INTERLABORATORY COMPARISON RESULTS FOR QUALITY CONTROL OF THE BIOETHANOL OF AFRICA AND LATIN AMERICA RELATED TO THE ACID NUMBER AND ELECTROLYTIC CONDUCTIVITY PARAMETERS

Paulo P. Borges, Isabel C. Serta Fraga, Fabiano B. Gonzaga, Mary Ane Gonçalves, Sidney P. Sobral, Carla de M. Ribeiro

National Institute of Metrology, Standardization and Industrial Quality - Chemical Metrology Division - Electrochemistry Laboratory, Av. Nossa Senhora das Graças, 50, Xerém, CEP 22250-020, Duque de Caxias, RJ, Brazil. E-mail: ppborges@inmetro.gov.br

Abstract: Some laboratories from Africa and Latin America involved with the quality control of biofuels have participated in an Interlaboratory Comparison (IC) in anhydrous bioethanol organized and coordinated by Inmetro. This IC has aimed to evaluate seven parameters which are important for the quality of this kind of fuel and that are specified by each country for trade. The results obtained from this exercise for the electrochemical parameters such as the acid number and the electrolytic conductivity will be shown in this paper.

Key words: bioethanol, interlaboratory comparison, acid number, electrolytic conductivity.

1. INTRODUCTION

Biofuels constitute a viable alternative in relation to the fuel derived from petrol. The worldwide demand for renewable fuels is increasing, especially because of the reduction of noxious emissions and sulfur-containing gases which are blamed for global warming [1].

Bioethanol can be produced from renewable sources, such as sugarcane and corn. The products of its combustion are lower pollutants. In order to guarantee the quality of this fuel, several analytical parameters and their limit values have been established so that bioethanol can be commercialized as fuel [2].

Inmetro, the Brazilian Metrology Institute, exerts a key role in the research of biofuels in general. Thus, Inmetro aims to contribute to fundamental research, development and production of reference materials to provide metrological traceability for national industrial laboratories, by means of certified reference materials (CRMs), in accordance with international procedures which are necessary to make biofuels a commodity [3].

In order to assist the National Metrology Institutes (NMIs) and independent quality laboratories from Africa and Latin America with technical qualification in measurement of some parameters in anhydrous ethanol, Inmetro, organized and coordinated an IC inside the Project named *Standards for the Ethanol of Africa and Latin America.* This exercise was performed to compare the measurement results of these laboratories with the reference values assigned by Inmetro for providing traceable results needed to develop reference methods and suitable reference materials in this important biofuel matrix.

In this IC, a total of 7 parameters were measured: acid number, electrolytic conductivity, copper content, density, sulphate content, water content and ethanol content. However, only the first two parameters were chosen to be shown in this paper since they were determined by electrochemical techniques.

The parameters which were evaluated in this IC define the quality of ethanol used as a fuel with international acceptance. It is extremely important to carry out the determination of these parameters with confidence and metrological traceability. Therefore, the IC was carried out with samples of ethanol fuel with certified values, allowing a more confident evaluation of the laboratories' performance regarding the determination of quality parameters for the bioethanol.

2. PURPOSE

This paper aims to present the results of the IC for the parameters acid number and electrolytic conductivity measured in anhydrous ethanol (bioethanol) obtained by the laboratories from Africa and Latin America.

3. MATERIALS AND METHOD
3.1. Sample
The comparison item was made up from samples of anhydrous ethanol. The samples of bioethanol from sugar cane (approximately 99.6 % ethanol content) were provided by a Brazilian producer in a container of 200 L. The bioethanol was bottled in about 2500 amber glass ampoules of 20 mL which had been evacuated with argon and flame-sealed. The number of bioethanol samples needed for the determination of each parameter was sent by Inmetro to the participating laboratories.

3.2. Characterization, Homogeneity and Stability Studies
Inmetro was responsible for the preparation, bottling, characterization, homogeneity and stability tests of the comparison item based on ISO GUIDE 35 [4].

For acid number characterization, the measurement was carried out in triplicate by automated volumetric titration (Metrohm 836 automated potentiometric Titrando) with potentiometric end-point detection by means of a combined

pH glass electrode with KCl internal filling solution previously checked by CRM of pH 6.86 and pH 4.00. The bioethanol samples were titrated with NaOH 0.02 mol L^{-1} solution standardized with HCl 0.01 mol L^{-1} (determined by the primary system of coulometry from Inmetro). The result was expressed as quantity of acetic acid, in milligrams of acetic acid per liter of bioethanol. For electrolytic conductivity characterization, the electrolytic conductivity was determined by means of one conductivity meter (Metrohm 712) coupled with a conductivity cell (Metrohm 6.0901.040) with constant value of 0.090 cm^{-1} (previously checked with CRM of 5 µS cm^{-1}), a magnetic stirrer and a resistance thermometer, Pt 100. All the measurements were carried out in duplicate at 25 °C.

After bottling, the homogeneity study of the batch of samples was carried out with the aim to determine the within and between-bottle variation. The measurements were performed under repeatability conditions. The homogeneity was assessed using a *one-w*ay analysis of variance.

Stabilities studies were conducted to establish both dispatch conditions (short-term stability) as well as storage conditions (long-term stability). Short-term stability studies were performed during four weeks. A long-term stability study was carried out using the classical design, where the measurements were taken under within–laboratory reproducibility conditions. The long-term stability study of test material was evaluated using regression analysis.

The uncertainty budget from these studies was estimated according to ISO GUM [5] and Eurachem/CITAC [6].

3.3. Statistical Analysis

z-score (zeta score) was used as the statistical test to evaluate the performance of the participant laboratories (Equation 1). The reference value and the variability (s) due to the uncertainty of the CRM (the comparison item) for the acid number and the electrolytic conductivity properties were assigned by Inmetro.

$$z_i = \frac{y_i - y_{ref}}{s} \tag{1}$$

Where: y_{ref} is the reference value; y_i is the average result of a specific laboratory i; s is the uncertainty of the CRM. The performance of the laboratory was classified as satisfactory, unsatisfactory or questionable, presented as follows: $|z| \leq 2$, satisfactory result; $2 < |z| < 3$, questionable result and $|z| \geq 3$, unsatisfactory result.

4. RESULTS

Table 1 shows the reference values with their expanded uncertainty (U) which was considered as the variability s (Equation 1) for the electrochemical parameters: acid number and electrolytic conductivity for this IC.

Table 1. Reference values for the electrochemical parameters.

Parameter	Reference value	U (*k*=2, 95%)	Unit
Acid number	45.2	2.1	mg L^{-1}
Electrolytic conductivity	0.54	0.15	µS cm^{-1}

In Figs. 1 and 2, the reference value (Ref) is given as a black solid line; the limits denoted by the gray lines are the reference values ± expanded uncertainty (Ref ± U), the limits denoted by the blue lines are Ref ± 2U and the limits denoted by the red lines are Ref ± 3U. The uncertainty bars of these values denote the standard deviation from the three measurements.

The results for acid number are given in Fig. 1. Eight laboratories reported acid number results. Two laboratories reported results below 45.2 mg L^{-1}. The laboratories 39 and 67 were outside of the plot scale.
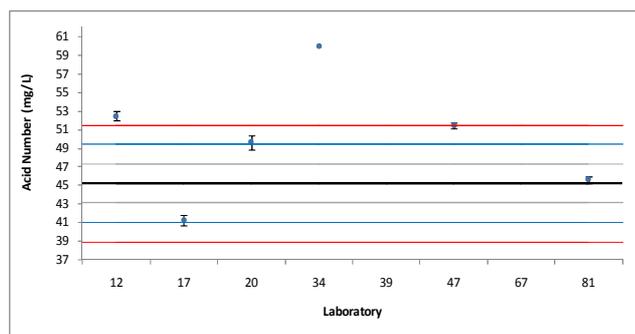

Fig. 1. Results for acid number parameter.

The results for electrolytic conductivity are shown in Fig. 2. Seven laboratories reported electrolytic conductivity results, of which only one laboratory reported results below 0.54 µS cm^{-1}. The laboratory 67 reported the results higher than the reference value; therefore its result can not be seen on the plot.
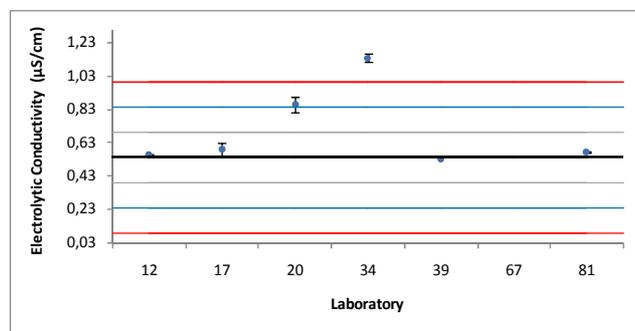

Fig. 2. Results for electrolytic conductivity parameter.

The *z*-score plot for measurements of acid number obtained by the participant laboratories in this IC is presented in Fig. 3.
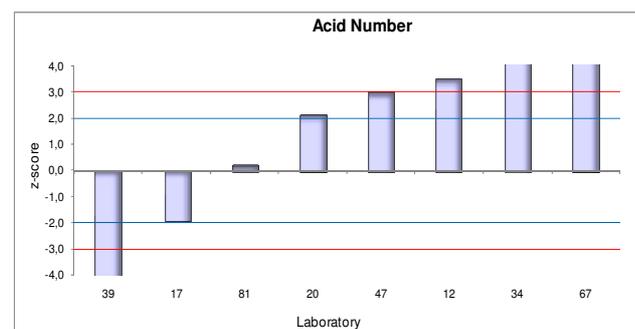

Fig. 3. Graph of z-score on the measurement of acid number.

In Fig. 4, the *z*-score plot for measurements of electrolytic conductivity obtained by the participant laboratories is shown.
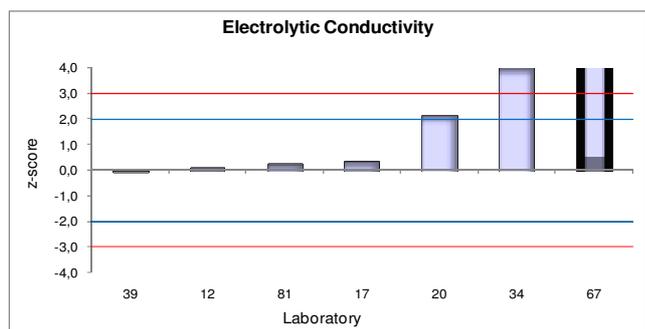

Fig. 4. Graph of z-score on the measurement of electrolytic conductivity.

5. DISCUSSION

After the studies of characterization, homogeneity and stability, the reference material was certified, providing reference value for this IC as shown in Table 1 as well as the variability (s) related to the expanded uncertainty value of the CRM shown in Equation 1. Laboratories from different countries participated in this exercise of IC. From the 8 laboratories which measured the acid number (Fig. 3), five laboratories presented unsatisfactory results; one laboratory presented a questionable result, and two laboratories presented satisfactory results. The participant laboratories presented different performances due to the use of different indicators, such as phenolphthalein (laboratories 20, 39, 47 and 81), bromothymol blue (laboratory 34), alpha-naphtolphthalein (laboratories 17 and 67) and also different standards such as ASTM D1613 or NBR 9866. The laboratory 12 used the colorimetric method with phenolphthalein as indicator; however, it did not mention if the requirements of ASTM D1613 standard were followed. Moreover, the laboratory 34 did not mention which standard was followed. From the 7 participant laboratories in the measurement of electrolytic conductivity parameter (Fig.4), 4 laboratories presented satisfactory results; 2 laboratories presented unsatisfactory results and only one laboratory presented questionable result. Three laboratories (12, 34 and 39) did not mention which standard was followed in the measurements, and 2 laboratories (20 and 81) carried out the measurements using the ASTM D1125 standard. The laboratories 17 and 67 followed the requirements of the NBR 10547 standard. Most of the participating laboratories used 3 ampoules for each measurement with a total of 9 measurements. It is worth to mention that the electrolytic conductivity measurement is strongly influenced by the temperature of the measurement. Thus, the use of calibrated thermometer inside the sample is needed to obtain good results, as well as the use of CRM which has its metrological traceability guaranteed for calibrating the conductivity cell.

6. CONCLUSIONS

The IC showed that the laboratory participants from Africa and Latin America obtained better performance in the measurement of electrolytic conductivity than in acid number measurement due to different standard procedures used as well as different indicators. The participation of the laboratories in the IC is a key role for the harmonic development of CRM of bioethanol and also for the improvement of the measurement for the electrochemical parameters to guarantee the traceability of the measurement in biofuels.

AKNOWLEDGMENTS

REFERENCES

[1] L.A.B. Cortez, "Sugarcane Bioethanol R & D for Productivity and Sustainability", São Paulo, Blücher, Fapesp, 2010.

[2] M.A. Gonçalves, et al., Evaluation study of different glass electrodes by an interlaboratory comparison for determining the pH of fuel ethanol. Sens. Actuators B: Chem., doi:10.1016/j.snb.2011.06.029, 2011.

[3] http://www.inmetro.gov.br/metcientifica/pdf/Final-Report-Anhydrous-Bioethanol-Project-PEAAL.pdf. Last accessed 8 July 2011.

[4] ISO GUIDE 35:2006 "Reference Materials – General and statistical principles for certification".

[5] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (2008), Evaluation of measurement data — Guide to the expression of uncertainty in measurement, first edition, GUM:1995 with minor corrections.

[6] Eurachem/CITAC, "Quantifying uncertainty in analytical measurement", 2nd edition, 2000.