Electrolytic (Contacting) Conductivity Measurement

Introduction

All solutions containing water conduct electricity to some extent. The measure of the ability of a solution to conduct electricity is called "conductance" (the reciprocal of resistance). Addition of electrolytes such as salts, acids or bases to pure water will increase the ability of the liquid to conduct electricity. This increases the solution's conductance (decreases the resistance).

An electrolytic conductivity measuring system measures solution conductance by using an analyzer interconnected with cable to a sensor immersed in the solution. The conductivity sensor is composed of a temperature sensor and two electrodes in contact with the solution. The analyzer circuitry impresses an alternating voltage between the two electrodes and the magnitude of the resulting current is linearly related to the solution conductivity.

When the temperature of a solution changes, its conductivity changes. Typically, a temperature change is compensated with a thermistor (temperature sensitive resistor) in the conductivity sensor to alter the gain of the measuring circuit. Regardless of the actual solution temperature, the display indicates what the solution conductivity would be if the solution temperature were 25°C (an internationally accepted reference). This temperature compensation may be achieved automatically or manually.

All solutions do not have the same amount of conductivity change for a given temperature change. For example, the change for hydrochloric acid is 1.5% per °C, and the change for sodium chloride is 2.1% per °C. The ratio of solution conductivity change to temperature change is referred to as the temperature compensation slope and is expressed as % per °C.

Electron Ion Transfer

When a voltage is applied between the electrodes of an electrolytic conductivity sensor, electrons are transferred and gases released. This electron transfer carries electrical current from one electrode to the other. As gases are released, they build upon the electrode. This build-up impairs the electrode's contact with the solution and creates a back EMF (electromotive force). This effect is known as

"polarization" which can be avoided by impressing a low, alternating current (AC) voltage on the electrodes rather than a direct current (DC) voltage. The duration of the AC cycle is too short and the voltage is too low to cause an electrode build-up of gases.

Conductivity Units of Measurement

Historically, the standard unit of conductivity measurement has been "mhos/cm" (mho is reciprocal of ohm). A resistivity of 100 ohms l cm is equivalent to a conductivity of l/l00 mhos/cm. The mhos/cm unit of measurement has been replaced throughout industry by an equal and interchangeable unit of measurement called the "Siemen/cm." Conductivity is usually expressed in microSiemens/cm (millionths of a Siemen) so that whole numbers can be used. A conductive solution with a resistivity of 100 ohms ● cm has a conductivity of 10,000 microSiemens/cm. [l/l00 (reciprocal of ohm) x 1,000,000 (multiplier to convert Siemens to microSiemens)].

MilliSiemen is occasionally used to represent l/l000 of a Siemen. To convert milliSiemens to microSiemens, multiply by 1000. (Example: 0.5 milliSiemens = 500 microSiemens.) MicroSiemens is abbreviated as µS; milliSiemens as mS. Since these terms and their abbreviations are similar, take care to avoid confusion.

For a given solution conductivity, microSiemens can be related to ppm (parts per million), which is a measure of concentration. Generally, microSiemens = 1.5 x TDS (total dissolved solids) ppm. Depending on solution concentration and composition, the 1.5 factor may change. If TDS in a solution is expressed in terms of sodium chloride, the microSiemen value is approximately twice the TDS NaCl ppm value. The table below illustrates this relationship.

TDS ppm	µS/cm	TDS NaCl ppm	TDS ppm	µS/cm	TDS NaCl ppm
10,000	15,000	8,400	500	750	365
6,660	10,000	5,500	400	600	285
5,000	7,500	4,000	250	375	175
4,000	6,000	3,200	100	150	71
3,000	4,500	2,350	66	100	47
2,000	3,000	1,550	50	75	35
1,000	1,500	750	40	60	28
750	1,125	560	25	37.5	17.5
666	1,000	490	6.6	10	4.7

Conductivity Sensor Design

A conductivity sensor generally consists of two electrodes that are insulated from each other. Electrode materials are typically 316 stainless steel, titanium-palladium alloy or carbon. Theoretically, any conductive material may be used if it will not dissolve in the solution. In practice, however, this does not always apply. Unexpected results may occur when current is impressed between the two electrodes. The magnitude of the voltage and current may have an effect on electrode life and measurement accuracy. No electrode material exists that suits all applications.

Electrodes are specifically sized and spaced at an exact distance apart to provide a known "cell constant." Theoretically, a cell constant of 1.0 has two electrodes, each one square centimeter in area, spaced one centimeter apart. The volume between these electrodes is one cubic centimeter. Figure 1 illustrates this relationship.
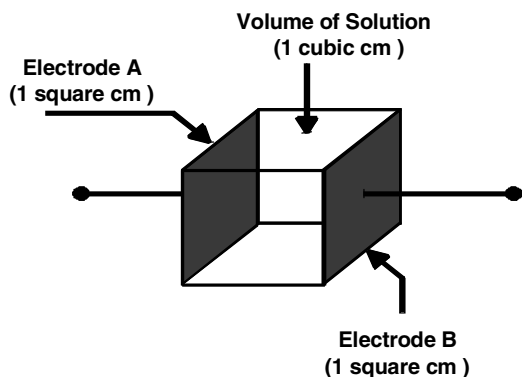

FIGURE 1
Theoretical Dimensions of 1.0 Cell Constant

Since the volume of measured solution is the area of the electrode times the distance between the two electrodes, the mathematical relationship does not change if one dimension increases and the other decreases proportionally. Theoretically, this is an accurate statement. However, variations and tolerances in electrode spacing and area may cause the volume to vary slightly.

Cell constants must be matched to the analyzer for a given range of operation. For example, if a conductivity sensor with a cell constant of 1.0 were used to measure pure water that has a conductivity of 1 microSiemen/cm, the cell would have a resistance of 1,000,000 ohms. Conversely, the same cell in seawater may have a resistance of 30 ohms. Because the resistances are so different, it is difficult for analyzers to accurately measure these extremes with only one cell constant.

In measuring the 1 microSiemen/cm solution, the cell would be configured with large electrodes spaced a small distance apart. This allows the cell to have a resistance of approximately 10,000 ohms, which can be measured quite accurately. By using sensors with different cell constants, it is possible for the measuring instrument to operate over the same range of cell resistance for both ultra pure water and high conductivity seawater.

Temperature-compensated Conductivity Measurements

Conductivity measuring system accuracy can only be as good as its temperature compensation. Since common solution coefficients are 2-3% per °C, proper care must be taken in the design and manufacture of measuring instruments with automatic temperature compensation. Similarly, the operator must take precise temperature measurements when setting instruments with manual temperature compensation to provide best measuring accuracy. Solution temperature coefficients are somewhat non-linear and usually vary with actual conductivity as well. Calibration at the actual measuring temperature will usually yield the best accuracy.

Most conductivity analyzers have manual temperature compensation capability. The operator should set the manual temperature compensation to the known solution temperature at the time the conductivity measurement is taken. Manual temperature compensation is usually suitable for applications where little temperature variation exists. However, automatic temperature compensation is preferred because after the instrument is operating it will not be susceptible to incorrect settings due to negligence or poor operating practice.