White Paper

Reducing Common Errors
in Conductivity Measurements

Conductivity measurement using electrochemical cells is a simple and cost-effective method frequently used to determine the concentration of dissolved substances in samples ranging from distilled water to concentrated acids and galvanic baths. While the parameters used for measuring conductivity are straightforward, they vary strongly depending on the sample being measured and the temperature at which the measurement is being made. Potential sources of error in conductivity measurements can be manifold, but with a better understanding of the theory behind conductivity, and a few useful tips on how best to measure conductivity, potential errors in measurement can be reduced and the accuracy of conductivity measurements can be increased.

1. Conductivity and Measuring Cells

The conductance of a solution, a physical property, can give important quantitative information regarding the ionic composition of a sample. Conductance is a measure of a sample's ability to pass a current and strongly depends on the concentration, mobility, and charge of ions in solution. [1] To determine the conductance of a solution, conductivity cells are often utilized.

A basic conductivity cell consists of a pair of poles between which the sample is placed and between which current is passed. The ratio of the distance between the poles (L) and their surface area (A) is known as the cell constant, K.

$$\mathrm{K} = {}^{\mathrm{L}\,[\mathrm{cm}]}\!\big/_{\mathrm{A}\,[\mathrm{cm}^2]}$$

The conductivity κ [$\mathrm{S} \cdot \mathrm{cm}^{-1}$] is given by the conductance G [S] multiplied by the cell constant K [cm^{-1}]. [1]

$$\kappa = \mathrm{G}\,[\mathrm{S}] \times \mathrm{K}\,[\mathrm{cm}^{-1}]$$

Every measuring cell has its own particular cell constant. The layout of the conductivity poles and the occurrence of inhomogeneous boundary effects prevent the calculation of the cell constant directly from the cell's dimensions. It has to be determined experimentally through calibration with a standard solution (of known conductivity) and is then stored in the conductivity meter that the conductivity cell is attached to.

Most conductivity sensors available on the market today are delivered with certified cell constants from the manufacturer. The user can simply enter these certified cell constants manually into the conductivity meter without actually having to measure the value in a standard prior to measurement.

Once the cell constant has been defined, it does not change with time, at least if the sensor is properly used and if adequately stored between measurements. The cell constant of a conductivity probe only changes if the surface of the electrode is altered, for example through grease from fingerprints, various deposits, and scratches. This behavior stands in stark contrast to a pH electrode, where the electrode's condition, including the gel layer forming over the glass membrane, may decay over time, requiring regular calibration.

2. Choosing the Right Conductivity Probe

A deciding factor in reducing conductivity measurement inaccuracies is choosing the right conductivity probe, respectively choosing the right cell constant based on the expected conductivity of the sample to be measured. The lower the expected conductivity of the sample, the smaller should the cell constant of the probe be. For samples with a high expected conductivity, a sensor with a large cell constant should be chosen (Fig. 1).

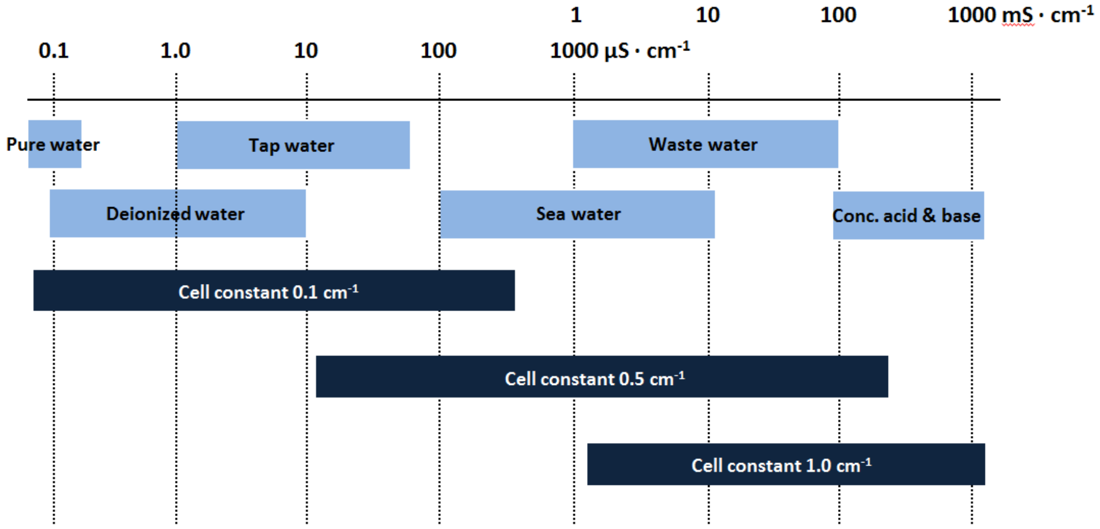

Figure 1: Cell constant versus sample conductivity. The figure depicts standard conductivity values for a set of samples and the range of recommended cell constants for a given conductivity probe.

3. Proper Cleaning and Storing of Conductivity Probes

If the conductivity probe is contaminated, it must be properly cleaned with ethanol, suitable detergents or solvents, or possibly via an ultrasonic bath. Poles made of graphite, platinum or steel can be carefully cleaned mechanically using a soft brush. It is extremely important not to damage the surface of a pole during cleaning.

After cleaning, it is best to thoroughly rinse the sensor with deionized water prior to usage or storage. Conductivity probes are ideally stored in dry conditions at room temperature.

4. Conductivity Measurements and Sources of Error

Sources of error in measurement are a frequent companion in day-to-day electrochemical measurements, including conductivity measurements. The following set of tips and tricks should aid in reducing errors made in measuring conductivity.

In general, one must always make sure that the poles' surfaces are completely immersed in the sample solution. Conductivity samples and standard solutions should never be diluted as the effect of dilution is not linear.

While dependent on the design of the electrode, the position of the sensor in the sample beaker can also greatly influence measuring results due to the occurrence of boundary effects outside the electrode surfaces. It is usually best to position the sensor in the middle of the beaker containing the solution.

A common source of error in conductivity measurements are air bubbles that may form on the surface of the poles. While frequent, bubbles are often not recognized by users as a source of error and should be removed during measurement by briefly stirring the sample using a magnetic stirrer prior to measurement or, if necessary, through tapping the conductivity probe. Successful removal of air bubbles often leads to a sudden jump in conductivity.

Since the accuracy of any measurement depends on proper calibration, a fresh standard must always be used. Ideally, sample beakers and sensor should be rinsed two to three times with the sample as the presence of contaminants can lead to additional errors in conductivity results.

Lastly, samples with low conductivities, such as pure or ultra-pure water samples, should be measured in a flow cell. The flow cell ensures that atmospheric CO_2 does not get into contact with low-conductivity samples and standards. Carbon dioxide dissolves in water, forming carbonic acid, which leads to higher than actual conductivity values. The usage of a flow cell is recommended for both calibration and for subsequent measurement. The flow cell and tubing must be thoroughly rinsed prior to use.

5. Impact of Temperature on Conductivity Measurements

Conductivity measurements are very temperature dependent. As the temperature of a sample increases, so does the observed conductivity of the probe. [2] For example, the conductivity of a 0.01 molar potassium chloride solution at 20 °C is 1278 $\mu S \cdot cm^{-1}$ but at 25 °C the conductivity is 1413 $\mu S \cdot cm^{-1}$. This means that measurements performed in the same sample but at different temperatures cannot sensibly be compared. For this exact reason, the concept of a reference temperature was introduced. The reference temperature usually equals either 20 °C or 25 °C.

In practice, the conductivity meter measures the actual conductivity (e.g. 1000 $\mu S \cdot cm^{-1}$) at a certain temperature (e.g. 27 °C) and converts the measurement value to the desired reference temperature (e.g. 25 °C) using a linear temperature coefficient (e.g. $\alpha = 2$ %/°C). In the example given above, the result displayed at the reference temperature of 25 °C would then be 962 $\mu S \cdot cm^{-1}$ instead of the uncompensated value of 1413 $\mu S \cdot cm^{-1}$.

Temperature correction for conductivity measurements should not be confused with temperature compensation in pH measurement. In a conductivity measurement, the conductivity value displayed is the calculated conductivity at the desired reference temperature. With pH measurement, the pH at the actual temperature (e.g. 27 °C) is displayed. Here temperature compensation involves adapting the slope of the pH electrode to the actual temperature being measured.

It is always important to note both the conductivity measured and the used reference temperature. While in general, conductivity results are recorded at a reference temperature of 25 °C, certain conductivity meters have a default reference temperature of 20 °C. These default settings will always yield differing conductivity results in comparison to a meter having a default reference temperature of 25 °C. Neither result is per se wrong – the respective measurements simply relate to different reference temperatures.

6. Temperature Compensation – A Closer Look

As temperature plays a key role in determining the conductivity measured, it is important to know the temperature dependence (= change of the conductivity per °C) of the measured sample.

The temperature dependence of every sample is different. As mentioned before, the higher the temperature of a sample, the higher the measured conductivity. While conductivity and temperature have a positive correlation, the change of the conductivity with increasing temperature is not linear, however. As the temperature of the aqueous sample increases, the mobility of the ions decreases (see Fig. 2). The higher the concentration of ions in solution, the lower is the increase in conductivity per °C. [3] A sample can exhibit completely different temperature dependence at different temperatures and different ion concentrations.

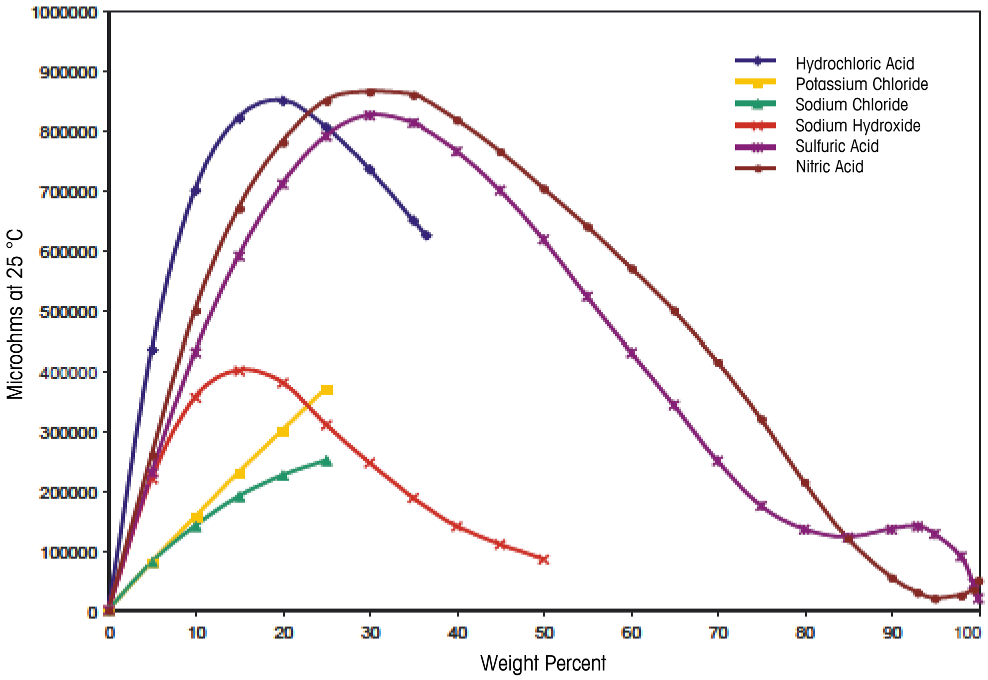

Figure 2: Change of the conductivity of a sample with increasing ion concentration.

To simplify the complex relationship between conductivity, temperature, and ion concentration, different temperature correction methods have been developed to accommodate users:

1. Linear (using temperature coefficient α)
2. Non-linear
3. No temperature correction

Depending on the sample in which conductivity is to be measured, one of the methods listed above is chosen.

For medium to strongly conducting solutions a linear equation can be used for temperature correction. Here, the temperature coefficient, which is manually entered by the user, is utilized. The linear temperature coefficient is unique to each sample type and valid only over a narrow temperature range.

In contrast, in natural waters the temperature dependence is strongly nonlinear so that non-linear correction has to be used. For more details on non-linear temperature correction refer to page 5 of this manuscript below.

Lastly, USP (United States Pharmacopeia) forbids any temperature correction methods and stipulates uncorrected conductivity measurements instead.

If large temperature differences exist between different samples in a measuring series, the sensor should be immersed in the sample of interest for 1 to 2 minutes before performing the actual measurement. Some built-in temperature sensors react more slowly than others to changes in sample temperature.

To achieve the highest measurement accuracy, the sample must be kept at the chosen reference temperature. In this case, temperature correction is not performed and any inaccuracies that may arise due to correction errors do not occur.

The temperature dependence of ordinary standard solutions used for calibration is usually programmed in the conductivity meter utilized and is automatically taken into account during calibration.

If the conductivity sensor remains in the standard solution after calibration, it is possible that the result displayed is different from the value at the point of calibration. This difference arises because during calibration, the values from the programmed table are utilized and not the values gained from the formula of the appropriate temperature correction method. Hence, for this measuring scenario, it is recommended that the user first turns off the automatic temperature correction given by the conductivity meter. Second, the real temperature is to be measured along with the conductivity of the sample and then compared to the temperature values listed in the temperature table on the bottle of the standard utilized.

7. Linear Temperature Compensation

In practice, linear temperature correction is used most frequently. The temperature coefficient is given in %/°C and is determined as follows:

1) The conductivity of the sample is measured without temperature compensation ($\alpha = 0$) at two temperatures, T1: Chosen reference temperature, T2: actual temperature of the sample.
A 0.01 molar KCl solution is used as an example. Upon measuring, the following conductivity values are obtained:

Measurement 1: $1278\ \mu S \cdot cm^{-1}$ at 20 °C
Measurement 2: $1413\ \mu S \cdot cm^{-1}$ at 25 °C

2) These values are then entered in the following equation to calculate the temperature coefficient [1]:

$$\alpha = \frac{(\kappa_{T2} - \kappa_{T1}) \times 100\%}{(T2 - T1) \times \kappa_{T1}}$$

$$\alpha = \frac{(1413\ \mu S \cdot cm^{-1} - 1278\ \mu S \cdot cm^{-1}) \times 100\%}{(25\ °C - 20°C) \times 1278\ \mu S \cdot cm^{-1}}$$

$$\alpha = 2.1\ \%/°C$$

As the temperature dependence of a sample is usually not linear over a large temperature range, the temperature coefficient (α) should be determined within the temperature range of the sample being measured. Below, a list of samples and their typical temperature coefficients can be found [2]:

Sample	Temperature Coefficient α (%/°C)
Acids	1.0 – 1.6
Bases	1.8 – 2.2
Salts	2.2 – 3.0
Drinking water	2.0
Pure water	5.2

Table 1: Listing of selection of typical samples and the accommodating temperature coefficients.

8. Non-linear compensation

The conductivity of natural waters from the sea, rivers and lakes exhibits strongly nonlinear temperature behavior. Additionally, in solutions with a conductivity of 1 µS/cm or less, the conductivity increases with temperature are nonlinear as well. [2] For these types of samples, such as ultra-pure water, a nonlinear compensation method should be used. [4] The measured conductivity, κ_T, is multiplied by the temperature-dependent factor, f_{25}, of the measured temperature and so referred to the reference temperature of 25 °C [3]:

$$\kappa_{T25} = \kappa_T \times f_{25}$$

Most modern conductivity meters have a f_{25} coefficient table programmed to make life a little easier. For example, if a different reference temperature, e.g. 20 °C, is desired, the conductivity result referenced to 25 °C is simply divided by 1.116 (the value was taken from the f_{25} table mentioned above):

$$\kappa_{T20} = \frac{(\kappa_T \times f_{25})}{1.116}$$

Many modern conductivity meters also offer temperature correction methods specifically for conductivity measurements in ultra-pure water, where the auto-hydrolsis of water is accounted for.

9. In Summary

While the parameters used for measuring conductivity are rather straightforward, care must be taken during measurement to avoid unnecessary sources of error. A deciding factor in reducing measurement inaccuracies is choosing the right equipment. Picking the right conductivity probe with the proper cell constant for the sample of interest along with the suitable conductivity standard for calibration are absolutely key. Next, proper handling and storage of the conductivity probe, correct calibration with fresh standards prior to measurement, and accounting for a sample's temperature and temperature dependence aid in reducing measurement error and in turn increase the accuracy of the conductivity measurement being made.

Acknowledgement:

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References:

1. Settle, Frank et al (1997). Handbook of Instrumental Techniques for Analytical Chemistry. Prentice-Hall Inc. Upper Saddle River, New Jersey. pp. 684-764.

2. Gray, James R. et al (2004). Conductivity Analyzers and Their Application. Found in the Environmental Instrumentation and Analysis Handbook. pp. 491–510. ISBN 978-0-471-46354-2.

3. Haynes, William M. et al (2011). Handbook of Chemistry and Physics. Taylor and Francis. 92nd edition. ISBN 978-1-439-85511-9.

4. Gray, David M. and Anthony C. Bevilacqua (1997). Cation Conductivity Temperature Compensation. Presented at the International Water Conference, Pittsburgh, PA, USA. Thornton Associates.