

TECHNICAL NOTES

Issue 4-1

CONDUCTIVITY THEORY AND MEASUREMENT

What is Conductivity?

Electrical conductivity is a measure of the ability of a solution to carry a current. Current flow in liquids differs from that in metal conductors in that electrons cannot flow freely, but must be carried by ions. Ions are formed when a solid such as salt is dissolved in a liquid to form electrical components having opposite electrical charges. For example, sodium chloride separates to form Na^+ and Cl^- ions. All ions present in the solutions contribute to the current flowing through the sensor and therefore, contribute to the conductivity measurement. Electrical conductivity can therefore be used as a measure of the concentration of ionizable solutes present in the sample.

Conductivity Units

Electrical resistivity uses the unit of ohm meter or $\Omega\cdot\text{m}$. Electrical conductivity is the reciprocal of electrical resistivity. Rather than use the units $\Omega^{-1}\cdot\text{m}^{-1}$, in 1971 the unit “siemens” (symbolized by the capital letter S) was adopted by the General Conference on Weights and Measures as an SI derived unit. The unit for electrical conductivity becomes siemens per meter. The siemens unit is named after Werner von Siemens, the 19th century German inventor and entrepreneur in the area of electrical engineering.

North American practice continues to see the use of unit mho/cm to measure conductivity, where the unit “mho” is a reciprocal ohm. The

word “mho” is the word “ohm” spelled backwards. Because of the history of conductivity measurements in micromho/cm and millimho/cm, it is common to see these measurements translated to microsiemens/cm and millisiemens/cm because there is a one-to-one correspondence between these units.

MEASUREMENT	UNITS
resistance	ohm
conductance	siemens, mho
resistivity	ohm
conductivity	siemens·cm ⁻¹ , ohm·cm ⁻¹

Table 1 Electrical conductivity measuring units

Conductivity Terminology and Formulas

$$\text{conductivity} = \frac{K_{\text{cell}}}{R} \frac{1}{1 + (\alpha/100) * (T - 25)}$$

where

conductivity is the temperature-compensated reading in siemens/cm;

K_{cell} = cell constant in cm^{-1} , typically in the range 0.01/cm to 50/cm;

R = measured resistance in ohms;

α = temperature compensation factor as % change per °C, typically close to 2.0;

T_{TC} = measured temperature of the sample in °C.

Conductivity measurement is typically read out as

microsiemens per centimeter ($\mu\text{S}/\text{cm}$)
millisiemens per centimeter (mS/cm)

$$\text{resistivity} = \frac{1}{\text{conductivity}}$$

$$\text{resistance} = \frac{1}{\text{conductance}}$$

$$\text{cell constant} = K_{\text{cell}} = \frac{l}{A}$$

where

l = distance in cm between the electrodes
 A = area in cm^2 of the electrodes

$$\frac{\text{siemens}}{\text{cm}} = \frac{\text{mho}}{\text{cm}} = \frac{1}{\text{ohm} \cdot \text{cm}}$$

$$1 \text{ S/m} = 10^4 \mu\text{S}/\text{cm} = 10^3 \text{ mS/m}$$

Conductance Data for Commonly Used Chemicals

Examples of conductance of various materials with changing concentration are shown in illustration 1. Sodium hydroxide (NaOH) exhibits variable temperature-related rates of concentration change. It is clear from the graph that both Sulfuric acid, (H_2SO_4), and nitric acid, (HNO_3), have unusual conductivity vs weight relationships as well. It clearly shows that there is no “conductivity constant” between chemical combinations.

Cell Constant

To determine the amount of current that will flow through a known amount of liquid, the volume between the two electrodes must be exact and the current must be kept consistent and moderate. This is known as the *cell constant*. Any effective volume change changes the cell constant and current, too much volume will result in noise (low

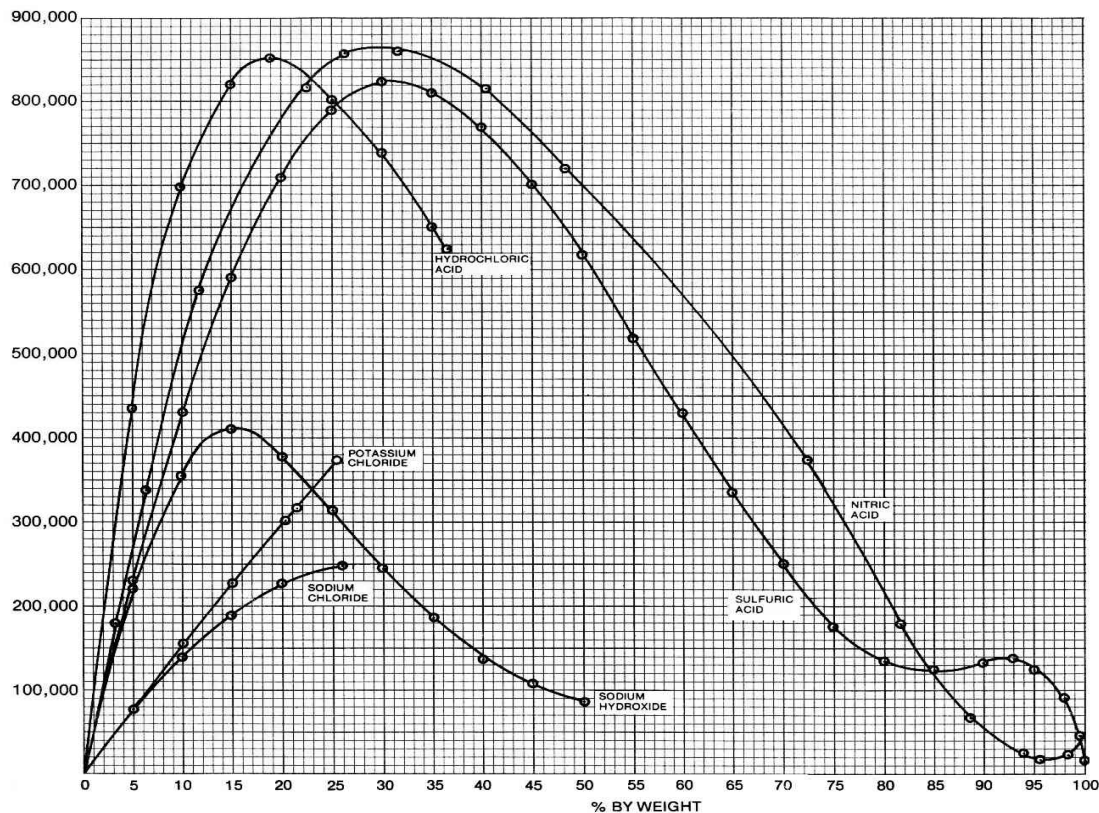


Illustration 1 Conductivity ($\mu\text{S}/\text{cm}$) vs chemical concentration

current), or *too little volume in electrolytic effects* (high current). The cell constant recommended will vary depending on the conductivity range of the solution. High conductivity requires a high cell constant and low conductivity requires a low cell constant.

Industrial users may have a wide range of applications with unpredictable variables. Ideally, IC Controls would check the ranges of conductance for all the applications and recommend appropriate cell constants. However, we may be dealing with unknowns and upsets. To provide for unknowns the IC Controls model 455 conductivity analyzer auto range capability allows for a tenfold increase or decrease in range by the microprocessor. The user can achieve full accuracy at a far greater range than was historically possible. For example, a 1.0/cm constant recommended for 0-1,000 $\mu\text{S}/\text{cm}$ can read accurately up to 0-10,000 $\mu\text{S}/\text{cm}$ or down to 0-100 $\mu\text{S}/\text{cm}$ full scale. Not only is accuracy assured over a greater conductivity range, but you can use fewer cell constants.

Temperature Compensation

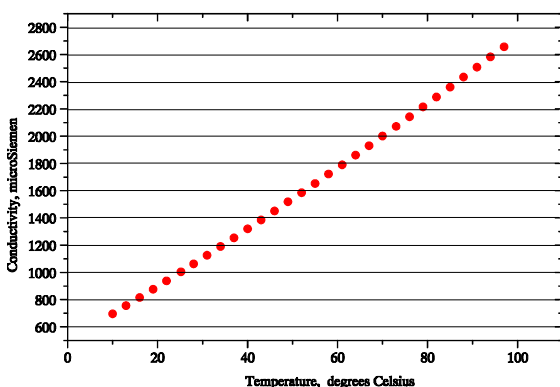


Illustration 2 Temperature compensation values

Ionic movement, and therefore conductivity measurement, is directly proportional to temperature (see illustration 2). The effect is predictable and repeatable for most chemicals, but unique to each chemical. The effect is instantaneous and quite large (typically 1%-3% / °C) with reference to the value at 25°C (see table 2 and illustration 3). Also refer to formula on page 1 of the report where α refers to % change.

substance	% change per °C
acids	1.0 to 1.6
bases	1.8 to 2.2
salts	2.2 to 3.0
neutral water	2

Table 2 Typical temperature response

In industrial applications, temperature often fluctuates and requires temperature compensation. This is generally accomplished by using an automatic, linear temperature compensation method. In most cases, the variations in temperature are corrected using automatic temperature compensation, 2% per °C is deemed acceptable.

Without temperature compensation big errors can result, $50^{\circ}\text{C} \times 2\%/^{\circ}\text{C} = 100\%$ off, or 50% error in reading! In laboratory applications, where measurements must be made with accuracy and consistency in various chemical combinations, manual temperature

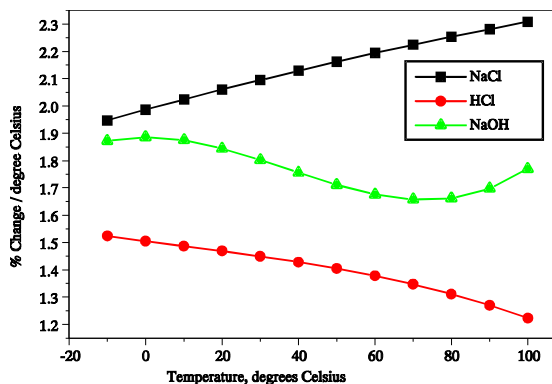


Illustration 3 Temperature response of typical solutions

compensation can be considered for each application. The temperature is set in the manual TC mode.

For on-line process applications the IC Controls 455 conductivity analyzer allows the user to set the TC constant in %/°C to match the curve in the known temperature range of the known process chemical. **Where the process mixture produces an unknown** the default 2% per °C can be used;

alternatively, tests can be performed and a custom value can be set in the 455. Some chemicals that are frequently diluted for use have changing non-linear temperature compensation requirements, so IC Controls has programmed special versions with TC in a graph in the memory; e.g. NaOH 455-21, H₂SO₄ 455-22, HCl 455-23, NaCl 455-24, that read out in % concentration. Additionally the 455-63 offers calibration and TC for high-purity water with very low conductivity.

Sensor Cleaning

As the volume (distance) between the two electrodes is exact, fouling of the sensor can alter the distance between the electrodes and change the cell constant. Therefore, keeping the electrode clean is important. The 455 analyzer will determine the cell constant at the point of calibration and condition of use and compensate accordingly. Changing cell constants will then not be a factor adversely affecting repeatability.

Conductivity Calibration

As mentioned above, a calibration schedule should be adhered to. While it is a quick, single point process, it is important that all applications be accurately reflected with acknowledgment of the set TC and cell constant. The 455 will keep in memory a record of calibration dates, values, and cell constants that can be downloaded to your computer for proof of performance or to trend the sensor cell condition. If the user calibrates using a laboratory bench top unit as a calibration standard, there is a grab sample method incorporated into the 455 analyzer that enables the user to standardize the reading to correspond with the lab unit. Using lab standardization or the high integrity of the model 455 calibration is the convenience choice of the user.

Theory of Calibration

Periodic calibration of conductivity sensors in continuous use is recommended. Various factors can affect the physical limits on the

liquid and the apparent cell constant (scale, biological growths, oils, wax, gum, etc). Reducing the area for current-carrying liquid.

A conductivity cell's physical size and shape are important. The only restrictions on an ion's movement are the physical limits of the liquid. A conductivity analyzer measures all the current that will flow between two electrodes; thus if there are no restrictions not only will the shortest path between the electrodes carry current, but also other roundabout paths will carry a smaller share of current. The controlled volume of a good conductivity sensor places physical limits on the liquid and controls current paths, which is identified by the cell constant. The cell constant can be accurately determined by dipping the sensor in a recognized conductivity standard, (preferably traceable to NIST since literature references are frequently in conflict over conductivity values). The standard should be near the high end of the range of operation for the cell constant of the sensor or in the range of interest.

Sensors with low cell constants like 0.01/cm tend to have large electrode surfaces which are close together, making for fairly large sensors. They need a long, slim container to be fully immersed in liquid for calibration. Sensors with medium cell constants like 0.1/cm and 1.0/cm are much smaller and more compact and can usually be calibrated in a beaker suspended above the bottom. High range cells with 10/cm, 20/cm and 50/cm constants usually include an internal liquid passage that requires a long thin vessel to be immersed or may require a pumped sample for calibration.

Use of NIST Traceable Standards

IC Controls manufactures conductivity standards and performs quality control using NIST materials. Certificates of traceability to NIST materials are available as P/N A1900333

Where to Perform Conductivity Calibrations

A suitable place to conduct a calibration is at a counter or bench with a sink in an instrument

Guide to Cell Constant Usable Ranges

CELL CONSTANT cm^{-1}	DESIGN RANGE $\mu S/cm$	LOWEST RANGE $\mu S/cm$	HIGH RANGE $\mu S/cm$	OVER-RANGE * $\mu S/cm$
0.01	0 to 10	0 to 1	0 to 100	0 to 1 000*
0.02	0 to 20	0 to 2	0 to 200	0 to 2 000*
0.1	0 to 100	0 to 10	0 to 1 000	0 to 10 000*
0.2	0 to 200	0 to 20	0 to 2 000	0 to 20 000*
0.5	0 to 500	0 to 50	0 to 5 000	0 to 50 000*
1.0	0 to 1 000	0 to 100	0 to 10 000	0 to 100 000*
2.0	0 to 2 000	0 to 200	0 to 20 000	0 to 200 000*
5.0	0 to 5 000	0 to 500	0 to 50 000	0 to 500 000*
10.0	0 to 10 000	0 to 1 000	0 to 100 000	0 to 1 000 000*
20.0	0 to 20 000	0 to 2 000	0 to 200 000	0 to 1 000 000*
50.0	0 to 50 000	0 to 5 000	0 to 500 000	0 to 1 000 000*

* *Note:* use over-range with caution. Some sensor designs may limit when used on over-range and may not reach the maximum shown.

Table 3 Cell constant usable ranges

shop or laboratory. However, IC Controls provides kits that are kept small and portable so that they can be taken to installation sites, along with a container of water for cleaning/rinsing and a rag/towel for wiping or drying. Calibration at the site offers the advantage of taking into account the wiring from the analyzer to the sensor, and correcting for any errors induced.

When calibrating, ensure there are no air

bubbles inside the cell; air bubbles will cause low conductivity readings. Remove bubbles by tapping the sensor or alternately raising and lowering the sensor to flush them out.

With the conductivity cell centered in the beaker and no air bubbles in the cell, monitor for the reading to stabilize and then calibrate the analyzer. Note: the reading may gradually change while the sensor equilibrates to the standard temperature. With analog conductivity analyzers the technician must decide when the temperature is stable and then turn the standardize adjuster. With a microprocessor-based analyzer such as the model 455, the program acts as an expert thermal equilibrium detector and flashes its reading until temperature stabilizes. A somewhat different but steady (non-flashing) reading indicates calibration is complete.

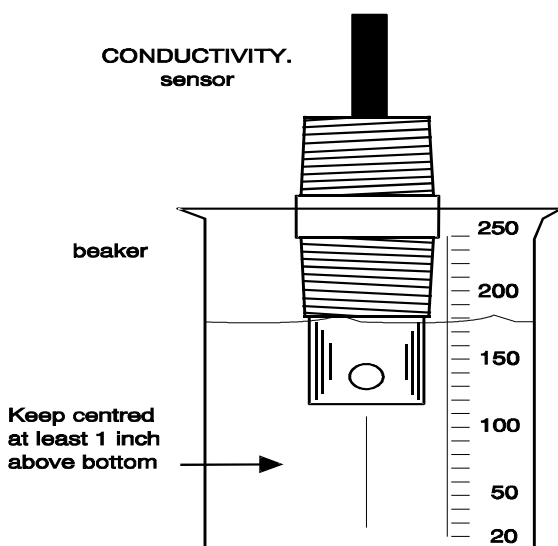


Illustration 4 Conductivity sensor calibration

Selecting Conductivity Sensors

In order to ensure integrity of conductivity readings, several steps are needed to consider the above factors. First, a survey should be made of all applications. The user should fill

in *Conductivity Application Analysis* sheets for each measurement point, factoring in varying chemical combinations, conductivity ranges and temperatures. This will allow for a selection of sensor styles and cell constants to allow standardization. At this time IC Controls would address the following:

1) Sensor recommendation - We will attempt to stay with as few cell constants and style variations as possible. For example, the IC Controls model 404-1.0 may be a suitable, economical choice.

2) Analyzer recommendation - The IC Controls model 455 may be recommended because of its wide range capability, accuracy and automatic compensation flexibility.

3) Cleaning Schedule - At least for fouling applications, to ensure sensor and cell constant integrity.

4) Calibration Schedule - To document accuracy and ensure repeatability is maintained.

IC Controls will be happy to answer any questions and work with users to ensure reliable conductivity readings. In North America we can be reached toll-free at 1-800-265-9161, or internationally contact us at:

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