STRATEGIES FOR THE ANALYSIS OF COMPLEX SAMPLES BASED ON REVERSING THE PHASE POLARITY IN GAS-LIQUID CHROMATOGRAPHY

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Introduction and Discussion

The successful design of multi-dimensional gas chromatographic applications is dependent on understanding the different characteristics of the phases that are used. Most methods increase the separation power based on some degree of orthogonality in phase polarity rather than on dimensional variations between columns.

The three-dimensional model of phase polarity described in Figure 1 considers the interactions between an analyte and a phase to be comprised of non-polar (essentially van der Waals interactions), π - π* orbital overlap and n-electron bonding effects. The latter type may take the form of heteroatomic loan pairs acting as a hydrogen bonding acceptor or an electron sump capable of n- π* interactions. The model defines the region of chromatographic space for conventional approaches to gas-liquid chromatography in terms of the type of intermolecular bonding between the analyte and GC phase. By defining the phases in this way, column selection may be more readily interpolated from the likely analyte-phase interactions rather than purely from empirical considerations.

The power of very polar separations is often lost in the single dimensional GC because the base method still relies on the association between retention time and vapour pressure. However, comparison of elution order for different classes of analytes from different GC phases is an effective demonstration of orthogonality.

While limitations of the GC technique and instrumentation mean that reversed-phase chromatography cannot be realized in the same sense as that achieved for liquid chromatography (both the stationary and mobile phase polarity is reversed), the advent of very polar GLC phases alters the fundamental retention chemistries between phase and analyte such that these very polar phases fulfill the requirements of a reversed-phase GLC column.
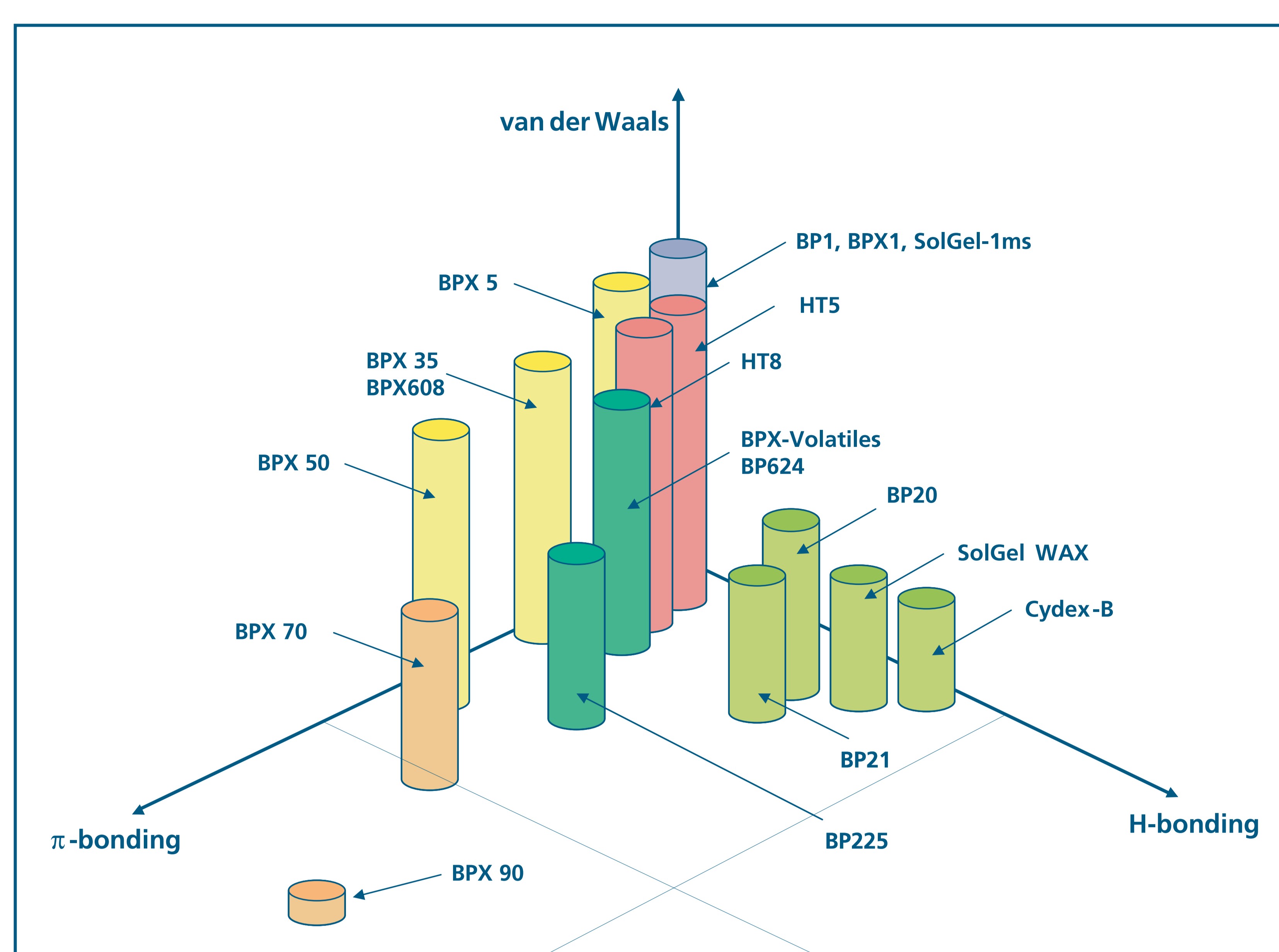

Figure 1: The 3-dimension GC phase polarity scale shows composite polarity arising from the three major retention types (van der Waals, H-bonding and π-bonding). BPX90 is considered to be a very polar phase and therefore expected to show much high selectivity towards unsaturated analytes than other phases.

ORTHOGONAL SEPARATION OF HYDROCARBONS

Petroleum samples are useful for demonstrating class specific chemistry because of the presence of compounds that exhibit relatively pure intermolecular bonding types. Alkanes bond by van der Waals interactions while aromatics exhibit a high level of π-bonding. When petroleum samples were analyzed isothermally on BPX5 and BPX90 columns of identical dimensions, a significant correlation for compounds that are structurally related was found (Fig 2). The use of an isothermal method limited the molecular weight range over which useful correlations could be determined but normalized other influences associated with thermal programming to allow retention time to be directly related to the degree of interaction between the phase and analyte. Retention characteristics are described by the gradient of the correlation plot for each class and hydrocarbon retention on BPX90 is found to be strongly 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.

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

EXPERIMENTAL CONDITIONS:

- Analysis used an Agilent 6890 GC -5973N MSD.
- BPX5 and BPX90 columns were 30 m x 0.25 mm i.d. 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 quadrupole 180 °C.
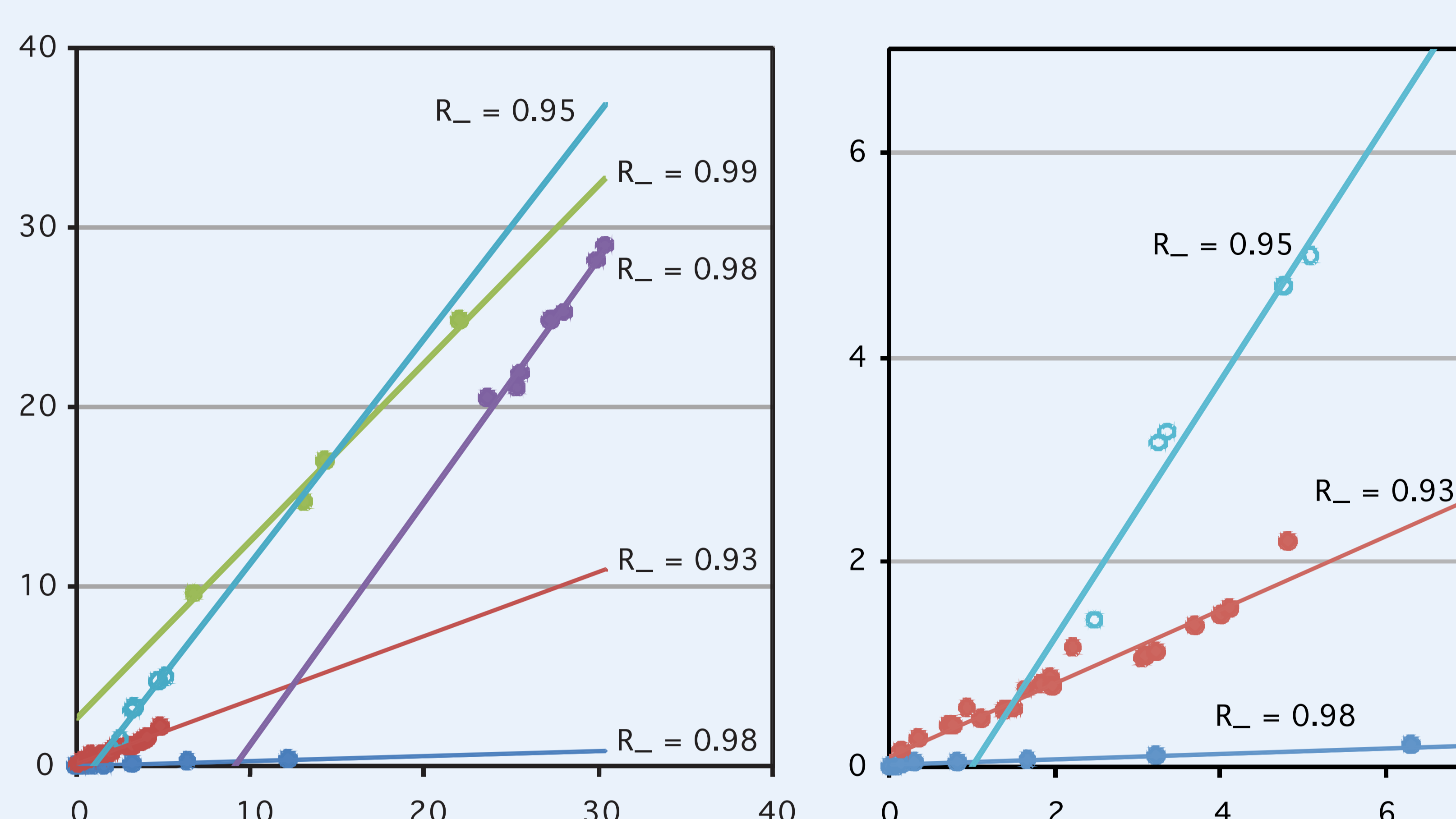- Scan range was 40-500 Da at 2 scan/sec.

PHASE SELECTIVITY TOWARDS POLYCHLOROBIPHENYLS (PCBs)

PCBs are a useful demonstration of phase selectivity towards aromatic compounds because they exhibit a very high capacity for π-bonding. Relative retention characteristics for the group also show the influence of steric hindrance arising from substitution and conformation (planarity).

Because the PCB congeners span a large molecular weight range (biphenyl M = 154 to decachlorobiphenyl M = 494) isothermal analysis is impractical. As retention times are influenced by volatility as well as mobility and solubility in the phase, the interaction between analytes and particular GC phases must be determined relative to a reference column. The relative influence of BPX90 and HT8 on PCB retention is shown by plotting retention data for the test columns against the same data for a BP5 reference column. The correlation plots are interpreted by comparing the deviation of the retention time for the test column away from the diagonal generated by plotting the reference against itself (Fig 3).

The carborane based HT8 phase shows an overall difference in PCB selectivity indicated by the 'S' shaped correlation plot. Not unexpectedly, selectivity differences are greater for congener groups that are more highly substituted (indicated by counterclockwise rotation of the congener correlation away from the diagonal) as the carborane is not affected by steric hindrance to the same extent as phenyl pendent phases. Longer retention times on HT8 demonstrate that the carborane-PCB interaction is stronger than the corresponding pendent phenyl-PCB interaction of BP5.

In contrast to the HT8 phase, BPX90 shows a high degree of selectivity both between congener groups and across all degrees of substitution. This is indicated by the counterclockwise rotation of congener correlation away from the diagonal and the spacing between the correlation lines for each congener group. The resulting separation may be attributed to BPX90's ability to overcome steric barriers by free rotational extension of bonding moieties (cyanopropyl groups). Early elution of analytes is the result of a negligible van der Waals contribution to retention that is typical of this phase.

CONCLUSION

HT8 and BPX90 provide selectivity for PCB analysis that is different to the selectivity of phenyl modified phases. The degree of selectivity is predictable when the dominant interactions between phase and analyte predicted by the three dimensional polarity scale are combined with an appreciation of the steric barriers associated with intermolecular bonding for highly substituted aromatic compounds.
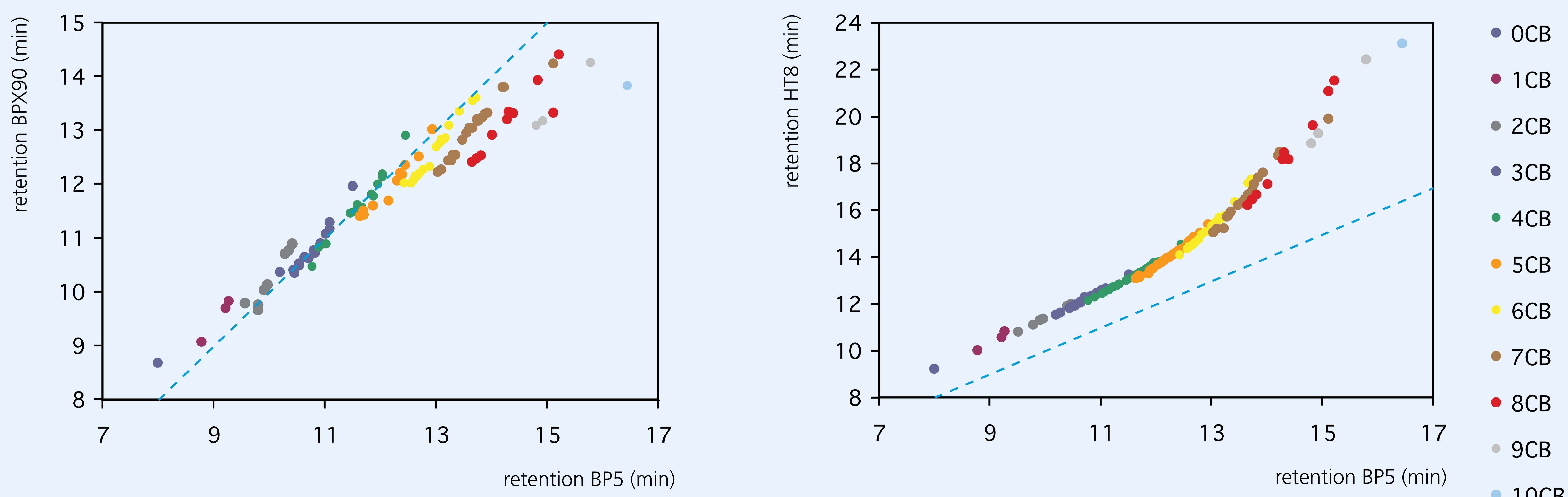

Figure 3: The correlation of PCB retention by a BP5 column versus a BPX90 column (left) and a HT8 column (right).

EXPERIMENTAL CONDITIONS:

- BP5, HT8 and BPX90 columns were 30 m x 0.25 mm i.d. with a 0.25 micron film thickness.
- Sample was a 2% w/v solution of transformer oil in dichloromethane.
- Analysis was performed on a 6890 GC-5973N MSD (Agilent Technologies) fitted with an ETP 14642 electron multiplier.
- Injection was split 50:1 with a split flow of 65 mL/min at a temperature of 250 °C.
- The carrier gas was helium with a nominal flowrate of 1.3 mL/min in constant flowrate mode and a nominal inlet pressure of 10.8 psi.
- The oven temperature was programmed from 50 °C (held for 2 minutes) to 270 °C (held for 15 minutes) at 20 °C/min.
- The transfer line was at 280 °C.
- MS scanned from 50-550 Da at 2.9 scan/sec.

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