Proof of Concept (POC) Case Study

Using Raman Spectroscopy to Measure Low Levels of Methane in Y-Grade

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Introduction

A 2019 report by the U.S. Energy Information Administration (EIA) estimated that there are 510 active natural gas processing plants in the United States. That is around 80.8 billion cubic feet of processing power just in the lower 48 states.

A modern processing plant has two primary production commodities: natural gas liquids, also known as Y-grade, and residue gas. Raw gas from a gathering network is processed through a cryogenic cooling tower, which cools the raw gas to extremely low temperatures. That process condenses most gaseous hydrocarbon components, such as C2-C6+ (ethane, propane, butane, etc.), into the liquid Y-grade product. Methane, the remaining hydrocarbon component, has a boiling point above the cooling tower's working temperature and primarily remains in the gas phase. This methane, now designated as residue gas, fuels power plants and residential and commercial buildings. However, a small amount of methane remains in the liquid Y-grade product, and the effective measurement and control of that quantity has significant implications for the process owner.

The methane found in Y-grade is considered a contaminant that impacts product quality and can result in process efficiency issues, custody transfer issues, and safety concerns. Some common methane specifications are that concentrations must be no greater than 0.5% (5000 ppm) or 1.5 x Ethane conc (ppm). NGL Fractionators (i.e., Y-grade customers) typically do not employ a methane scrubber (a demethanizer column) as an initial unit operation. Therefore, when the methane spec is exceeded, it can impact the fractionator columns' processing speed rate, efficiency, and quality. High methane Y-grade can be accommodated via blending, but this affects process efficiency and profitability. Excess methane also poses potential outgassing issues during the subsequent pipeline transfer of the NGLs to customers. Beyond the practical implications, off-spec Y-grade can incur financial penalties and jeopardize contracts.

Monitoring the methane concentration is critical to ensuring the Y-grade producer's cryogenic tower is operating properly and on target. Traditional online analysis methods, such as gas chromatography (GC), report cooling tower operating status as a C1/C2% ratio value, which is a common metric used to tune tower performance. Individual measurement cycles for online GC instruments can take 5 to 20 minutes to report.

Raman spectroscopy has recently demonstrated its utility and value in the online measurement of hydrocarbon products in the midstream and refinery spaces. Due to its selectivity, speed, stability, and sensitivity, it has proven itself to be the premier optical approach for composition and physical property measurement in NGL, natural gas, and purity products.

Many industrial processes, including cryogenic cooling towers, can change more quickly than a typical GC measurement cycle can be completed. A slow cycle time when attempting to measure a rapidly changing process provides operators with effectively no useful information during the GC cycle times, and means key events and transitions may be missed or detected late. In comparison, a Raman measurement can be completed in 3 to 5 seconds, which is significantly faster than the comparable GC measurement and can be used to ensure continuous monitoring and timely detection of process changes. This speed allows operators greater insight into processes as they occur, and it provides the ability to optimize process outcomes relative to specifications—for example, to ensure ethane concentrations in the cryogenic cooling towers are at acceptable levels. An argument against using Raman spectroscopy is its perceived low sensitivity compared to other techniques like gas chromatography. However, this study demonstrates that Raman can detect low concentrations (down to 130ppm) of methane in NGLs with good precision in real time.

Experimental

All spectra were collected on a Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer. The acquisition parameters were set such that a new dark-subtracted spectrum was collected for each sample analyzed, optimizing acquisition times and averages for the collected samples (Figure 1). Spectra were collected using a Thermo Scientific™ MarqMetrix™ FlowCell Sampling Optic (Figure 2). After collection, the data were processed and modeled using Solo 9.2.1 (Eigenvector Research, Inc., Manson, WA). Extended multiplicative signal correction (EMSC) was performed to mitigate minor, non-chemical variations among the spectra.

Figure 2. Integrated high-pressure low-temperature FlowCell, rated to 2,500 psi and a temperature range from cryogenic temperatures to 350 K.

This study introduced liquid samples to the FlowCell in a stopped-flow manner from pressured piston cylinders with backpressure maintained at >1000psi. Back pressure was provided on the exit leg of the FlowCell to facilitate stop-flow manipulation and enable measurement under pressure to maintain volatile compounds in solution. Laboratory reference values were obtained by GPA 2177 analysis of the same samples. Nine samples were analyzed in this experiment for the Proof-of-Concept (POC) study.

Results/Discussion

This study demonstrates the potential for measuring low-level methane in a Y-grade product down to a level comparable to the typical GC measurement. The methane model suggests a RMSEC of 100ppm is achievable based on this POC model, which contains only nine samples (Figure 3).

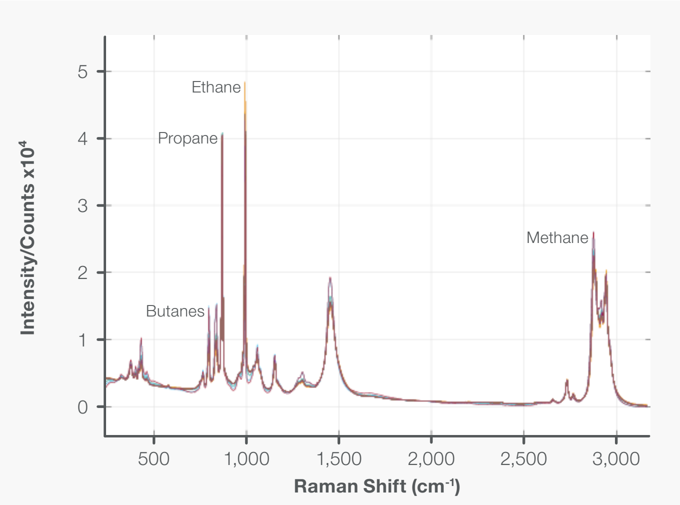

Figure 1. Y-grade spectra collected on a MarqMetrix All-In-One Process Raman Analyzer and FlowCell Sampling Optic. The acquisition parameters were set to collect a new dark-subtracted spectrum for each sample analyzed.

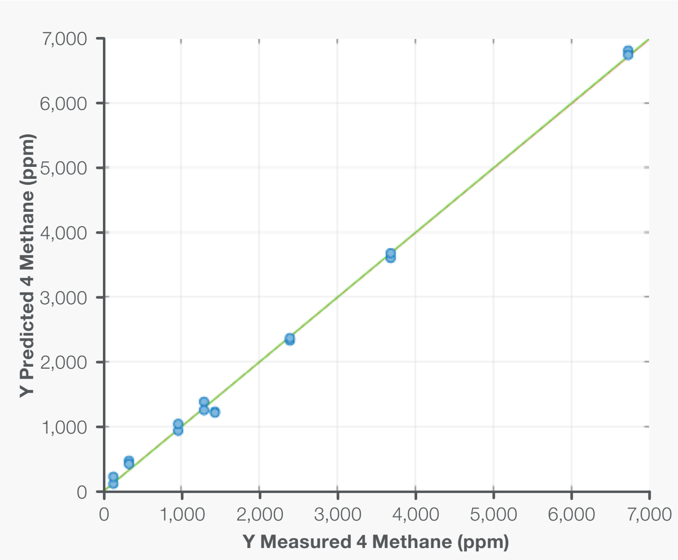

Figure 3. The methane model suggests that a prediction RMSE of 100ppm is achievable based on this POC model, which contains only nine samples.

The capability of a given multivariate model is always dependent on the quality and characteristics of the calibration dataset. This dataset was important to the methane response's independence relative to the other hydrocarbon species. A proper calibration dataset forces the modeling to rely solely on the methane Raman spectral features for modeling, as demonstrated by the Regression Vector (Figure 4).

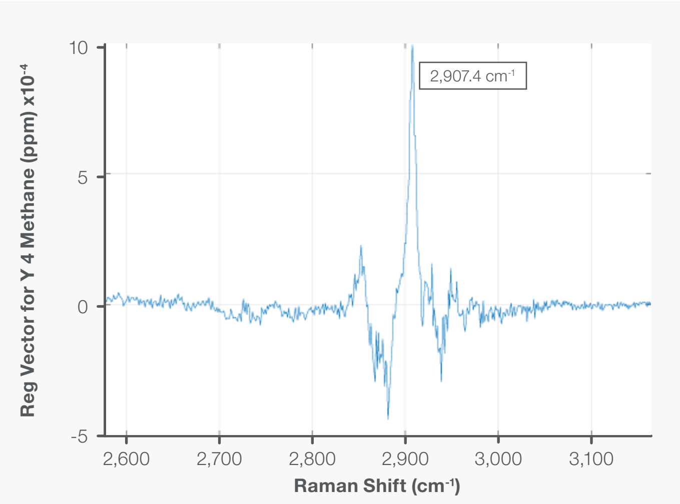

Figure 4. Regression Vector showing methane has a single strong Raman band at approximately 2910 cm^{-1}, demonstrating that Raman can detect methane in low concentrations.

Among a few Raman bands, methane has a single strong Raman band at approximately 2910 cm^{-1}, making it the best region for measuring and modeling methane at low levels. The methane model's PLS regression vector demonstrates the specificity potentially achievable with Raman spectroscopy models; the methane band is observable as the key feature in the PLS model regression vector. While this band is nearly always highly overlapped by other hydrocarbons, a robust calibration set design coupled with multivariate modeling allows for using the small but strongly overlapped methane Raman peak.

Additionally, the concentrations of the other hydrocarbons in Y-grade products are of interest. Raman spectroscopy can easily measure and predict these other bulk-level components. The RMSEC values and component ranges from this modeling study are tabulated in Table 1, illustrating the prediction capability for all Y-grade species based on Raman spectroscopy.

Species	RMSEC	Range
Methane (ppm)	100.3	130 – 6720 ppm
Ethane (LV%)	0.129	16.0 – 47.7%
Propane (LV%)	0.078	31.7 - 34.7%
n-Butane (LV%)	0.126	10.1 - 25.9%
i-Butane (LV%)	0.075	3.2 - 7.0%
n-Pentane (LV%)	0.151	2.2 - 5.2%
i-Pentane (LV%)	0.110	2.0 – 4.8%
Hexanes+ (LV%)	0.108	2.4 - 6.4%
CO_2 (LV%)	0.0038	0 – 0.083 LV%

Table 1. Y-Grade PLS Model RMSE Metrics.

Conclusion

This study demonstrates that Raman spectroscopy is a feasible technique for measuring low levels of methane in Y-grade products. The rapid measurement frequency, as fast as 3 to 5 seconds, makes Raman very attractive for process monitoring and control.

Solid-state Raman analyzers, such as the MarqMetrix All-In-One Process Raman Analyzer, are factory-calibrated and do not require any consumables. This means that the customer can conduct their analysis without costly interruptions. This efficiency, along with the combination of Raman spectroscopy with chemometric methods, has already facilitated the adoption of Raman in a broad array of industrial applications.

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