Stage 4

G-03: CONDUCTIVITY OF SOLUTIONS

CP: USP

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INTRODUCTION

This chapter provides information on how to apply electrical conductivity measurements (hereafter referred to as “conductivity”) of fluid solutions, including pure fluids. ♦This chapter does not replace the official Water Conductivity <645> procedure, which is used to ensure the ionic purity of compendial waters such as Water for Injection, Purified Water, Pure Steam condensate, and Sterile Water for Injection, among others. ♦ This chapter is intended for other fluid applications when conductivity is used to measure, monitor, or control chemical dispensing, chemical purity, ionic concentration, and other applications where the ionic character of the fluid needs to be known or controlled.

Applications include, but are not limited to, solutions that may be used in clean-in-place, chromatography detection, ionic solution preparations, end point detection, dosing, fermentation, and buffer production. In some cases, conductivity measurements can be extended to pure organic fluids such as alcohols and glycols where a weak conductivity signal exists, and the signal can be significantly increased if the organics become contaminated with water or salts. ♦ [NOTE – For additional background information, see Theory and Practice of Electrical Conductivity

Measurements of Solutions <1644>.]♦

Conductivity is the measurement of the ability of a fluid to conduct electricity via its chemical ions. The ability of any ion to electrically conduct is directly related to its ion mobility. Conductivity is directly proportional to the concentrations of ions in the fluid, according to *Equation 1*:

$$\kappa = 1000 \sum_{i}^{all\ ions} C_i \lambda_i \qquad (1)$$

κ = conductivity (S/cm)

C_i = the concentration of chemical ion i (mol/L)

λ_i = the specific molar conductance of ion i ($S \cdot cm^2/mol$)

Although S/m is the appropriate SI unit for conductivity, historically the unit S/cm has been selected by industry as the accepted unit.

Based on Equation 1, conductivity is not ion-selective because it responds to all ions. Furthermore, the specific molar conductance of each ion is different. As a result, unless the percentage composition of ions of the solution is limited and known, the precise concentrations of ionic species cannot be determined from conductivity measurements. However, for examples such as a solution of a single salt or acid or base, such as a caustic solution used in cleaning, the precise concentration can be directly determined. Despite the lack of ionic specificity, conductivity is a valuable laboratory and process tool for measurement and control of total ionic content because it is proportional to the sum of the concentrations of all ionic species (anions and cations) as described in *Equation 1*. Conductivity measurements cannot be applied to solids or gases, but they can be applied to the condensate of gases.

Another variable that influences conductivity measurements is the fluid temperature. As fluid temperature increases, the ion conductance increases, making this physicochemical phenomenon the predominant reason for the temperature-compensation requirement when testing conductive fluids.

The conductivity, κ, is proportional to the conductance, K (S), of a fluid between two electrodes (*Equation 2*):

$$\kappa = K \times \left(\frac{d}{A} \right) = K \times \theta \tag{2}$$

κ = conductivity (S/cm)

K = conductance (S)

d = the distance between the electrodes (cm)

A = the area of the conducting electrodes (cm^2)

θ = the cell constant (cm^{-1}), which also equals the ratio of d/A.

The resistivity ρ (Ω-cm), of the fluid is, by definition, the reciprocal of the conductivity (*Equation 3*):

$$\rho = \frac{1}{\kappa} = \frac{1}{K \times \theta} = \frac{R}{\theta} \tag{3}$$

ρ = resistivity (Ω-cm)

κ = conductivity (S/cm)

K = conductance (S)

θ = the cell constant (cm^{-1})

R = the resistance (Ω), which is the reciprocal of the conductance, K.

APPARATUSAn electrical conductivity measurement consists of the determination of resistance of the fluid between and around the electrodes of the conductivity sensor. To achieve this measurement, the primary instrumentation is the resistance-measuring circuit and the conductivity sensor, and they are usually connected by a cable when the sensor and the user interface are separated.

The resistance measurement is made by applying an AC (alternating current, meaning the flow of electric charge periodically reverses direction) voltage (or current) to the electrodes, measuring the current (or voltage), and calculating the resistance according to Ohm's Law. The alternating source is utilized to prevent the polarization (collection of ions) at the electrodes. The measuring frequency of the AC signal adjusts automatically according to the measuring conditions of the instrument, and there may be multiple resistance-measuring circuits embedded in the measuring system. The resistance-measurement circuit may be embedded in the transmitter or in the sensor.

The conductivity sensor consists of at least two electrical conductors of a fixed size and geometry, separated by an electrical insulator. The electrodes, insulator and any other wetted materials should be constructed of materials that are unreactive to fluids with which they may come into contact. Also, the sensor construction should withstand the environmental conditions (process or ambient temperature, pressure, cleaning applications) that it would be subjected to.

Most conductivity sensors have temperature devices such as a platinum RTD (resistance temperature device) or NTC (negative temperature coefficient) thermistor embedded inside the sensor, although external temperature measurement is possible.

The purpose of the temperature measurement is for temperature compensation of the conductivity measurement.

CELL CONSTANT DETERMINATIONThe purpose of the sensor’s cell constant is to normalize the conductance (or resistance) measurement for the geometrical construction of the two electrodes.

The cell constant is determined by immersing the conductivity sensor in a solution of known conductivity. Solutions of known conductivity can be obtained by 1) preparation of specific recipes according to national authoritative sources, 2) procurement of commercially available certified and traceable standard solutions, or 3) comparison to other reference conductivity measuring systems. These recipes or certified solutions can range from 5 to 200,000 µS/cm depending on the level of accuracy desired. [NOTE - Conductivity measurements are not perfectly linear with concentration. Dilution of a reference solution by x-fold does not imply that the conductivity of that diluted fluid is x-fold less. Negative deviations from linearity range from 5% to 10% for commonly used reference solutions.]

The measured cell constant of the conductivity sensor must be within 5% of the value indicated by the sensor certificate.

Modern conductivity sensors normally do not change their cell constant over their lifetime. If a change of the cell constant is detected during calibration, a cleaning of the sensor is appropriate according to the manufacturer’s recommendations. Following that, the calibration procedure should be repeated. Sometimes "memory effects" appear, particularly when changing from high to low concentrations if the sensor is not well flushed.

TEMPERATURE COMPENSATION

Because the conductivity of a fluid is temperature dependent, temperature compensation of the conductivity measurement is normally necessary. An appropriate temperature compensation algorithm will ensure that changes in the conductivity measurement can be ascribed to concentration changes and not temperature changes, Conductivity measurements are normally referenced to 25°C. A common form of linear temperature compensation uses *Equation 4*:

$$\kappa_{25} = \frac{\kappa_T}{\left[1 + \alpha(T - 25)\right]} \qquad (4)$$

κ_{25} = the conductivity compensated to 25°C

κ_T = the conductivity at T

α = the linear temperature compensation factor

T = the measured temperature

A value of 0.021 for a temperature coefficient of 2.1% per °C is commonly used for many salt solutions. Most salt-based solutions have linear compensation factors ranging from 1.9% to 2.2% per°C. Depending on the application, other values can be used for acids, bases, and other fluids. Another known, non-linear form of temperaturecompensation is described in ISO *7888 Water Quality – Determination of Electrical Conductivity*. Depending on the fluid samples, other forms of temperaturecompensation may be appropriate. In cases of very low conductivity, (<10μS/cm), such as purified pharmaceutical waters, two compensations need to be made. One is for the intrinsic conductivity of water, and the other is for the other ionic species in water. These compensations are normally combined and embedded in the microprocessor-controlled conductivity measurement systems. This is not supplied in all conductivity measurement technologies.

CALIBRATION OF TEMPERATURE AND MEASUREMENT

In addition to verifying the sensor's cell constant, the embedded temperature device (or external temperature device) should be appropriately calibrated for the application in order to apply the temperature compensation algorithm accurately. The temperature accuracy that is required depends on the criticality of the temperature to the application. An accuracy of ±1°C typically suffices.

The measurement circuit of the system is fundamentally an AC resistance measuring device. Appropriate verification and/or calibration of the measuring circuit is required. This is accomplished by disconnecting the measuring circuit from the sensor's electrodes, attaching traceable resistors of known value to the measuring circuit, and verifying that the measured resistance agrees with the resistor value to an acceptable level. A typical acceptance criterion for the resistance accuracy is <2% of the reading at resistances greater than 100 ohms, and increasing to 5% at lower resistances. However, the application criticality should ultimately determine the desired accuracy.

For conductivity systems that cannot have the resistance-measuring circuit disconnected from the electrodes, it may be difficult to directly adjust or verify the circuit accuracy, depending on the sensor design. An alternative method of verifying the circuit accuracy can be used by performing a sensor cell constant calibration at two (or more) measurement points for each measuring circuit that is intended to be used.

If verification/calibration of the sensor’s cell constant, temperature device, and measuring circuit are done at the same service interval, the measuring circuit should be verified first, the temperature device next, and the cell constant last. Because all of these parameters are typically very stable due to modern electronics and stable sensor construction, frequent calibration (such as daily) is not usually required. Comparison to qualified reference systems is also a proper means of calibration. Calibration cycles range from 6 to 12 months.

CONDUCTIVITY MEASUREMENT OF FLUIDS

For off-line batch measurements, rinse the cleaned sensor with the fluid to be measured. Then immerse the sensor in the fluid to be measured and record the temperature and the temperature-compensated conductivity as required. Be sure that the position of the sensor in the container does not impact the conductivity measurement, as the container walls can impact the measurement for some electrode designs.

For continuous on-line or at-line measurements, install the cleaned sensor into the pipe, tank, or other containment vessel, and flush, if necessary. Make sure proper installation procedures are applied to prevent bubbles or particles from collecting between the electrodes. Be sure that the position of the sensor in the pipe or tank does not impact the conductivity measurement, as the nearby surfaces can impact the measurement for some electrode designs. Record the temperature and the temperature-compensated conductivity as required.

For all batch or continuous measurements, ensure that the wetted components of the sensor are compatible with the fluid and the temperature to be measured.