SHIMADZU
Excellence in Science

Application News

No. GC-2102

System GC

Trace Level Alcohols in Hydrocarbon Streams via GC-FID

■ Background

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 as 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.

■ Instrumentation

The GC-2030 gas chromatograph equipped with an LVO-2030, AOC20i, FID-2030, and 6-port gas loop sampling valve was used for this analysis. No specialized detectors or injectors were required for this analysis.

■ Experimentation and Observation

Liquid standards were made by the dilution of equal parts methanol, ethanol, and butanol standard into a 1 to 1 solution of Hexane and Iso-octane that was used to simulate heavier hydrocarbons found within hydrocarbon gas streams. Standards contained each analyte at concentrations of 3.3,33.3, 66.7, 166.7 and 333.3 ppm. In addition to the liquid standards, a premade natural gas standard containing hexane was used to test the hydrocarbon only via gas phase while bridging between the gas and liquid injections. Each standard was injected three times and used to generate calibration curves for each component.

Method conditions

Optimal method conditions were selected based on the highest resolution between methanol and ethanol while avoiding tailing for the nonpolar peaks. The optimal isothermal conditions were found to be at 55 C.

Table 1: Method Parameters

Parameter	Value
Column	Supelco SBL-IL111i, 30 m, 0.25 mm, 0.2 um 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 Ramp	Isothermal 55° C
FID Temperature	180° C
FID Gas Flows	Makeup (He): 24 mL/min, H_2: 32 mL/min, Air: 200 mL/min

Calibration Curve

The standards were injected and applied to the calibration processing within LabSolutions. Baseline resolution was achieved between methanol, ethanol and butanol from the iso-octane and hexane matrix.

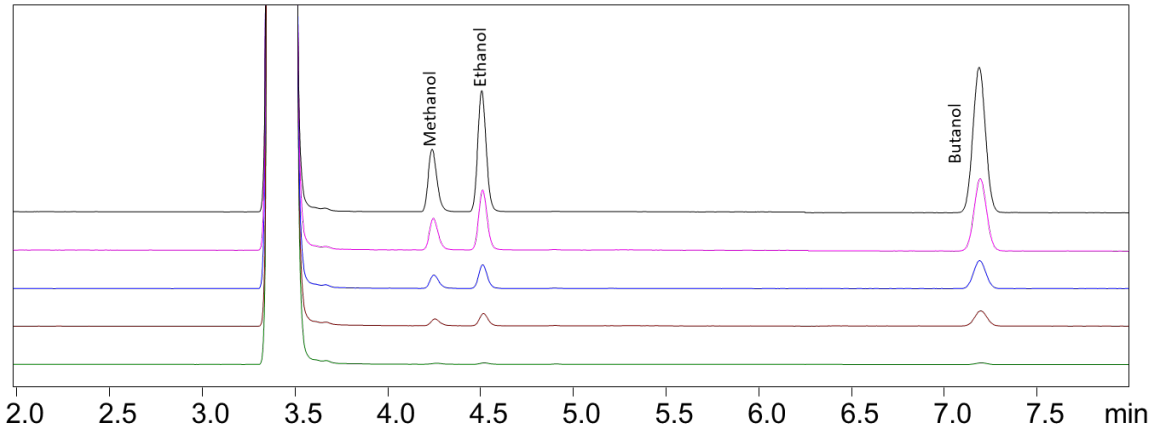

Figure 1: Stacked chromatograms of calibration curve points

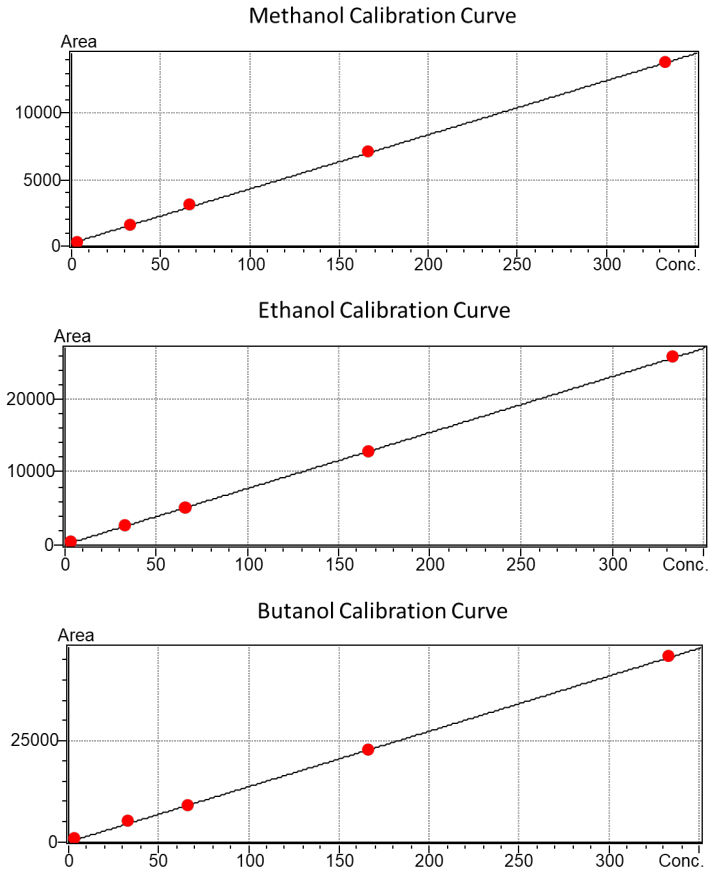

Figure 2: Calibration curves for Methanol, Ethanol and Butanol

Table 2 shows the calculated limits of detection and quantitation and r^2 assessment of linearity of the calibration curve. A high degree of linearity was observed within the calibration curve range with calculated limits of detection below 3 ppm for each analyte.

Table 2: Calibration Curve Analysis

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)

To assess the viability of analyses of samples that are either gaseous or liquid phase, a natural gas standard containing hexane was injected. The resulting chromatogram in Figure 3 shows the natural gas peak matching the retention time of the hexane peak of the liquid standards and no interference from alcohol peaks. With the high degree of flexibility of the GC-2030 platform, the system can be reconfigured with appropriate sample introduction components and further optimized for other liquid samples, gaseous samples, and LPG samples containing alcohols.

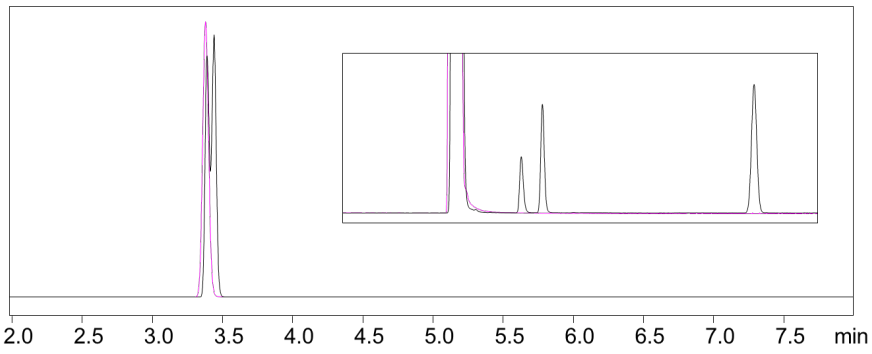

Figure 3: Overlay of Natural Gas Chromatogram and 333 ppm liquid standard.

■ 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.

Given the flexibility of the GC-2030 platform and capabilities of Shimadzu, the analysis can be expanded to additional liquid, gaseous, and pressurized liquid streams.

First Edition: January 2021

SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com