Measurement of Conductivity

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Theory of Operation

The term conductance refers to the readiness of materials to carry an electric current. Liquids which carry an electric current are generally referred to as electrolytic conductors. The flow of current through electrolytic conductors is accomplished by the movement of electric charges (positive and negative ions) when the liquid is under the influence of an electrical field. The conductance of a liquid can be defined by its electrical properties — the ratio of current to voltage between any two points within the liquid. As the two points move closer together or further apart, this value changes. To have useful meaning for analytical purposes, a dimension needs to be given to the measurement; i.e., the physical parameters of the measurement.

By defining the physical parameters of the measurement, a standard measure is created. This standard measure is referred to as specific conductance or conductivity. It is defined as the reciprocal of the resistance in ohms, measured between the opposing faces of 1 cm cube of liquid at a specific temperature. The units used to define conductance are: 1/ohm = 1 mho = 1000 mS = 1,000,000 µS. S.I. units may be used in place of mhos; 1 mho = 1 Siemen (S). Conductivity units are expressed as uS/cm (1.0 *dS/m = 1.0 µS/cm*) or mS/cm.

Design of the Conductivity Cell

In theory, a conductivity measuring cell is formed by two 1 cm square surfaces spaced 1 cm apart. Cells of different physical configuration are characterized by their cell constant, K. This cell constant (K) is a function of the electrode areas, the distance between the electrodes and the electrical field pattern between the electrodes. The theoretical cell just described has a cell constant of K = 1.0. Often, for considerations having to do with sample volume or space, a cell's physical configuration is designed differently. Cells with constants of 1.0 cm-1 or greater normally have small, widely spaced electrodes. Cells with constants of K = 0.1 or less normally have large closely spaced electrodes. Since K (cell constant) is a "factor" which reflects a particular cell's physical configuration, it must be multiplied by the observed conductance to obtain the actual conductivity reading. For example, for an observed conductance reading of 200 µS using a cell with K = 0.1, the conductivity value is 200 x 0.1 = 20 µS/cm.

In a simplified approach, the cell constant is defined as the ratio of the distance between the electrodes, d, to the electrode area, A. This however neglects the existence of a fringe-field effect, which affects the electrode area by the amount AR. Therefore $K = d/(A + AR)$. Because it is normally impossible to measure the fringe-field effect and the amount of AR to calculate the cell constant, K, the actual K of a specific cell is determined by a comparison measurement of a standard solution of known electrolytic conductivity. The most commonly used standard solution for calibration is 0.01 M KCl. This solution has a conductivity of 1412 µS/cm at 25 °C. *(Note: Some sources in literature quote this value at 1409 or 1413 µS/cm at 25 °C. Differences exist due to the use of kilogram of water rather than liters, as well as changes in assigned molecular weights, definitions of the Siemen, the use of different temperature scales, and whether or not the inherent conductivity of water was subtracted out. Regardless, for normal laboratory calibration the use of 1409 µS/cm versus 1413 µS/cm is insignificant.)*

In summary, the calibration of a conductivity probe is to compensate for the fact that the K is not specifically known and changes as the electrode ages. Calibration simply adjusts the measured reading to the true value at a specified temperature.

The Affect of Temperature

The conductivity of a solution with a specific electrolyte concentration will change with a change in temperature. By definition, temperature compensated conductivity of a solution is the conductivity which that solution exhibits at the reference temperature. This temperature is chosen to be either 25 °C or 20 °C. A measurement made at reference temperature, therefore, needs no compensation. Generally for most aqueous samples, a coefficient of 2.1% per degree Celcius is used in temperature compensation, with the apparent value being 2.1% high for each degree C above 25 °C; or conversely the apparent value being 2.1% low for each degree °C below 25 °C. For soil and irrigation water analysis, the standard temperature for measurement is 25 °C. A useful algorithm for temperature correction is:

$$C_T = C_{25} [1 + 0.021 (T - 25)]$$

Where C_T = the measured conductivity of a solution at sample temperature; C_{25} = the conductivity of the solution at 25 °C; and T = the sample temperature (°C).

Many conductivity meters today automatically compensates for temperature if the conductivity probe includes a thermistor. However, as will be explained later, this can be a major source of error in analysis if the thermistor is not accurate or if the instrument is improperly calibrated.

Note the two following examples to explain the effect and compensation of the fringe-field effect and temperature.

Example #1 - Manual Temperature Compensation: An analyst wishes to calibrate a conductivity probe and measure an unknown sample. The conductivity probe is specified to have a cell constant of 1.0. The analyst is calibrating in a 0.01 M KCl (EC = 1412 µS/cm at 25 °C) solution at a temperature of 22 °C. Automatic temperature compensation (ATC) is not available.

1. Determine the conductivity of the 0.01 M KCl at 22 °C.

    EC KCl 22 °C = 1412[1 + 0.021(22-25)]
    EC KCl 22 °C = 1412 [0.937]
    EC KCl 22 °C = 1323 µS/cm

2. Immerse the conductivity probe into the standard and adjust the value to 1323 µS/cm. Any adjustment being made is compensating for the difference between the specified cell constants and the true cell constant.

3. The analyst now measures an unknown sample whose temperature is at 19 °C and obtains an apparent value of 967 µS/cm. How is this value adjusted to 25 °C?

    967 µS/cm = C_{25} [1 + 0.021(19-25)]

    C_{25} =   967 µS / [1 + 0.021(19-25)]

    C_{25} =   967 µS / [1 + 0.021(-6)]

    C_{25} =   967 µS / 0.874

    C_{25} =   1106 µS/cm

Example #2 - Automatic Temperature Compensation: An analyst wishes to calibrate the conductivity probe and measure a sample. The conductivity probe is specified to have a cell constant of 1.0. The analyst is calibrating in a 0.01 M KCl (EC = 1412 µS/cm at 25 °C) solution at a temperature of 22 °C. Automatic temperature compensation (ATC) at 25 °C is available.

> 1. Immerse the conductivity probe into the standard and adjust the value to 1412 µS/cm. Any adjustment being made is compensating for the difference between the specified cell constants and the true cell constant. NOTE: On most modern instrumentation, the true temperature is displayed along with the temperature compensated conductivity value. In this case the display would show a conductivity of 1412 µS/cm and of 22 °C.

> 2. Once the electrode has been calibrated, it is cleaned, placed into the unknown sample at 19 °C. Once temperature is stable, the correct conductivity value (1106) µS is displayed.

Sources of Error in Measurement

Temperature Compensation

Since many conductivity probes now include a thermistor for ATC it is important to determine if the thermistor reading is accurate at the temperatures that samples are being measured. If not, then the automatic temperature corrected value will be inaccurate. Compare the measured value from the thermistor with that of a quality laboratory thermometer. If the values differ significantly, contact the manufacturer as to the defect or consider manual temperature compensation.

Improper Calibration

Too often, calibration standards have been sitting around a laboratory for extended periods. Standards should be fresh and known to be correct within at least ± 1% before attempting a calibration. Since the conductometric response is not perfectly linear at all ranges it is best to calibrate the probe in the same magnitude of range as the samples being measured. In other words don't calibrate your conductivity probe in a 100 µS/cm standard if your samples are typically in the >1000 µS/cm range. Standard conductivity solutions:

KCl Concentration	Conductivity uS/cm [1]
0.001 N	0.147
0.010 N	1.413
0.020 N	2.767
0.050 N	6.668

[1] Temperature KCL Solutions 25 ºC

Condition of Probe

Probes can become inaccurate when they become coated with interfering substances on the probe element. During normal use, rinse the probe thoroughly with laboratory grade water between each measurement. This will help to minimize the buildup of the coating substances. If the probe needs cleaning first try ethanol which is good for removing most organics. If this isn't successful, clean the probe with a strong detergent solution. Rinse thoroughly with demineralized water.

The cells may occasionally need replatinization to refresh the cell plates and return them back to the original cell constant. The cell constant changes when the platinum black layer becomes partially removed or contaminated. Follow the manufacturer's directions on this procedure.