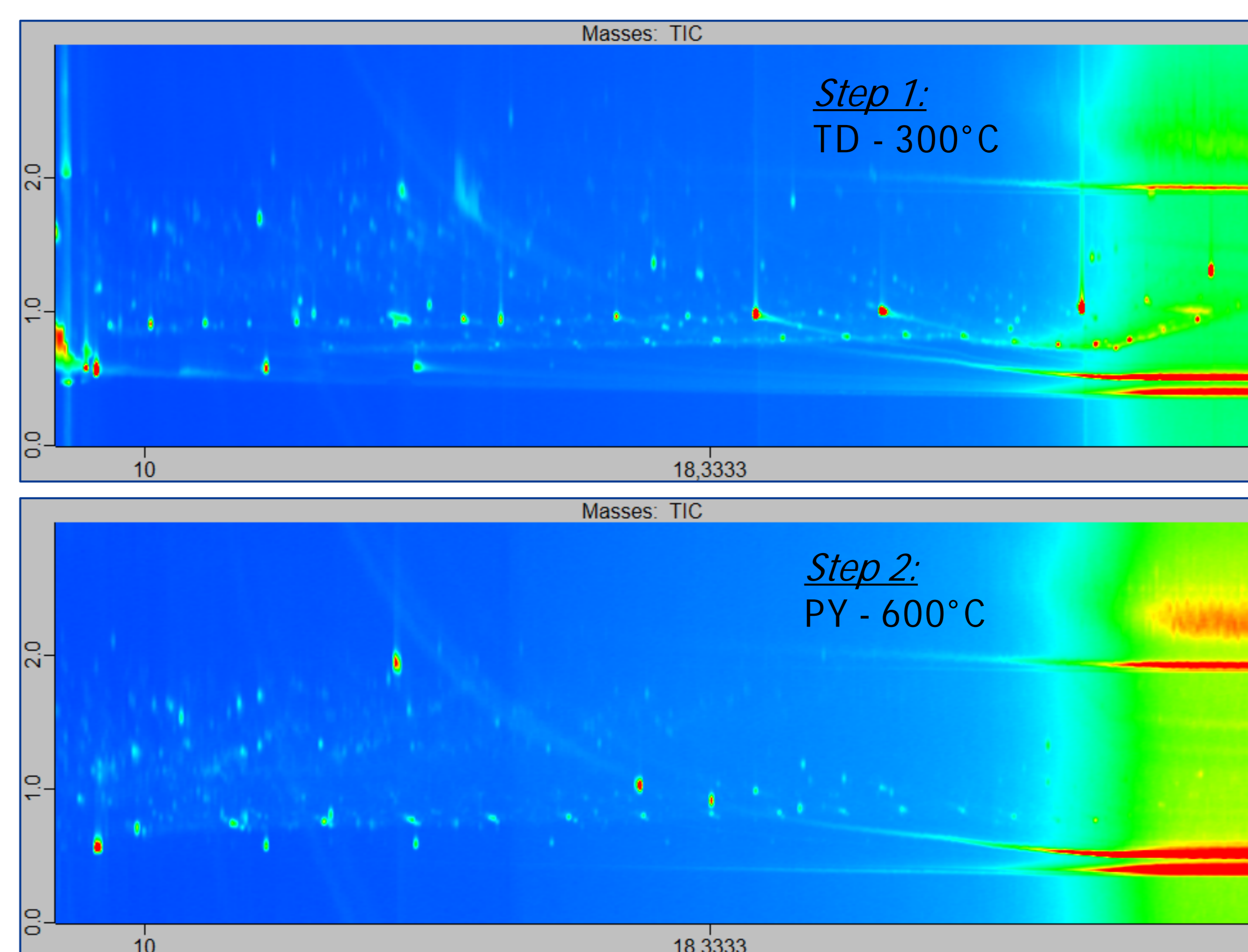


Figure 3: 2-Dimensional contour plots of the 2-step TD/Py-GCxGC-TOFMS analysis of a PM10 urban air sample.

The ability to differentiate between the origin of common chemical markers is highly important in understanding the relative prevalence of polymer particles in comparison with non-particle chemical compositions in various locations. For example, we were able to confirm the presence of polystyrene (PS) polymer particles in these samples (Figure 4); found following the Py step, but not significantly present during the prior TD step.

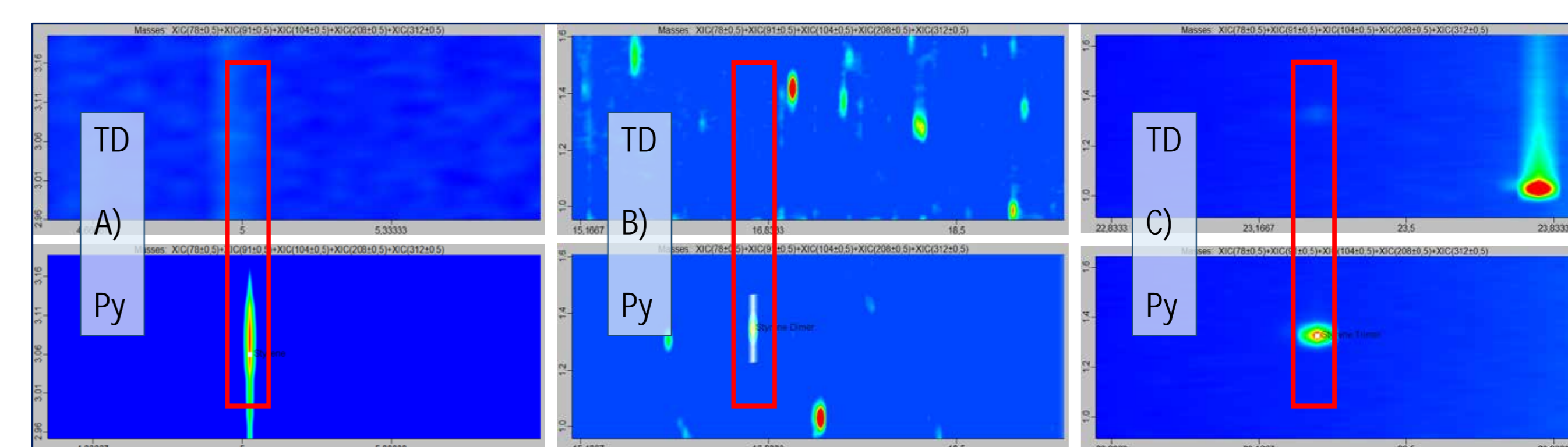


Figure 4: Zoomed contour plots of TD (Top) and Py (Bottom) analyses of the same sample, demonstrating presence of PS particles by formation of styrene monomer (A), dimer (B), and trimer (C) during the step-2 pyrolysis.

Additionally, it was possible to evaluate homogeneity of the filter sample surfaces and therefore the sub-sampling process by analysing replicate samples from the different filter sections (groups). Data was processed using ChromaTOF Tile statistical software which uses an algorithm to separate GCxGC chromatograms into multiple regions (Tiles). Applying this to multiple samples and groups allows comparison of Fisher Ratios (F-Ratios) to determine similarities and differences between multiple chemical classes. We were able to determine that the centre regions and direct middle of filter samples showed less analyte variability and were most similar overall compared with the outer region, for example with Styrene (Figure 5). However, F-Ratios were low across all sample classes between regions.

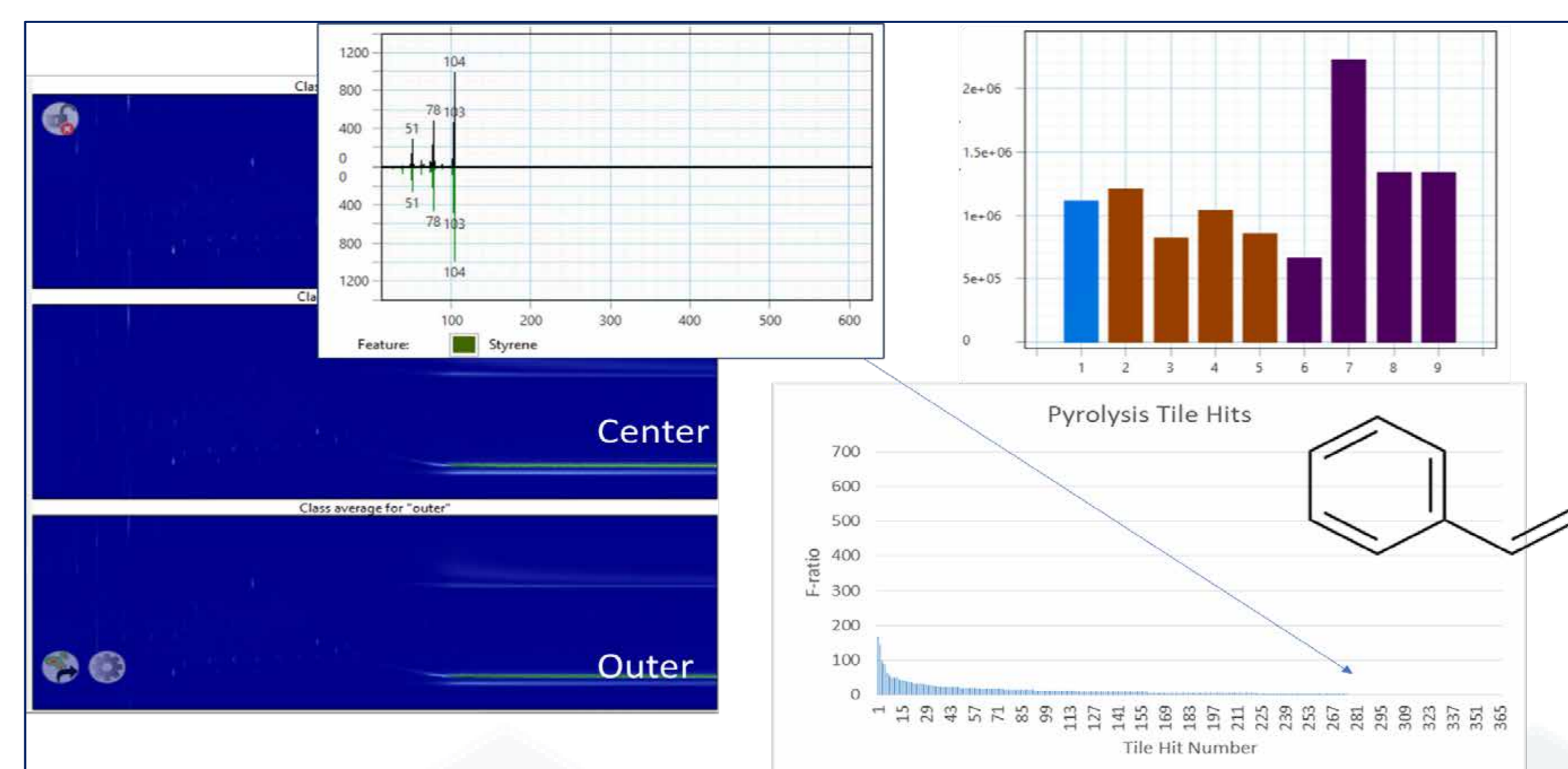


Figure 5: Styrene feature comparability across filter groups.

CONCLUSION

This study demonstrated that the use of a 2-Step TD/Py-GCxGC-TOFMS analysis approach enabled high quality separation and detection of multiple chemicals collected using PM10 filters, plus the differentiation of chemical markers from either associated air or directly from particulate polymer origins. Additionally, the application of ChromaTOF Tile software enabled fast and informative statistical comparisons of the sub-sampling workflow to be made.