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

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Key words: combustible blends, FT-Raman spectroscopy, spectral chemical analysis

Received in November 2011. Published in March 2012.

### **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  $\lambda {=} 632.816 nm)$  was used. The resulting spectral data are in the range of 0·cm<sup>-1</sup> to 3500·cm<sup>-1</sup>. The resolution of these Raman spectra is 1.66·cm<sup>-1</sup>. 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

<sup>\*</sup> Presented at the Third International Environmental Best Practices Conference, 13-16 September 2011, Offenburg, Germany

ratio method (Larkin 2011; Ye et al. 2009). The ratio method is not always adequate, since a low proportion of certain element can lead to a poor Raman signal on its evaluation peak and it can also be hidden by the spectral noise. On the other hand, information hiding in the CH stretch region (around 2800·cm<sup>-1</sup>) of organic materials can be used to determine the proportion of a specific material contained on a sample under inspection.

This work presents detailed Raman spectral information from different proportion binary gasoline-ethanol blends and a tertiary gasoline-ethanol-methanol blend. The aim of such measurements was the qualitative and approximated quantitative analysis of certain chemical components used on specific combustible blends in a clean and rapid way. The spectral data was presented in the range of 0·cm<sup>-1</sup> to 3500·cm<sup>-1</sup> with a resolution of 1.66·cm<sup>-1</sup> (most liquid and solid samples require resolutions between 3·cm<sup>-1</sup> and 10·cm<sup>-1</sup> (McCreery 2000) ). The measurement has been performed using a frequency precise, low-cost, self-designed FT-Raman spectrometer prototype (Ortega Clavero et al. 2011). This FT-Raman spectrometer was able to deliver a reliable frequency accuracy and high resolution Raman spectra from the sample under observation. The frequency precision and resolutions obtained with this FT-Raman setup was comparable to the Raman standards used as calibration on commercial devices at a significantly lower cost.

## **MATERIAL AND METHODS**

## Chemical compound samples

For the Raman spectral analysis the following chemical component samples were used: pure ethanol ( $C_2H_6O$ ), pure methanol ( $CH_4O$ ), and pure gasoline (petroleum ether from Riedel-De Haen AG) with a boiling range of 50-70°C, with approximately 0.02% of water content. Gasoline-ethanol blends with known volume proportions (5%, 10%, 15%, 20% and 50%) were prepared for a first experiment (Table 1). For an additional experiment, a sample containing the same volume amount of gasoline, ethanol and methanol was used. A sample of pure cyclohexane ( $C_6H_{12}$ ) was measured separately for calibration and validation purposes.

Each liquid sample was contained in a 5ml cuvette, and placed in front of a  $20 \times \text{microscope}$  objective. The observed samples were prepared using an Eppendorf Research® variable pipette holder (0.5ml to 5.0ml with a maximum measurement deviation of  $\pm 2.4\%$ ). All the described samples were measured at room temperature.

## FT-Raman spectrometer setup

The robust and low-cost setup used for the spectral measurements is depicted in Figure 1. This FT-Raman spectrometer setup consisted of a Michelson interferometer, an in-house-design and low-cost photon counter based on a silicon avalanche photodiode (Perkin Elmer C30921SH) cooled down to  $-40^{\circ}$ C, and a reference photo-detector. For sample excitation a Helium-Neon laser ( $\lambda$ =632.816nm, Power=30mW) was used. A second low-power Helium-Neon laser signal (approximately 10nW) was used to generate a reference interference pattern, which helped in determining the optical path accurately (Connes advantage). The Raman scattered light and interference pattern were coupled with 62.5/1.25 $\mu$ m multi-mode optical fibers.

### **Evaluation methodology**

The Raman spectra from the samples under observation were obtained by sampling the Raman scattered light,  $P_i$ , and the interference pattern,  $R_i$ , from the Michelson interferometer output (Hariharan 2007; Kauppinen and Partanen 2001; Sumner et al. 2001). The raw data obtained were evaluated off-line. A corrected interferogram,  $I_j$ , was first calculated by re-sampling the photon counter information using the optical path,  $O_i$ , as a new axis. The real optical path was extracted from the reference signal  $R_i$  and was defined by

$$O_i = \frac{\phi_i \lambda}{2\pi} \tag{1}$$

where  $\phi_i$  was the unwrapped phase from  $R_i$ , and  $\lambda=632.816$ nm. The unwrapped phase,  $\phi_i$ , was calculated by applying a Hilbert transform to the reference signal  $R_i$ . The jth value of the corrected interferogram  $I_j$ , where  $i \le j \le i+1$ , was calculated by taking the photon counter array  $P_i$  as an amplitude along the optical path  $O_i$ 

$$I_{j} = \frac{j \cdot O_{i}}{O_{i+1} \cdot O_{i}} [P_{i+1} \cdot P_{i}] + P_{i}$$
(2)

After this operation the resulting interferogram  $I_j$  was a re-sampled version of the photon array obtained having the information about the real optical path (including the mechanical imperfections and thermal drift). Similar results were obtained when other interpolation schemes were used e.g. spline or cubic interpolation. The Raman spectrum was extracted by applying a fast Fourier transform (FFT) to this corrected interferogram  $I_j$ . The experimental measurements have been performed with no additional hardware for mechanical vibration or thermal drift compensations and the

Table 1. Chemical samples used on the measurements and their different proportions.

Material in sample	Chemical samples						
	E05	E10	E15	E20	E50	ME33	
Gasoline (ml)	4.75	4.50	4.25	4.00	2.50	1.50	
Ethanol (ml)	0.25	0.50	0.75	1.00	2.50	1.50	
Methanol (ml)	0.00	0.00	0.00	0.00	0.00	1.50	

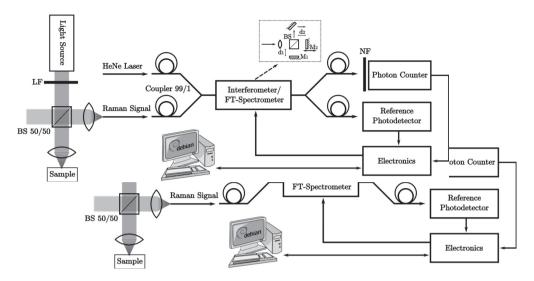


Figure 1. General diagram of the FT-Raman spectrometer setup.

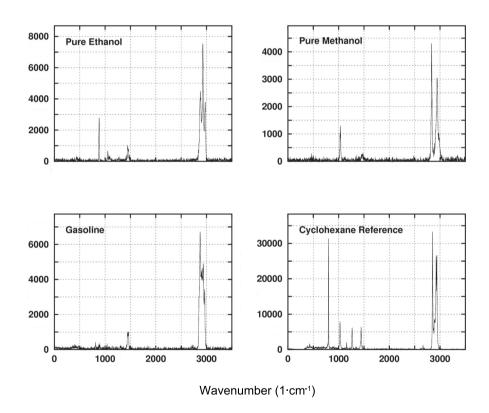


Figure 2. Raman spectra from the different pure chemical compounds used.

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

information of the pure chemical compounds, x was an n column vector with the unknown proportions present in the blend, and b was a column vector of m entries holding the experimental Raman spectrum obtained for the blend. The quantitative analysis was performed under the assumption that the changes in the Raman signal coupled into the Raman spectrometer oscillates around a certain average value and therefore using several consecutive scans can help to reduce this effect. Since the nature of the data obtained can be arranged as an over-determined system, it can be solved by using QR decomposition (QR Factorization) for computing time improvement.

#### **RESULTS**

Detailed, frequency precise and repetitive Raman spectra of ethanol, methanol, gasoline, five binary gasoline-ethanol blends with different proportions and an equally proportioned gasolineethanol-methanol blend have been obtained in the range of 0·cm<sup>-1</sup> to 3500·cm<sup>-1</sup> with a resolution of 1.66·cm<sup>-1</sup> using the FT-Raman spectrometer prototype and the evaluation method that we proposed. Higher resolutions could be achieved using this FT-Raman setup since longer optical paths are possible. Figure 2 shows the Raman spectra of the pure materials (ethanol, methanol, gasoline and cyclohexane) observed with the FT-Raman spectrometer. Figure 3 shows the Raman spectra from four gasoline-ethanol binary blends.

The quantitative analysis of the materials allowed an approximated calculation on the proportion of ethanol and methanol in a gasoline mixture without using any Raman marker or complex calibration method. Table 2 shows the calculated proportion from the gasoline-ethanol blends and the equally proportioned gasoline-ethanol-methanol blend. Figure 4 shows the linear regression from the quantitative evaluation of the gasoline-ethanol binary blends. This result demonstrates a fairly linear behavior of the gasoline-ethanol mixtures, with a coefficient of determination of  $R^2$ =0.99695.

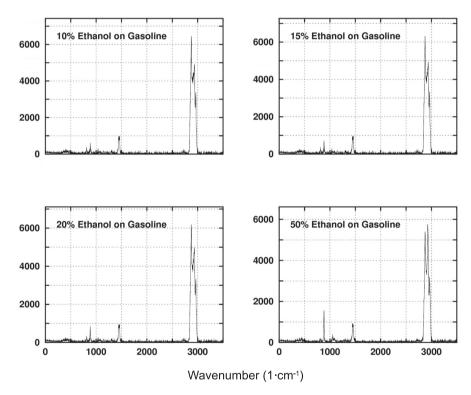


Figure 3. Raman spectra from the different proportions gasoline-ethanol blends observed.

Table 2. Calculated proportion values from the observed binary ethanol-gasoline blends, and the equally proportioned 33% gasoline-ethanol-methanol blend blends.

Materials	E05	E10	E15	E20	E50	ME33
Gasoline	0.93118	0.88029	0.81380	0.75986	0.49470	0.33030
Ethanol	0.06881	0.11971	0.18620	0.24014	0.50530	0.35030
Methanol	0.00	0.00	0.00	0.00	0.00	0.31940

The Raman spectrum of cyclohexane (C<sub>6</sub>H<sub>12</sub>), which is an alkane widely used to calibrate spectrometers since it exhibits very strong Raman lines at 801·cm<sup>-1</sup> and 2852·cm<sup>-1</sup>, 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 <sup>-1</sup> )						
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.

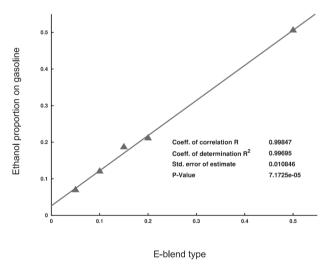


Figure 4. Linear regression calculated for the gasoline-ethanol blends observed.

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.

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.

## **ACKNOWLEDGEMENTS**

The authors would like to thank Mrs. Regina Brämer, Mrs. Barbara Milz, B.Sc., and Mrs. Andrea Siegel from the Chemie, Analytik, Umweltanalytik laboratory from the University of Applied Sciences Offenburg for all the support on providing and storing the required chemical samples and laboratory material used to perform the presented Raman spectral analysis. We would like also to thank Mr. Ernst Klausmann, Mr. Heiko Haufe, and Mr. Thomas Retzlik from the Elektro/Mechanische Werkstatt for providing the components for the proper functioning of the FT-Raman spectrometer.

This work has been partially funded by the Consejo Nacional de Ciencia y Tecnología - CONACYT (National Council for Science and Technology).

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