Methane detection using Wavelength Modulation Spectroscopy and a multiline quantitation method

Ana M. Cubillas *, Olga M. Conde, María Ángeles Quintela, Adolfo Cobo, José Miguel López-Higuera

Photonics Engineering Group, University of Cantabria, Avda. de Los Castros S/N, Santander, Cantabria, Spain

ABSTRACT

In this paper the application of the Inverse Least Squares algorithm (ILS) to the detection of methane using its behaviour in the near-infrared band is presented. In order to test the effectiveness of this method, different methane concentrations were measured. Wavelength Modulation Spectroscopy (WMS) was employed to obtain the first and second harmonics of the modulation signal. The use of both harmonics in spectroscopy eliminates the dependence of the measured absorbance on parameters such as: fiber misalignments, optical power fluctuations, etc. This property greatly increases the accuracy of the concentration readings. The benefits of analysing multiple lines in gas detection are discussed together with the capabilities of the ILS algorithm. The ILS algorithm is based on the Beer-Lambert law. This law is extended to include multiple wavelengths and rearranged in such a way that the concentration of the chemical species depends on the measured absorbances. In order to apply the previous algorithm, three absorption lines centered at 1665.961 nm, 1666.201 nm and 1666.483 nm were used. The obtained results are compared with the most usual single-line calibration method based on linear regression. This comparison shows that ILS gives a superior performance. Specifically, results indicate that the ILS multiline algorithm is less noise dependent and has a higher reliability than single-line calibration methods.

Keywords: Methane, Wavelength Modulation Spectroscopy (WMS), Inverse Least Squares (ILS).

1. INTRODUCTION

Methane (CH_4) is a very inflammable and asphyxiating gas which is found easily in the environment, making it necessary to develop systems to ensure that its concentration does not exceed a permissible limit. Therefore, the detection of methane is of such an importance for security reasons in chemical plants or mines, as well as in environmental applications as water treatment plants or wastelands [1, 2]. Traditionally, conventional sensors as electrolytic or catalytic ones have been used in the applications described above, but they are not able of remote sensing. Furthermore, sometimes they can hardly distinguish between methane and other chemical species [3]. On the other hand, optical sensors based on the absorption of light are appropriate for remote sensing and, additionally, they have the advantages of being immune to electromagnetic fields, high sensitivity, fast response and high molecular sensitivity [4]. Currently, there are few systems that use absorption spectroscopy to measure the concentration of chemical species [2], that is why a lot of research is being done in order to apply this technique not only in industrial and environmental applications but also in biomedicine.

To achieve great sensitivity, the strongest absorption lines of the gas are required. Methane, as the majority of chemical species of interest (nitrogen dioxide, carbon monoxide, etc.) has its principal absorption bands in the mid-infrared region, wavelengths ranging from 3 to 10 μm. In this region, the line strengths are very high, around 100 or 1000 times greater than the lines of the near infrared region. Despite this difference, detecting in the near infrared is more effective than in the mid-infrared due to other aspects that must be considered [1, 2].

* ana@teisa.unican.es; phone +34 942 20 08 77 Ext. 16; fax +34 942 20 08 77; http://grupos.unican.es/gif

Photonics Applications in Industry and Research IV, edited by Ryszard S. Romaniuk, Stefan Simrock, Vladimir M. Lutkovski, Proc. of SPIE Vol. 5948, 59482J, (2005) · 0277-786X/05/$15 · doi: 10.1117/12.623141

At the moment, it is very difficult to obtain laser diodes with wavelengths above 2 μm working at room temperature. Besides, thanks to the great development of fiber communications, there are a great variety of low–cost and high emission power lasers in the market, emitting at the typical windows of optical communications. Taking into account that absorption spectroscopy is aimed at detecting the biggest spectral power, which is due to both the light source and the absorption lines of the gas, the smaller lines of the near infrared region are fairly compensated by the higher emission power of commercial lasers. For this reason, the present paper focuses on the detection of methane in the near infrared region where also the optical fiber presents its lowest degree of attenuation.

The spectrum of methane is mainly composed of two strong bands, centered at 3.3 μm (ν_3) and 7.6 μm (ν_4) respectively. The strongest line below 2 μm, named $2\nu_3$, is centered at 1.665 μm. Additionally, this band has two branches: R-branch (between 1.637 and 1.654 μm) and Q-branch (from 1.665 to 1.667 μm), the latter composed of several close lines. This Q-branch is the one to be analyzed in the present paper. A figure of the methane Q-branch with the estimated absorbance for the conditions of our experiment can be seen in Figure 1.

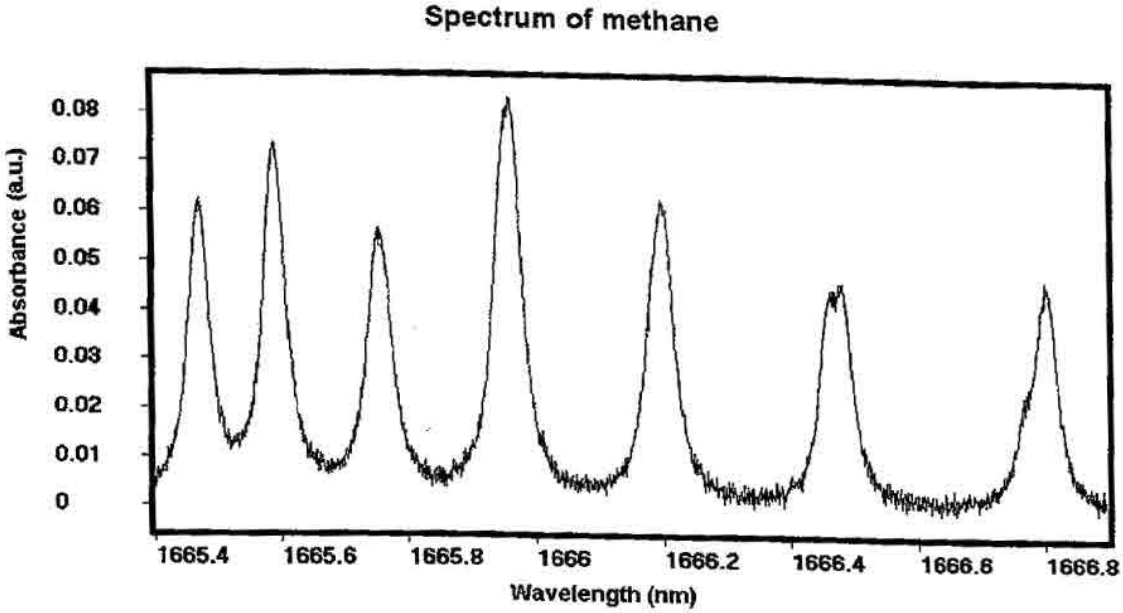

Figure 1: Q-branch of the 1.66 μm band of methane

In this work, a multi-line quantitation method will be used, choosing for this purpose the three strongest lines of methane in the Q branch at 1.66 μm. Specifically, the employed lines are centered at 1665.961 nm, 1666.201 nm and 1666.483 nm.

Due to the interest in methane, a lot of research has been done in this topic. One of the first articles about the detection of methane with frequency modulation spectroscopy was from Uehara in 1992 [3]. Using Q(6) line at 1.66 μm, a minimum detectable concentration of 0.3 ppm·m was achieved. Tanaka patented a gas detection device in 1993. Likewise, methane was detected at Q(6) line at 1.66 μm with a modulation scheme, resulting in a minimum detectable concentration of 1.3 ppm·m [6]. Schäfer compared Photoacoustic Spectroscopy (PAS) with Wavelength Modulation Spectroscopy (WMS) at R(3) (1.6537 μm) [7]. With the first approach, a minimum detectable concentration of 6ppm·m was obtained, whereas WMS managed to detect methane with a detection limit of 1.15 ppm. Iseki developed a portable remote methane detector using the $2\nu_3$ band R(3) line of methane with a WMS detection scheme. The estimated detection limit was 1.3 ppm·m with a measurement time of 100 ms [4,5]. Wainner also developed a handheld detector for detection of industrial gas leaks based on FMS. Using R(3) line, they achieved a detection sensitivity of 12 ppm·m [8]. Finally, Whitenett installed

fiber-optic methane sensor on a landfill site in Glasgow. Using Q(6) absorption line with the aid of WMS, methane was detected from 50 ppm to 100% with a 5 cm length gas cell [9].

On the other hand, chemometrics deals with the application of mathematical or statistical methods to the analysis of chemical data. Attending to the dimension of data, chemometrical methods can be classified as univariate and multivariate. Univariate methods, such as linear regression, use a single predictor to model a property, while multivariate methods take into account several predictable variables to model the system more accurately. Multivariate methods, despite being a more recent technique, have attracted a lot of interest [10,11]. The main reason of this success is that conventional univariate methods are unlikely to perform a good calibration of the system of interest, whereas multivariate methods, such as Classical Least Squares (CLS), Inverse Least Squares (ILS), Partial Least Squares (PLS), etc. are capable of better prediction due to the use of more complex models [12,13].

The aim of this paper is to demonstrate the benefits of applying multivariate calibration methods to the detection of gas species. For this purpose, this work combines the Inverse Least Squares (ILS) method with Wavelength Modulation Spectroscopy (WMS). We enclose the preliminary results of applying this combination of techniques to the detection of methane. Despite some problems with the stability of the laser used, which will be explained later, we demonstrate the superior performance of multi-line quantitation methods compared to that of single line methods.

2. WAVELENGTH MODULATION SPECTROSCOPY (WMS)

Wavelength Modulation Spectroscopy (WMS) presents great benefits compared to direct absorption spectroscopy. Although the main advantage of direct absorption is its ease of use, the sensitivity obtained with this technique is fairly smaller than that of WMS. This is due to the fact that, in WMS, the detection bandwidth is shifted from DC to higher frequencies to get rid of the excess noise (1/f). This technique is possible thanks to the laser diodes property of being easily modulated through its injection current [14]. Since is not the purpose of this paper to explain WMS thoroughly, only the most important equations will be introduced. A detailed study of wavelength modulation spectroscopy can be found in [15].

When a small sinusoidal modulation (with modulation frequency f_m) is applied to the injection current of a laser diode, the following equations are obtained:

$$\nu(t) = \overline{\nu} + \nu_o \cdot \cos(2\pi f_m t) \tag{1}$$

$$Io(t) = \overline{I}_o + i_o \cdot \cos(2\pi f_m t + \Psi) \tag{2}$$

where $\nu(t)$ is the instantaneous frequency, $I_o(t)$ is the output intensity, ψ the phase shift between the intensity modulation and the wavelength modulation, whereas ν_o and i_o are the modulation amplitudes around $\overline{\nu}$ and $\overline{I}_o$, respectively.

The second harmonic of the detected signal, after being absorbed by the gas of interest, is typically measured by a lock-in amplifier. The reason is that it contains the most important information of the WMS signal and, besides, it quite reduces the offset and baseline of the signal detected. To improve the sensitivity of the method, it is of great importance to choose the right value of the index of modulation, m, which is defined as the ratio between ν_o and the spectral width (HWHM) of the absorption line, $\Delta\nu$:

$$m = \frac{\nu_o}{\Delta\nu} \tag{3}$$

Taking into account that absorption lines in a gas at atmospheric pressure follow a Lorentzian profile, the optimum value for this parameter is m~2.2.

Usually, the second harmonic is normalized to the first harmonic in order to correct for misalignments, power fluctuations, etc. [18, 19]. In the following work, the ratio of the second and the first harmonic will be calculated in order to obtain more accurate measurements.

3. INVERSE LEAST SQUARES (ILS)

As stated before, Inverse Least Squares (ILS), also known as Multiple Linear Regression (MLR) or P matrix, is an example of multivariate method, where the dependent variable is calculated from multiple independent variables. ILS is based on the inverse Beer-Lambert equation, which rearranges the extended Beer-Lambert equation to multiple wavelengths so as to make the concentration dependent of the absorbance. The resulting equation represents the concentration as a linear combination of different absorbances, as can be seen below [20, 21].

$$C = A_\lambda \cdot P + E \tag{4}$$

where C is the matrix of concentrations with dimensions $m \times p$, A_λ is the matrix of absorbances at wavelength λ (dimensions $m \times k$), P the unknown matrix of coefficients ($k \times p$) and E the matrix of concentration errors ($m \times p$). On the other hand, m represents the number of calibration samples, p is the number of chemical species presented in the mixture and k, the number of wavelengths used for calibration ($k \geq p$).

To calculate the matrix of coefficients P, the error is assumed to be produced in the concentrations, and therefore, the mean square error in the concentrations is minimized. The solution to the previous equation is:

$$\hat{P} = (A_\lambda^T \cdot A_\lambda)^{-1} \cdot A_\lambda^T \cdot C \tag{5}$$

Then, to obtain the estimated concentration value, the following equation is used:

$$\hat{C} = A_{med,\lambda 1} \cdot \hat{P}_{\lambda 1} + A_{med,\lambda 2} \cdot \hat{P}_{\lambda 2} + A_{med,\lambda 3} \cdot \hat{P}_{\lambda 3} \tag{6}$$

This method has the advantage of calculating the concentration of very complex mixtures easily. The only requirement is to select the most appropriate wavelengths for detection. Nevertheless, it is limited by the fact that more samples than variables are required, which restricts the number of wavelengths to just a few. If the number of wavelengths is too big, the model can fail to predict new data. This phenomenon is called "over-fitting" and must be avoided [12].

4. EXPERIMENTAL SET-UP

The experimental set-up, shown in Figure 2, is composed of a Thomson DFB laser diode, model H-954, with central wavelength of 1666 nm. This laser diode is controlled in temperature and intensity by the LDC-3742B ILX controller in order to scan the three lines that will be used to detect the concentration of methane. Furthermore, the system has two Lock-in amplifiers. The first one, model SR-850, is used to measure the first harmonic and it also provides the laser modulation amplitude, whereas the second one measures the second harmonic. As can be seen in the diagram, the modulated intensity of the laser goes through a 7-cm-length transmissive gas cell where the light is absorbed by the gas. After going through the cell, it is detected by a Thorlabs PDA400 detector. The resulting signal is finally measured with the two Lock-in amplifiers and the ratio of the second and first harmonic calculated.

As stated before, there was a problem with the stability of the laser. When the measurements were taken, the laser introduced a lot of noise due to its long life. In consequence, the results here obtained are not as good as they are supposed to be. However, as it will be shown later, ILS approach gives better results in presence of noise.

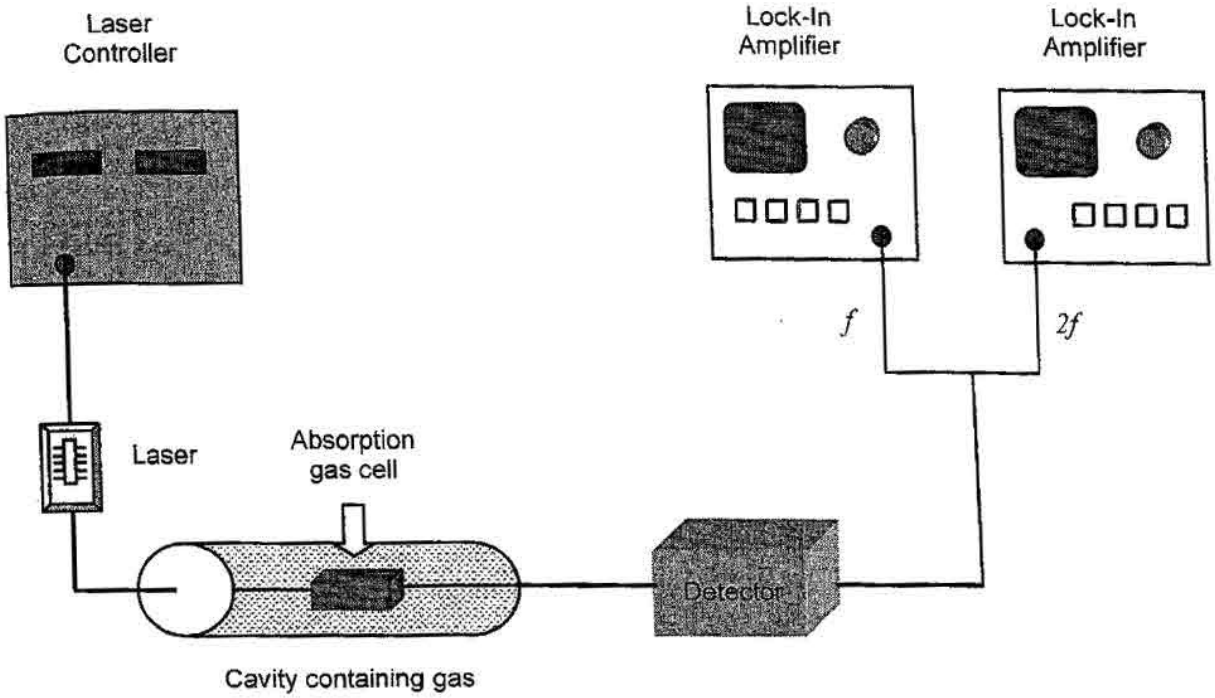

Figure 2: Measurement set-up

5. RESULTS

To calibrate the sensor system with the ILS method, four concentrations of methane have been used, specifically: 2.5%, 1%, 0.5% and 0.1%. It has been checked that the system is able to detect up to this last concentration. For each of the previous concentrations, three different measurements have been made, that will be the input data of the ILS method.

Then, the value of some of the parameters of the Inverse Least Squares method can be pointed:

- m= 4 number of calibration samples, i.e., number of concentrations used to calibrate.
- p= 1 number of chemical species.
- k= 3 number of wavelengths

With the above information, the dimensions of the ILS matrix are:

- Dimension of C and E: $m \times p$ = 4x1
- Dimension of A_λ: $m \times k$ = 4x3
- Dimension of P: $k \times p$ = 3x1

For this purpose, a program in Matlab has been developed which finds the peaks of the absorption lines and calculates the coefficients of matrix P from the ratio of the second and first harmonic. The coefficients P obtained are shown below:

$$P = \begin{pmatrix} 128.208 \\ 97.295 \\ 162.863 \end{pmatrix}$$

After the calibration process, the system is ready to calculate the methane concentration of an unknown sample from the absorbance values of the three absorption lines.

The estimated concentration as a function of the real concentration which results of applying the method is depicted in Figure 3.

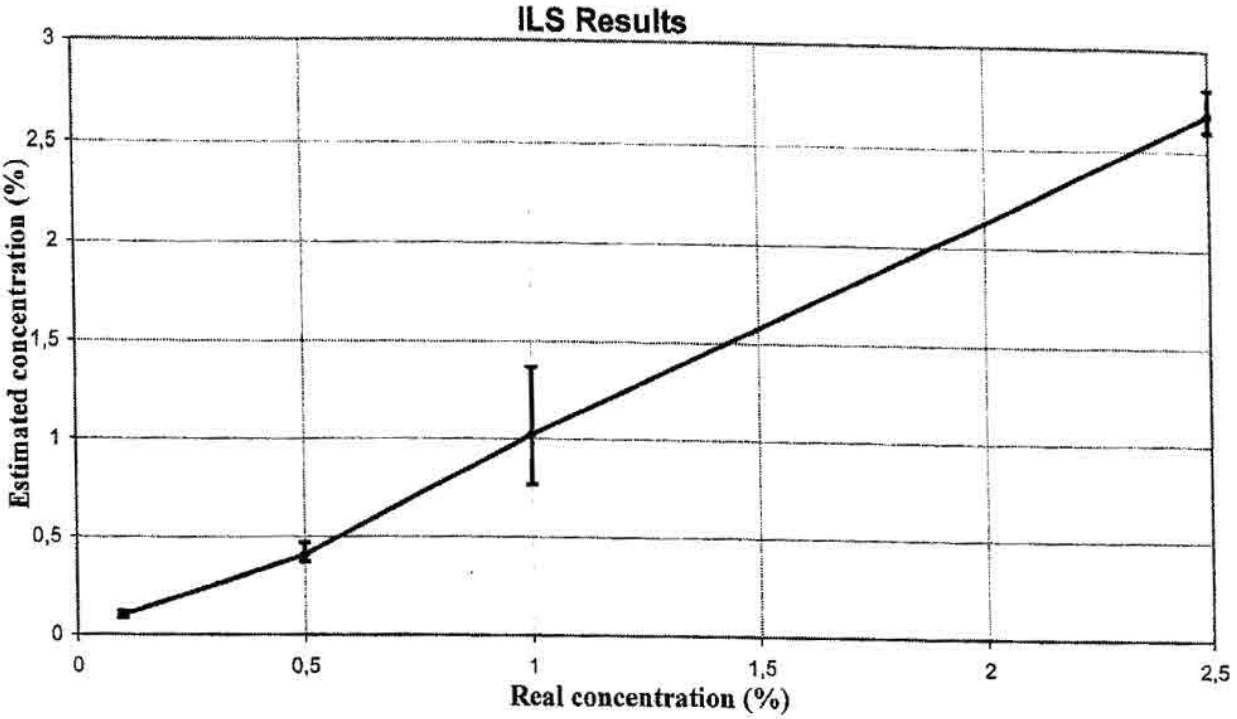

Figure 3: Result of applying the Inverse Least Squares method.

In Figure 3, the vertical axis represents the estimated value of concentration obtained with the algorithm whereas the horizontal axis shows the real value of concentration. This graph has been calculated from the mean of three values of estimated concentration. The error bars represent the maximum deviation from the mean in the set of the three measurements. Ideally, the estimated concentration should be equal to the real concentration and this curve as linear as possible. Besides, the error bars should be equal to zero.

As said before, multivariate methods are more adequate than univariate models, mainly because they reduce noise due to the use of more measurements, among other advantages [22]. If we compare the results obtained with ILS method (using three absorption lines of methane) with the results from the most usual single-line calibration method, i.e. linear regression (using for this purpose the Q(6) line of 1.66 μm band of methane), it can be seen that the Inverse Least Squares method gives better concentration readings in terms of accuracy and reliability. Furthermore, ILS method is less affected by system losses.

The comparison between both methods can be seen in Figure 4.

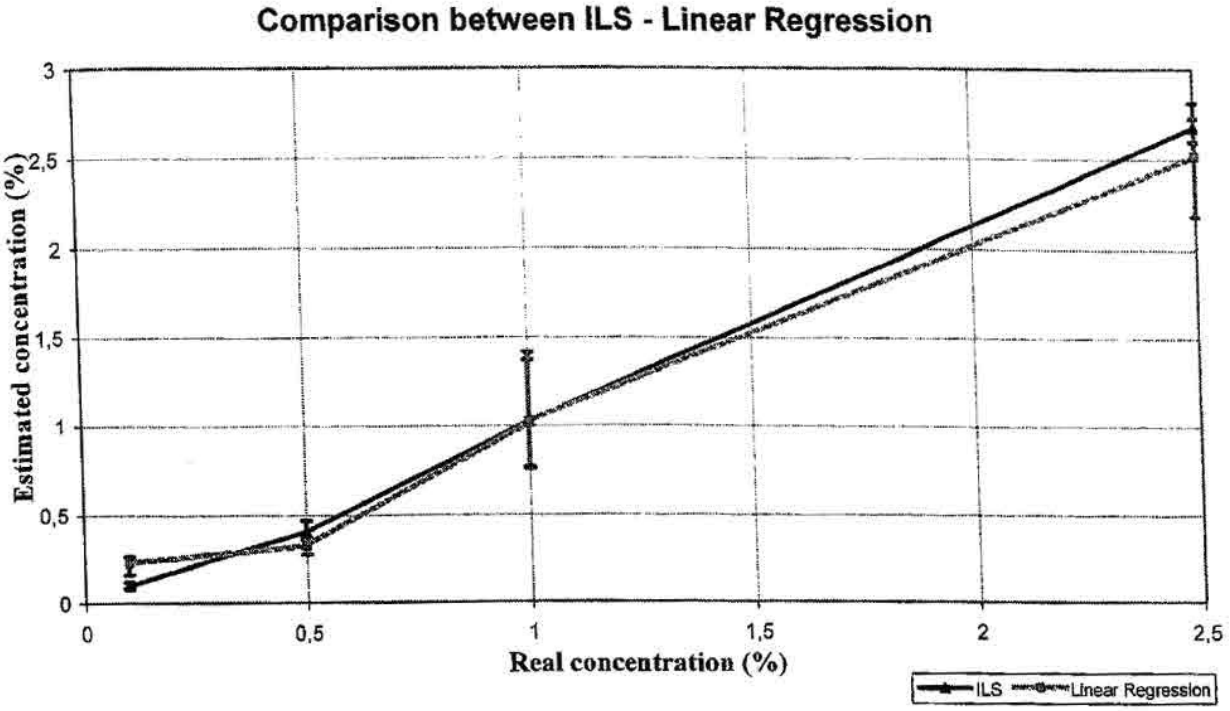

Figure 4: Comparison between the estimated concentration resulting of applying the Inverse Least Squares and the Linear Regression methods. Note that ILS presents less variability and that it is able to predict in a better way in a noisy ambient, as it happens in our experiment.

This figure demonstrates that ILS gives a superior performance in small concentrations, where the influence of noise is more important. Besides, the curve obtained is more linear. It can also be noticed that the error bars are smaller in ILS approach, meaning that the values calculated are more stable. Nevertheless, it must be taken into account that more time is needed to scan the three lines in the ILS approach than with single-line calibration methods, and must be considered if a fast response is required.

6. CONCLUSIONS

In this paper, a new combination of methods, Inverse Least Squares (ILS) with Wavelength Modulation Spectroscopy (WMS), to measure methane has been presented. Additionally, the preliminary results of applying this combination of techniques have been included.

It has also been demonstrated the benefits of using multi-line quantitation methods instead of single-line methods. Among the advantages of the former approach, it can be highlighted the better accuracy due to the use of three lines instead of just one and the no necessity of a calibration cell filled with 100% methane thanks to the calibration curve. On the other hand, it has the drawback of requiring more time to scan the three lines. It must be noted that the results here presented were affected by a lot of noise and instability and that will be improved in further research.