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ELECTROLYTIC CONDUCTIVITY AS A QUALITY INDICATOR FOR BIOETHANOL

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Abstract: This work introduces the European Metrology Research Project on the SI traceability of electrolytic conductivity measurements in bioethanol. As a first step to this aim secondary conductivity measurements have been performed to characterise reproducibility, stability, measurement uncertainty and the significance of the measurement results. The standard measurement uncertainty is in the order of 0.3 %. Two samples from different sources show significantly different conductivity values. The results indicate that conductivity is an appropriate quality indicator for bioethanol.

Keywords: **electrolytic conductivity, bioethanol, SI traceability**

Introduction

Electrochemical characterisation is of increasing interest in terms of the identification of impurities at trace levels within bioethanol to assess risk of corrosion and potential damage to engines. High measurement accuracy, and a strict application of metrological principles in establishing traceability for these measurements, is mandatory to achieve meaningful measurements. In particular, electrolytic conductivity is a ‘quality indicator’ for bioethanol that is needed as an easy-to-use tool to assess the amount of impurities. Substantial work is still required to underpin the traceability of this parameter in order to guarantee metrological comparability [1] of the results. Comparability is a prerequisite for standardization of measuring procedures and essential for the reliability of measured material properties for engineering. Moreover, an assessment of the sensitivity, significance and uncertainty of these measurements is required.

To establish comparability of measurement results they must be traceable to an agreed common metrological reference, which, whenever possible, should be the International System of Units (SI). Nowadays, the result of an electrolytic conductivity measurement (at the application level) is linked to the conductivity value of a reference solution. Typically, the conductivity value of the reference solution is measured traceable to the SI by National Metrology Institutes by means of a primary reference measurement procedure [2]. The value indicated by a conductivity measuring system is usually adjusted by a calibration measurement, such that the actually measured resistance R_{ref} is scaled by the so called cell constant K_{cell} to match the conductivity value κ_{ref} of the reference solution:

$$\kappa_{\mathrm{ref}} = K_{\mathrm{cell}} / R_{\mathrm{ref}}. \quad (1)$$

Cells, which cell constants are adjusted in this way, are referred to as secondary cells in contrast to primary cells, where the cell constant is determined by geometric measurements [2]. The measured resistance is affected by the electric field distribution and the correlated spatially distributed current density within the measuring cell [3] and by electrode polarisation. Both effects depend on the design of the cell, the kind of solution and its ion concentration. Consequently, when non-matrix matched reference solutions are used for calibration, conductivity cells of different cell design can provide different conductivity results for an equivalent biofuels sample, even if their cell constant is adjusted with the same reference solution. Therefore the comparability of conductivity measurement results is the more questionable, the more the properties of the solution under investigation deviate from those of the reference solution. At least, the measurement uncertainty must consider the effect of matrix-mismatch.

Concerning bioethanol, reference solutions based on ethanol are inappropriate mainly due to stability issues. Aqueous KCl solutions are typically used for cell calibration [4]. It must be emphasised that the nominal conductivity value of the lowest stable aqueous KCl reference solution recommended by OIML and IUPAC is, at 25°C, 140.82 mS m^{-1}[5] and that of ASTM solution D is 14.693 mS m^{-1}[6], while the conductivity of bioethanol is in the order of 0.1 to 0.2 mS m-^{1}. Hence, the common calibration procedure make use of a reference solution that significantly differs in the matrix and the in the conductivity value of bioethanol. As a consequence, it must be investigated, if they can nevertheless be used as reference solutions and to what extend the measurement uncertainty must be increased due to the matrix-mismatch. In particular

comparison measurements, in which cells of different design are used, could give more insight into the effect of the matrix-mismatch.

Currently, there exist no conductivity measurements of bioethanol, based on primary reference procedures, which could be used as a basis for providing traceability of measurement results at the application level. Therefore, a work package has been established within the European Metrology Research Project [7] ENG09 [8] that covers among others two main objectives, related to the use of electrolytic conductivity as an important 'quality indicator' for bioethanol:

(i) Research into the measurement of electrolytic conductivity from the primary level to the application level in order to establish SI traceability and
(ii) providing exemplary reference data of bioethanol.

As a first step to establish traceability, the conductivities of two bioethanol samples from different origins, one from Brazil and one from a German producer, were measured with a secondary conductivity measurement cell. The cell constant was adjusted after calibration with a glycerol based KCl solution, which conductivity was in the conductivity range of bioethanol. A method, which has recently been investigated by the authors [9], has been used to determine the solution resistance from impedance spectroscopy measurements of the cell/solution system. This method has particularly been developed to minimize the effect of electrode polarisation on the derived solution resistance in the low conductivity range. Additionally, the measurement uncertainties which particularly include contributions from stability and reproducibility have been determined from the derived solution resistances. Significant differences in the conductivity values of the two different bioethanol samples have been observed.

Measurement of conductivity

Conductivity measurements were performed with a two electrode Jones-type like cell. The general design of the cell is similar to that described in [5], but does not have a removable centre section. Two round and flat electrodes (diameter 2 cm), made of blank platinum, are arranged opposite to each other in a cylindrical body (inner diameter 2.2 cm), made of bore silicate glass. The distance between the electrodes is around 1 cm. Two glass pipes are connected to the main cylinder to fill and empty the cell. The cell constant was adjusted after calibration with a glycerol based KCl solution at 25°C. The conductivity value κ_{ref} of the reference solution has been determined with the primary conductivity measurement setup of PTB [2] to be $(133.0 \pm 0.17)\ \mu\mathrm{S\ m^{-1}}$. The resulting cell constant is $0.1861\ \mathrm{cm^{-1}}$. If not mentioned otherwise all stated uncertainties are standard uncertainties according to the "*Guide to the expression of uncertainty in measurement*" (GUM) [10].

The cell was placed in an air thermostat. Temperature of the solution was measured with a calibrated Pt-100 temperature sensor connected to the measurement bridge MKT50 from Anton Paar. The senor is coated with PTFE and was placed in one of the filling tubes to measure the temperature directly in the solution. After the cell was filled, it took about 60 to 90 minutes until stable temperature conditions were achieved. Then the temperature variation was less then ±2 mK around the mean temperature.

Two different kinds of samples, one from Brazil (sugar cane) and one from Germany (sugar beet) were measured. 2 L of each sample have been homogenized and finally bottled into 250 mL bore silicate bottles under argon atmosphere. The measurements where performed according to the following steps.

1. The conductivity measurement cell was cleaned several times with ultra pure water and finally filled with ultra pure water. Then, the bottle with the sample and the cell were put into the air bath at 25 °C for at least 12 hours before the measurement.
2. The cell was emptied and flooded with Argon for about half an hour until it was dry. Using a peristaltic pump and chemical inert Norprene® tubes the sample was pumped into the cell until it was filled almost up to the rim of the filling tubes. Finally the inlets were sealed with tape. The contact of bioethanol with ambient air and evaporation within the small filling pipes were not completely prevented during this filling step. However, the surface of the solution that was exposed to air or argon was small and the filling time was less than 30 s. The main objectives of the measurements were to characterize measurement stability, reproducibility and uncertainty, rather than measuring the precise conductivity value of bioethanol samples actually having unknown impurities. Hence, the assessed measurement uncertainties due to the mentioned influences are acceptable. They are considered in the uncertainty budget.
3. An impedance spectrum between 20 Hz and 500 kHz, 5 steps per decade, was measured and the best frequency range (see below) was chosen for the measurement.
4. Afterwards impedance spectra were recorded together with temperature for more than 2 h measuring time.
5. Finally the cell was emptied and cleaned several times with ultra pure water.

Calculation of conductivity

The determination of the resistance R_{sol} of the solution between the electrodes is based on an analysis of impedance spectra of various low conductivity solutions measured with different cell types. The basic concept has been developed within the Imera+ European metrology research program TP2-JRP10 [9] and will be discussed in a forthcoming paper. In brief, the determination of the solution resistance is based on the equivalent circuit shown in figure 1. The corresponding impedance spectrum can be separated into two regions. The low frequency part of the spectrum is dominated by electrode polarisation, which is represented by the CPE element and the polarisation resistance R_{p}. The latter accounts for a residual charge transfer across the electrodes. In a complex plane plot this part of the spectrum is nearly a linear line, slightly curved due to the influence of R_{p}. In the high frequency part of the spectrum polarisation effects can

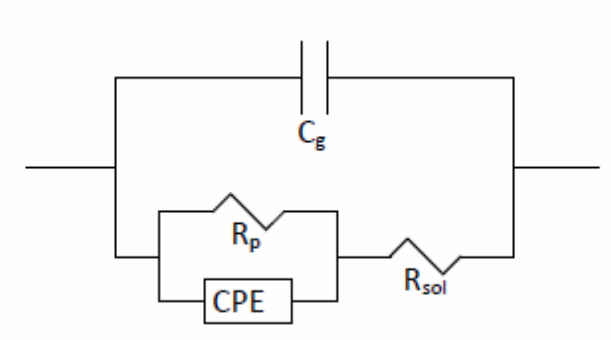

Figure 1 Equivalent circuit used to model the cell solution system to derive the solution resistance R_{sol}. Electrode polarisation is represented by the CPE element and the polarisation resistance R_p, and the geometric capacitance of the electrodes by C_g.

be neglected and the spectrum is dominated by the solution resistance R_{sol} in parallel to the geometric capacitance C_g of the electrodes. In a complex plane plot this part of the spectrum is a semi circle. Concerning the cell used in this investigation for high resistive solutions like ethanol the effect of electrode polarisation on the spectrum can be neglected above 10 kHz. So in this region the equivalent circuit simplifies to the parallel of C_g and R_{sol}.

We have chosen measurement frequencies between around 10 and 400 kHz that result in fairly equidistant impedance values across the semi circle. From all impedances measured at a frequency a mean impedance was calculated. These mean values were used for the semi circle fit. The solution resistance was derived from the corresponding radius r: $R_{sol} = 2r$. This procedure has turned out to be more robust against small (systematic) impedance measurement errors than simply calculating the solution resistance from the impedances by assuming the parallel of R_{sol} and C_g. A typical impedance

spectrum of bioethanol and the semi circle fit is shown in figure 2. The average relative deviation of the measured data points from the fit is less then 0.1 %. The impedance measurements were performed with a high precision commercial LCR-meter (Agilent 4284A).

The conductivity value $\kappa_{sol}(t)$ at the mean measurement temperature t is calculated from R_{sol} and the calibrated cell constant K_{cell} in analogy to equ. (1). The impedances are typically not measured at the exact set temperature of 25 °C, but the measurement temperature deviates about a few tens of mK. The conductivity value at the measurement temperature t is therefore linearly corrected to its value κ_{sol} (25) at 25°C using

$$\kappa_{sol}(25) = \kappa_{sol}(t)/(1+\alpha_\kappa(t-25°C)) \qquad (2)$$

For bioethanol a linear relative temperature coefficient $\alpha_{\kappa be}$ = (2.0 ±0.15) % C^{-1} at 25°C has been determined from

conductivity measurements between 20 and 27°C. The linear temperature coefficient $\alpha_{\kappa ref}$ of the reference solution

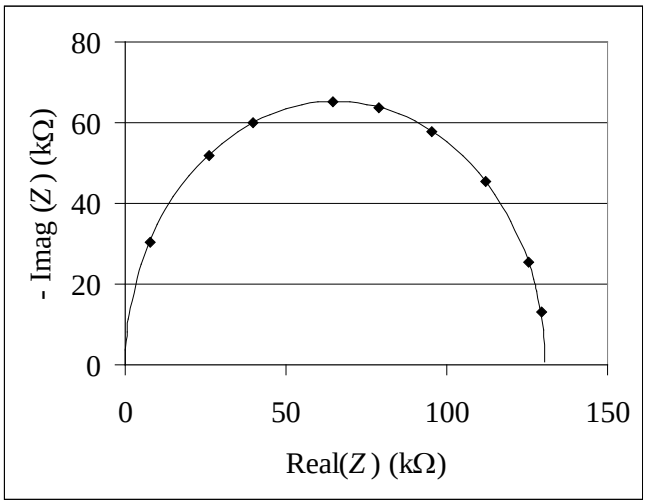

Figure 2 Impedance spectrum of a bioethanol sample in a complex plane plot. The dots are the measured impedances Z, the solid line is a semi circle fit. Frequency range is from 10 to 400 kHz.

is 5.09 % $°C^{-1}$ at 25°C. Using equations (1) and (2) the final conductivity value $\kappa_{be}(25)$ of a bioethanol sample at 25°C has been calculated from the input variables from

$$\kappa_{be}(25) = \frac{\kappa_{ref}(25) R_{ref}(1+\alpha_{\kappa ref}(t_{ref}-25°C))}{R_{be}(1+\alpha_{\kappa be}(t_{be}-25°C))} \qquad (3)$$

In equ. (3) the index “ref” refers to the reference solution and the index “be” to bioethanol.

Results

The measured conductivity values of the two bioethanol samples are

Brazilian sample: (108.37 +/-0.33) µS m^{-1},
German sample: (142.67 +/- 0.43) µS m^{-1}.

The values are significantly larger compared to pure synthetic ethanol, which has a conductivity of a few µS m^{-1}. Additionally, the difference of the results is much larger than their uncertainties. Consequently, conductivity measurements can well serve to characterise bioethanol samples. There are no details available about residual ion concentrations or the production conditions of the samples. So it is difficult to reason the difference. Using ion chromatography, we have performed a first analysis of one of the samples. The anionic ion chromatogram (not calibrated) showed a significant and predominant amount of chloride compared to a measurement of pure synthetic ethanol. Therefore the measured difference of the conductivity values could be the result of residual dissolved chloride salts. However, this assumption still needs to be verified quantitatively.

Figure 3 demonstrates the stability of the measurement results after temperature equilibrium has been reached. The error bars indicate the expanded measurement uncertainty (coverage factor 2). An unspecific, small drift can be seen. The reason for it is not clear. However, the drift within the

measurement period is considered in the stated measurement uncertainty.

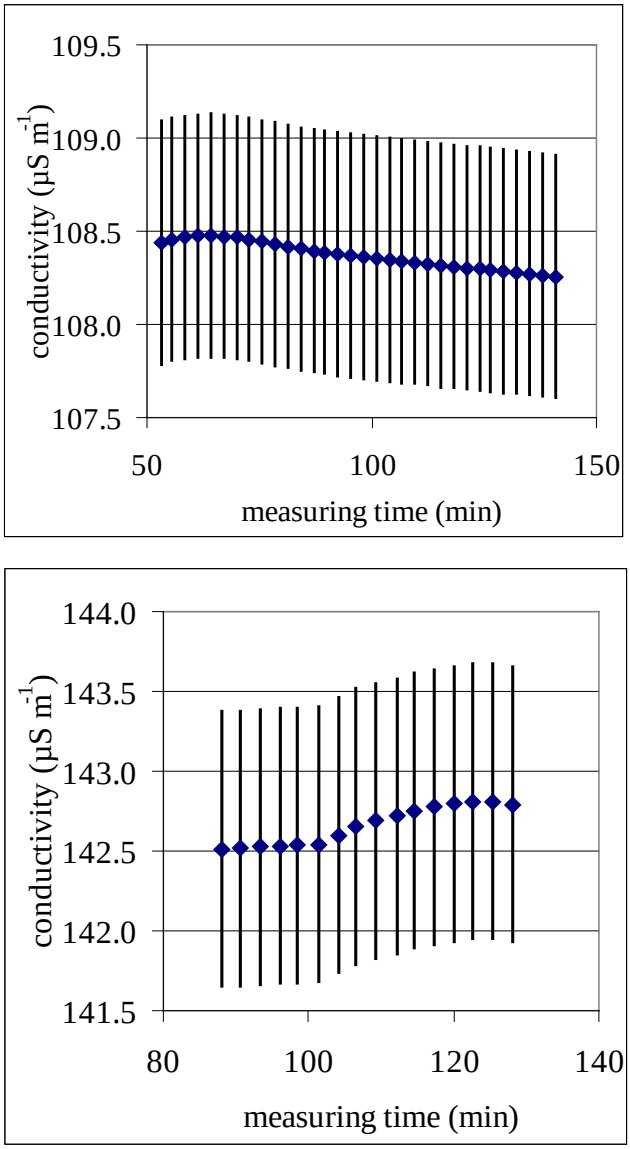

Figure 3 Stability of the conductivity measurement results of bioethanol from Brazil (above) and Germany (below). The error bars indicate the expanded ($k = 2$) uncertainty.

Table 1 identifies the main sources of uncertainty (first column) and their estimated standard uncertainties (second column) exemplarily for the bioethanol sample from Germany. Note that resistance and temperature uncertainties have been separated into a systematic part and a statistical part. This has not been indicated in equ. (3) for reason of readability. Inaccuracies of the measuring devices and, in case of the resistances, of the method to derive them, entered into the systematic contributions. It should also be noted that the systematic uncertainties of the solution resistances have been calculated with a Monte Carlo method [11], since it is practically impossible to use the analytical GUM framework to handle the complex-valued impedances and the fitting procedures involved in resistance calculation. The statistical contributions reflect the measurement stability and were calculated from the standard deviation of the mean of the measured values.

Source of uncertainty of input quantity x_i	**uncertainty $u(x_i)$**	**$u_{xi}(\kappa_{be})/\kappa_{be}$ (%)**
conductivity of reference solution	0.17 µS m^{-1}	0.128
temperature of reference solution (systematic)	10 mK	0.051
temperature stability of reference solution	0.4 mK	0.002
temperature of bioethanol (systematic)	10 mK	0.020
temperature stability of bioethanol	1.6 mK	0.002
resistance of reference solution (systematic)	124 Ω	0.099
resistance stability of reference solution	2.3 Ω	0.002
resistance of bioethanol (systematic)	149 Ω	0.114
resistance stability of bioethanol	2.9 Ω	0.022
reproducibility	0.27 %	0.27

Table 1 Contributions to the combined measurement uncertainty of the conductivity value κ_{be}, exemplarily for the bioethanol sample from Germany. $u_{xi}(\kappa_{be})$ is the propagated uncertainty contribution of x_i to the uncertainty of κ_{be}.

Uncertainty propagation has then been calculated straight forward from equ. (3) according to the general GUM uncertainty framework [10]. The last column shows the relative uncertainty contributions of the input variables to the uncertainty of the conductivity value.

The main contributions to the measurement uncertainty result from the conductivity of the reference solution and the reproducibility of the measurement results. The latter has been determined from independent measurements of four samples that have been homogenised and afterwards bottled as described above. The observed variation of the values within a relative standard deviation of 0.27 % is probably due to the instability of the measurement shown in figure 3.

The uncertainty calculation accounted for correlations between the input quantities

(i) R_{ref} and R_{be} (the resistance of bioethanol) values with respect to the systematic uncertainty contributions,

(ii) temperature measurement results of calibration measurement and bioethanol measurement with respect to the systematic uncertainty contributions,

(iii) temperature values and temperature corrected conductivity values (corresponding resistance values, respectively), which are measured at the same time.

For (i) and (ii) a correlation coefficient of one has been assumed, since all the measurements have been performed with the same system, using the same evaluation method. Any systematic measurement error in (i) or (ii) due to an offset is therefore nearly equal in the measurement of the reference solution and the solution under investigation. Scaling effects have been neglected, since the measurement results are compatible. As a consequence, although the relative uncertainties of the measured resistances are compatible to that of the conductivity reference value and to that attributed to reproducibility, they barely contribute to the combined uncertainty of the conductivity value. For (iii) the correlation coefficient has been statistically calculated from temperature corrected resistance values and the corresponding temperatures, in order to account for correlations that are not covered by the linear temperature correction. Here the correlation coefficient is typically around -0.5 to -0.7.

Conclusion

The results indicate that conductivity measurements can well serve to measure differences in the composition of bioethanol samples. Under laboratory conditions the combined relative standard uncertainty of such measurements is around 0.3 %. This particularly includes contributions from the stability of the solution during the measurement and the reproducibility of the measurement results. However, the measured conductivities have been related to the conductivity value of the glycerol based KCl solution that has been used to adjust the cell constant. The measured cell constant of a secondary cell depends on the matrix of the reference solution. Therefore the matrix-mismatch of bioethanol and the reference solution cast doubts on the comparability of the measured values, if these are measured using a different cell type. In other words measurements of the same solutions using another cell type could provide different conductivity values, even if the cell constant is adjusted with the same reference solution as used in this work. However, getting consistent, i.e. comparable, measurement results is a prerequisite for any standardisation work and a reliable data bases for engineering. Therefore further work is needed to achieve this aim. The next steps within the European Metrology Research Project ENG09 will be to investigate conductivity measurements of bioethanol on the primary level and to perform comparison measurements to investigate the effect of different designs of secondary cells on the measured values.

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