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Methane-Hydrogen Raman Spectra Analysis in Binary Gaseous Mixtures

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Summary:
The combined Raman spectra of methane and hydrogen have been analyzed in a way to estimate the concentration of the two species in binary gaseous blends. The acquisitions were made with an industrial tailored Raman instrument appositely developed to measure the natural gas mixtures composition. Once acquired, the Raman spectra have been fitted using a MATLAB® routine. The results show a high correlation between the estimated and the certified gases concentrations.

Keywords: Raman spectroscopy, methane, hydrogen, gas analysis, measurement

Motivation

Hydrogen is light, storable, reactive, has high energy content per unit of mass, and it can readily produce at industrial scale. Supplying hydrogen to industrial users is now a major business globally. Demand for hydrogen in its pure form is around 70 million tons per year (MtH_2/yr) [1]. In the next few years, hydrogen will be injected in the natural gas networks in several European countries and around the world. For example, in Germany the hydrogen concentration can reach 2% by volume, growing up to 10% concentration under certain circumstances [2].

Given its intrinsic capability to determine multiple species simultaneously with a non-invasive approach, Raman spectroscopy is a suitable candidate to analyze complex gas mixtures. Starting from the results obtained from a feasibility study [3], a novel system which implements Raman spectroscopy to determine the main natural gas components has been used to analyze the combined Raman spectra of methane and hydrogen. The aim of this study is to first determine the performance and the reliability in CH_4-H_2 binary mixtures concentration detection. The focus has been set on detection and concentration estimation in four CH_4-H_2 binary mixtures.

Methods

The system employed in this study is designed to operate with a low power absorption and in a wide operative temperature range. Its final use is intended to be the on-the-field analysis of natural gas directly on the transport and distributions networks. In this experiment the instrument was kept at a fixed laboratory temperature, minimizing the sources of variability.

The Raman system employed in the experiment is shown in Fig. 1. The laser source is a solid state multi-mode diode source centered at 455 nm with an optical power set to 2W.

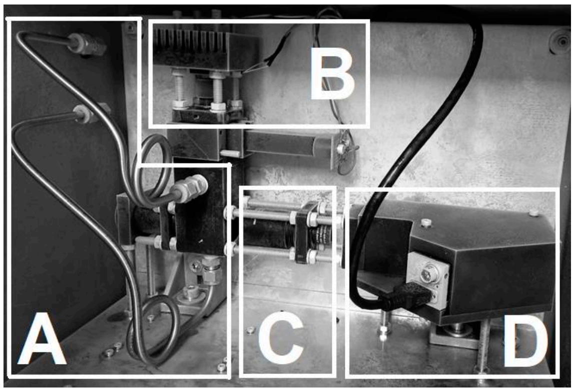

Fig. 1. Raman system employed in the experiment. Section A: gas cell, gas-in and gas-out pipes. Section B: laser source. Section C: Raman signal collecting optics. Section D: diffraction grating spectrometer.

Raman calibration spectra of methane and hydrogen were generated by averaging 30 acquisitions with 2-seconds camera exposure. The bottles used in this phase had concentrations equal to 100% for both methane and hydrogen. The calibration spectra of methane and hydrogen are plotted in Fig. 2.

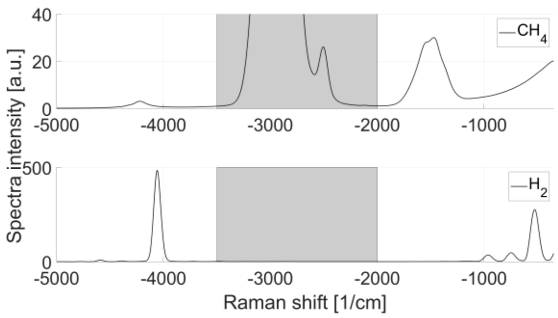

Fig. 2. Calibration Raman spectra, 100% concentration of methane (top) and hydrogen (bottom).

In Table 1 the concentrations of the four analyzed mixtures are reported.

Tab. 1: Certified mixtures concentration [%]

Label	CH_4	H_2
MIX1	98.000	2.000
MIX2	94.977	5.023
MIX3	89.940	10.060
MIX4	79.758	20.242

The analysis is performed on two spectral regions: from -350 cm^{-1} to -2000 cm^{-1} and from -3500 cm^{-1} to -5000 cm^{-1}. For each mixture, 20 experimental spectra were fitted using a fit routine appositely developed in MATLAB®, using a nonlinear least-square solver which finds the linear combination of the two calibrations that fits at best the acquired spectra. The average of the 20 fit solutions is intended to be the final estimated concentration.

Results

As an example, the elaboration for MIX3 is represented in Fig. 3. The acquired spectra and the best fit solution are plotted on the top. The residues between the acquired spectra and the synthetic spectra are plotted on the bottom.

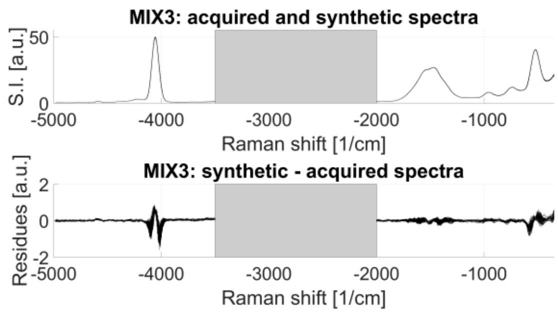

Fig. 3. Fit elaboration: acquired and synthetic spectra (top) and elaboration residuals (bottom).

The measured concentrations and the related errors are reported in Table 2. The precision of the measuring method in the measurement of concentrations is anyway better than 0.1%mol/mol for concentration of hydrogen in methane as high as 20%.

Tab. 2: Experimental mixture concentrations [%] and errors [% mol/mol]

Fit results		Result CH_4	Result H_2
MIX1	Result	98.003	1.997
	Error	0.003	-0.003
MIX2	Result	94.928	5.072
	Error	-0.049	0.049
MIX3	Result	89.849	10.151
	Error	-0.091	0.091
MIX4	Result	79.667	20.333
	Error	-0.091	0.091

Conclusions

The ability to estimate the compositions of binary methane-hydrogen mixtures has been proven, to assess the feasibility to analyze mixtures with a hydrogen content up to 20%. Mixtures containing hydrogen in natural gas will be the object of next studies.

Acknowledgments

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