Application note

Natural Gas Analysis in Hazardous Locations Using Raman Spectroscopy and Chemometric Modeling

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Summary

Precise natural gas measurements are critical in any environment, and this note describes how Raman spectroscopy combined with chemometric modelling provides a potent solution. The Thermo Scientific™ MarqMetrix™ All-In-One X Process Raman Analyzer is designed to provide inherently and intrinsically safe optical power in hazardous locations. It was used with a Thermo Scientific™ MarqMetrix™ Flow Cell Sampling Optic, which meets ATEX Zone 0, IECEx, and Class 1 Division 1 certification standards, to collect and analyze spectra from six natural gas standards. Operating at a consistent pressure of 100 psi with an ATEX-compliant laser (35 mW), the system delivered high-quality data.

Chemometric modeling developed robust regression models for key chemical constituents, with optimized variable selection enhancing model accuracy and reliability. Model performance metrics showed excellent linearity, resolution, and sensitivity, demonstrating that Raman spectroscopy combined with chemometric modeling is a powerful solution for precise natural gas analysis in hazardous locations.

Introduction

Natural gas is a fossil fuel composed primarily of methane, with smaller amounts of other hydrocarbons and impurities. Formed from ancient marine organisms under heat and pressure, natural gas is used as a combustion source for heating, electricity generation, vehicle fuel, and as a feedstock in chemical production. It is considered to be a cleaner-burning alternative to other fossil fuels, contributing to reduced greenhouse gas emissions and air pollutants.

The measurement and analysis of natural gas is a vital process that demands both speed and precision. Accurate natural gas measurements have far-reaching implications. They ensure revenue accuracy and facilitate fair financial transactions between producers, which is crucial for the economic integrity of the industry. Additionally, these measurements are essential for regulatory compliance, as they ensure adherence to stringent government and industrial standards.

Operational efficiency of gas-using industries is also impacted by accurate natural gas measurement. By obtaining trustworthy and precise data, operators can optimize their processes, reduce waste, and ultimately enhance the overall efficiency of their operations. Furthermore, the measurement of natural gas plays a significant role in safety assurance and environmental protection. By accurately measuring methane content and detecting any irregularities in the natural gas stream, operators can address potential safety hazards and mitigate environmental issues, thereby promoting safer and more sustainable practices within the industry.

Raman spectroscopy is an exceptionally powerful tool that can effectively address the myriad challenges associated with natural gas measurements. The MarqMetrix All-In-One X Process Raman Analyzer, when equipped with a flow cell or an immersion probe, offers the capability for non-invasive, in-situ measurements of natural gas directly within pipelines or process equipment. This innovative approach eliminates the need for traditional sampling systems or loops, thereby significantly reducing both the cost and operational disruptions typically associated with gas sampling.

The versatility of the MarqMetrix All-In-One X analyzer is underscored by its ability to operate reliably across a wide range of conditions, performing consistently under varying temperature and pressure regimes. Moreover, the hazardous location configuration enhances the instrument's capabilities even further, enabling the analyzer to function safely and effectively in some of the harshest and most hazardous operating environments. This robust configuration ensures that accurate and reliable natural gas measurements can be obtained even in extreme conditions, providing a critical tool for maintaining operational efficiency, safety, and regulatory compliance.

The analyzer is specifically designed for hazardous environments, ensuring intrinsic and inherent safety for use in ATEX Zone 0, IECEx, and Class 1 Division 1. It provides intrinsically safe operation and allows for on-location real-time compositional insights, allowing operators to make faster, safer, and more informed decisions in high-risk areas. The analyzer also features probe options engineered for safe operation in hazardous locations, meeting ATEX Zone 0, IECEx, and Class 1 Division 1 certification standards. These probes allow real-time analysis of gases, liquids, and solids using a single analyzer, making it an adaptable solution for demanding industrial applications.

Coupling the MarqMetrix All-In-One X Process Raman Analyzer with advanced chemometric modeling significantly enhances its capabilities, enabling rapid compositional analysis, environmental monitoring, and near real-time detection of impurities. This powerful combination provides a comprehensive solution for addressing the complex requirements of natural gas analysis.

The spectra of natural gas are characterized by minimal background fluorescence, which simplifies the analytical process. The primary components of natural gas exhibit distinct, well-resolved spectral peaks, facilitating the development of highly accurate and robust chemometric models. These models can effectively analyze the compositional nuances of natural gas, ensuring precise identification and quantification of its various constituents.

By leveraging the strengths of both the MarqMetrix All-In-One X analyzer and Thermo Fisher's global chemometric support, operators can achieve rapid and reliable assessments of natural gas quality and composition. This integration not only enhances operational efficiency but also supports stringent regulatory compliance and environmental stewardship. The ability to monitor and detect impurities in near real time further underscores the value of this approach, providing a critical tool for ensuring the safety and integrity of natural gas operations.

This application note will showcase the viability and applicability of Raman spectroscopy for analyzing natural gas in hazardous locations, highlighting its potential effectiveness and reliability under stringent operational conditions.

Cylinder	Methane (mol%)	Ethane (mol%)	Propane (mol%)	Isobutane (mol%)	N-Butane (mol%)	Isopentane (mol%)	N-Pentane (mol%)	Hexane (mol%)	Nitrogen (mol%)	Carbon dioxide (mol%)
1	90	2.5	2.5	0.5	2	0.3	0.5	0.2	1.5	0
2	89.01	4.8	1	0.3	0.3	0.1	0.1	0.08	2.4	1.9
3	81.7	4.2	1.9	0.9	0.3	0.2	0.1	0.4	0.2	10.1
4	77.8	6.5	4.6	0.9	0.9	0.5	0.5	0.3	1	7
5	81.85	3	1	0.4	1	0.2	0.4	0.05	9	3
6	72.7	10	4	0.9	0.8	0.4	0.3	0.3	0.2	10.4

Table 1. Natural gas standard composition.

Materials and Methods

The MarqMetrix All-In-One X Process Raman Analyzer, equipped with a flow cell, was employed to collect the spectra of six natural gas standards as detailed in Table 1.

To ensure consistent and accurate sampling, the sample cylinders were connected to the analyzer via a gas sampling rig, and the pressure was carefully maintained at 100 psi throughout the entire process. For the spectral analysis, a laser with a power output of 35 mW was used, with each sample undergoing a 1-minute acquisition period. The laser power applied to the sample was in accordance with ATEX 0 requirements.

To enhance the reliability of the data, each acquisition was averaged over six measurements. The spectra obtained from this process were subsequently imported into Solo 9.5 software (Eigenvector Research, Inc., Manson, WA USA 98831) for comprehensive chemometric modeling, enabling detailed analysis and interpretation of the chemical composition of the natural gas samples.

Figure 1 illustrates the primary component peaks from the mean spectra collected for each cylinder, highlighting the impressive resolution and sensitivity of the MarqMetrix All-In-One X Process Raman Analyzer.

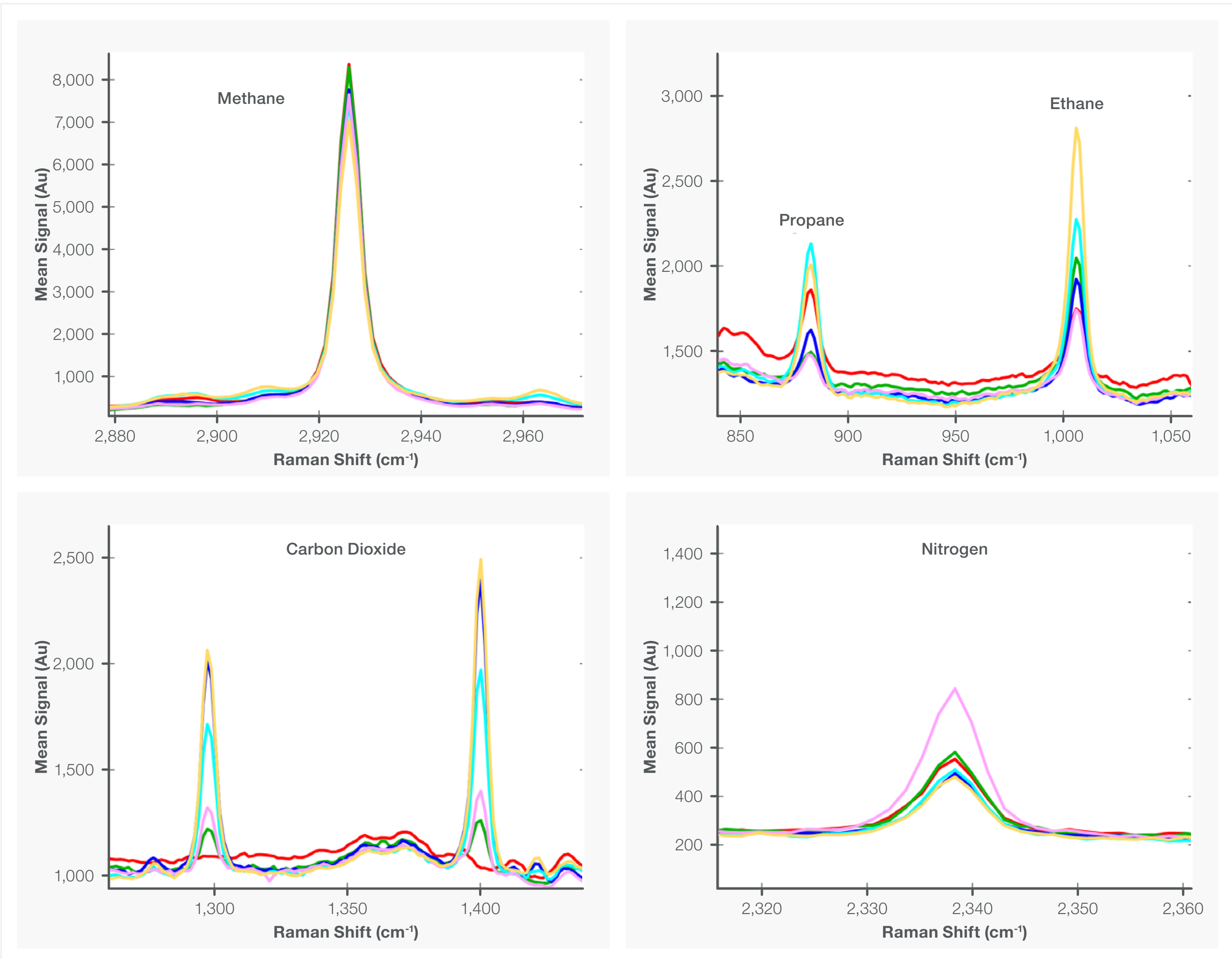

Figure 1. Peaks for the main natural gas components at various concentrations.

Results

The spectra produced, along with the reference data obtained from the certificates of analysis accompanying the gas cylinders, were imported into SOLO software. Using this dataset, Partial Least Squares (PLS) regression models were constructed for each of the hydrocarbons present in the natural gas standards. The models underwent rigorous optimization processes, focusing on variable selection, determination of latent variables, and appropriate preprocessing techniques.

Variable selection emerged as a crucial step in the modeling process due to the significant covariance observed among the different hydrocarbons within the natural gas standards. By carefully selecting specific regions of the spectra that correspond exclusively to the hydrocarbons of interest in each model, the independence and relevance of the information utilized in the model were significantly enhanced. This careful selection process ensures that the PLS regression models are robust and accurate, leading to more reliable predictions and analyses of the hydrocarbon content in the natural gas samples.

Given the lower concentration and relatively lower intensities of the butane and pentane peaks, a wider range of variables were selected to build the models.

Table 2 shows the specific regions of the spectra that were chosen for constructing the regression models.

Components	Region (cm^{-1})
Methane	2880 - 2960
Ethane	975 - 1050
Propane	850 - 950
Butanes	370 - 700, 800 - 875
Pentanes	370 - 700, 800 - 875
Nitrogen	2320 - 2360
Carbon dioxide	1250 - 1500

Table 2. Selected spectral regions for model development.

Given the limited number of samples in the dataset, the performance of the models was assessed using the Root Mean Square Error in Cross-Validation (RMSECV). To ensure robust cross-validation, the Venetian blinds technique was employed; additionally, all replicates of the samples were held out simultaneously during the validation process. The 95% Confidence Interval (CI) for the RMSECV was estimated by multiplying the RMSECV value by 1.96, providing a measure of the uncertainty associated with the model predictions. The results of the chemometric models, including their performance metrics, are reported in Table 3.

Components	Range	LVs	RMSECV (mol%)	R^2	95% CI (mol%)
Methane	72.7 - 90	5	1.91	0.993	3.74
Ethane	2.5 - 10	4	0.075	0.999	0.147
Propane	1 - 4.6	3	0.095	0.995	0.187
i-Butane	0.3 - 0.9	3	0.059	0.948	0.115
n-Butane	0.3 - 2	5	0.084	0.966	0.165
i-Pentane	0.1 - 0.5	2	0.046	0.785	0.091
n-Pentane	0.1 - 0.5	4	0.066	0.814	0.129
Nitrogen	0.2 - 9	4	0.575	0.968	1.13
Carbon dioxide	0 - 10.4	3	0.182	0.999	0.357

Table 3. Model parameters and performance metrics.

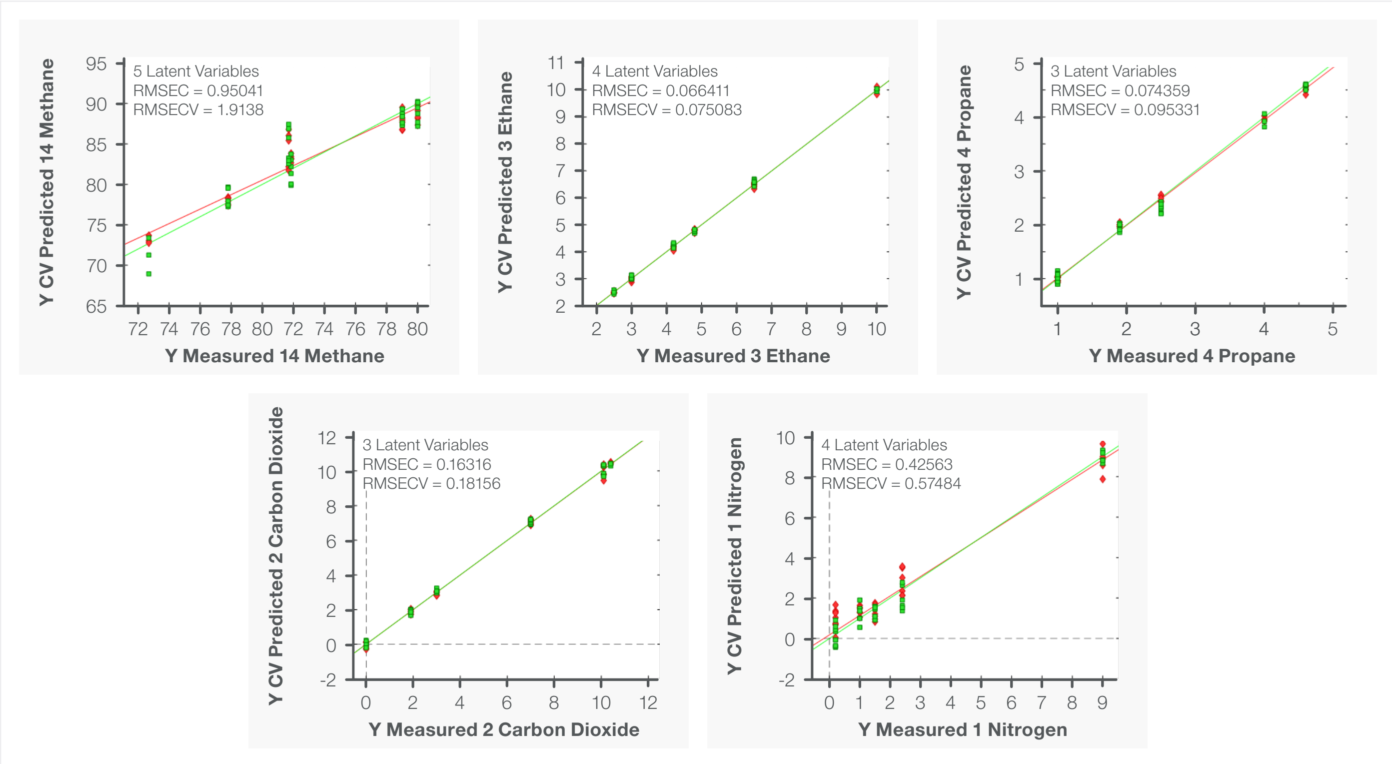

Figure 2. Regression models of key natural gas species.

Figure 2 presents the regression models for the primary natural gas species. Each of these models demonstrates excellent linearity, high resolution, and remarkable sensitivity, underscoring the robustness and accuracy of the analytical approach used.

Conclusion

In conclusion, the MarqMetrix All-In-One X Process Raman Analyzer along with a Thermo Scientific™ MarqMetrix™ FlowCell™ Sampling Optic, both developed to be operated in ATEX Zone 0, proved to be a highly effective solution for collecting and analyzing the spectra of natural gas standards. The resulting data produced robust PLS regression models for each hydrocarbon component. Careful variable selection and optimization enhanced the independence and relevance of the models, resulting in accurate and reliable predictions. The performance of these models demonstrated excellent linearity, resolution, and sensitivity across the range of natural gas components. This study underscores the viability and applicability of Raman spectroscopy, coupled with advanced chemometric modeling, for precise and reliable natural gas analysis in hazardous environments.

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