Article

Evaluation Study of an Ion Selective Field Effect Transistor Electrode for Measuring Quality Parameters of Fuel Ethanol

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Um eletrodo íon seletivo baseado em transistor de efeito de campo (ISFET) foi avaliado na medição de pH e índice de acidez (IA) de etanol combustível e comparado a dois eletrodos de vidro contendo soluções de referência diferentes: solução aquosa de KCl (eletrodo glass-KCl) e solução etanólica de LiCl (eletrodo glass-LiCl). O pH foi determinado utilizando diferentes tempos de medição e AN foi determinado utilizando titulação potenciométrica automática. Para pH, o eletrodo glass-KCl apresentou as melhores precisão e estabilidade, com uma repetibilidade média cerca de quatro vezes melhor quando comparado ao eletrodo ISFET para o tempo de medição de 30 s (norma ASTM D6423). Para AN, os eletrodos glass-KCl e glass-LiCl apresentaram repetibilidades similares, as quais foram cerca de três vezes melhor do que a apresentada pelo eletrodo ISFET. Além disso, os resultados de um estudo de recuperação demonstraram a melhor exatidão do eletrodo glass-LiCl, com uma recuperação de 100,1%.

An ion selective field effect transistor (ISFET) electrode was evaluated for measuring pH and acid number (AN) of fuel ethanol and compared to two glass electrodes with different reference filling solutions: KCl aqueous solution (glass-KCl electrode) and LiCl ethanolic solution (glass-LiCl electrode). pH was determined at different measurement times and AN was determined using automatic potentiometric titration. For pH, the glass-KCl electrode showed the best precision and stability, with an average repeatability about four times better when compared to the ISFET electrode for the measurement time of 30 s (as indicated in the ASTM D6423 standard). For AN, the glass-KCl and glass-LiCl electrodes showed similar repeatabilities, which were about three times better than that of the ISFET electrode. In addition, the results from a recovery study demonstrated better accuracy of the glass-LiCl electrode, with a recovery value of 100.1%.

Keywords: ISFET electrode, glass electrode, fuel ethanol, acid number, pH

Introduction

Ethanol is becoming an important alternative to petroleum derived fuels as it can be produced from renewable sources, such as sugarcane and corn, and the products of ethanol combustion are lower pollutants and contain lower amounts of greenhouse gases.[1,2] In order to guarantee the quality of this fuel, several analytical parameters and their limit values have been established in international regulations, so that ethanol can be commercialized as fuel.[3-5] Among these, pH and acid number (AN) indicate the corrosive potential of ethanol, which can reduce the lifetimes of fuel tanks and automobile engines. Although both parameters are related to the content of acids, whose presence in fuel ethanol is derived from both the fermentation and distillation processes, as well as from possible contaminants, pH is predominantly related to the amount of strong acids. The AN, also referred to simply as acidity and commonly expressed as mass fraction of acetic acid (in % m/m) or mass of acetic acid (in mg) *per* volume of sample (in L), represents the total content of all titratable acids.[6,7]

Thus, regional standards and regulations have established official methods for determining pH and AN of ethanol.[8-14] For pH, the measurements are based on potentiometry using combination glass pH electrodes with different reference filling solutions (KCl aqueous solution or LiCl ethanolic solution). For AN, the measurements are based on volumetric titrations, with colorimetric (using different dyes) or potentiometric detections (using a glass combination pH electrode). However, only a few published works have dealt specifically with the determination of

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these quality parameters in fuel ethanol. Recently, two works were published about pH determination in fuel ethanol, both evaluating different types of combination glass pH electrodes.[15,16] For AN determination in ethanol, three works reported volumetric titration,[17] coulometric titration,[18] and flow injection analysis[19] based methods, employing conductometric or potentiometric detection.

In the early 1970s, a new type of pH electrode was developed, based on a technology called ion selective field effect transistor (ISFET), derived from field effect transistors used in electronics. In an ISFET electrode, the metallic coverage of the gate of the transistor is replaced by a layer of an appropriate crystalline material (such as Si_3N_4, Al_2O_3, or Ta_2O_5). The surface of this crystalline layer, in contact with the sample, interacts with H^+ ions, working as a sensitive surface to them. In principle, the ISFET electrode presents important advantages over the glass electrode, such as its smaller size, faster response time, lower impedance, no need for hydration of its sensitive surface for the device to work, and, mainly, its higher robustness (it does not have an easily breakable sensitive surface).[20,21] Due to these special properties, ISFET electrodes have been used in food,[22,23] medical,[24-26] environmental[27-29] and biotechnology applications,[30,31] in which robust and/or miniaturized systems are needed. In addition, nowadays several combination ISFET pH electrodes are commercially available.

Although the glass electrode is the most commonly used sensor for measuring pH, it is not an ideal sensor for pH measurements in non-aqueous samples, such as ethanol, because this type of solvent causes dehydration of the glass membrane. This phenomenon affects the pH signal stability, thus requiring periodic treatment of the glass membrane for its recovery.[9] On the other hand, although the ISFET electrode needs no hydration, only a few works evaluating its use for pH monitoring in non-aqueous media exist,[32,33] and no works studied its use in ethanol media.

Therefore, this work describes an evaluation study of an ISFET electrode, in comparison with glass electrodes, for measuring pH and AN of several hydrous and anhydrous fuel ethanol samples. The precision, accuracy and stability of the electrodes were studied, as well as possible similarities among their results. Principal component analysis (PCA)[34] was used to evaluate the large amount of pH data.

Experimental

Equipment

Three commercial combination pH electrodes (two glass electrodes and one ISFET electrode) were used to measure the pH value and AN of several fuel ethanol samples. The three electrodes had the same type of reference electrode (Ag/AgCl), with single liquid junctions. The only difference between the two glass electrodes was the reference filling solution: a 3 mol L^{-1} KCl aqueous solution for one (named glass-KCl electrode) and a 2 mol L^{-1} LiCl ethanolic solution for the other (named glass-LiCl electrode). The ISFET electrode had a Si_3N_4 gate coverage and a KCl gel reference filling solution. A glass sample cell, a magnetic stirrer and a Mettler Toledo S40 SevenMulti potential/pH meter were used to measure pH. AN was measured using the same potential/pH meter and magnetic stirrer, together with a glass titration vessel and a 20 mL Metrohm 785 DMP automatic burette.

Samples

The pH value and AN were determined for ten fuel ethanol samples: five anhydrous fuel ethanol samples (about 0.4% water mass fraction, called AE) and five hydrous fuel ethanol samples (about 7.2% water mass fraction, called HE). Additionally, AN was also determined for a pure ethanol sample (Merck, purity higher than 99.9% in mass fraction) before and after doping it gravimetrically with acetic acid (Merck, purity higher than 99.8% in mass fraction).

Experimental procedures

For each pH determination, an aliquot of approximately 20 mL of the sample was added to the sample cell and pH was measured, at room temperature (21 ± 1 °C), under continuous stirring, 30 s after the immersion of the electrode into the sample. This procedure is similar to the one described in an international standard.[9] In addition, pH measurements were also taken at 10, 20, 60, 120 and 180 s for every sample aliquot in order to evaluate the stability of the pH signal. For each AN determination, an aliquot of approximately 20 mL of the sample was added to the titration vessel and volumetrically titrated, at room temperature and under continuous stirring, using a 0.02 mol L^{-1} NaOH aqueous standard solution and potentiometric detection. Around the end point (EP) of the titration, the volume step was set to 10 μL. All analyses were carried out in five replicates using each electrode.

Evaluation of the data

For pH, the average results taken at 30 s (as indicated in the ASTM D6423 standard) and the standard deviations of the replicates were used to evaluate possible similarities

between the electrodes, using statistical *t*-tests, and for a preliminary evaluation of their precision. Then, all pH data from the anhydrous or hydrous samples (3 electrodes × 5 replicates × 6 measurement times × 5 anhydrous or hydrous samples = 450 pH data for each type of sample) were analyzed at once, using PCA with no data pre-treatment and employing the software CAMO The Unscrambler 9.7. In order to evaluate the precision of the electrodes, the data had been previously arranged according to the replicate number, resulting in five data lines for each electrode, each line representing a given replicate number (5 anhydrous or hydrous samples × 6 measurement times = 30 pH data *per* line). To evaluate the stability of the electrodes, the data had been previously arranged according to the measurement time, resulting in six data lines for each electrode, each line representing a given measurement time (5 anhydrous or hydrous samples × 5 replicates = 25 pH data *per* line). For AN, the average results and the standard deviations of the replicates were used to evaluate possible similarities between the electrodes, using statistical *t*-tests, and their precision. The accuracy was also evaluated by comparing the experimental AN increase found for the doped ethanol sample (in relation to the non-doped sample) with the expected theoretical AN increase (acetic acid concentration added to the sample).

Results and Discussion

pH value

Figure 1 shows the average pH results taken at 30 s, with the standard deviations of the replicates. As can be seen, the lowest pH results were obtained using the glass-LiCl electrode, whereas, for eight samples, the highest pH results were obtained using the ISFET electrode. Moreover, statistical comparisons between the average results using *t*-tests (95% confidence level) showed that the results of the ISFET and glass-KCl electrodes were similar to each other for only four samples (AE1, AE2, HE1 and HE3 samples), while the results of the ISFET and glass-LiCl electrodes were similar to each other for only one sample (HE3 sample). In addition, the glass-KCl electrode presented the best repeatability, with an average standard deviation of the replicates about 2.5 and 4 times lower than those of the glass-LiCl and ISFET electrodes, respectively. The differences between the average pH results from the different electrodes can be associated with the different mobility of the ions Li^+ and K^+ and to the different flow speeds of the different solvents (water, ethanol and gel), both leading to different residual liquid junction potentials (RLJP).[9,35] RLJP is the difference in

the junction potentials between measurements with the standard solutions and the sample. It is a peculiar source of error in pH measurements and is generally difficult to evaluate and control.[36] As aqueous standard solutions were used to calibrate the electrodes (as stated in the standard procedure)[9] and the samples had less than 8% of water, the pH measurements probably involved significant RLJP values. Therefore, as the electrodes contained different reference filling solutions, the measurements taken with the different electrodes probably involved distinct RLJP values, thus resulting in different pH values.
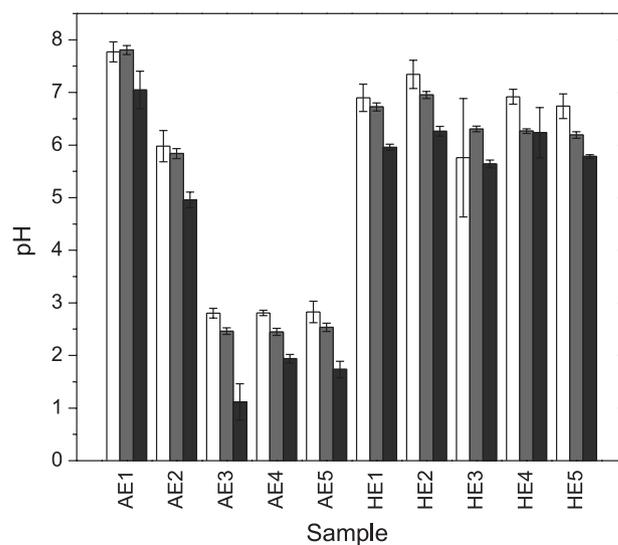

Figure 1. Average pH results (30 s measurement time), with standard deviations of the replicates, obtained using ISFET (white columns), glass-KCl (light grey columns) and glass-LiCl (dark grey columns) electrodes.

Figure 2 shows four score plots in the first two principal components (PC) resulting from PCA, using all pH data from the anhydrous or hydrous samples. In Figures 2a and 2b, related to the anhydrous and hydrous samples, respectively, each point represents a given replicate number of a given electrode, considering all anhydrous or hydrous samples and measurement times. Similarly, in Figures 2c and 2d, related to the anhydrous and hydrous samples, respectively, each point represents a given measurement time of a given electrode, considering all anhydrous or hydrous samples and replicates. Therefore, the dispersion of the data from each electrode is related to its overall precision in Figures 2a and 2b, and to its overall stability in Figures 2c and 2d. As can be seen, the glass-KCl electrode presented the best performance in terms of precision and stability, regardless of the type of fuel ethanol sample. In addition, for the anhydrous samples, the ISFET electrode presented a better performance (precision and stability) than the glass-LiCl electrode, and stability similar to the glass-KCl electrode. On the other hand, for
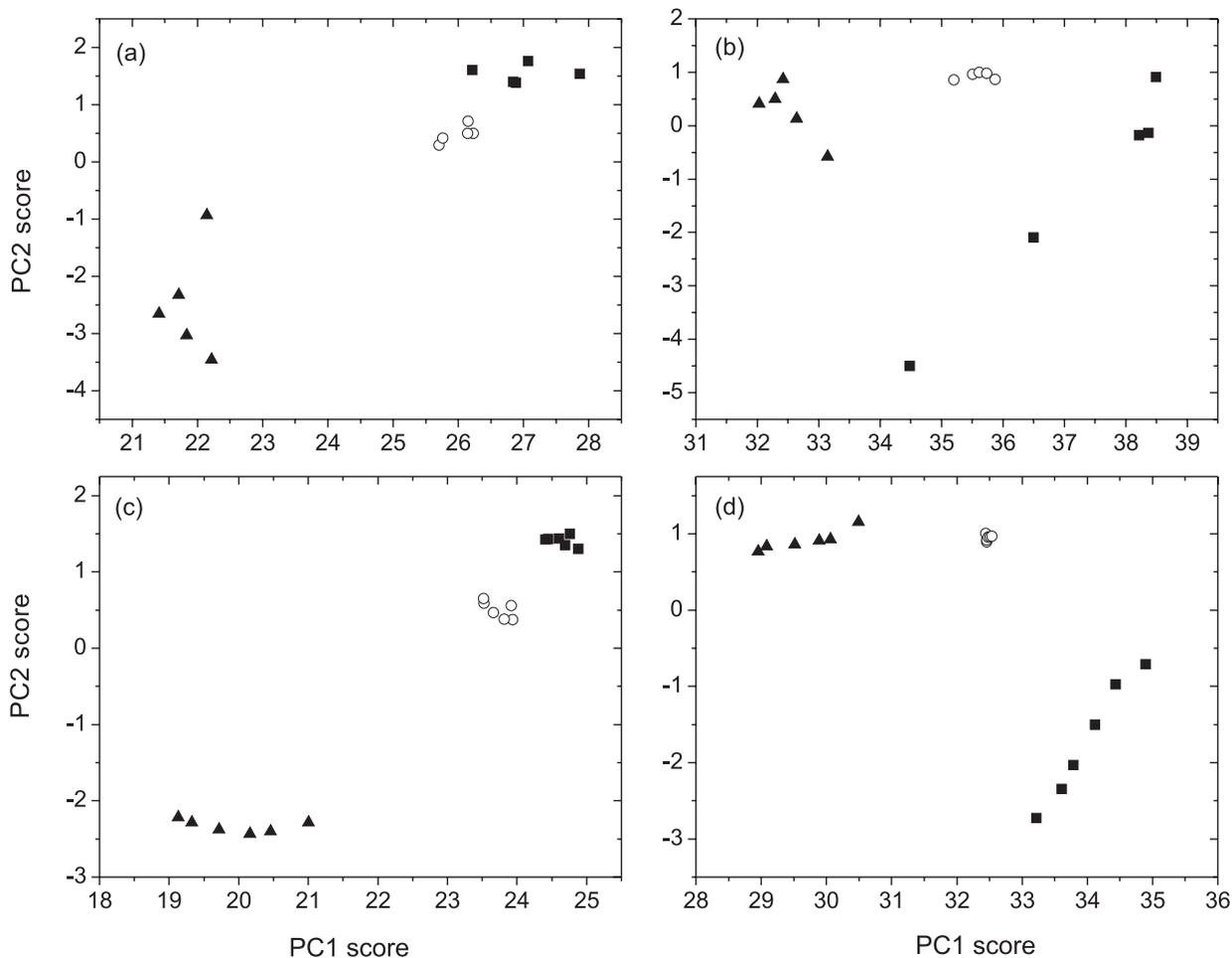
Figure 2. Score plots in the first two principal components (PC1 and PC2) resulting from PCA, using raw pH data from ISFET (■), glass-KCl (○), and glass-LiCl (▲) electrodes: (a) data from anhydrous samples and previously arranged according to the replicate number, (b) data from hydrous samples and previously arranged according to the replicate number, (c) data from anhydrous samples and previously arranged according to the measurement time, and (d) data from hydrous samples and previously arranged according to the measurement time.

the hydrous samples, the glass-LiCl electrode presented a better performance than the ISFET electrode. The better stability of the glass-KCl electrode can also be seen in the pH results along time for a given fuel ethanol sample, as shown in Figure 3.

Comparisons among different electrodes for measuring pH in ethanol media had already been reported in previous works,[15,16] also showing lower pH results for glass-LiCl electrodes. However, they did not study the stability of the electrodes and an ISFET electrode. Previous works also reported higher pH results from an ISFET electrode compared to glass electrodes in other types of samples.[24,29]

Acid number

Figure 4 shows the average AN results with the standard deviations of the replicates. For eight samples, the lowest AN results were obtained using the glass-LiCl electrode and, for seven samples, the highest AN results were obtained using

the ISFET electrode. In addition, statistical comparisons between the average results using *t*-tests (95% confidence
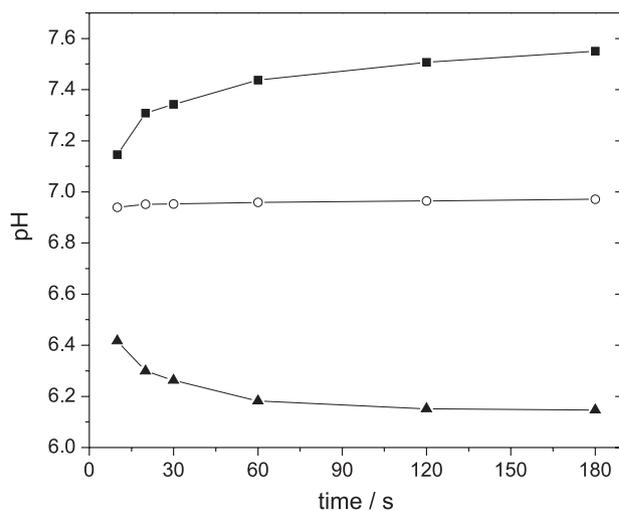

Figure 3. Average pH results *vs.* time for one fuel ethanol sample, obtained using ISFET (■), glass-KCl (○) and glass-LiCl (▲) electrodes.

level) showed that the results of the ISFET electrode were similar to the results of both glass electrodes for eight samples (except to AE1 and AE3 samples), demonstrating that the AN parameter is less affected by the type of electrode than the pH parameter for fuel ethanol. However, the ISFET electrode presented the worst repeatability, with an average standard deviation of the replicates about three times higher than those of both glass electrodes.
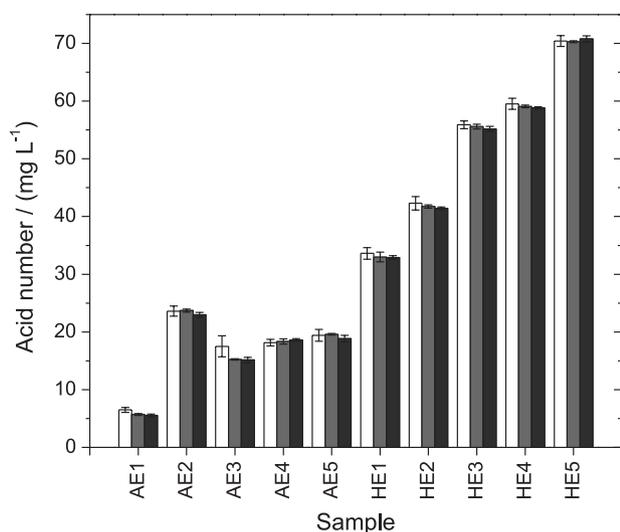

Figure 4. Average AN results, with standard deviations of the replicates, obtained using ISFET (white columns), glass-KCl (light grey columns) and glass-LiCl (dark grey columns) electrodes.

The differences found in the AN results are related to the response of the electrodes along the titration curves, as can be observed in the second derivatives of the titration curves obtained for a given fuel ethanol sample, shown in Figure 5.

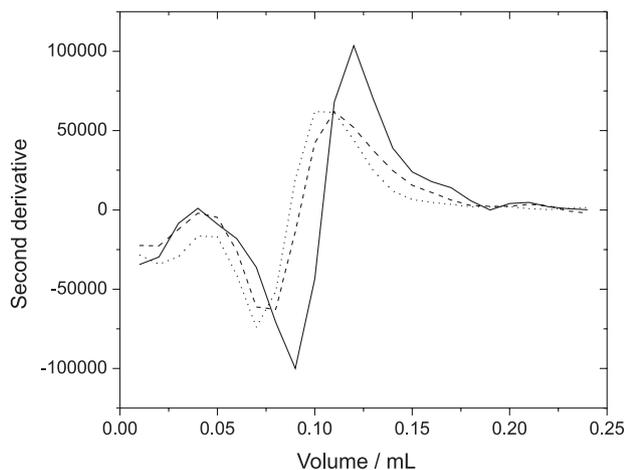Although the ISFET electrode presented a more abrupt potential variation around the EP of the titration curves

Figure 5. Second derivative titration curves for one fuel ethanol sample, obtained using the ISFET (straight line), glass-KCl (dashed line) and glass-LiCl (dotted line) electrodes.

(higher slope of the second derivative titration curve around the zero value derivative), it sensed the EP at higher titrand volumes for most of the samples, as seen in Figure 5, resulting in higher AN values. On the other hand, the glass-LiCl electrode typically sensed the EP at lower titrand volumes, explaining its lower AN results for most of the samples. This behavior also affected the accuracy of the electrodes, as can be seen in the results of the recovery study that was performed using a pure ethanol sample and acetic acid as dopant, shown in Table 1.

Table 1. Results of the recovery study, using acetic acid for doping a pure ethanol sample

Electrode	Addition of acetic acid / (mg L^{-1})	Experimental AN increase / (mg L^{-1})	Recovery / %
ISFET		15.719	106.8
Glass-KCl	14.721	15.000	101.9
Glass-LiCl		14.729	100.1

Similarly to the AN results of the fuel ethanol samples, the ISFET electrode presented the highest recovery value, while the glass-LiCl electrode presented the lowest recovery value and closest to 100%, evidencing the better accuracy of the latter. This better performance is probably related to the reference filling solution contained in the glass-LiCl electrode, which is more similar to the samples in terms of chemical composition, allowing a faster and more accurate sensing around the EP of the titration curves of fuel ethanol. In addition, the worst performance of the ISFET electrode, as for pH as for AN measurements, can also be related to its sensitive surface. The sensitive area of an ISFET electrode is commonly much smaller than those of glass electrodes, making the ISFET electrode easier to be miniaturized, but also making its signal less stable. Moreover, the signal of ISFET pH electrodes having Si_3N_4 as sensitive material (such as the ISFET electrode used in this work) is usually less stable than those of ISFET pH electrodes having other types of sensitive materials, such as Ta_2O_5 or Al_2O_3.[37,38]

Conclusions

Due to its potential advantages over glass electrodes, especially the fact that no hydration of its sensitive surface is required, an ISFET electrode was evaluated, for the first time, to measure pH and AN of fuel ethanol samples in comparison with two glass electrodes. For both quality parameters studied, the results were affected by the type of electrode used, with a greater influence in the pH results.

For pH, although the glass-LiCl electrode contained a reference filling solution more similar to the samples in

terms of chemical composition, and the ISFET electrode did not experience dehydration of its sensitive surface, the glass-KCl electrode presented the best performance. The measurements taken at 30 s showed a better precision of the glass-KCl electrode, with an average repeatability about four times better when compared to the ISFET electrode. Furthermore, the evaluation of the pH data from all measurement times at once also revealed a better overall precision and stability of the glass-KCl electrode, regardless of the type of fuel ethanol sample, and a better performance of the ISFET electrode, compared to the glass-LiCl electrode, for the anhydrous samples.

For AN, although ISFET electrodes are known to exhibit faster response times than glass electrodes, the ISFET electrode presented the worst performance. The glass-KCl and glass-LiCl electrodes showed similar repeatabilities, which were about three times better than that of the ISFET electrode. In addition, the results from a recovery study, using acetic acid and pure ethanol, demonstrated better accuracy of the glass-LiCl electrode, with a recovery value very close to 100%, and 6.7% lower than that of the ISFET electrode.

The results indicate a need for harmonization of the different regional standard methods used for measuring pH of fuel ethanol, primarily regarding the specifications of the electrode and preferably indicating a glass-KCl type electrode, so that pH can be internationally established as a quality parameter of this fuel. For AN determination, a regional standard method based on automatic potentiometric titration was recently proposed,[14] already indicating the use of a glass-LiCl type electrode; however, there is still a need for a similar international standard in order to avoid the use of different electrodes.

References

1. Balat, M.; Balat, H.; *Appl. Energy* **2009**, *86*, 2273.

2. Gnansounou, E.; Dauriat, A.; *J. Sci. Ind. Res. India* **2005**, *64*, 809.

3. EN 15376: *Automotive Fuels. Ethanol as a Blending Component for Petrol. Requirements and Test Methods*; European Committee for Standardization: Brussels, Belgium, 2011.

4. ASTM D4806: *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel*; American Society for Testing and Materials: West Conshohocken, PA, USA, 2009.

5. Resolution ANP No. 07; Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP), Brasília, Brazil, 2011.

6. Oliveira, M. F.; Saczk, A. A.; Okumura, L. L.; Stradiotto, N. R.; *Energy Fuels* **2009**, *23*, 4852.

7. Fraga, I. C. S.; Ribeiro, C. M.; Sobral, S. P.; Dias, J. C.; Gonçalves, M. A.; Borges, P. P.; Gonzaga, F. B.; *Talanta* **2012**, *99*, 99.

8. EN 15490: *Ethanol as a Blending Component for Petrol. Determination of pHe*; European Committee for Standardization: Brussels, Belgium, 2007.

9. ASTM D6423: *Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol*; American Society for Testing and Materials: West Conshohocken, PA, USA, 2008.

10. ABNT NBR 10891: *Álcool Etílico Hidratado - Determinação do pH - Método Potenciométrico*; Brazilian Association of Technical Standards: Rio de Janeiro, RJ, Brazil, 2006.

11. EN 15491: *Ethanol as a Blending Component for Petrol. Determination of Total Acidity. Colour Indicator Titration Method*; European Committee for Standardization: Brussels, Belgium, 2007.

12. ASTM D1613: *Standard Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products*; American Society for Testing and Materials: West Conshohocken, PA, USA, 2006.

13. ABNT NBR 9866: *Etanol Combustível - Determinação da Acidez Total por Titulação Colorimétrica*; Brazilian Association of Technical Standards: Rio de Janeiro, RJ, Brazil, 2012.

14. ABNT NBR 16047: *Etanol Combustível - Determinação de Acidez Total por Titulação Potenciométrica*; Brazilian Association of Technical Standards: Rio de Janeiro, RJ, Brazil, 2012.

15. Borges, P. P.; Fraga, I. C. S.; Marques, B. S. R.; Dias, J. C.; Cunha, V. S.; *J. ASTM Int.* **2010**, *7*.

16. Gonçalves, M. A.; Gonzaga, F. B.; Fraga, I. C. S.; Ribeiro, C. M.; Sobral, S. P.; Borges, P. P.; Rocha, W. F. C.; *Sens. Actuators, B* **2011**, *158*, 327.

17. Avelar, H. D.; Barbeira, P. J. S.; *Fuel* **2007**, *86*, 299.

18. Gonzaga, F. B.; Gonçalves, M. A.; Sobral, S. P.; Ribeiro, C. M.; *Fuel* **2012**, *94*, 70.

19. Fatibello-Filho, O.; Borges, M. T. M. R.; *Anal. Chim. Acta* **1998**, *366*, 81.

20. Bergveld, P.; *Sens. Actuators, B* **2003**, *88*, 1.

21. Lübbers, B.; Schober, A.; *Chem. Anal.(Warsaw)* **2009**, *54*, 1121.

22. Jansen, M. L.; *Meat Sci.* **2001**, *58*, 145.

23. Roseiro, L. C.; Santos, C.; Almeida, J.; Melo, R. S.; *Meat Sci.* **1994**, *38*, 347.

24. Hemmink, G. J. M.; Weusten, B. L. A. M.; Oors, J.; Bredenoord, A. J.; Timmer, R.; Smout, A. J. P. M.; *Eur. J. Gastroenterol. Hepat.* **2010**, *22*, 572.

25. Mayanagi, G.; Igarashi, K.; Washio, J.; Nakajo, K.; Domon-Tawaraya, H.; Takahashi, N.; *J. Dent. Res.* **2011**, *90*, 1446.

26. Roh, J. H.; Shin, K. S.; Cho, N. K.; Lee, D. H.; Moon, B. M.; Lee, D. S.; *Sensor. Mater.* **2008**, *20*, 417.

27. Martz, T. R.; Connery, J. G.; Johnson, K. S.; *Limnol. Oceanogr.-Meth.* **2010**, *8*, 172.

28. Matthiesen, H.; *J. Archaeol. Sci.* **2004**, *31*, 1373.

29. Poghossian, A.; Baade, A.; Emons, H.; Schöning, M. J.; *Sens. Actuators, B* **2001**, *76*, 634.

30. Nemeth, B.; Tsuda, S.; Busche, C.; Cronin, L.; Cumming, D. R. S.; *Electron. Lett.* **2012**, *48*, 144.

31. Chiang, J. L.; Chou, J. C.; Chen, Y. C.; *J. Med. Biol. Eng.* **2001**, *21*, 135.

32. Izutsu, K.; Yamamoto, H.; *Anal. Sci.* **1996**, *12*, 905.

33. Izutsu, K.; Ohmaki, M. *Talanta* **1996**, *43*, 643.

34. Wold, S.; Esbensen, K.; Geladi, P.; *Chemom. Intell. Lab. Syst.* **1987**, *2*, 37.

35. Frant, M. S.; *Today's Chemist at Work*, 1st ed.; American Chemical Society: Washington, DC, USA, 1995.

36. Kadis, R.; Leito, I.; *Anal. Chim. Acta* **2010**, *664*, 129.

37. Bousse, L.; Mostarshed, S.; van der Schoot, B.; de Rooij, N. F.; *Sens. Actuators, B* **1994**, 17, 157.

38. Chou, J. C.; Weng, C. Y.; *Mater. Chem. Phys.* **2001**, *71*, 120.