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A copper interdigitated electrode and chemometrical tools used for the discrimination of the adulteration of ethanol fuel with water

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ABSTRACT

A new approach for the discrimination of the adulteration process of ethanol fuel with water is reported using a copper interdigitated electrode and chemometrical tools. The sensor was constructed using copper sheets with non-chemical modification of the electrode surface. The discrimination process was performed using capacitance values recorded at different frequencies (1000 Hz to 0.1 MHz) as the input data for non-supervised pattern recognition methods (PCA: principal component analysis and HCA: hierarchical cluster analysis). The relative standard deviation for the capacitance signals obtained from ten independent interdigitated sensors was below 5.0%. The ability of the device to differentiate non-adulterated ethanol samples from those adulterated with water was demonstrated. In all analysed cases, there was good separation between the different samples in the score plots and the dendrograms obtained from PCA and hierarchical cluster analyses, respectively. Furthermore, the water content was quantified using a PCA approach. The results were consistent with those obtained using the Karl–Fischer method at a 95% confidence level, as measured using Student's *t*-test.

1. Introduction

In recent years, many countries have begun to invest in the research and development of alternative energy sources such as ethanol and biodiesel. The rapid growth in this field reflects the need to reduce greenhouse gases and our dependence on fossil fuels [1]. Brazil is the world's largest producer of ethanol, and it derives this alternative energy source from sugar cane. The cost of producing ethanol from this source is lower than that from other sources due to minimal losses during energy conversion, i.e. the increased efficiency of the conversion of sugars into ethanol and their higher energy values compared to other sources such as corn, beet, wheat, and cassava [2]. Although Brazil is the world's largest consumer of ethanol fuel in the form of hydrated ethyl alcohol fuel (HEAF) [3], the use of this fuel has increased across the globe due, among other factors, to the explosion of the sales of flex-fuel cars in recent years.

Given its popularity, the adulteration of ethanol fuel has increased dramatically. The addition of foreign substances or substances above the permitted level without payment of the taxes on the sold fuel is a practice that is engaged in by many traders across the country with the aim of achieving higher profits. Such practices directly impact consumers since they pay for a product that harms their engines, is illegal, and can lead to imprisonment for 1–5 years and a fine [4]. The fight against this crime is hampered by both the large size of Brazil and problems with enforcement given the absence of a rapid, *in situ*, accurate, and inexpensive screening method for detecting adulteration.

There are several methods of adulterating ethanol fuel that result in a fuel that does not comply with the specifications established by the ANP (Agência Nacional do Petróleo; in English, National Petroleum Agency). The most common form of adulteration of ethanol fuel is through the addition of water above the threshold value. The ANP states that the maximum allowable water content in ethanol fuel is 7.4% (v/v) [5]; however, due to the properties of water and HEAF, water can easily be added to the fuel without obvious visible effects.

The amount of water in ethanol fuel can be measured using the Karl–Fischer method (ASTM E203) [6]. However, this method must be employed in a laboratory, and it requires a range of reagents and equipment that makes its *in situ* implementation difficult. The search for new analytical methods for ethanol fuel analysis is essential to assess the addition of impurities to fuel by counterfeiters in an attempt to make the identification of fraud using traditional methods such as hydrometers and conductivity meters difficult.

Therefore, this study aims to develop a low-cost analytical method that could be applied in the field or even attached directly to the fuel tank of a car to qualitatively detect the adulteration of ethanol fuel with water. Capacitance measurements were used to extract information from samples of ethanol fuel in order to develop

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a device that could assess the quality of the ethanol fuel. Additionally, a different approach was investigated to quantify the water content in ethanol fuel within a specific range. To the authors' knowledge, this is the first example of an electrochemical sensor with chemometrical tools being used to discriminate the process of the adulteration of ethanol fuel with water. Previous approaches used electronic noses to discriminate and/or quantify different analytes in gasoline [7,8], biodiesel [9], diesel [10,11], and ethanol fuels [12]. Additionally, impedance methods were used to characterize gasoline blends with ethanol and/or water [13,14].

2. Experimental

2.1. Chemicals and materials

Acetonitrile was purchased from Fisher Scientific (NJ, USA). Ferric chloride, sulphuric acid, and ethanol were obtained from Merck (Darmstadt, Germany) and used without further purification. Binary standard solutions (ethanol/water) were prepared by diluting the ethanol in deionised water that was processed through a water purification system (Direct-Q 5 Ultrapure Water Systems, Millipore, USA).

2.2. Electrodes and instrumentation

A μAutolab (Eco Chemie, Netherlands) with a FRA2 module was used in combination with the FRA.4.9.005 software for the electrochemical measurements. Preliminary experiments were carried out using a homemade copper disk working electrode ($d = 3$ mm) [15] and a homemade Ag/AgCl (saturated KCl) electrode [16]. A Karl–Fischer instrument (Metrohm, model 831 KF, Netherlands) was used to standardize the ethanol fuel samples.

2.2.1. Fabrication of the interdigitated sensor

The procedure for the fabrication of the interdigitated sensor was based on the use of toner masks to protect the metallic surface during the chemical etching process, as was previously reported for gold and copper electrodes [17–20]. The layout of the electrodes was designed using graphic software (OpenOffice.org 2.4, Sun Microsystems Inc.), and it comprised a pair of interdigitated electrodes. The layout was then printed on the same type of waxed paper that is used as a support for adhesive label paper using an HP Laser Jet P2015. The toner mask with the layout of the electrodes was heat-transferred to the copper substrate (copper sheets obtained from Pertech® of Brazil, which comprise copper electroplated on a substrate composed of paper and phenolic resin) using an HLM 230 thermal press (Metalnox, Santa Catarina, Brazil) at 120 °C for 1–2 min. Any exposed copper that was not protected by toner was removed via exposure to a ferric chloride (42%, w/v) solution for approximately 6 min. The toner mask was then removed using acetonitrile on cotton swabs to expose the electrode layout. Fig. 1 shows a schematic of the procedure. Each pair of interdigitated electrodes contained 10 digits. The width and length of each digit was 1000 μm and 7000 μm, respectively, and the interdigit distance was 500 μm. This interdigit distance was the smallest that could be obtained with good reproducibility using the proposed fabrication process. The relative standard deviation for the capacitance signals obtained from ten interdigitated sensors in a standard ethanol solution was below 5.0%.

2.3. Ethanol fuel samples

Four different brands of ethanol fuel purchased from different gas stations in São Paulo (Brazil) and Santo André (Brazil) were used in this study. The measurements were performed directly on the ethanol fuel samples without the addition of other chemical species. All samples were previously standardized using the Karl–Fischer method [6]. The water content in each sample as determined using the Karl–Fischer method was as follows: BR1 = 5.5 ± 0.1, BR2 = 5.6 ± 0.1, SHELL = 5.60 ± 0.05, and ESSO = 5.5 ± 0.2% (v/v).

2.4. Chemometrics

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed using Statistica 8.0 (StatSoft Inc., USA). The analyses were carried out using the capacitance values recorded without any prior preprocessing and scaling using the interdigitated electrodes or a homemade copper disk electrode plus a homemade Ag/AgCl (saturated KCl) electrode as the input. All capacitance curves as a function of frequency (1000 Hz to 0.1 MHz, total of 50 points or variables) were recorded in triplicate for each independent sample or reference binary ethanol/water solution in a random order using the different electrodes.

3. Results and discussion

3.1. Qualitative determination of water

To verify the ability to obtain an analytical signal capable of discriminating samples of water and ethanol, capacitance values were measured as a function of frequency (1000 Hz to 0.1 MHz) using a homemade copper disk electrode and a homemade saturated potassium chloride Ag/AgCl reference electrode (Fig. 2). The geometry of distance was placed the reference electrode parallel to the copper electrode.

Fig. 2 shows that the capacitance values at low frequencies were dependent on the composition of the solution, which supports the possibility of differentiating samples of ethanol with different amounts of water. The variation in the capacitance values could be attributed to the differences in the dielectric constants of the liquids studied. To confirm this hypothesis, we calculated the ratio of the capacitances ($C_{\text{water}}/C_{\text{ethanol}}$) measured in the region of the steady-state value with the frequency (568,980 Hz) and obtained a value of 3.19. It is worth noting that the capacitance value measured in air was subtracted from the capacitance values measured in water and ethanol. This procedure is required in order to obtain only the capacitance value of the liquid since the value

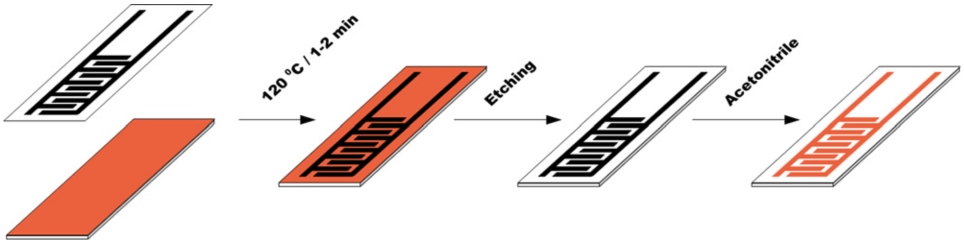

Fig. 1. Schematic representation of the fabrication process of the interdigitated sensor.

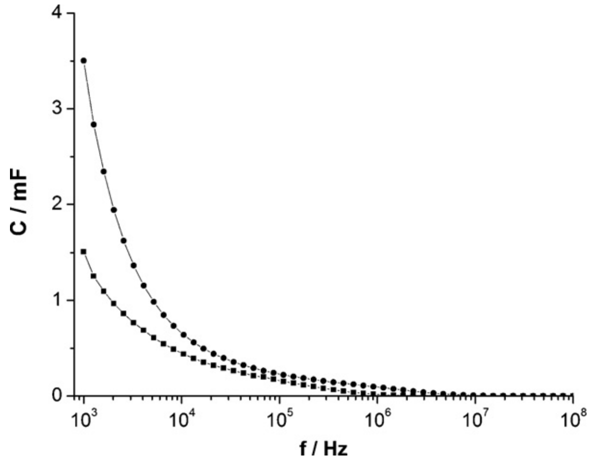

Fig. 2. Capacitance values recorded as a function of frequency (1000 Hz to 0.1 MHz) using a commercial copper electrode and a saturated potassium chloride Ag/AgCl reference electrode in pure solvents: water (●) and ethanol (■). The distance between the electrodes was 2.5 cm.

measured by the device is the sum of capacitance values of the substrate, the distance between the electrodes, and the liquid studied. Note that the value obtained experimentally was consistent with the ratio of the dielectric constants reported in the literature [21] for these two liquids ($\varepsilon_{\text{water}} = 79.99$ and $\varepsilon_{\text{ethanol}} = 25.02$, $\varepsilon_{\text{water}}/\varepsilon_{\text{ethanol}} = 3.197$).

To evaluate the possibility of differentiating water and ethanol using capacitance values recorded at different frequencies, capacitance values were recorded using disk electrodes made of different materials (platinum, gold, glassy carbon, and copper) in binary reference solutions of ethanol/water (5–25% (v/v)) with the additional aim of evaluating the best material for manufacturing the electronic tongue. The analysis of the capacitance data by PCA (Fig. 3) demonstrated that the copper electrode showed the best differentiation of the binary samples. This conclusion was based on the dendograms constructed by HCA (not shown) for each electrode material: the copper electrode was the only material that did not misclassify any of the binary reference solutions studied. For this reason, copper was selected as the device material.

As briefly mentioned earlier, the distance between the two electrodes used for the measurements is one of the parameters that influence the capacitance values. To illustrate this influence, three capacitance curves were measured with (Fig. 4A) and without (Fig. 4B) changing the distance between the commercial copper electrode and the saturated potassium chloride Ag/AgCl reference electrode in an ethanol solution containing 25% water (v/v). Fig. 4A shows that the capacitance value change with the distance between the electrodes and the relative standard deviation of the values of capacitance measured at 2×10^5 Hz was 40% versus 0.21% for three measurements performed with a static distance between the electrodes.

To ensure that the distance between the electrodes did not influence the capacitance values recorded, a device containing a pair of copper electrodes with a fixed distance between the electrodes was fabricated to record the capacitance values extracted from the liquid samples. The layout of the electronic tongue is described in the experimental section. Using this new device, capacitance curves were directly recorded in both real non-adulterated and adulterated ethanol fuel samples. The amount of water in all samples was quantified using the Karl–Fischer method. The capacitance data were treated with PCA resulting in the score plot presented in Fig. 5. Under these conditions, the electronic tongue was able to differentiate ethanol fuel samples with water contents ranging from 5.6 to 15% (v/v); this indicates the possibility of using this device for the qualitative discrimination of adulterated and non-adulterated samples according to Brazilian legislation [5]. HCA was performed on the capacitance data to complement the PCA results and to quantitatively demonstrate the degree of similarity of the analysed samples using the data's full dimensionality (Fig. 5B). The HCA dendrogram (Fig. 5B) showed four different clusters that were distinguished by the amount of water in the sample; there were no misclassifications (0% error rate) and all classifications were consistent with the PCA results (Fig. 5A).

To evaluate the possibility of discriminating brands of ethanol fuel, capacitance curves were obtained from samples of ethanol fuels from different suppliers. The capacitance data were analysed

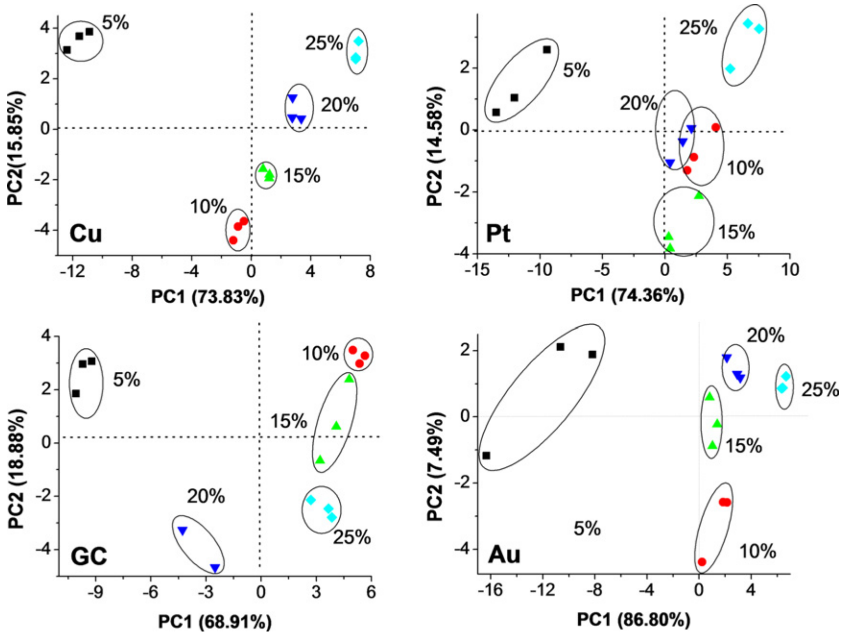

Fig. 3. PCA score biplot of ethanol/water solutions using capacitance data obtained using different electrode materials and a saturated potassium chloride Ag/AgCl reference electrode. Number of replicates per sample: 3. Values shown on the PCA score plots indicate the water concentration (v/v).

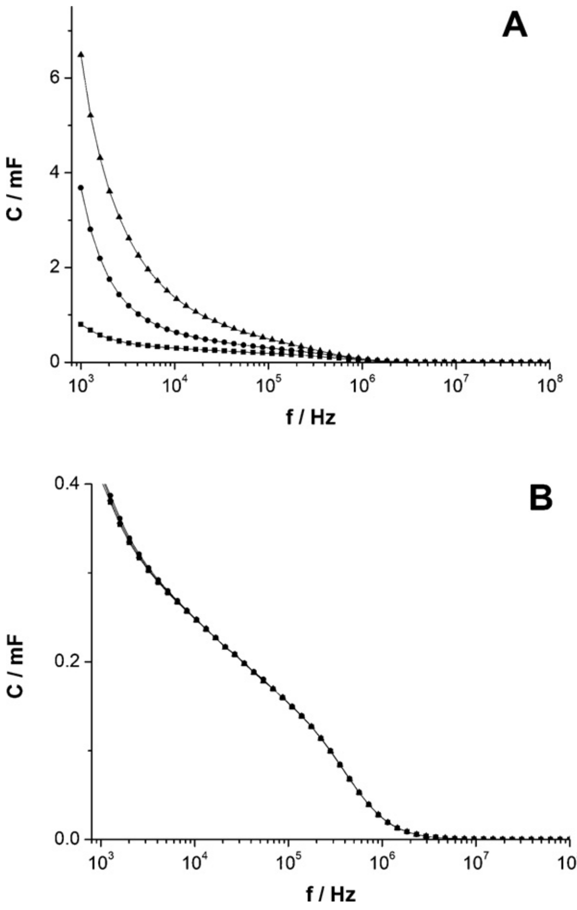

Fig. 4. Capacitance values recorded as a function of frequency (1000 Hz to 0.1 MHz) using a commercial copper electrode and a saturated potassium chloride Ag/AgCl reference electrode with (A) changing and (B) static distances between the electrodes in a binary ethanol (75% (v/v))/water (25% (v/v)) reference solution. In panel A, the distances between the electrodes were 4.5 (▲), 3.0 (●), and 2.0 cm (■). In panel B, the distance between the electrodes was 2.0 cm. Number of replicates per sample: 3.

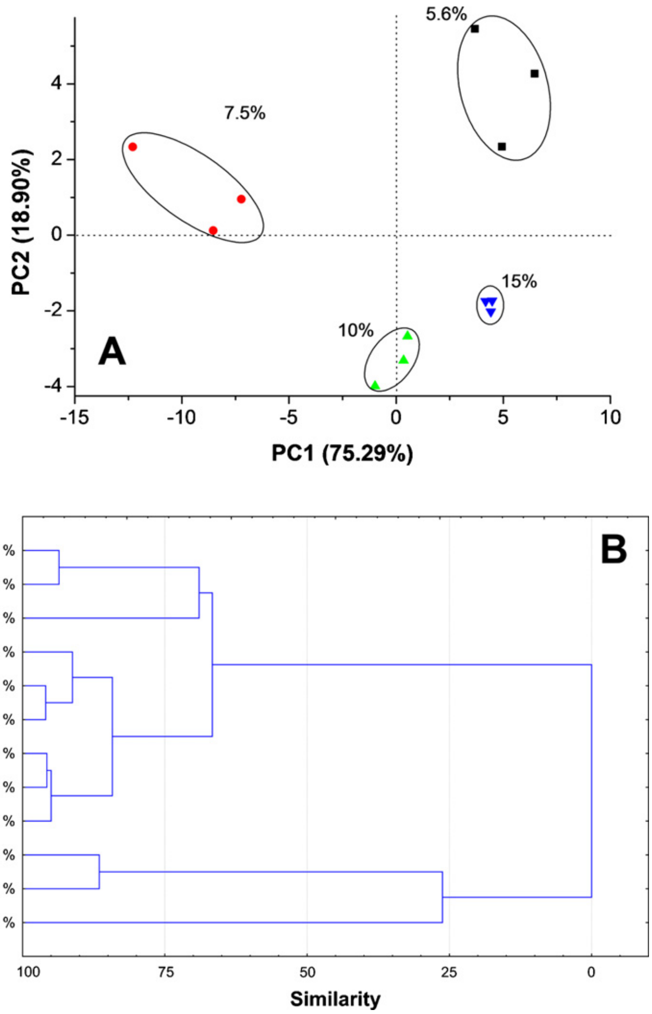

Fig. 5. (A) PCA score biplot of a commercial ethanol fuel before (■) and after the addition of water (●, ▲, and ▼). PCA was obtained from the capacitance data. (B) Dendrogram using HCA algorithm and Euclidian distances of a commercial ethanol fuel before and after the addition of water from the impedance data (capacitance values) obtained using a Cu interdigitated electrode. Number of replicates per sample: 3.

using PCA, resulting in the score plots presented in Fig. 6. The PCA plots prove that discrimination between different brands of ethanol is possible. Such discrimination may be possible due to the different levels of sodium salts, which are limited to a maximum concentration of 2.00 mg L^{-1} in ethanol fuel samples according to regulation no. 45 of the ANP [22]. This limit is in place to prevent the accumulation of sodium salts in alcohol-fuelled engines. The different values of capacitance could reflect the different ionic concentrations of each sample or the different amounts of water in each sample. However, in this case, all samples had similar water contents (see Section 2).

3.2. Potential quantification of water using PCA data

Once the ability to qualitatively discriminate samples of ethanol fuel adulterated with water above and below the content permitted by Brazilian law was verified, the quantification of the water content and the range of concentrations in which the sensor could work were investigated.

Takagi et al. [23] demonstrated the ability to quantify bitterness using a standard calibration plot based on the results of a PCA versus quinine concentration. Using the same approach, we constructed two curves using the PCA results (PC1 and PC2) versus the concentration of water in the range of 10–25% (v/v). A nonlinear regression was obtained for the relationship between PC1 and water content, which indicates that the variable related to water content is not associated with this principal component. The relationship between PC2 and the water content from the data for different standard binary solutions (ethanol/water) with water concentrations in the range of 10–25% (v/v) is shown in Fig. 7. This suggests that PC2 characterizes the water response obtained from the capacitance values, and therefore, it results in a straight line ($(\mathrm{PC2}/\%) = 8.72 + 0.47\ (C_{\mathrm{water}}/\%\ (\mathrm{v/v}))$, $R^2 = 0.9992$). Below 10% (v/v), it was not possible to perform a quantitative measurement of the water content due to a nonlinear relationship between PC2 and the concentration of water. This indicates that the quantification limit is 10% (v/v) of water. However, qualitative discrimination could be possible for samples in the range of 7.5–10% (v/v) using the quantitative process, as shown previously.

Using linear regression to correlate the water content with the PC2 values, we quantitatively analysed two intentionally adulterated samples (samples in Fig. 5, up and down triangles) (Table 1). The values obtained were consistent with those obtained using the Karl–Fischer method at a 95% confidence level according to the Student's *t*-test. The water contents of these two samples were evaluated using an external analytical curve constructed from different standard binary solutions (ethanol/water). However, when we tried

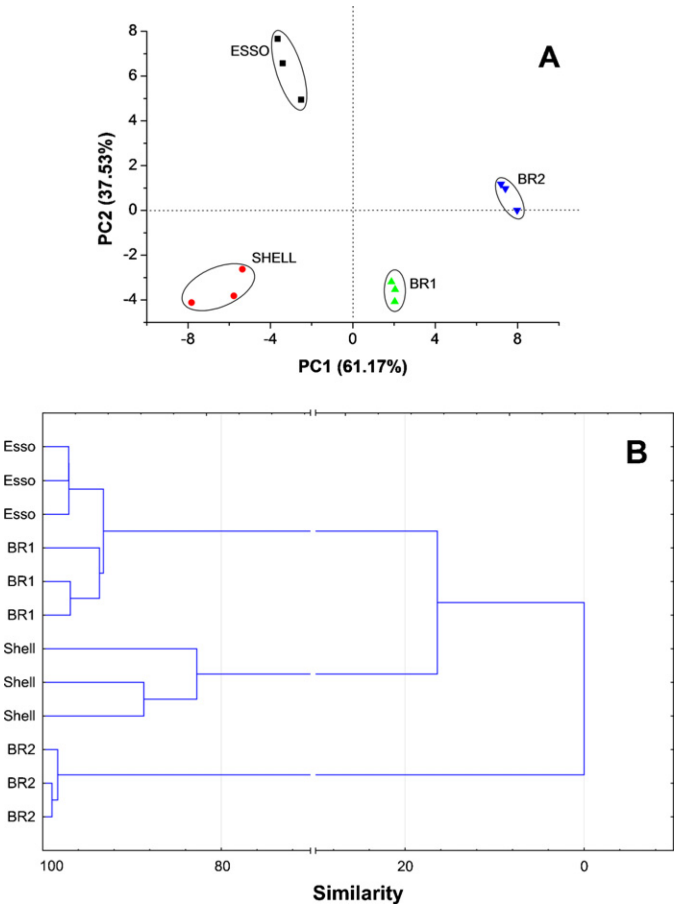

Fig. 6. (A) PCA score biplot of four commercial ethanol fuel samples from different suppliers using capacitance data. (B) Dendrogram using HCA algorithm and Euclidian distances of four commercial ethanol fuels from the impedance data (capacitance values) obtained using a Cu interdigitated electrode. Number of replicates per sample: 3.

Table 1
Water content measured by the proposed method and the Karl–Fischer method.

Sample	Proposed method water content[a] [% (v/v)]	Karl–Fischer water content[a] [% (v/v)]
BR2 adulterated with water	(10 ± 2)	(10.5 ± 0.2)
BR2 adulterated with water	(14 ± 1)	(15.0 ± 0.3)
ESSO adulterated with water[b]	(19 ± 4)	(17.3 ± 0.4)

[a] All measurements were performed in triplicate.
[b] Achieved by standard addition method (number of additions = 3).

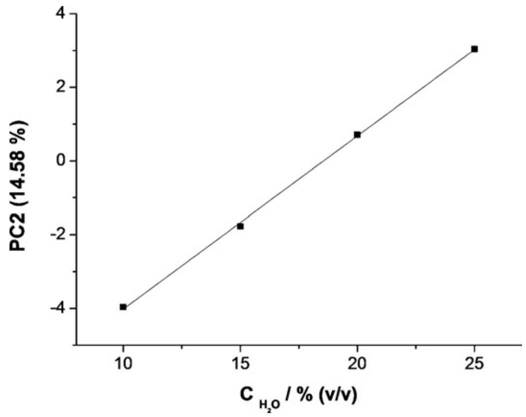

Fig. 7. Calibration curve for the PC2 values of the PCA score plot obtained using the Cu interdigitated electrode in different ethanol/water solutions. Linear regression: (PC2 (14.58%)) = –8.7 + 0.47 (C_{water}/% (v/v)), R^2 = 0.9993.

to use the linear regression obtained from this external analytical curve to quantify the water content in another brand of ethanol, the value obtained was not consistent with that obtained using the Karl–Fischer method due to the differences in the composition of the brands of ethanol from that reported previously. For this reason, we constructed a standard addition curve for the ESSO sample and found that the slopes of the external analytical curve and the standard addition curve were different, which indicates a matrix effect. To circumvent this problem, we used the standard addition curve obtained for the ESSO sample to quantify a sample of the same origin that was intentionally adulterated with water using both the proposed method and the Karl–Fischer method (Table 1). In this case, the two values were consistent according to 95% confidence levels, as measured using the Student's *t*-test. This indicates the need to evaluate the slopes of the external analytical and standard addition curves prior to measurements.

3.3. *Qualitative determination of different solvents*

Finally, we evaluated the ability of the interdigitated Cu electrode to discriminate different solvents including gasoline, diesel, ethanol, water, hexane, methanol, and acetone (Fig. 8). As shown in Fig. 8, the electronic tongue was able to discriminate between different solvents, indicating the possibility of evaluating other types of fuel adulteration such as the addition of methanol to ethanol, which is prohibited in Brazil, or the addition of different solvents to gasoline in order to adulterate this fuel [8].

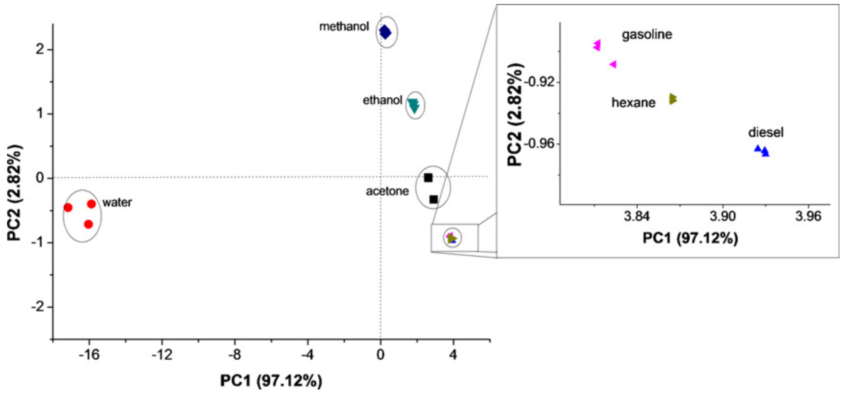

Fig. 8. PCA score biplots for different solvents. PCA scores were obtained from the capacitance data directly from pure standard solvents using a Cu interdigitated electrode. Number of replicates per sample: 3.

4. Conclusions

An interdigitated electrode fabricated from two copper electrodes was found to be useful for discriminating ethanol fuel samples with different water contents using a non-supervised pattern recognition method. This indicates the real possibility of using the electrode to differentiate adulterated and non-adulterated samples. In addition, it was possible to quantify water contents ranging from 10 to 25% in biofuel samples. Preliminary experiments also demonstrated the possibility of differentiating other solvents using the same electronic tongue.

Acknowledgments

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