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Short communication

Water content in hydrated ethanol fuel measured by a photothermal chamber with a transparent transducer

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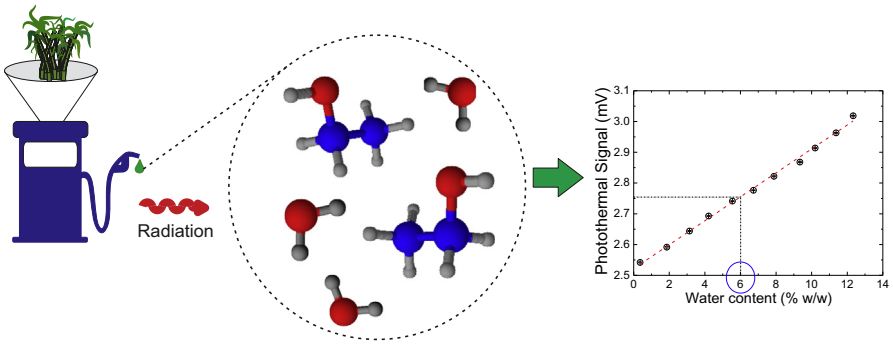
HIGHLIGHTS

- The water content in ethanol fuel was assessed by a transparent transducer.
- The data were compared with reference values certified by Karl-Fischer titration.
- A good agreement between these two methodologies was achieved.
- Low-cost and portable devices for *in situ* and *on-line* analysis may be developed.

GRAPHICAL ABSTRACT



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ABSTRACT

A photothermal chamber with a transparent transducer and a 1450 nm laser were used to measure the water content of hydrated ethanol biofuel. The values of water content in the fuel samples assessed using the photothermal chamber were compared with reference values certified by Karl-Fischer titration. The results indicate good agreement between these two methodologies. Detection thresholds of 0.73 and 0.89 (% w/w) and sensitivity of 0.039 and 0.014 mV/(% w/w) were assessed at the laser powers of 340 and 125 mW, respectively. This study proves that the analytical approach based on the photothermal chamber with a transparent transducer is convenient to determine the water content in ethanol fuel because it is capable of providing reliable results in a quick and accurate way.

1. Introduction

We have been increasingly dependent on fossil fuels as the primary energy source since the industrial revolution [1]. The combustion of those fuels releases a number of toxic compounds that contribute to the greenhouse effect and acid rain, among other issues, and the international prices charged depend on the political stability of the producing countries [2]. The search for renewable, low-cost and environmentally safe sources of energy has motivated the gradual replacement of that energy matrix due to the global problems.

Numerous countries have sought alternative fuels without the same drawbacks associated with fossil fuels. In this context, ethanol is regarded as a good candidate biofuel because it is biodegradable, renewable and may be produced advantageously from

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biomass [3]. The USA could supply approximately 60 billion gallons of ethanol fuel, 30% of U.S. liquid transportation fuel needs [4], if all biomass derived from its agricultural and forest residues could be sustainably produced and harvested, showing the potential of this biofuel. Conversely, the presence of water in this biofuel should be monitored because the polar end of the ethanol molecule makes it soluble in water, facilitating product adulteration and contributing to tax evasion [5]. Furthermore, ethanol absorbs water from atmospheric air during its storage, transport and distribution due to its hygroscopic character [6].

The Brazilian National Agency of Petroleum, Natural Gas and Biofuels (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis, ANP) stipulates that the concentration of water in hydrated ethanol fuel may not exceed 7.4 (% w/w) [7,8]. The methodology recommended by the ANP for the assessment of water content in ethanol fuel is the Karl-Fischer titration method, although this method requires reagents and skilled labor [9]. Thus, alternative methods have been developed due to the significance of ethanol not only as a biofuel but also for its broad use in medicine, pharmaceutical products and chemistry [10]. Various analytical methodologies have been proposed, many of them based on optical spectroscopy, individually or in combination with chemometric methods, such as dual-beam near-infrared spectrometry, wave acoustic methods, optic sensors and surface acoustic wave sensors [6,8–25].

In 2013, Omido et al. demonstrated the viability of a photothermal camera using a transparent transducer to monitor water in ethanol pro analysis (PA) [5]. Samples with different concentrations of water and ethanol PA were evaluated using focused radiation derived from a diode laser operating at 1450 nm, corresponding to the first overtone vibration of the water OH group [26]. The photothermal signal was monitored as a function of power, frequency and water content, assessing the best experimental configuration for system optimization.

The potential of that photothermal method to assess the water content of ethanol fuel from several fuel stations of different Brazilian distributors has been demonstrated in this study. The water content in biofuels was quantified and compared to values assessed using Karl-Fischer titration through simple regression analytical methods.

2. Materials and methods

The chamber for liquid samples (LC) is made of aluminum with a lithium tantalate ($LiTaO_3$) window covered with an indium tin oxide (ITO) film. One of the faces of the crystal is in contact with the liquid and the other with air, receiving and transmitting incident radiation. Instrumental details may be found in previous publications [5,27].

A diode laser operating at 1450 nm was used as a radiation source to excite the first overtone vibration of the water OH group [26]. The optical excitation power derived from the laser was monitored using a power meter (Newport, 1918-C). Optical powers of 125 and 340 mW were measured using optical neutral density filters. The radiation was modulated using a mechanical chopper (Stanford-SR540) maintaining a constant frequency of 18 Hz. The radiation, passing through the chopper and a converging lens, focuses on the crystal window and strikes the sample. The sample undergoes a change in its temperature with the absorption of radiation because of the non-radiative relaxation of water molecules to the ground state. This change in temperature produces a potential difference across the pyroelectric crystal detected by a lock-in amplifier (Stanford Research Systems, SR-530). Samples of biofuels were individually inserted into the photothermal chamber, and the values associated with the measurements were calculated from the mean of the data collected for a period of 2 min.

Eleven water/ethanol mixtures were prepared in the laboratory using mixtures of ethanol PA (Dinâmica® 99.5% purity) and distilled water in the nominal range of 0–12.5 (% w/w). Samples of hydrated ethanol fuel from four fuel distributors in Brazil were collected from two different fuel stations of each distributor, totaling eight samples. These samples were identified as A, B, C and D, letters associated with the distributors, and the respective indices, 1 and 2, were associated with fuel stations. For example, A_1 and A_2 are biofuels from different fuel stations of the same distributor. The water content of all water/ethanol mixtures prepared in the laboratory and acquired from the fuel stations was analyzed by external laboratory calibration according to the International Organization for Standardization (ISO) 17025 certification using Karl Fischer titration. All experiments were performed at room temperature.

3. Results and discussion

Fig. 1 show the photothermal signal as a function of the water content of the samples produced in the laboratory and assessed using the Karl-Fischer method. Those results were obtained for 340 and 125 mW laser power, respectively. The graphs show an increase in the photothermal signal with the concentration of water. That result is explained by the increased concentration of water molecules, which absorb incident radiation, producing an increase in vibration and thereby heating the medium. Although the vibrational contribution of ethanol molecules can occur at approximately 1450 nm, the coefficient of absorption is much lower than the value shown by water in the same spectral region [28]. Furthermore, the contribution of ethanol molecules decreases with the concentration of water in the medium.

Detection thresholds of 0.73 and 0.89 (% w/w) were assessed using the regression approach method for the higher [Fig. 1(a)] and lower [Fig. 1(b)] excitation power, respectively [29]. Furthermore, the sensitivity [30] of the method was also determined from the slopes of analytical curves shown in Fig. 1. When operating the laser at a power of approximately 340 and 125 mW, the results were 0.039 and 0.014 mV/(% w/w), respectively, showing that the highest sensitivity was reached in the high power excitation regime.

The following linear regression equations were calculated from the curves shown in Fig. 1(a) and (b): y (mV) = 2.52 + 0.039C (% w/w) and y (mV) = 0.926 + 0.014C (% w/w), respectively. Then,

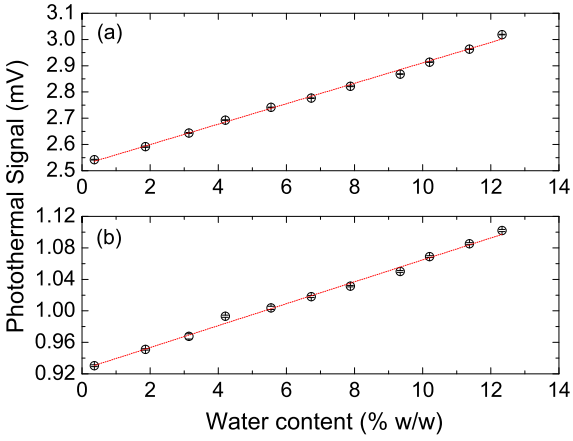

Fig. 1. Photothermal signal of the water/ethanol solutions using power laser of (a) 340 mW and (b) 125 mW. The error bars are smaller than the symbols.

Table 1
Water content measured in hydrated ethanol fuel by Karl Fischer and photothermal chamber method.

Karl Fischer		Photothermal method	
		340 mW	125 mW
Sample	(% w/w)	(% w/w)	
A_1	7.23	(7.2 ± 0.6)	(6.9 ± 0.7)
A_2	7.11	(6.8 ± 0.6)	(6.7 ± 0.7)
B_1	7.11	(7.1 ± 0.6)	(7.1 ± 0.7)
B_2	7.04	(7.2 ± 0.6)	(7.3 ± 0.7)
C_1	7.20	(7.3 ± 0.6)	(7.4 ± 0.7)
C_2	7.21	(7.3 ± 0.6)	(7.4 ± 0.7)
D_1	7.22	(7.4 ± 0.6)	(7.3 ± 0.7)
D_2	7.03	(6.9 ± 0.6)	(6.9 ± 0.7)

photothermal signals from the ethanol fuel samples acquired from fuel stations were measured, and the mean value of each measurement was represented by y_0. The concentration of water in the biofuel sample (C_0) was assessed, replacing y_0 in the regression equation. However, the C_0 value accumulates a series of errors derived from the experimental method and calculations performed. Estimating the error associated with the value resulting from the regression curve is a complex process. We adopted Eq. (1) to estimate the standard deviation (S_{x0}) of the measurement in this study [29]:

$$S_{x0} = \frac{S_{x/y}}{b}\sqrt{1+\frac{1}{n}+\frac{(y_0-\bar{y})^2}{b^2\sum_i(C_i-\bar{C})^2}} \quad (1)$$

wherein $S_{x/y}$ estimates the random errors in the *Y*-axis (y), b is the slope, n is the number of points of the calibration curve, $\bar{y}$ and $\bar{C}$ represent the mean photothermal signal and water concentration of the n samples, respectively, and y_0 is the experimental value of y from which the concentration value C_0 is calculated. The water content calculated using the photothermal method for each sample is thus represented by $(C_0 \pm t_{(n-2)}S_{x0})$, where $t_{(n-2)}$ represents the Student's t coefficient for a confidence level of 95%.

The values of water concentrations in the samples from the distributors assessed using the photothermal method and the Karl-Fischer titration method are summarized in Table 1. The results indicate good agreement between the two methodologies for both excitation powers, 340 mW and 125 mW. The values remained virtually unchanged despite a significant change in the power of the radiation source, indicating good stability in the measurements. Furthermore, the data indicate that all tested samples meet the Brazilian standard.

Thus, this study shows the viability of using a photothermal chamber with a transparent transducer and a laser operating at 1450 nm for the quantification of water in ethanol fuel. The system proves convenient for this type of analysis because it is capable of providing reliable results quickly and accurately and may be used in measurements both at fuel stations and in laboratories. Furthermore, studies involving other experimental settings could be performed to improve the detection limit and sensitivity, among other factors. For example, the absorbance of water near 1940 nm is approximately four times greater than the absorbance at 1450 nm [6]. Thus, changes in photothermal signal intensity should be expected.

4. Conclusions

The results of this study indicate that the method proposed is a promising alternative for the quantification of water in samples of hydrated ethanol fuel. Furthermore, there is a possibility of developing low-cost and portable devices to enable monitoring *in situ* and *on-line* during fuel storage. It is noteworthy that the method is proposed herein as an alternative for biofuel quality control, although it may also have various applications, for example, in studies of contaminants in liquids.

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