Ionic Liquid Stationary Phases:

Application in Gas Chromatographic Analysis of Polar Components of Fuels and Lubricants

by Sam Whitmarsh, Investigational Analysis, BP Research and Technology
Global Lubricants Technology, Pangbourne, Berkshire, RG8 7QR
samuel.whitmarsh@bp.com

The capillary gas chromatographic analysis of polar components within fuels and lubricants was investigated using commercially available ionic liquid coated columns. The improved temperature stability and high polarity of these phases relative to polyethylene glycol were studied in one and two dimensions. In one dimension, the reduction in hydrocarbon matrix interference presents opportunities for improved quantitation and less sample preparation. In two dimensions, a reduction in second dimension retention was observed as phase polarity was increased providing a reminder that column sets should be correctly matched to sample composition for effective separation.

Engine oils are complex mixtures of hydrocarbon base fluids which can act as lubricants by virtue of their viscometric properties. These fluids also act as carriers for a range of additive components which have a chemically active role in the engine. These additives function as viscosity modifiers, anti-oxidants, detergents, dispersants and surface active molecules which protect against wear. Analysis of these materials in both fresh and used lubricants is critical to the behavioural understanding of these materials for practical troubleshooting, performance monitoring and as indicators of the fundamental processes involved in internal combustion engines.

Gas chromatography is one of the primary analytical techniques involved in the investigation of these compounds. Whilst mass spectrometry and statistical analysis have enabled sophisticated deconvolution of overlapping peaks, it is still highly desirable to achieve a physical separation of the analyte of interest from the matrix and other signals. Evaluation of column chemistries which enable such separations continue to be an important part of laboratory development. Analytes of interest in lubricant samples are typically more polar that the hydrocarbon base fluids due to the degradation pathways of oxidation and nitration and because additive components tend to contain heteroatoms. Therefore, separation of these polar materials from the non-polar matrix would allow for the study of the analytes of interest with reduced interference from the matrix.

Ionic liquids are a class of compounds which can be defined as organic salts that are liquid below 100°C. They find use in many areas of chemistry as highly tuneable non-molecular solvents in synthesis, electrochemistry and analytical chemistry [1]. The properties of extremely low vapour pressure even at high temperatures, high viscosity, high thermal stability and high polarity make them suitable as phases for gas chromatography [1]. The first commercial ionic liquid column was launched by Supelco in 2008 [2] and further development has yielded an additional five column phases. A range of columns are now available encompassing different phase types, from polyethylene glycol equivalent polarity with improved thermal stability (SLB-IL59) to phases with extremely high polarity (SLB-IL111).

This combination of high polarity and high temperature stability along with new selectivity has great potential to impact methods within our labs. This report describes initial work studying the application of these columns to commonly observed problems within the group. Namely: the removal of hydrocarbon matrices from analytes of interest in a single dimension and improved orthogonality for use in 2D GCxGC separations.

Experimental

Two capillary gas chromatographs were employed. Firstly, an Agilent 6890N (Agilent Technologies, Santa Clara, CA, USA) equipped with an ATAS Optic 4 PTV inlet (ATAS GL International B.V., Eindhoven, NL), Agilent 5973MSD single quadrupole EI mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) operated in positive ion mode and a nitrogen/phosphorus detector. Secondly, an Agilent 7890A (Agilent Technologies, Santa Clara, CA, USA) equipped with a split/splitless inlet, flame ionisation detector and Agilent G3486A capillary flow GCxGC modulator (bypassed for use in single dimension studies). System control and data processing were carried out using Agilent ChemStation (Agilent Technologies, Santa Clara, CA, USA).

Methods in the single dimension: A 0.1 µl injection volume was used for undiluted samples (diesel, B20, gasoline) and 1.0 µl used for diluted samples (test mixes, methanol extract, lubricant samples). Injections were made into a split/splitless injector with a single gooseneck liner containing quartz wool at 275°C. Split ratios of 200:1 were typically used. The column flow was 1 ml/min constant with helium as carrier gas. The temperature program was as follows: 50°C with hold for 5 minutes, then 8°C/min until maximum column temperature reached, then hold until 45 minutes total run time reached. Detection was carried out using either mass spectrometry (scan mode 20-500 AMU, 70 eV, interface constant 270°C), nitrogen phosphorus detection (310°C, 60 ml/min air, 3 ml/min H_2, make up flow 2 ml/min He and electrometer voltage auto optimised) or flame ionisation detection (300°C, 40 ml/min H_2, 400 ml/min air, make up flow 40 ml/min He).

Methods in two dimensions were as follows: Inlet and injection conditions as in single dimension with 500:1 split ratio. First

dimension column flow was 1 ml/min on 30 m x 0.25 mm x 0.25 µm Agilent HP5 phase and second dimension column flow was 32 ml/min on 5 m x 0.25 mm (phase thickness described below). Oven temperature program as single dimension. Microfluidic modulator settings as follows: Modulation delay 1.2 sec, modulation period 1.55 sec, sample time 1.45 sec. Detection carried out by flame ionisation detector conditions as in the single dimension.

Columns used: All columns were conditioned according to the manufacturer's specifications.

Agilent J&W HP5 30 m x 0.25 mm x 0.25 µm (max temp 350°C) Agilent J&W DBwax 30 m x 0.25 mm x 0.25 µm and 5 m x 0.25 mm x 0.15 µm (max temp 280°C) in single and dual dimensions respectively. Supelco columns SLB-IL59 (max temp 300°C), SLB-IL61 (max temp 290°C), SLB-IL76 (max temp 270°C), SLB-IL82 (max temp 270°C), SLB-IL100 (max temp 230°C) and SLB-IL111 (max temp 270°C) were all 30 m x 0.25 mm x 0.20 µm when referred to in single dimension and 5 m x 0.25 mm x 0.25 µm in dual dimensions.

Sample preparation: Hydrocarbon standards were purchased from Sigma-Aldrich (Sigma-Aldrich Company Ltd, Gillingham, Dorset, UK). Diesel, soya bean methyl ester (SME), and lubricating oil samples were obtained from BP stocks. Diesel B20 samples were prepared by mixing by weight diesel and soya bean methyl ester so that 20% solution of SME in diesel was obtained. Methanol extracts of lubricating oil were prepared by taking a 1:1 mixture (by volume) of lubricating oil and methanol in a vial and shaking by hand and vortex, after the phases were allowed to separate the top methanol fraction was removed and analysed.

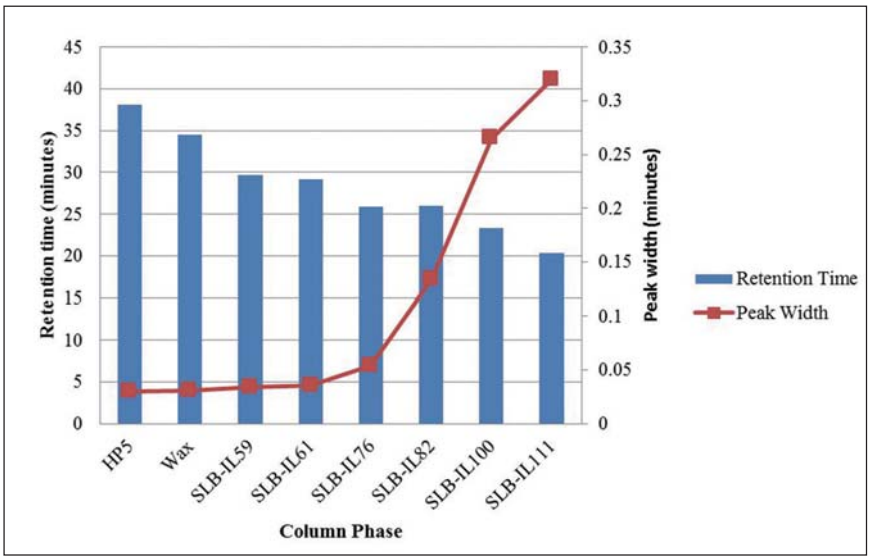

Figure 1: Changes in Retention time and Peak width at base of C31 n-alkane with increasing column phase polarity

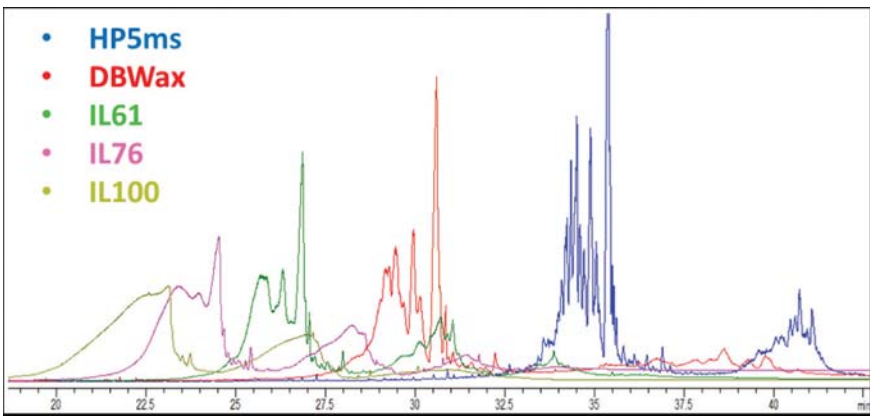

Figure 2: Elution of a lubricant product on various column phases.

Results and Discussion

Analysis in a single dimension:

As expected, increasing column polarity reduces retention time for non-polar hydrocarbons as shown in Figure 1. This occurs to such an extent that Hentriacontane (C31 n-alkane) elutes almost twice as quickly using an identical temperature program on SLB-IL111 when compared to a HP5 phase. This corresponds to a reduction in elution temperature of approximately 100°C. At a constant concentration of approximately 3 ng on column, the peak width at base of n-C31 increases and peak shape worsens (greater fronting) with column polarity so that on IL100 and IL111 the peak shape is poor. These changes are likely to be caused by the relative importance of different retention mechanisms acting in each column phase. In the HP5 retention is prominently due to London dispersion forces (instantaneous dipole – induced dipole attractions) since there are no polar moieties to introduce other interactions. This mechanism appears to dominate in HP5 to IL61 also, though to a decreasing degree. From IL86 to IL111 the dominant retention mechanism changes so that dipole/dipole and electrostatic interactions are most important, retention decreases as the analyte does not dissolve in the liquid phase and peak width increases due to poor wetting of the surface. The peak width increase is most noticeable on the larger hydrocarbons. C11 is approximately Gaussian at the same concentration on IL111. Polar analytes of interest are present at concentrations in the order of 100-10000 times lower than the hydrocarbon matrix in our typical samples. Without sample pre-treatment hydrocarbon concentrations will inevitably be large and the observed poor peak shape of the hydrocarbons at higher on-column loadings may inhibit analysis if compounds of interest elute in a similar region of the chromatogram as shown in Figure 2.

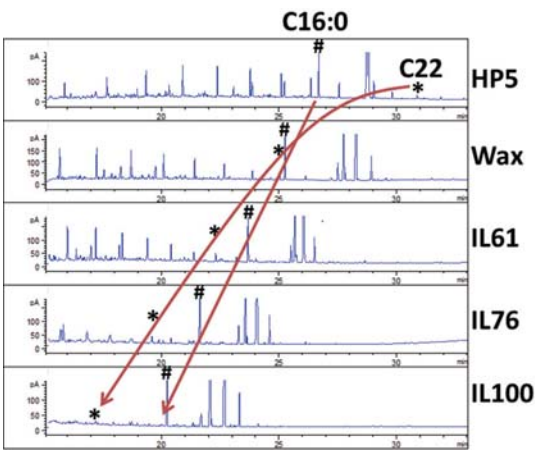

Figure 3: Elution of B20 biodiesel on various column phases showing peak position of n¬-Docosane – C22 (*) and palmitic methyl ester - 16:0 (#).

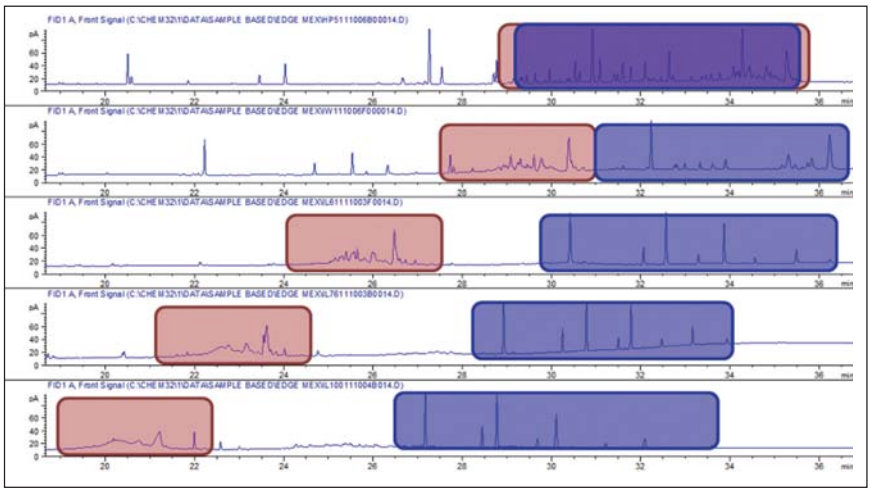

Figure 4: Chromatograms showing separation of a lubricant product methanol extract using different column coatings. The red box indicates the bulk of nonpolar hydrocarbon oil matrix, blue indicates bulk of polar anti-oxidant and anti-ware additive components.

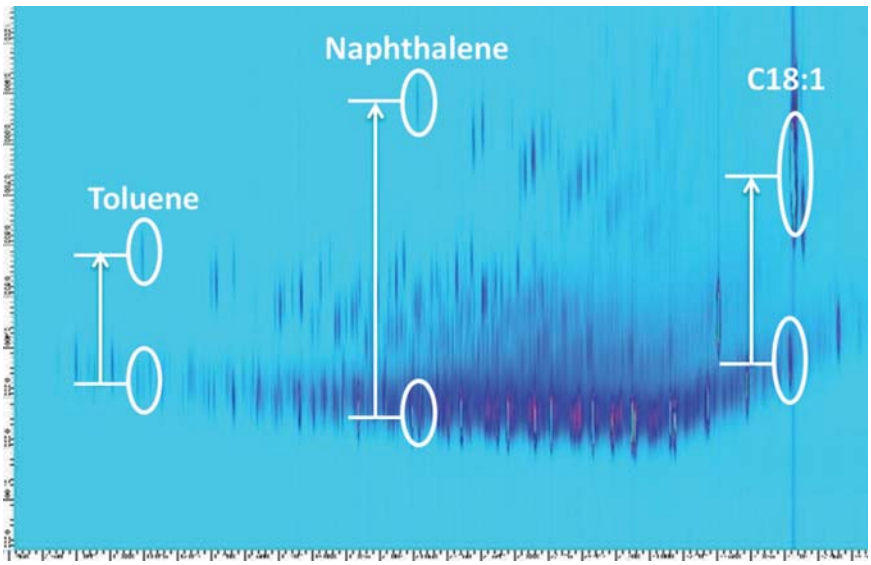

Figure 5: Flow modulated comprehensive GCxGC chromatogram of B20 biodiesel. Retention time in the second dimension is highlighted by arrows.

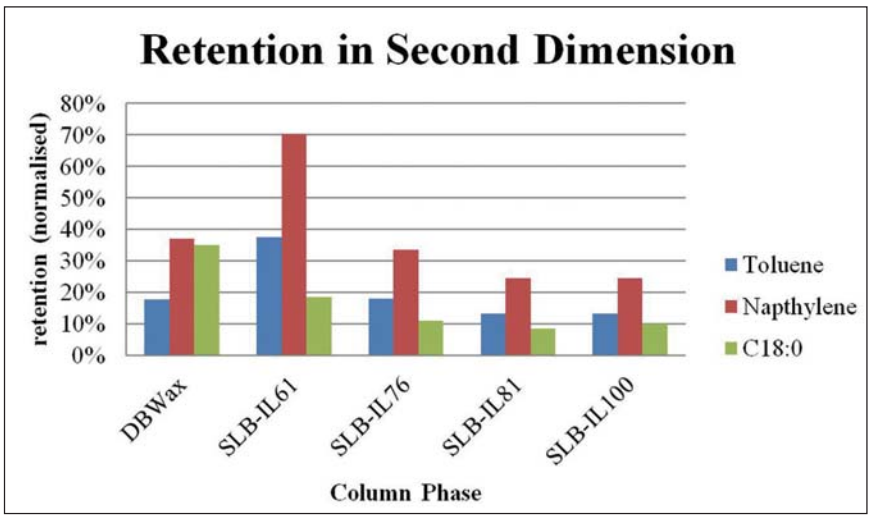

Figure 6: Graphical representation of analyte retention in the second dimension from Figure 5.

Many discussions of the analysis of fatty-acid methyl esters (FAMES) using ionic liquid coated GC columns can be found in the literature [3-7]. In addition to the analysis of difficult to separate isomers, the high polarity enables the bulk of the hydrocarbon envelope to be eluted before the methyl esters reducing the amount of sample preparation required to achieve good analysis. A more detailed discussion of this type analysis has been published by Ragonse et al [7]. In the current work the elution order of palmitic (C16:0) methyl ester as first major peak of soya methyl ester and docosane (C22 n-alkane) as the last major peak of diesel respectively, was investigated. The advantages of using a highly polar column in this analysis can be clearly seen from Figure 3. On a non polar HP5 phase, C16:0 elutes after C19, but as polarity is increased C22 elutes more quickly relative to C16:0. So that on a wax phase C16:0 elutes after C22, on IL61 after C23, on IL76 after C24 and after C26 on IL100. Contribution of saturated alkanes after C22 is low and very low after C26, interferences from high boiling mono and poly aromatics are also low at these carbon numbers.

An alternative application utilising the same principles as discussed above is the analysis of methanol extracts of fully formulated lubricating oils. As previously described, lubricants are complex mixtures of hydrocarbons and additional components designed to carry out specific functions. These additives are typically polar in nature finding application as surfactants, anti-oxidants and anti-wear compounds. Base oil and additives co-elute using HP5 columns as shown in Figure 4. The increased polarity of the wax column improves the situation significantly but not fully. Separation is only achieved using the more polar IL76 and IL100 ionic liquid phases. This separation of the analytes of interest allows for a number of improvements: more accurate quantitation - less baseline noise due to low levels of hydrocarbon matrix, greater ease of chromatogram overlaying – for observation of changes between samples, and additional chemical information (well retained components with good peak shape are likely to possess significant polarity).

Highly polar ionic liquid columns therefore present improvements for the analysis of polar components in hydrocarbon matrices. The improved maximum column temperatures when compared to traditional polar phases such as polyethyleneglycol and even 1,2,3-tris(2-cyanoethoxy)propane (TCEP) increase the boiling range of materials amenable to analysis and allow for the study of lubricants and lubricant extracts.

Analysis in two dimensions

One of the major drawbacks of comprehensive GCxGC where both columns are in the same oven is that the maximum possible temperature is limited by the polar

second dimension phase. This limits elution from the first dimension (typically non-polar) to that which is significantly less than the temperature required to elute hydrocarbons in the lubricant boiling range. Current means of addressing this issue involve a reduction in the second dimension polarity so that parity of T_{max} is found between the two phases. DB17 and 35 type high temperature phases have been successfully employed in our labs. However, this change reduces the orthogonality between the first and second dimensions and limits the accessible chromatographic space. Highly polar phases which have an equivalent maximum temperature to 5% phenyl 95% methyl polysiloxane phases would address this issue. Ionic liquids have the potential to achieve this aim and promise to make a significant impact on multi-dimensional GC.

A quick method of comparing column phases in the second dimension was devised. Samples were run on a range of columns and the difference between the test compound and the closest eluting hydrocarbon in the first dimension were compared. This is shown in Figure 5, where the arrow length describes retention time in the second dimension. This was normalised to a ratio of the modulation period and data is shown in Figure 6. The different selectivities of the phases can be observed by the changes in relative peak height across the columns studied. A number of trends can also be observed. Naphthalene appears to be well retained on all columns, IL 61 appears to be effective at retaining aromatic compounds; and retention tends to decrease with column polarity (N.B. Wax and IL61 are similar). It is this final observation which is most interesting and not what might be expected at first glance. The aim of increasing polarity in the second dimension was to improve column orthogonality and therefore improve separation between compounds. In general this is not what is shown in Figure 6, and leads to two observations. Firstly, the retention differences between non-polar and polar materials displayed on polar phases in one dimension is negated in two dimensions. This is because as compound elutes from the first dimension it is already near or above the elution temperature for the second column and is poorly retained. Secondly, increasing the polarity differences between the two dimensions improves the potential chromatographic space but this is only useful if the analytes can access the entire space. If there is not the range of differently retained components in a mixture, increasing the orthogonality between the two dimensions will condense elution in the second dimension to a smaller region. It is better in this case to reduce the differences between columns to maximise the 'useful' chromatographic space.

In addition to these observations it is still the case that whilst significant improvements have been made in the maximum temperature of the polar ionic liquid phases, these commercially available columns are still 30-50 °C away from true parity with non-polar DB1 and 5 phases. Many reviews in the literature describe research phases [8] that can achieve these higher temperatures but these have yet to come to market for general use.

Conclusions and future work

The ability of ionic liquid coated GC columns to separate polar analytes of interest from the bulk hydrocarbon matrix in petroleum products has been investigated in both one and two dimensions. As polarity increases a number of effects were observed:

- A reduction in the loading of larger hydrocarbons.
- A reduction in the overall retention of components.
- An increase in the separation between non-polar and polar compounds.

In particular, fatty acid methyl esters and polar lubricant additives have been shown to elute in areas of the chromatogram less congested with hydrocarbon matrix. The increased temperature stability of the ionic liquid phases allows for lubricant products to be analysed in a single dimension. However, in two dimensions and in a single oven, analysis is still restricted by the maximum operating temperature of the polar phase.

In two dimensions, the use of highly polar columns as the second dimension was found to be unsuitable for the samples chosen. Analytes interacting with the polar phase above their retention temperature were poorly retained. Poorly matched column sets did not make full use of the available modulation time.

Future work will concentrate on two specific areas. The first area of research will be reversing the column order so that the polar column is in the first dimension. This will reduce issues of poor retentivity at higher temperatures. The second area will investigate the effect of placing the columns in separate ovens, such as the Agilent LTM module, which allows for independent control of the two phases. This would overcome issues of maximum temperature and improve retention at high temperatures.

Acknowledgements

The author would like to thank Supelco for provision of the SLB-ionic liquid columns and Tom Lynch and the Investigational Analysis team for support.

[1] L.Vidal, M-L. Riekkola, A. Canals, Anal. Chim. Acta. 715 (2012) 19-41.

[2] D.W. Armstrong, T. Payagala, L.M. Sidisky, LCGC North Am. 27 (2009) 596 598 600.

[3] F. Destaillats, M. Guitard, C. Cruz-Hernandez, J. Chromatogr. A. 1218 (2011) 9384-9389.

[4]J. V. Seeley, C. T. Bates, J. D. McCurry, S. K. Seeley, J. Chromatogr. A, In Press, Corrected Proof, Available online 30 July 2011.

[5] Q.Gu, F. David, F. Lynen, P.Vanormelingen, W. Vyverman, K. Rumpel, G. Xu, P. Sandra, J. Chromatogr. A.1218 (2011), 3056-3063.

[6] P. Delmonte, A-R. Fardin Kia, J. K.G. Kramer, M. M. Mossoba, L. Sidisky, J. I. Rader, J. Chromatogr. A. 1218 (2011) 545-554.

[7] C. Ragonese, P. Quinto Tranchida, D. Sciarrone, L. Mondello, J. Chromatogr. A. 1216 (2009) 8992-8997.

[8] C. F. Poole, S.K. Poole, J. Sep. Sci. 34 (2011) 888–900.