Characterisation of lubricant polymers and deposits using an OPTIC-4/SilFlow(TM) based thermal desorption/pyrolysis heart-cut GC with multiple detection.

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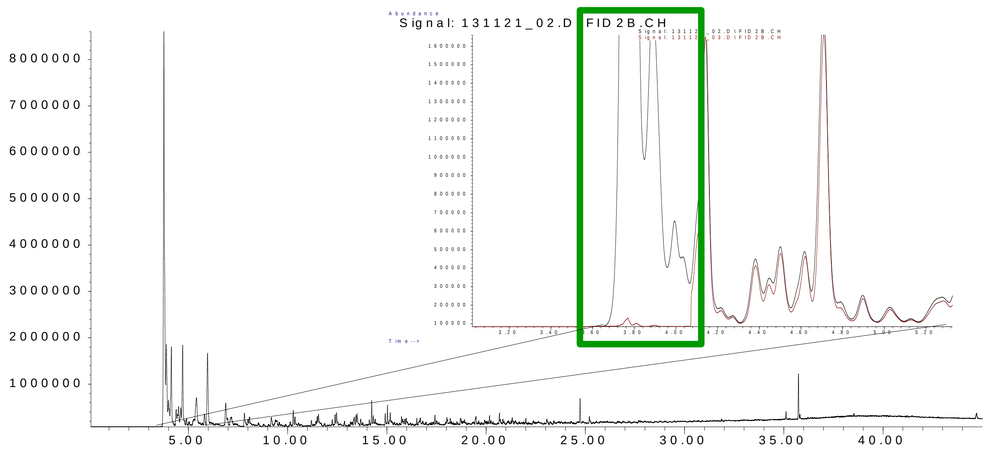
Introduction:

Viscosity modifiers and Engine deposits:
Polymeric materials, are added to engine oils in order modify the viscometric characteristics of the fluid. This ensures the hydrodynamic properties of oil are tailored to suit the different temperature regimes present within the engine. Analysis of these materials can be carried out using a range of techniques. Within the BP labs in Pangbourne UK our focus has been NMR, IR, SEC and pyrolysis GCMS. This poster presents development of a heart cut method suitable for the analysis of these materials in collaboration with ATAS GL and SGE, namely the ATAS GL OPTIC 4 with new deans switch valve and control and SGE SilFlow™ microfluidic devices.



Instrument Configuration:

Instrument configuration: An Agilent 6890N GC equipped with FID and NPD detectors and a 5973 MSD were coupled to an ATAS GL OPTIC 4 multimode inlet and SGE Silflow microfluidic switches.

Flow path description: The Auxiliary electronic flow controller on the OPTIC was used to drive a high pressure pneumatic switch which directed flow to an SGE Silflow deans switch. An SGE 4 port splitter was pressure controlled using an Aux EPC channel on the 6890.Column connections are shown in figure 3: The OPTIC inlet was connected to a SGE BPX50 30 m x 0.25 mm x 0.25 mm (primary column) the column exited at the Silflow deans switch and was split either to a transfer line which fed a 4 port splitter or an Agilent GS-CarbonPLOT 30 m x 0.32 mm x 1.5 mm (secondary column) which exited at the FID. Output from the 4 port splitter was to the NPD or the MS via transfer lines. In total 12 gas line connections are present in the oven connecting 5 columns and transfer lines. All transfer lines were selected to minimise transfer time whilst balancing pressures across the microfluidics. Ensuring leak tight connections was particularly important due to the number of connections and inclusion of the mass spectrometer.

Figure 3: **(see right)** Schematic of instrument flow path. Description in text above. Photograph of the connections within the oven.

Rationale: Our lab carries out analysis on a wide range of sample types. We require instrumentation that can be adapted to suit the analysis in question with minimal user input. The OPTIC 4 is a highly flexible GC inlet which allows gas, liquid and solid samples to be processed including large volume injections, thermal desorption and pyrolysis.

The OPTIC 4 can heat 5 mm OD quartz liners up to 600 °C at 3600 °C/min and thus carry out pyrolysis of organic compounds. Under the condition set available to the OPTIC 4 the pyrolysis of engine oil polymers (poly-ethyene, -propylene, -methylmethacrylate, -styrene, -isobutene, -ethylene oxide, -butadiene, -isoprene) produces fragments of polymeric materials typically between C1 and C24. Using standard column chemistry (BPX1, BPX5, BPX50) the highly volatile materials (to C4) elute as a single unretained peak (see figure 1). However, characteristic components such as methyl acrylate, styrene and higher level oligomers of hydrocarbon polymers are retained and can be used to identify the polymer present. It is more difficult to differentiate between the hydrocarbon based polymers such as Poly-ethyene, -propylene, -isobutene, -butadiene, and -isoprene (structures shown in figure 2) without reference to the highly volatile pyrolysis fragments.

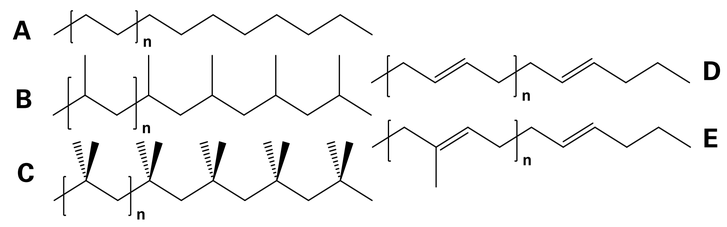
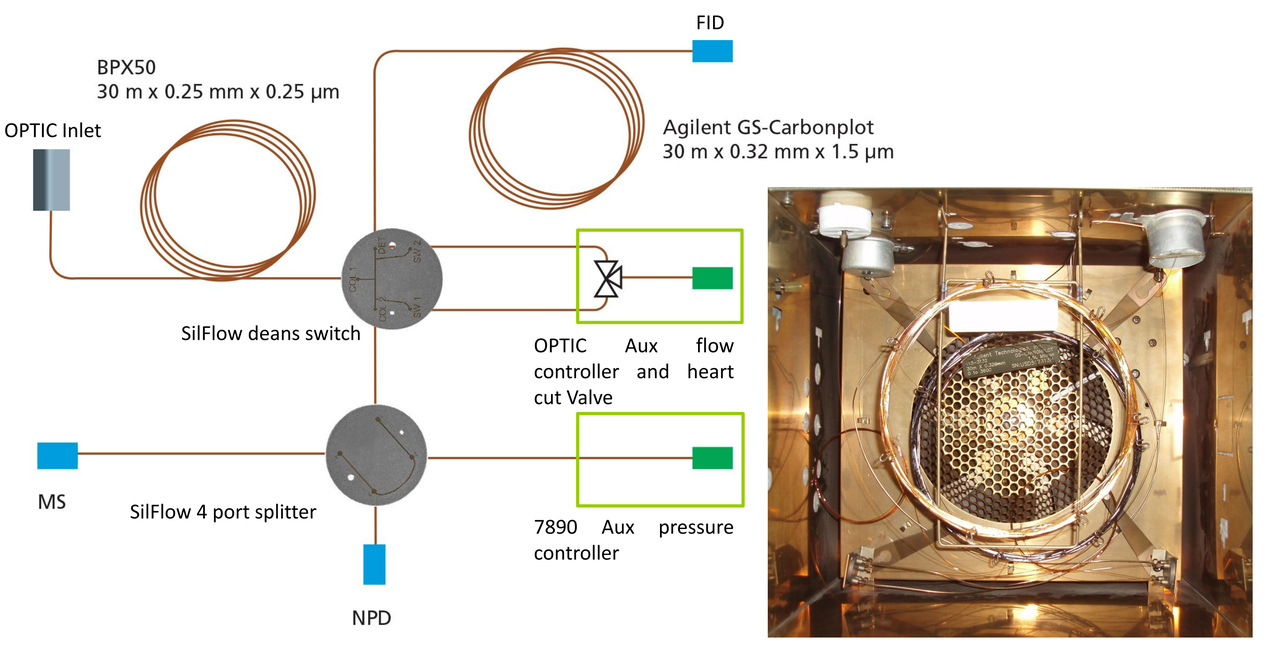


Figure 2: (right) Hydrocarbon polymer structures.
A Polyethylene. **B** Poly propylene. **C** Polyisobutene.
D Polybutadiene. **E** Polyisoprene.

Collaboration: This application describes collaboration between BP, ATAS GL and SGE to produce a flexible deans switch solution to interrogate the highly volatile pyrolytic fragments produced from analysis of polymeric lubricant additives and engine deposits.

Figure 1: **(left)** Main: Pyrolysis chromatogram of a polyethylene/propylene co polymer. **Inset** Region of heart cut shown by the green box.



Results:

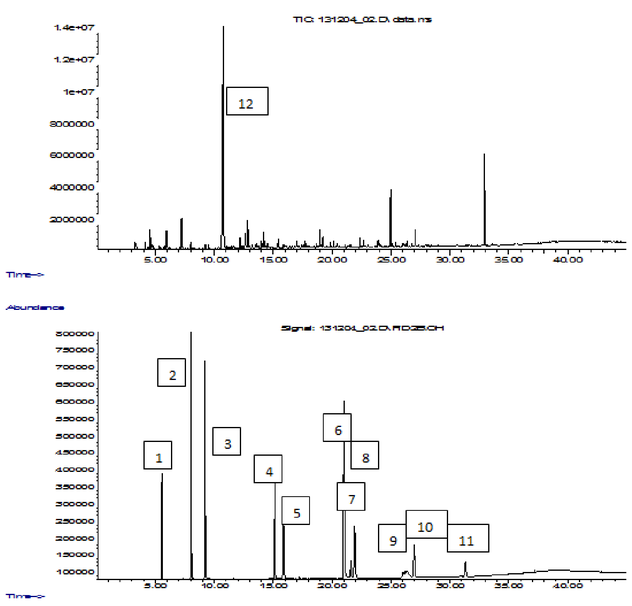


Figure 4: Pyrolysis GCMS of Syrene/isoprene copolymer **(top)** Annotated Primary Chromatogram (BPX50) **(bottom)** Annotated secondary chromatogram (GS-CarbonPLOT). 1) methane, 2 ethene, 3) ethane, 4) propene, 5) propane, 6) butene, 7 butene (isomer), 8) butane, 9) pentenes, 10) pentane, 11) hexane, 12) styrene.

Figure 4 shows primary (top) and secondary heart cut (bottom) chromatograms for a styrene isoprene co-polymer. A range of C1-C6 hydrocarbon pyrolytic fragments are produced. The ratios of this fragmentation changes with polymer composition as shown in figure 6 which allows for the identification of unknown polymers. Figure 5 shows an overlay of the secondary (heart cut) chromatogram for polyisobutylene, a polyethylene/propylene copolymer and polyisoprene.

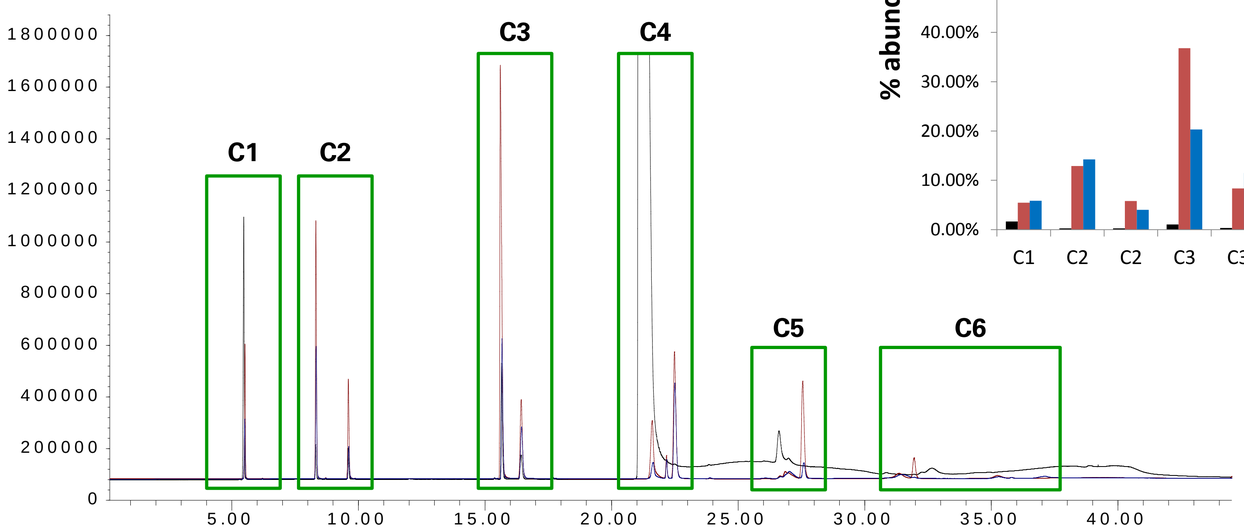


Figure 5: Overlaid secondary chromatograms of Poly isobutene (black); Poly propylene/ethylene (red) polyisoprene (blue). Regions of Carbon number elution are marked.

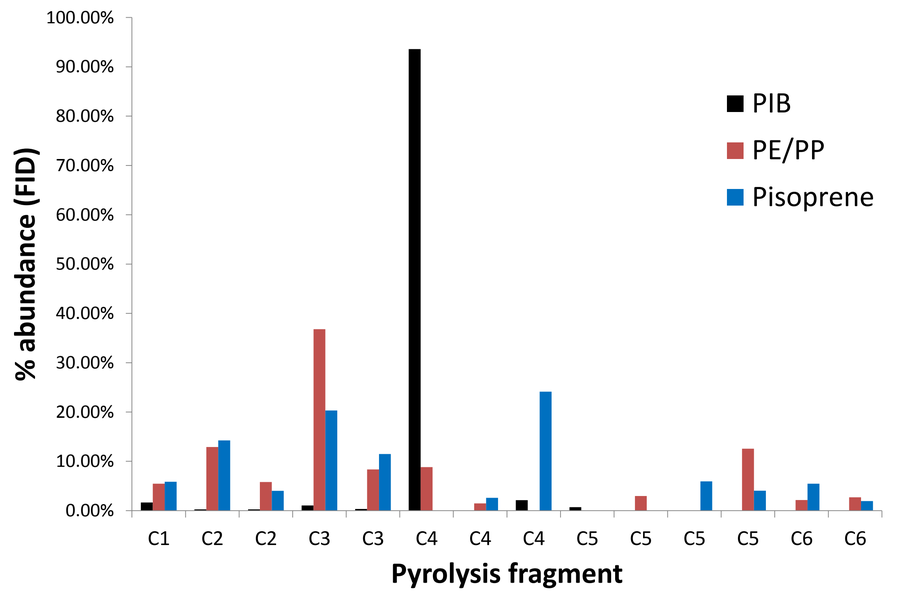


Figure 6: Graphical representation of normalised peak areas shown in figure 5. Each polymer type shows shows a characteristic profile which can be used as a finger print to identify unknown polymers.

Conclusions:

The addition of the SGE deans switch to the OPTIC 4 increases the range of applications that this already highly flexible inlet can investigate. The equipment allows the production, collection and separation of very volatile pyrolysis fragments produced from viscosity modifier polymer samples. A characteristic chromatogram is produced from the secondary column where the normalised ratios of peak areas are compared to a database of known samples. In summary, a GC system that can investigate volatile fragments of pyrolysis, heavy hydrocarbons (upto C50+), solids, liquids and gases has been produced which maximises the range of applications the OPTIC 4 can access.

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