

Detailed spectral monitoring of different combustible blends based on gasoline, ethanol and methanol using FT-Raman spectroscopy*

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ABSTRACT

The use of mixtures of oil-based fuels with organic chemical components (e.g. ethanol, methanol) has been gaining ground in recent years. Several countries try nowadays to replace part of the fossil fuels for various reasons including economics, sustainability or optimization of resources. The characteristics of these combustible-related chemical component blends can be analyzed by different means. Optical spectral analysis (e.g. Raman, Fourier-transform infrared, etc.) can extract in many cases most of the required information concerning the molecular structure of a determined chemical sample in an effective and clean manner. Experimental detailed Raman spectra from various gasoline-ethanol blends and a gasoline-ethanol-methanol blend are presented. The Raman spectral information obtained has been used for approximated quantitative analysis with no additional chemical marker or complicated calibration methods.

The analysis has been performed using a self-designed, low-cost, robust and frequency precise Fourier transform Raman (FT-Raman) spectrometer. This proposed FT-Raman spectrometer has been constructed with a Michelson interferometer, an in-house designed photon counter, and a sensitive trans-impedance photo-detector. Additional complex hardware was not used to compensate the mechanical or thermal drifts disturbances in the interferometer. For accurate spectral calculation an interference pattern generated by a low-power Helium-Neon laser (wavelength $\lambda=632.816\text{nm}$) was used. The resulting spectral data are in the range of 0-cm^{-1} to 3500-cm^{-1} . The resolution of these Raman spectra is 1.66-cm^{-1} . Higher resolutions are possible since the scanning distances in the Michelson interferometer can be extended substantially before instrumental effects appear. A comparison of the experimental results obtained with standard Raman shift values revealed a satisfactory accuracy and precision in frequency detection.

INTRODUCTION

The combination of oil-based fuels with organic chemical components, such as ethanol and methanol, has been gaining importance in the recent years due to high fuel prices and the strong trend towards sustainable development. Different spectral analytical methods can help to determine the characteristics of pure or blended chemical components: temperature, pressure, composition, purity, proportions, etc. (Al-Ghouti et al. 2008; Balabin and Safieva 2011). Different experiments based on spectral techniques have explored the possibility of detecting not only qualitatively but also quantitatively the combination of fuel

blends with ethanol or methanol (Fernandes et al. 2008; Pereira et al. 2006; Xu et al. 2010; Ye et al. 2009). For proper quantitative Raman spectroscopy measurements, it is necessary to overcome the instability (light coupling, temperature drift, sample holder, etc.) on a specific Raman spectroscopy setup. One technique for quantitative Raman analysis requires that the sample under test is mixed with an additional marker for calibration purposes (Sasic 2008), which is compared to the spectrum of interest. This procedure is not always suitable and in some cases can represent a drawback in this spectral analysis technique. Another approach is to compare the main Raman shift lines from the related chemical compounds in a specific mixture. This is known as the

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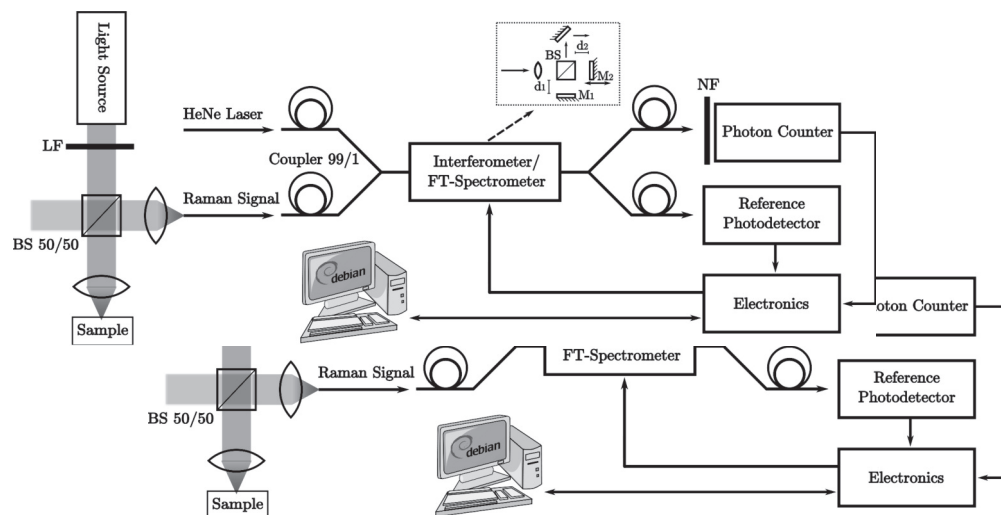


Figure 1. General diagram of the FT-Raman spectrometer setup.

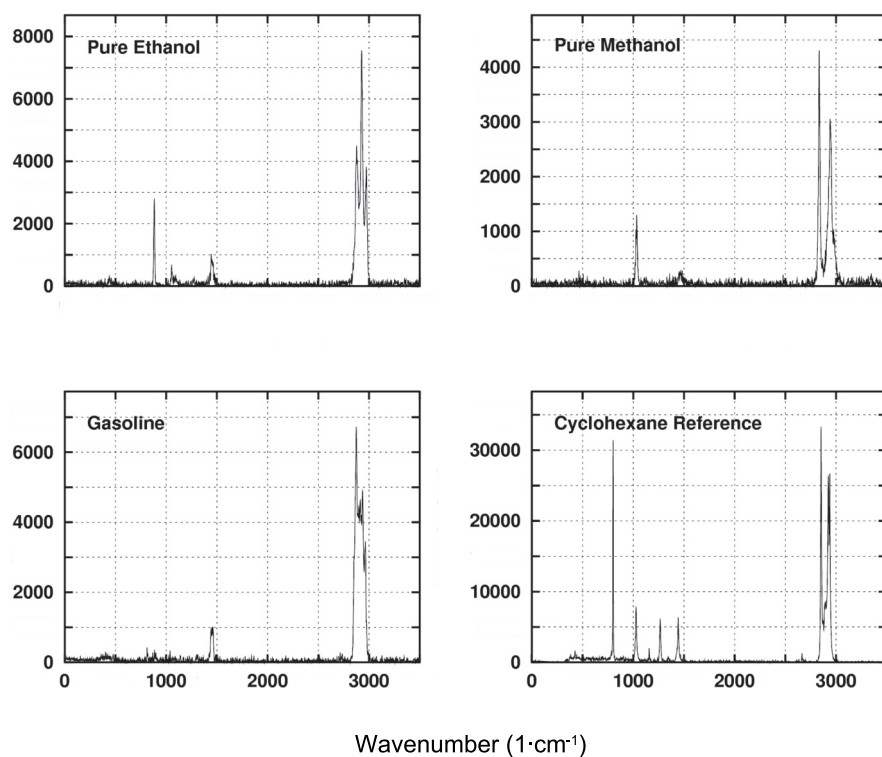


Figure 2. Raman spectra from the different pure chemical compounds used.

non-ideal instrument effects (e.g. finite entrance size, finite optical path length, and radiation non-uniformities) have not been taken into account. Each spectrum was obtained by averaging 20 successive scans.

The approximated quantitative measurements of the binary ethanol-gasoline blends and the gasoline-ethanol-methanol blend were performed by solving the $Ax=b$ matrix system, where A was a $m \cdot n$ matrix containing Raman spectral

The Raman spectrum of cyclohexane (C_6H_{12}), which is an alkane widely used to calibrate spectrometers since it exhibits very strong Raman lines at 801-cm^{-1} and 2852-cm^{-1} , has been obtained for comparison, validation and calibration purposes. Table 3 shows the comparative position of the main Raman peaks of standard cyclohexane (McCreery 2000) vs.

that obtained with the proposed FT-Raman setup. The observed Raman spectrum shows a reduced deviation from the standard cyclohexane Raman shift, despite having no instrumental effect compensation, demonstrating the reliability of the this low-cost device in spectral accuracy, resolution, and robustness.

Table 3. Main values of theoretical vs. observed cyclohexane (C_6H_{12}) Raman spectrum using the FT-Raman setup presented in Figure 1. The observed Raman spectrum has not been compensated for instrumental effects.

Spectrum type	Cyclohexane main Raman shift peaks (cm^{-1})				
Standard	801.3	1028.3	1266.4	1444.4	2852.9
Observed	801.9	1028.4	1266.7	1443.7	2853.1

CONCLUSIONS

The different techniques based on vibrational spectroscopy can help in determining the nature of a sample under observation. These related technologies can offer a wide range of possibilities for precise and sustainable chemical and physical analysis of materials. Raman spectroscopy can be used for analyzing several types of chemical components including sustainable combustible-related mixtures, like those mentioned in the present work. In most of the cases the use of such a tool is environment-friendly and non-polluting, since the required information is obtained optically.

The FT-Raman setup offers high flexibility and robustness and its results obtained are comparable to those obtained using commercial devices. The frequency precision has been demonstrated by observing the Raman spectrum of cyclohexane, which is widely used for calibration purposes and comparing it to its standard Raman spectrum.

The whole range of spectral information has been used to perform Raman quantitative analysis of the samples for calculating the proportion of the chemical compounds present in the sample. The quantitative analysis has shown approximated proportion results in the sample despite the molecular complexity of the mixed samples observed. This analysis has been done without using additional chemical markers or comparison (main peak ratio) between the main shift peaks of the chemical compounds present in a specific blend. The quantitative results have shown approximated values of the proportion of gasoline and ethanol present in E05, E10, E15, E20, and E50 mixtures. The main advantage of this analysis is that with enough scans and setup stability, it is possible to determine a low proportion of ethanol in gasoline at low cost and without using a chemical calibration marker and hence with no additional sample preparation being required. This analysis can also be applied where the peak ratio analysis is difficult due to the poor signal of the ethanol in the gasoline blend or other sample of complex molecules.

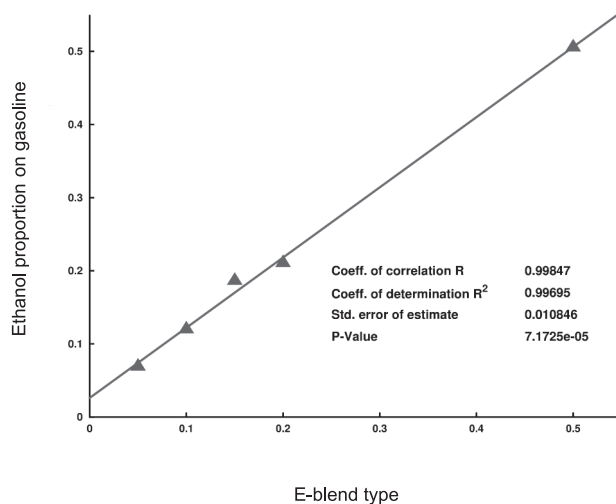


Figure 4. Linear regression calculated for the gasoline-ethanol blends observed.

The proposed self-designed FT-Raman spectrometer prototype, and the methods used for spectral evaluation are capable of extracting detailed and frequency precise Raman spectra from gasoline-ethanol and gasoline-ethanol-methanol mixtures in a clean and cost-accessible manner.

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