

How to Supercharge an Ordinary Contacting Conductivity Sensor Using Multipoint Calibration

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The range of conductivity values that water—or any other liquid for that matter—can measure is enormous. From ultrapure water at 0.055 $\mu\text{S}/\text{cm}$ to concentration acids at 500,000 $\mu\text{S}/\text{cm}$ or greater the range is 10 million to 1. No one probe can measure it all so manufacturers adjust the sensitivity of their conductivity sensor to match the range needed. For the ubiquitous contacting conductivity sensor, they do this by “playing” with the geometry of the two (or more) electrodes. Make the surface area of the electrodes larger and/or space them closer together and the probe is more sensitive so that it can measure solutions of low conductivity. And vice versa. For planar, parallel electrodes the ratio of the spacing between the electrodes (d) to the surface area (A) is the cell constant (K). It should be clear that K has units of inverse length, typically cm^{-1} .

$$K = \frac{d}{A}$$

The smaller K is the more sensitive the probe is. Since conductivity sensors nowadays rarely use planar electrodes, one can either use sophisticated mathematics involving integrals to calculate K or one can think of K as simply a geometric factor that converts the conductance of the sample to the intrinsic conductivity. A cell constant of 0.1 is appropriate for pure water whereas a cell constant of 10 is optimal for highly saline water. A cell constant of 1 is used for everything in between.

After one chooses the cell constant appropriate for the application the question then is: How low and how high in conductivity values can it go? The upper limit of the range is determined by the polarization of the electrodes. At sufficiently high ion concentrations the alternating voltage applied across the electrodes cannot keep up with the build-up of charge on them. The measured conductivity rolls over with increasing values. At the lower limit there are simply not enough ions to yield a current large enough to rise above the noise level. The measured conductivity is stuck at a value near zero. Any measured current is internally generated, analogous to so-called “dark current” of light sensors. In the middle of the curve is the “sweet spot”—the range over which the sensor output responds linearly (in a straight line) to the conductivity of the sample. The overall result is an S-shaped response curve that holds for just about any type of sensor—from photographic film to gravity wave detectors.

For an alternative explanation of the measurement range consider the electronics of the measurement. The conductivity analyzer sends a current through a fixed, precision (reference) resistor in series with the sample, thus creating a voltage divider. So, the usable range of the probe is a resistance in the neighborhood of the reference resistor. By “neighborhood” I mean a factor of 10 below and above the reference resistance. For a 10 $\text{k}\Omega$ resistor and a cell constant of 1.0 that means a conductivity in the neighborhood of 100 $\mu\text{S}/\text{cm}$ —or 10 to 1000 $\mu\text{S}/\text{cm}$. If we want to measure water outside this range, then we change the geometry of the probe—and the cell constant—to brings the resistance of the water to be measured into this range. (Some laboratory analyzers can change the value of the reference resistor.)

We expect the response of a conductivity sensor to a range of conductivity to be linear in the neighborhood of this “sweet spot,” where the resistance of the sample is within an order of magnitude of the resistance of the precision resistor. Outside of this range the response is non-linear. This is the range defined by the reference resistor.

Figure 1 shows the response for a conductivity sensor in solutions of NaCl. We made conductivity measurements using an AquaMetrix ASM-1 conductivity sensor and AM2250 controller. (We use the term “analyzer” to refer to the combination of a sensor and controller or transmitter.) The probe has a cell constant of 1.0 and we have always advertised its range as approximately 100 to 5000 $\mu\text{S}/\text{cm}$. The blue dots represent the actual conductivity and the red dots represent the measured conductivity. Keep in mind that the conductivities of all electrolytes roll over at high enough concentrations. Let’s not confuse this rollover with the rollover caused by the limitations of the conductivity analyzer. A magnification of the left side of the figure shows that the measured conductivity starts falling below the true conductivity by more than 10% at about 0.4% concentration (or 4000 ppm). This corresponds to a conductivity limit of about 8000 $\mu\text{S}/\text{cm}$, which is considerably higher than our advertised limit. We can clearly see the high-end rollover of the ASM sensor. The low end of the range did not reveal the smooth beginning of the

S-curve as described. That’s because the digital conversion of the miniscule voltage signal at very low ion concentration creates huge swings in the calculated conductivity. But, as POTUS would say, “Believe me.” It’s there; we just couldn’t see it.

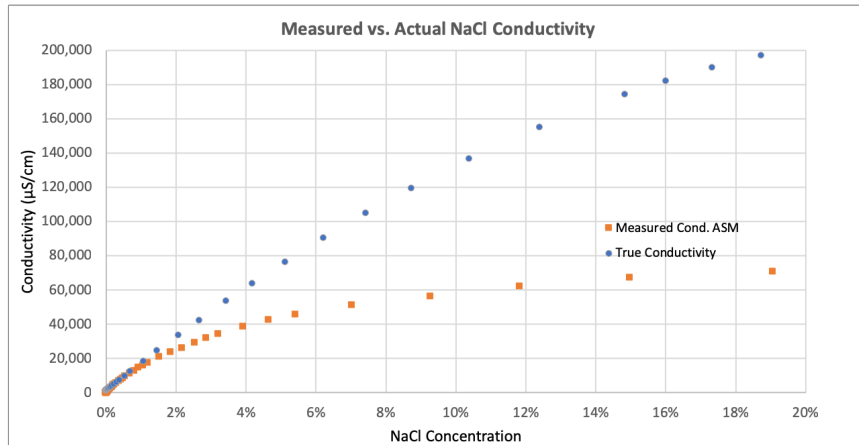


Figure 1 - Actual conductivity for NaCl solutions compared to actual values.

The useful measurement range—the width of the straight-line portion of the S-curve—lies between 20 and 8000 µS/cm. But that straight line is not truly straight, which begs the question, “How straight is straight enough?” Certainly, if we accept a 20% error the range is going to be a lot wider than if we insist on accuracy better than 2%.

In the world of conductivity measurements high precision is hard to come by. The temperature dependence of the conductivity measurement is between 1.5% and 2% per degree Celsius. That means, being off by 2 °C can incur a 4% error. Placing the sensor too close to the walls of a container or pipe can throw off the measurement by more than 10%. The error can be positive for a metallic wall or negative for a plastic one. Coatings on the electrodes can reduce the measured conductivity by more than 10%. So, 5% is achievable with careful and frequent calibration. For most routine conductivity measurements 10% is about as good as one can reasonably expect.

Most conductivity analyzers offer one-point calibration. (Figure 1 is actually data from a one-point calibration.) Since all linear calibrations require two points this method assumes that the second point is (0,0). If the calibration curve were a straight line from the zero point to the one calibration measurement, then this would work fine but the analyzer might have an offset so that zero conductivity gives a small, but measurable, reading. In addition to the limits of accuracy due to the curved response of a conductivity sensor we suffer the added insult of an inaccurate slope. To be fair, this error is significant only for very low conductivity solutions—less than approximately 20 µS/cm.

If one-point calibration is problematic, then two points at least eliminates the error of the zero offset. But we want more! What if we calibrate the sensor at multiple points? Then we can model more of the S-curve than just the quasi-straight-line portion. We ought to be able to squeeze just a little more headroom on both ends of the measurement range. Can we do it? Yeah you betcha. Calibration with as many as 16 points is a feature on all AM2250 series controllers.

I’d like to say that supercharging contacting conductivity sensors was our intention all along when we designed our 2250 series of controllers. But we weren’t that prescient. We did it so that the user can use conductivity to measure the concentration of strong acids and bases when pH readings lose accuracy above 12 or below 2. Conductivity curves are so highly curved for acids and bases that their values actually turn over and decrease after a certain value. See Figure 2. When it occurred to us that the same strategy might extend the conductivity range of dissolved salts, we realized we had a simple, powerful method for turning any sensor into a wide range sensor.

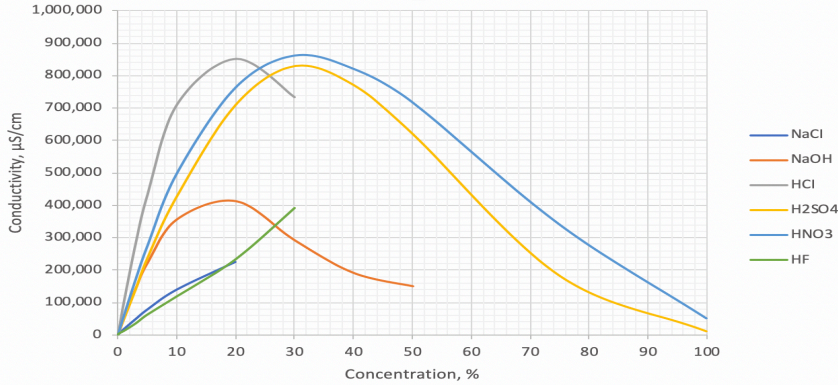


Figure 2- Conductivity of 3 acids (HCl, H₂SO₄, HNO₃ and HF), NaCl and NaOH.

Figure 3 shows the results adding more calibration points. We measured the conductivity for a series of solutions of KCl for which the true conductivity values were determined by a NIST-calibrated laboratory conductivity analyzer (YSI). The calibration solutions were 2.4, 5.2, 11.3, 18.6, 4994, 19,210, 99,700 and 110,000 µS/cm. The figure plots the ratio of the measured conductivity to the actual conductivity. A value of 100% means that the two are exactly equal and the error is zero.

For the sake of comparison, we made two sets of measurements over the same conductivity range: Measurements using a one-point calibration are shown in red while those using a seven-point calibration are shown in blue. The rectangular shaded areas indicated the range within which the measurement error is within ±10%. At first glance the extension of measurement range afforded by the 7-point calibration might not seem that impressive. But keep in mind that the conductivity values are plotted on a log 10 scale. The 1-point calibration range is approximately 20 to 8,000 µS/cm. But the 7-point calibration range is 5 to greater than 100,000 µS/cm. (The AM-2251 maxes out at 6 digits so we did not beyond 100,000 µS/cm.) That's an expansion by a factor of fifty! In fact, this range is about as wide as that of a conventional toroidal conductivity sensor, which is known for its expansive range. And, it covers the low end better than a toroidal probe. I say "conventional" because our new AM2251 controller expands the range of the toroidal sensor even further, especially into the low range.

The bottom line is that multi-point calibration can turn an inexpensive contacting conductivity probe into one that can compete with a conventional toroidal probe and analyzer costing at more than three times as much. All you need are a series of calibration standards, which you can make by buying one high concentration standard from which you make serial dilutions. And—oh yeah—a controller that lets you calibrate at several points.

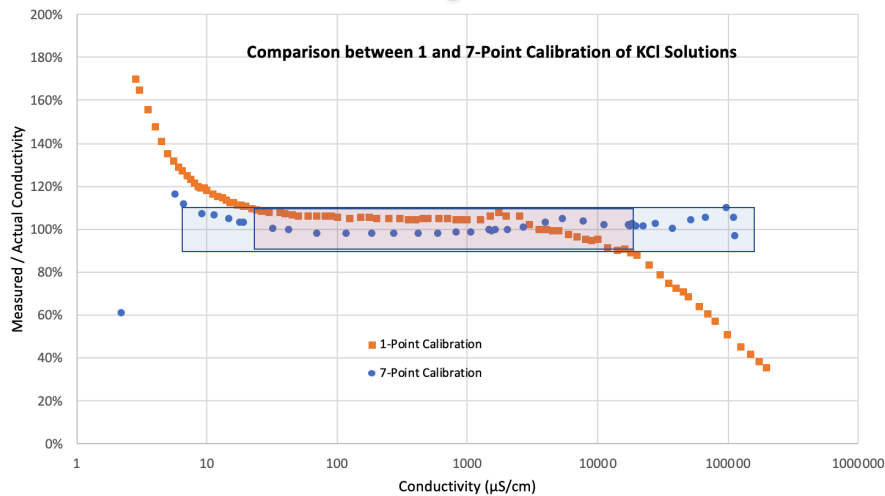


Figure 3 - Accuracy for 1-point calibration vs. 7-point calibration. The shaded rectangles display the range of conductivity for which the error is ±10%; red for 1-point calibration and blue area for 7-point calibration.