Sensing ethanol-blended gasoline with long-period fiber grating: a metrological perspective

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Abstract—This work shows a standard metrological characterization of an optical fiber sensor based on long period grating for assessing ethanol-blended gasoline. The sensor performance is evaluated according to the following metrological characteristics: response curve, calibration curve, sensitivity, resolution, repeatability, reproducibility, conformity, detection peak uncertainty, calibration system uncertainty, combined standard uncertainty and expanded uncertainty. The results showed that the sensor can determine ethanol concentrations in ethanol-gasoline blends as small as 0.14 % v/v, for a range between 0 and 40.0 % v/v (range I), and 0.30 % v/v, for a range between 40.0 and 100.0 % v/v (range II). However, the uncertainty analysis indicated that sensor response is mainly influenced by reproducibility and repeatability uncertainties. The result of measurement inherent to sensor can fluctuate up to ± 2.00 and ± 3.88 % v/v, for ranges I and II, respectively, for a confidence level of 95.45 %. Such complete performance characterization is fundamental to not overestimate the sensor capabilities.

Index Terms—Ethanol-blended gasoline, long period fiber grating, metrological characterization, optical fiber sensor

I. INTRODUCTION

Although fossil fuels have been historically considered the most important source of power for industrial process and machines, the use of biofuels has increased worldwide in last few years for reasons of energy security, diversity, and sustainability [1], [2]. Among the biofuels, ethanol has been widely employed in order to minimize the global dependency of non-renewable fossil fuels. Ethanol has also been used to mitigate the greenhouse effect and to support the sustainable development [1]-[3]. Additionally, ethanol is an octane booster with anti-knocking properties used as a substitute for both tetra-ethyl lead and methyl tertiary butyl ether (MTBE) in gasoline blends [4].

The ethanol-blended gasoline increases the engine torque, brake power, volumetric and brake thermal efficiencies and fuel consumption, while reduces the brake specific fuel consumption and equivalence air-fuel ratio. Besides, the ethanol can minimize the exhaustion emissions of carbon monoxide and hydrocarbons inherent to gasoline combustion [4], [5]. On the other hand, excessive ethanol concentrations in blends can induce structural problems, such as premature corrosion of the
fuel tank and the internal engine components, as well as can be associated with practice of adulteration for increasing illegally profits [6]. In this context, knowledge of ethanol concentration in ethanol-blended gasoline is fundamental for fuel distributors and consumers, engine manufacturers, fleet operators and regulatory agencies.

Aqueous extraction method is the standard test employed to assess the ethanol-blended gasoline [7]. Despite of widespread, this method has drawbacks such as high response time (approximately 15 minutes), poor resolution and human dependence. Besides, it demands segregation of compounds and is subject to parallax errors. Alternative techniques able to assess ethanol-gasoline blends have been reported on the literature [8]-[18]. These techniques are based on microfluidic sensor [8], infrared, near infrared and Fourier transform Raman spectroscopy [9]-[11], and optical fiber Fresnel-reflection-based and Raman-based sensor [12], [13]. Some works also report optical fiber sensors based on long period grating (LPG) employed to measure ethanol concentration in ethanol-blended gasoline [14]-[17], but with a lack of information about metrological performance of the sensor. In 2009, a preliminary metrological characterization of an LPG-based sensor applied to the analyses of ethanol-blended gasoline was reported [18]. Despite the well known LPG-based refractometric sensor ability, its worldwide acceptance depends on both specification and testing according to metrological standards [19]. The use of standard metrological characterization avoids misinterpretations about the sensor performance and establishes parameters that allow comparing different devices or methods. Recently, a set of tools for metrological evaluation of optical fiber grating sensors was reported [20], including uncertainty analysis of the measurements based on International Standard Organization’s Guide to the Expression of Uncertainty in Measurement (GUM) [21]. This metrological standard approach is used in this work to characterize an LPG-based sensor able to quantify ethanol-blended gasoline.

II. FUNDAMENTALS OF METROLOGY APPLIED TO LPG-BASED SENSOR

An LPG is an intrinsic optical fiber device produced by a periodic refractive index modulation in the fiber core along its length. This device shows periodicities of hundreds of micrometers and couples the optical power guided by the core fundamental mode to forward-propagating cladding modes at distinct wavelengths [22]. These modal couplings give rise to several attenuation bands in the fiber transmission spectrum which amplitude and central wavelength depend on the difference between the effective refractive indices of the core and the cladding modes, besides the grating period [22]. As changes in the surrounding medium refractive index result in cladding effective refractive index changes, the resonant bands amplitude and position are parameters that allow the employment of the LPG as a refractometric sensor.

When the ethanol-blended gasoline is analyzed by the LPG refractometric sensor, the measurand is the ethanol concentration in the sample. The LPG transmission spectrum for different samples can be measured by an interrogation unit and the resonances central wavelengths can be obtained with a
Gaussian fitting. These wavelengths correspond to the sensor responses and must be compared with the previously known \textit{calibration curve} of the sensor. In this specific application of the LPG refractometric sensor, the \textit{calibration curve} relates the sensor response to the ethanol concentration on the blend. This is the first step to obtain the ethanol concentration or the \textit{result of the measurement}.

In order to complete this information it is necessary to supply the \textit{expanded uncertainty} inherent to the \textit{result of the measurement}. This procedure can be straightforward if the main metrological characteristics of the sensor are known. Nevertheless, to assure an efficient metrological evaluation of the sensor performance, it is necessary to define and understand the terminology associated with the measurement procedure. A comprehensive guide for this procedure can be found in [20].

III. METHODOLOGY

An LPG, with period of 540 μm and total length of 21.6 mm, was written in a standard telecommunication optical fiber (SMF-28®, from Corning) by the point-by-point technique applying electrical arc discharges from a fusion splicer. A super-luminescent LED (MRV Communications, central wavelength at 1547.1 nm, half bandwidth of 54.8 nm) and an optical spectrum analyzer (OSA, Anritsu-MS9710B, resolution of 0.1 nm, minimum wavelength stability of ± 5 pm) were used to acquire the LPG transmission spectra. These spectra were recorded in a personal computer connected to OSA by RS-232 interface. Gaussian curves were fitted to the recorded spectra in order to determine the central wavelength of the resonance bands.

To keep the LPG immersed in the sample it was inserted into a glass cell. In order to avoid the effects of cross-sensitivity in the LPG response [23], the optical fiber tips were held, keeping the grating under constant longitudinal strain. Additionally, the temperature of the liquid samples was monitored with a type-K thermocouple, with a resolution of 0.05 °C, positioned close to the LPG. Throughout the measurements the temperature was kept at (20.0 ± 0.5) °C.

The LPG response for different ethanol-blended gasoline samples, prepared by adding 0.0, 20.0, 40.0, 60.0, 80.0 and 100.0 % v/v of anhydrous ethanol to pure gasoline, was measured. The estimated limit of error inherent to the samples preparation procedure was 0.1 % v/v. The experiments were carried out by introducing each one of the ethanol-gasoline blends into the glass cell, in increasing order of ethanol concentration. Twelve consecutive measurements of the LPG response under repeatability conditions and four consecutive measurements under reproducibility conditions were carried out. In order to minimize errors and to clean the grating, a sample of anhydrous ethanol was introduced into the glass cell, after each ethanol-gasoline blend was drained from it. Moreover, the LPG response was measured relatively to its response when the grating was in contact with anhydrous ethanol, which was used as a reference substance [16].

These procedures allowed establishing the main metrological characteristics of the LPG-based sensor. In a sense, the following characteristics of the sensor were obtained according to standard approach reported in [20]: \textit{response curve}, \textit{calibration curve}, \textit{sensitivity}, \textit{resolution}, \textit{repeatability},
reproducibility, conformity, detection peak uncertainty, calibration system uncertainty, combined standard uncertainty and expanded uncertainty for a confidence level of 95.45%. The analytical expressions to compute the combined standard and expanded uncertainties were also obtained.

IV. RESULTS AND DISCUSSIONS

Figure 1(a) shows the response curve (the set of experimental points, including the error bars associated with the sensor response to the measurands) of the LPG-based sensor for the ethanol concentration range from 0.0 up to 100.0 % v/v at (20.00 ± 0.50) °C. The square symbols are the arithmetic mean of four cycles of independent measurements performed under reproducibility conditions. The error bars are the combined standard uncertainties and were calculated according to standard uncertainties inherent to the following sources: experimental standard deviation of the mean of the LPG resonance wavelength measured under repeatability and reproducibility conditions (Type A uncertainties), OSA minimum wavelength stability uncertainty (Type B uncertainty), Gaussian fitting uncertainty associated to the determination of the LPG resonance wavelength (Type B uncertainty), and the limit of error inherent to the samples preparation procedure (Type B uncertainty). All Type B uncertainties were considered characterized by symmetric rectangular probability distributions. As LPG responses were evaluated relatively to a reference substance (anhydrous ethanol), error bars were calculated by considering the uncertainty propagation resulting from the subtraction between data. In order to express all uncertainties in nanometer (the same unit of the LPG response), the limit of error inherent to the samples preparation procedure (expressed in % v/v), was multiplied by the LPG preliminary sensitivity curve. This preliminary sensitivity curve corresponds to the numerical derivative of the preliminary calibration curve obtained by fitting a non-linear function to the LPG responses without taking into account their error bars.

Calibration curve of the LPG-based sensor was obtained by fitting a non-linear empirical function [15]-[18] to the LPG responses according to the method of least squares, taking into account the error bars. The calibration curve is the dotted line shown in Fig. 1 and its mathematical expression is:

\[
\delta \lambda_{LPG} (E%) = a - b \cdot c \cdot E% \\
(1),
\]

where, \(\delta \lambda_{LPG}\) is the LPG resonance wavelength shift relatively to the resonance wavelength when the grating was in contact with the reference substance, \(E%\) is the ethanol concentration in the ethanol-gasoline blend, and \(a = (1.12705 ± 0.04909)\) nm, \(b = (4.59028 ± 0.04588)\) nm, and \(c = (0.98568 ± 0.0003)\) are constants. The determination coefficient obtained was \(r^2 = 0.99995\).

If \(\delta \lambda_{LPG}\) is measured, the ethanol concentration \((E%)\) can be determined by:

\[
E% = \ln \left( \frac{a - \delta \lambda_{LPG}}{b} \right) \cdot (\ln c) \cdot \mathcal{P} \\
(2).
\]

Consequently, the standard uncertainty inherent to ethanol concentration \(u_{E%}\) can be computed by:
\[ u_{E_x}^2 = \sum_{i=1}^{4} \left( \frac{\partial E_x}{\partial x_i} \right)^2 u_{x_i}^2 + \sum_{i=1}^{4} \sum_{j=1}^{4} \left\{ \frac{1}{2} \left( \frac{\partial^2 E_x}{\partial x_i \partial x_j} \right)^2 + \frac{\partial E_x}{\partial x_i} \frac{\partial E_x}{\partial x_j} \right\} u_{x_i}^2 u_{x_j}^2 = \sum_{i=1}^{4} \left( \frac{\partial E_x}{\partial x_i} \right)^2 u_{x_i}^2 + \psi \]  

(3)

where, \( x_i \) are \( i \)-variables that characterize \( E_{E_x} \) (\( \delta \lambda_{LPG} \), \( a \), \( b \), or \( c \)), \( u_{x_i} \) is the \( i \)-standard uncertainty estimated for the \( i \)-variables that characterize \( E_{E_x} \) and \( \psi \) represents the higher-order terms in the Taylor series expansion associated with non-linearity of \( E_{E_x} \).

The expanded uncertainty inherent to ethanol concentration measurements (\( U_{E_{E_x}}^p \)) is computed by:

\[ U_{E_{E_x}}^p = u_{E_{E_x}} \cdot k_{v_{E_{E_x}}}^p \]  

(4)

where, \( k_{v_{E_{E_x}}}^p \) is the respective coverage factor commonly available in statistical tables with the name of \( t \)-Student coefficient as a function of both the required confidence level (\( p \)) and the number of effective degrees of freedom (\( v_{E_{E_x}} \)), which is obtained by Welch-Satterthwaite formula [21]:

\[ v_{E_{E_x}} = u_{E_{E_x}} \left[ \sum_{i=1}^{4} \left( \frac{\partial E_{E_x}}{\partial x_i} \right)^2 \left( \frac{u_{x_i}}{x_i} \right)^2 \right]^{-1/2} \]  

(5)

In the last expression, \( v_{x_i} \) is the \( i \)-number of degrees of freedom associated with \( u_{x_i} \). Therefore, a result of the measurement from LPG-based sensor can be provided by \( E_{E_x} \pm u_{E_{E_x}} \) or \( E_{E_x} \pm U_{E_{E_x}}^p \). However, the expressions (3), (4) and (5) are rather complex and not desirable for final users of the sensor. Besides, the use of these expressions depends on replicate measurements in optical domain. So, in order to simplify the procedure for obtaining \( u_{E_{E_x}} \) and \( U_{E_{E_x}}^p \), it is recommended to use the standard approach based on metrological characteristics of the sensor already expressed in terms of measurand unit [20].

Figure 1 (b) shows the sensitivity and resolution curves for the LPG-based sensor. Both curves are non-linear as the LPG-based sensor calibration curve is markedly non-linear. The sensitivity curve was obtained by numerical derivative of the calibration curve with respect to ethanol concentration.
The resolution curve was obtained dividing the OSA minimum wavelength stability by the sensitivity curve. For an ethanol concentration range between 0 and 100.0 % v/v, the resolution varies from 0.09 up to 0.45 % v/v, being the lower resolution value 5 times smaller than the higher one. As a consequence, only one value of resolution is not representative of the sensor performance along the whole range of concentrations. In order to overcome this drawback, the sensor metrological characteristics were calculated for two concentration ranges: 0.0 – 40.0 % v/v (range I); 40.0 – 100.0 % v/v (range II). For each range, the average sensitivity was computed by the slope of the linear fit to experimental points resulting in (0.0506 ± 0.0036) nm / % v/v, and (0.0237 ± 0.0023) nm / % v/v for the ranges I and II, respectively.

Table I summarizes the sensor metrological characteristics and uncertainties for both concentration ranges. Initially, the metrological characteristics were obtained in nanometer (nm); afterwards, they were individually divided by the average sensitivity for the respective concentration range and expressed in ethanol concentration units (% v/v). The resolution was calculated based on OSA minimum wavelength stability and the detection peak uncertainty, repeatability and reproducibility are the maximum values for each range.

<table>
<thead>
<tr>
<th>Metrological characteristic</th>
<th>Uncertainty</th>
<th>Range</th>
<th>LPG sensor (% v/v)</th>
<th>Type</th>
<th>( u_i ) (% V/V)</th>
<th>( v_i )</th>
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<tbody>
<tr>
<td>resolution</td>
<td></td>
<td>I</td>
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<td>B</td>
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<tr>
<td></td>
<td></td>
<td>II</td>
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<td></td>
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<td>repeatability</td>
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<td></td>
<td></td>
<td>II</td>
<td>0.89</td>
<td></td>
<td>0.89</td>
<td></td>
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<tr>
<td>reproducibility</td>
<td></td>
<td>I</td>
<td>0.65</td>
<td>A</td>
<td>0.65</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>1.24</td>
<td></td>
<td>1.24</td>
<td></td>
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<tr>
<td>conformity</td>
<td></td>
<td>I</td>
<td>0.11</td>
<td>B</td>
<td>0.06</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>0.65</td>
<td></td>
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<tr>
<td>detection peak uncertainty</td>
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<tr>
<td>calibration system</td>
<td></td>
<td>I, II</td>
<td>0.10</td>
<td>B</td>
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<td>standard uncertainty</td>
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<td></td>
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<tr>
<td>(( u_i ))</td>
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<tr>
<td>expanded uncertainty</td>
<td></td>
<td>I</td>
<td></td>
<td></td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>(( U^{95.45%} ))</td>
<td></td>
<td>II</td>
<td></td>
<td></td>
<td>3.88</td>
<td></td>
</tr>
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</table>

The metrological characteristics supplied in Table I consider the uncertainty propagation from the subtraction between LPG responses for ethanol blended gasoline sample and reference substance. In order to estimate the combined uncertainty, each metrological characteristic was considered one uncertainty source and, consequently, each one was transformed in standard uncertainty (\( u_i \)). After, the standard uncertainties were combined among themselves and with the calibration system.
uncertainty, which is the limit of error inherent to the samples preparation procedure. All Type B uncertainties were considered characterized by symmetric rectangular probability distributions. Then, the combined standard uncertainty \( (u_c) \), the expanded uncertainty for a confidence level of 95.45 % \( (U_{95.45\%}) \), the number of effective degrees of freedom \( (v_{eff}) \), and the coverage factor for a confidence level of 95.45 % \( (k_{v_{eff}}) \) were determined according to [26] and considering that standard uncertainties are independent among themselves. The computed values for \( v_{eff} \) and \( k_{v_{eff}} \) were respectively: 6.30 and 2.516 (range I), 7.42 and 2.429 (range II).

It is also important to observe that in general the uncertainties obtained for range I are smaller than uncertainties for range II. This proves that is pertinent to sub-divide the ethanol concentration range in order to not overestimate the sensor performance. The values of \( u_c \) and \( U_{95.45\%} \) can be used as uncertainties in the result of the measurement when only one measurement is executed. In this case, it is not necessary to apply the expressions (2), (3) and (4). Hence, a result of the measurement from LPG-based sensor can straightforward be provided by \( E_\% \pm u_c \) or \( E_\% \pm U_{95.45\%} \). If we follow the GUM recommendation [21] about to determine uncertainties when corrections from a calibration curve are not applied, the next combined standard uncertainty \( (u_c) \) values are obtained, without taking into account the conformity uncertainty: 0.79 % v/v (for range I), and 1.54 % v/v (for range II). These values are smaller than the values shown in Table I. In this case, a final uncertainty \( (U_{final}) \) should be estimated based on the sum between the conformity and the expanded uncertainty. The \( U_{final} \) values for both ethanol concentration sub-range (2.10 % v/v, for range I; 4.53 % v/v, for range II) are higher than expanded uncertainty \( (U_{95.45\%}) \) shown in Table I.

Finally, the contribution of each standard uncertainty \( (u_i) \) to the value of combined standard uncertainty \( (u_c) \) is shown in Fig. 2.

![Fig. 2. Percentual contribution to combined standard uncertainty of each standard uncertainty estimated for each concentration range.](image)

It is possible to observe that the major contributions (more than 90 %) for each range are associated with both the repeatability and the reproducibility uncertainties, which are Type A uncertainties.
Additionally, the contribution of the *Type B uncertainties* in $u_c$ is much smaller than the contribution of the *Type A uncertainties*. If the reference substance was not used, then the *combined standard* and *expanded uncertainties* would increase at least 2 times for range *I* and at least 4 times for range *II*, due to the increase of both the *repeatability* and the *reproducibility uncertainties*.

### V. Conclusions

A standard metrological characterization of an LPG-based sensor for assessing ethanol-blended gasoline was described, following the global trends foreseen for the optical fiber sensor technology and fuel analysis method. Although some works have reported that it is possible to use an LPG for this purpose, it was the first time that a paper provides further information about performance of the sensor, including uncertainties analysis. Under the light of the standard approach recently reported in the literature, the LPG-based sensor metrological characteristics were investigated for a *confidence level* of 95.45%.

It was estimated that LPG-based sensor can determine ethanol concentrations in ethanol-gasoline blends as small as 0.14 or 0.30 % v/v, depending on the concentration range. On the other hand, the *uncertainty* analysis indicated that the *result of measurement* inherent to sensor can fluctuate up to ± 2.00 or ± 3.88 % v/v for the same ranges, taking into account a *confidence level* of 95.45 %. This thorough characterization of the sensor by means of a metrological perspective leads to a well-specified and more reliable device.

In order to provide a useful comparison with other sensing techniques, the whole set of uncertainties to each specific sensing application must be carefully identified and evaluated. A comparison that takes in account just type B uncertainties is not enough to provide information about the performance of the sensors. The combined uncertainty is the main parameter, which contains information about both types A and B uncertainties. It was observed that *repeatability* and *reproducibility uncertainties*, both *Type A uncertainties*, are dominant in LPG-based sensor. The *uncertainties* associated with *reproducibility* represented more than 60 % of all *uncertainties* sources. Besides, *uncertainties* associated with *repeatability* represented more than 30 % of all *uncertainties* sources. In a sense, the *Type B uncertainties* could be disregarded, probably due to combined action between the cross-sensitivity of the LPG-based sensor and environmental conditions of the measurement. In order to minimize the *Type A uncertainties* it is recommended to increase the number of the measurements, to implement a stable control of the environmental conditions and to use a reference substance. Here, the use of reference substance diminished the *combined standard* and *expanded uncertainties* at least 2 times, for range *I*, and 4 times, for range *II*.

In conclusion, the standard metrological characterization of the LPG-based sensor provides a reliable tool for fuel industry. The sensor can determine ethanol-blended gasoline in real time and without human intervention, avoiding the drawbacks inherent to aqueous extraction method. The sensor is adequate for controlling industrial process in an automatic way. Besides, the sensor presents
a small physical size and can be easily integrated to portable measurement systems which are useful for fuel blenders, distributors and consumers, engine manufacturers, fleet operators, and regulatory agencies.

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