Good Practices in Evaluating the Uncertainty of Measurements for the Conductivity of the Electrolyte Solutions

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This paper intends to present the theoretical background as well as practical illustrations for good laboratory practices in conductivity measurements, ways to increase the accuracy of conductivity measurements as well as how one may evaluate the uncertainty of conductivity measurements for the electrolyte solutions. Practical measurements for prepared standards of 1 M KCl and 0.1 M KCl solutions are carried out and the values of repeatability, composed uncertainty and expanded uncertainty are presented.

Keywords: errors, uncertainty, conductivity, traceability

Measurements of the electrolytic conductivity tend to become *sine qua non* determinations as time goes by due to their inherent advantages such as simplicity, state of the art conductivity meters provided with automatic temperature compensation, possibility to interface the meters in computerized data acquisition systems etc. [1-8]. However, as the demand for precision and accuracy of measurements increases more and more, one may no longer disregard some errors factors overlooked in the past. In order to increase accuracy one should pay particular attention to some factors such as: measurement carried out in small sample volumes, selecting the proper measurement range as close to the actual value, the use of the appropriate conductivity probe and cell constant, calibrating the meter with standards of proven traceability [1, 2]. Although many fundamental books and papers define the conductivity based on the analogy with the electrical conductivity of solid state electronic conductors considering the resistance of that particular electrolyte solution:

$$R = \rho \cdot \frac{l}{A} \quad (1)$$

where ρ is the specific resistivity and hence the opposite of resistivity, the conductivity:

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A} \quad (2)$$

the actual determination of the conductivity of an electrolyte solution is carried out from the impedance measurements. Measurement of alternating current impedance is a way to reduce the electrodes polarization effect. The ration of l / A from eq. 1 and 2 defines the conductivity cell/probe constant, K_{cell}, where l is the distance between the electrodes and S is the common surface area [1-10].

$$K_{cell} = \frac{l}{S} \quad (3)$$

A single conductivity cell cannot satisfy the huge range of conductivity values, therefore one should pay particular attention to this and use conductivity probes with cell constant directly related to the considered conductivity range [10]:

Table 1
RECOMMENDED VALUES FOR CELL CONSTANT [10]

Cell Constant cm^{-1}	Recommended conductivity range µS/cm
0.1	0.5 to 400
1	10 to 200
10	1000 to 200,000

Factors affecting the conductivity measurements

Cell Geometry

The cell geometry is a significant factor in measuring the conductivity as the distance between electrodes can affect the impedance values of the solution. If the distance between the electrodes is too small, one will measure low impedance values, resulting in a strong influence of electrodes upon the ionic strength, affecting not only the ions that come into contact with their surfaces, but also those in the electrodes proximity, known as the field effect; its influence decreases with increasing the electrodes distance [11].

Electrodes polarization

The polarization of electrodes is a direct result of the accumulation of ionic species with opposite sign on the electrode surface, due to the existence of the electrical field. To reduce this polarization effect, it is necessary to use AC and not in DC voltage at a frequency range from 800 Hz up to 5 kHz. [1]-[8]. The frequency is a key factor when one wishes to eliminate the effect of polarization. Applying a working frequency too high, one may run the risk to induce a capacitive effect, the electrodes playing this time the role of a capacitor plates. At the other end, low frequencies values, below kHz range can be applied when one deals with at low conductivity values [12]. Manufacturers came with an innovation to overcome this effect by applying a variable frequency controlled voltage, where the frequency is increased as the conductivity values grow [2, 12]. Platinizing the electrodes with black platinum, increasing the electrodes actual specific surface, is another method to reduce the effect of polarization.

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CO_2 effect

The conductivity of the electrolytic pure waters equilibrated with CO_2 is 1.05 mS/cm [1]. Besides the existence of protons and hydroxide ions in solution, even in the pure water, the effect of carbon dioxide is sensed by the conductivity probe as it is in equilibrium with the water and these are the reasons why even the pure water will have a readable conductivity value [1].

Temperature effect

An increase in temperature will cause a decrease of viscosity and an increase in ion mobility in solution. When the temperature increase, the dissociation increases, increasing the total amount of ions in solution. In order to compensate for this effect, one may use conductivity meters with automatic temperature compensation or to apply a linear compensation procedure. In the latter case, the temperature conductivity coefficient of variation, depicted in equation 4:

$$\alpha_{\theta,25} = \frac{\kappa_\theta - \kappa_{25}}{\kappa_{25} \cdot (\theta - 25)} \cdot 100 \quad (4)$$

is assumed to be the same regardless of the temperature measurement and the measured value is used to transpose the conductivity value to the corresponding conductivity value at 25°C:

$$\kappa_{25} = \frac{\kappa_\theta}{1 + (\alpha_{25}/100) \cdot (\theta - 25)} \quad (5)$$

where θ and 25°C are temperatures at which conductivities k_θ and k_{25} respectively are measured.

The standard uncertainty of temperature should be u = 0.1K or better. However to achieve low levels of uncertainty, it is preferred that the sample should be measured in thermostated cells, for acceptable replicated results as well as for a good cell calibration [12, 13].

Good laboratory practices and ways to increase the accuracy of conductivity measurements

The quality of the measurement results of conductivity are part of the contribution of several factors, namely: the human factor, the standard used, the working procedure, the measuring, the measuring unit used, the nature of the sample analyzed. It should be noted that without a certain traceability of the standards used, the conductivity measurements may not be reliable, especially when it comes to those sectors which require a close monitoring of food safety, human health, human safety and environmental protection.

Good laboratory practices impose a series of intercomparison tests with respect to the standards used for calibrating the meters, their purpose being to improve the existing standards, the quality results or to further the development of other standards, which will be used in those areas where the existing standards can not be integrated into the measuring process and to carry out validation according to ISO17025 [12-17].

Traceability

According to International vocabulary of metrology [15], *traceability is property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.* The International Metrology Organization specifies three reference values of conductivity standards as presented in table 2 [14]:

Table 2

RECOMMENDED VALUES FOR STANDARD CONDUCTIVITY [14]

Concentration [mol/L]	Conductivity value [µS/cm]		
	0^0C	18^0C	25^0C
1	65.140	97.81	111.31
0.1	7.134	11.163	12.852
0.01	773.3	1220.1	1408.3

Accuracy of measurement and determination of the uncertainty of measurement

In the case of conductivity measurements, the accuracy is a key factor to achieve the required quality of the expected results, as no matter if one had a good repeatability of measurements, there are always some other factors that can occur, of a technical or human nature, inducing the measurement errors. When one is calculating the uncertainty of measurement, all identified sources of potential errors that can affect the measurement process must be taken into account. Knowing these possible sources of error will help in decreasing or totally eliminating the causes which can affect the results, and by its definition it is the parameter that characterizes the dispersion of associated values [14-17].

Achieving highly accurate measurements is done by using a primary standard; however using this type of standard is very costly, so that using a secondary standard is a better choice and also a common practice, particularly in calibration procedures and/or metrological verification.

The evaluation of uncertainty

Type A evaluation

For type A evaluation, the standard uncertainty, *u,* is given by:

$$u_A = \frac{s}{\sqrt{n}} \quad (6)$$

where s is the standard deviation and is number of terms [14-16].

Type B evaluation

A Type B evaluation of standard uncertainty takes into consideration information coming from previous experimental data, calibration certificate, manufacturer specification, and baseline data from reference sources [12, 14-17].

By combining the type A and B evaluation, one may get a combined standard uncertainty:

$$uc = \sqrt{u_A^2 + u_B^2} \quad (7)$$

Standard expanded uncertainty is achieved by multiplying the combined standard uncertainty with a multiplication factor, which is m = 2 for a probability p = 95% [18].

The uncertainty determination of the conductivity measurements

In order to determine de uncertainty in conductivity measurements, one must identify the sources affecting the measurement: the cell constant and the electrochemical system as an integrated unit *including the auxiliaries.

For the first case, the following factors must be considered: resolution, reproducibility, temperature

distribution, uncertainty of calibration, thermometer precision, thermometer resolution, while for the second one: measuring device accuracy, resolution, reproducibility, temperature distribution, thermometer precision, thermometer resolution.

The scope of this paper is to present the theoretical background as well as practical illustrations for good laboratory practices in evaluating the conductivity of electrolyte solutions and how one may determine the uncertainty in the case of the conductivity measurements of electrolyte solutions.

Experimental part

Methods and materials

The KCl was of p.a grade and was purchased from ChimReactiv SRL. A HACH HQ40D conductivity meter used in connection with a thermostated bath, calibrated thermometers and a thermostated cell was used for the determination of conductivity values. A Kern ABJ analytical scale was used to weigh the solid KCl samples to prepare the electrolyte solutions.

Results and discussions

For 1 M KCL, one has determined the influence of temperature on conductivity for electrolyte solutions prepared with reagent taken directly from the reagent jar and with the same reagent subjected to a drying procedure. In figure 1 and figure 2 are shown the differences between the values when the KCl used for solution preparation was dried and when it was taken as it was direct from the reactive jar. The differences between them is obvious as the main error source for the lower conductivity values is the water which was evaporated during the drying procedure, e.g. at 25^{0}C the conductivity was almost 119.1 mS/cm for substance taken direct from the jar, with a certain water content, the wet substance, while for the dry substance was 119.64 mS/cm. In both cases one may see the linear trend versus temperature.

At 25^{0}C the conductivity value for sample taken from the reagent jar without any intervention is 13.03mS/cm, while for dried sample is 13.28mS/cm. The relative error with reference to a standard value is:

$$\varepsilon_r = \frac{(\kappa_m - \kappa_{ca})}{\kappa_{ca}} \cdot 100\% \quad (8)$$

where κ_m is the average of experimental conductivity data, and κ_{ca} is the reference value of conductivity. In the tables

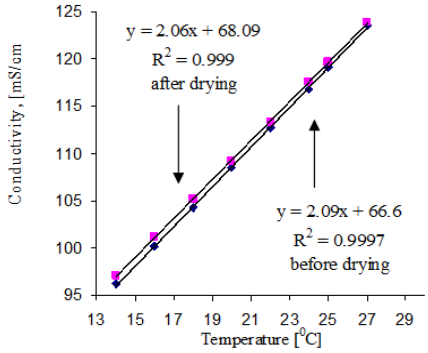

Fig.1. The values of conductivity before drying and after drying the KCl for standards preparations versus temperature for 1 M

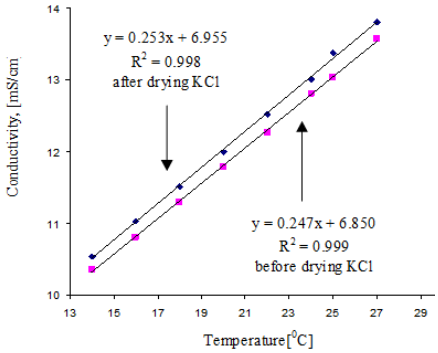

Fig. 2 . The values of conductivity before drying and after drying the KCl for standards preparations versus temperature for 0.1M KCl

3 and 4 one may see the values of the relative errors for 1M KCl standards before and after being processed and similarly for 0.1M KCl.

Error programation

If one considers a randomly error propagation using a Taylor's series for u=f(x,y,z), where *u* is the final result:

$$du^2 = \left(\frac{\partial u}{\partial x}\right)^2_{y,z}(dx)^2 + \left(\frac{\partial u}{\partial y}\right)^2_{x,z}(dy)^2 + \left(\frac{\partial u}{\partial z}\right)^2_{x,y}(dz)^2 + 2\cdot\left(\frac{\partial u}{\partial x}\right)_{y,z}\cdot\left(\frac{\partial u}{\partial y}\right)dxdy +$$

$$+2\cdot\left(\frac{\partial u}{\partial y}\right)_{x,z}\cdot\left(\frac{\partial u}{\partial z}\right)dxdz + 2\cdot\left(\frac{\partial u}{\partial x}\right)_{y,z}\cdot\left(\frac{\partial u}{\partial z}\right)_{x,y}dxdz \quad (9)$$

and if one considers that the variables *x, y, z* are independent, so that *dxdy*=0; *dydz*=0; *dxdz*=0:

$$\sigma_u = \sqrt{\left(\frac{\partial u}{\partial x}\right)dx^2 + \left(\frac{\partial u}{\partial y}\right)dy^2 + \left(\frac{\partial u}{\partial z}\right)dz^2} \quad (10)$$

Table 3

RELATIVE ERRORS WITH RESPECT TO STANDARD VALUE OF 1M KCl

Temperature ^{0}C	1M unprocessed sample			1M dried sample		
	Standard Value	Measured Value	Error	Standard Value	Measured value	Error
	mS/cm	mS/cm	%	mS/cm	mS/cm	%
16	94.400	101.160	7.160	94.400	100.160	6.100
18	98.200	105.180	7.110	98.200	104.300	6.210
20	102.100	109.120	6.880	102.100	108.500	6.270
22	105.900	113.280	6.970	105.900	112.700	6.420
24	109.800	117.580	7.090	109.800	116.860	6.430
25	111.800	119.640	7.010	111.800	119.100	6.530
27	115.700	123.920	7.100	115.700	123.540	6.780

	0.1 M dried sample			0.1 M unprocessed sample		
Temperature	Standard value	Measured value	Error	Standard value	Measured Value	Error
^{0}C						
	mS/cm	mS/cm	%	mS/cm	mS/cm	%
16	10.720	11.038	2.970	10.720	10.806	0.800
18	11.190	11.508	2.840	11.190	11.300	0.980
20	11.670	11.990	2.740	11.670	11.786	0.990
22	12.150	12.524	3.080	12.150	12.264	0.940
24	12.640	13.012	2.940	12.640	12.806	1.310
25	12.880	13.380	3.880	12.880	13.036	1.210
27	13.370	13.810	3.290	13.370	13.572	1.510

Table 4
RELATIVE ERRORS WITH RESPECT TO STANDARD VALUE OF 0.1M KCl

We consider standard deviation equivalent with differential equation, $\sigma_u = du$; $\sigma_x = dx$

$$\sigma_z = dz : \sigma_u = \sqrt{\left(\frac{\partial u}{\partial x}\right)_{y,z} \sigma_x^2 + \left(\frac{\partial u}{\partial y}\right)_{x,z} \sigma_y^2 + \left(\frac{\partial u}{\partial z}\right)_{x,y} \sigma_z^2} \quad (11)$$

$$\text{as:} \quad \begin{matrix} u = x + y + z \\ u = x - y - z \end{matrix} \quad (12)$$

it results:

$$\sigma_u = \sqrt{\sigma_x^2 + \sigma_y^2 + \sigma_z^2} \quad (13)$$

Systematic error propagation

If the determination is taken as a series of measurements x, y, z:

$$d_u = \left(\frac{\partial u}{\partial x}\right)_{y,z} dx + \left(\frac{\partial u}{\partial y}\right)_{x,z} dy + \left(\frac{\partial u}{\partial z}\right)_{x,y} dz \quad (14)$$

The total error is:

$$\sigma_{total} = \sqrt{\sigma^2_{aleator} + \sigma^2_{systematic}} \quad (15)$$

In all cases or error propagation it is important not to confuse the error propagation with the uncertainty of measurement [19].

Considering a 1 M conductivity standard corresponding to 111.8 mS/cm at 25^{0}C , one may identify 2 types of errors, as presented in table 5 and it is possible now to calculate the total error, as depicted in table 5.,

For 0.1 M, at 25^{0}C with a conductivity value of 128.8mS/cm one may identify also 2 types of errors, as presented in table 6 and it is possible now to calculate the total error, as depicted in table 6.

The repeatability is a good indicator of the conductometer accuracy, and in metrology it is the same with the value of the standard deviation:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}} \quad (16)$$

where x_i baseline value, x is the average and n is the number of terms.

The main factor affecting the overall uncertainty are the uncertainty of the standard (1% from measured value), the sensivity, which is 0.01 and the associated uncertainty, $\frac{0.01}{\sqrt{12}}$ and the repeatability, so that one may now calculate the overall or the composed uncertainty, u_c :

$$u_c = \sqrt{SD^2 + u_{standard}^2 + u_{sens}^2} \quad (17)$$

where:

SDis the standard deviation (repeatability), $u_{standard}$ is the uncertainty of used standard and

u_{sens} - represent associated uncertainty of sensivity.

The expanded uncertainty, u_{exp}, is given by:

$$u_{exp} = m \cdot u_c \quad (18)$$

Sources	Value %	Sources	Value %	Preparation error	3.325
weighing	0.013	measuring device	1	Measurement error	1.005
marking	1.77	temperature variation	0.02	Total error	2.080
purity	2	CO_2 effect	-		
dilution	2	Scale	0.1		

Table 5
RESULTS FOR 1M KCl

Preparation		Measurement		Calculated errors, %	
Sources	Value %	Sources	Value %	Preparation error	3.361
weighing error	0.013	measuring device	1	Measurement error	1.005
marking	1.81	temperature variation	0.02	Total error	2.089
purity error	2	CO_2 effect	-		
dilution error	2	Scale	0.1		

Table 6
ERRORS RESULTS FOR 0.1 M KCl

Temperature	Average mS/cm	Standard Value mS/cm	Repeatability mS/cm	Composed Uncertainty %	Expanded Uncertainty %
16	11.038	10.720	0.008	0.510	1.020
18	11.508	11.190	0.008	0.510	1.020
20	11.990	11.670	0.010	0.510	1.020
22	12.524	12.150	0.005	0.504	1.008
24	13.012	12.640	0.011	0.510	1.020
25	13.380	12.880	0.011	0.504	1.008
27	13.810	13.370	0.010	0.510	1.020

Table 7
UNCERTAINTY DETERMINATION FOR 1 M AFTER KCl DRYING

Temperature ^{0}C	Average mS/cm	Standard Value mS/cm	Repeatability mS/cm	Composed Uncertainty %	Expanded Uncertainty %
16	101.160	94.400	0.110	0.513	1.026
18	105.180	98.200	0.130	0.517	1.034
20	109.120	102.100	0.180	0.529	1.058
22	113.280	105.900	0.130	0.520	1.040
24	117.580	109.800	0.080	0.510	1.020
25	119.640	111.800	0.090	0.505	1.010
27	123.900	115.700	0.080	0.505	1.010

Table 8
UNCERTAINTY DETERMINATION FOR 0.1 M AFTER KCl DRYING

where m is a multiplication factor, m=2, for a probability p=95%.

The results are presented in table 7 and table 8.

The values of the composed uncertainty are below 1% and that of the expanded uncertainty is around 1% values normally accepted for measurements within the limits of the good laboratory practices.

Conclusions

When determining the conductivity one should take into account a series of key factor to achieve the required quality for the results intended to be used in further applications or evaluations.

One has proven that, in certain instances, is not enough to rely only on the information provided by the reagent manufacturer when preparing the standards and it is recommended that the reagent should be subjected to certain preliminary treatments (drying in this particular case) as this will decrease the errors associated with the conductivity meter calibration and the evaluation of conductivity.

The results obtained for the prepared standards of 1 M KCl and 0.1 M KCl solutions have proven that if one takes certain precautionary steps, the values of the repeatability, composed uncertainty and expanded uncertainty are well within the limits of the good laboratory practices.

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