

# CALIBRATING CONTACTING CONDUCTIVITY SENSORS

## BACKGROUND

A typical contacting conductivity sensor consists of two metal electrodes separated by a fixed distance. When the sensor is placed in an electrolyte solution and an alternating voltage is applied to the electrodes, a current, carried by the motion of ions in the solution, passes between the electrodes. The conductance of the solution is the ratio of the current to the voltage. The conductance depends on the total concentration of ions in the solution as well as on the length and area of the solution through which the current passes. Thus, even if the concentration of the ions remains the same, the conductance will change if the length or area of the current path changes. The geometry of the current path is defined by the sensor geometry, or cell constant. Multiplying the conductance by the cell constant corrects for the effect of sensor geometry on the measurement. The result is the conductivity, which depends only on the concentration of ions in the electrolyte solution.

The cell constant is simply a calibration factor that converts conductance (measured in  $\mu\text{S}$ ) to conductivity (measured in  $\mu\text{S}/\text{cm}$ ). The units of cell constant are  $1/\text{cm}$ . Figure 1 illustrates the relationship. Note that the slope of the calibration line is the cell constant.

Because the electric field is not strictly confined between the two electrodes, it is not possible to calculate the cell constant from the dimensions of the sensor. Instead, the cell constant must be measured by placing the sensor in solution having known conductivity and measuring the conductance. The cell

constant is calculated by dividing the conductivity by the conductance.

Normally, the cell constant is measured at the factory. When the sensor is first placed in service, all that is necessary is to enter the cell constant into the analyzer. However, the cell constant can change over time, making recalibration necessary.

## CALIBRATION METHODS

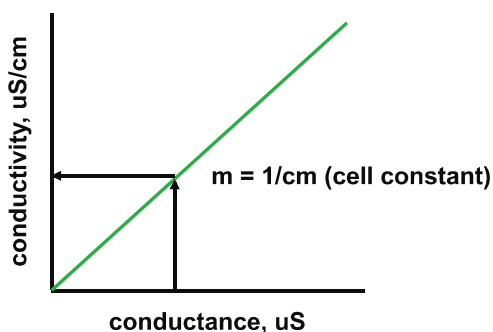
There are two basic ways to calibrate a conductivity sensor: against a standard solution or against a referee meter and sensor. A referee meter and sensor is an instrument that has been previously calibrated and is known to be accurate and reliable. The referee instrument can be used in either an in-process calibration or a grab sample calibration. In-process calibration involves connecting the process and referee sensors in series and measuring the conductivity of the process liquid simultaneously. Grab sample calibration involves taking a sample of the process liquid and measuring its conductivity in either the laboratory or shop using the referee instrument. No matter which calibration method is used, the analyzer automatically calculates the cell constant once the known conductivity is entered.

### Calibration against a standard solution

Standard solutions having conductivity between 5 and 20,000  $\mu\text{S}/\text{cm}$  (at 25°C) are commercially available. Standards can also be prepared in the laboratory following procedures in ASTM D1125 or Standard Methods 2510. For reasons discussed later the use of conductivity standards below 100  $\mu\text{S}/\text{cm}$  is not recommended.

The calibration procedure is fairly straightforward. Immerse the rinsed sensor in the standard solution and adjust the analyzer reading to match the conductivity of the standard. For an accurate calibration, however, several precautions are necessary.

- Choose a calibration standard near the midpoint of the recommended conductivity range for the sensor. Because the optimum range depends on the analyzer, consult the analyzer manual or product data sheet to determine the range.
- Do not use calibration standards having conductivity less than 100  $\mu\text{S}/\text{cm}$ . Low conductivity standards are susceptible to contamination by atmospheric carbon dioxide, which can increase the conductivity by a variable amount up to about 1.2  $\mu\text{S}/\text{cm}$ . At 100  $\mu\text{S}/\text{cm}$ , the potential error from carbon dioxide contamination is



**FIGURE 1.** Graphical representation of the cell constant. The analyzer measures the conductance (x-axis) and converts the result to conductivity (y-axis) using the calibration line. The slope of the calibration line is the cell constant.

about 1%. Low conductivity standards are also subject to contamination during handling.

- Turn off automatic temperature compensation in the analyzer. Almost all process conductivity analyzers feature automatic temperature compensation in which the analyzer applies one of several temperature correction algorithms to convert the measured conductivity to the value at a reference temperature, typically 25°C. Although temperature correction algorithms are useful for routine measurements, they should not be used during calibration. There are two reasons. First, no temperature correction is perfect. If the assumptions behind the algorithm do not perfectly fit the solution being measured, the temperature-corrected conductivity will be in error. Second, if the temperature measurement itself is in error, the corrected conductivity will be in error. To minimize the error in the cell constant, all sources of avoidable error, e.g., temperature compensation, should be eliminated.

- Use a standard for which the conductivity as a function of temperature is known. The information will usually be on the bottle label. If not, it can often be calculated if the identity of the electrolyte is known. Most Rosemount Analytical conductivity standards are aqueous potassium chloride solutions. The table gives the conductivity of these standards as a function of temperature. The nominal conductivity of the standard is the value at 25°C.

Temp (°C)	Part number				
	SS-6 and SS-6A	SS-5 and SS-5A	SS-1 and SS-1A	9210004	SS-7 and SS-7A
15	162	813	1145	1625	4063
20	181	906	1276	1811	4528
25	200	1000	1409	2000	5000
30	219	1098	1547	2196	5490
35	238	1197	1687	2394	5986

- Use a good quality calibrated thermometer to measure the temperature of the standard solution. The thermometer error should be less than  $\pm 0.1^\circ\text{C}$ . Allow adequate time for the solution and sensor to reach thermal equilibrium.

- If the conductivity of the standard is known only at 25°C, the temperature of the solution must be adjusted to  $25.0 \pm 0.1^\circ\text{C}$  before completing the calibration. Use a water bath to adjust the temperature. Do not use a hot plate. Use a good quality thermometer to measure the temperature. Do not place the thermometer in the water bath; place it in the standard solution.

- Follow good laboratory practice. Rinse the beaker and sensor at least twice with standard. Be sure the rinse solution reaches between the inner and outer electrodes by tapping and swirling the sensor while it is immersed in the standard. Discard all rinses and the standard after it has been used to calibrate the sensor. Do not attempt to recycle used standard. Keep the bottle of standard tightly capped unless you are pouring from it.

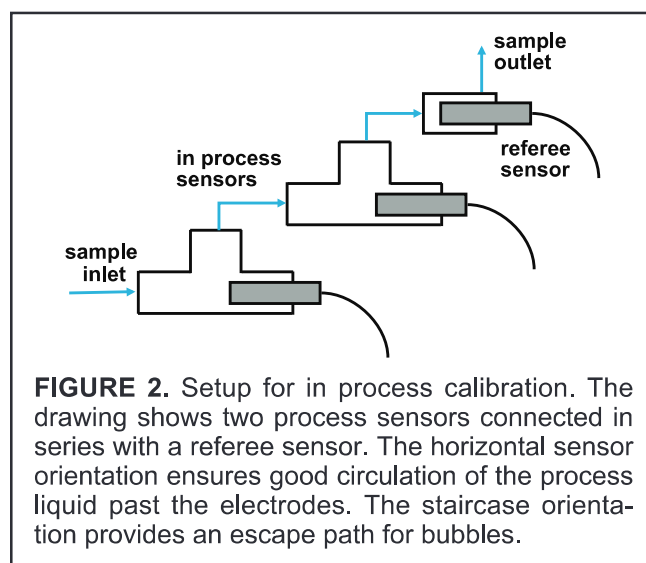
- Be sure air bubbles are not trapped between the electrodes. Place the sensor in the standard and tap and swirl to release bubbles. Note the reading. Then,

remove the sensor and return it to the standard. Tap and swirl again and note the reading. If the two readings agree, trapped bubbles are absent. If they do not agree, bubbles are present. Continue the process until two subsequent readings agree.

- While making the measurement, do not allow the sensor to touch the sides and, particularly, the bottom of the beaker. Keep at least 1/4 inch (6 mm) clearance.

### Calibration against a referee – in-process

This method involves connecting the process and referee sensors in series and allowing the process liquid to flow through both. The process sensor is calibrated by adjusting the process analyzer reading to match the conductivity measured by the referee instrument. The method is ideal for calibrating sensors used in low conductivity water (0.01/cm cell constants) because the calibration system is closed and cannot be contaminated by atmospheric carbon dioxide. Figure 2 illustrates the setup.



**FIGURE 2.** Setup for in process calibration. The drawing shows two process sensors connected in series with a referee sensor. The horizontal sensor orientation ensures good circulation of the process liquid past the electrodes. The staircase orientation provides an escape path for bubbles.

For a successful calibration, several precautions are necessary.

- If the normal conductivity of the process liquid is less than about 1.0 uS/cm, adjust the conductivity so that it is near the upper end of the operating range. This reduces the influence of fixed error on the calibration. The difference between the conductivity measured by the process and referee analyzers usually has both a fixed (constant error) and relative (proportional error) component. Because the cell constant calibration assumes the error is proportional only, calibration at low conductivity allows the fixed component to have an outsized influence on the result. For example, assume the **only** difference between referee and process sensor is fixed and the process sensor always reads 0.002 uS/cm high. If the process sensor is calibrated at 0.100 uS/cm, the new cell constant will be changed by 0.100/0.102 or 2%. If the sensor is calibrated at 0.500 uS/cm, the change will be only 0.500/0.502 or 0.4%. Calibration at higher conductivity produces a better result because it minimizes the effect of the offset.

- Orient the sensors so that air bubbles always have an easy escape path and cannot get trapped between the electrodes.
- Turn off automatic temperature compensation in the analyzer. Almost all process conductivity analyzers feature automatic temperature compensation in which the analyzer applies one of several temperature correction algorithms to convert the measured conductivity to the value at a reference temperature, typically 25°C. Although temperature correction algorithms are useful for routine measurements, they should not be used during calibration. There are two reasons. First, no temperature correction is perfect. If the assumptions behind the algorithm do not perfectly fit the solution being measured, the temperature-corrected conductivity will be in error. Second, if the temperature measurement itself is in error, the corrected conductivity will be in error. The purpose of calibrating the sensor is to determine the cell constant. To minimize the error in the cell constant, all sources of avoidable error, e.g., temperature compensation should be eliminated.
- Keep tubing runs between the sensors short and adjust the sample flow as high as possible. Short tubing runs and high flow ensure the temperature of the liquid does not change as it flows from one sensor to another. If the process temperature is appreciably different from ambient, high flow may not be enough to keep the temperature constant. In this case, pumping sample at room temperature from a reservoir through the sensors might be necessary. Because such a system is likely to be open to atmosphere, saturate the liquid with air to prevent drift caused by absorption of atmospheric carbon dioxide.
- To prevent contamination of low conductivity (<1 uS/cm) process liquids, use clean tubing to connect the sensors. To prevent drift caused desorption of ionic contaminants from tube walls, keep the sample flow greater than 6 ft/sec (1.8 m/sec).

### Calibration against a referee – grab sample

This method is useful when it is impractical to remove the sensor for calibration or to connect a referee sensor to the process line. It involves taking a sample of the process liquid, measuring its conductivity using a referee instrument, and adjusting the reading from the process analyzer to match the measured conductivity. Because the method involves exposing the sample to air, it should not be used if the conductivity of the process liquid is less than about 100 uS/cm.

For a successful calibration, several precautions are necessary.

- Take the sample from a point as close to the process sensor as possible. Be sure the sample is representative of what the sensor is measuring.
- Keep temperature compensation turned on. There is likely to be a lag time between sampling and analysis, so temperature is likely to change. Therefore, temperature compensation, although imperfect, must be used. Be sure the referee and process instruments are

using the same temperature correction algorithm. Grab sample calibration should be used only when the conductivity is fairly high, in which case, the temperature compensation algorithm will most likely be linear slope. Confirm that both instruments are using the same temperature coefficient in the linear slope calculation. If the referee instrument does not have automatic temperature correction, calculate the conductivity at 25°C using the equation:

$$C_{25} = \frac{C_t}{1 + \alpha(t - 25)}$$

where  $C_{25}$  is the conductivity at 25°C,  $C_t$  is the conductivity at  $t^\circ\text{C}$ , and  $\alpha$  is the temperature coefficient expressed as a decimal fraction.

- Confirm the temperature measurements in both the process and referee instruments are accurate, ideally to within  $\pm 0.5^\circ\text{C}$ .
- Follow good laboratory practice when measuring the conductivity of the grab sample.
  - Rinse the beaker and sensor at least twice with sample. Be sure the rinse solution reaches between the inner and outer electrodes by tapping and swirling the sensor while it is immersed in the sample.
  - Be sure air bubbles are not trapped in the sensor. Place the sensor in the sample and tap and swirl to release bubbles. Note the reading. Then, remove the sensor and return it to the sample. Tap and swirl again and note the reading. If the two readings agree, trapped bubbles are absent. If they do not agree, bubbles are present. Continue the process until two subsequent readings agree.
  - While making the measurement, do not allow the sensor to touch the sides and, particularly, the bottom of the beaker. Keep at least 1/4 inch (6 mm) clearance.
- Be sure to compensate for process conductivity changes that might have occurred while the grab sample was being tested. Newer Rosemount Analytical conductivity analyzers (Models 1056, 1066, and 56) do this automatically. They save the value of the process conductivity at the time the sample was taken and use that value to calculate the new cell constant when the user enters the result of the grab sample test. Older analyzers do not remember the process conductivity value. Therefore, the user must enter a value adjusted by an amount proportional to the change in the process conductivity. For example, suppose the process conductivity is 810 uS/cm when the sample is taken and 815 uS/cm when the test result is entered. If the grab sample conductivity is 819 uS/cm, the user should enter  $(815/810) \times 819$  or 824 uS/cm.



## LIMITATIONS

The calibration methods described above have two important characteristics. First, the calibration is done at a single point. There is no certainty that the cell constant calculated at the calibration point will be exactly the same at other conductivity values. However, as long as the sensor is used in the conductivity range recommended for its cell constant, the cell constant will be reasonably close to the value at the calibration point. For example, when a 0.01/cm sensor is used with a Model 1056 analyzer between 0.01 and 200  $\mu\text{S}/\text{cm}$ , the variability in the apparent cell constant is about 0.5%. The second limitation is the analyzer and sensor are calibrated as a unit. Thus, any error in the conductance (at the calibration point) measured by the analyzer is automatically incorporated into the cell constant. When the sensor is used with a different analyzer, which may have a slightly different error at the calibration point, the cell constant may be slightly in error.

## ACCURACY

The accuracy of the calibration depends on the calibration method. For calibration against a standard solution, the accuracy depends on the accuracy of the standard itself and the accuracy of the temperature measurement. For routine work using a good quality standard and thermometer, the uncertainty is probably between 0.5 and 1.0%. For calibration against a referee instrument, either in process or using a grab sample, the errors are greater. Error in the conductivity measured by the referee instrument, which includes the uncertainty in the conductivity of the standard used to calibrate it, and the variability of the cell constant over the operating range of the referee sensor are the major causes of the increased error. Of course, if the in-process calibration is done at the same conductivity the referee instrument was calibrated, the error will be less. For calibration using a grab sample, the error will be even greater. The additional uncertainty arises from temperature measurement errors and the likelihood that the temperature correction will not be perfect.



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