Editorial

Dear Reader,

The determination of pH value, conductivity and related parameters such as ion concentration, resistivity, and salinity, are frequent and ordinary tasks in many labs. Samples may originate from many different areas. Sample composition, i.e. solvent and major components, can differ considerably and cover a wide concentration range. The most common solvent of pH and conductivity samples is water. However, other solvents are used as well. In addition, user needs in the lab reach from simple, manual determination to fully automated analysis systems including data gathering via software and other features.

To meet this array of requirements, a big number of methods exist and a wide variety of instrument solutions have been developed by meter and sensor manufacturers. Standard methods are in use for numerous applications. For special needs many dedicated solutions exist as well. However, the vast number of possibilities can make selecting the right instrument and/or sensor cumbersome.

This guide provides some insights into meter and sensor characteristics and performance, enabling users to make better decisions and find the right instrument and electrode. Tips and hints for sensor maintenance and care help to exhaust their usable life and achieve reliable results. METTLER TOLEDO’s Intelligent Sensor Management (ISM) and the three-stage method to determine conductivity in ultra-pure water are also explained. This wealth of information helps finding the most suitable instrument solution but as well measuring successfully each time.

METTLER TOLEDO

Disclaimer

This guide represents selected, possible application examples. Examples have been tested with all possible care in our lab with the analytical instrument mentioned in the applications. The experiments were conducted and the resulting data evaluated based on our current state of knowledge. However, this guide does not absolve you from personally testing its suitability for your intended methods, instruments and purposes. As the use and transfer of an application example are beyond our control, we cannot accept responsibility.

When chemicals and solvents are used, the general safety rules and the directions of the producer must be observed.
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1. General Introduction

Water is essential to life. The growth of human civilization has been dependent on harnessing this natural resource in the 10,000 years since humanity’s gradual evolution to agrarian, and therefore stationary, societies. This massive shift from hunter-gatherer to farmer forever changed humanity’s relationship with water. As we settled down, ensuring we had the water we needed to drink, bathe, and move waste became paramount. The earliest records of intricate systems for water delivery date back to Bronze Age Minoan and Mycenaean cultures in Crete and Greece about 4000 years ago[1].

Because of the importance of this resource, water quality analysis and monitoring are highly relevant to civilizations and have been a major focus since the beginning of modern chemical analysis. pH value and electric conductivity are two fundamental quality parameters of water as well as water-containing solutions and preparations.

1.1 pH Value

The pH value indicates strength and concentration of the acids or leaches present in the given sample. Sample solutions with a pH below 7 are acidic. If the pH is above 7, the solution is basic (also called alkaline). At pH 7.0 the solution is neutral. By definition, the pH value is related to the concentration of the hydronium ion H₃O⁺ which is formed when an acid such as citric, acetic, nitric or sulfuric is dissolved in water. According to Sørensen the pH is defined as the negative logarithm of the H₃O⁺ ion concentration:

\[
\text{pH} = -\log [\text{H}_3\text{O}^+] \]

The response of a pH electrode, i.e. correlation between the pH value and the potential measured with an electrode, is defined by the Nernst equation:

\[
E = E_0 - 2.3 \frac{RT}{nF} \times \text{pH} \\
E \quad \text{measured potential} \\
E_0 \quad \text{constant (zero potential)} \\
R \quad \text{gas constant} \\
T \quad \text{temperature in Kelvin} \\
n \quad \text{ionic charge} \\
F \quad \text{faraday constant} \\
\text{slope factor}
\]

The slope factor at 25 °C has a value of 59.16 mV which is called the theoretical or ideal slope factor.

Strictly speaking, the pH is defined for diluted aqueous solutions of acids and bases. However, the principle of pH is also applied to concentrated and even non-aqueous acidic or basic solutions. In non-aqueous solutions the solvent water is replaced e.g. by hydrocarbons or alcohols.

Because of the importance of the pH value, we recommend to apply a two or three point calibration. If samples disperse below and above pH 7, three calibration points at pH 4, 7 and 9 (or 10) are good practice. It ensures that acidic and basic pH values are measured correctly. If samples are always acidic, also a two point calibration between 4 and 7 is acceptable and yields reliable results.

Nowadays, pH buffers need to be traceable to generally accepted reference standards (e.g. NIST). Please respect the expiry date of buffers (“best before…”) to ensure reliable calibrations. We recommend using ready-to-use buffers in order to avoid any errors due to dilution or impurities. Discard used buffers. Backfilling them may contaminate the remaining buffer solution.

1.2 Conductivity

Electrical conductivity is a non-specific sum parameter over all dissolved ionic species such as salts, acids and bases. The reading is proportional to the combined effect of all ions in the sample and it gives a quick overview of the total dissolved solids in the water. Conductivity does not differentiate between diverse kinds of ions. It is an important tool for monitoring and surveying of a wide range of water types (pure water, drinking water, process water, sea water, etc) and other mainly water based samples.

The higher the content of dissolved solids, the higher the conductivity. Ultra-pure water has a conductivity of 0.055 µS/cm due to self-ionization. Sea water containing about 35 g salt per liter reaches 55 mS/cm.

The conductivity of a solution increases with temperature. Thus, conductivity measurement results are related to a reference temperature (usually 20 or 25 °C). The effect of temperature dependance is represented by the temperature coefficient $\alpha$ of this solution.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration</th>
<th>Temperature coefficient $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride NaCl</td>
<td>10%</td>
<td>2.14</td>
</tr>
<tr>
<td>Potassium chloride KCl</td>
<td>10%</td>
<td>1.88</td>
</tr>
<tr>
<td>Hydrochloric acid HCl</td>
<td>10%</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Table 1: temperature coefficient $\alpha$
2. Meter Selection

2.1 Does Your pH Meter Meet Your Needs?

Users of pH and conductivity meters have to fulfill many different needs and requirements. Therefore, manufacturers offer a variety of meters to match as many of them as possible. Considering the following points will facilitate the selection process and allows you to choose the best possible instrument to cover the user needs and the requirements of the laboratory.

Keep in mind that such needs may change over time due to customer requests or regulatory amendments. Therefore, it is also a good idea to take into account potential future requirements.

2.2 Type of Meter

When choosing a meter, first define which parameters need to be measured and where they will be measured (e.g., in a lab or outdoors).

Electrochemical instruments offer the following measurement parameters:

- potentiometric pH/ISFET pH
- ORP (oxidation reduction potential)
- conductivity (and related values e.g., resistivity, salinity, total dissolved solids)
- ion concentration
- dissolved oxygen (DO)/Biochemical oxygen demand (BOD)

Instruments are available as single-, dual- or multi-channel meters. Besides traditional single or dual-channel meters, there are also modular multi-channel meters. Modular instruments can be expanded at any time by plugging in new measurement modules.

<table>
<thead>
<tr>
<th>Meter Example</th>
<th>Channels</th>
<th>pH</th>
<th>ISFET pH</th>
<th>ORP</th>
<th>Conductivity</th>
<th>Ion conc.</th>
<th>DO</th>
<th>BOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>SevenExcellence</td>
<td>Multi-channel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SevenCompact</td>
<td>Single-channel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SevenGo Duo</td>
<td>Dual-channel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seven2Go</td>
<td>Single-channel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: available meters

There are two answers to the question of where to measure: in a laboratory and outdoors. Accordingly, electrochemical meters can be split into two groups:

- **Benchtop meters** are designed and optimized for use in laboratories or similar spaces. They have an external power supply. Modern benchtop meters come with a large screen, which enhances readability and offers further benefits to users.

- **Portable meters** are optimized for outdoor measurements and use in rough environments. They are dust and waterproof (IP67). The internal power supply makes them independent from plug sockets.

However, portable meters are also used in labs. Their small footprint and easy storage, e.g., in a small drawer, are two advantages appreciated by many lab operators.
2.3 Technical Specifications

Technical specifications are quantifiable parameters describing the meter. They can be found in the meter’s datasheet. Basic specs include:

- Measuring range
- Resolution
- Accuracy
- Connectors
- Size
- Weight

Depending on the use of the meter, the relevance of these basic specification data can be defined.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Benchtop meters</th>
<th>Portable meters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring range</td>
<td>highly relevant</td>
<td>highly relevant</td>
</tr>
<tr>
<td>Resolution</td>
<td>highly relevant</td>
<td>less relevant</td>
</tr>
<tr>
<td>Accuracy</td>
<td>highly relevant</td>
<td>less relevant</td>
</tr>
<tr>
<td>Connectors</td>
<td>highly relevant</td>
<td>less relevant</td>
</tr>
<tr>
<td>Size</td>
<td>less relevant</td>
<td>highly relevant</td>
</tr>
<tr>
<td>Weight</td>
<td>less relevant</td>
<td>highly relevant</td>
</tr>
</tbody>
</table>

Table 3: relevance of basic specifications

Although such technical figures can be easily compared, they cannot provide more than a preliminary qualification. The most important meter requirements are of course precision and accuracy. Both of them are mainly influenced by the quality and stability of the meter circuitry including sensor connectors. Neither big measuring range nor high resolution indicate the circuitry’s quality per se. Circuitry quality depends rather on the knowledge and capacity of the meter manufacturer.

In addition, accuracy sums up all uncertainties of the entire measuring system including meter, sensor and calibration procedures. Typically, sensor quality and buffer status (calibration) contribute considerably more to uncertainty than the meter itself.

2.4 Operation

As explained above, more decision points are necessary to evaluate the most suitable meter. Aspects like ease of use, compliance with SOPs\(^1\) and regulations, display type and options, and available calibration procedures are just as important as technical specifications – especially since basic specifications are very similar for most meters. Therefore, true differentiation comes mainly from these other aspects of meter performance. Hence, here some additional considerations:

**User interface, ease of use**

The easy exchange of information between the user and meter is crucial for reliable results. The meter should always perform exactly as the user wants it to. And the user should always know what the meter is doing. The user interface masters this information exchange. The scope of user interface types ranges from segmented LED or LCD displays with cryptic symbols to color touch screens enabling intuitive menus and full sentences in different languages. Clearly, ease of use, user friendliness and operator guidance are highly improved by modern touch screens.

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\(^1\) SOP: Standard operating procedure
**Readability of display**

Good and easy readability of the display avoids reading errors and increases operation safety. Especially helpful to achieve better reading is the uFocus™ display mode, which enables to indicate just the most important data on the display, such as result, unit and temperature.

**Calibration and measurement**

Modern meters provide many features to simplify and optimize the workflow and ensure its accurate completion. Again, some of these features can be easily found and compared using specs tables. Other properties need to be used in real practice to prove their benefits. For best use, watch for the following:

Calibration:
- Up to 5 calibration points
- Linear or segmented calibration curve
- Predefined and user-defined buffer groups
- Automatic buffer recognition
- Calibration reminder
- Electrode status icon (showing the quality of the last calibration)

Measurement:
- Different endpoint formats (automatic, manual, timed)
- Different stability criteria (fast, standard, strict, user-defined)
- User-defined interval measurement

**Data management and processing**

After results are measured, they need to be processed. Result validation, reporting and archiving are typical steps. Modern meters can support users on different levels. Nevertheless, comparisons may be difficult just from specs without practical tests.

Principally, there are three different possibilities to process data
- Store results locally in the meter – big storage capacity is a plus
- Print results on an external printer – simple and fast printer connection required
- Export data to a PC or a data management system – safe and easy data export options necessary

According to the chosen approach, requirements have varying importance. However, it is decisive whether data-handling tools are present in the meter itself or accessed via suitable, dedicated software solutions.

**Helpful accessories**

Accessories can support the workflow greatly. It is advisable to check if accessories are available for the meter under consideration and the intended use.

- Electrode holder: Simplifies the work and reduces the risk of vessel tipping over and potential damage to the sensor. We recommend the uPlace™ holder which enables a straight up and down movements of electrodes.
- Stirrer: Stirring reduces response time and improves reproducibility. The uMix™ stirrer connects to Seven meters and is automatically operated from them as well.
- Barcode reader: Enables fast and easy sample identification
- Printer: Offers printed results even without a PC
- Sample changer: Allows automated and unassisted analyses of multiple samples
**Ingress protection**

Benchtop meters for laboratory use are IP54 protected. For portable meters, however, protection according to IP67 is an important advantage.

<table>
<thead>
<tr>
<th>Solid particle protection</th>
<th>Liquid ingress protection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IP54</strong></td>
<td>Dust protected, dust cannot enter in sufficient quantity to interfere with the satisfactory operation of the meter</td>
</tr>
<tr>
<td><strong>IP67</strong></td>
<td>Dust tight, no ingress of dust</td>
</tr>
</tbody>
</table>

*Table 4: Liquid and particle protection*

**2.5 Compliance**

Meters can offer additional security functions supporting workflow that help meet compliance requirements during all phases of calibration, measurement and archiving. These function can greatly improve the reliability of results.

- GLP support: Different functions that support Good Laboratory Practice (GLP) are available such as time and date, sample ID, user ID, several user levels. User levels are PIN protected and accommodate measurements limits.
- Radio clock: A radio-controlled clock gives absolute certainty that the displayed date and time is correct. When the radio-controlled clock is used, results are marked accordingly (applies to both internal data memory and printout).
- Methods: The method concept should provide a high degree of compliance and security ensuring that analyses are always performed the same way with identical - and ideal - settings and parameters. So methods fully support SOPs.
- Nonetheless, comparison of different method concepts and their benefits based just on factsheets alone can be very demanding. At least checking that the meter provides a method concept and supports methods is the first step.
- ISM (Intelligent Sensor Management): With ISM, sensor calibration and identification data are stored in the sensor. Meters automatically recognize sensors via ISM and transfer calibration data automatically. This increases ease-of-use and eliminates potential error sources. For further information about ISM, see in chapter 5.10 Intelligent Sensor Management.
- User management: A multilevel user management offers different user rights on different levels. This allows rights assignments that match user’s authorization level. The risk of unintentional or unauthorized changes of settings and methods or deletion of results can be eliminated.
- Services: Are tools for a standardized installation and instrument-specific qualification available? Is a regular instrument certification with traceable tools possible?
## 2.6 General Requirements for Benchtop Meters

### Expected solutions

<table>
<thead>
<tr>
<th>Typical Requirements</th>
<th>Professional Performance Level</th>
<th>Routine Performance Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Display</td>
<td>Large size, color Touch screen with One Click™ operation</td>
<td>Monochrome or color LCD</td>
</tr>
<tr>
<td>Extended memory</td>
<td>Memory for methods and analysis incl. statistics</td>
<td>Data memory</td>
</tr>
<tr>
<td>Data export functions</td>
<td>Export to USB stick, network printer and RS232</td>
<td>Export to USB stick and RS232 printer</td>
</tr>
<tr>
<td>Enhanced compliance with regulations</td>
<td>4 user levels Calibration reminder Radio controlled automatic clock</td>
<td>Routine and expert mode Calibration reminder Set data and time</td>
</tr>
<tr>
<td>Buffers</td>
<td>8 pre-defined and 20 user-defined</td>
<td>8 pre-defined and 1 user-defined</td>
</tr>
<tr>
<td>Automation option</td>
<td>Sample changer, stirrer, LabX direct pH software</td>
<td>Stirrer, LabX direct pH software</td>
</tr>
<tr>
<td>ISM functionalities [1]</td>
<td>full</td>
<td>full</td>
</tr>
</tbody>
</table>

Table 5: general requirements for benchtop meters  
[1] ISM: Intelligent Sensor Management. Relevant sensor data (name, S/N, calibration data) are automatically added to the meter upon connection.

Find more information about METTLER TOLEDO’s meter portfolio on www.mt.com/pH
3. **pH Electrode Selection**

3.1 **Electrode Selection and Handling**

For optimal pH measurements, the correct electrode must first be selected. The most important sample criteria to be considered are: chemical composition, homogeneity, temperature, pH range and container size (length and width restrictions). The choice becomes particularly important for non-aqueous, low conductivity, protein-rich and viscous samples where general purpose glass electrodes are subject to various sources of error.

The response time and accuracy of an electrode is dependent on a number of factors. Measurements at extreme pH values and temperatures, or low conductivity may take longer than those of aqueous solutions at room temperature with a neutral pH. The significance of the different types of samples is explained below by taking the different electrode characteristics as a starting point. Again, mainly combined pH electrodes are discussed in this chapter.

3.2 **Different Kinds of Junctions**

**a) Ceramic junctions**

The opening that the reference part of a pH electrode contains to maintain the contact with the sample can have several different forms. These forms have evolved through time because of the different demands put on the electrodes when measuring diverse samples. The ‘standard’ junction is the simplest one and is known as a ceramic junction. It consists of a porous piece of ceramic which is pushed through the glass shaft of the electrode. This porous ceramic material then allows the electrolyte to slowly flow out of the electrode, but stops it from streaming out freely. This kind of junction is very suitable for standard measurements in aqueous solutions; the METTLER TOLEDO InLab® Routine Pro is an example of such an electrode. A schematic drawing of the principle of this junction is shown below in figure 3.

Even though this is probably the most widely used junction because of its simplicity of use with aqueous solutions, it has one main drawback. Because of the porous structure of the junction it is relatively easy for samples to block the junction, especially if the sample is viscous or if it is a suspension.

One sometimes also has to be careful with some aqueous samples such as those with a high protein concentration, since proteins may precipitate within the porous junction if they come in contact with the reference electrolyte, which is often KCl. This reaction will cause the porous structure to be filled with protein debris blocking the junction and rendering the electrode useless. Measurements are not possible if the electrolyte cannot flow freely since the reference potential will no longer be stable. The same problem can also be caused if the inner electrolyte reacts with the sample solution being measured and the two meet in the junction.

This reaction can create a precipitate which may block the junction, e.g. if KCl electrolyte saturated with AgCl is used with samples containing sulfides, the silver and sulfides react to form Ag₂S which then blocks the ceramic junction.

**b) Sleeve junctions**

The ceramic junction has its limitations and is not suitable for more difficult samples, so several other junctions have been developed to facilitate the measurements with these samples. The problems that the ceramic junction has with viscous samples or suspensions can be solved with a larger junction which cannot be so easily blocked and which can be easily cleaned.

One such junction is the sleeve junction. This junction consists of an electrode shaft with a ground glass part over which a ground glass or plastic sleeve can be moved. The electrolyte comes out of the electrode via a hole which is covered with the ground glass or plastic sleeve.
The sleeve can be pulled more or less securely over the ground glass part of the shaft to regulate the flow of the electrolyte out of the reference element. A representation of the ground glass junction is given in figure 4.

METTLER TOLEDO has for example the sleeve junction electrode InLab® Science. The advantage of this junction is that the electrolyte flow is faster than with the ceramic junction, which is beneficial for some samples such as ion-deficient media. Cleaning is also very easy with this junction as the sleeve can be lifted up completely and all the pollutants can be removed from the junction with deionized water or cleaned with a tissue (as long as the pH membrane isn’t touched!). This stronger electrolyte flow also makes the junction ‘self-cleaning’ to a certain extend. The main application for this junction is in areas where the benefits of having fast electrolyte flow and a blockage resistant junction are required for accurate pH measurements.

The fast ion flow is particularly useful in media that have a low ion concentration of a few mmol or lower. These media are considered to be ion-deficient or ion-poor and have very low conductivity. This again causes increased resistance at the junction and leads to contact problems between the reference electrolyte and the measuring solution, giving a very unstable signal. However, this problem is solved by using a circular ground glass junction which creates optimal contact between the reference electrolyte and the measuring solution. Ion-poor media are also difficult to measure but this example will be discussed later on in this chapter.

The fact that the junction can easily be cleaned and is more resistant to blockages comes in handy with very viscous samples like oil, suspensions and emulsions e.g. milk. The electrode can perform longer without having to be cleaned and cleaning is easier. The larger junction contact area is also of benefit for oily samples as this solves the low ion concentration problem that oil samples generally have.

c) Open junctions

The third type of junction is the open junction. This reference electrode is completely open to the environment and has full contact between the reference electrolyte and the sample solution. This is only possible with a solid state polymer reference electrolyte. A schematic diagram of this junction is shown below. The great advantage of this junction is clearly the fact that it is completely open and can therefore seldom clog. Open junctions can easily cope with very dirty samples constantly providing good measurements. The disadvantage of the solid state polymer reference electrolyte which is used for this open junction is that it has slower reaction times and low electrolyte flow. This means that the samples measured need to have a high enough ion concentration for stable measurements to be possible. Nevertheless, these electrodes are suitable for most samples and are very robust.

figure 4: electrode with sleeve junction

figure 5: example of electrode with open junction
3.3 Reference Systems and Electrolytes

Of all the possible reference systems developed for reference elements, only a few are of practical importance. These are the silver/silver chloride, iodine/iodide and the mercury/calomel systems, as well as some of their adaptations. Due to environmental considerations, however, the calomel reference electrode is no longer widely used. Here we only discuss the most important reference system, the silver/silver chloride system.

The potential of the reference electrode system is defined by the reference electrolyte and the reference element (silver/silver chloride). The conventional construction of this reference system is a silver wire coated with AgCl. For this version of the Ag/AgCl reference system it is important that the reference electrolyte has a very high (saturated) AgCl concentration to ensure that the reference element wire doesn’t get stripped of the AgCl. If this were to happen the reference element would stop working.

A recent improvement of this type of reference element was made with the development of the ARGENTHAL™ reference element. The ARGENTHAL™ reference element consists of a small cartridge filled with AgCl particles that provide the silver ions for the chemical reaction at the lead off wire. This cartridge contains enough AgCl to last the lifetime of the electrode. Which type of reference electrolyte is used in an electrode strongly depends on the reference system and on the type of sample used. Whereas the reference system can either be conventional silver wire or ARGENTHAL™, the sample can be divided into two classes namely aqueous and non-aqueous matrices.

For both aqueous and non-aqueous solutions it is important that the reference electrolyte contain plenty of ions to keep the reference system working well. Ideally, the salts used to provide these ions in the reference electrolyte are very soluble in the solvent, are pH neutral (so that they do not influence the measurements when flowing out of the electrode) and do not precipitate out by reacting with other ions present in sample or buffer. KCl matches these requirements best for aqueous solutions and LiCl is best suited for use with non-aqueous solutions.

The conventional Ag/AgCl reference system needs the presence of an electrolyte saturated with AgCl so that the lead off wire does not get stripped of AgCl. The reference electrolyte of choice is therefore, 3 mol/L KCl saturated with AgCl. The disadvantage of this electrolyte is that silver ions can react with the sample to form an insoluble precipitate thereby blocking the junction.

The ARGENTHAL™ reference system has a cartridge with AgCl granules which ensure that AgCl is constantly available. This cartridge contains enough AgCl to last the lifetime of the electrode. Typically this ARGENTHAL™ system comes in combination with a silver ion barrier which stops silver ions from passing into the electrolyte. The advantage of these features of the ARGENTHAL™ reference system is that one can use standard 3 mol/L KCl as a reference electrolyte rather than 3 mol/L KCl saturated with AgCl, so in combination with the silver ion trap there are no free Ag⁺ ions in the electrolyte which could cause a precipitate after reaction with the sample.

A phase separation in the contact area between electrolyte and sample solution at the junction can cause an unstable signal, therefore deionized water is used as a solvent for the reference electrolyte in aqueous samples.
and ethanol or acetic acid is used as solvent for non-aqueous systems. A brief overview of the possible reference system/electrolyte combinations is given below:

<table>
<thead>
<tr>
<th>Electrolyte for aqueous samples</th>
<th>Electrolyte for non-aqueous samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARGENTHAL™ reference</td>
<td>Conventional reference</td>
</tr>
<tr>
<td>3 mol/L KCl + H₂O</td>
<td>3 mol/L KCl + AgCl + H₂O</td>
</tr>
<tr>
<td>ARGENTHAL™ reference</td>
<td></td>
</tr>
<tr>
<td>LiCl + Ethanol</td>
<td></td>
</tr>
<tr>
<td>LiCl + Acetic acid</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: overview of reference electrolytes to be used

In addition to the above-mentioned liquid electrolytes, there are also gel and solid polymer electrolytes. Electrodes delivered with these electrolytes cannot be refilled.

The electrode response time is strongly dependent on the type of electrolyte used. Liquid electrolyte electrodes show a very quick response time and give the most accurate measurements. Gel and solid polymer electrolyte electrode both have longer response times, but they are virtually maintenance-free.

### 3.4 Types of Membrane Glass and Membrane Shapes

The pH glass membrane of an electrode can have several different shapes and properties, depending on the application the electrode is used for. The selection criteria here are sample consistency, volume and temperature, the required measurement range and the concentration of ions present in the sample.

The most obvious property is the shape of the membrane. In figure 7 a selection of membrane shapes is shown together with their properties and proposed usage.

**figure 7: differently shaped pH membranes**
The membrane glass is also important for the measurement properties of the electrode. The table below gives an overview of the various types of METTLER TOLEDO pH membrane glasses.

<table>
<thead>
<tr>
<th>Type of membrane glass</th>
<th>Properties/samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA – High alkali glass</td>
<td>For high temperatures and high pH values: extremely low alkali error</td>
</tr>
<tr>
<td>LoT – Low temperature glass</td>
<td>For low temperatures and low ion concentrations: low resistance glass</td>
</tr>
<tr>
<td>A41</td>
<td>For high temperatures; resistant to chemicals</td>
</tr>
<tr>
<td>U – Universal glass</td>
<td>For standard applications</td>
</tr>
<tr>
<td>HF – Hydrofluoric acid resistant glass</td>
<td>For samples containing Hydrofluoric acid (up to 1 g/L)</td>
</tr>
<tr>
<td>Na – Sodium sensitive glass</td>
<td>Only used for sodium detecting electrodes: sodium specific glass</td>
</tr>
</tbody>
</table>

Table 7: various membrane glasses

### 3.5 pH Electrodes for Specific Applications

Now that we have seen what different types of junctions, electrolytes and membranes exist in pH electrodes, we will have a look at what this means for the measurement of the pH in different systems.

#### Easy samples

A simple pH electrode is sufficient for routine measurements in chemistry labs where a lot of aqueous chemical solutions are tested. The advantage of the simple pH electrode is that it is very easy to use and is also very robust. In general, these electrodes are made of glass and have a ceramic junction. They are also refillable, which means that you can refill the electrolyte thereby cleaning the electrode and prolonging its lifetime. An electrode of choice for these simple lab measurements is the InLab® Routine with or without temperature sensor. The InLab® Routine Pro has an integrated temperature sensor for automatic temperature measurement and compensation during measurement.

#### Complex samples or such of unknown composition

Measuring the pH of complex samples can be somewhat tricky, since the dirt in the sample can hinder correct measurements. Examples of such applications are soil acidity measurements, quality control in foodstuffs such as soups and measurements in colloidal chemical systems. The risk of blockages with such samples would be very high if one were to use a pH electrode with a ceramic junction. Therefore it is best to use a pH electrode with an open junction such as the InLab® Expert which has a solid state polymer reference electrolyte. This electrode has an open junction which allows direct contact between the electrolyte and sample. For temperature compensation during the measurement it is possible to use an electrode with a built-in temperature sensor such as the InLab® Expert Pro.

#### Emulsions

Another class of samples that require special care when doing pH measurements are emulsions, for example paints, oil in water dispersions, milk and other dairy products. Such samples can also block the junction of pH electrodes when the dispersed phase of the emulsion (the ‘mixed-in’ part) blocks the junction. The emulsion particles which can cause blockages are very small; therefore it is not necessary to measure with an open junction. Since electrodes with solid state polymers have relatively slow reaction times compared to electrodes with a liquid electrolyte, it is best to measure emulsions with electrodes that have a sleeve junction. The sleeve junction cannot be blocked easily and has a large contact area with the sample. If the junction should get blocked, it can easily be cleaned by moving the sleeve away from the junction and cleaning the electrode.
An example of this kind of electrode is the InLab® Science, or the InLab® Science Pro which has a built-in temperature sensor. Electrodes with a sleeve junction have a large contact area between the reference electrolyte and sample solution and therefore are also suitable for samples which cause an unstable signal.

**Semi-solid or solid samples**

Standard pH electrodes are generally not able to withstand the pressure of being pushed into a solid sample; therefore one needs a special electrode which is able to penetrate the sample in order to measure the pH. The shape of the membrane is also important as it needs to be formed in such a way as to ensure a large contact area with the sample, even if the electrode is pushed into the sample with force. The METTLER TOLEDO electrodes most suitable for these kinds of applications are the InLab® Solids or InLab® Solids Pro. While their spear shaped point enables them to pierce the sample, the membrane shape ensures accurate measurements. The InLab® Solids also has an open junction, which further prevents the junction from being blocked by the (semi-) solid sample. This electrode is typically used for quality control or checking production processes of cheese and meat.

**Surfaces**

One sometimes needs to measure the pH of a sample with a volume so small that it doesn’t cover the tip of a pH electrode. For these kinds of measurements there is only one solution, namely a flat pH electrode. This electrode only needs a surface to be able to measure pH. Applications for this type of electrode include the determination of the pH of skin during a health check-up and the pH of paper as required in the manufacture of archival grade paper for important documents. There are many other applications where only very small volumes are available for pH determinations, such as when measuring the pH of a drop of blood. Here the flat pH electrode is placed directly on the drop spreading out the sample over the surface of the flat membrane. Other applications involve very expensive biochemical samples of which only a tiny amount is available. The METTLER TOLEDO electrode best suited for this purpose is the InLab® Surface.

**High sample throughput or very viscous samples**

For certain challenging applications it is advantageous to use an electrode with SteadyForce® reference. The InLab® Power and InLab® Power (Pro) has been designed so that the inner electrolyte is under pressure, which has the advantage of preventing the sample from getting into the electrode regardless of the characteristics of the sample or application. This means that the measurements are both reliable and fast since the electrolyte flow is always sufficient for stable measurements. For very viscous samples the InLab® Viscous works best: the combination of SteadyForce reference and specially designed tip allows for quick measurements despite the applicative challenges.
3.6 Measuring Small Samples

The more precious or rare the sample, the greater the challenge to use it for analysis. Some pH applications call for an electrode which only needs a small sample volume or can reach into difficult sample vessels, such as when measuring pH values in test tubes, Eppendorf tubes or narrow NMR sample tubes. Such containers with small sample volumes generally require a small and narrow pH electrode which can reach the sample and allow for pH determinations.

METTLER TOLEDO’s micro and semi-micro pH sensors fit any size of sample container – particularly handy for precious or rare samples because they eliminate the need for larger volumes in electrochemical analysis.

Mini technological marvels

While the InLab® 751-4mm conductivity sensor still manages to encompass an integrated temperature probe, the micro pH sensors are too small to feature one.

InLab® Nano – cutting edge pH technology

The InLab® Nano measures pH in volumes as small as 5 µL. Its steel needle does not break easily, despite its super small diameter of 1.7 mm. Its slanted tip protects the pH membrane against mechanical damage, at the same time allowing for puncturing septa.

InLab® Ultra-Micro – an evolved micro sensor

Compared to the InLab® Micro, this electrode has a shorter sensor shaft of 40 mm for easier handling and less breakage. The ceramic junction is placed lower in order to make it possible to measure small sample volumes down to 15 µL, e.g. in well plates, centrifuge vials etc.

InLab® Micro – the tried and trusted classic

The InLab® Micro is ideal for measuring pH in deep vials and centrifuge tubes thanks to its 60 mm long shaft. Rigorously tried and tested, it reliably meets most standard micro applications. It has become a true classic amongst the InLab® Micro family.

InLab® Micro Pro – temperature corrected pH

The InLab® Micro Pro has an integrated temperature sensor supporting automatic temperature compensation (ATC). The position of the temperature probe close to the pH membrane enables exact ATC.
**InLab® Semi-Micro – maintenance and contamination free pH measurements**

The InLab® Semi-Micro contains the latest in polymer electrolytes: XEROLYT® EXTRA. Service and operation could not be simpler thanks to the polymer electrolyte and the open reference connection. With no junction, there is no possibility of contamination or blockage.

**InLab® Flex-Micro – pliable pH precision**

This pH electrode will flex before breaking, so no more headaches over damaged micro electrodes. Relax knowing that one wrong move will not result in an expensive electrode replacement. An efficient member of the team.

**InLab® Redox Micro – easy oxidation-reduction potential**

ORP (oxidation reduction potential), also known as redox potential, is important in biology and easily determined with the InLab® Redox Micro. This traditional INGOLD product is based on the tried and true platinum ring design.

---

**Minimum sample volume in this specific container type**

<table>
<thead>
<tr>
<th>Container type and typical sample size</th>
<th>pH diameter</th>
<th>Conductivity diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.7 mm</td>
<td>3.0 mm</td>
</tr>
<tr>
<td>InLab® Nano</td>
<td>50 μL</td>
<td>100 μL</td>
</tr>
<tr>
<td>InLab® Ultra-Micro</td>
<td>20 μL</td>
<td>25 μL</td>
</tr>
<tr>
<td>InLab® Micro</td>
<td>20 μL</td>
<td>25 μL</td>
</tr>
<tr>
<td>InLab® 751-4mm</td>
<td>10 μL</td>
<td>20 μL</td>
</tr>
<tr>
<td>LiteTouch Tubes 1.5–1.7 mL</td>
<td>20 μL</td>
<td>25 μL</td>
</tr>
<tr>
<td>Sample tubes 0.5 mL</td>
<td>20 μL</td>
<td>25 μL</td>
</tr>
<tr>
<td>96 well plates 200–300 μL</td>
<td>10 μL</td>
<td>20 μL</td>
</tr>
<tr>
<td>384 micro plates 5–100 μL</td>
<td>5 μL</td>
<td>15 μL</td>
</tr>
</tbody>
</table>

*Table 8: minimum sample volume*

For more information, please visit:

> [www.electrodes.net](http://www.electrodes.net)
4. **Conductivity Sensor Selection**

4.1 **Selecting the Right Sensor**

Choosing the right conductivity sensor is a decisive factor in obtaining accurate and reliable results. As shown in the previous sections, the different construction types and materials used lead to sensors with a variety of strengths and weaknesses. Therefore, it does not make sense to speak of good or bad sensors. The right sensor is the one which fits the needs of the application best.

A basic requirement is that no chemical reactions occur between the sample and the sensor. For chemically reactive samples, glass and platinum are often the best choice because they have the best chemical resistance of all commonly used cell materials. For field application and also a lot of laboratory applications, the mechanical stability of the sensor is a more important factor. A conductivity sensor with an epoxy body and graphite electrodes is often used, as this has been shown to be extremely durable and it also has good chemical resistance. For low reactive aqueous solutions and organic solvents, the use of cells made of steel or titanium is often a good alternative.

The next point which should be considered in order to select an optimal sensor is the cell constant and the construction type. A suitable cell constant correlates with the conductivity of the sample. The lower the expected conductivity of the sample, the smaller the cell constant of the sensor should be. Figure 21 shows a set of samples and the range of recommended cell constants which should be used for the measurement. To make a decision between a 2-pole cell and a 4-pole cell the following rough-and-ready rule can be used: For low conductivity measurements, a 2-pole cell should be used. For mid to high conductivity measurements a 4-pole cell is preferred, especially for measurements over a wide conductivity range.

Sometimes standards or norms contain requirements concerning the conductivity sensor. If a conductivity measurement is performed according to such a standard, then the chosen sensor must completely fulfill all the described requirements.

Furthermore, there are some special sensors with a very low cell constant for a high precision measurement or with a small shaft diameter which allow conductivity measurements in small sample vessels. Table 15 gives an overview over the METTLER TOLEDO laboratory conductivity sensor portfolio. For further information, please check: [www.electrodes.net](http://www.electrodes.net)
Conductivity Sensor Selection

**Generalist**
- **Configuration:** 4 platinum pole glass shaft
  - **Cell Constant:** 0.80 cm\(^{-1}\)
  - **Measuring Range:** 0.01–500 mS/cm
  - **Sensor Name:** InLab® 710
- **Configuration:** 4 graphite pole epoxy shaft
  - **Cell Constant:** 0.57 cm\(^{-1}\)
  - **Measuring Range:** 0.01–1000 mS/cm
  - **Sensor Name:** InLab® 731

**Specialist**
- **Pure water and high precision**
  - **Configuration:** 2 titanium pole titanium shaft
    - **Cell Constant:** 0.01 cm\(^{-1}\)
    - **Measuring Range:** 0.0001–1000 µS/cm
    - **Sensor Name:** InLab® Trace
  - **Configuration:** 2 steel pole steel shaft
    - **Cell Constant:** 0.105 cm\(^{-1}\)
    - **Measuring Range:** 0.001–500 µS/cm
    - **Sensor Name:** InLab® 741
  - **Configuration:** 2 platinum pole glass shaft
    - **Cell Constant:** 0.06 cm\(^{-1}\)
    - **Measuring Range:** 0.1–500 µS/cm
    - **Sensor Name:** InLab® 720
- **Micro**
  - **Configuration:** 2 platinum pole glass shaft
    - **Cell Constant:** 1.0 cm\(^{-1}\)
    - **Measuring Range:** 0.01–100 mS/cm
    - **Sensor Name:** InLab® 751-4mm
  - **Configuration:** 2 platinum pole glass shaft
    - **Cell Constant:** 1.0 cm\(^{-1}\)
    - **Measuring Range:** 0.01–112 mS/cm
    - **Sensor Name:** InLab® 752-6mm

**Bio-ethanol**
- **Configuration:** 2 platinum pole glass shaft
  - **Cell Constant:** 0.1 cm\(^{-1}\)
  - **Measuring Range:** 0.1–500 µS/cm
  - **Sensor Name:** InLab® 725

Table 9: Conductivity Sensor Portfolio of METTLER TOLEDO

**InLab® 751–4mm – micro-conductivity made easy**
With a diameter of only 4 mm, the InLab® 751–4mm still features an integrated temperature probe and corrects conductivity readings to a defined reference temperature. For correct results, immerse the sensor to the minimum immersion level marked on the probe.

**InLab® 752–6mm – versatile semi-micro conductivity**
With a measuring range of 10 µS/cm to 200 mS/cm this unique semi-micro conductivity sensor is a real generalist – ideal for direct measurements in test tubes or micro titrations. Its 6 mm diameter allows for a minimum immersion depth of only 17 mm.
4.2 Materials of Conductivity Sensors

Different materials are used to build conductivity cells. Platinum, platinized platinum, graphite, stainless steel, and titanium are qualified materials for the electrodes, while epoxy and glass are often used as shaft material. With steel and titanium, it is also possible to produce the electrodes and shaft in one piece.

Important characteristics of the materials used are:

- Chemical resistance
- Mechanical resistance
- Polarization resistance
- Carry-over effect

Chemical reactions between the sensor material (especially the electrodes) and the sample are highly undesirable because this leads to incorrect measurements and to a permanent change of the cell. The cell can also be destroyed by mechanical influences. Electrodes which are built from a material with a low mechanical strength like platinum or graphite are normally surrounded with a more robust material which makes the electrode less sensitive to mechanical damage.

The surface texture of the electrode has an influence on the polarization resistance. Porous or roughened surfaces have a lower interface resistance and therefore a reduced polarization effect. Uncoated platinum electrodes have very high resistance; electrodes made of platinized platinum have the lowest.

Porous layers such as platinized platinum or graphite can adsorb some parts of the sample, which leads to a carry-over effect and a longer response time if solutions with different concentrations are measured. These effects are contrary to the polarization resistance of the electrode material. Depending on the requirements, an electrode material with a low polarization resistance, large carry-over effect and longer response time or an electrode material with a high polarization resistance, a small carry-over effect and short response time can be chosen.

For more information, please visit:

- www.electrodes.net
5. Care and Measurement Technique

This section provides an overview of how to properly care for pH and conductivity sensors and some hints regarding measurement techniques. In addition, the advantages of Intelligent Sensor Management (ISM®) and the testing of ultra-pure water are explained.

5.1 pH Electrode Maintenance

Regular maintenance is very important for prolonging the lifetime of any pH electrode. Electrodes with liquid electrolyte need the electrolyte to be topped up when the level threatens to become lower than the level of the sample solution. This way a reflux of the sample into the electrode is avoided. The complete reference electrolyte should also be changed regularly, e.g. once a month. This ensures that the electrolyte is fresh and that no crystallization occurs despite evaporation from the open filling port during measurement. Be careful not to get any bubbles on the inside of the electrode, especially near the junction. If this happens the measurements will be unstable. To get rid of any bubbles, gently shake the electrode in the vertical motion like with a fever thermometer.

5.2 pH Electrode Storage

Electrodes should always be stored in aqueous and ion-rich solutions. This ensures that the pH-sensitive gel layer which forms on the pH glass membrane remains hydrated and ion rich. This is necessary for the pH membrane to react in a reliable way with respect to the pH value of a sample.

**Short term storage**
In between measurements or when the electrode is not being used for brief periods of time, it is best to keep the electrode in a holder containing the special InLab® storage solution[1], its inner electrolyte solution (e.g. 3 mol/L KCl), or in a pH 4 or pH 7 buffer. Ensure that the level of solution in the beaker is below that of the filling solution in the electrode.

**Long term storage**
For long term storage, keep the electrode wetting cap filled with the InLab® storage solution[1] or, alternatively, with the inner electrolyte solution, pH buffer 4 or 0.1 mol/L HCl. Make sure that the filling port for reference and combination electrodes is closed so as to avoid loss of the electrolyte solution through evaporation, which can cause the formation of crystals within the electrode and junction. Never store the electrode dry or in distilled water as this will affect the pH-sensitive glass membrane and thus shorten the lifetime of the electrode. Although an electrode that has been incorrectly stored can be restored by regeneration procedures, following the above mentioned recommendations will ensure that your electrode is always ready to use.

**Temperature sensors**
Rinse the temperature sensors after use and store dry in the packing box to prevent damage.

5.3 pH Electrode Cleaning

To clean the electrode, rinse it with deionized water after each measurement but never wipe it clean with a tissue. The rough surface of the paper tissue will scratch and damage the pH-sensitive glass membrane removing the gel-layer and creating an electrostatic charge on the electrode. This electrostatic charge causes the measured signal to become very unstable. Special cleaning procedures may be necessary after contamination with certain samples. These are described in greater detail below.

[1] This InLab® storage solution can be ordered from METTLER TOLEDO (30111142)
[2] This thiourea solution can be ordered from METTLER TOLEDO (51340070)
Blockage with silver sulfide (Ag₂S)
If the reference electrolyte contains silver ions and the sample being measured contains sulfides, the junction will get contaminated with a silver sulfide precipitate. To clear the junction of this contamination, clean it with 8% thiourea in 0.1 mol/L HCl solution.¹

Blockage with silver chloride (AgCl)
The silver ions from the reference electrolyte can also react with samples that contain chloride ions, resulting in an AgCl precipitate. This precipitate can be removed by soaking the electrode in a concentrated ammonia solution.

Blockage with proteins
Junctions contaminated with proteins can often be cleaned by immersing the electrode into a pepsin/HCl (5% pepsin in 0.1 mol/L HCl) solution for several hours.²

Other junction blockages
If the junction is blocked with other contaminations, try cleaning the electrode in an ultrasonic bath with water or a 0.1 mol/L HCl solution.

5.4 pH Electrode Regeneration and Lifetime
Even electrodes that have been well maintained and properly stored may start performing poorly after some time. In such cases it may be possible to regenerate the pH-sensitive glass membrane and restore the electrode to its previous level of performance using an ammonium bifluoride regeneration solution.³ This regeneration solution is based on a highly diluted solution of hydrofluoric acid which etches away a very thin layer of the glass membrane, exposing a fresh surface area.

When using the regeneration mixture, do not leave the electrode in the solution for longer than 1–2 minutes or the whole pH-sensitive membrane will be corroded away and the electrode rendered useless. The expected lifetime of a correctly used and maintained pH electrode is around one to three years. Factors that contribute to a reduction of the lifetime of an electrode include high temperatures and measuring at extreme pH values.

5.5 Measuring pH – Temperature is a Critical Component
pH results are only correct if the sample temperature is taken into account. With these simple but effective rules for avoiding negative temperature effects, it’s easy to obtain accurate, reproducible results.

Automatic Temperature Compensation (ATC)
ATC works best with normal-size samples.

• Use a sensor with integrated temperature probe and wait for a stable signal. The meter automatically corrects the pH signal. ATC works best in samples larger than 10 mL.

• Any “Pro” type InLab® sensor – InLab® Micro Pro, Science Pro, Expert Pro – has integrated temperature probes, eliminating worries over wrong temperature settings or not capturing temperature.

• For sensors without an integrated temperature probe, using a separate temperature probe is recommended.

¹ This regeneration solution can be ordered from METTLER TOLEDO (51350104)
² This pepsin solution can be ordered from METTLER TOLEDO (51340068)
Manual Temperature Compensation (MTC)
MTC is extremely accurate, but can be time-consuming.

- If the temperature of your sample is known (you are working in a climate-controlled room or the samples just came out of the refrigerator) enter this known temperature in the measuring settings of your instrument to correct the pH (or conductivity) signal.

- When measuring samples with different temperatures, MTC can be time-consuming, because the setting must be changed with every temperature change.

Measure the sample, not your sensor
With very small samples, the sensor can take so long to reach equilibrium that the sensor temperature is wrongly interpreted as the sample temperature. The sample mass is negligible compared with the sensor mass, so take the time necessary to ensure that you actually measure the sample temperature. Best practice is to keep the sensor with the sample. Make sure temperatures match by storing the sensor with samples in the refrigerator or incubator, or at room temperature. This guarantees the highest accuracy because the pH membrane, reference system and sample are at the same temperature.

5.6 Contamination Control of pH Electrodes
When measuring samples there is always the risk of contamination, either by sample carry-over or by microbiological or genetic contamination. Conventional pH electrodes can also be damaged by electrolyte outflow when measuring TRIS-based buffers or proteinaceous samples. This is not the case when working with InLab® electrodes.

Avoid sensor contamination with TRIS buffers
Accurate pH measurement is a key factor in buffer quality. TRIS-based buffers – widely used in biological research ranging from molecular biology to histology – can damage standard pH equipment.

How does TRIS do its damage?
When measuring pH during TRIS buffer preparation, the reference junction on conventional pH electrodes can clog when TRIS reacts with silver ions in the fill solution. This reaction can also occur with protein in the buffer, such as BSA (bovine serum albumin). The eventual result is slow or fluctuating readings, or even entirely wrong results.

InLab® electrodes by METTLER TOLEDO are specifically designed for compatibility with TRIS-based buffers, assuring reliable results and accurate buffer values. The electrolyte in InLab® electrodes is guaranteed to be free of silver ions, eliminating the possibility of contamination.
Clean with RNase and DNase cleansers and autoclave to eliminate biohazard

The pH electrode models InLab® Power, Power Pro, Viscous and Viscous Pro can be sterilized by autoclaving. By cleaning the sensors with RNase and DNase decontamination solutions first, the potential for biological contamination is significantly reduced.

![figure 27: special InLab® sensors can be autoclaved](image)

5.7 Some Tips for Conductivity Measurements

- Avoid electrostatic charges from the sample vessel. Electrostatic forces adversely influence the conductivity measurement.
- Avoid air bubbles in the probe. Carbon dioxide CO₂ may be absorbed from the sample deteriorating the original conductivity. In addition, air bubbles also interfere with the conductivity measurement.
- Use low conductivity standards like 10 or 84 μS/cm as quickly as possible and discard after use. They react with carbon dioxide from the ambient air, which changes the conductivity of the standard solution and leads to erroneous calibrations of the conductivity cell constant.
5.8 Three-stage Method for the Measurement of Conductivity in Ultra-pure Water

Pure and ultra-pure water is easily polluted by the smallest amount of impurities and contaminants such as salts or carbon dioxide. The assurance of pure and ultra-pure water quality needs meticulous testing. The most widespread test of ultra-pure water is the three-stage method according to USP <645>, which is described in detail in the following section. However, other pharmacopoeias stipulate different methods.

The three-stage method <645> contains three stages of different measurements, conditions and requirements. Testing stops at the first stage that passes. If all three stages fail, the water does not meet requirements. It is important to switch-off the temperature correction when testing according to <645>.

Stage 1
Measure the non-temperature-compensated conductivity and temperature. The measurement may be performed online (with flow cell) or offline (with sample bottle). Round the temperature down to the next lowest 5 °C interval. Look up the Stage 1 limit for that temperature (see table 10). If the measured conductivity is not greater than the limit in the table, the water meets the requirements for <645>. If the conductivity is higher than the table value, proceed with Stage 2.

USP <645> Stage 1 Requirements
For non-temperature compensated conductivity measurements

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum Conductivity (µS/cm)</th>
<th>Temperature (°C)</th>
<th>Maximum Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
<td>55</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>60</td>
<td>2.2</td>
</tr>
<tr>
<td>10</td>
<td>0.9</td>
<td>65</td>
<td>2.4</td>
</tr>
<tr>
<td>15</td>
<td>1.0</td>
<td>70</td>
<td>2.5</td>
</tr>
<tr>
<td>20</td>
<td>1.1</td>
<td>75</td>
<td>2.7</td>
</tr>
<tr>
<td>25</td>
<td>1.3</td>
<td>80</td>
<td>2.7</td>
</tr>
<tr>
<td>30</td>
<td>1.4</td>
<td>85</td>
<td>2.7</td>
</tr>
<tr>
<td>35</td>
<td>1.5</td>
<td>90</td>
<td>2.7</td>
</tr>
<tr>
<td>40</td>
<td>1.7</td>
<td>95</td>
<td>2.9</td>
</tr>
<tr>
<td>45</td>
<td>1.8</td>
<td>100</td>
<td>3.1</td>
</tr>
<tr>
<td>50</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10: stage 1 maximum conductivity limits

Stage 2
Adjust the temperature of the sample to 25 ±1 °C and stir or agitate until the conductivity stops rising and is equilibrated with ambient air. The reading must not exceed 2.1 µS/cm.

Stage 3
Add saturated KCl solution (0.3 mL/100 mL) to the sample from stage 2 and measure the conductivity value. The conductivity reading from stage 2 must not exceed the allowed conductivity for that pH (see table 11).
### USP <645> Stage 3 pH and Conductivity Requirements

<table>
<thead>
<tr>
<th>pH</th>
<th>Maximum Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.9</td>
<td>3.8</td>
</tr>
<tr>
<td>7.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 1: Stage 3 maximum conductivity limits

#### 5.9 Intelligent Sensor Management

Avoid mistakes and save time with Intelligent Sensor Management (ISM®). Whether you are measuring pH, conductivity or dissolved oxygen, the revolutionary ISM® technology supports you in your daily work.

The SevenExcellence, SevenCompact and SevenGo Duo™ meters incorporate Intelligent Sensor Management. This ingenious system offers great advantages such as:

- **Secure and efficient** – After connecting an ISM sensor the current sensor calibration data and the sensor ID are immediate transferred to the meter. No need to calibrate again.
- **Always up to date** – After the calibration of an ISM sensor the new calibration data are instantaneously transferred from the meter to the sensor chip, where they belong!
- **Backup certificate guaranteed** – The initial factory calibration data of an ISM sensor can be reviewed and transferred to a PC or printer. Print out your certificate any time.
- **Conclusive calibration history** – The last five calibrations data are stored in an ISM sensor, including the current calibration; can be reviewed and transferred to a PC or printer.
- **Easy lifetime monitoring** – The maximum temperature that the ISM sensor has been exposed to during measurement is monitored automatically and can be reviewed for valuation of electrode lifetime.

METTLER TOLEDO supplies pH electrodes for all possible applications. The most important electrode models are available with ISM. They all come with an integrated temperature probe for automatic temperature compensation (ATC):

- **InLab® Expert Pro-ISM (waterproof to IP67)**
  Easy-to-use pH generalist with polymeric XEROLYT® electrolyte and two open reference junctions
- **InLab® Routine Pro-ISM**
  Classical, refillable glass pH electrode for routine measurements of aqueous samples
5.10 Good Electrochemistry Practice™

In just 5 steps, the METTLER TOLEDO Good Electrochemistry Practice (GEP) program provides the right tools, procedures and services to evaluate and select the right products, to install and qualify a measurement system properly and to operate and maintain it correctly during its entire life time.

Thus, GEP gives peace of mind to all lab personnel concerned about the proper performance of pH and conductivity systems and to responsibles for instrument qualification procedures.

For more detailed information and helpful tips, please refer to the GEP program.

▶ www.mt.com/GEP
6. METTLER TOLEDO Solutions

Customers can select any meter, electrode and accessory combination from the comprehensive METTLER TOLEDO offering. However, we have prepared several application-specific kits to guide customers through the options and propose proven combinations.

6.1 Excellence Performance Level

<table>
<thead>
<tr>
<th>Kit</th>
<th>Application</th>
<th>Parts [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S400-Kit</td>
<td>General pH application</td>
<td>SevenExcellence S400 meter, Expert Pro-ISM sensor</td>
</tr>
<tr>
<td>S400-Bio</td>
<td>pH in proteinaceous media, enzyme solutions, serums</td>
<td>SevenExcellence S400 meter, Expert Pro-ISM sensor</td>
</tr>
<tr>
<td>S400-Micro</td>
<td>pH measurement in small samples, down to 15 µL</td>
<td>SevenExcellence S400 meter, Expert Pro-ISM sensor</td>
</tr>
<tr>
<td>S8-Field kit</td>
<td>General pH application with portable meter</td>
<td>Seven2Go S8 meter, Expert Pro-ISM-IP67 sensor</td>
</tr>
<tr>
<td>S700-Kit</td>
<td>General conductivity application</td>
<td>SevenExcellence S700 meter, 731-ISM sensor</td>
</tr>
<tr>
<td>S700-Trace</td>
<td>Low and very low conductivity application</td>
<td>SevenExcellence S700 meter, Trace conductivity sensor, flow cell</td>
</tr>
<tr>
<td>S7-Field kit</td>
<td>General conductivity application with portable meter</td>
<td>Seven2Go S7 meter, 738-ISM sensor</td>
</tr>
<tr>
<td>S470-Kit</td>
<td>General pH and conductivity application (dual channels)</td>
<td>SevenExcellence S470 meter, Expert Pro-ISM pH and 731-ISM conductivity sensors</td>
</tr>
<tr>
<td>S470-USP/EP</td>
<td>Pure water pH and conductivity application according to pharmacopeias (dual channels)</td>
<td>SevenExcellence S470 meter, Pure Pro-ISM pH and 741-ISM conductivity sensors</td>
</tr>
</tbody>
</table>

[1] Parts can include: uPlace electrode holder, cover, LabX direct pH software, buffer sachets, guides or uGo carrying case

6.2 Routine Performance Level

<table>
<thead>
<tr>
<th>Kit</th>
<th>Application</th>
<th>Parts [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S220-Kit</td>
<td>General routine pH application</td>
<td>SevenCompact S220 meter, Expert Pro-ISM sensor</td>
</tr>
<tr>
<td>S220-Bio</td>
<td>pH in proteinaceous media, enzyme solutions, serums</td>
<td>SevenCompact S220 meter, Routine Pro-ISM sensor</td>
</tr>
<tr>
<td>S220-Micro</td>
<td>pH measurement in small samples, down to 15 µL</td>
<td>SevenCompact S220 meter, ultra micro sensor</td>
</tr>
<tr>
<td>S2-Field kit</td>
<td>General pH application with portable meter</td>
<td>Seven2Go S8 meter, Expert Pro-ISM-IP67 sensor</td>
</tr>
<tr>
<td>S230-Kit</td>
<td>General routine conductivity application</td>
<td>SevenCompact S230 meter, 731-ISM sensor</td>
</tr>
<tr>
<td>S230-USP/EP</td>
<td>Pure water conductivity application according to pharmacopeias</td>
<td>SevenCompact S230 meter, 741-ISM sensor</td>
</tr>
<tr>
<td>S3-Field kit</td>
<td>General routine conductivity application with portable meter</td>
<td>Seven2Go S3 meter, 738-ISM sensor</td>
</tr>
</tbody>
</table>

[1] Parts can include: uPlace electrode holder, cover, LabX direct pH software, buffer sachets, guides or uGo carrying case
### 6.3 Examples

<table>
<thead>
<tr>
<th></th>
<th>Benchtop meters</th>
<th>Portable meters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Professional</strong></td>
<td>SevenExcellence S470 meter</td>
<td>Seven2Go S8 pH and ion meter</td>
</tr>
<tr>
<td><strong>Performance Level</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Routine</strong></td>
<td>SevenCompact S220 pH/ion meter</td>
<td>Seven2Go S2 pH meter</td>
</tr>
<tr>
<td><strong>Performance Level</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 14: examples benchtop and portable meters for professional or performance level
7. Conclusion

We have presented characteristics and performance data of a comprehensive portfolio of pH and conductivity meters and sensors. Such data form the basis for thorough product evaluations to match needs of the users and requirements of the laboratory.

Meters and sensors for pH and conductivity and related solutions from METTLER TOLEDO empower you to perform these testing tasks with the confidence that your results will be accurate. Depending on your needs, different solutions can be applied:
• single or multichannel meters
• benchtop or portable meters
• generally applicable or highly specialized sensors
• several degrees of automation from purely manual to fully automated
• standard or excellence performance level

METTLER TOLEDO experts have contributed tips and hints for maintenance and care to this guide to advise you on best practices and ensure you get the most out of your instruments and equipment. It’s important to us that you achieve your target of correct, efficient and reliable sample testing.
8. More Information

8.1 Guides
Guide pour les mesures de pH, Mettler-Toledo AG, 51300185, (2013)
Anleitung zur Messung von pH, Mettler-Toledo AG, 51300058, (2013)

Guide des mesures de conductivité, Mettler-Toledo AG, 30099123, (2013)
Ein Leitfaden für Leitfähigkeitsmessungen, Mettler-Toledo AG, 30099122, (2013)
Guía para la medición de la conductividad, Mettler-Toledo AG, 30099124, (2013)

Selected Water Analysis Methods, Application Brochure 37, Mettler-Toledo AG, 51725072 (2007)

8.2 Webinars
We provide web-based seminars (webinars) on different topics. You can participate in on-demand webinars at any convenient time and place.
Live webinars offer the added benefit of allowing you to ask questions and discuss points of interest with METTLER TOLEDO specialists and other participants.
> www.mt.com/webinars
Good Measuring Practices
Five Steps to Improved Measuring Results

The five steps of all Good Measuring Practices guidelines start with an evaluation of the measuring needs of your processes and their associated risks. Using this information, Good Measuring Practices provide straightforward recommendations for selecting, installing, calibrating and operating laboratory equipment and devices.

- Preservation of the accuracy and precision of results
- Compliance with regulations, secure audits
- Increased productivity, reduced costs
- Professional qualification and training

Good Electrochemistry Practice™
Reliable pH measurements – thanks to GEP™
› www.mt.com/gep

Good Titration Practice™
Dependable titration in practice – reliable results with GTP™
› www.mt.com/gtp

Learn more about Good Measuring Practices program
› www.mt.com/gp

www.mt.com
For more information

Mettler-Toledo International Inc.
Laboratory Division
CH-8606 Greifensee, Switzerland
Tel +41 44 944 22 11

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