THE ANALYSIS OF PETROLEUM HYDROCARBONS WITH BPX90

Paul Wynne,Yi Huang, Roy Hibbert, Dan DiFeo, Peter Dawes
SGE Analytical Science, 7 Argent Place, Ringwood VIC 3134 AUSTRALIA
SGE Inc, 2007 Kramer Lane, Austin TX 78758, USA

Introduction and Discussion

The recent development of thermally robust very polar phases has realized the simple application of gas chromatography to the separation of complex mixtures on the basis of functional chemistry. The speciation of complex hydrocarbon mixtures is particularly difficult to demonstrate. The components have few substituents or ring heteroatoms and all hydrocarbons, regardless of their degree of unsaturation, exhibit significant van der Waals interactions. Orthogonality of separation for hydrocarbon samples requires the non-polar mechanism to be reduced to a low level and a π-π* retention mechanism to be dominant.

The isothermal elution of petroleum hydrocarbons from BPX5 and BPX90 columns shows significant correlation for compounds that are structurally related (Fig 1). Retention characteristics are described by the gradient of the correlation plot for each class. BPX90 exhibits a low affinity for alkanes and a high affinity for aromatic compounds. The specificity towards aromatics is sensitive enough to separate benzenes, styrenes, naphthalenes and dialkylnaphthalenes into separate groups (Fig 1).

The specificity towards hydrocarbon classes is described by a three-dimensional polarity scale for GC phases (Fig 2) in which very polar phases exhibit strong π-bonding capacity and weak van der Waals capacity. Bonding of this type gives class specificity for hydrocarbons (Fig 3).

Conclusion

The selectivity of BPX90 towards unsaturation supports the use of this column for petroleum applications targeting aromatics in the presence of a high aliphatic background or in combination with a non-polar phase such as BPX5 for orthogonal separation in multidimensional techniques.

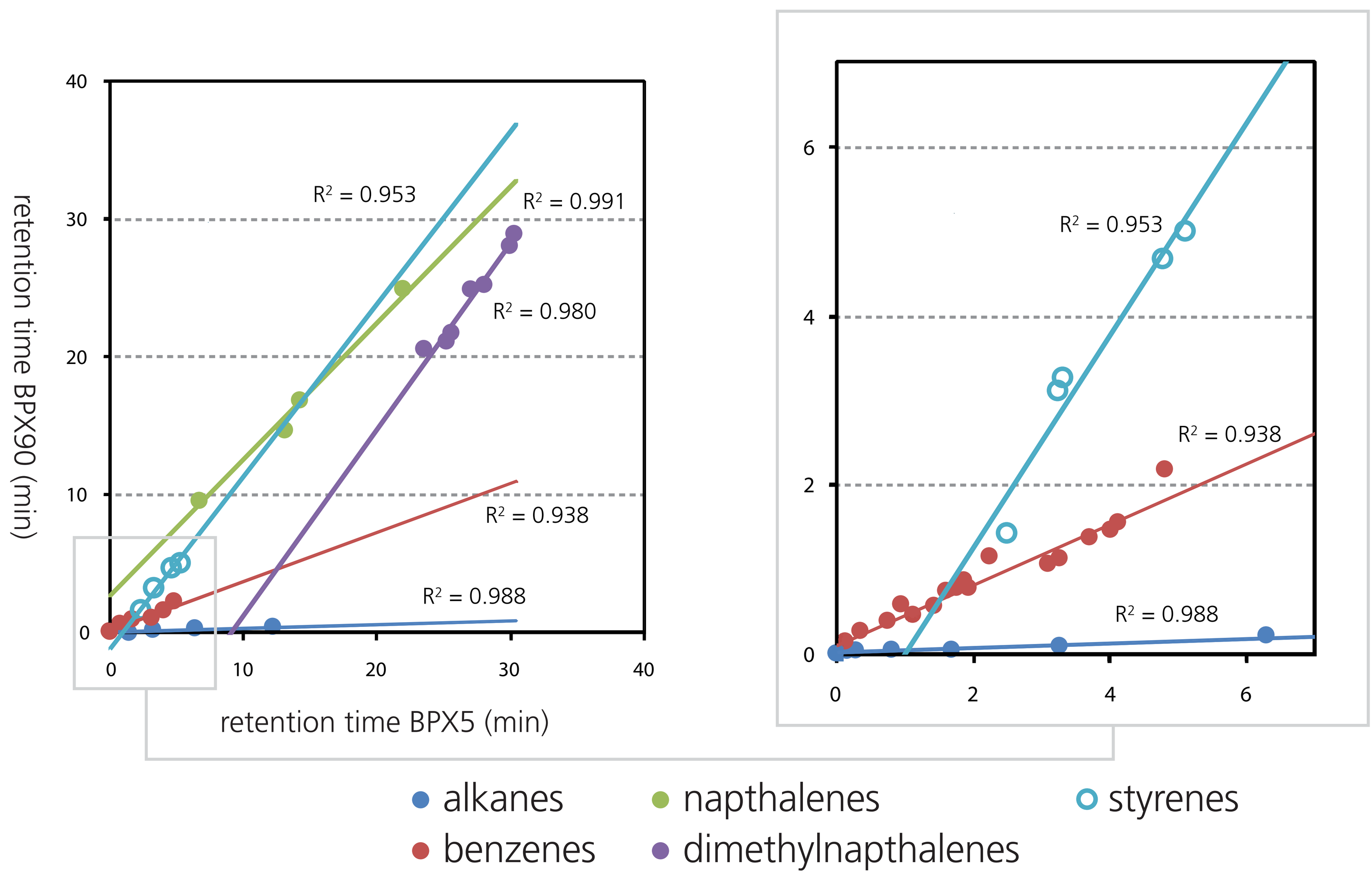

Figure 1: Correlation of retention times for hydrocarbons chromatographed on BPX5 and BPX90. Retention times are corrected for the solvent front.

Experimental conditions: Analysis of petroleum samples used an Agilent 6890 GC-5973N MSD. BPX5 and BPX90 columns were 30 m x 0.25 mm ID with a 0.25 µm film thickness. Injector was 270 °C and injection of 0.05 µL of petroleum was split 200:1. Oven temperature was isothermal at 100 °C. Transfer line was 280 °C, source 230 °C and quadrapole 180 °C. Scan range was 40-500 Da at 2 scan/sec.

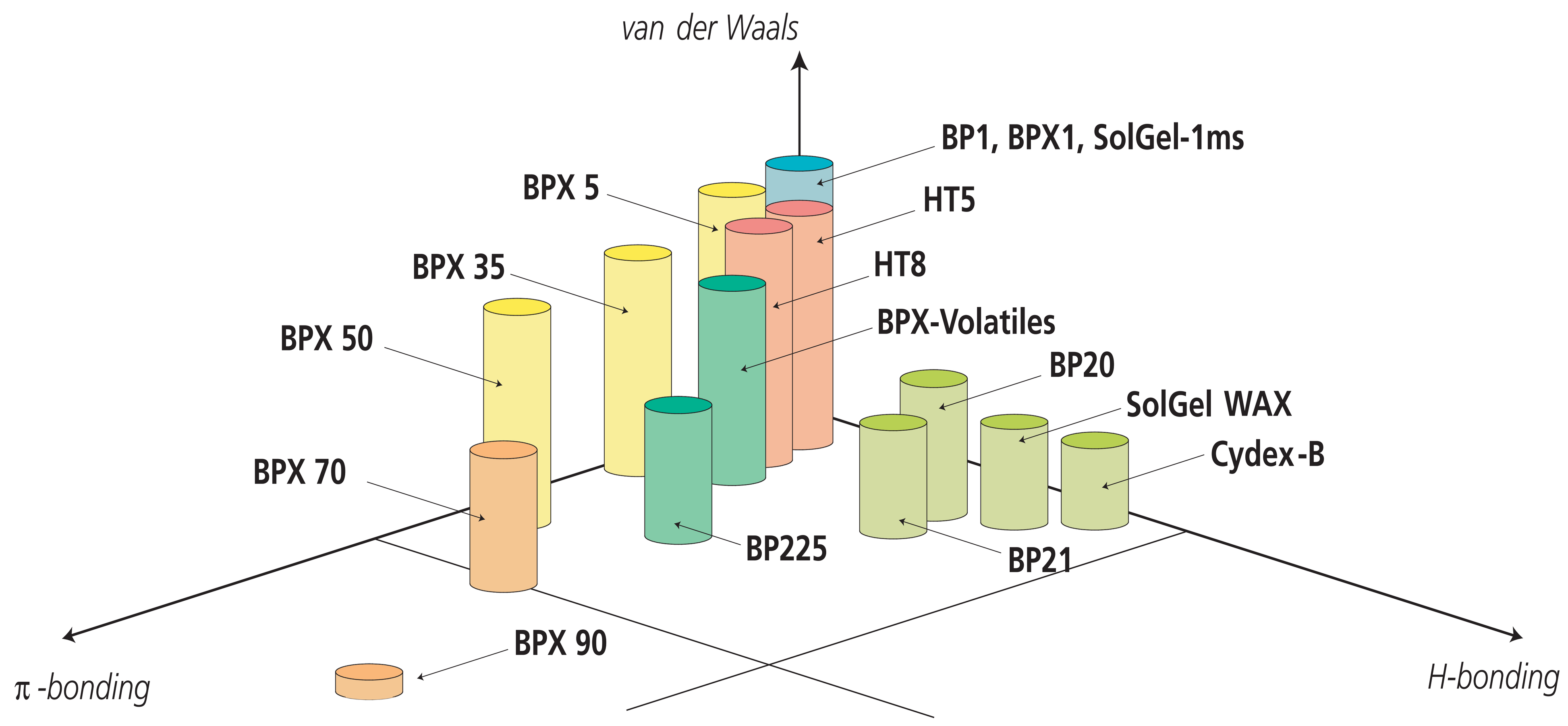

Figure 2: The 3-dimensional GC phase polarity scale shows composite polarity arising from the three major retention types (van der Waals, H-bonding and π-bonding). BPX90 is considered to be a very polar phase and therefore expected to show much higher selectivity towards unsaturated analytes than other phases.

HYDROCARBON ANALYSIS USING VERY POLAR PHASES

Hydrocarbon retention on BPX90 is influenced by degree of unsaturation. Aromatic compounds are strongly retained while aliphatic compounds are eluted with almost no retention provided they are mobile.

Alkenes are retained more strongly than alkanes on BPX90 but retention is also affected by steric factors and low aliphatic solubility in the phase. Aromatic compounds may be separated on the basis of class. Benzenes, styrenes and naphthalenes showed family dependent retention on BPX90.

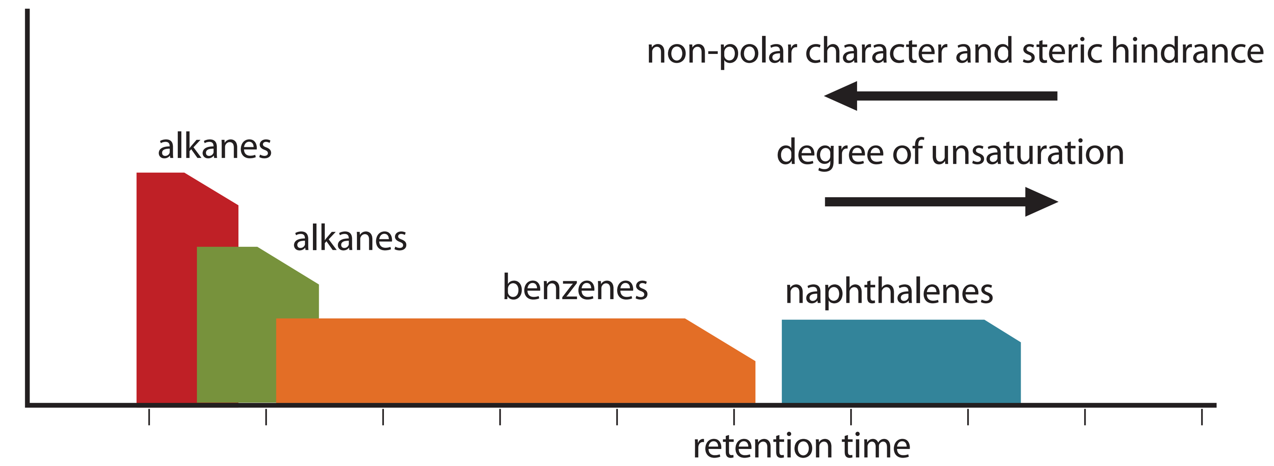

Figure 3: The highly polar phase BPX90 speciates hydrocarbons on the basis of their degree of unsaturation rather than vapor pressure and molecular weight. Steric hindrance of unsaturated moieties and the introduction of non-polar characteristics reduce retention.

ANALYSIS OF LEADED PETROL AND HEATING OIL

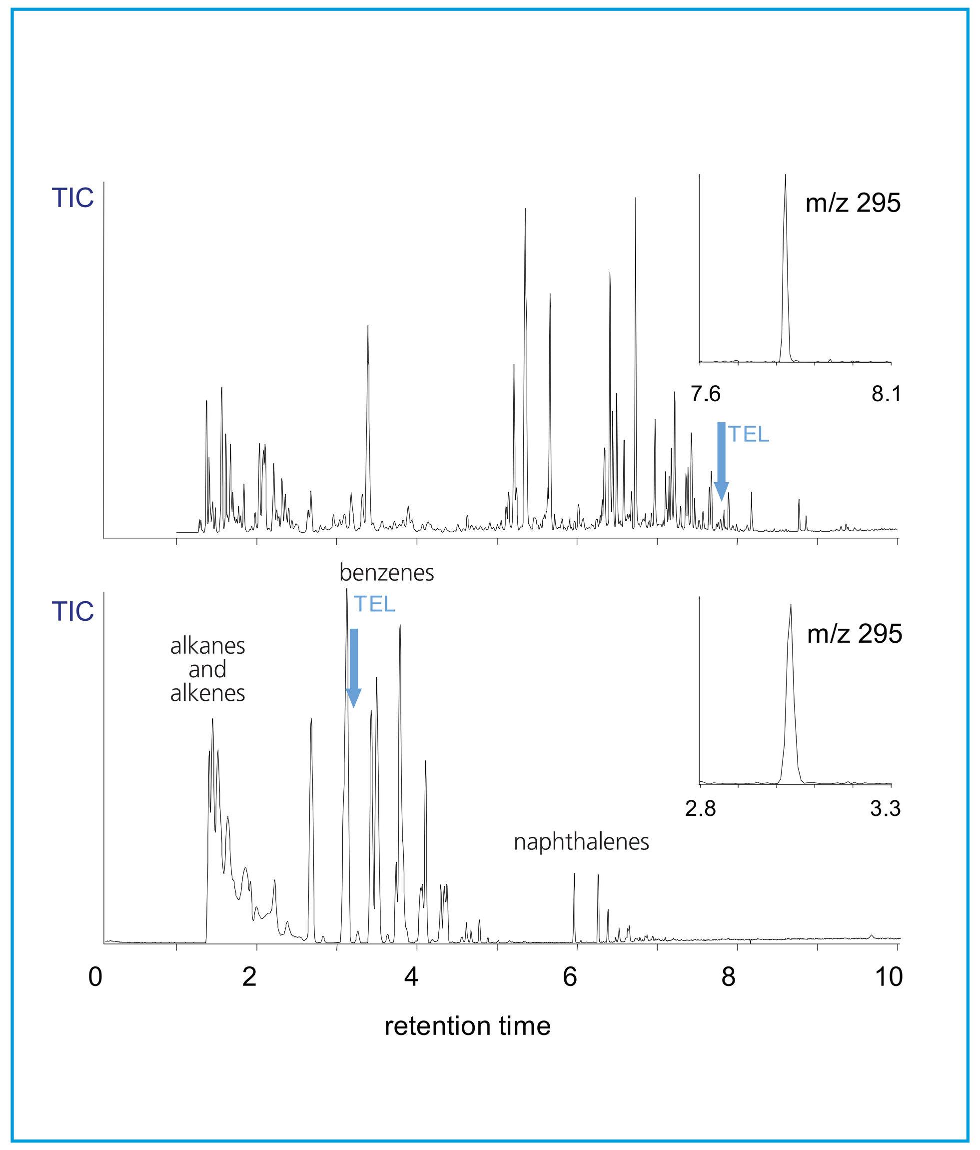

Figure 4: The GCMS analysis of pre-2001 leaded petrol on BPX5 (top) and BPX90 (bottom) columns under identical operating conditions. Insets are for the tetraethyl lead ion m/z 295. Experimental conditions as for Fig 1 excepting that the oven temperature was 40 °C (1 min) then heated at 30 °C/min to 200 °C (10 min).

Petrol (gasoline) is speciated into hydrocarbon families by BPX90. Retention is influenced by unsaturation rather than by molecular weight and vapor pressure as is seen for BPX5 (Fig 4). The additive tetraethyl lead (TEL) is a useful indicator of retention mechanism. Retention on BPX5 is influenced by molecular weight (323), vapor pressure (0.027 kPa at 20 °C) and the non-polar ethyl surface. Free rotation along the C-C bond axis shields the plumbate core and, consequently, polar retention is poor relative to non-polar phases (Fig 4).

Analysis of heating oil aromatics is complicated by coeluting C9 – C15 alkanes (Fig 5, bottom). Because alkanes have poor solubility in BPX90 they coat the phase surface after injection. At low temperatures this effect can be used in combination with their vapor pressures to eliminate them as interferences by using a low temperature sweep (Fig 5, top). The passage of the alkanes through the column is neither phase compatible nor optimized chromatographically and so they appear as poorly shaped and resolved peaks. The aromatics, having higher solubility in the BPX90, are retained until mobilized by the temperature program applied.

Elution on the basis of unsaturation supports either standalone application of BPX90 or its use as a complement to BPX5 in multidimensional techniques requiring a highly orthogonal approach.

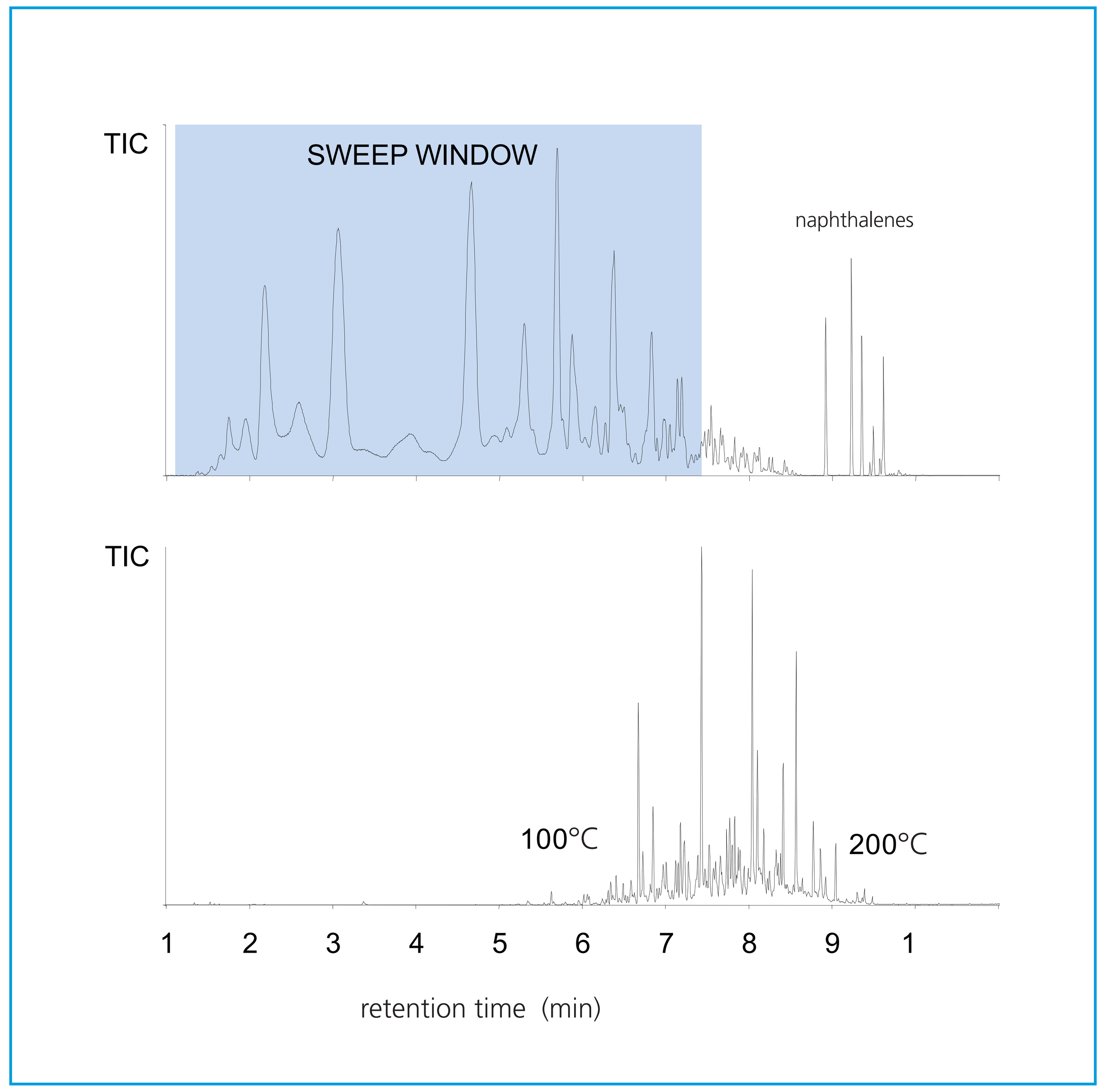

Figure 5: The GCMS analysis of commercial heating oil using BPX90 (top) and BPX5 (bottom) columns. Experimental conditions as for Fig 1 excepting that the oven temperature was 40 °C (4 min) then heated at 30 °C/min to 200 °C (10 min).

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