

Is tyre wear an underestimated source of air pollution? Assessing PM 2.5 for evidence of tyre emissions

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Introduction

As technology for managing exhaust emissions has improved, the impact of non-exhaust emissions is now the topic of growing concern for human health and the environment. It is important to obtain a comprehensive view of all possible sources of emissions from vehicles, including those generated through tyre wear.

Pollution from tyres is of particular concern as they are thought to generate more particulate and VOC emissions than exhausts, as well as being a source of microplastics. This emission is then increased in heavier battery electric vehicles, which are typically 40% heavier than combustion engine vehicles.



However, the analysis of tyre emissions remains a challenge due to sample and matrix complexity.

In this study, we look for tyre marker compounds using thermal desorption (TD)-GC×GC-TOF MS. That information is then applied to real particulate matter samples in the form of a "routine" analysis.

Figure 1: The popularity of large, heavy vehicles, such as SUVs, exacerbates tyre wear related pollution.

Experimental

Sample prep and analytical workflow for investigation of tyre marker compounds



Tyre samples placed into a micro-chamber. Evolve compounds collected onto TD tubes

TD tubes placed into TD100-xr™, thermally desorbed and injected to GC

Enhanced separation by INSIGHT®-GC×GC and confident identification by BenchTOF2™

Sample prep for routine screening of PM 2.5 filters for evidence of tyre particles



Sections taken of a PM 2.5 filter

Place inside empty TD tube for direct desorption

Analysis using TD100-xr™ automated TD unit coupled to GC-MS with H₂ carrier gas

Results and discussion

Investigation of tyre marker compounds

The 2D chromatography revealed a complex extraction profile for the tyre rubber samples. One of the benefits of GC×GC is the stratified structure of the chromatogram where compounds with a similar chemistry elute in bands; this enables a quick a group type analysis as a first step in processing.

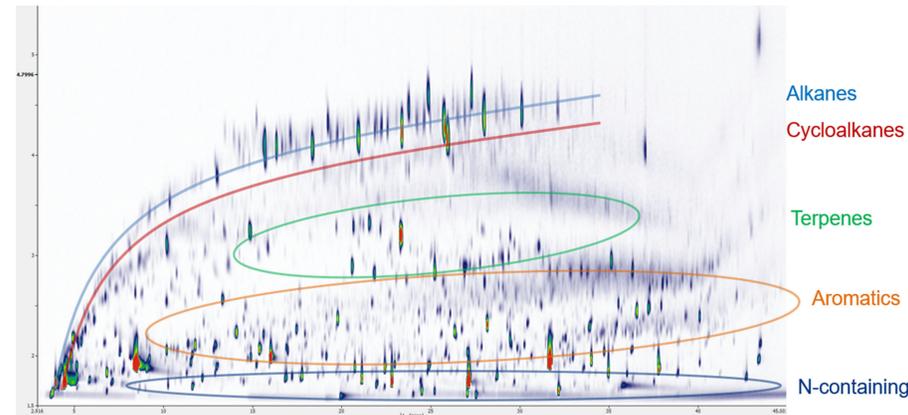


Figure 2: Tyre extracted at 100°C in a Micro-Chamber under a flow of air. The nitrogen containing compounds would have been difficult to see in a 1D chromatogram due to the large number of aromatic compounds and alkanes at a much higher abundance.

Closer investigation of the compounds within the samples and comparison with published literature enabled the creation of a target list of 22 compounds.

The tyre emission profile has many features in common with what would typically be expected in particulate matter. The target list of 22 compounds combines 16 PAHs which would be assessed in any particulate matter sample, limonene and targets from tyre and plastics manufacture. 6PPD is thought to be unique in its use in tyre production and could act as a definitive marker for qualitative assessment of presence/absence.

Table 1: List of chosen compounds for targeted analysis. The list combines expected compounds in PM samples and tyre "marker" compounds. The tyre marker compounds are picked out in bold.

Benzonitrile	Limonene	Naphthalene	Benzothiazole	2-tert-Butyl-4-methylphenol	Acenaphthylene
Acenaphthene	Butylated Hydroxytoluene	Fluorene	Phenanthrene	Anthracene	Fluoranthene
Pyrene	6PPD	Benz[a]-anthracene	Chrysene	Benzo[b]-fluoranthene	Benzo[k]-fluoranthene
Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene	Dibenzo[a,h]-anthracene	Benzo[ghi]-perylene		

Validation of the method for routine screening of particulate filters

Prior to running any samples or filter papers, the analytical method was validated with standards for the target compounds which were spiked onto sorbent tubes. Reproducibility, linearity and carryover testing was assessed, followed by assessment of the limit of detection (LOD) and limit of quantification (LOQ) for the instrument. Any future work would include an assessment of the method detection limit and improvement of the carryover, which was 0.5% out of the desired specification.

The validated method was run in SIM with a total run time of 17 minutes, and enabled with use of hydrogen carrier, which significantly compressed the chromatography without sacrificing separation.

Table 2: Validation criteria and detection limit results.

	Pass criteria	Average	Min	Max	Achieved for all compounds
Linearity of calibration	> 0.999	0.9977	0.993	0.999	Yes
Reproducibility	< 5%	3.82%	0.72%	4.81%	Yes
Carryover	< 2%	1.14%	0.09%	2.53%	No
LOD	-	0.004 ng	0.001 ng	0.017 ng	-
LOQ	-	0.013 ng	0.002 ng	0.056 ng	-

Analysis of filter papers

Sections of paper (4 mm x 6 mm) were cut from the centre of the filter. Once cut, they were inserted into empty stainless steel sorbent tubes, which had been conditioned with a small plug of quartz wool inside.

Three PM 2.5 filter samples were analysed which had been collected from an urban environment. The 6PPD marker was found not to be present in any of them, but at least three other tyre marker compounds were found in each sample. In each sample at least 14 PAHs were also positively identified and quantitated.

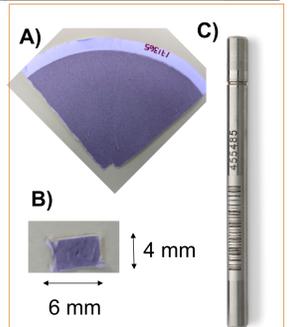
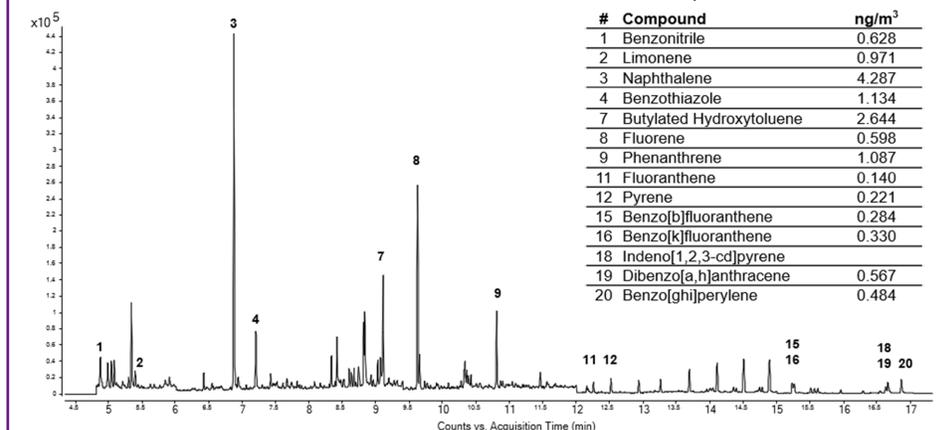


Figure 3 (above):
A) Sample filter
B) Cut filter section
C) stainless steel tube

Figure 4 (below): EIC chromatogram for sample 171365 with some identified compounds picked out.



Conclusions

Assessment of tyre samples using micro-chamber extraction with pre-concentration and analysis by TD proved easy and suitable for capturing a wide range of organic compounds non-selectively. The enhanced separation enabled through GC×GC, and NIST quality spectra from the BenchTOF, meant that finding and identifying compounds of interest was possible with increased confidence.

Utilising the same non-selective approach by using the TD instrument for sample introduction enabled a list of target analytes with mixed chemistries to be quantitated in the real samples. The method itself was shown to be robust, and use of a hydrogen carrier significantly increased possible throughput and decreased cost per analysis.

Acknowledgements

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