



An Ionic GC Column for 3 Petroleum Related Applications

Sigma - Aldrich • Michael D. Buchanan, Katherine K. Stenerson, and Leonard M. Sidisky
595 North Harrison Road, Bellefonte, PA 16823-0048 USA
Web sigma-aldrich.com • Tel (800) 247-6628 (814) 359-3441

Gas chromatography (GC) is commonly employed for many applications in the petroleum industry. Two specific applications, the determination of benzene and other aromatics in gasoline, and the fatty acid methyl ester (FAME) profile of B20 biodiesel, present special challenges and require the use of a highly polar column. The SLB™-IL111 column utilizes a stationary phase with extreme polarity and has a 270 °C maximum temperature; features which can be leveraged to perform these specific separations in a timely manner.



Ionic Liquids

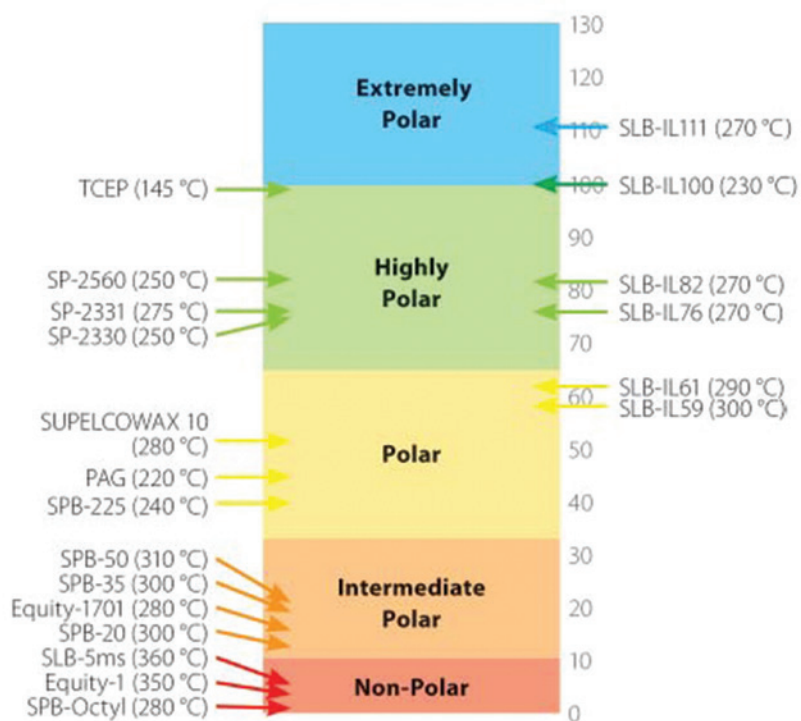
GC Column Polarity Scale

A visual depiction of our GC column polarity scale is shown in Figure 1, showing the relationship of several columns to one another. The positions/maximum temperatures of several non-ionic liquid capillary GC columns are shown to the left of the scale. Listed to the right of the scale are the positions/maximum temperatures of Supelco® ionic liquid capillary GC columns. All polarity number values are relative to both squalane (0 on the scale) and SLB-IL100 (100 on the scale). This simple but useful scale allows multiple columns to be quickly compared. Detailed information concerning the scientific basis used to generate this scale can be found at sigma-aldrich.com/il-gc

Observations are:

- On the non-polar Equity®-1 column, elution was by boiling point; resulting in benzene eluting between C6 and C7. The last analyte to elute was C12, at 56 minutes. C13-C15 did not elute prior to the end of the run, which was terminated after 60 minutes. The long retention of the heavier n-alkanes is due to the very strong dispersive interaction this stationary phase exhibits.
- On the polar SUPELCOWAX™ 10 column, benzene elutes between C9 and C10. Retention of benzene is slightly longer than on the Equity-1 due to induced dipole interaction. However, due to the comparatively weaker dispersive interactions, the n-alkanes are less retained.
- On the highly polar TCEP column, dispersive interaction is not as strong as the Equity-1 or SUPELCOWAX 10. This results in even less retention of the n-alkanes, and as a result, benzene elutes between C11 and C12. The last analyte to elute is C15, at 25 minutes. This would translate to ~12.5 minutes if a 30 m TCEP were used. Peak shapes of the heavier n-alkanes exhibit fronting due to the low solubility of long hydrocarbon chains in this phase.
- On the extremely polar SLB-IL111, the n-alkanes have the shortest retention of the four columns studied. As a result, benzene elutes between C12 and C13, and C15 elutes in <5 minutes, prior to o-xylene. Peak shapes of the heavier n-alkanes exhibit fronting due to the low solubility of long hydrocarbon chains in this phase. Under the conditions used, the TCEP and SLB-IL111 were able to elute benzene after C11, which will allow the analysis of benzene free from aliphatic interference in a gasoline sample. Toluene, which is another analyte of interest in gasoline, also elutes after the C5-C11 hydrocarbon range. The SLB-IL111 resulted in the shortest analysis time, even when extrapolating the TCEP data to a 30 m column length.

Figure 1. GC Column Polarity Scale, Positions/Maximum Temperatures of Columns



Standard: C5-C15 n-Alkanes and BTEX

The C5-C11 n-alkanes represent the prevalent carbon range of the aliphatics found in gasoline. Therefore, to measure benzene and other aromatics free from aliphatic interference, the aromatics should elute after C11. A 17-component neat mixture of C5-C15 n-alkanes, plus the six BTEX compounds (benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene), was prepared. This mix was analyzed on four columns to illustrate the selectivity of each for the separation of BTEX compounds, and their elution in relation to the aliphatics.

Analyses were performed isothermally, to allow comparison to retention index data. With the exception of TCEP, which is only available in a 60 meter length, 30 meter columns were used. Resulting chromatograms are shown in Figure 2 (Page 2). To highlight selectivity, only the time range demonstrating the elution of the BTEX compounds is shown.

Application: Benzene and Other Aromatics in Reformulated Gasoline

The amount of benzene in gasoline is a concern because it is a known human carcinogen, and exposure to it has been linked to leukemia. The challenge with the analysis lies in the complex composition of gasoline, which consists of hundreds of different compounds that include aliphatic, aromatic, and oxygenated constituents. Reformulated gasoline contains additives to produce more complete combustion, and subsequent lower emissions of harmful compounds. These additives are compounds that boost the oxygen content of the gasoline, and are commonly referred to as "oxygenates." Ethanol is a commonly used oxygenate, and its level in reformulated gas varies, but can be as high as 10%. Therefore, to measure benzene in reformulated gasoline, a column must resolve it from the C5-C11 aliphatic portion, other aromatics, and also ethanol. An aliquot of reformulated gasoline was analyzed on each of four columns with oven temperature programming. Resulting chromatograms are shown in Figure 3. To illustrate selectivity, only a time range including the elution of the C5-C11 aliphatics, benzene, and ethanol is shown for each column.

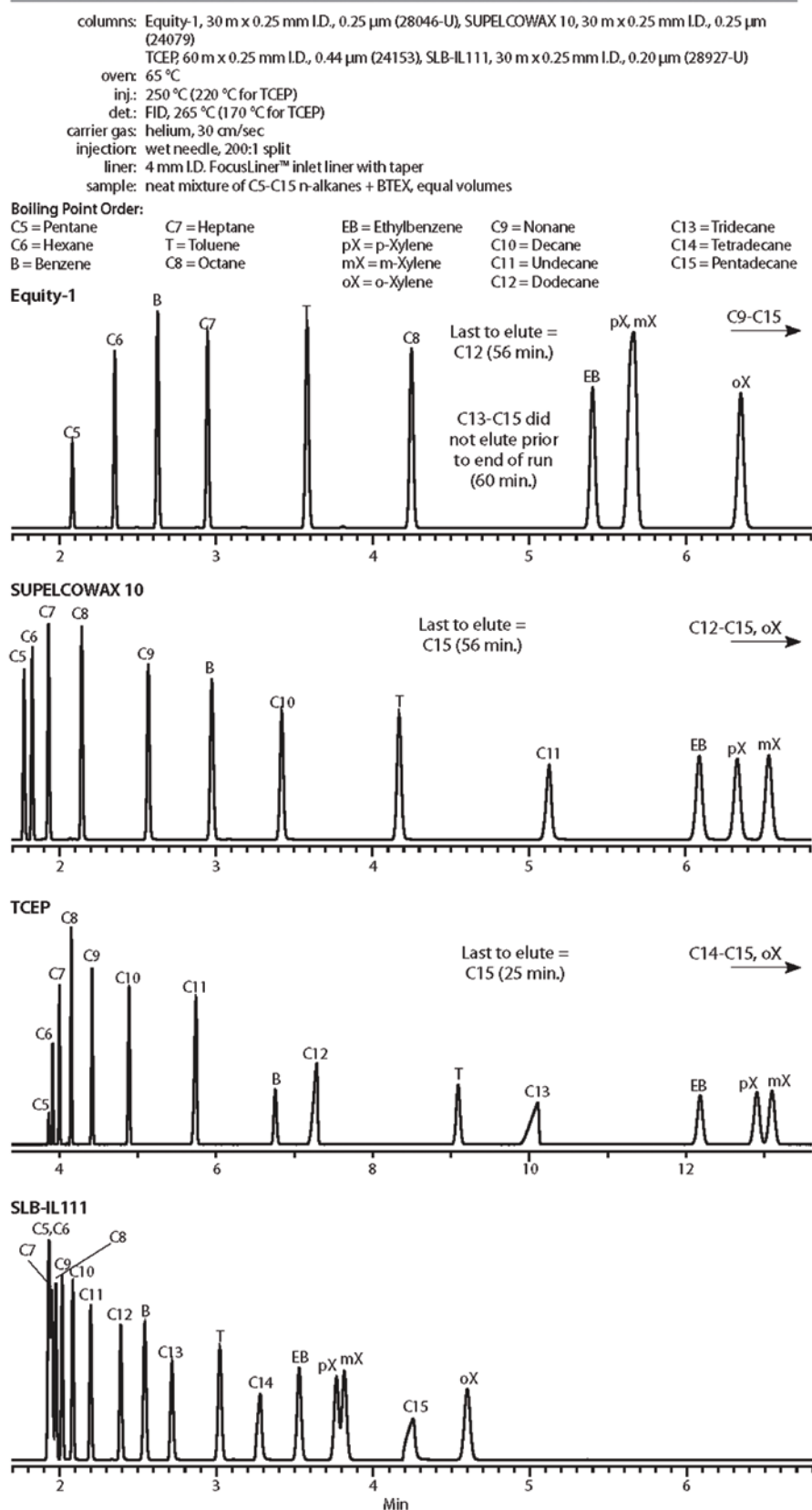
The Equity-1 and SUPELCOWAX 10 both exhibited overlap in the elution range of the aliphatic and aromatic fractions, making these columns unsuitable for this application. The high polarity of the TCEP and SLB-IL111 resulted in elution of benzene and toluene after the aliphatic portion, and resolution of benzene and ethanol. Note the reversal in elution order between the two columns. However, if the TCEP was used for this application, a much longer analysis time would be required.

In addition, the phase stability of the SLB-IL111 gives it a distinct advantage over the TCEP in that it exhibits a stable baseline when subjected to a temperature ramp, and can be used up to 270 °C, allowing the timely elution of the heavy constituents in gasoline. By comparison, the maximum temperature of the TCEP is 145 °C, so it is often used as part of a two-column switching set-up for this analysis.

Application: FAME Profile of B20 Biodiesel

In its undiluted, just-manufactured state, 100% biomass-based diesel is known as B100 biodiesel. It is composed of various fatty acid methyl esters (FAMES). The properties and performance of the B100 biodiesel are affected by the composition of the FAMES it contains. As a result, determining the FAME

Figure 2. C5-C15 n-Alkanes and BTEX



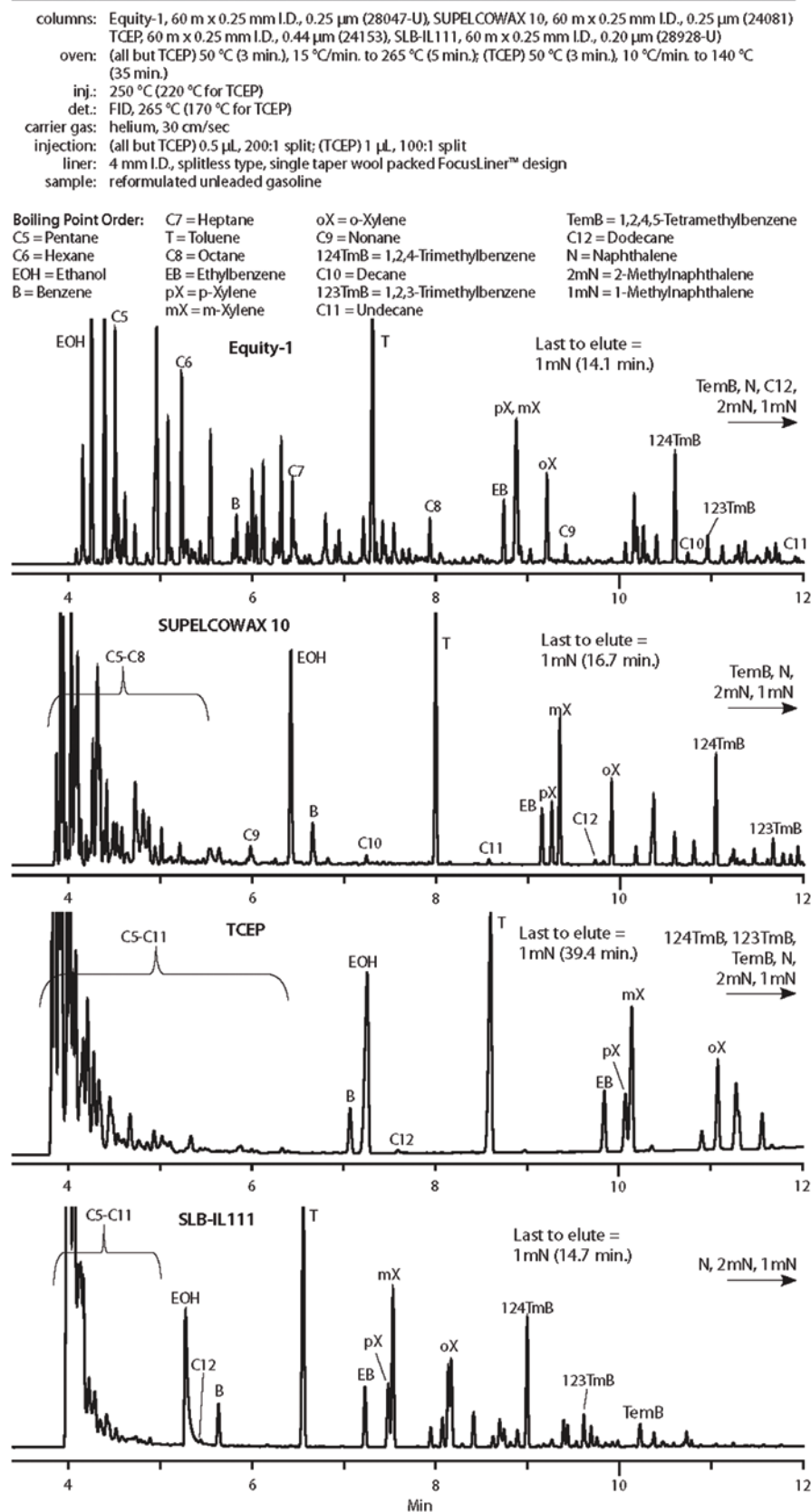
profile of B100 biodiesel is a test that is used in some cases to ensure fuel quality. B100 material is typically blended with petroleum-based diesel prior to consumer use. A common blend is B20 biodiesel, which contains 20% biomass-based diesel and 80% petroleum-based diesel. Once blended, the FAME profile cannot be easily determined, as the petroleum-based diesel compounds interfere with the biomass-based diesel compounds.

To analyze a blended biodiesel sample, a column that can separate the FAMES from the alkanes must be used. In this evaluation, the SLB-IL111 was compared with an Omegawax™ column for the analysis of a blended biodiesel sample. The Omegawax uses a polar phase, poly(ethylene glycol), as the stationary phase. This column was originally designed for, and is specifically tested for, the analysis of omega 3 and omega 6 fatty acids as their methyl esters. A B20 biodiesel sample was made by mixing a soy source biomass-based diesel and a petroleum-based diesel to a 20:80 ratio. This mixture was diluted 1:20 with hexane prior to analyses on Omegawax and SLB-IL111 columns. Resulting chromatograms are shown in Figure 4 (page 4), displayed using the same time scale for ease of comparison. On the Omegawax, there is some overlap of the n-alkane and FAME fractions. Specifically, the C16:0 FAME (the first major FAME in the sample) elutes after the C22 n-alkane. Modifications to these analysis conditions did not result in a decrease in the overlap of the n-alkane and FAME fractions. The SLB-IL111, being more polar than the Omegawax, was expected to exhibit less overlap of these fractions. It was found that the C16:0 FAME elutes after the C25 n-alkane (the last significant n-alkane in the sample). With less overlap between the elution range of the FAMES and n-alkanes on the SLB-IL111, the FAME profile of the B20 biodiesel sample can be more easily determined.

SLB-IL111

• **Application:** This extremely polar ionic liquid column was the world's first commercial column to rate over 100 on our GC column polarity scale. As such, it has the most orthogonal selectivity

Figure 3. Reformulated Gasoline



compared to commonly used nonpolar and intermediate polar columns, providing increased selectivity for polar and polarizable analytes. Its temperature limit of 270 °C is very impressive for such an extremely polar column. The 60 m version is excellent at resolving benzene and other aromatics in gasoline samples. The 100 m version is suitable for detailed cis/trans FAME isomer analysis, and is a great complementary column to the SP-2560. Launched in 2010.

- **USP Code:** None
- **Phase:** Non-bonded; proprietary
- **Temperature Limits:** 50 °C to 270 °C (isothermal or programmed)

Conclusion

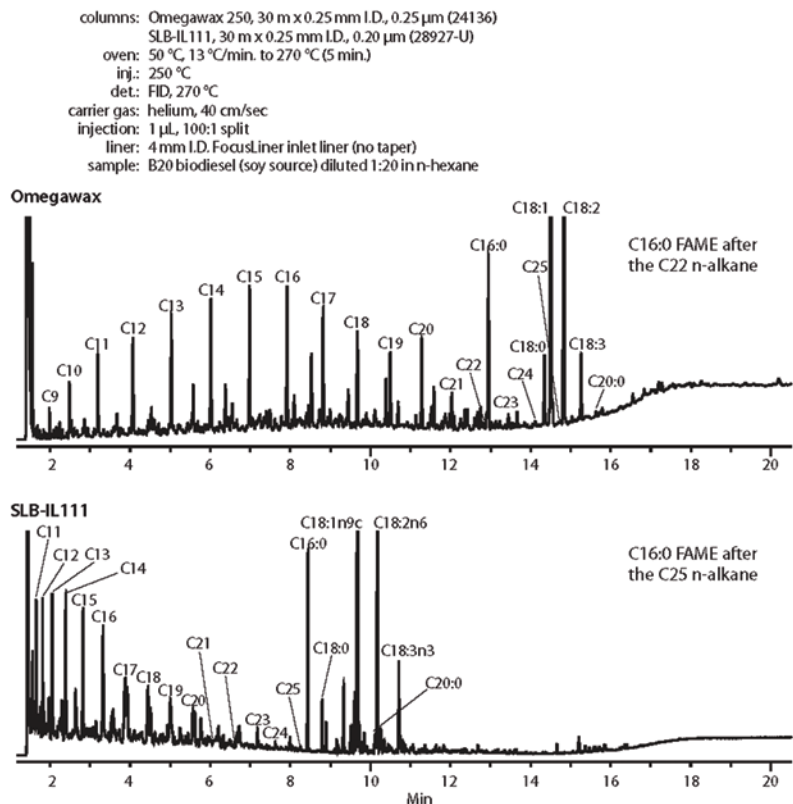
The extreme polarity of the SLB-IL111 phase, in combination with a 270 °C maximum temperature, makes the SLB-IL111 useful for two petroleum applications. Specifically:

- Benzene and other aromatics in gasoline: allows more accurate and reproducible aromatic reporting, plus it may eliminate the need for a two-column switching procedure
- FAME profile of B20 biodiesel: allows the FAME profile (a measure of purity) of blended fuels to be more easily determined

Both applications highlight the suitability of the SLB-IL111 for group separation analyses of aromatics from aliphatics, and FAMES from aliphatics. In addition, it offers high phase stability in conjunction with extremely high polarity. This characteristic can be utilized for both class separations, as shown here, isomeric separations, and for the analysis of samples containing a wide boiling range of components.

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Figure 4. B20 Biodiesel



Ordering Information

Description

SLB-IL111 Column

15 m x 0.10 mm I.D., 0.08 μ m
30 m x 0.25 mm I.D., 0.20 μ m
60 m x 0.25 mm I.D., 0.20 μ m
100 m x 0.25 mm I.D., 0.20 μ m

Cat. No.

28925-U
28927-U
28928-U
29647-U

References

1. ASTM D3606, "Benzene and Toluene in Unleaded Gasoline and Aviation Fuel"
2. DIN EN 14103, "Fat and Oil Derivates - Fatty Acid Methyl esters (FAME) - Determination of Ester and Linolenic Acid Methyl Ester Contents"

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