Using Conductivity to Measure Salinity

What is salinity?

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What is salinity? Salinity was originally defined as the amount of dissolved salts present in seawater. Early measures typically involved weighing the solids left when seawater was dried. Unfortunately, drying is not only tedious but it is relatively inaccurate because some of the solids are driven off as gases before all of the water is removed. Consequently, scientists have developed a wide array of techniques for measuring salinity, including conductivity, refractive index and density. While all of these are suitable for hobbyists, conductivity is recognized by scientists as being the most precise, and this article will provide an understanding of the how's and why's of this technique.

It is beyond the scope of this article to describe why one is interested in controlling salinity in a marine aquarium. Suffice it to say that all organisms have a range of salinities that they can exist in, and a smaller range in which they thrive. Once that range is established, one need only keep them within it. If a range has not established, then keeping them within the range experienced in their natural environment would seem the next best choice.

Let's start by discussing what it is that we are interested in measuring when we talk about salinity. In previous articles in Aquarium Frontiers, the nature of the constituents in seawater has been described in detail. In the context of salinity, seawater consists primarily of inorganic ions dissolved in water. It is the aggregate concentration of these ions that we want to quantify. To a first approximation, these ions (such as sodium, Na^+, and chloride, Cl^-) are all independent of each other, and are moving around freely in the water.

Because these ions are both charged and free to move, they are capable of responding to an electric field imposed on them. Thus, positively charged ions will move toward a negatively charged electrode, and negatively charged ions will move toward a positively charged electrode. Because these ions are charged and moving, they constitute an electrical current. So, to measure conductivity, one simply measures the flow of electricity through the water in an electrical field.

In practice, the measured electrical flow is dependent upon several things: 1) the number of ions that are moving, 2) the types of ions that are present — some move more rapidly than others, and 3) the strength of the electrical field imposed. If we assume that the water has the right ratios of ions (so that number 2 isn't a variable; see below) then the measured electrical flow can be a good measure of the total number of ions present, or, in other words, a good measure of salinity.

In order to understand whether the types of ions are a significant issue for marine aquaria, we need to understand a few facts about conductivity. The most important is that most ions contribute to conductivity to about the same extent. Table I shows the relative conductivity of several ions. Ions with higher charges tend to have higher conductivity because they not only carry more charge but they respond more strongly to an electrical field. Good examples are sulfate (SO_4^{--}) and calcium (Ca^{++}), which have higher conductivities than sodium (Na^+) or chloride (Cl^-).

Another effect is that larger ions tend to have more "drag" as they move through the water, and thus have lower conductivity. In such comparisons one needs to take into account the tightly bound water molecules that get dragged along as well, so one cannot simply look at molecular weights or ionic radii. This is, for example, why lithium (Li^+) is so much less conductive than sodium, which in turn is less conductive than potassium (K^+). Table II shows the ionic mobility — a measure of how readily the ion can move through water — for several ions. This value tracks well with the conductivity of the ions, except that ions with more charge and the same mobility, such as calcium or sulfate, conduct more.

Table I
Relative Conductivity of Various Ions

Cations	Relative Conductivity	Anions	Relative Conductivity
H^+	7.0	OH^-	4.0
Li^+	0.8	Cl^-	1.5
Na^+	1.0	Br^-	1.6
K^+	1.5	I^-	1.5
Mg^{++}	2.1	NO_3	1.4
Ca^{++}	2.4	acetate	0.8
Zn^{++}	2.1	SO_4	3.2

Another interesting factor is the unusually large conductivity displayed by hydrogen ions (H^+) and hydroxide ions (OH^-). They have very high apparent conductivities and high mobilities, but not because they are especially small. Instead, they conduct without actually moving very far. In this mechanism, a hydrogen ion, for example, makes a new bond with a nearby water molecule. The water molecule then releases a new hydrogen ion off its other side, resulting in the apparent motion of a hydrogen ion without any single ion actually moving. This process continues

Table II
Relative Conductivity of Various Ions

Cations	Relative Conductivity	Anions

Relative Conductivity	
H^+	7.0
OH^-	4.0
Li^+	0.8
Cl^-	1.5
Na^+	1.0
Br^-	1.6
K^+	1.5
I^-	1.5
Ca^{++}	1.2
NO_3	1.4
La^{++}	1.4
acetate	0.8
SO_4	1.6

through the solution (Figure 1), resulting in high conductivities for H^+ and OH^-. The most important fact for measuring seawater salinity is that anything that is not present at relatively high concentrations just doesn't contribute significantly to the total. Even H^+ and OH^- , with their high inherent conductivities, do not contribute much because they are present at very low concentrations. In fact, Na^+ and Cl^- really dominate in seawater, comprising >90 percent of the total ions present. Magnesium adds another 5 percent and sulfate adds another 2.5 percent. Thus, as long as these four ions are roughly right (>97 percent of the total ions), imbalances in the other ions will have relatively small contributions to the conductivity. So, for this measure of salinity, reasonable variations in phosphate, calcium and other ions that are so important for other aspects of marine aquaria are of no consequence.

Can I just drop some electrodes into the water and measure the resistance with a meter? No. Several factors make that impossible. The size and shape of the electrodes are significant, but more important is what happens at those electrodes. If you apply a DC current to seawater, numerous reactions take place when the ions hit the electrodes. Some ions will plate out on the electrodes, some may bubble off as gasses, and the electrodes themselves may dissolve. These and other effects all serve to change the nature of the solution at the electrode, impacting the measured conductivity.

So how do conductivity probes get around this problem? They, in fact, use an AC current rather than DC. Using fields that oscillate, there is no overall movement of ions toward one electrode or the other. The ions move one way for a tiny fraction of a second, and then back the other direction for the second half of the cycle. Overall, the solution and electrodes stay unchanged and the conductivity is accurately measured. Modern conductivity meters use complex AC waveforms to minimize additional complications such as capacitance, which can interfere with simple conductivity measurements.

In practice, commercial conductivity probes have either two or four electrodes, with the four-electrode version being more resistant to fouling and other effects that can cause degradation of the measurement. The electrodes are made of nonreactive materials such as epoxy/graphite, glass/platinum or stainless steel. The choice depends primarily on the nature of the solution to be tested. For occasional use in seawater, all of these are acceptable.

One final complication is that the conductivity of ions in water depends upon temperature. There are a number of factors that cause this in seawater, but one big one is simply that the ions are naturally moving around faster as they get warmer. When the same number of ions are moving faster, the apparent conductivity is increased. The conductivity of seawater at 41 degrees Fahrenheit, for example, is a little over half of that at 56 degrees. For this reason, all conductivity meters simultaneously measure the conductivity and the temperature. The internal electronics then take the temperature into account, and normally provide a value that is "corrected" to what the conductivity would be at a standard temperature (47 degrees). Consequently, you can measure the salinity of water regardless of the temperature of the sample.

The exact dependence of the conductivity of seawater on temperature is well known, and some meters use this exact relationship. Other use a slightly different correction — that for simple aqueous solutions. Still others provide several temperature correction options. The closer that you are to 47 degrees, the smaller the correction is and the less important the nature of the correction used. Nevertheless, if you have a choice, select the correction used for seawater. If you don't, you won't be far off.

Commercial conductivity meters range from about a hundred dollars to several thousand. For typical marine aquaria purposes, most lower end models are likely adequate. If you are going to take the plunge and buy a conductivity meter, make sure that it spans the range of interest to you. Full strength seawater has a conductivity of 53 mS/cm (milliSiemens per centimeter), so the range should include this value. Some conductivity meters are designed only for use in lower conductivity solutions, and while these have their uses, they won't work for seawater salinity.

Finally, if you are going to manage the salinity in an aquarium based on conductivity, you should get a conductivity standard with which you can either calibrate or confirm the proper operation of the meter. Some meters permit calibration and others do not. The ability to calibrate is not necessarily a sign of a higher quality unit, with some very high performance units not permitting calibration. Conductivity is, in a sense, an absolute measurement, and calibration isn't always necessary. Further, a meter permitting calibration is also, by definition, one permitting miscalibration. Nevertheless, confirmation with a known standard is always a good idea. Standards are relatively inexpensive and can be obtained from most sources that sell meters. Be sure, however, to get a calibration solution that is in the range of the measurement that you are taking (say, between 20 and 70 mS/cm).

If the meter reads in conductivity units (mS/cm) you may want to convert that into seawater salinity. Some manufacturers provide conversion tables, and there are many available in reference books such as the CRC Handbook of Chemistry and Physics. More simply, however, you may choose, as I do, to simply target natural seawater (35 parts per thousand; ppt) with a conductivity of 53 mS/cm. To bracket this figure, a salinity of 30 ppt has a conductivity of 46 mS/cm, and 40 ppt has a conductivity of 60 mS/cm.

As you might have guessed by this point, conductivity probes have other uses as well. One of my favorites is to measure the concentration of limewater, but that’s another story for another day....