

The Selection, Use, Care and Maintenance of Sensors for Accurate Conductivity Measurement

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Abstract

As is the case with all measurements, the selection of appropriate sensors and their correct use is essential for the accurate measurement of conductivity. This paper outlines the different types of conductivity sensors that are available to the analyst and the factors that should be considered when selecting conductivity sensors for measurement applications. As well as giving recommendations on the suitability of different types of conductivity sensors for various applications, recommendations are given on the calibration, use and maintenance of conductivity sensors to maximize the accuracy of test measurements and provide increased confidence in conductivity measurements.

1 Introduction

All conductivity instrumentation systems consist of a conductivity meter and a conductivity sensor, commonly referred to as a conductivity cell. There is a wide range of different conductivity cells available to the analyst. The selection and correct use of an appropriate conductivity cell is essential to the quality of analytical conductivity measurements.

Conductivity meters provide an electrical input signal to the conductivity cell and monitor the output signal from the cell. The meter determines the conductivity of the test sample from the ratio between the cell's input and output signals and from the cell's properties. The conductivity cell must be compatible with the meter so that the electrical signals used are within the operating range of both the cell and the meter. Besides compatibility with the conductivity meter, the selection of a suitable conductivity cell will depend on the following factors:

- Where the analysis is performed – e.g. on-line, in the field or in a laboratory
- The conductivity range of the samples to be analysed
- The nature of the samples to be analysed – corrosion resistance may be required
- The temperature range of the samples
- The required accuracy of analysis
- Budgetary requirements

This paper outlines the different designs of conductivity cells that are available and their suitability for various conductivity measurement applications. Advice is also given on the calibration of conductivity cells and their correct use and maintenance in order to maximise the quality of the analytical measurements and comply with the requirements of good laboratory practice.

2 Definition of Conductivity

The electrical resistance of a sample of any material will be dependent on the dimensions of the sample and the material's ability to resist the flow of an electric current. The resistance, R , between two parallel electrodes is inversely proportional to the cross-sectional area of the electrodes, a , and is proportional to the distance between the electrodes, l , and the material's specific resistance or resistivity, ρ .

$$R = \frac{\rho \times l}{a} \quad \text{Equation 1}$$

The specific conductance or conductivity, κ , of a solution is a measure of its ability to conduct an electrical current. As conductivity is the reciprocal of resistivity, then it can be defined as shown in Equation 2.

$$\kappa = \frac{1}{a \times R} \quad \text{Equation 2}$$

3 Cell Types & Measurement Principle

Conductivity cells can be classified according to the technique by which they interact with the sample and also by the geometry of the cell design. The two operating techniques are the contacting technique and the inductive or toroidal technique. In both cases, the conductivity meter provides an AC electrical input signal to the conductivity cell and measures the resultant AC electrical output signal from the cell.

The AC input signal magnitude, AC input signal waveform and the system for measuring the output signal must be optimized for both the conductivity value of the sample and the characteristics of the measuring cell. Care must be taken to ensure that the conductivity cell and meter can provide this compatibility – failure to do so will result in erroneous readings and a reduced range of linear response.

3.1 Contact Technique Cell Designs

Cells that measure conductivity using the contacting technique have their electrodes in

direct contact with the sample. There a number of different electrode geometries used in modern contacting cells.

3.1.1 2-Plate Cells

The earliest design of contacting cells consists of two parallel plate electrodes, made from platinized platinum. An AC voltage is applied across the plates resulting in an AC current flowing through the solution - see Figure 1.

The geometry of the plates used will affect the magnitude of the AC current generated and this needs to be accounted for when measuring the solution's conductivity. This is achieved by the introduction of a Cell Constant, K, into the calculation. Using the traditional design of two parallel plates, the cell constant can be defined as the distance between the plates, l, divided by the surface area of the plates, a:

$$\text{Cell Constant, } K = \frac{l}{a} \quad (\text{cm}^{-1}) \quad \text{Equation 3}$$

The cell constant can be introduced into the definition of conductivity given in Equation 2:

$$\text{Conductivity, } \kappa = \frac{K}{R} \quad \text{Equation 4}$$

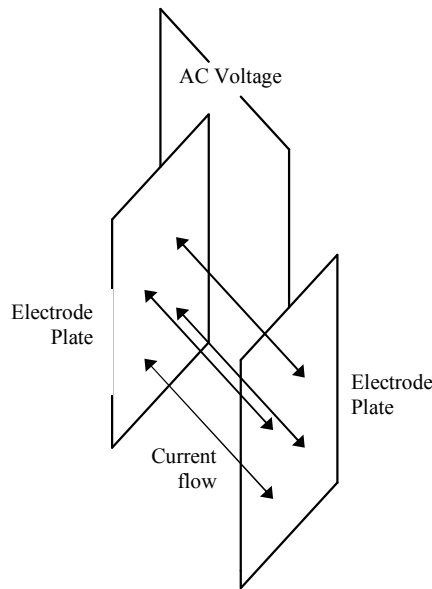


Figure 1: Design of 2-plate conductivity cells

A conductivity cell can be manufactured with a low cell constant by reducing the distance between the electrode plates and increasing the surface area of the plates, see Figure 2. 2-plate conductivity cells with low cell constants are particularly suited to the measurement of ultra-pure water. 2-plate conductivity cells with very high cell constant ($K > 10$) would require very small plates separated by a large distance and would thus be impractical.

Capacitance effects at the plates' surfaces mean that the maximum conductivity at which most 2-plate cells can be used for accurate measurements is $200,000\mu\text{S}/\text{cm}$. Highly sophisticated conductivity meters can be used to overcome these capacitance effects but, due to the instrument cost, the use of 2-plate cells for high conductivity measurement is limited to research applications.

The accuracy of conductivity measurements will depend on the conductivity meter's range and accuracy for resistance measurement. By using a range of conductivity cells with different cell constants, this will reduce the resistance measurement range that the conductivity meter has to operate over. A reduced resistance measurement range will enable an economical conductivity meter to give accurate readings for an extended range of conductivity values. Cells with a low cell constant should be used for low conductivity measurements and cells with a high cell constant should be used for high

conductivity measurements.

3.1.2 2-Pin Cells

2-pin cells are most commonly used for field analysis with portable conductivity meters. The pins are usually made of graphite or stainless steel and are mounted on an epoxy body. The 2-pin cell uses the same measurement technique as the 2-plate cell – i.e. an AC voltage is applied across the pins and the resulting AC current traveling in the sample between the pins is measured. The electrodes are more rugged than the platinized platinum electrodes used in the 2-plate cells, are cheaper to manufacture and are easier to clean; but the measurement accuracy is reduced. Due to the size of the pins, these cells cannot be manufactured with low cell constants and hence they cannot be used for the accurate measurement of low conductivity.

3.1.3 2-Ring Cells

2-ring cells utilize ring-shaped electrodes mounted on a plastic shaft. To ensure that a constant volume of the sample conducts the AC voltage applied across the cells then an outer sheath of non-conducting plastic is placed on the cell. 2-ring cells are more expensive and less robust than 2-pin cells and are widely used for field applications that require higher accuracy than can be offered by 2-pin cells. 2-ring cells are less accurate than 2-plate cells; but are used for laboratory applications where a high degree of accuracy is not essential, as they are cheaper and more robust than 2-plate cells.

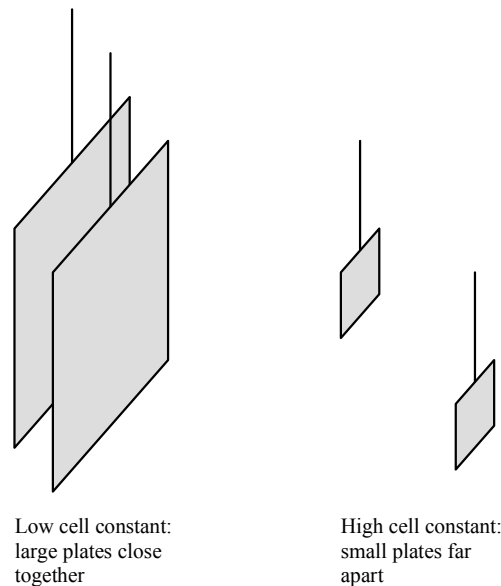


Figure 2: Different Cell Constants

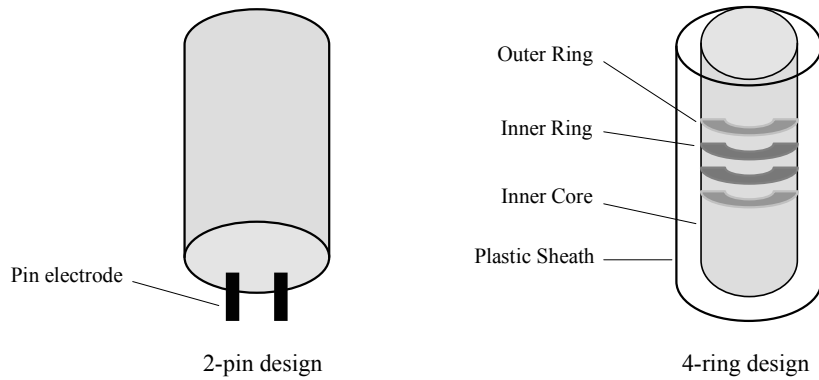


Figure 3: Design of Contacting Conductivity Cells – 2-pin & 4-ring

3.1.4 4-Ring Cells

The 4-ring cell has a pair of voltage electrodes and a separate pair of current electrodes. An AC voltage is applied to the two outer rings - see Figure 3. The two inner rings, which are sited within the resultant electric field in the sample, are used to measure the field's current. The magnitude of this current also depends upon the volume of the solution and so an outer sheath of non-conducting plastic is placed on the electrode to maintain a constant volume. 4-ring cells do not suffer from the capacitance effects shown by 2-electrode cells in high conductivity samples and so can be used beyond the limit of 200,000 $\mu\text{S}/\text{cm}$ for 2-electrode cells. The manufacture of 4-ring cells with a very low cell constant is not practical and so 4-ring cells cannot be used for accurate low conductivity measurements

3.2 Inductive (or Toroidal) Technique

Inductive or Toroidal cells consist of two

toroidal coils, known as a drive toroid and a sensing toroid. The toroid coils are not in contact with the solution and are coated with chemically resistant, electrically insulating materials, e.g. PEEK^{TM(1)} and Kevlar^{TM(2)}.

An AC current is passed through the drive toroid coil, which induces a current in the conducting solution. This induced current in turn induces a current in the sensing toroid, which is proportional to the conductivity of the solution. As the toroidal coils are not in direct contact with the sample, then these cells are particularly suited to measurement in aggressive samples or at high temperature or pressure. However, the increased cost of inductive cells means that their use tends to be limited to on-line conductivity measurement. Inductive cells are not as sensitive as plate and ring contacting cells and so cannot be used for low conductivity measurement – e.g. ultra-pure water.

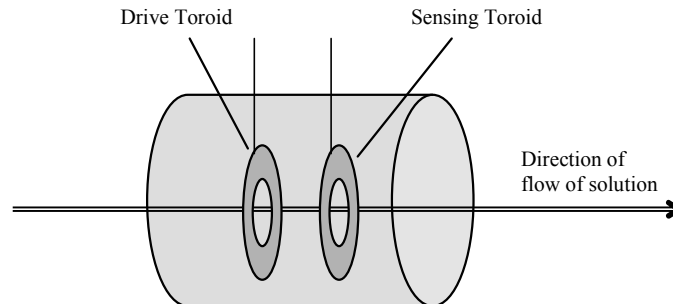


Figure 4: Toroidal Cell

3.3 Polarization errors for 2-electrode contacting cells

Polarization is the build up of ions at the oppositely charged electrode, resulting in a reduction in the current flow between the electrodes and the solution's conductivity being under reported – hence an AC voltage is applied across the electrodes rather than a DC voltage. If the frequency of this AC voltage is too low then partial polarization will occur during the voltage cycle. For higher conductivity solutions then the solution's resistance is reduced and higher frequencies are required to prevent polarization. However, if too high a frequency voltage is applied then capacitance effects will interfere with the measurement.

Manufacturers of modern conductivity meters overcome the effects of polarization by applying an AC voltage with a complex waveform and increasing the frequency of this waveform as the measured conductivity value increases. Polarization can be further reduced by stirring the sample or using a flow-through chamber around the conductivity cell, see Figure 5. Polarization only affects 2-electrode contacting cells – 4-ring contacting cells and inductive cells are not affected by polarization.

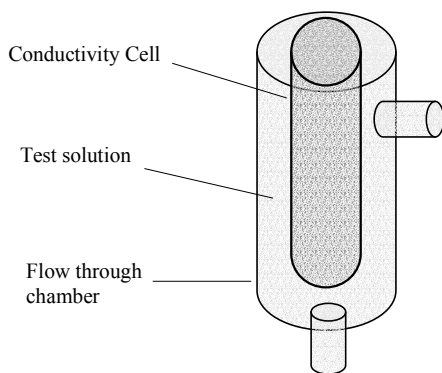


Figure 5: Flow Through Cell

3.4 Temperature Sensors

The conductivity of all solutions is dependent on the temperature of the material. The measurement temperature must be recorded and

the influence of the measurement temperature on the conductivity reading must be taken into account⁽³⁾. Temperature measurement is made using conductivity cells with integral temperature sensors or by using separate temperature sensors. The temperature sensor output must be compatible with the conductivity meter. The most commonly used temperature sensor output types are Pt 1000 and NTC 30kΩ. Both of these sensor output types have a wide range (0 - 100°C) and a high resolution (0.1°C).

4 Selection of Cells for Different Measurement Ranges

Examination of literature from the manufacturers of conductivity cells shows a wide range of cell constants available to the analyst. Conductivity cells are available with cell constants ranging from 0.01 to 50. The most commonly used cells have nominal cell constants of approximately 0.1, 0.5, 1.0 and 10. By correctly matching cells of various cell constants to a meter, the analyst can use one meter to accurately measure conductivity over a wide range. Generally, a cell with a low cell constant should be used to measure solutions of low conductivity. Table 1 outlines the recommendations of ISO 7888⁽⁴⁾.

Measuring Range (μS/cm)	Recommended Cell Constant, K (cm ⁻¹)
< 20	0.01
1 to 200	0.1
10 to 2000	1.0
100 to 20,000	10

Table 1: Recommendations of ISO 7888⁽⁴⁾

Individual instrument manufacturers may recommend specific cells and conductivity instruments for different applications, taking into consideration the measuring range and the nature of the sample solution. The suitability of this instrumentation for a particular measurement application should be verified by using an appropriate control standard, as described in Section 6.1.2.

Cell Type	Accuracy	Robustness	Cost	Measuring Range & Typical Applications
2-Plate	Excellent	Poor – care required to prevent electrode damage	High	Very low conductivity (including ultra pure water) up to 200,000µS/cm. Accurate laboratory measurements. On-line ultra pure water measurement.
2-Pin	Poor	Very good	Low	Field measurements where low accuracy is acceptable. Limited linear response range compared with other types of cells. Not suitable for low conductivity measurement
2-ring	Good	Good	Moderate	Routine laboratory & online measurements. Accurate field measurements. Not suitable for very high conductivity measurement
4-ring	Good	Good	Moderate	Routine laboratory & online measurements. Accurate field measurements. Not suitable for low conductivity measurement.
Toroidal	Fair	Excellent – including extreme temperatures and pressure	Very high	On-line measurements – Cost can be offset by robustness and low maintenance requirements. Not suitable for low conductivity applications.

Table 2: Summary of Properties of Different Cell types

5 Selection of Cells for Measurement Applications

The selection of a suitable conductivity cell must take into account the following factors for all of the sample types that the cell will be used to measure:

- Compatibility with the conductivity meter.
- The accuracy required for the test measurements. The use of Control Standards described in Section 6.1.2 is essential for full confidence in the test measurements.
- The conductivity range of the samples to be analysed. This will determine the cell constant that will be required. If a wide range of conductivity values is to be covered then a range of cells with different cell constants may be required.
- The test environment – for online measurement the conductivity cell must have a suitable specification that covers the complete range of temperatures and pressures that will be encountered for measurement and Cleaning In Process (CIP). For field analysis the conductivity cell should be sturdy enough to withstand

transportation and should only need care and maintenance that can easily be conducted in the field.

- The nature of the samples – corrosion resistance will be a requirement for cells used with aggressive sample types.
- Conformance with any regulatory requirements that apply to the conductivity measurement.
- Any potential future requirements.

Table 2 outlines a summary of the properties of the different types of conductivity cells and their suitability for various conductivity measurement applications. It should be noted that there can be substantial variation in the quality of each cell type from different cell manufacturers – hence Table 2 should be used for general guidance only.

For field and online analysis, it is essential that the conductivity cell must be positioned correctly to ensure that the analysed samples are representative of the material being measured. The factors that must be considered when positioning conductivity cells used for field and online analysis are detailed in a further Reagecon publication⁽⁵⁾.

6 Calibration of Conductivity Sensors

For accurate conductivity measurement, it is essential that the cell constant, K , is accurately assigned and this is achieved by calibration of the conductivity cell. Any changes in the cell constant over time, caused by damage to the electrodes or fouling by the sample, will result in errors in conductivity readings – hence calibration should be frequently performed.

The classical definition of the cell constant for 2-plate cells given in Equation 3 describes it as the distance between the plates divided by the plate area. This definition does not account for the fringe lines of conductance that occur outside the electrode plates, as shown in Figure 6, and excludes toroidal cells and pin and ring type electrodes. Additionally, the classical definition of the cell constant will not account for exclusions in the plates' surface coating or the plates not being exactly parallel. For these reasons it is impossible to produce a conductivity cell to a precise cell constant value and the cell constant must be determined empirically.

Cell constant determinations are carried out by measuring the cell's response in a solution of

known conductivity. A correction factor is applied to the meter's reading - this correction factor is the cell constant. For the example shown in Figure 7, a cell constant of 1.040 cm^{-1} ($= 1413 \text{ } \mu\text{S/cm} \div 1359 \text{ } \mu\text{S}$) will need to be applied to achieve correct readings. Modern conductivity meters have a calibration mode that automatically assigns and applies the corrected cell constant.

6.1 Good Laboratory Practice Requirements for Calibration

For accurate results and for compliance with good laboratory practice, conductivity standards of high quality should be used for calibration. The calibration standard should be accurate, should be traceable to Certified Reference Materials and should have quantified uncertainty and proven stability⁽⁶⁾. If possible, the calibration standard should be matrix-matched to the sample. The selection of the conductivity value of the calibration standard depends on the nominal cell constant of the cell being calibrated – i.e. the standard used must be within the linear response range of the cell. Table 3 shows recommended calibration standard values for a range of nominal cell constant values.

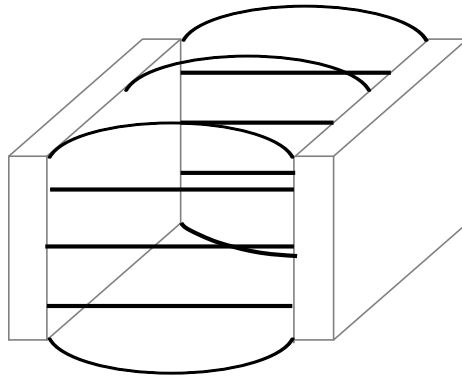


Figure 6: Conductance lines including fringe lines

Cell Constant, K (cm^{-1})	Standard Solution ($\mu\text{S/cm}$ @ 25°C)
50	12,880
10	12,880
1.0	1,413
0.1	147
0.01	147

Table 3: Recommended Calibration Values

$$\text{Measured Conductance} \times \text{Cell Constant} = \text{Measured Conductivity}$$

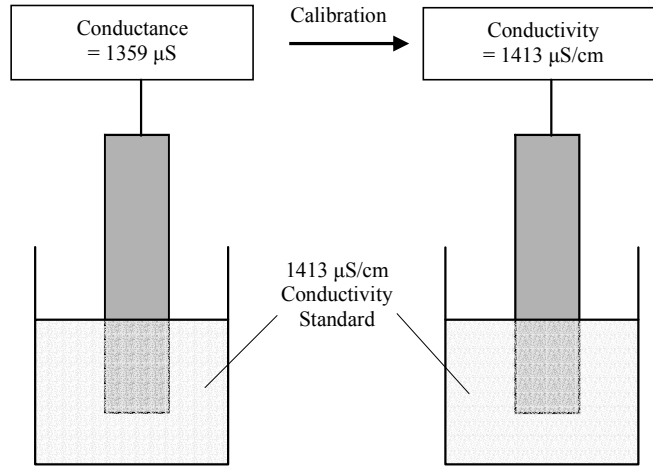


Figure 7: Cell Constant Determination

For compliance with the requirements of good laboratory practice, the calibration procedure should be fully documented and the following information should be recorded regarding the calibration results:

- Date and location
- Serial or identity number of the conductivity meter
- Serial or identity number of the conductivity cell (and temperature sensor if a separate temperature sensor is used)
- Manufacturer, product and lot number of the calibration standard
- Calibration temperature
- The analyst's name
- Assigned cell constant value

6.1.1 Use of Control Charts

The assigned cell constants for each cell and meter pair should be recorded against time on a Control Chart, which also includes Action Limits. Action Limits should be assigned to the determined value of the cell constant and to the change in cell constant between consecutive calibrations. The value of the Action Limits will be dependent on the accuracy of the meter, the accuracy of the standard, the sample type and variations in calibration conditions.

Minor variations in successive determined values of the cell constant will occur due to the uncertainty of measurement of the cell constant

determination and slight changes in the cell constant with time, caused by exposure to the sample or operating conditions. The Action Limits should be set to detect changes that cannot be reasonably explained by these factors. Exceeding an Action Limit indicates a change in the measurement system that requires investigation.

If the calibration produces a cell constant within the Action Limits then the cell should be labelled as being calibrated. The date of calibration, the initials of the analyst performing the calibration and the due date for the next calibration should also be recorded on the calibration label. Some modern, high-specification conductivity meters include a Calibration Protocol function that automatically records this information and provides an alarm message if the calibration interval has been exceeded. Further details of the functions and requirements of conductivity instruments are given in a further Reagecon publication⁽⁷⁾.

When an Action Limit is exceeded, the conductivity meter and cell should be clearly labelled as having failed calibration and should not be used for sample measurement. The reason for the calibration failure should be investigated and this investigation should be documented for future reference. Calibration failure reports and Control Charts should be reviewed periodically in order to identify recurring problems.

If an Action Limit is exceeded, all of the test sample measurements taken since the previous successful calibration must be assumed invalid and should, if possible, be repeated. In many instances, sample measurements cannot be repeated at a later date, but it is essential that the measurement procedure can provide confidence in sample readings between calibrations. This is achieved by the use of Control Standards.

6.1.2 Use of Control Standards

The use of an appropriate cell and high quality calibration standards are essential for accurate conductivity measurement. However, this is not sufficient to provide maximum confidence in sample test measurements – the following criteria must also be met:

- Proof that the instrument and cell used have a suitable Limit of Detection (LOD) for the samples' range of conductivity values.
- Proof that the instrument and cell have a linear response across the samples' range of conductivity values.
- Proof that the instrumentation used is functioning correctly, has been used correctly and that environmental factors, such as temperature, are not adversely affecting the measurements.

The only means for satisfying these criteria is by the use of appropriate Control Standards of similar values to the samples being measured. The same stringent criteria used in selecting Calibration Standards should also be applied to the Control Standards.

Measurement of the Control Standards should be made with each batch of samples or at fixed intervals for online conductivity cells. A Control Standard test should also be performed after each calibration to verify the validity of the assigned cell constant. An out of specification result on the Control Standard will immediately highlight an error in measurement and this will prevent incorrect sample results from being reported. In addition to satisfying the above criteria, the use of Control Standards is essential to satisfy the requirements of good laboratory practice.

The use of Control Standards should be documented in the measurement procedure. The test measurements of the Control Standard should be recorded and monitored using Control Charts, as described in Section 6.1.1.

The frequency of use of Control Standards will be determined by the criticality of the measurement results, the feasibility of repeating sample measurements and the robustness of the test method. For a new conductivity test method or a modified test method, it should be assumed that the method is not robust. Hence the frequency of use of Control Standards should be high and should only be reduced if analysis of the Control Charts shows that this will not reduce confidence in the analytical results⁽⁸⁾.

7 Maintenance and Use of Conductivity Cells

The accuracy of conductivity measurements and the working life of the cell will be severely compromised if the conductivity cell is not used and maintained correctly. Incorrect use of conductivity cells may also compromise test samples. This may have substantial ramifications, e.g. contamination of an entire production batch from an online conductivity cell.

7.1 Care & Maintenance of Conductivity Cells

The working life of a conductivity cell can be several years if correct care and maintenance is employed. The following guidelines are general recommendations only – the cell manufacturer's instructions on care and maintenance should always be followed.

- Visually inspect the cell's electrodes and electrode housing on a regular basis and instigate cleaning if required.
- Mechanical cleaning should be avoided as scratching of the electrodes' surfaces may result.
- Oil and salt deposits may be removed by soaking in a mild non-ionic detergent, followed by repeated rinsing with purified water to remove all traces of the detergent.
- In extreme cases, deposits may be removed by soaking in a mild acid solution, followed by repeated rinsing with purified water to remove all traces of the acid.
- Platinum electrodes are coated in platinum black and they require regular re-platinizing to maintain the integrity of the platinum black coating. This

should be done in accordance with the cell manufacturer's instructions.

- Cleaning may alter the cell constant and so calibration must be performed after any cleaning process.
- Cells can be stored in purified water for short-term storage; for long-term storage, they can be stored dry. Some cells may require re-conditioning after long-term storage by soaking in purified water for one hour before being used for measurements.

7.2 Use of Conductivity Cells

The correct use of conductivity cells is essential to ensure the accuracy of cell constant assignment and test sample readings. The following guidelines will assist the analyst to achieve improved conductivity measurement accuracy:

- Thoroughly rinse the measurement container or beaker, the conductivity cell and the temperature sensor at least 3 times with the solution being measured. This applies equally to test samples and calibration and control

standards. This must be performed to prevent carry-over from the previous measured solution.

- Ensure that the conductivity cell and the measurement samples are at the same temperature before taking readings. Temperature has a significant influence on conductivity - accurate temperature measurement is required for accurate conductivity measurement⁽³⁾.
- Ensure that the cell's electrodes are fully immersed in the measurement sample.
- Ensure that there are no air bubbles lodged on the electrode surfaces – these can be dislodged by gently tapping the cell.
- Rinse the cell with purified water after each measurement.

In addition to the recommendations given above, analysts must ensure that they comply with the requirements of any applicable regulations or standard methods for their measurement application. This is of particular relevance for conductivity measurements taken for pharmaceutical applications⁽⁹⁾.

8 Conclusion

There is a wide range of different conductivity cells available to the analyst. The required accuracy of the test measurements, compatibility with the conductivity meter, the conductivity range of the samples, the nature of the samples and the test environment must all be taken into account when selecting an appropriate conductivity cell for a measurement application.

The cell constant of the conductivity cell will affect the cell's output signal to the conductivity meter. The cell constant will change if there is damage to the electrode surface or fouling of the cell and so the cell constant must be regularly re-determined during the working life of the conductivity cell. Calibrating the conductivity cell performs this cell constant determination. Calibration is carried out by measuring the cell's response in a solution of known conductivity value. This requires the use of a quality conductivity standard that has high accuracy, quantified uncertainty of measurement, proven stability and traceability to Primary Standards. The use of a Control Standard will demonstrate that the cell and meter have the linearity of response required for accurate measurement of the samples – this cannot be demonstrated by the single point calibration used for cell constant determination.

As is the case with all sensors, conductivity cells must be used and maintained correctly or their performance will be impaired. However, if conductivity cells are used correctly then they require minimal maintenance and can have a service life of several years.

References

- 1 PEEK is a registered trademark of Victrex plc.
- 2 Kevlar is a registered trademark of E.I. du Pont de Nemours and Co.
- 3 J.J. Barron & C. Ashton, "The Effect of Temperature on Conductivity Measurement" *
- 4 "Water Quality – Determination of Electrical Conductivity", ISO 7888:1985
- 5 J.J. Barron & C. Ashton, "Sampling Strategies and Sample Handling Requirements for Accurate Conductivity Measurement" *
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- 7 J.J. Barron & C. Ashton, "The Selection and Use of Instruments for Accurate Conductivity Measurement" *
- 8 J.J. Barron & C. Ashton, "Method Validation for conductivity measurements" *
- 9 J.J. Barron & C. Ashton, "Conductivity Measurement in the Pharmaceutical Industry" *

* These papers form part of a comprehensive series of papers that the authors have written covering all of the practical requirements for accurate conductivity measurement. These papers and the authors' book, "A Practical Guide to Accurate Conductivity Measurement" are available via Reagecon's website - www.reagecon.com.

Biographical Notes:

John J Barron is Managing and Technical Director of Reagecon Diagnostics Limited. The company, which was founded in 1986, is the largest producer worldwide of Conductivity Standards and is also a major producer of other chemical standards. Mr. Barron is an expert in several areas of analytical chemistry, including electro-chemical analysis, good laboratory practice (GLP) and chemical metrology. He has written and lectured extensively and is credited with several scientific discoveries including stable low level conductivity standards

Colin Ashton has worked in the Reagecon group since 1994 and is currently Head of the Chemical Metrology Department. A graduate of the University of Southampton, he has developed particular expertise in the development, stabilisation, manufacture and validation of cation, anion and electro-chemical standards. He has particular scientific interest in all aspects of on line chemical analysis and has lectured and published on several areas of this field.

Acknowledgements

The authors wish to extend their gratitude to Ms V. Byrne for her assistance in compiling this paper and Mr L. Geary and Ms R. Cooney for proofing this paper. The authors wish to thank all of their colleagues who have provided technical assistance in compiling Reagecon's series of conductivity measurement papers.

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