Primary certification of reference material for electrolytic conductivity of bioethanol

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Abstract: Nowadays the preservation of the planet is spreading into the international scene with the use of renewable energy sources such as bioethanol. The challenge is to guarantee the quality of produced bioethanol, and the electrolytic conductivity (EC) is one of the specified parameters for this purpose. However, is necessary to demonstrate the metrological traceability of the measurement results for EC in this matrix. This study presents the primary certification of a reference material for EC in bioethanol, value of (0.77 ± 0.06) μS.cm⁻¹, and its use will provide the metrological traceability needed for measurement results in laboratories.

Keywords: bioethanol, electrolytic conductivity, metrology.

1. INTRODUCTION

The production of biofuels has attracted the attention of society due to social, economic and environmental aspects. It has highlighted the possibility of using these energy sources to replace fossil fuels as they can lead to the reduction of global warming and the greenhouse effect [1,2]. In addition, the biofuels are considered renewable energy sources as their obtainment involves the processing of raw materials that can be continuously produced through agriculture (sugar cane, vegetable oils, etc.) or from animal fats.

Bioethanol plays an important role in biofuels, and Brazil is one of the leaders in the production and development of technologies related to its use [3]. Therefore, efforts to ensure the quality of this matrix are required, for example, the operation of automotive engines without corrosion damage. Aiming for this control, there are international and national specifications [4] for quality parameters in bioethanol (pH, electrolytic conductivity (EC), etc.) and standards for measurement methodologies [5] in order to harmonize the results of these measurement parameters in Brazil and in other countries.

National Institute of Metrology, Quality and Technology (Inmetro) has been active since 2006 in the production of Certified Reference Materials (CRMs) [6]. In 2007, the primary system of electrolytic conductivity (PSEC) was implemented; its objectives are to provide metrological traceability and to characterize (property value) a CRM at a primary level. Inmetro participates in several international comparisons in order to compare the results to those of its peers. In 2014, there was an international comparison (Pilot Study) in the ambit of the Consultative Committee for Amount of Substance (CCQM): Metrology in Chemistry and Biology, in order to determine the EC of bioethanol, and Inmetro coordinated it. For this, a batch was previously submitted to studies of certification (homogeneity, stability and property...
value) [7,8] by PSEC. The main results of these studies are presented and discussed in this work.

2. MATERIALS AND METHODS

2.1 Bioethanol batch production

The bioethanol, from a national supplier, was collected at Sugarcane Technology Center (CTC), in the city of Piracicaba in the state of São Paulo. The bioethanol was homogenized by magnetic stirring for 24 h in a container of polyvinyl chloride (PVC) at room temperature (20 ± 1) ºC. The bioethanol was bottled in 500 mL amber bottles in a batch of 120 units individually sealed with Parafilm® identified and stored in the laboratory at the same temperature.

2.2 Equipment

The PSEC used in the measurements has a piston-type cell with a cylindrical ceramic body made with aluminum oxide (Al₂O₃) and two platinum electrodes (Pt). In addition, the system is composed of a series of equipment for measuring the quantities that are used to determine EC [6].

2.3 EC Measurement

The EC is defined (1) being inversely proportional to the electrical resistance of the solution and directly proportional to the constant of the cell used. This constant is defined by its geometric dimensions and for a cylinder with parallel electrodes at each side, it is equal to its length (or the distance between the electrodes, ∆L) divided by the cross-sectional area (A) inherent.

\[ k = \frac{1}{R} \cdot K_{cel} = \frac{1}{R} \cdot \frac{\Delta L}{A} \]  

Where \( k \) is the EC (S.m⁻¹), \( R \) is the electrical resistance from the solution (ohm) and \( K_{cel} \) is the cell constant (m⁻¹).

In the PSEC measurement, the solution resistance is given by the resistance variation between two electrode positions (\( \Delta R = R_i - R_f \)) with the length of the cell given by the variation (\( \Delta L = L_i - L_f \)) while the cell diameter is fixed (0.049998 m) and determined through calibration. The most complete representation for determination of EC (2) takes into account the correction of the values to the reference temperature of 25 ºC (for which all the results of this study are expressed). Usually, thirty repetitions are performed to obtain the EC value of a single sample and the final value it is the average of these results.

\[ \kappa = \left[ \frac{\Delta (L_i - L_f)}{(R_i - R_f) \cdot \Delta P^2} \right] \cdot \left[ \frac{1}{1 + \alpha (T_m - T_o)} \right] \]  

Where \( \alpha \) is the temperature coefficient of the solution (ºC⁻¹), \( T_m \) is the temperature of the measurement (ºC) and \( T_o \) is the reference temperature (25 ºC).

3. RESULTS

3.1 Homogeneity study

The homogeneity of bioethanol was verified through the determination of the EC in six samples randomly chosen from the produced batch. This study aims to obtain the standard uncertainty associated with the degree of heterogeneity inherent to the material and contributing to the overall uncertainty of the material.

The estimation (3) of this uncertainty (\( u_{hom} \)) follows the concepts defined in ISO guide 35 [8] being equal to the variance observed between the bottles (\( S_{bb} \)).

\[ u_{hom} = S_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n_0}} \]  

Where \( MS_{among} \) is the mean square between the bottles studied; \( S_{bb} \) is the between-bottle (in) homogeneity standard deviation; \( MS_{within} \) is the mean square inside the bottles studied and; \( n_0 \) is the number of repetitions (30) done.
The EC measurement results of this study are presented in the graph of figure 1. They were statistically analyzed by analysis of variance (ANOVA) for the bottles with numbers 3, 30, 54, 56, 113 and 116.

The results show a weak correlation (fitting a simple linear regression model) for EC variation with time (correlation coefficient, $R = 0.44$) that indicates a good stability of the material. Furthermore, applying a significance test, the $F_{\text{statistic}}$, with 95% confidence level (CL), is 1.19 with an associated $p_{\text{value}}$ of 0.29 ($>0.05$), which does not allow the rejection of the null hypothesis that the slope is zero and, therefore, the material could be considered stable.

Despite this, a slight variation in the EC value is observed and could be explained by the evaporation of the matrix over time, leading to an increase in the ionic strength of the solution. This effect must be incorporated in the evaluation of the standard uncertainty due to long-term stability ($u_{\text{tls}}$) multiplying the slope from the linear fit obtained (0.0003 $\mu$S.cm$^{-1}$.week$^{-1}$) by the time studied (4).

\[ u_{\text{tls}} = a \cdot t \quad (4) \]

Where $a$ is the slope from linear regression model ($\mu$S.cm$^{-1}$.week$^{-1}$) and $t$ is the time studied (week).

The uncertainty associated with the instability of the material can be estimated as 0.02 $\mu$S.cm$^{-1}$. As the material was studied over 64 weeks (01 year and 03 months), this period also could be estimated as the shelf life of the material.

### 3.3 Property value

The characterization, or the determination of the property value of the material, was performed in duplicate with randomly chosen samples. The standard uncertainty associated due to characterization ($u_{\text{char}}$) takes into account the repeatability and the individual uncertainties of each measurement (5).

\[ u_{\text{char}} = \sqrt{\frac{s^2}{\sqrt{n}}} + \sum_{i=1}^{2} u_i^2 \quad (5) \]

Where $s$ is the standard deviation of the two samples; $n$ is the number of samples (two bottles).
and $u_i$ is the standard uncertainty associated with each individual sample.

The property value was 0.77 $\mu$S.cm$^{-1}$ with an estimated standard uncertainty of 0.02 $\mu$S.cm$^{-1}$. The electrical resistance values in the EC measurements were in the order of $1.4 \times 10^5$ $\Omega$, with an associated frequency range from 60 to 100 Hz.

### 3.1 Certified reference material value

The evaluation of the combined standard uncertainty ($u_{CRM}$) for the material takes into account the standard uncertainties of the three previously studies (6).

$$u_{CRM} = \sqrt{u_{Hom}^2 + u_{ie}^2 + u_{Char}^2}$$

This combined standard uncertainty is expanded, multiplying the result by the convergence factor $(k) = 2$ (95% CL) then the CRM value is $(0.77 \pm 0.06)$ $\mu$S.cm$^{-1}$.

### 4. CONCLUSION

The EC primary measurements prove the possibility of establishment and the production of CRM in alcoholic matrixes. However, the final uncertainty from the material $(0.06 \mu$S.cm$^{-1})$ shall be improved as this value is approximately 8% of the property value of the material.

This improvement involves the investigation of the matrix effects (alcoholic media) and the methodology of the measurements where smaller associated uncertainties should be studied. However, the obtained values do not invalidate the use of this type of CRM because it allows the establishment of a traceable and metrological chain. As the first work with primary measurements for this matrix, it was achieved with the highest level of accuracy possible. Laboratories analysis will present reliability of the issued results.

### REFERENCES


Prezados revisores, seguem as respostas aos questionamentos realizados.

- No tópico 3.2 o gráfico foi alterado, pois realmente foram realizadas medições até 64 semanas. O gráfico anterior não foi expandido até a data final do estudo.
- Na equação 5, o "n" é o número de amostras (garrafas) analisadas. Foram mensuradas duas garrafas para a determinação da caracterização sendo que cada uma delas foi lida em 30 replicatas. Foi reescrito o texto explicando a equação 5 para a melhor compreensão (logo abaixo da equação) e foi incluído antes da equação 2 um texto explicando que toda amostra analisada no trabalho foi feita com 30 repetições.
- Sim, as incertezas dos estudos de homogeneidade, estudo de longa duração e caracterização todas deram iguais a 0.02 µS/cm. Isso, porém após arredondamento para duas casas decimais (os valores originais foram de 0.019, 0.020 e 0.017 para homogeneidade, longa duração e caracterização respectivamente).