Structure-retention relationships on different 5 % phenyl equivalent GC phases

Roy Hibbert[1], Phillip Marriott[2], Naza Lahoutifard[3] and Paul Wynne[1],
[1]SGE Analytical Science, Ringwood, Victoria, Australia
[2]School of Physical Sciences, RMIT University, Melbourne, Victoria, Australia
[3]SGE Europe, France

Introduction

In this study, we examine the retention of closely eluting aromatic analytes as a function of GC phase chemistry under identical chromatographic conditions. The approach allows the generation of a retention matrix based on phase chemistry and analyte structure that is a useful predicitve tool for describing retention mechanisms and for column selection.

Results and discussion

The chromatographic results and analytes are shown in figure 1.

In the first group, the separation of PAH components is considered. Two minor components (peaks 3 and 5) chromatograph close to pyrene. Increasing phase aromaticity reduces the retention of the more saturated component (peak 5) relative to other components. The diphenyl phase (BP5) shows less selectivity towards extended aromaticity than BPX5 because of steric limitations on each interaction that do not influence silphenylene phases. The m-carborane modified HT8 is similar in selectivity to BPX5 because PAHs are not sufficiently hindered to realise angle of approach differences.

In the second group, isopropylphenol (13) shows the effect of higher aliphatic substituents in hindering analyte interactions with the phase. It elutes earlier, relative to less hindered phenols (12), with increasing phase aromaticity.

The resolution of xylenols 8 and 9 for BP1 and BPX5, but not for more aromatic phases may be attributed to the less favourable phenyl pendant intercalation shown by the 2,4- over 2,6-isomer. In contrast, differences between 4-ethyl and 3,5-dimethylphenols appear to be electronically influenced (the strength of the π-donor/acceptor) with the consequnce that the HT8 phase is less retentive for the ethyl phenol than BPX5. A similar mechanistic interpretation may also be adopted for the shift in retention of 2-nitrophenol with phase type where the analyte's structure is influenced by an intramolecular hydrogen bonded form.

In the third group, safrole isomers show little change in separation for cis-trans isomerism or ene-aryl spacing for either silphenylene content or m-carborane modified phases. The analytes are all relatively small with aromaticity-extending substituents that offer equally low barriers to interaction with silphenylene or phenyl substituents. In contrast, naphthalendione and 1,4-dinitrobenzene are rigid or restricted systems and both show greater retentive character for increasing phase aromaticity in line with their highly unsaturated and planar character.

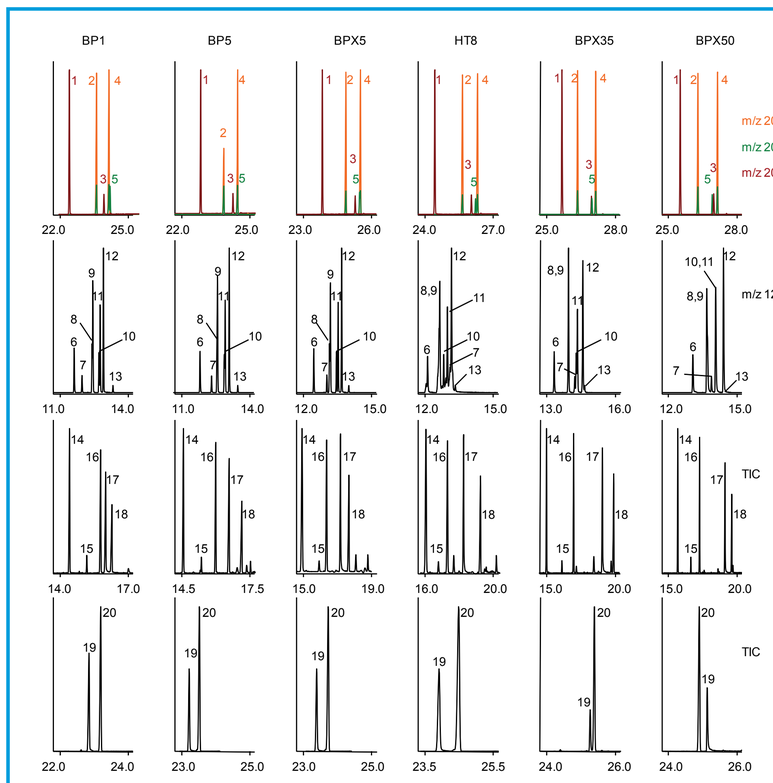

Figure 1: GCMS used a 6890-5973N MSD (Agilent Technologies, CA, USA) with either a BP1, BP5, BPX5, HT8, BPX35 or BPX50 column (30 m x 0.25 mm i.d., 0.25 µm film thickness). Injections of 1 µL were splitless at a temperature of 260 °C and a pressure of 93 kPa. The oven was 40 °C (hold for 4 min) to 300 °C (hold for 10 min) at 10 °C/min. Transfer line was 260 °C and helium flow was 1.2 mL/min. Detection was by EI-MS between 40-500 Da at 2 scan/sec and the source was 230 °C.

In the fourth mix, the separation of methapyrilene and isodrin changes with increasing phase aromaticity and culminates in a reversal of elution order for BPX50. This phenomenon can be attributed to the aromatic moieties and nitrogen lone pairs on the metapyrilene and the boat like form of isodrin in which the two double bonds are hindered by a relatively high halogen count. Contrasting behaviour is seen with the m-carborane modified HT8 phase where the boat form of isodrin is able to wrap around the carborane, allowing simultaneous interaction with both enic bonds, but with little halogen induced steric interference.

Conclusion

Retention of aromatic analytes by GC phases is based on the ability of the analyte to approach the aromatic moieties in the GC phase without steric or electronic interference. Silphenylene (BPX5, BX50 and BPX 35) and carborane phases (HT8) are capable of unique selectivity over non-polar or phenyl modified PDMS phases because interaction with aromatic analytes is not dependent on a sterically sensitive intercalation mechanism.