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The Trace Level Alcohols in Hydrocarbon Streams via GC-FID

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Introduction

Determining concentrations of alcohols and other oxygenates in hydrocarbon streams is important in the petrochemical industry due to their corrosiveness and their effects on the physical and chemical characteristics of the product. Methods such UOP845, a retracted method for quantifying residual alcohols in liquified petroleum gases (LPG), are still commonly used to monitor and report alcohol concentrations within hydrocarbon gas streams. With current improvements in column technology, new column phases can be utilized for applications such as these while simplifying the hardware required for analysis. The Supelco SBL-IL111i columns utilize ionic liquids to create a highly polar column that is more rugged than traditional polar phases. This application aims to utilize these properties for the separation of alcohols and nonpolar analytes of natural gas and LPG.

Alcohols in Hydrocarbon Streams

- Commonly produced by processing of natural gas
- Can help reduce greenhouse gas emissions, increase octane rating
- Can cause increased corrosion
- Various methods used for alcohol analysis often require multiple columns, valves, detectors, or specialized equipment.

Ionic Liquid GC Columns

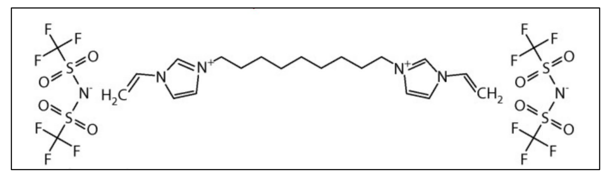


Figure 1: Structure of IL-111i column phase

- Uses cation/anion linkages in place of silica backbone
- Highly polar phase
- More stability/less column bleed
- Can be tailored for custom selectivity

Instrument Parameters

Figure 2: Image of the GC-2030

Table 1: Instrument parameters used for this analysis

Parameter	Value
Column	Supelco SBL-IL111i, 30 m, 0.25 mm, 0.2 µm DF (29883-U)
Valve Box Temperature	80° C
Injection Volume	1 mL gas sampling loop, 1 µL liquid injection
Injector Temperature	180° C
Linear Velocity	31.6 cm/sec He
Split Ratio	20:1
Oven Temperature	Isothermal 55° C
FID Temperature	180° C
FID Gas Flows	Makeup (He): 24 mL/min, H_2: 32 mL/min, Air: 200 mL/min

Separation and Calibration

Liquid standards were made by the dilution of equal parts methanol, ethanol, and butanol standard into a 1:1 solution of Hexane and Iso-octane that was used to simulate heavier hydrocarbons found within hydrocarbon gas streams.

Table 2: Calibration curve dilution scheme for alcohol standards used.

Component	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Methanol, Ethanol, Butanol	3.3 ppm	33.3 ppm	66.7 ppm	166.7 ppm	333.3 ppm

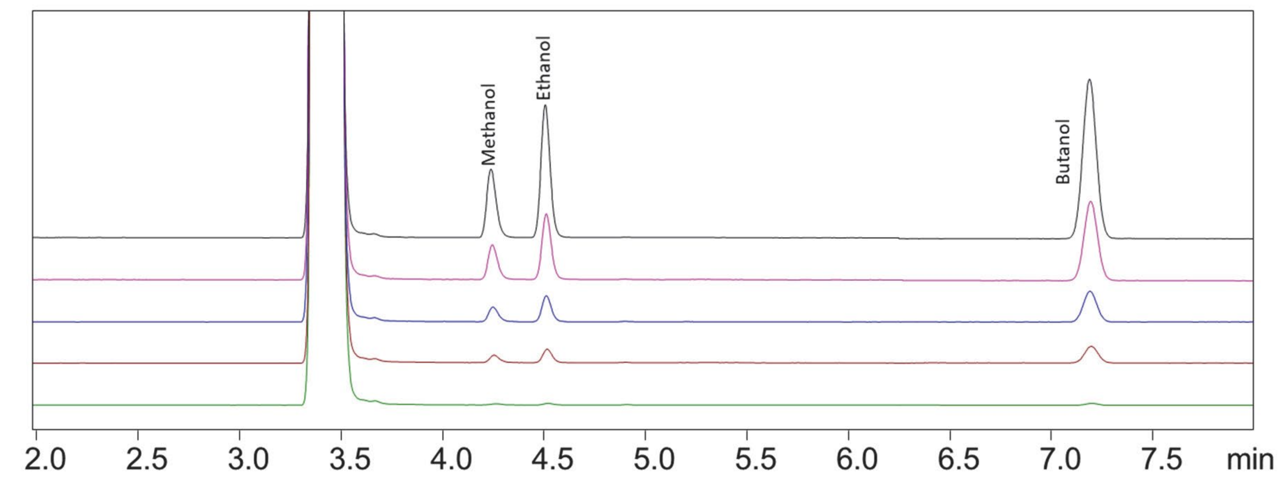
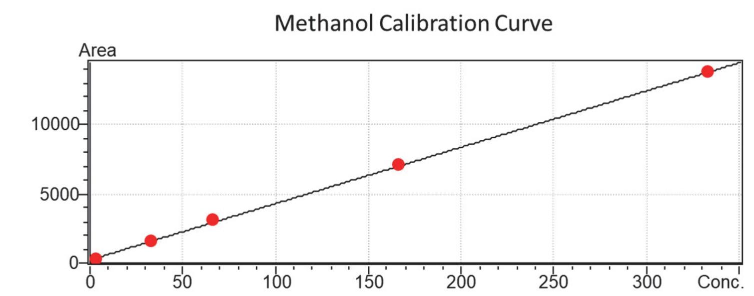
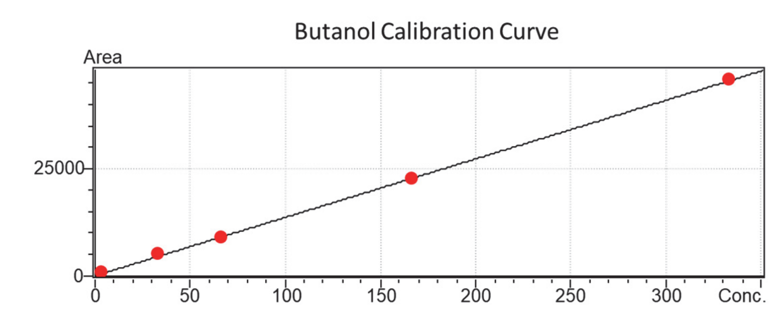
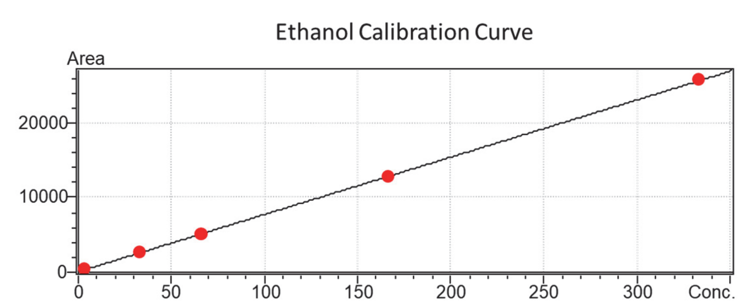


Figure 3: Overlay of 3.3, 33.3, 66.7, 166.7 and 333 ppm alcohol standard chromatograms

- Baseline resolution for methanol, ethanol and butanol was achieved
- No interferences from nonpolar hydrocarbon matrix







Analyte	R^2 value	LOD (ppm)	LOQ (ppm)
Methanol	0.99970	2.7 (± 0.3)	8.3 (± 0.8)
Ethanol	0.99997	1.8 (± 0.2)	5.6 (± 0.6)
Butanol	0.99980	1.4 (± 0.1)	4.3 (± 0.3)

Figure 4: Calibration curves for methanol, ethanol and butanol and calculated LOD/LOQ values for each.

- A high degree of linearity for methanol, ethanol and butanol between 3.3 ppm and 333.3 ppm
- Limits of detection were calculated below 3 ppm for each analyte

Natural Gas Bridging

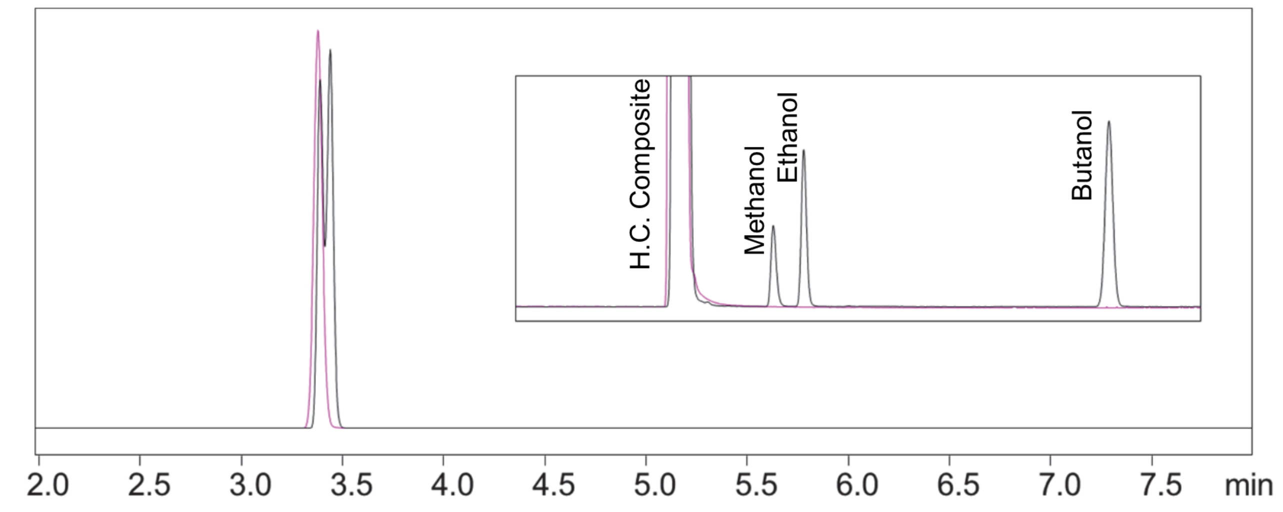


Figure 5: Natural Gas (pink trace) overlaid with 333 ppm standard (black trace)

- A natural gas standard containing n-Hexane was analyzed to bridge between the characteristics of gas and liquid standard injections
- The composite hydrocarbon peak between the liquid injection and gas injection is superimposable.
- The natural gas trace fully elutes prior to methanol elution

Conclusion

The GC-2030 with the Supelco SBL-IL111i column is an effective means to separate, speciate, and detect 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. Bridging experiments have shown full separation between the natural gas analytes and light alcohols which shows viability for direct detection of light alcohols in a gaseous hydrocarbon matrix.

Future Directions

Future directions will include expanding to additional analytes including additional alcohols and oxygenates, heavier hydrocarbon matrices, and different samples including pressurized liquids and gas samples. To allow the ambient liquids, gases and pressurized liquids to be analyzed, the system will be reconfigured with an internal loop valve, and gas sample valve in the following configuration:

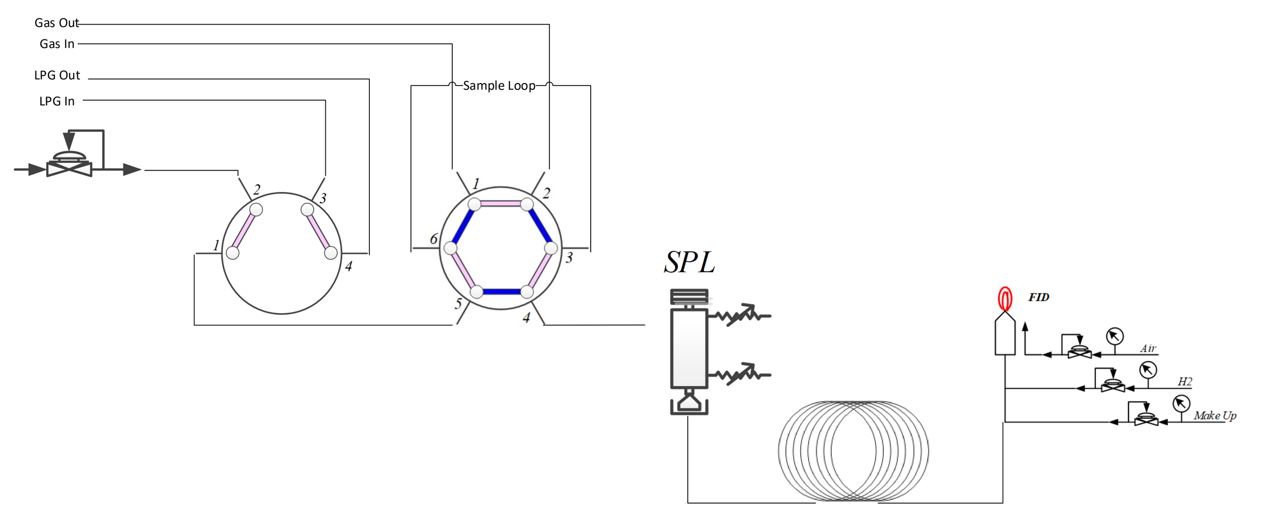


Figure 6: Diagram of proposed analyzer for LPG, natural gas and ambient liquids

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