Long Period Grating Transducer for Measurement of Ethanol Concentration in Water Solution

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***Abstract*— This work shows results of the applicability of an optical fiber device, the long period grating, as a transducer to determine the ethanol concentration in samples obtained by the mixture of ethanol and pure water in different proportions. The amplitude and central wavelength of the grating resonance attenuation was measured with the device immersed in samples with ethanol concentration ranging from 0 % to 99.6 %. The device performance, when interrogated in wavelength and amplitude, was analyzed considering its sensitivity, resolution, repeatability, linearity and uncertainty. The results showed that the transducer can be used to measure the ethanol-water concentration with resolution of up to 0.23 %.**

***Index Terms*—** Concentration measurement, Ethanol-water solution, Long period fiber grating, Optical transducer.

I. INTRODUCTION

The ethyl alcohol or ethanol has a widespread use in several sectors as beverage industries, personal care products, pharmaceutical and chemical industry. At room temperature, ethanol is an organic molecule (CH_3CH_2OH), liquid, colorless, volatile, flammable and soluble in water, with characteristic flavor and smell. As the ethanol molecule also has a non-polar end, it also dissolves non-polar substances, including most essential oils, as well as numerous flavoring, coloring and medicinal agents.

Furthermore, along the past few years the search for alternative and renewable energy sources, besides the biomass availability and the great ethanol applicability as a fuel for the internal combustion engines [1]-[3], encouraged the ethanol production. As a consequence, the ethanol industry becomes a very attractive market to invest. This interest comes from the ethanol high-performance as a motor fuel that cuts poisonous exhaust emissions, being harmless for the environment. Besides, it is a renewable fuel made from plants, provides high octane at low cost, can be used in all petrol engines without modifications, and is biodegradable without harmful effects to the environment.

However, ethanol is a versatile solvent miscible in all proportions with water. Consequently, a carefully monitoring of water content in ethanol is fundamental for the product commercialization as the product cost and destination are specified as a function of its purity.

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In despite of the existence of traditional techniques to measure the ethanol concentration in water, optical fiber intrinsic devices like long period gratings (LPG) applied as transducers present a potential capability for in-situ and real-time monitoring without the need for handling the substance under test, as well as they can be easily multiplexed for multipoint sensing. Besides, fiber optic transducers present surpassing properties as low weight and size, electromagnetic immunity and electrical passivity [4]-[7]. Furthermore, the device sensitivity, resolution and measuring range can exceed the characteristics of standard transducers. In the past few years, LPGs were produced and applied with success as temperature, strain and refractive index sensors for several applications [8]-[14].

This work investigates the applicability of a LPG as a transducer device to measure the concentration of ethanol in water solutions. The device performance was analyzed considering its sensitivity, resolution, repeatability, linearity and uncertainty for two different ranges of operation and when the device was interrogated whether in wavelength or amplitude.

II. THEORY

A LPG is a periodic modulation of the fiber core refractive index produced along its length. The resultant device present periodicities ranging from 100 μm to 1 mm, and couples light from the guided fundamental mode to forward-propagating cladding modes at distinct wavelengths [8]-[9]. *Fig.* 1 depicts the LPG principle of operation, showing the coupling between the fiber modes that fulfill a specific phase matching condition.

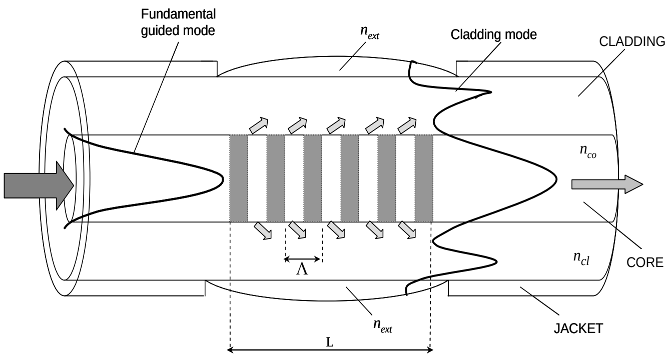

Fig. 1. LPG principle of operation.

The optical power coupled to the cladding modes are strongly affected by fiber imperfections, micro and macro bending, and by boundary condition at the cladding-external medium interface. Thus, as the optical fiber propagates several cladding modes, the light coupled from core to the cladding modes leaks out the fiber, leaving *n* dips in the transmission spectrum, each one corresponding to a specific coupling [8]-[9] with resonance wavelengths (λ_n) governed by

$$\lambda_n = \left(n_{eff}^{co} - n_{eff}^{cl,n}\right)\Lambda = \delta n_{eff}\Lambda \tag{1}$$

In this equation, n_{eff}^{co} and $n_{eff}^{cl,n}$ represent the effective refractive indices of the fundamental core guided mode and the *n*-th LP_{0n} cladding mode, respectively, Λ is the grating pitch, and δn_{eff} represents the difference between the effective refractive indices.

For resonant wavelengths the transmission (T_n) through the core is given by the following relation, when a sinusoidal profile of modulation is produced in the fiber core [8]-[9]:

$$T_n = \cos^2(\kappa_n L) = \cos^2\left(\pi \Delta n_{co} I \lambda_n^{-1} L\right) \tag{2}$$

where L is the grating length, κ_n is the coupling coefficient for the n-th LP_{0n} cladding mode, Δn_{co} is the amplitude of refractive index modulation induced in core fiber and I is the integral of superposition between the resonance modes.

Changes that occur in the refractive index of surrounding medium will affect the cladding effective refractive indices and, as a direct consequence, attenuation dips experience both changes in its amplitude (T_n) and shifts in the resonance wavelengths (λ_n). These spectral changes can be used to measure the external medium refractive index and allows the LPG to be used as a transducer device, for example to determine the concentration of a specific substance in a binary mixture.

III. METHODOLOGY

A LPG (Λ= 595 µm and L = 3.5 cm) was written in a standard telecommunication optical fiber applying an electrical arc discharge from a fusion splicer using the point-to-point technique [11]. The device was inserted into a glass cell specially designed to keep the sample in contact with 25 cm^3 of liquid sample, see *Fig.* 2. After the LPG insertion into the container, the fiber ends are held immobile to keep constant the longitudinal strain and to avoid fiber-bending interference on the sensor response. Another parameter controlled during the measurements is the sample temperature, which remained constant within (20 ±0.5) ºC.

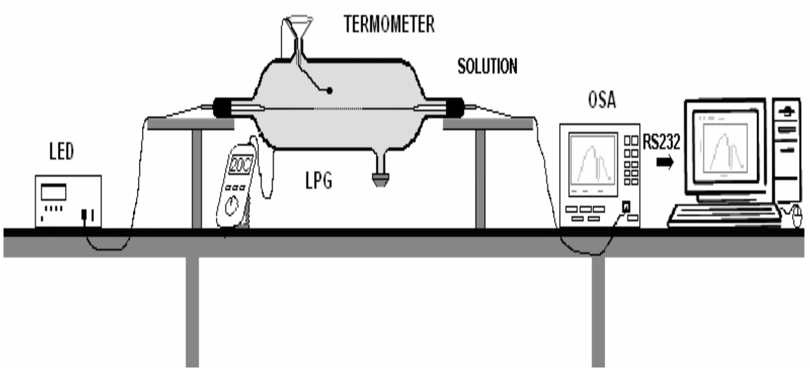

Fig. 2. Experimental set-up employed to characterize the LPG transducer.

A super-luminescent LED (MRV Communications, central wavelength 1547.1 nm and half bandwidth of 54.8 nm) and an optical spectrum analyzer (OSA, Anritsu-MS9710B, wavelength stability of ± 5 pm and level stability accuracy of ± 0.02 dB), are employed for the transmission spectrum measurements. The amplitude and resonance wavelength of the LPG dip was measured with the device immersed in samples obtained from the mixture of ethanol and pure water in different proportions. Samples were prepared with percentages of 99.6, 94.6, 89.6, 84.7, 79.7, 59.8, 39.9, 19.9 e 0.0 of ethanol in pure water. For all the samples analysis, the wavelength shifts are measured

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relatively to the LPG immersed in pure water sample used as a reference fluid. The use of a reference fluid serves two purposes: to remove any trace of each sample between two different measurements and to assure that the LPG dip returns to the original wavelength after each measurement. An Abbe refractometer (Bausch & Lomb, resolution of ± 0.0001, operating at 589.3 nm) was employed to measure the samples' refractive indices, just after the sample was drained from the glass cell.

The experiments were carried out by introducing individually each one of the samples into the glass cell following a crescent order of ethanol concentration, and making seven consecutive measurements of the LPG spectrum with the device immersed in each sample. This procedure allows the LPG calibration in the used range of ethanol concentrations. Then a linear fit to the experimental points were done for two different ranges of ethanol concentrations, lower and higher than 89.6 % named range A and range B, respectively. For each range, the angular coefficient of the straight line fitted to the experimental points is the transducer sensitivity, and the major absolute deviation presented by the experimental points with respect to the fitted line is the device linearity. For each range of measurement, the minimum detectable unit of measure was considered as the transducer resolution and the repeatability was obtained by the average standard deviation. The LPG transducer characteristics were calculated in units of volume concentration and compared with those obtained with the Abbe refractometer.

IV. RESULTS AND DISCUSSIONS

The samples' refractive indices were measured with the Abbe refractometer and are presented in the graph of *Fig*. 3. The refractive index shows a non-linear dependence with the increase of ethanol concentration in the samples from 0% to 100%, which is in accordance with the literature [12].

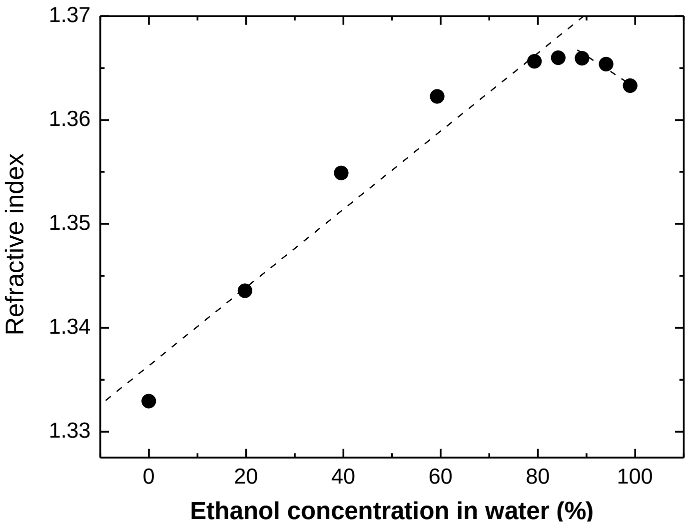

Fig. 3. Samples refractive indices measured with the Abbe refractometer and the best linear fit for samples with ethanol concentration lower and higher than 89.6%.

From the graph it is possible to distinguish two distinct ranges of ethanol concentration to which the refractive index variation shows an approximately linear behavior, below and above 89.6 %. Samples' refractive indices rise with the increase of ethanol concentration in the first concentration range and decrease in the second one.

Fig. 4 shows the LPG transmission spectrum when the device was immersed in samples obtained from the mixture of ethanol and pure water in different proportions. As the increase of ethanol proportion in pure water samples results in samples with different refractive indices, the LPG sensor immersed in such samples shows different wavelengths and transmission intensities for the resonance dip. It can be observed that the resonance wavelength shifts towards lower wavelengths when the external medium refractive index increases while its amplitude decreases.

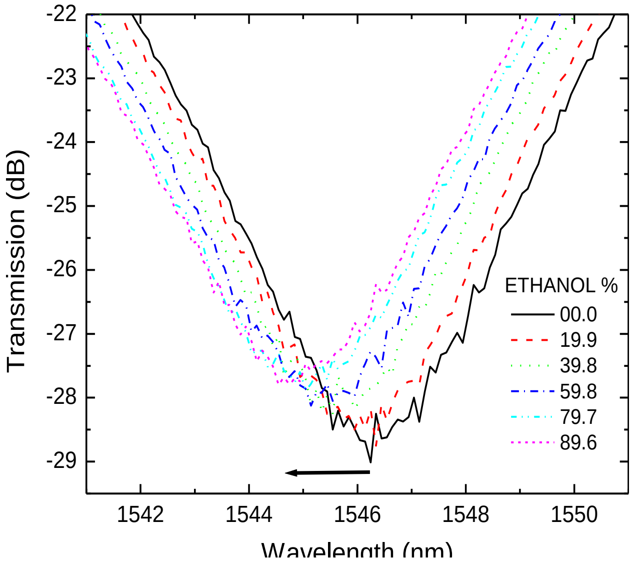

Fig. 4. Transmission spectra of LPG immersed in samples of water with ethanol in different proportions.

Figs. 5 and 6 show the changes in the wavelength and amplitude of the LPG resonance related to the samples' refractive indices. In these graphs the experimental data of LPG wavelength shift and amplitude were obtained with respect to the LPG immersed in pure water.

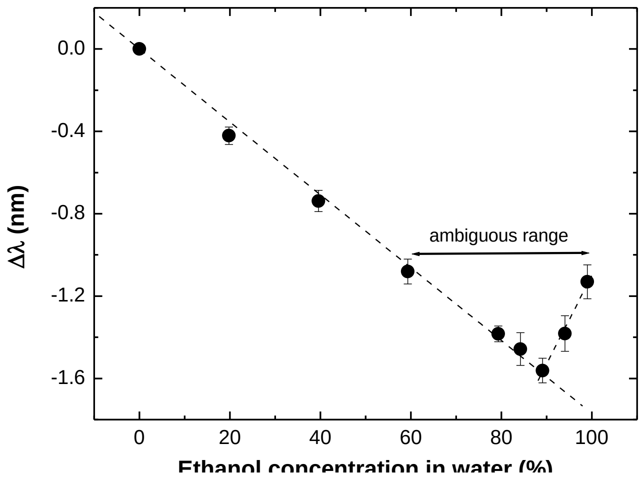

Fig. 5. LPG response measured in wavelength when immersed in samples of water with ethanol in different proportions and the best linear fit to samples with ethanol concentration lower and higher than 89.6%.

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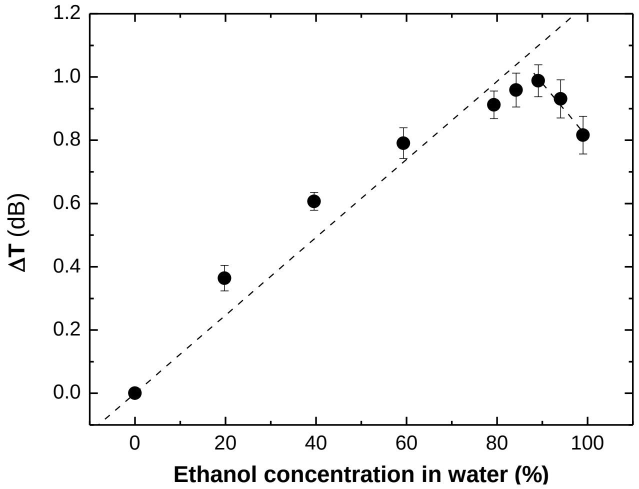

Fig. 6. LPG response measured in intensity when immersed in samples of water with ethanol in different proportions and the best linear fit to samples with ethanol concentration lower and higher than 89.6%.

As the refractive index changes from 1.3329 to 1.3660, with the increase of ethanol proportion in water from 0 % to 89.6 %, a monotonic behavior was observed for the LPG response in wavelength. For ethanol proportions higher than 89.6 %, the sample refractive index decreases, as shown in *Fig.* 3, and the LPG wavelength shifts towards higher values. Besides, the dip amplitude shows a behavior similar to that presented by refractive index.

From the results presented in *Figs.* 3, 5 and 6, were obtained the sensitivity, resolution, repeatability, linearity and uncertainty for the LPG and refractometer in two distinct ranges of ethanol concentration, see Table I. The columns A correspond to the ethanol proportion ranging from 0 % to 89.6 %, and the columns B to higher ethanol proportions up to a maximum value of 99.6 %.

Better linearity and resolution were obtained with the LPG transducer wavelength coded. In despite of the refractometer presents more repeatability, the uncertainties in its measurements are superior than the uncertainties obtained for the LPG wavelength coded.

TABLE I. CHARACTERISTICS OF MEASUREMENT (% REFERS TO THE ETHANOL PROPORTION IN WATER).

	Abbe refractometer n (*RIU x10^{-4})		LPG $\Delta\lambda$ (*nm x 10^{-2})		LPG ΔT (*dB x 10^{-2})	
Concentration range / Characteristic	A	B	A	B	A	B
Sensitivity (unit* / %)	3.74	-3.04	-1.76	4.27	1.23	-1.70
Resolution (%)	0.53	0.66	0.57	0.23	3.26	2.36
Repeatability (%)	0.89	1.48	2.71	1.79	3.09	3.34
Linearity (%)	5.28	1.70	2.01	0.62	4.89	1.18
Combined uncertainty (%)	5.38	2.35	3.42	1.90	6.64	4.25

Although the results of *Figs.* 5 and 6 summarized in Table I show that the LPG device can be employed to distinguish samples with different ethanol concentrations, the ambiguous result obtained for samples with ethanol proportions in water ranging from 60 % to 100 % (see *Fig.* 5) is detrimental for sensing purposes. However, this ambiguity problem is easily solved when a controlled amount of pure water is intentionally added to the sample under analysis. The water addition to a specific sample corresponds to a decrease in the ethanol concentration, resulting in a shift in the sample's refractive index towards higher or lower values, depending on the initial ethanol concentration. Two samples within this ambiguous range, with initial ethanol concentrations of 60 % and 99.6 %, were chosen to exemplify the tests to solve the ambiguity. With the LPG immersed in these samples, its wavelength response was followed after two consecutive decreases of 1% in the initial ethanol concentration; *Figs.* 7 and 8 show the wavelength shifts measured in the LPG resonance.

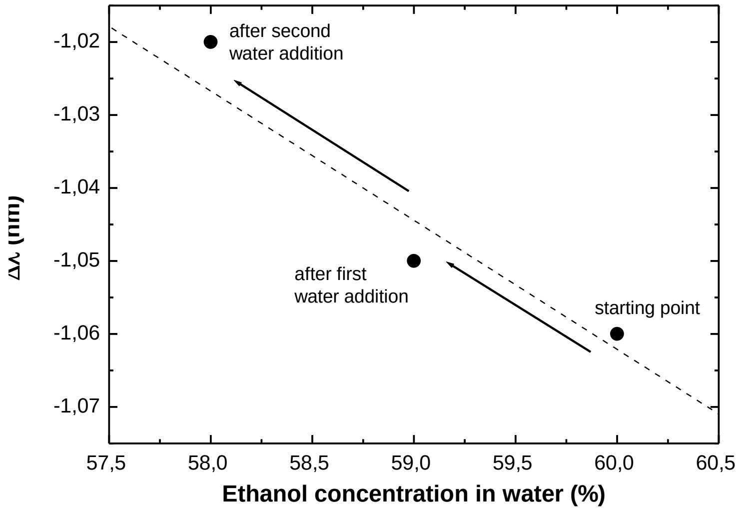

Fig. 7. LPG response when water is added to a sample with initial ethanol concentration of 60%, resulting in two consecutive decreases of 1% in the initial ethanol concentration. The dashed line corresponds to the best linear fit of figure 5.

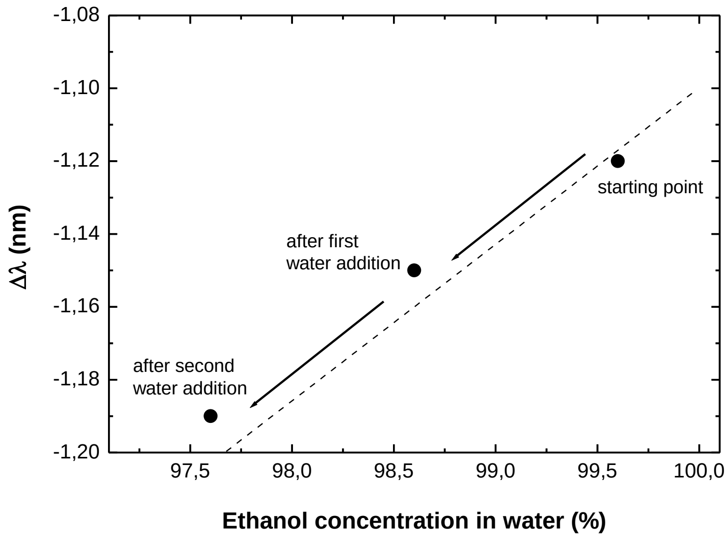

Fig. 8. LPG response when water is added to a sample with initial ethanol concentration of 99.6 %, resulting in two consecutive decreases of 1% in the initial ethanol concentration. The dashed line corresponds to the best linear fit of figure 5.

When the sample has an ethanol concentration lower than 89.6 %, a controlled addition of water produces a red shift in the LPG resonance, whereas for a sample with concentration higher than 89.6 %, a blue shift is observed. The measurement of this wavelength shift allows identifying the

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correct range of the sample (range A or B for ethanol concentrations lower or higher than 89.6 %, respectively), as well as its correct concentration.

V. CONCLUSION

The results obtained in this work showed that the LPG wavelength coded can be used to determine the ethanol concentration in water samples with better linearity and equivalent or better resolution then an Abbe refractometer. The LPG can operate either as a transducer wavelength coded or amplitude coded; however, minor uncertainty was obtained when the device was wavelength coded, as in this case the sensor is not affected by fluctuations in the light source intensity.

When samples are obtained by the mixture of ethanol and pure water in different proportions, the samples' refractive indices present a non-linear behavior with the increase of ethanol concentration. For the samples with lower ethanol proportions, between 0 % and 89.6 %, the refractive index rises with the increase of ethanol concentration. However, when the ethanol proportion is higher than 89.6 %, the refractive index turns back to lower values. Consequently, the LPG transducer wavelength coded will present an ambiguous result when samples with ethanol concentrations in water ranging from 60 % to 100 % are analyzed. This behavior can be detrimental to the transducer performance when the device is intended to be employed in the analysis of fuel hydrated ethyl alcohol (AEHC-Álcool Etílico Hidratado Combustível), which has an allowed minimum ethanol proportion of 95.1 %. In despite of this fact an extra and controlled ethanol addition to the sample under analysis will change the refractive index to lower (or higher, depending on the case) values and the corresponding LPG response allows identifying an illegal sample.

The LPG transducer can be also applied to analyze the conformity of other products as alcoholic drinks, and in this application the samples will be in the first range of ethanol concentrations where the LPG response is almost linear. The LPG response to the sample refractive index and, consequently, to the ethanol proportion in the samples resulted in a transducer resolution of 0.57 % for samples with ethanol concentrations ranging from 0 % to 89.6 %.

Besides of the high sensitivity to refractive index changes, LPG is an in-fiber compact and cheap device that presents real time response, and can be easily integrated in an optical link. In addition, by measuring the LPG response in the intensity domain instead of the frequency domain, the OSA can be replaced by a less expensive and suitable instrumentation for an industrial process.

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