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Certified reference material of bioethanol for metrological traceability in electrochemical parameters analyses

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ABSTRACT

Bioethanol has become an important biofuel because it is a source of renewable energy and can help to decrease global warming. However, the quality of bioethanol needs to be guaranteed so that it can be trusted and accepted in international trade. The Brazilian Metrology Institute (Inmetro) has been developing a certified reference material (CRM) for bioethanol to ensure quality control for measurement in the bioethanol matrix. Inmetro has certified 11 quality parameters. Using these, the CRM of bioethanol will contribute to guaranteeing metrological traceability and reliable measurement results. These factors can be used to compare different bioethanols produced to comply with legislation in different countries in order to avoid technical barriers and thus increase the international trade in Brazilian bioethanol. The aim of this paper is to present the results of certification studies using three important electrochemical quality parameters in the CRM of bioethanol–total acid number, pHe and electrolytic conductivity–which are crucial in protecting the metallic parts of a vehicle from corrosion. The certified results obtained for total acid number, pHe and electrolytic conductivity parameters were (16.2 ± 1.7)mg L^{-1}, 6.07 ± 0.30, and (1.03 ± 0.11)μS cm^{-1}, respectively. The uncertainties for all parameters were the expanded uncertainty obtained by multiplying the combined standard uncertainty by a coverage factor of $k=2$, which represents an approximately 95% confidence level.

1. Introduction

The use of bioethanol as a biofuel is currently increasing for many reasons, such as its application in flex-power vehicles, along with its status as a renewable and less pollutant fuel. The development of flex-power vehicles in Brazil and other countries has underpinned the high consumption of this biofuel: around 86% of these vehicles were sold in the Brazilian internal market in 2011, and the consumption of bioethanol in the same year was around 15 billion litres [1]. Studies on the projected consumption of biofuels from 2010 to 2017 in Brazil have estimated that 53.2 billion litres of bioethanol will be consumed in 2017. Bioethanol has a key role as a source of alternative energy, contributing to the economy of countries that adopt it; this encourages policies for the production and use of bioethanol as a biofuel. In the world trade of biofuels, bioethanol is a renewable biofuel that can reduce the environmental impact caused by greenhouse gases and particulate material emissions [2–5].

Since 2005, the Brazilian Metrology Institute (Inmetro) has been studying different quality parameters of bioethanol with the aim of developing a certified reference material (CRM). These parameters are established by the National Agency of Petroleum, Natural Gas and Biofuels (ANP), which is the agency responsible for the quality control of biofuels consumed in Brazil. It regulates the limits for several parameters of biofuels [6] according to Brazilian and international standards.

To trade bioethanol on the market, the analytical measurements of its quality parameters of bioethanol [6] must present traceability and reliability that can be obtained by using CRM [7–9]. Inmetro has certified 11 quality parameters of bioethanol; however, only the three electrochemical parameters will be focused on in this paper: total acid number, pHe and electrolytic conductivity.

Reliable determination of the total acid number is necessary ($\leq$30 mg acetic acid per litre of bioethanol [6]) to avoid corrosion in the fuel chain. Acid levels higher than 30 mg acetic acid per litre contribute to the corrosion of the metallic parts present in the production process, transport and motors. The same issues pertain to the determination of the electrolytic conductivity and pHe; conductivity values up to 350 μS m^{-1} (3.5 μS cm^{-1}) and pHe of bioethanol in the range from 6.0 to 8.0 will contribute to corrosion [6].

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There is a lack of metrological traceability on the pHe measurements in bioethanol [10–21]. Nowadays, only pH CRM from aqueous solutions is available to calibrate a pH meter. The use of this pH CRM in the bioethanol matrix can provide an unreliable pH measurement result. However, three national metrological institutes (in Germany, France and Brazil) are developing a project from 2011 to 2013 to harmonise the pHe measurements at a global level. The project's goal is to stress the study of pHe measurement and develop a pH buffer in the ethanol matrix.

The certification process of a candidate CRM depends on the preparation of the sample, the analytical determination and material characteristics, since the metrological traceability of the values of properties will be recorded on one certificate, according to ISO Guide 31 [22].

For the certification of a CRM candidate, a homogeneity study, stability study (short- and long-term stability) and characterisation of the material must be carried out. Homogeneity study is necessary in batch certification projects to demonstrate that the batch of bottles (units) is sufficiently homogeneous. Aspects of quality assurance are as important as the determination of the remaining batch between-bottle variation, which is an uncertainty component to be included in the uncertainty estimate of the value of properties in CRM [23]. A stability study aims to determine the remaining degree of instability of the candidate reference material (RM) after preparation, or to confirm the stability of the material. Even "stable" materials may show instability in terms of one or more property values. Such a stability study is carried out by simulating transport and storage conditions, where the temperature and the time are varied [23]. The characterisation of an RM determines its property values as part of the certification process [23]. ISO Guide 34 [24] distinguishes between four basic approaches to characterisation. They are implemented in many different variants by producers and certification bodies of RMs as follows:

a) measurement by a single (primary) method in a single laboratory;
b) measurement by two or more independent reference methods in one laboratory;
c) measurement by a network of laboratories using one or more methods of demonstrable accuracy;
d) a method-specific approach giving only method-specific assessed property values, using a network of laboratories.

After all the certification studies have been performed, the values of uncertainties from homogeneity, stability and characterisation are combined to obtain the uncertainty of the CRM [9,24].

Recently, Inmetro and the National Institute of Standards and Technology (NIST) collaborated to certify a batch of bioethanol CRM [25]. Additionally, Inmetro participated in a European project called BIOREMA [26] to certify RMs for bioethanol and biodiesel and coordinate in an interlaboratory comparison on a global level. In 2010, Inmetro coordinated an interlaboratory comparison of anhydrous bioethanol for the project 'Standards for the Ethanol of Africa and Latin America'. This project aimed to assist the National Metrology Institutes (NMIs) and independent quality laboratories in technical qualification, identified and invited by the NMIs; these laboratories are involved in the quality control of biofuels in their respective countries [27].

The aim of this paper is to present the steps needed to develop a CRM of bioethanol to guarantee the metrological traceability and reliability of bioethanol measurements for the control of the electrochemical parameters of total acid number, pHe and electrolytic conductivity.

It is important to highlight that these electrochemical parameters are specified because of their relevance to some regional standards such as Technical Specifications (Res. ANP no. 7/2011) (Brazil), Draft prEN 15376 (11/09/2009) (European Community) and ASTM International D4806 (USA) [28], which are in place for bioethanol trading in the world.

The main motivation of this paper is to build on studies that were carried out in recent years for the development of CRM for measurements of the electrochemical parameters of bioethanol. These studies have started from planning activities, including the bottling of the bioethanol material and the certification steps up to the issuance of a CRM certificate. This CRM allow the measurement results to be improved in sample analyses because the results can be reliably compared. Moreover, this improvement can be directly related to the quality assessment of bioethanol in order to avoid technical barriers to this biofuel in international trade.

2. Materials and methods

2.1. Equipment

The equipment used for the total acid number experiments consisted of an automatic potentiometric titrator (Titrando 836, Metrohm, Herisau, Switzerland) composed of Dosino 800 automatic burettes, stirrer 801, a combination pH electrode (6.0232.100) with internal solution 3 mol L^{-1} KCl, a robotic USB sample processor XL 815 and pump unit 772. For characterisation studies, pH meter 713 (Metrohm) was used; furthermore, pH meter 780 (Metrohm) was employed for measurements of pHe related to the homogeneity and stability studies. A combination pH electrode 6.0232.100 (Metrohm) with internal solution 3 mol L^{-1} KCl was coupled to each pH meter whenever necessary. The electrolytic conductivity was measured using conductivity meter 712 (Metrohm) coupled with conductivity cell 6.0901.040 (Metrohm), with a cell constant of 0.090 cm^{-1}.

2.2. Materials

The total acid number was measured by potentiometric titration with 0.02 mol L^{-1} NaOH solution (99%, Merck, Darmstadt, Germany) as the titrant. The NaOH reagent was from Merck (99% purity). The titrant was standardised with a CRM of HCl 0.01 mol kg^{-1} (code 8134, batch 08.2/10.0003, Inmetro, Brazil) for internal use certified by the primary coulometry system from Inmetro [29,30]. CRMs of pH 4.00 (code 8832, batch 03.1/08.0001, Inmetro) and 6.86 (code 8855, batch 03.2/10.0005, Inmetro) were used to calibrate the pH meter. A CRM of 5 $\mu S\,cm^{-1}$ was used for the calibration of the conductivity meter (code 8435, batch 04.5/09.0001, Inmetro). All solutions were prepared with deionised water from Millipore® (Milli-Q), with an electrolytic conductivity value less than 0.1 $\mu S\,cm^{-1}$.

2.3. Preparation of the CRM of bioethanol

Initially, a batch of approximately 40 L of raw material of bioethanol from sugarcane, provided by a Brazilian producer, was generated with an ethanol content of 99.5% in the mass fraction. The bioethanol was bottled in approximately 200 amber glass bottles of 500 mL for the determination of the total acid number, pHe and electrolytic conductivity parameters. The preparation of the CRM candidate of bioethanol and the studies for its certification in terms of the three electrochemical parameters were performed according to the ISO Guide 30 to 35 series [8–13].

2.4. Procedures

An aliquot of 70 mL of bioethanol sample was used for each determination of acid number. The result for total acid number is represented by a quantity of acetic acid expressed as milligrams of acetic acid per litre of bioethanol.

Each of the measurements of pHe was performed in a sample of bioethanol with a volume of 40 mL at 25 °C using a Pt 100 resistance thermometer. The samples were homogenised with a magnetic stirrer until 25 °C was reached. Then, the stirrer was turned off and the pHe measurement was carried out after 30 s. Because of the harmful effect of the bioethanol medium on the electrode glass membrane, the glass membrane of the pH electrode was regenerated by alternately introducing the pH electrode to HCl 1.0 mol L^{-1} and NaOH 1.0 mol L^{-1} solutions after 10 measurements of pHe in the bioethanol samples. Electrolytic conductivity measurements of the bioethanol for certification studies were carried out using a volume of 30 mL at 25 °C, a Pt 100 resistance thermometer and a magnetic stirrer; these were immersed in a glass recipient containing a conductivity cell.

2.5. Homogeneity study

The homogeneity study was performed for the three parameters, and all of the measurements were taken on the same day. The storage temperature for the bioethanol samples was 21 °C (room temperature of the laboratory), and the analysis of variance (ANOVA) statistical test was applied. For the total acid number (the first parameter), 10 bottles were analysed, and for each analysis, 70.0 mL of bioethanol was needed. The measurements of total acid number were performed in triplicate. For pHe (the second parameter), 10 bottles were analysed, and for each analysis, 25 mL of bioethanol was required. The pHe measurements were performed in duplicate. For electrolytic conductivity (the third parameter), 10 bottles were analysed, and for each analysis 50 mL of bioethanol were used. The measurements of electrolytic conductivity were performed in triplicate.

2.6. Characterisation study

The characterisation study approach [9] involves one primary method or two different methods for measurements in bioethanol for each parameter certified in the batch described in this paper. All measurements were carried out in triplicate for each parameter. These methods presented metrological traceability involving calibrated equipment and the use of CRM. The estimated uncertainty of each parameter was calculated considering all of these factors.

2.7. Stability studies

A short-term stability study was not applied to the bioethanol batch considered in this paper because previous studies [9,25,26] have been carried out to simulate the extreme conditions of transport (at 4 °C and 50 °C) from other bioethanol batches. These studies have shown that this factor has no influence on the results of certification studies for bioethanol. Instead, a long-term stability study was carried out over seven months, and the storage temperature was 21 °C. Linear regression was the statistical test used to calculate the bioethanol samples' stability.

2.8. Uncertainty calculation

The uncertainty calculation for certification of bioethanol's RM was estimated for each parameter. Eq. (1) was used to estimate the combined uncertainty associated with each electrochemical value from the contributions of the characterisation, homogeneity and stability studies [9].

$$u_{CRM} = (u_{char}^2 + u_{bb}^2 + u_{lts}^2)^{1/2} \quad (1)$$

where u_{CRM} is the uncertainty associated with the property value of a CRM, u_{char} is the characterisation standard uncertainty, u_{bb} is the between-bottle (homogeneity) standard uncertainty and u_{lts} is the long-term stability standard uncertainty.

The expanded uncertainty (U) for each parameter of this bioethanol RM was calculated by multiplying the combined uncertainty by a coverage factor of $k=2$, which corresponds to an approximately 95% confidence level according to GUM [31].

3. Results and discussion

3.1. Homogeneity study

Table 1 shows the results of the homogeneity study performed for the three electrochemical parameters, using ANOVA as a statistical tool; this includes the values of $F_{experimental}$ and F_{table}. As can be observed in the table, the results of $F_{experimental}$ for all parameters presented values lower than F_{table}, with a p-value > 0.05. Therefore, these parameters are considered homogeneous in this batch of bioethanol because they do not present significant differences within and between bottles.

3.2. Long-term stability study

Previous experience was evaluated concerning bioethanol matrix CRM through a short-term stability study carried out at different temperatures of 4 °C and 50 °C. Based on the results obtained in these studies, no changes in the parameters were observed when the storage conditions were altered. Therefore,

Table 1
Results of ANOVA homogeneity study of three electrochemical parameters in bioethanol.

Parameters	$F_{experimental}$	F_{tabled}
Total acid number	1.2965	3.0557
pHe	1.9165	2.3928
Electrolytic conductivity	1.4140	2.0889

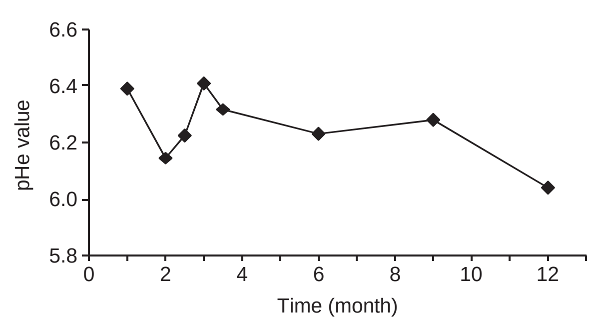

Fig. 1. Results of pHe long-term stability study for bioethanol CRM.

Table 2
Linear regression of the long-term stability study at 21 °C.

Parameters	p-value	Standard deviation (sb)
Total acid number	0.243011	0.061550
pHe	0.838133	0.012790
Electrolytic conductivity	0.155521	0.001567

there was no need to take precautions concerning temperature during transportation of the bioethanol CRM in the temperature range studied.

A long-term study was performed on bioethanol for the three parameters using the classical stability study [9], in which individual samples are prepared at the same time under identical conditions and measured as a function of time. In this case, the study was carried out under reproducibility (within-laboratory) conditions. As an example of this study, the results of linear regression for the pHe parameter are presented in Fig. 1; it can be seen that the batch remained stable for more than seven months. It is worth mentioning that this batch will be monitored in relation to the property values while there are bottles available on the shelf.

The calculation of long-term stability was based on linear regression, and the results can be observed in Table 2. The *p*-value indicates that the regression was insignificant (it becomes significant for a level of confidence of, for example, 95% for $p<0.05$). Therefore, the batch of bioethanol was stable.

In Table 3, the uncertainty budget–estimated according to GUM [31] and Eurachem [32]–can be observed; the sources considered for the characterisation of the acid number parameter are presented. The value for total acid number was 16.20 ± 0.80 mg L^{-1}.

For pHe characterisation, two methods were employed using two commercial pH meters from the same manufacturer but different models, specifically models 713 and 780. The uncertainty budget for the first method used in the pHe measurement [33] is shown in Table 4.

Table 3
Uncertainty budget for characterisation of total acid number.

Uncertainty source	Value	Units	Standard uncertainty	Sensitivity coefficient	Contribution of standard uncertainty
NaOH standard solution	0.0217	mol L^{-1}	0.0003	7.4463×10^{2}	2.1315×10^{-1}
Repeatability	0.1945	mg L^{-1}	0.0435	1	4.3496×10^{-2}
Titrator	−400 a 400	mV	0.0450	-1.7023×10^{1}	-7.6601×10^{-1}
Automatic burette (NaOH)	3.9665	mL	0.0021	2.5690×10^{1}	5.4084×10^{-2}
Automatic burette (sample)	40.1008	mL	0.0015	-4.0321×10^{-1}	-6.1896×10^{-2}
Molar weight (CH_3COOH)	60.0520	g mol^{-1}	0.0010	2.6926×10^{-1}	2.6919×10^{-4}
End-point titration	0.0080	mL	0.0017	2.5819×10^{1}	4.3493×10^{-2}
		Combined standard uncertainty			0.80

Table 4
Characterisation uncertainty of measurement of pHe parameter.

Uncertainty source	Value	Unit	Standard uncertainty	Sensitivity coefficient	Contribution of standard uncertainty
pH 6.86 CRM	6.859		0.0115	−0.7240	−0.0083
pH 4.00 CRM	4.005		0.0130	0.2760	0.0036
Liquid junction	0.0057[a]	V	−0.0033	16.9035	−0.0556
Repeatability	3.45		0.0136	1	0.0136
pH meter			0.0375	1	0.0375
Temperature	25	°C	0.1	−0.0026	−0.0003
			Combined standard uncertainty		0.069

[a] Ref. [14].

Table 5
Results for characterisation of pHe considering two different pH meters.

	Bottle 1	Bottle 2	Bottle3
Average of the measurements with two pH metres ($n=14$)	6.031	6.117	6.059
Combined uncertainty value from the first pH meter ($u_{pH\ meter1}$)	0.069		
Combined uncertainty value from the second pH meter ($u_{pH\ meter2}$)	0.075		
Combined standard uncertainty value from the two pH meters	0.102		
Characterisation value (pHe)	6.07		

Table 6
Characterisation uncertainty for the electrolytic conductivity parameter.

Uncertainty source	Value	Unit	Standard uncertainty	Sensitivity coefficient	Contribution of standard uncertainty
CRM	5	μS cm^{-1}	0.0500	1	0.0500
Repeatability	1.03	μS cm^{-1}	0.0045	1	0.0045
Conductivity metre	0.014	μS cm^{-1}	0.0070	1	0.0070
Temperature		°C	0.0772	0.02	0.00154
Cell constant	0.090	cm^{-1}	0.0010	0.02	0.00002
CO_2 concentration	0.004	μS cm^{-1}	0.0023	1	0.0023
			Combined standard uncertainty		0.10

Table 7
Results of the certification of the electrochemical parameters for the development of bioethanol CRM.

	Total acid number (mg L^{-1})	pHe	Electrolytic conductivity (μS cm^{-1})
Characterisation uncertainty	0.80	0.07	0.051
Homogeneity uncertainty	0.05	0.019	0.005
Stability uncertainty	0.25	0.13	0.016
Certified reference material value[a]	16.2 ± 1.7	6.07 ± 0.30	1.03 ± 0.11

[a] Expanded uncertainty (k=2; approximately 95% of confidence level).

Table 5 shows the summary of the characterisation study in which three samples (bottles) were used. The average obtained from 14 measurements for each bottle can also be seen in the same table. The value of combined standard uncertainty of two pH meters (0.102) was calculated by combining the values (as the square root of the squared sum of both values) of standard uncertainty from each pH meter (0.069 and 0.075). The characterised value for pHe in bioethanol samples was 6.07 ± 0.10.

In Table 6, the uncertainty budget for the characterisation of the electrolytic conductivity parameter can be seen. The value obtained from the characterisation study for the electrolytic conductivity parameter was (1.03 ± 0.10)μS cm^{-1}.

3.3. Certified values

Table 7 presents the results for certification of the electrochemical parameters of the bioethanol batch. These results include combined uncertainties values of homogeneity, stability, and characterisation studies with their respective estimated expanded uncertainties values [9].

4. Conclusions

This work was motivated by the importance of the electrochemical parameters in the development a bioethanol CRM. It focused mainly on the total acid number, pHe and electrolytic conductivity parameters because of their relevance in biofuel analysis, wherein they indicate the risk of corrosion in motor vehicles. This CRM will be used in different applications, mainly to guarantee the quality of the results of the measurements and the validation of the methodologies needed for electrochemical analysis and to assess the quality of bioethanol. The studies of homogeneity and stability required for the certification of bioethanol showed that the batch was homogeneous and stable for more than seven months. After the CRM begins to be used commercially, its stability concerning the electrochemical parameters will be monitored continuously as long as there are CRMs of bioethanol batches on the shelf. The results obtained for the CRM of bioethanol regarding homogeneity, stability and characterisation studies for total acid number, pHe and electrolytic conductivity parameters were (16.2 ± 1.7)mg L^{-1}, 6.07 ± 0.30, and (1.03 ± 0.11)μS cm^{-1}, respectively. These results were obtained with the improvements established in recent Inmetro studies of other batches of the CRM of bioethanol. Therefore, this paper can contribute to the quality of the bioethanol trade because it presents an important tool, specifically the use of a CRM, which is needed to guarantee the results of the measurements with metrological traceability and reliability.

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