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 certification of a reference material for EC in bioethanol by using only primary measurements. The value of primary certified reference material (CRM) is \((0.77 \pm 0.06) \, \mu \text{s} \cdot \text{cm}^{-1}\), 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 factors. This increased attention has also highlighted the possibility of using these energy sources to replace fossil fuels, as they can facilitate the reduction of global warming and the greenhouse effect [1,2]. In addition, biofuels constitute a viable alternative in relation to fuel derived from petrol, and they are considered renewable energy sources because obtaining them involves the processing of raw materials (e.g., sugarcane, vegetable oils, etc.) that can be continuously produced through agriculture or from animal fats. The participation of biofuel in the energy matrix depends on a complex array of factors involving many aspects of production (i.e., raw material and technology) and the sustainability (e.g., social, economic, and environmental) of this energy source.

Since the start of the PROALCOOL program, the quality of bioethanol has been connected with the performance of engines working with hydrated alcohol. Playing an important role in bioethanol’s economic sustainability, Brazil is one of the leaders in the production and development of technologies related to its use [3-5]. Therefore, efforts to ensure the quality of this matrix are required, such as achieving the operation of automotive engines without corrosion damage. Aiming for this control are international and national specifications [6-8] for quality parameters in bioethanol (e.g., pH, electrolytic conductivity (EC), etc.) and standards for measurement methodologies [9-11] to harmonise the results of these measurement parameters in Brazil and other countries.

The validation of biofuel is markedly dependent on three basic factors: normalised specifications; official methods of analysis, and certified reference materials (CRMs). The normalised specifications are a set of characteristics required to guarantee the quality of the biofuels. The official methods of analysis are the tools necessary to construct a correct evaluation of the normalised specifications of the fuel. The CRMs are tools utilised in the validation and official method control of fuel analysis [5].

The National Institute of Metrology, Quality and Technology (Inmetro) in Brazil has been active since 2006 in the production of CRMs [12-15]. In 2007, Inmetro implemented the primary system of electrolytic conductivity (PSEC); its objectives are to provide metrological traceability and to characterise (i.e., define the property value of) a CRM at a primary level. Inmetro participates in several
international comparisons within the ambit of the Consultative Committee for Amount of Substance (CCQM): Metrology in Chemistry and Biology and the Inter-American Metrology System (SIM) in order to compare the results to those of its peers [16-20]. In 2014, Inmetro coordinated an international comparison (via pilot study) within the ambit of the CCQM to determine the EC of bioethanol. In preparation for the study, a batch of bioethanol was submitted to studies of certification (specifically, homogeneity, stability, and property value) [21,22] 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 the Sugarcane Technology Center (CTC) in the city of Piracicaba in the state of São Paulo. The bioethanol was homogenised by magnetic stirring for 24 hour in a container made of polyvinyl chloride (PVC) at room temperature (20 ± 1) °C. 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 [13-20].

2.3 EC measurement
The EC is defined (1) as 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, ΔL) divided by the cross-sectional area (A) inherent.

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

(1)

Where \( k \) is the EC (S.m⁻¹), \( R \) is the electrical resistance from the solution (Ω), 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 °C (at which all the results of this study are expressed). Usually, 30 repetitions are performed to obtain the EC value of a single sample, and the final value is the average of these results.

\[ \kappa = \left[ \frac{4 \cdot (L_i - L_f)}{(R_i - R_f) \cdot \pi \cdot D^2} \right] \cdot \left[ \frac{1}{1 + \alpha (T_m - T_o)} \right] \]  

(2)

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

3. RESULTS
3.1 Study of the impedance spectrum
Prior to the certification studies (i.e., the homogeneity, characterisation, and long-term stability study), it is relevant to obtain a profile of the electrical behaviour of the material by studying the electrochemical
impedance spectroscopy (EIS) of the solution. This profile is related to the fact that for electric current applied (or potential difference) with different electrical frequency bands, the electrical resistance may assume different values.

This occurs because, in the cell model used, the total resistance to the passage of electrical current is subdivided into components, such as the electrical resistance (the real component of impedance), the reactance (the imaginary component of the impedance), and the capacitance originating from the cell geometry, and also into parasitic effects such as the polarisation of the electrodes and effects of adsorption and desorption of ions on the surface of the electrodes used. Therefore, it is important to choose a model in which these effects can be minimised, such that the impedance values observed experimentally are dominated by its real component (electrical resistance) that is used in the determination of the electrolytic conductivity of the solution.

Experimentally, this occurs when, for a wide range of frequencies studied (wide frequency study), some regions of the impedance spectrum indicate stable values for the real component of the impedance within specified ranges of electrical frequencies. In these regions, it is observed that the values of the imaginary component are minimal and, therefore, the spectrum of the solution is dominated by the electrical resistance of the solution. Another important aspect is that around this particular ‘ideal’ frequency range, the parasitic effects can be minimised by extrapolating the measured values of the electrical resistance in this region to the limit of high frequency (or its inverse to zero). In this situation, the system can be modeled simply as an equivalent circuit in which there is electrical resistance of the solution in parallel to the capacitance of the electrodes [13,23,24].

The impedance spectrum of bioethanol samples is shown in Figure 1, in the Nyquist plot (a) that presents the variation of the reactance values and electrical resistance for different associated electrical frequencies. The bioethanol samples were subjected to a wide range of frequencies (20-100000 Hz).

![Figure 1. Impedance spectrum for the bioethanol samples.](image)

For the samples of bioethanol, it was observed that the minimum reactance values (a) were found for an associated frequency band that comprises a range between 20 and 200 Hz. For this same range, the observed electrical resistance values are of the magnitude of 558.000 Ω (b). These values must be extrapolated linearly to infinite frequency values in order to minimize parasitic effects, as mentioned above. For this work, all subsequent measurements were performed in the electrical frequency range...
between 60 and 100 Hz. This is a more specific working range in which there is an intersection with the optimum working range observed in the study of the impedance spectrum of the samples.

3.2 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 aimed to obtain the standard uncertainty associated with the degree of heterogeneity inherent in the material and contributing to the overall uncertainty of the material [25,26].

The estimation (3) of this uncertainty ($u_{hom}$) follows the concepts defined in ISO Guide 35 [22], being equal to the variance observed between the bottles ($s_{bb}$).

$$u_{hom} = s_{bb} = \sqrt{\frac{(MS_{among} - MS_{within})}{no}}$$

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, $no$ is the number of repetitions (30) done.

The EC measurement results of this study are presented in the graph in Figure 2. They were statistically analysed by analysis of variance (ANOVA) for the bottles numbered 3, 30, 54, 56, 113, and 116.

![Figure 2. Bioethanol homogeneity study.](image)

The results demonstrate the convergence of values because, for each individual measurement, there is an intersection with the subsequent measurement. The estimated value of the standard uncertainty was 0.02 μS.cm⁻¹.
3.3 Stability study

The stability of the batch was determined with EC measurements on samples randomly chosen more than one year after the preparation of the batch. The results of these measurements are presented in the graph in Figure 3.

![Figure 3. Bioethanol stability study.](image]

The results presented a weak correlation (fitting a simple linear regression model) for EC variation with time (correlation coefficient, $R = 0.44$) that indicates good stability of the material. Furthermore, applying a significance test, the $f_{\text{statistics}}$, 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 was observed, which 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 into the evaluation of the standard uncertainty due to long-term stability ($u_{\text{ltS}}$), multiplying the slope from the linear fit obtained (0.0003 $\mu$S.cm$^{-1}$.week$^{-1}$) by the time studied (4).

$$u_{\text{ltS}} = \alpha \times t \quad (4)$$

Where $\alpha$ is the slope from the 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 (1 year and 3 months), this period also could be estimated as the shelf life of the material.

3.4 Property value

The characterisation, or the determination of the property value of the material, was performed in duplicate with randomly chosen samples. The associated uncertainty determined by characterisation ($u_{\text{char}}$) takes into account the repeatability and the individual uncertainties of each measurement (5).
\[ u_{\text{char}} = \sqrt{\frac{s^2}{n} + \sum_{i=1}^{2} u_i^2} \]  

(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 [25,26] 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.

3.5 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 previous studies (6).

\[ u_{CRM} = \sqrt{u_{hom}^2 + u_{ltc}^2 + u_{char}^2} \]  

(6)

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

4. CONCLUSION

The EC primary measurements indicate the possibility of establishment and the production of CRM in alcoholic matrices. However, the final uncertainty from the material (0.06 \( \mu \)S.cm\(^{-1}\)) should be improved, because this value is approximately 8% of the property value of the material. It is important to emphasise that this value is very low (0.77 \( \mu \)S.cm\(^{-1}\)) and is therefore not easy to measure.

This improvement will involve 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 this is the first work of primary certification of a CRM for measurements of the bioethanol matrix, the purpose was achieved with the highest level of accuracy possible. Laboratory analysis will confirm reliability and metrological traceability of the issued results of the measurements of EC.

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