ACTA IMEKO
September 2014, Volume 3, Number 3, 38 – 42
www.imeko.org

Electrolytic conductivity as a quality indicator for bioethanol

Steffen Seitz[1], Petra Spitzer[1], Hans D. Jensen[2], Elena Orrù[3], Francesca Durbiano[3]

[1] *Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany*
[2] *Danish Fundamental Metrology Ltd., Matematiktorvet 307 DK-2800 Kgs. Lyngby, Denmark*
[3] *Istituto Nazionale di Ricerca Metrologica, Strada delle Cacce 91, 10135 Turin, Italy*

ABSTRACT
We present results of 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 characterize reproducibility, stability, measurement uncertainty and the significance of the measurement results. The relative standard measurement uncertainty is of the order 0.3 %, while inter-laboratory reproducibility is around 6.9 %. The measured conductivities of two samples from different sources show a relative difference of around 30%. These results show that conductivity is an appropriate quality indicator for bioethanol. However, it also demonstrates that inter-laboratory reproducibility has to be improved, in particular with respect to SI traceability.

Section: RESEARCH PAPER

Keywords: bioethanol; electrolytic conductivity; measurement uncertainty

Citation: Steffen Seitz, P. Spitzer, F. Durbiano, H. Jensen , Electrolytic conductivity as a quality indicator for bioethanol, Acta IMEKO, vol. 3, no. 3, article 9, September 2014, identifier: IMEKO-ACTA-03 (2014)-03-09

Editor: Paolo Carbone, University of Perugia

Received June 12th, 2013; **In final form** May 27th, 2014; **Published** September 2014

Funding: This work was supported by Measurement Science Consultancy, The Netherlands

Corresponding author: Steffen Seitz, e-mail: steffen.seitz@ptb.de

1. INTRODUCTION

Electrochemical characterisation of bioethanol is of interest in terms of the identification of impurities at trace levels 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 measurement procedures and essential for the reliability of measured material properties for engineering. Moreover, an assessment of 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:

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

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 dimensional measurements [2]. The measured resistance is affected by the electric field distribution and the correlated spatial distribution of the current density within the measuring cell [3]. Additionally it is affected by electrode polarisation. Both effects depend on the design of the cell, the kind of solution and its ion concentration. Consequently, conductivity cells of different cell

design can provide different conductivity results for an equivalent sample, even if their cell constant is adjusted with the same reference solution. Therefore the comparability of conductivity measurement results is more questionable, the further the properties of the solution under investigation deviate from those of the reference solution. It is practically not possible to provide a matrix-matched primary reference solution for any kind of solution. However, in any case 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 is 140.83 mS m^{-1}, [5], that of IUPAC is 140.82 mS m^{-1}) [6] at 25°C and that of ASTM solution D is 14.693 mS m^{-1}[7], while the conductivity of bioethanol is in the order of 0.1 to 0.2 mS m^{-1}. Hence, the common calibration procedure makes use of a reference solution that significantly differs in the matrix and 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 extent 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 ENG09 [8, 9] 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) to provide 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 determined 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 [10], 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.

2. MEASUREMENT PROCEDURE

Conductivity measurements were performed with a two electrode Jones-type like cell. A sketch of the setup is shown in Figure 1. The general design of the cell is similar to that described in [6], 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 determined 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 ± 0.17) μS m^{-1}. The resulting cell constant is 18.61 m^{-1}. If not mentioned otherwise all stated uncertainties are standard uncertainties according to the "*Guide to the expression of uncertainty in measurement*" (GUM) [11].

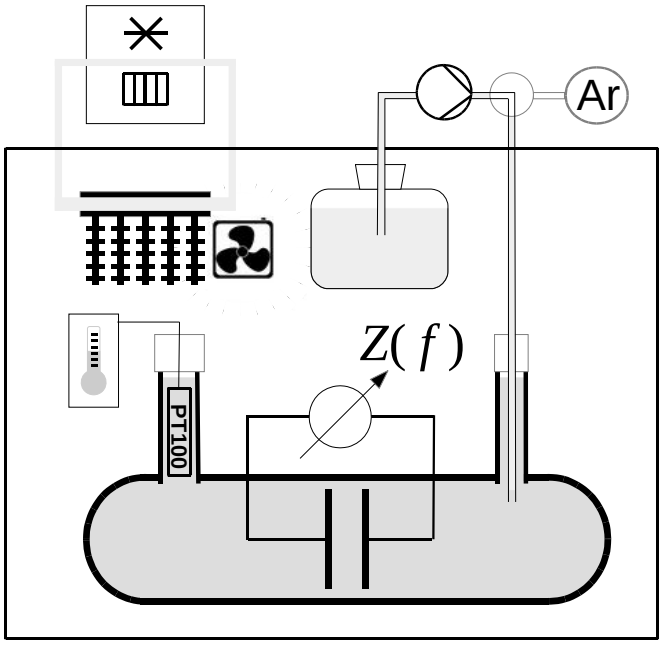


Figure 1. Sketch of the measurement setup, using a two electrode cell that is placed in a temperature controlled air bath. The contact of the sample with ambient air is minimised by pumping it into the cell. Argon is used to dry the cell after cleaning it with ultra pure water.

The cell was placed in an air thermostat. Temperature of the solution was measured with a calibrated Pt-100 temperature sensor connected to a measurement bridge MKT50 from Anton Paar. The sensor 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 than ±2 mK around the mean temperature.

Two different kinds of bioethanol samples, one from Brazil (produced from sugar cane) and one from Germany (produced from sugar beet), were measured. 2 L of each sample have been and finally bottled into 250 mL bore silicate bottles under an argon atmosphere that had been bubbled through ethanol in a gas washing bottle before. 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, a 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. Evaporation of ethanol within the cell was 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 corresponding measurement uncertainty has been considered in terms of measurement reproducibility.
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.

At the end the cell was emptied and cleaned several times with ultra pure water.

3. CONDUCTIVITY CALCULATION

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-Plus European metrology research program TP2-JRP10 [10]. In brief, the determination of the solution resistance is based on the equivalent circuit shown in Figure 2. 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 be neglected and the complex plane plot in this part of the spectrum is a semicircle. Concerning the cell used in this investigation the effect of electrode polarisation on the spectrum can be neglected above 10 kHz for high resistive solutions like ethanol. 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 semicircle. At each given frequency the mean impedance was calculated from at least 15 measurements. These mean values were used for the semicircle fit. The solution resistance was derived from the corresponding radius r: $R_{sol} = 2r$. This procedure has turned out to be more robust than calculating the solution resistance analytically from the impedances by assuming the parallel of R_{sol} and C_g. The latter way usually shows a significant dependence of the resistance on frequency resulting from small impedance measurement errors. Figure 3 shows the impedances of a typical measurement of bioethanol and the corresponding semicircle fit in a complex plane plot. The average relative deviation of the measured data points from the fit is less than 0.1%. The impedance measurements were performed with a high precision commercial LCR-meter (Agilent 4284A).

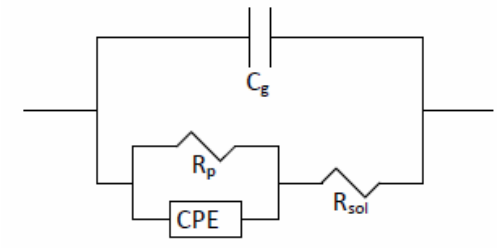


Figure 2. Equivalent circuit used to model the cell solution system to derive the solution resistance R_{sol}. Electrode polarisation is represented by the CPE element and the polarisation resistance R_p. C_g is the geometric capacitance of the electrodes.

The conductivity value $\kappa_{sol}(t)$ at the mean measurement temperature t, given in the unit °C, is calculated from R_{sol} and the calibrated cell constant K_{cell} in analogy to equation (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 the value $\kappa_{sol}(25°C)$ at 25°C using

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

For bioethanol a linear relative temperature coefficient $\alpha_{\kappa be} = (2.0 \pm 0.15)\%\ °C^{-1}$ at 25°C has been determined from conductivity measurements between 20°C and 27°C. The linear temperature coefficient $\alpha_{\kappa ref}$ of the reference solution is 5.09% °C^{-1} at 25°C. Using equations (1) and (2) the final conductivity value $\kappa_{be}(25°C)$ of a bioethanol sample has been calculated from the input variables:

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

In equation (3) the index "ref" refers to the reference solution and the index "be" to bioethanol.

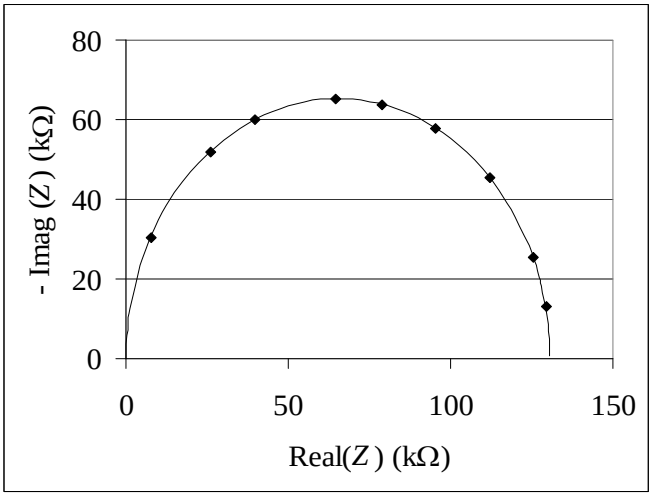
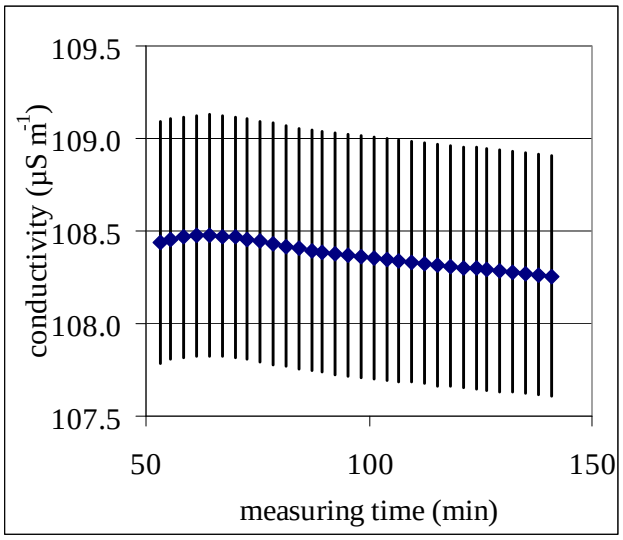


Figure 3. Impedances of a bioethanol sample in a complex plane plot. The dots are the measured impedances Z, the solid line is a semi circle fit. Frequency range is from 10 to 400 kHz.



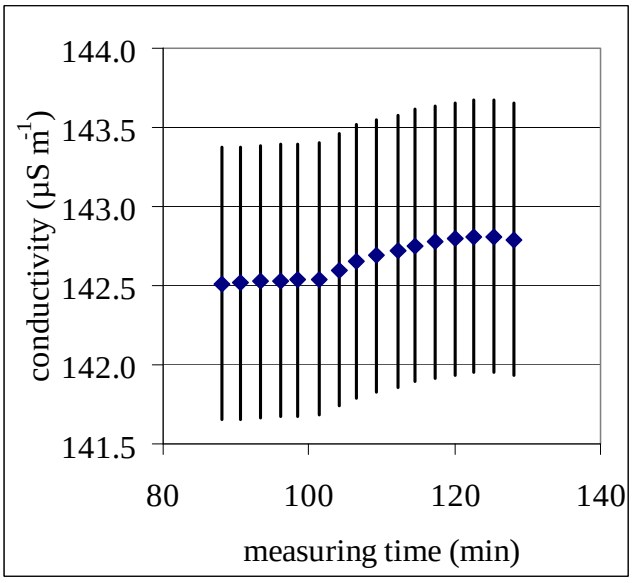


Figure 4. Stability of the conductivity measurement results of bioethanol from Brazil (above) and Germany (below). The error bars indicate the expanded ($k = 2$) uncertainty.

4. RESULTS

The measured conductivity values of the two bioethanol samples are

Brazil 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.

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}.

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
repeatability	0.27 %	0.27

Figure 4 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.

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 considered systematic and statistical contributions. 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 [12], 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.

Uncertainty propagation has then been calculated straight forward from equation (3) according to the general GUM uncertainty framework [11]. 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 repeatability 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 4.

The uncertainty calculation also accounted for correlations between the input quantities:

(i) R_{ref} and R_{be} 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 of similar magnitude. 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 repeatability, 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.

The described measurements have been performed at the Physikalisch-Technische Bundesanstalt (PTB) and reflect the characteristics of the setup used there. In order to estimate inter laboratory reproducibility a conductivity comparison measurement of bioethanol was performed, including the German (PTB), the Danish (Danish Fundamental Metrology) and the Italian (Istituto Nazionale di Ricerca Metrologica) metrology institutes. All participants used secondary cells for the measurements. Two institutes calibrated the cells with glycerol based KCl solutions, and one institute used a water based KCl solution. The relative standard deviation of the results was 6.9%, which is significantly larger than the individually reported standard measurement uncertainties (0.3% to 1%). This cannot be explained by inhomogeneity of the samples. It is more likely due to differences in sample handling, in cell design, in measurement and data evaluation procedure. The comparison will be repeated with more institutes and a more detailed sample handling and measurement instruction. However, the result of the comparison gives an upper limit for inter laboratory reproducibility of conductivity measurements of bioethanol, even though it is, for the time being, rather large compared to typical conductivity measurements.

5. 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 repeatability of the measurement results (at a single institute). 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. This assessment is also supported by the relatively bad inter laboratory reproducibility of 6.9%. In other words measurements of the same solutions using another cell type could provide different conductivity values, even if the cell constant is determined with the same reference solution. However, getting consistent, i.e. comparable, measurement results is a prerequisite for any standardisation work and a reliable data base for engineering. Therefore further work is needed to achieve this aim. The next steps will be to investigate conductivity measurements of bioethanol on the primary level and to perform further comparison measurements to investigate the effect of different designs of secondary cells on the measured values.

ACKNOWLEDGEMENT

The research leading to these results has received funding from the European Union on the basis of Decision No 912/2009/EC.

REFERENCES

[1] International Vocabulary of Metrology, ISO/IEC, 2012.
[2] F. Brinkmann, N. E. Dam, E. Deák, F. Durbiano, E. Ferrara, J. Fükö, H. D. Jensen, M. Máriássy, R. H. Shreiner, P. Spitzer, U. Sudmeier, M. SurduL. Vyskocil, Primary methods for the measurement of electrolytic conductivity, Accred Qual Assur 8 (2003), pp. 346-353.
[3] S. L. Schiefelbein, N. A. Fried, K. G. RhoadsD. R. Sadoway, A high-accuracy, calibration-free technique for measuring the electrical conductivity of liquids, Rev. Sci. Instrum. 69 (1998), pp. 3308-3313.
[4] J. Barthel, F. Feuerlein, R. NeuederR. Wachter, Calibration of Conductance Cells at Various Temperatures, Journal of Solution Chemistry 9 (1980), pp. 209-219.
[5] Standard solutions reproducing the conductivity of electrolytes, OIML, 1981.
[6] K. W. Pratt, W. F. Koch, Y. C. WuP. A. Berezansky, Molality-based primary standards of electrolytic conductivity, Pure Appl. Chem. 73 (2001), pp. 1783-1793.
[7] Standard test methods for the electrical conductivity and resistivity of water, ASTM-International, 1995.
[8] European Metrology Research Project. Available: http://www.emrponline.eu/
[9] Publishable JRP summary: EMRP JRP- ENG09 (2009). Available: http://www.euramet.org/fileadmin/docs/EMRP/JRP/JRP_Summaries_2009/ENG09_Publishable_JRP_Summary.pdf.
[10] Publishable JRP summary: EMRP T2 JRP10 - Tracebioactivity (2007). Available: http://www.euramet.org/fileadmin/docs/EMRP/JRP/iMERA-plus_JRPs_2010-06-22/T2.J10_TRACEBIOAVTIVITY_publishable_summary_April10_V1.pdf
[11] Guide to the expression of uncertainty in measurement, JCGM, 2008.
[12] Guide to the expression of uncertainty in measurement, Supplement 1: Propagation of distributions using a Monte Carlo method, JCGM, 2008.