POLAR PHASES FOR GAS CHROMATOGRAPHY

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Introduction

BPX90 is a new generation of very polar gas chromatography phase of the biscyanopropylpolysiloxane type that offers thermal stability not normally associated with this class. Some areas of analysis make greater use of these phases for improved separation and/or speciation of analytes. Highly polar phases can be useful alternatives to non-polar phases for some difficult analyses and used to maximum advantage when their parallel versus orthogonal capabilities are understood across analyte classes.

We describe here the separation of several aromatic amines on a non-polar phase (BPX5) and compare that with the separation under identical conditions on a highly polar BPX90 phase. The two phases are described on the basis of their primary and secondary retention mechanisms and separation is rationalized according to functional interactions between the phase and the analytes. This technique is then representative of how these columns can be used in practice and the information used to develop an understanding of the principles underlying selectivity and suitability for purpose of the very polar phases.

What is BPX90?

BPX90 is a biscyanopropylpolysiloxane type phase. The very high cyano content of the phase gives the column its defined high polarity and, conversely, defines its lack of non-polar character. BPX90 is a localized π -donor type and is therefore capable of interacting strongly with aromatic and other unsaturated analytes by π-π* mechanisms as well as with n-electron containing heteroatomic species (Figure 1).

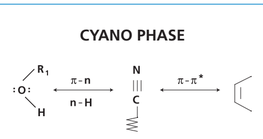

Figure 1: Illustration of the major liquid phase - analyte interactions that operate for biscyanopropylpolysiloxane phases.

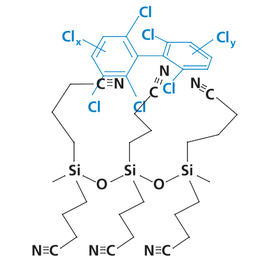

Figure 2: Stylized illustration of how biscyanopropylpolysiloxane phase can adapt to the shape of the analyte and thereby minimize steric barriers.

The cyanopropyl chains allow the cyano groups to adapt to the shape of individual analytes (for example a PCB shown in Figure 2). Such adaptive chemistry presents a very low steric barrier to analyte-phase interactions.

Electronic insulation of the cyano groups give very specific enthalpies of interaction with analytes and so there is significant contribution from Hammett-Taft substituent effects to elution order.

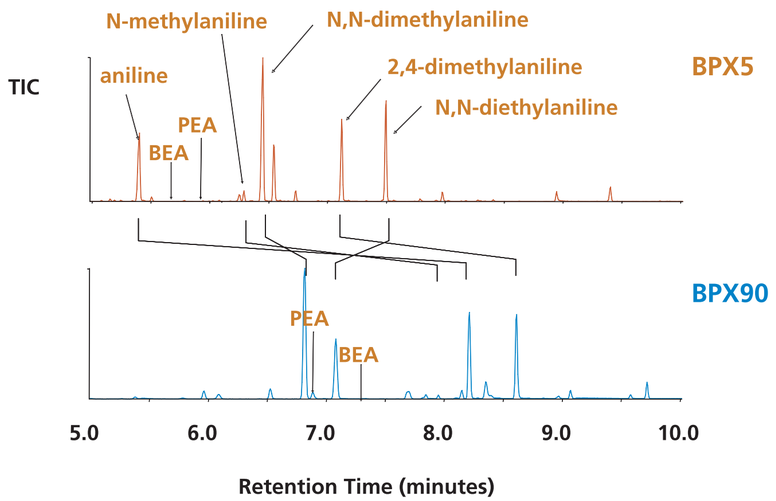

Figure 3: Separation of anilines on a BPX5 columns (top) and a BPX90 column (bottom). Separation was performed under identical conditions on 30m x 0.25mm i.d, 250µm columns.

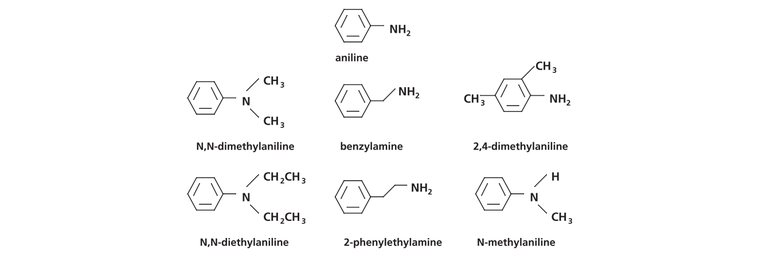

Figure 4: Structure of aromatic amines compared in the study.

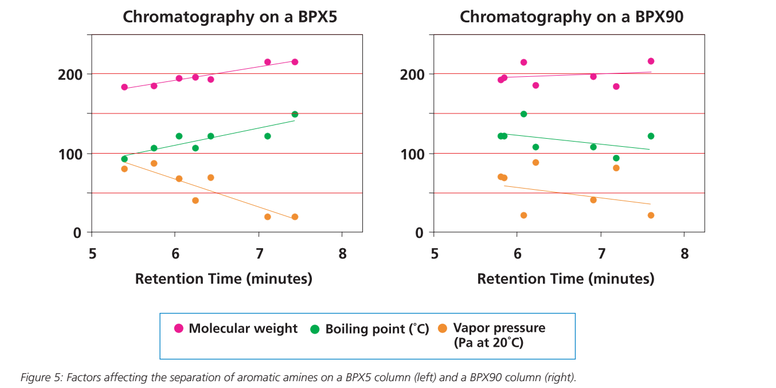

Figure 5: Factors affecting the separation of aromatic amines on a BPX5 column (left) and a BPX90 column (right).

Application of BPX90

Mixtures of aromatic amines (Figure 3) were subjected to gas chromatographic separation under identical conditions on BPX5 and BPX90 columns of identical dimensions. Chromatograms for the anilines are shown in Figure 4.

Separation of analytes on a BPX5 column is essentially non-polar and shows the expected dependence on vapor pressure and molecular weight (Figure 5).

For BPX90, these relationships are no longer apparent indicating that separation is determined by a fundamentally different process (Figure 5). The shift in retention time between BPX5 and BPX90 shows a strong familial dependence on the partition coefficient, pK_{ow} (Figure 6). Such a relationship, if typical, indicates that the selectivity of the highly polar phases are due largely to the ability of the phase to dissolve analytes and therefore suggests significant orthogonality to the non-polar phases.

Conclusion

BPX90 is orthogonal to non-polar phases and shows very little non-polar character. It is thermally stable up to 280˚C and is therefore particularly useful in 2-D GC systems.

The selectivity of highly polar phases like BPX90 results from the adaptive chemistry of the phase (i.e. the enthalpy associated with the analyte interaction) while the speciation characteristics are more likely related to the solubility of analyte in the phase (i.e. the frequency of interaction).

BPX90 has a dominant π-π* retention mechanism and insignificant non-polar retention which gives high selectivity towards aromatic electron density and structurally significant double bonds.

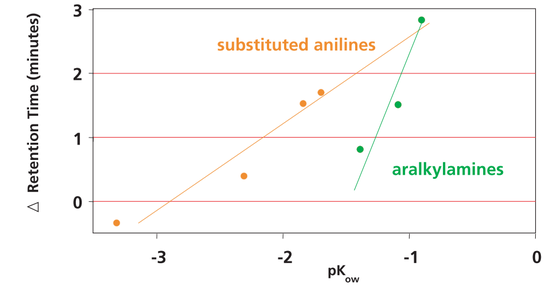

Figure 6: The phase dependent change in retention time between BPX5 and BPX90 can be correlated with measures of polarity such as the octanol-water partition coefficient.

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