

Orion Conductivity Theory

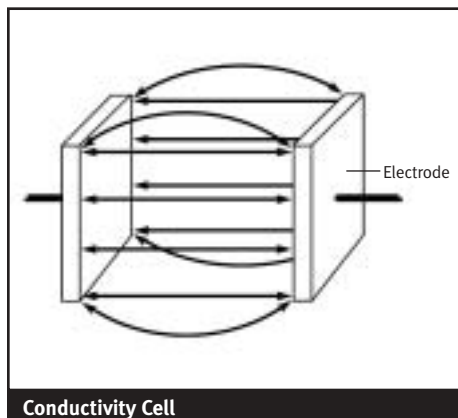
Background

Electrical conductivity is an inherent property of most materials, and ranges from extremely conductive materials like metals to very non-conductive materials like plastics or glass. About halfway between the two extremes in conductivity are aqueous solutions, such as sea water and plating baths. In metals, the electrical current is carried by electrons, while in water it is carried by charged ions. In both cases, the conductivity is determined by the number of charge carriers, how fast they move, and how much charge each one carries. Thus, for most water solutions, the higher the concentration of dissolved salts, which will lead to more ions, the higher the conductivity. This effect continues until the solution gets “too crowded,” restricting the freedom of the ions to move, and the conductivity may actually decrease with increasing concentration. This can result in two different concentrations of a salt having the same conductivity. See Table 1. Some species ionize more completely in water than others do, and their solutions are more conductive as a result. Each acid, base, or salt has its own characteristic curve for concentration vs. conductivity. Metals are extremely conductive because electrons move almost with the speed of light; while in water, ions move much slower and the conductivity is much lower. Raising the temperature makes water less viscous, and the ions can move faster. Because the ions are of different sizes, and carry different amounts of water with them as they move, the temperature effect is different for each ion. Typically, the conductivity varies about 1–3% per degree C, and this temperature coefficient may itself vary with concentration and temperature. See Tables 1 and 2.

Definitions

The conductivity of a material is an inherent property—that is, pure water at a particular temperature will always have the same conductivity. The conductance of a sample of pure water depends on how the measurement is made—how big a sample, how far apart the measuring electrodes are, etc. It is defined as the reciprocal of the resistance in ohms, measured between the opposing faces of a 1 cm cube of liquid at a specific temperature. See Conductivity Cell Figure. The basic unit of conductance is the Siemens (S) and was formerly called the mho. Because a measurement gives the conductance, techniques have been worked out to convert the measured value to the conductivity, so that results can be compared from different experiments. This is done by measuring a cell constant (K) for each setup, using a solution of known conductivity.

$$\text{Cell Conductance} \times \text{Cell Constant (K)} = \text{Conductivity} \quad (\text{Equation 1})$$



The cell constant is related to the physical characteristics of the measuring cell. K is defined for two flat, parallel measuring electrodes as the electrode separation distance (d) divided by the electrode area (A). Thus, for a 1 cm cube of liquid,

$$K = d/A = 1 \text{ cm}^{-1} \quad (\text{Equation 2})$$

In practice, the measured cell value is entered into the meter, and the conversion from conductance to conductivity is done automatically. The K value used varies with the linear measuring range of the cell selected. Typically, a cell with $K = 0.1 \text{ cm}^{-1}$ is chosen for pure water measurements, while for environmental water and industrial solutions a cell with K of 0.4 to 1 cm^{-1} is used. Cells with up to $K = 10 \text{ cm}^{-1}$ are best for very high conductivity samples. For some solutions, such as pure water, the conductivity numbers are so low that some users prefer to use resistivity and resistance instead. The resistivity is the reciprocal of the conductivity ($R = 1/C$), and the resistance is the reciprocal of the conductance. Resistance units are in ohms, and $1 \text{ ohm} = 1/\text{Siemens}$. From Eq. 1 and 2, it can be seen that conductivity units are in Siemens/cm, and therefore resistivity units are in $\text{ohm}\text{-cm}$. The resistivity of ultrapure water is 18 megaohm-cm.

How is conductivity measured?

In the simplest arrangement (a 2-electrode cell), a voltage is applied to two flat plates immersed in the solution, and the resulting current is measured. See Conductivity Cell Figure. From Ohm's Law, the conductance = current/voltage. Actually there are many practical difficulties. Solution conductivity is due to ion mobility. Use of DC voltage would soon deplete the ions near the plates, causing polarization, and a higher than actual resistance. This can be mostly overcome by using AC voltage, but then the instrument designer must correct for various capacitance and other effects. Modern sophisticated 2-electrode conductivity instruments use complex AC waveforms to minimize these effects, and by using the cell constant, measured temperature, temperature coefficient and reference temperature, will report sample conductivity.

Table 1

Sample at 25 °C	Conductivity, $\mu\text{S/cm}$
Ultrapure Water	0.055
Power Plant Boiler Water	1.0
Drinking Water	50
Ocean Water	53,000
5% NaOH	223,000
50% NaOH	150,000
10% HCl	700,000
32% HCl	700,000
31.0% HNO ₃ (Highest Known)	865,000

Some Conductivity Values of Typical Samples

Table 2

Sample	Percent/°C (at 25 °C)
Ultrapure Water	4.55
Salt solution (NaCl)	2.12
5% NaOH	1.72
Dilute Ammonia Solution	1.88
10% HCl	1.32
5% Sulfuric Acid	0.96
98% Sulfuric Acid	2.84
Sugar Syrup	5.64

Some Typical Temperature Coefficients

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4-Electrode Cell Theory and Practical Advantages

The approaches discussed earlier cannot correct for deposits which form on the surface of the electrodes, and which subtract from the measured conductivity of the sample. A more sophisticated approach uses the 4-electrode technique. The operational theory is discussed below. Not only is the 4-electrode technique superior in terms of ability to function in "dirty" solutions, but one cell with a single cell constant can cover almost the entire seven decade range (except for pure water) of three ordinary 2-electrode cells. A number of technical advancements allow this.

4-Electrode Cell Measurement Theory

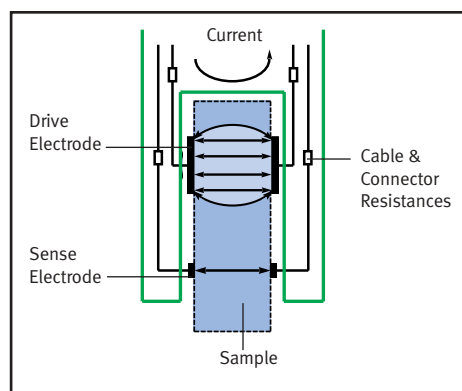
4-electrode conductivity measurements offer the user significant advantages, particularly in high conductivity solutions. These advantages include minimizing the effect on measurement accuracy from electrode polarization and contamination, as well as eliminating error from cable resistance and connector resistance. 4-electrode conductivity cells contain two drive (current) electrodes and two sense (voltage) electrodes. See 4-Electrode Cell Schematic. The drive electrodes are powered by an alternating voltage, and the alternating current that flows is measured to determine the conductivity. The amplitude of the alternating voltage applied to the drive electrodes is controlled by the voltage measured at the sense electrodes. Since the sense electrodes are positioned in a low current area of the cell, and this voltage is measured using a high impedance circuit, it represents with high accuracy the strength of the electric field within the cell. Using this signal to maintain the cell field strength at a constant, the current that flows at the drive electrodes is proportional to the conductivity of the sample, and the errors due to polarization, contamination and cable resistances are minimal.

Polarization Errors

Polarization errors occur in the case of 2-electrode cells at the boundary layers between the measuring electrode and the ion conducting measuring medium. These effects can be compensated for with the 4-electrode system, and do not contribute an error.

Contamination of Electrode Surfaces

Deposits on the electrode surface of a 2-electrode cell have a similar effect to polarization errors, that is the conductivity reading is lower than actual. These effects are also compensated with the 4-electrode system. Conductive deposits will have no effect on the accuracy of the cell, and errors due to insulating deposits have been shown to be three times lower than comparable 2-electrode cells.



4-Electrode Cell Schematic

Cable Resistance

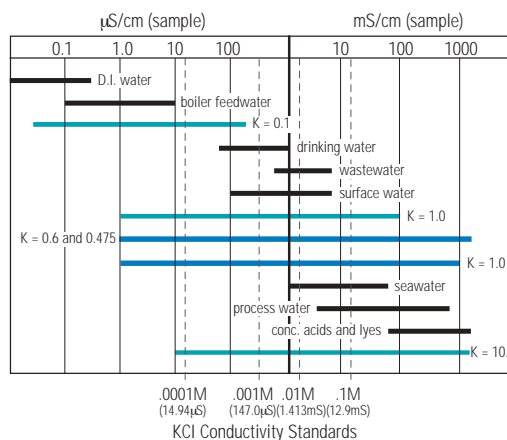
Cable resistances add to the measured sample conductance in the case of a 2-electrode cell. This resistance is compensated for with the 4-electrode cell, and no error occurs. This is of particular importance in environmental work, where measurement in wells and boreholes may require cable lengths of up to 100 meters.

Geometry Related Errors—Fringe Field Effects

Errors are also caused by fringe field effects. See 4-Electrode Cell Schematic. This is the part of the measuring field that "bulges" outside the theoretical 1 cm cube described previously. This error can be calibrated out of the measurement, but can subsequently affect the measurement if anything interferes with the field, such as the side of the measuring vessel. Advanced conductivity cells are designed to minimize this effect. If the entire measuring field is contained within the body of the electrode, then fringe field errors cannot be caused by the side of the sample vessel.

Durability

Cell materials should be chosen to fit the needs of the application. For field and demanding laboratory applications, many users choose a cell constructed with an epoxy body and carbon measuring electrodes, as this has been shown to be extremely durable and chemically resistant. For especially demanding applications, some manufacturers supply probe guards, which can be attached to the probe for additional protection. For pure water applications such as USP injectable water testing, stainless steel is the material of choice. It is very durable, can be manufactured to precise tolerances, and for low conductivity, low contact resistances are not required. For chemically reactive samples, glass and platinum are frequently the optimum choice, as they have the best overall chemical resistance of all commonly used cell materials.



Legend

- Conventional 2-Electrode Cells
- DuraProbe 4-Electrode Cells

Chart represents general guidelines for choosing a cell for your application. Performance characteristics of some cells may vary. See individual cell specifications, or call Technical Service at 800.225.1480.