Application Note

SPORIAN®
MICROSYSTEMS, INC

Using Enhanced Raman Spectroscopy for Fuel Gas Composition Monitoring

Authors

Kevin F. Harsh
Duc Nguyen
Melissa Mezger
Sporian Microsystems, Inc.

Introduction

Modern, lean-burning, low-emission gas turbines require fine-tuned control of the combustion process to achieve their optimal operation. Upsets to the operating point, which may be caused by fluctuations in the fuel gas composition, can result in reduced efficiency, high pollutant emissions, or even turbine damage. Fuel gas sources are highly variable, including syngas from coal/biomass gasification, natural gas (both conventional and shale gas), liquefied natural gas, hydrogen-blended gas, and coal bed methane.

Compositional differences in these fuels have created significant challenges achieving efficient control of the combustion process. To achieve higher efficiencies, lower emissions, improved reliability and availability, and stable control and operation, fossil energy power generation facilities (e.g. emerging modular power systems) need real-time fuel gas composition data to identify any post-production cleanup options and allow fine-tuned control of the combustion process.

Additionally, as part of the strategy to decarbonize the U.S. Energy sector, there is a move to add hydrogen, renewable methane (e.g., biomethane), and other renewable constituents to the natural gas grid in order to deliver renewables to end markets [1]. If implemented at appropriate concentrations, this strategy of storing and delivering hydrogen and other additions appears to be viable without significantly increasing risks associated with utilization, overall public safety, or durability and integrity of the existing natural gas pipeline network. The introduction of new constituents to the natural gas grid will require monitoring technologies capable of providing real-time constituent composition of gas blends.

Raman spectroscopy is a powerful analytical technique that quickly gives highly specific information for the analysis of chemical compounds, and can be used for multi-compound analysis. Raman-active species exhibit spectra with distinct peaks and provide "fingerprint" information on the vibrational transitions within a molecule. This feature makes Raman spectroscopy ideal for implementing a robust automated molecular identification system.

Cavity-enhanced Raman spectroscopy (CERS) overcomes the limitations of conventional Raman spectroscopy by concentrating or enhancing the Raman scattering efficiency through the use of optical cavities to increase the likelihood (by orders of magnitude) of excitation from a light source [2,3]. When implemented correctly, many CERS formats are unaffected by surface contamination, making them highly suitable for complex or dirty liquid/gas composition monitoring.

In this application note, we'll explore the use of Sporian Microsystems SpecIQ™ enhanced Raman spectroscopy monitoring instrument for the measurement of fuel gas composition.

Methods

Data presented here was collected using a Sporian Microsystems SpecIQ™ cavity enhanced Raman gas/fluid composition monitoring system. The Raman-spectroscopy-based measurement system has the capability to provide in-situ, real-time monitoring of various gas/fluid environments, such as those encountered in fossil fuel energy generation, fuel gas distribution and production, water/wastewater monitoring, emissions monitoring, petrochemical production, and chemical/gas manufacturing.

Key system specifications are shown in Table 1 and the system is designed to operate in one of two possible modes: (1) as an autonomous monitoring device that measures and applies machine-learning-based algorithms to provide classification of salt constituents and quantified concentrations to higher-level control systems, and (2) as a user-operated instrument with specific feature/function control options.

Table 1: Key SpecIQ™ specifications

Spec/Feature	Unit
Excitation Wavelength	532 nm
Wavenumber Range (Shift)	100-5400 cm^{-1}
Resolution	6 cm^{-1}
Communications	Ethernet
Measurement Temp. Used	25-100°C
Max Measurement Temp. Capable	950°C
Raman Enhancement Mechanism	Cavity

Gas standard mixtures were acquired from MESA Specialty Gases & Equipment, and included high purity, reference grade 99.9% methane (P1971), 99.9% propane (P1075) and BTU-4 natural gas (K2I5585), as well as industrial grade propane and butane. The industrial grade propane and butane was selected as it was likely to have a high but uncertain level of other fuel gas constituents. Gas regulators were used to flow gas sampled though 1/8th inch stainless steel tubing to a Raman measurement cell which was vented via ignition-safe ventilation systems. The pressure at the point of measurement would have been ~1 atm.

The Raman measurement cell contained the gas and included the front-end optics to excite, enhance, and collect signal from the gas. The enhancement test cell/chamber was sealed from the environment to prevent air/oxygen from mixing into the gas sample during measurement, and enclosed in an air-tight, light-tight enclosure continuously flushed with purge air to prevent potential gas buildup in case of leaks. The laser source and spectrometer hardware were kept outside of the enclosure, using optical fibers to transmit excitation light in and signal out. Gas leak detector/alarms were inside and outside the enclosure to ensure safety. Because of the high danger of combustion when using fuel gas all safety measures and steps were/should be taken when performing such testing.

The setup included the capability to purge nitrogen through the system or to flush the system with cleaning solutions as needed. The instrument was configured to measure and send data to a database file that could be subsequently used to process/view resulting data. Gas was allowed to flow though the test cell at approximately 10 cc/min, as only a very small volume of gas is required for each measurement.

One of the benefits of the Sporian Microsystems SpecIQ™ Raman Monitoring System is the ability to provide very high dimensionality measurements by using many pixels to measure a broad spectral range, thereby enabling it to measure many different species within a sample. However, this poses a challenge in analyzing the data as there are many dimensions, or variables, to process.

All spectral data were processed and analyzed by performing a sequence of pre-processing, dimension reduction, and machine learning classification and/or regression. Preprocessing included the stabilization of signal fluctuations based on laser output and the removal of background signal. When classification and regression predictions are required, principal component analysis (PCA) can be performed on training data for select components and mixtures to find the optimal variance in the data as well as transform the data and reduce the dimensionality. Supervised machine learning models can then be implemented to train on the known dataset, analyzing their relationships.

Results

Figure 1, shows the measured spectra for the methane gas calibration-grade standards. To maintain concentration control, gases were measured at their nominal mixture/compositions and not diluted. At the short integration times used, the noise floor that was limiting low-end detection ranges was ~ 0.05%.

This noise/sensitivity limit reduces proportionally with increased integration time, and thus if longer integrations/measurement times are acceptable, lower-end precision/detection limits are similarly reduced (0.05-.005%). These Raman shifts are expected with differing methane cations [4]: methane v1 (CH symmetric stretching), methane v2 (CH bending), and Methane v3 (CH stretching).

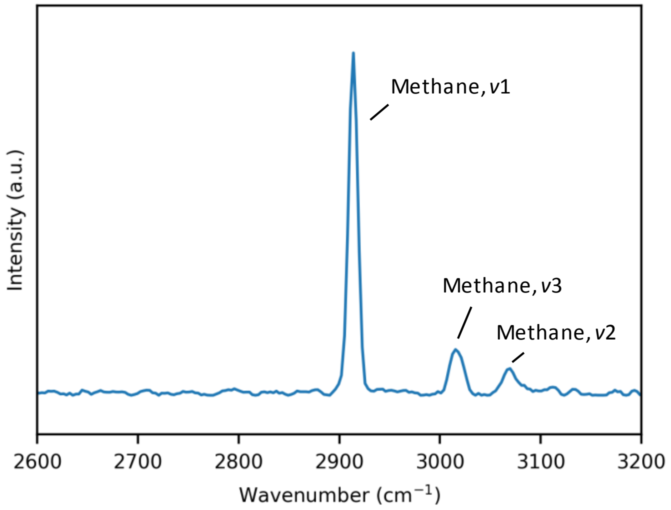

Figure 1: Measured spectra for calibration-grade methane gas standard

Figure 2 and Figure 3 show the measured spectra for industrial/utility-grade propane and butane respectively, and shows how the methods can be used to characterize complex fuel gas mixtures. In each plot, the peaks from the primary gas as well as other common gases/hydrocarbons (methane, ethane, N_2, sulfur compounds) as well as other unidentified constituents in low concentrations.

Once the components of a fuel mixture are identified based on peak analysis, the concentration of each component can be identified by correlating peak intensity to a calibration curve for each component. Determining the concentration of each component offers the ability to analyze many important aspects of a fuel gas [5] including: Wobbe index and the resulting turbine operating parameters, H:C ratio, and theoretical emissions/combustion byproducts. Such a real-time capability can enable feed-forward turbine control systems to maintain optimal combustion conditions through rapid, localized feedback and adjustment, and similarly enable safe and effective blended fuel gas transportation, distribution, and storage.

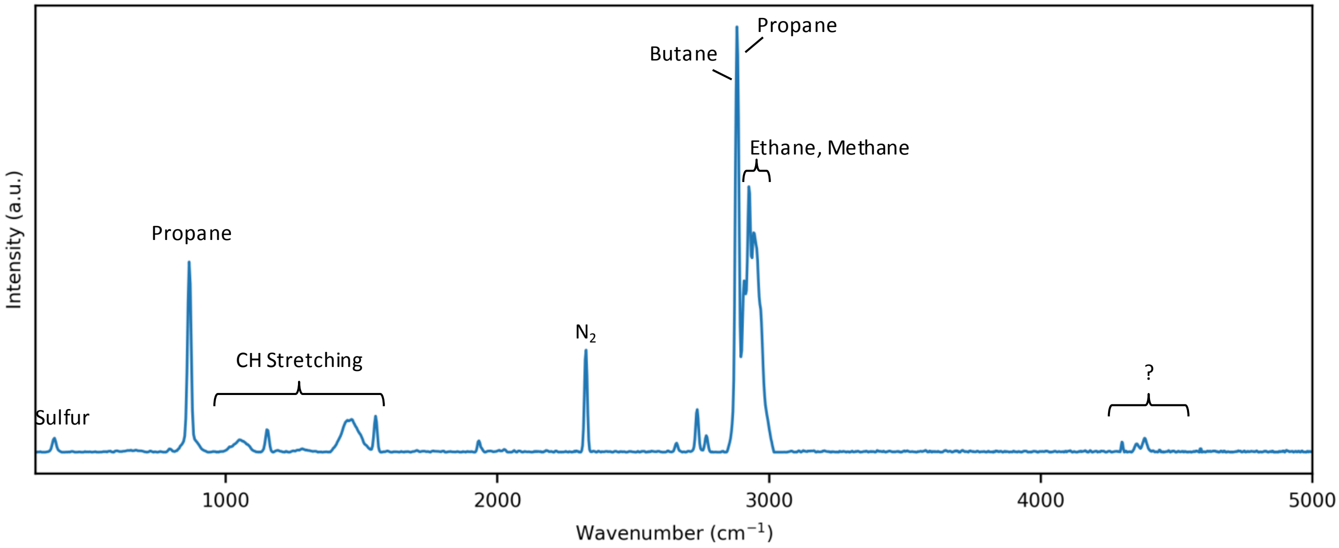

Figure 2: Measured spectra for industrial/utility-grade propane gas

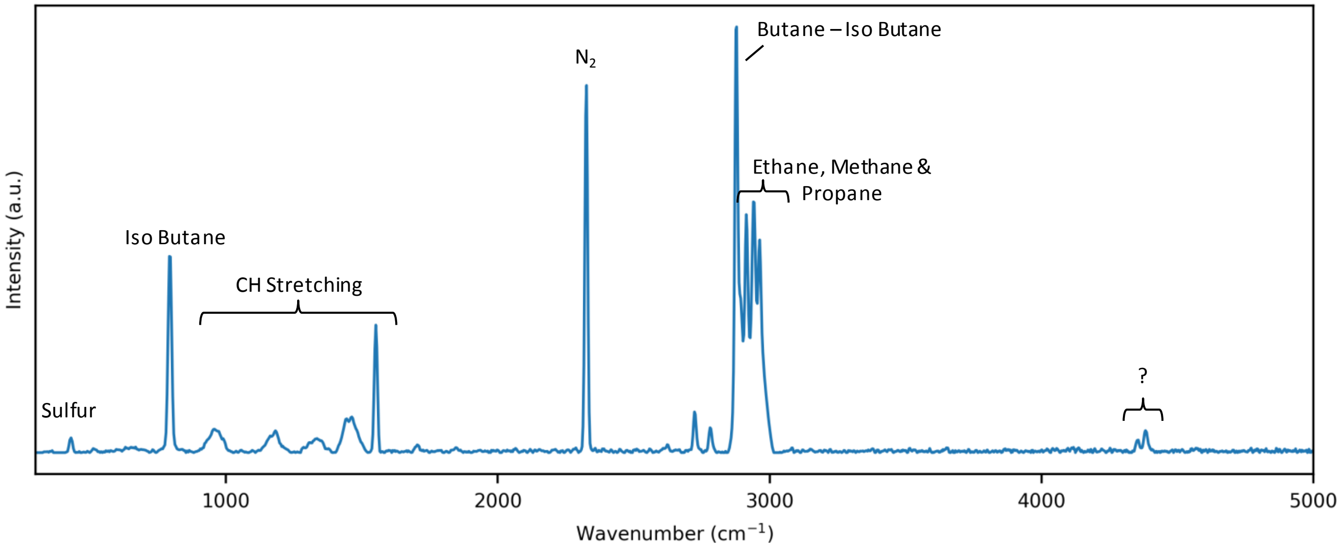

Figure 3: Measured spectra for industrial/utility-grade butane gas

Conclusions

There is a need within multiple fossil fuel related industries for real-time, low-cost, rugged, fuel gas chemical composition-sensing technologies for use as part of power generation systems as well as gas production and distribution. Sporian Microsystems' SpecIQ™ enhanced Raman gas/fluid composition monitoring systems are effective tools to provide in-situ, real-time monitoring of gas mixtures and to provide constituent and contaminant classification and quantification. This real-time capability can enable a feed-forward turbine control system to maintain optimal combustion conditions through rapid, localized feedback and adjustment to facilitate operation in both standard operation and flex-fuel mode via blending coal-based syngas with low-cost feedstock or other fuel gas types. It can also enable safe and effective blended fuel gas transportation, distribution, and storage and benefit any other market utilizing any type of fuel gas by providing real-time composition information.

---

1 "HyBlend Project To Accelerate Potential for Blending Hydrogen in Natural Gas Pipelines." Accessed February 17, 2021. https://www.nrel.gov/news/program/2020/hyblend-project-to-accelerate-potential-for-blending-hydrogen-in-natural-gas-pipelines.html.

2 Thorstensen, J., et al. "Low-cost resonant cavity Raman gas probe for multi-gas detection." Journal of the European Optical Society-Rapid publications 9 (2014).

3 Salter, Robert, Johnny Chu, and Michael Hippler. "Cavity-enhanced Raman spectroscopy with optical feedback cw diode lasers for gas phase analysis and spectroscopy." *Analyst* 137.20 (2012): 4669-4676.

4 Welsh, H. L., Stansbury, E. J., Romanko, J., & Feldman, T. (1955). Raman spectroscopy of gases. *JOSA*, *45*(5), 338-343.

5 Sandfort, V., Trabold, B., Abdolvand, A., Bolwien, C., Russell, P., Wöllenstein, J., & Palzer, S. (2017). Monitoring the wobbe index of natural gas using fiber-enhanced Raman spectroscopy. *Sensors*, *17*(12), 2714