Using soft ionisation GC×GC-ToF-MS to characterise SVOC from nanoparticles in diesel exhaust emissions

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Despite intensive research over the last 20 years, a number of major research questions remain concerning the sources and properties of road traffic-generated particulate matter. There are major knowledge gaps concerning the composition of primary vehicle exhaust aerosol, and its contribution to secondary organic aerosol (SOA) formation (Gordon *et al* 2014). These uncertainties relate especially to the semi-volatile component of the particles (Donahue *et al* 2006). Semi-Volatile Organic Compounds (SVOC) are compounds which partition directly between the gas and aerosol phases under ambient conditions. The SVOC in engine exhaust are typically hydrocarbons in the C_{15}-C_{35} range. They are largely uncharacterised, other than the *n*-alkanes, because they are unresolved by traditional gas chromatography and form a large hump in the chromatogram referred to as Unresolved Complex Mixture (UCM) (Chan *et al* 2013).

In this study, 2D Gas-Chromatography Time-of-Flight Mass-Spectrometry (GC×GC-ToF-MS) was exploited to characterise and quantify the composition of SVOC from the exhaust emission. The GC×GC-ToF-MS technique has been demonstrated capable of resolving specific components of the UCM, which typically makes up 95% of the area of chromatogram using conventional 1D separation (Alam *et al* 2013). Samples were collected from the exhaust of a diesel engine, changing variables such as, sulphur content in fuel, with and without abatement devices fitted, and different engine starting temperatures. Engine exhaust was diluted with air and collected using both filter and impaction (nano-MOUDI), to resolve total mass and size resolved mass respectively. Absorption tubes were utilised to collect SVOC in the gas phase, while particle size distribution was evaluated by sampling simultaneously with a Scanning Mobility Particle Sizer (SMPS).

The SVOC was observed to contain predominantly *n*-alkanes, branched alkanes, alkyl-cyclohexanes and cyclopentanes, PAH and various aromatic compounds. Using a soft ionization technique di-, tri-, tetra- and penta- substituted aliphatics were positively identified and quantified tentatively. Figure 1, shows a typical 3D chromatogram of diesel fuel.

Assessing the chromatography of both lubricating oil and diesel fuel, preliminary results indicate that the contribution of diesel fuel to the exhaust SVOC composition is dominant at high engine speeds, and a more pronounced contribution from lubricating oil is observed at low speeds. Differences were observed in the particle size distribution and SVOC composition when using different fuel types, engine lubricants, starting tem,peratures and collecting samples with and without abatement devices fitted.

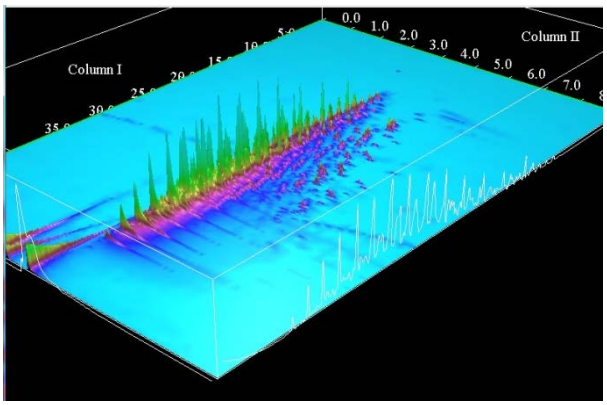

Figure 1. A typical 3D chromatogram generated from GCxGC-ToF-MS.

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