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

Isabel Cristina Serta Fraga*, Carla Matos Ribeiro, Sidney Pereira Sobral, Júlio Cesar Dias, Mary Ane Gonçalves, Paulo Paschoal Borges, Fabiano Barbieri Gonzaga

National Institute of Metrology, Quality and Technology—Inmetro Chemical Metrology Division—Dquim, Electrochemistry Laboratory—Label Av. Nossa Senhora da Graças 50, Prédio 4, 25250-020 Xerém, Duque de Caxias, Rio de Janeiro, Brazil

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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 $(16.2 \pm 1.7)\,\mathrm{mg\,L^{-1}}$, 6.07 ± 0.30, and $(1.03 \pm 0.11)\,\mu\mathrm{S\,cm^{-1}}$, 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 (≤ 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 $\mu\mathrm{S\,m^{-1}}$ (3.5 $\mu\mathrm{S\,cm^{-1}}$) and pHe of bioethanol in the range from 6.0 to 8.0 will contribute to corrosion [6].

* Corresponding author. Tel.: +55 21 26799134; fax: +55 21 26799069.
E-mail address: icfraga@inmetro.gov.br (I.C. Serta Fraga).

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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 μS 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 μS 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].