A Novel Approach to the Analysis of Alcohols in Hydrocarbon Streams by Gas Chromatography

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The analysis and quantification of alcohols in hydrocarbon streams is important for quality control, compliance with product specifications, and ensuring process efficiency. These analyses are traditionally conducted using gas chromatography (GC) with a flame ionisation detector (FID) using polyethylene glycol (PEG) or wax analytical capillary columns. To assess an expanded scope of these analyses, FID, barrier discharge ionisation detector (BID) and mass spectrometry (MS) were compared for quantification of alcohols in hydrocarbons. A novel, highly-polar ionic liquids capillary column facilitated chromatographic separations.

The BID showed the highest sensitivity and raises the possibility of quantification of other non-hydrocarbon analytes. The FID yielded slightly less sensitivity but a larger linear range. The MS provided high selectivity and allowed for definitive analyte identification. The use of novel detectors and column phases may be beneficial in the petrochemicals industry where existing methods are less sensitive, rely on complicated analytical configurations, or are limited by the chemistry of traditional column phases.

The quantification of alcohols and other oxygenates in hydrocarbon streams is important in the petrochemical industry due to the corrosiveness of these compounds and their effects on the combustion characteristics of the final product (e.g., [1, 2]). Alcohols and oxygenates can also deactivate catalysts used in the refining process, reducing their efficiency by occluding active sites through fouling from coke formation (e.g., [3]). Alternatively, alcohols and other oxygenates may intentionally be blended into hydrocarbon-based fuels to improve their performance or reduce reliance on conventional fossil fuels (e.g., [4]).

Standard test methods from Universal Oil Products (UOP) and American Society for Testing and Materials International (ASTM International) are commonly used in the refining and petrochemicals industries for analysis of oxygenates in hydrocarbons. UOP 845, a now retracted method, is used for quantifying trace or residual concentrations of alcohols in liquified petroleum gases (LPG) and other hydrocarbon sample types [5]. Another method, UOP 960 describes the analysis of trace oxygenates up to C6 in LPG, including ethers, ketones, esters, and alcohols [6]. ASTM D7423 specifies methodology for analysis of oxygenates in up to C5 hydrocarbon mixtures [7]. An overview of these methods is provided in *Table 1*.

Traditional analytical methods for alcohols and other polar compounds in LPG and hydrocarbon matrices, such as those outlined above, employ gas chromatography (GC) and may be limited by traditional column phases and/or complex instrument hardware requirements. These methods commonly use column phases with a strong affinity for polar compounds, such as dimethylpolysiloxane or polyethylene glycol (PEG / Wax) phases. However, these column phases have certain limitations, including the inability to be significantly chemically modified and/or temperature limitations [8]. Other methods specify the use of multidimensional analysis and switching using a rotary valve or a fluidic switch, which adds complexity to the instrument itself and adds to its cost and potential challenges associated with operation.

The methods and hardware required for these types of analyses for oxygenates, alcohols, and other polar compounds can be simplified through the use of novel, highly-polar column phases. So-called ionic liquids columns are a relatively novel type of column phase that is comprised of two or more organic cations joined by an organic link and associated with anions. They can be advantageous for analysis as they are much more polar than DMPS and PEG column phases, are less susceptible to damage by oxygen and water, can be easily modified, and are stable at higher temperatures compared to traditional wall-coated open tubular (WCOT) and porous-layer open tubular (PLOT) columns (e.g., [9, 10]). Whereas traditional methods may require multiple valves and columns, these properties of ionic liquids columns allow for a simple 'injector to detector' configuration, simplifying the instrument and the analytical workflow.

These historic methods also specify the use of GC with a flame ionisation detector (FID) due to its high sensitivity for carbon-based compounds. However, other detectors may be applicable for these analyses. The barrier discharge ionisation detector (BID) is a highly-sensitive, universal detector manufactured by Shimadzu that is capable of detecting organic and inorganic compounds, whereas a mass spectrometer (MS) can be used to definitively identify eluting analytes and is highly selective. Antoniadou et al. (2019) go into more detail on the performance and functionality of the BID and comparison to the FID [11].

The purpose of this study is to assess the feasibility and performance of ionic liquids column phases as well as different detection methods (i.e., FID, BID, MS) for the separation and quantification of C1-C4 alcohols in natural gas and LPG.

Table 1. Generalised overview of standard test methods for alcohols and/or oxygenates in hydrocarbon mixtures.

	UOP 845	UOP 960	ASTM D7423
Target Analytes	≤ C4 alcohols	C1-C5 alcohols, C2-C6 carbonyls and ethers, C2-C4 methyl esters, 1,4-dioxane	'Organic oxygenates' e.g., ethers, alcohols, aldehydes, acetone
Sample Matrix	C3 and C4 olefin/paraffin streams	Up to C4 LPG, light isomerate, naphtha	C2, C3, C4, C5 hydrocarbons with final boiling point ≤ 200° C
Instrumentation	GC	GC	Multidimensional GC actuated by rotary valve or Deans' switch
Detection	FID	FID	FID
Column(s)	1) Nukol™ WCOT column (acid-modified polyethylene glycol)	1) CP-SimDist Ultimetal (5% diphenyl, 95% 2) CP-Lowox (proprietary polar PLOT phase) dimethylpolysiloxane)	1) Nonpolar pre-column (e.g., methyl siloxane WCOT) 2) Polar analytical column (e.g., barium sulfate PLOT)

Experimental

Instrument Configuration and Method Parameters

A Shimadzu GC-2030 gas chromatograph equipped with an FID and a BID was used for these analyses. In addition to the GC-2030, a Shimadzu GCMS-QP2020 NX was used for identification and confirmation of analytes. A Supelco® SLB®-IL111i ionic liquids column was used to facilitate chromatographic separations. The method conditions used for analysis were optimised by maximising the resolution between methanol and ethanol while also minimising peak tailing of nonpolar compounds. The GC-2030 oven was programmed to run isothermally at 55°C and helium carrier gas was set to 19.2 cm/sec at a constant linear velocity. A schematic of the instrument configuration is provided in *Figure 1* and the method parameters are provided in *Table 2*.
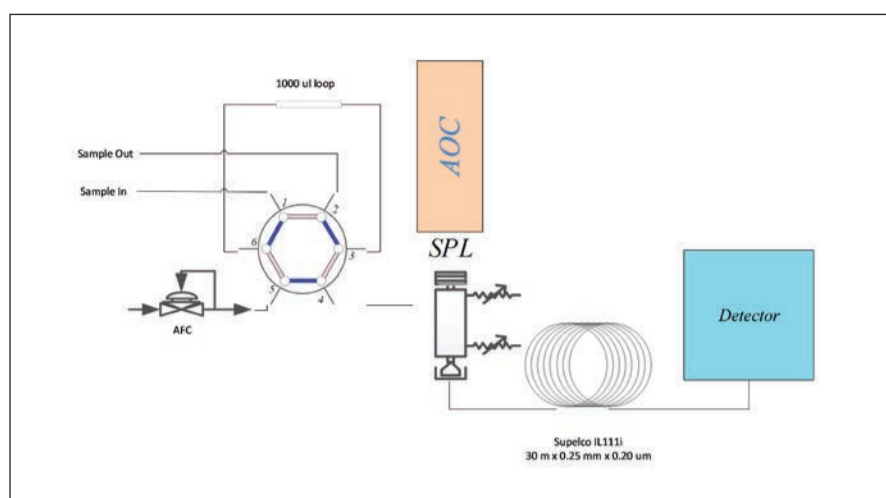
Figure 1. Diagram of GC-2030 configuration used for this study. The detector is either FID, BID, or MS.

Table 2. Instrument and detector parameters and method conditions.

General	
GC	Shimadzu GC-2030
GC-MS	Shimadzu GCMS-QP2020 NX
Column	Supelco® SLB®-IL111i, 30 m, 0.25 mm, 0.2 µm DF
Valve Box Temp.	80°C
Injection Vol.	Gas injection - 1 mL; Liquid injection - 1 µL
Injector Temp.	200°C
Carrier Gas	He
Linear Velocity	19.2 cm/sec
Split Ratio	20:1
Oven Temp.	Isothermal 55°C
FID	
FID Temp.	200°C
FID Gas Flows	Makeup (He) - 24 mL/min; H2 - 32 mL/min; Air - 200 mL/min
BID	
BID Temp.	200°C
BID DCG Flow	50 mL/min (He)
MS	
MS Interface Temp.	150°C
MS Source Temp.	230°C
MS Scan Range	28-500 m/z
Acquisition Time	2.2 to 5.5 min

Standards and Samples

Liquid standards were made by the dilution of equal parts methanol, ethanol, propanol, and butanol into a 1:1 solution of hexane and isooctane, which was used to simulate heavier hydrocarbons found within typical hydrocarbon gas streams. Concentrations for each analyte were 2.5, 5, 25, 50, 100, 500, and 2500 ppm. In addition to the liquid standards, a premade natural gas standard containing hexane was used to analyse hydrocarbon via gas phase. It also served as a proxy for a 'wet gas' sample, with compositional and physical properties intermediate between gas and liquid injections. Finally, two gas samples prepared using 500 µL of the 2500 ppm alcohol mixture injected into a 300 mL sample cylinder, pressurised to approximately 650 kPa with nitrogen gas and heated to 150°C was also used for analysis. Each standard was injected three times and used to generate calibration curves for each component. Details of the standards are outlined in *Table 3*.

Table 3. Calibration levels and concentrations.

Level	Conc. of each alcohol (ppm)
1	2.5
2	5
3	25
4	50
5	100
6	500
7	2500

Results and Discussion

Separation

Baseline separation was established between the four alcohols of interest and the hydrocarbon matrix of isooctane and hexane (Figure 2). Spiking experiments confirmed the elution order is methanol (1, RT:4.084 min), ethanol (2, RT: 4.350 min), propanol (3, RT: 5.205 min) and butanol (4, RT: 6.923 min). Definitive confirmation of compound identity was performed using MS.

The LabSolutions data acquisition and analysis software can calculate a variety of valuable statistics based on the data set, which are useful in assessing data quality and are presented in *Table 4*. The peak symmetry, or tailing factor, indicates the degree of Gaussian distribution of each peak where a number less than one indicates peak fronting and a number greater than one indicates peak tailing. Methanol and ethanol demonstrate slight peak tailing whereas butanol displays slight peak fronting. All peaks are resolved from one another with a calculated peak resolution of greater than 3 for each analyte with a high number of theoretical plates (NTP) indicating the column is effective for separating the alcohols both from the hydrocarbon matrix and from each other even at higher concentrations.
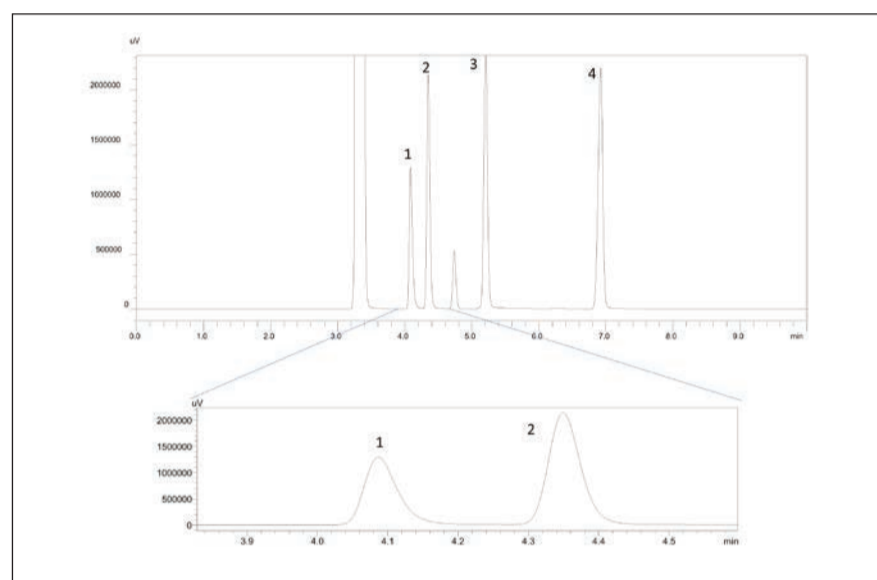

Figure 2. Chromatogram of 2500 ppm alcohol standard generated using the BID and zoomed in chromatogram to show baseline resolution between methanol and ethanol.

Table 4. Analytical statistics for IL111i separation and analytical characteristics.

Peak	Analyte	RT (min)*	NTP (USP)*	Resolution (USP)	Tailing Factor
1	Methanol	4.087	36385	11.117	1.371
2	Ethanol	4.350	43072	3.101	1.190
3	Propanol	5.205	45585	9.434	1.045
4	Butanol	6.923	45898	15.148	0.886

*RT - Retention Time; NTP - Number of Theoretical Plates

Mass Spectrometry Confirmation

Analysis by GC-MS was performed to confirm elution order of the analytes by using a NIST library search. Although the elution order was maintained between BID and MS analyses, the elution time shifted ~1.5 minutes earlier due to the vacuum applied by the mass spectrometer (Figure 3). The fragment ions chosen for methanol, ethanol, propanol, and butanol were m/z = 31, 45, 59, and 56, respectively *(Figure 3)*.
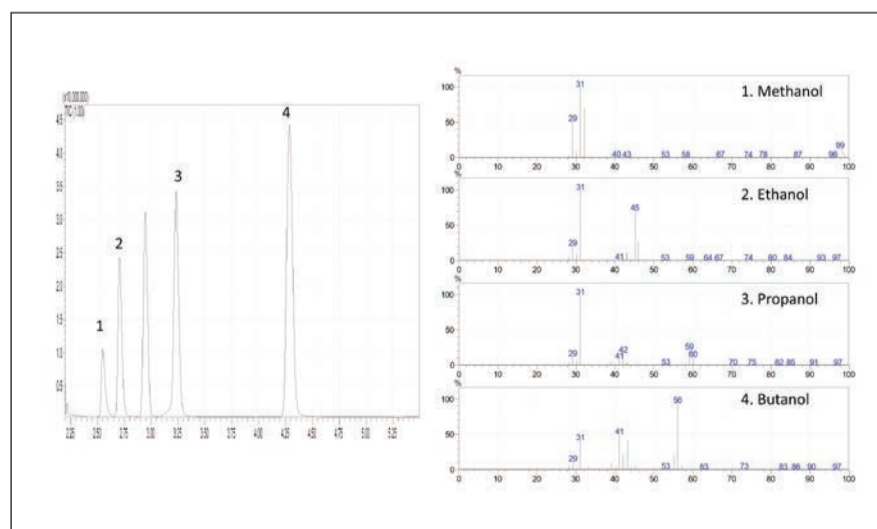

Figure 3. Chromatogram and resulting mass spectrum for 500 ppm alcohol standard on GC-MS.

Barrier-discharge Ionisation Detector (BID) Analysis

The BID was able to detect the lower concentration standards with a high degree of sensitivity while maintaining separation for all analytes. The calibration curves for methanol and ethanol show some non-linearity above 500 ppm which was not observed in propanol or butanol.
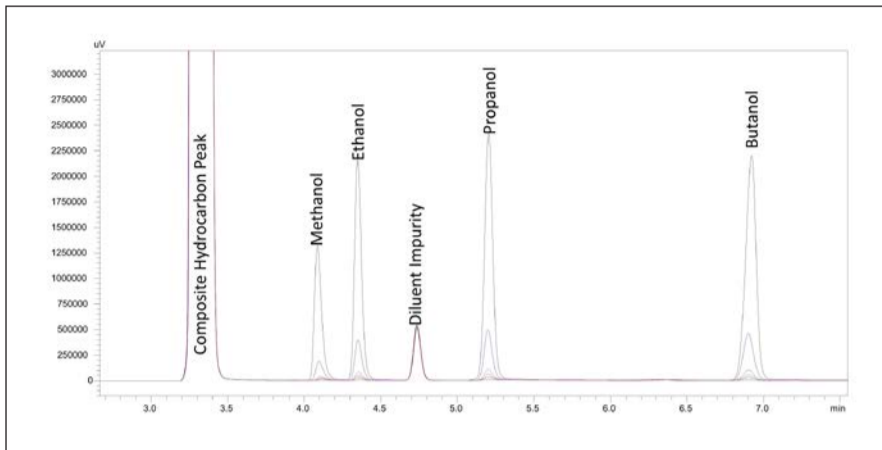

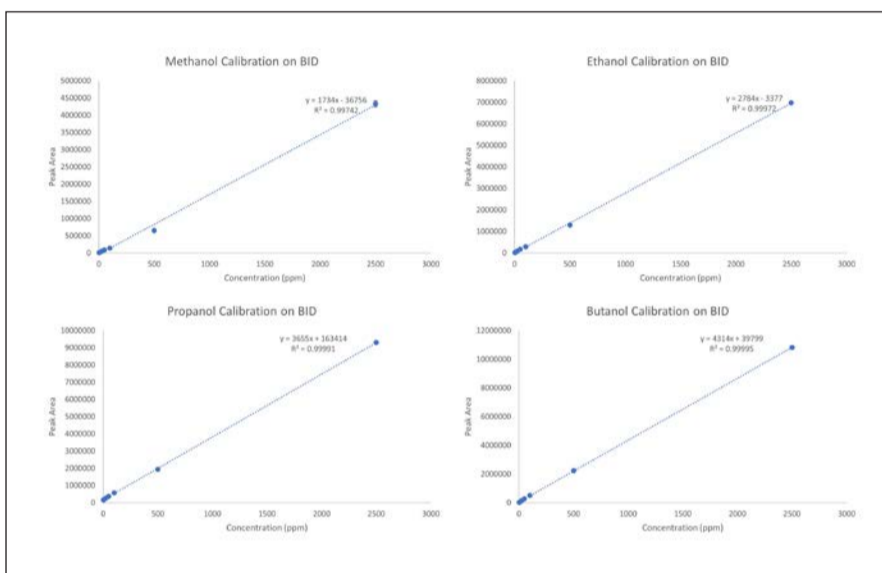Figure 4. Stacked chromatogram of the calibration curve on BID.

Figure 5. Calibration curves for methanol, ethanol, propanol, and butanol on BID.

Flame Ionisation Detector Analysis

The FID displayed a high degree of linearity across the full calibration range and was able to detect the lowest concentration of 2.5 ppm. Separation was maintained for all analytes with the FID.
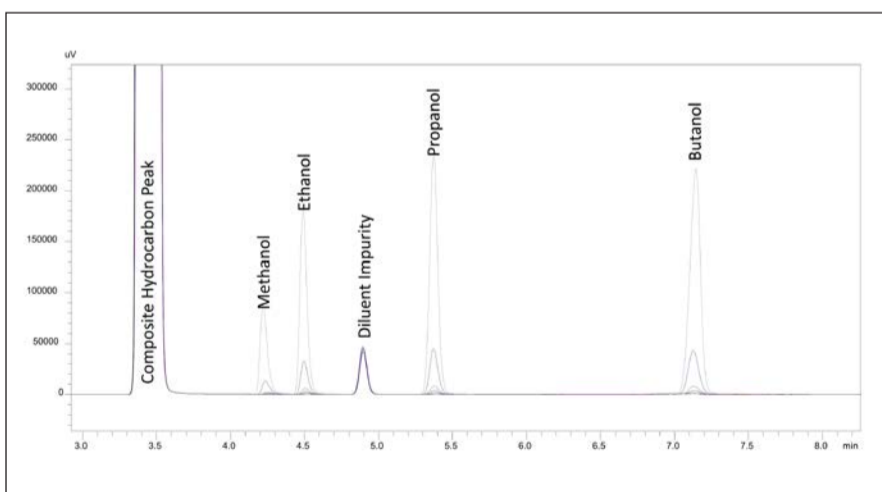

Figure 6. Stacked chromatogram of the calibration curve on FID.

Limits of Detection and Quantification

Limits of quantification and detection for the BID and FID were calculated using a mid-point on the calibration curve, the 50 ppm standard. Both detectors displayed a high degree of sensitivity for each alcohol. Methanol displayed the highest limits of detection and quantification for each detector. The BID results showed the highest sensitivity with calculated LOD at sub ppm levels, whereas the FID yielded calculated LOD of low ppm and sub ppm levels.
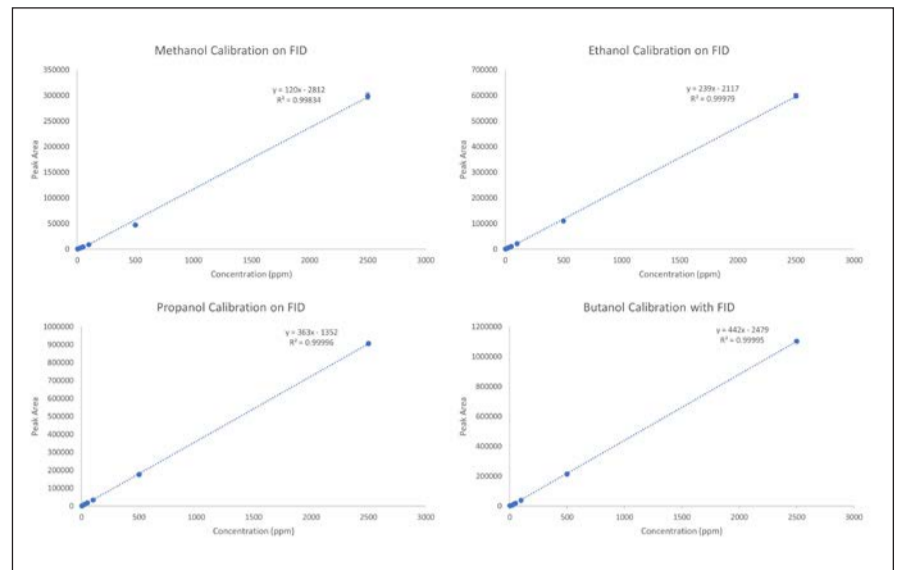

Figure 7: Calibration curves for methanol, ethanol, propanol and butanol on FID.

Table 5. Calculated LOD and LOQ for BID and FID detectors*.

	BID		FID	
	LOQ (ppm)	LOD (ppm)	LOQ (ppm)	LOD (ppm)
Methanol	0.75 (± 0.03)	0.17 (± 0.01)	12.56 (± 1.11)	2.76 (± 0.24)
Ethanol	0.31 (± 0.02)	0.07 (± 0.01)	4.09 (± 0.34)	090 (± 0.07)
Propanol	0.23 (± 0.01)	0.05 (± 0.01)	2.74 (± 0.17)	0.60 (± 0.05)
Butanol	0.24 (± 0.01)	0.05 (± 0.01)	2.85 (± 0.28)	0.63 (± 0.06)

*LOQ - Limit of quantification; LOD - Limit of detection; Generated using 50 ppm standard

Spiked Natural Gas Analysis

A premade natural gas standard was injected to assess any coelutions that may occur in a C1 through C6 matrix on the BID and FID instrument configurations. On both detectors the hydrocarbon peak eluted around the same time as the isooctane/hexane matrix peak from liquid injections. Given the nearly universal nature of the BID, peaks such as water were visible that would not be observed on the FID. A small peak was observed around 5.2 minutes which is suspected to be water on the BID chromatogram.

To simulate a vapourised LPG sample, two qualitative alcohol-spiked gas samples were created, one for analysis using FID and one using BID. Although the two spiked samples were prepared similarly, the differences in calculated concentration are likely related to imprecision when creating the two different samples, resulting in different calculated concentrations.

For both detectors, the alcohol peaks and the isooctane/hexane matrix were observed. Repeatability was determined for each detector. Results are presented in Table 6. On both detectors, repeatability was excellent with % RSD ≤ 2.22% for all analytes. Methanol, which had the lowest sensitivity on FID displayed the most variability at 2.22% RSD. The higher RSD for methanol on the FID is suspected to be a result of the lower signal intensity or stratification of the sample during the sampling process. On the BID, propanol displayed the highest variability of 1.88% RSD, which is suspected to be related to the observed water peak.
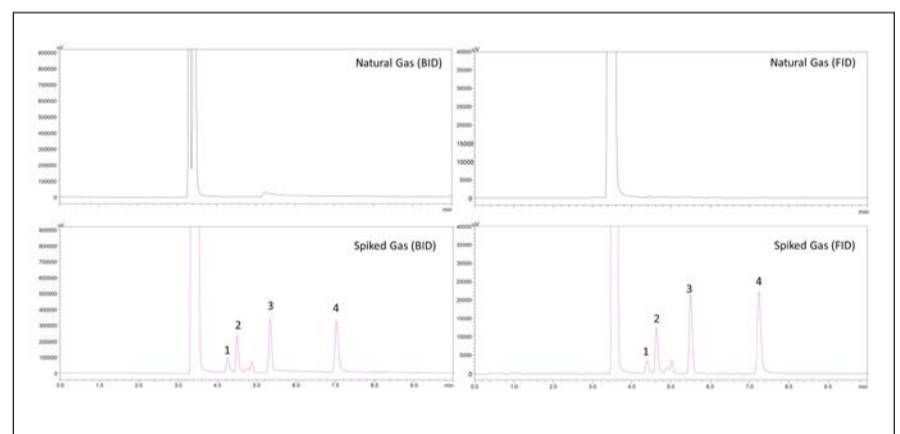

Figure 8. Representative chromatograms for premade natural gas standard and generated alcohols gas standard on BID and FID.

Table 6. Quantification and repeatability results from spiked natural gas samples.

		BID		FID	
Peak	Compound	Conc. (ppm)	%RSD	Conc. (ppm)	%RSD
1	Methanol	305.89	0.10%	170.52	2.22%
2	Ethanol	410.10	0.17%	263.15	0.37%
3	Propanol	583.21	1.90%	319.78	0.23%
4	Butanol	477.69	0.34%	333.13	1.01%

Conclusions and Future Directions

The Shimadzu GC-2030 with the Supelco® SLB®-IL111i column equipped with various detectors is an effective means to separate, speciate, quantify, and detect common alcohols in hydrocarbon matrices. With a high degree of linearity and low limits of detection established, the GC-2030 is a suitable system for this analysis. Given the flexibility of the GC-2030 platform, the analysis can be expanded to additional liquid, gaseous, and pressurised liquid streams.

All three detectors demonstrated viability for this style of analysis and each have individual benefits and drawbacks. The BID demonstrated the highest sensitivity but may suffer from detection of coeluting peaks (e.g., water) that are not detected on the FID. Using FID provided increased linearity, no interference from coeluting non-hydrocarbon peaks, and a wide linear range but slightly less sensitivity. The MS is critical when selectivity and positive identification is required and can be further explored with fine-tuning method parameters.

It is likely that ionic liquids columns can be used for separation and speciation of other polar compounds within hydrocarbon matrices that are challenging to separate with conventional column phases. It is worth considering these applications and adoption of evolving column and detection technologies into industry standard test methods for simplified analyses of alcohols, oxygenates, and other polar compounds in hydrocarbon streams. For example, analysis of methanol and ethanol content in gasoline can be facilitated by ionic liquids columns and GC-BID, effectively separating and detecting the alcohols independent of other hydrocarbon constituents *(Figure 9)*. These types of analyses are of interest given the nearly universal availability of E10 gasoline (i.e., 10% ethanol-gasoline mixture) and growing adoption of E15 gasoline, particularly in the US market.
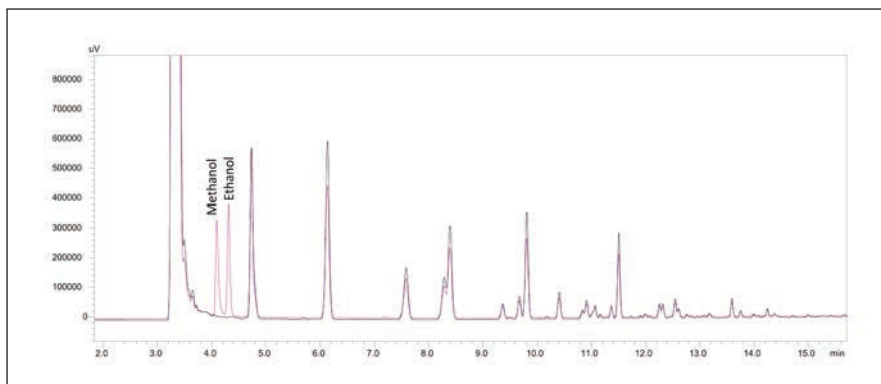

Figure 9. Stacked chromatogram of a gasoline standard (black) and a gasoline standard spiked with methanol and ethanol (pink) generated using BID.

The analysis of fuels, their constituent hydrocarbons, as well as non-hydrocarbon components by gas chromatography are long-standing and mature techniques. However, the evolution and improvement in common analytical technologies, separations chemistry, and detection methods warrant further study for these applications. These technological improvements can yield better separation, higher sensitivity, faster analytical times, less complex instrumentation, and other advantages that can be beneficial compared to traditional workflows.

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