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ELECTROLYTIC CONDUCTIVITY MEASUREMENT Theory & Application

What is Conductivity

Conductivity (or Electrolytic Conductivity) is defined as the ability of a substance to conduct electrical current. It is the reciprocal of the resistivity.

In the chemical water treatment field our interest is in measuring the conductivity of waters which consist of ionic compounds dissolved in the water.

This conductivity is quite easily measured by electronic means and this offers a simple test or control level which can tell much about the quality of the water.

A broad line of conductivity equipment is now available to measure from ultrapure water (very low conductivity) to concentrated chemical streams (high conductivity).

Units of Conductivity

The basic unit of resistance is the ohm, - conductance is the reciprocal of resistance and its basic unit is the siemens, formerly called the mho.

In discussions of bulk material it is convenient to talk of its specific conductance, or more commonly called its conductivity.

Conductivity is the conductance as measured between the opposite faces of a 1- cm cube of the material. This measurement has units of Siemens/cm. More common in water treatment the units $\mu\text{S}/\text{cm}$ (microsiemens) and mS/cm (millisiemens) are used as they are more meaningful.

The corresponding terms for specific resistance (or resistivity) is ohm-cm, megohm-cm and kilohm-cm. Ultrapure water users normally prefer to use resistivity units of Megohm-cm as this spreads the scale out in their area of interest, and use kilohm-cm when dealing with less pure water such as tap water.

Most of us tend to use the units $\mu\text{S}/\text{cm}$ and mS/cm when dealing with quite pure water to concentrated chemical solutions. The use of conductivity in these applications has the advantage of an almost direct relationship with impurities especially at low ionic concentrations such as boiler and cooling water applications. Thus an increasing conductivity reading shows increasing impurities, and control levels can be set to control the maximum level of impurities.

Conductivities of Waters @ 25 °C

	Conductivity	Resistivity
Absolute Pure Water	0.055 $\mu\text{S}/\text{cm}$	18.3 Megohm/cm
Distilled Water	0.5 $\mu\text{S}/\text{cm}$	2.0 Megohm/cm
Demineralised Water	5 $\mu\text{S}/\text{cm}$	200 Kilohm/cm
Electricity Gen. Boiler Condensate	5 - 75 $\mu\text{S}/\text{cm}$	Rarely Used
Cairns Water Supply	40 $\mu\text{S}/\text{cm}$	"
Brisbane (Wivenhoe)	450 $\mu\text{S}/\text{cm}$	"
Oakey (Qld) Supply	1500 $\mu\text{S}/\text{cm}$	"
Cooling Towers	500 - 3000 $\mu\text{S}/\text{cm}$	"
Ind. Boilers	2500 - 5000 $\mu\text{S}/\text{cm}$	"

Conductivities of 1000 ppm Solutions

Compound	$\mu\text{S}/\text{cm}$ @ 25 °C	$\mu\text{S}/\text{ppm}$
Sodium Bicarbonate	870	0.87
Sodium Sulphate	1300	1.30
Sodium Chloride	1990	1.99
Sodium Carbonate	1600	1.60
Sodium Hydroxide	5820	5.82
Ammonium Hydroxide	189	0.19
Hydrochloric Acid	11000	11.10
Hydrofluoric Acid	2420	2.42
Nitric Acid	6380	6.38
Phosphoric Acid	2250	2.25
Sulphuric Acid	6350	6.35

Conductivities of Major Water Supplies

	$\mu\text{S}/\text{cm}$ @ 25 °C	
	Minimum	Maximum
Adelaide	400	600
Alice Springs	300	450
Brisbane	200	500
Canberra	40	60
Cairns	30	40
Darwin	80	120
Hobart	80	120
Melbourne	50	120
Newcastle	80	200
Perth	300	600
Sydney	125	175
Townsville	100	200

TECHNOLOGY FOR THE YEAR 2001 AND BEYOND

Applications for Conductivity

Conductivity is extensively used in the measurement of water supplies for municipal, commercial, hospital and industrial uses. Whilst individual ions cannot be differentiated this is usually not needed and conductivity gives a measure of the total impurities present.

Some "rules of thumb" which are in wide use are as follows:-

Conductivity in $\mu\text{S}/\text{cm} \times 0.5 = \text{T.D.S. ppm as NaCl.}$

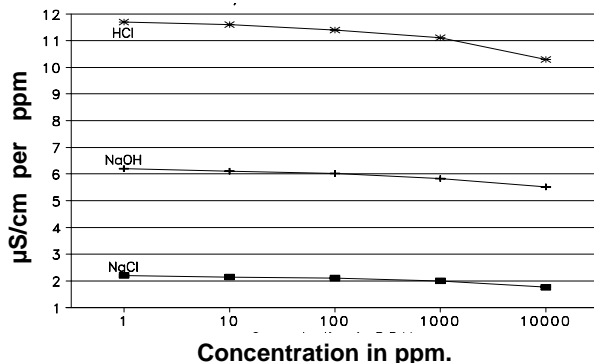
Conductivity in $\mu\text{S}/\text{cm} \times 0.75 = \text{T.D.S. ppm as such.}$

The major drawback of conductivity measurements is that they are non specific, they cannot distinguish between different types of ions, giving instead a reading that is proportional to the combined effect of all the ions present, and some ions such as NaOH, HCl and others contribute far more than others.

Refer to "Conductivities of 1000 ppm Solutions" on previous page

Another minor drawback in referring conductivity to concentration is that concentrated solutions show a slightly lower $\mu\text{S}/\text{cm}$ for each ppm than do dilute solutions as shown by the following graph. This effect is due to the decrease in ionic velocity with increasing concentration and is the basis of the **Interionic Attraction Theory**

Conductivity versus Concentration @ 25°C



Some of the compounds may also reduce the accuracy by coating the sensor or probe, e.g. Calcium Carbonate and Silica scales. In most cases these difficulties are not serious, or can be circumvented and a quite accurate reading of the desired components can be obtained. In general conductivity offers a fast, reliable, in-line, non destructive, inexpensive, and durable means of measuring the ionic content of a sample stream. Typically repeatability is about 1% of the upper range value.

Temperature increases ionic mobility and the conductivity and data is usually referenced to 25 °C

See information later on temperature and automatic temperature compensation.

Both conductivity test meters and controllers are very widely used in a broad spectrum of areas.

Industries using Conductivity

Agriculture	Air Conditioning
Brewing	Beverage
Chemical	Electroplating
Food Processing	Hospitals
Iron & Steel	Marine
Mining	Paper
Petroleum	Semiconductor

Conductivity Applications

Aquaculture	Boiler Blowdown
Cooling Towers	Condensate Return
Demineralisers	Desalination
Effluent Control	Fruit Peeling
Laboratory Analysis	Level Detection
Oceanography	Reverse Osmosis
Rinse Tanks	Waste Streams

Effect of Temperature

Conductivity in aqueous solutions is by means of ionic motion and invariably increases with increasing temperature, opposite to metals but similar to graphite. It is affected by the nature of the ions, and by the viscosity of the water. In low ionic concentrations (very pure water) the ionization of the water provides a appreciable part of the conducting ions.

All these processes are quite temperature dependant and thus conductivity has a substantial dependence on temperature. This dependence is usually expressed as a relative change per degree C. at a particular temperature, commonly as **percent per degree C.**, called the slope of the particular solution.

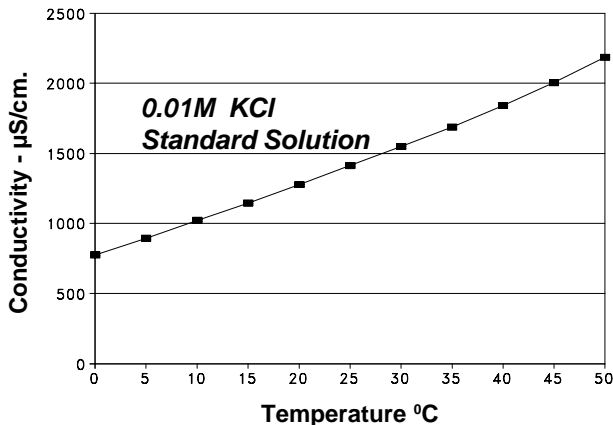
Ultrapure water has the largest slope at 5.2% per degree C., whilst **most water supplies and cooling systems are in the 1.8 - 2.0% per degree C. range.** Concentrated salt solutions, acids and alkali solutions have slopes of about 1.5% per degree C.

It is now obvious that a small difference in temperature makes a considerable difference in conductivity, and for this reason conductivity readings are normally referenced to 25 °C.

Fortunately temperature sensors are available which have characteristics similar to those of the solutions we are interested in, and with the use of additional resistors and electronic circuitry, the temperature - conductance curves can be shaped to match closely virtually any solution. The temperature sensor is used as a gain control element in the circuitry and the conductivity value is brought to its equivalent value at 25 °C. automatically by the circuitry.

A very modern technique uses a microprocessor and an associated "look up" table which contains the temperature response of the solution. The solution temperature is measured and converted to digital form, from this information and data in the "look up" table a very accurate temperature compensation can be derived. All temperature sensors have a time lag dependant on the position and the mounting of the sensor.

Temperature versus Conductivity



Cell Constant or Cell Factor

A very simple conductivity sensor can be constructed as a cell consisting of a cube 1 cm on a side, where the electrodes form the two opposite ends having an area of 1 cm and distance between as 1 cm. This cell has a cell constant of 1.0 which can be calculated for other cells from the formula:-

Resistivity cell constant = distance between electrodes divided by the electrode area.

For very dilute solutions the electrodes can be placed closer together so that the distance is reduced and cell constants of 0.1 and 0.01 result. This has the effect of raising the conductance as read by the electrodes and produce a value more easily handled by the electronic circuitry

For more conductive solutions the distance between the electrodes is increased so that cell factors of 10 or more result.

Aquarius Technologies sensors (used in controllers) with their respective housing use graphite as the electrodes. Graphite has a similar temperature coefficient to conductance, and is less affected by polarisation that common metals such as stainless or nickel, and less expensive than platinum which is commonly used in laboratory sensors.

The common Aquarius Technologies sensors have cell constants in the 3 - 5.0 range and are suited to the range of 50 - 10,000 µS/cm. Thermistors having similar temperature characteristics to the conductivity being measured are embedded in the epoxy mold of the electrode to provide for accurate temperature compensation or ATC.

Polarisation

Polarisation can cause formation of gas at metallic surfaces even though high frequency AC is used in measurement, the effect can take place in the half cycle of one polarity. Another reason is a depletion of anions or cations around the electrode due to the charge build up. Polarisation is an insidious effect in that conductivity readings can be lower than the true

value but by an unknown amount and a reading is obtained from the instrument with no indication that it is incorrect. Similar effects are noted if grease or oil are present in the solution, or if the electrodes are fouled or scaled in any way. Polarisation can be reduced by using high frequency AC, keeping the current density low by the correct choice of cell constant and by making surfaces rough such as graphite, and by operating in conductivities of less than 30,000 µS/cm, and in the case of fouling, by removal of the sensor and cleaning frequently.

Conductivity Standard Solutions

The standards against which conductivity is measured are solutions of potassium chloride (KCl) which are measured to very high accuracy per ASTM Standard D1125-77.

Approx. Normality	µS/cm. @ 25 °C
0.001	146.93
0.01	1408.8
0.1	12,856
1.0	111,342

A precisely weighted amount of thoroughly dry KCl is specified to be dissolved in an exact volume in a volumetric flask. The normalities of the resulting solution are close to, but not the same as the values shown, due to traces of conductivity in the distilled water used. e.g. 0.01N KCl is normally taken as 1413 µS/cm @ 25 °C

Sensor Considerations

The choice of correct sensor materials, cell constant and method of mounting, so that the sensor has a good sample of solution are the most important considerations in a conductivity control system.

The following should be considered:-

- (a) The proper cell constant
- (b) Adequate range on the controller and
- (c) The correct choice of materials for the environment.

Under proper sensor mounting the following should be observed:-

1. The sensor should be installed with its Tee or its housing as supplied (to which it was calibrated)
2. The solution at the sensor is representative of the solution as a whole.
3. A moderate flow is maintained past the sensor to provide an up-to-date solution sample. Excessive flow rates, however can cause cavitation, resulting in low readings, and damage to the sensor.
4. The sensor should be mounted in a carefully designed manifold incorporating all of the above features, and where it is easy to remove the sensor for periodic cleaning and calibration.

Conversion Factors

1.0 Siemens/cm. = 1000 millisiemens/cm.
1.0 millisiemen/cm = 1000 microsiemens/cm.

T.D.S. expressed as ppm.

Note that all meters supposedly measuring T.D.S. are actually measuring conductivity and using a conversion factor to give a reading as ppm. T.D.S.

This reading is at best an approximation as different waters have different ionic concentrations, and that even conductivity per ppm. reduces slightly with increasing concentration.

Accurate T.D.S. can only be measured by carefully evaporating a measured sample of the water to dryness, under strict laboratory conditions, and carefully weighing the amount of dry solids remaining.

Note that boiler waters require to be neutralised to approx. pH 7.00 when estimating the T.D.S. as ppm. (NaOH alkalinity has approx. 6 times the conductivity of the other corresponding salts)

With condensate some of the conductivity measured may well be from dissolved gases e.g. carbon dioxide or ammonia, as well as a trace of mineral salts from carry over, Boiling a sample of condensate for 5-10 mins. in the laboratory will remove these dissolved gases and allow T.D.S. from the "carry over" to be estimated.

Acknowledgements

1. Elements of Physical Chemistry - Macmillan
2. Hanna Instruments Information
3. Myron L Company Information
4. Foxboro Technical Information.
5. Chemical Treatment of Boiler Waters
6. Aquarius Technologies Pty. Ltd.

