Calibrating Ion-Selective Electrodes: The Difference Between Activity and Concentration

January 2013

eureka™
water probes

Here's the short answer:

The more ions trying to move around in a water solution, the more they get in each other's way and so decrease all the ionic "activity". An ion-selective electrode (ISE) measures an ion's activity, which is always a lower than the ion's real concentration. The number on the bottle of an ISE calibration solution is the activity of the specified ion. When you calibrate an ISE, you have to type in that activity number because the Manta knows the ISE isn't smart enough to give a concentration number. Then the much-smarter Manta uses the solution's conductivity reading to estimate how much it needs to boost the ISE's activity reading to produce a concentration reading. That's why the reading immediately after calibration is higher than the calibration number you had just typed in.

Ionic Concentration

If you stir 0.05 milligrams (mg) of table salt (sodium chloride, NaCl) into 1 liter of pure water, then clearly you have a concentration of 0.05 mg/liter of NaCl. But what is the chloride concentration? We know that sodium and chlorine have molecular weights of 11 and 17 respectively. So:

- 17 / (11 + 17) = 61%, meaning that the chloride ion makes up 61% of the weight of NaCl

- 61% (0.05 mg/l) = 0.03 mg/l, meaning that the chloride ion concentration in your solution is 0.03 mg/l (and we can assume that the sodium ion makes up 0.02 mg/l, in case anyone asks)

Standard analytical chemistry methods can be used to confirm the chloride concentration.

Chemical Activity

Suppose you are a guy running laps at the gym. There are only two other guys running laps, so you can run as fast as you want in any direction you want. But suppose it's just after New Year's and the gym is offering membership discounts. Suddenly, 2000 women show up to run laps in the gym at the same time you're running. Now, you have to run a lot slower to avoid hitting someone.

Notice that the concentration of guys remained constant at 3 guys per gym. But their activity decreased markedly when the concentration of women jumped to 2000 women per gym. It's the same way with ions. If you dump a double handful of calcium carbonate (CaCO3) into that solution with the 0.03 mg/l chloride ion concentration, the chloride ion concentration does not change. But, like the guys in the gym, the chlorides just can't move around like they used to – the crowding causes a reduction in their activity. We professional chemists refer to this phenomenon of activity as "activity".

Even after adding the CaCO3, those standard analytical chemistry methods mentioned earlier will still correctly tell you that the chloride ion concentration is 0.03 mg/l. But a chloride ISE will not tell you 0.03 mg/l, because it measures activity, not concentration. The more CaCO3 you dump in, the more the activity of the chloride drops, and the more the reading from the chloride ISE falls away from the concentration value.

What to do?

If you knew how much CaCO3 you dumped into the water containing 0.03 mg/l chloride ion, you could calculate the activity coefficient, and use it to convert a chloride ISE's activity reading into a concentration reading, i.e. 0.03 mg/l. A solution containing only a vanishingly small amount of some salt would have an activity coefficient of 1.00; as you add more and more salt, the activity coefficient decreases. (If you're interested, google DeBye-Hückel to see how activity coefficients are calculated.)

Suppose you've got a solution for which you calculated an activity coefficient of 0.85, and your chloride ISE is giving a reading of 2 mg/l. Because the activity coefficient is less than one, you know that the chloride ISE's activity reading is going to be less than the real concentration. Here's all you have to do:

2 mg/l / 0.85 = 2.35 mg/l

So the actual concentration is 2.35 mg/l, not 2 mg/l like that lyin' ISE said.

But what if I don't know how much of what chemicals are in my water sample?

I assume that if you're reading this you are the proud owner of a Eureka Environmental Manta multiprobe, the finest water-quality analyzer in the world, and that your Manta is equipped not just with an ISE, but with a conductivity sensor as well. The Manta uses the conductivity reading, which is gross indicator of ionic activity in the water, to estimate the activity coefficient and then corrects the ISE's reading. This correction is not perfect, because some ions have a greater effect on the activity coefficient than others - but it's not half bad considering you are the one who doesn't know what's in your own water.

By the way, the activity-killing ions don't have to be another type of ion. If you have a high concentration of chloride ions in your water, they will get in each other's way just like any other ion would. But that's taken care of using Eureka's conductivity estimation of activity coefficient.

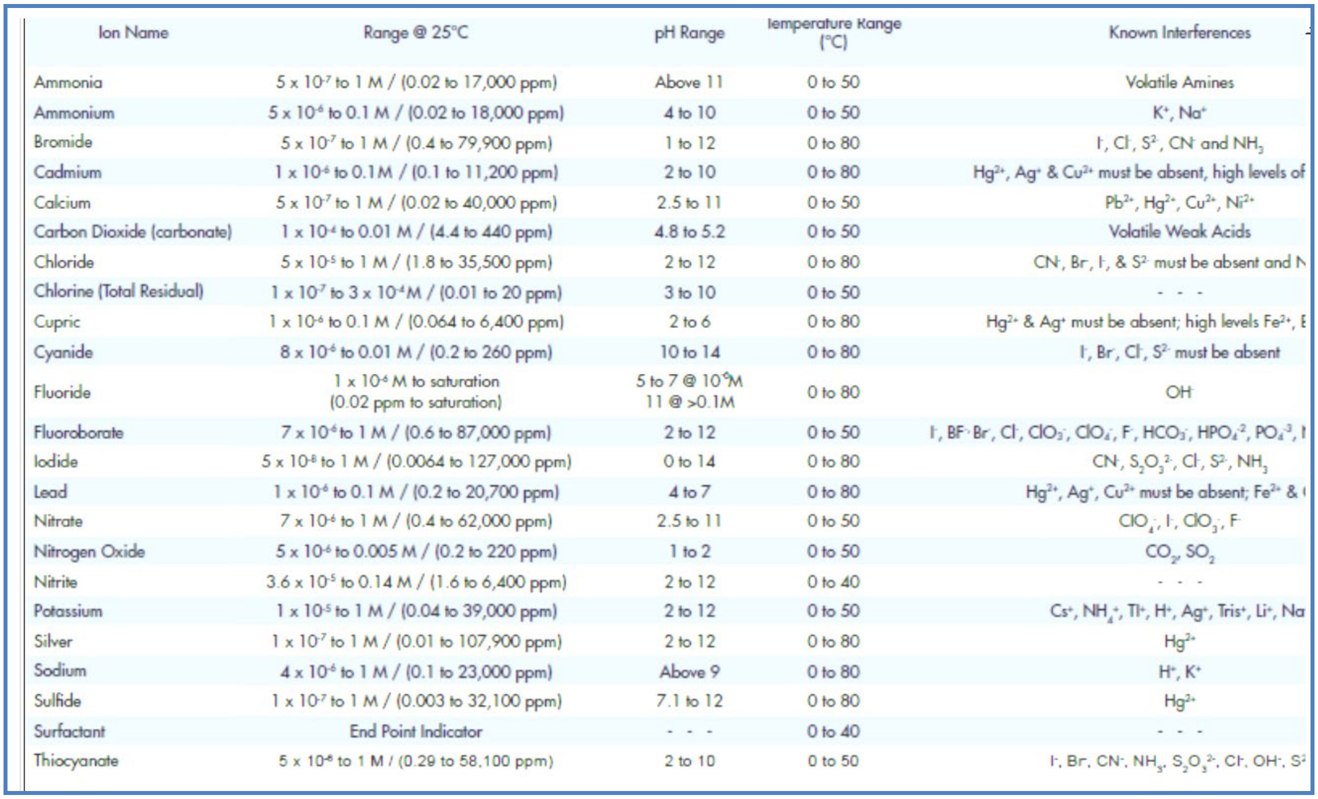
So how does that affect calibration of an ion-selective electrode?

The number marked on an ISE calibration bottle is the activity of the ion in question, not the ion's concentration. So that's the number you type in as the calibration value. But the Manta automatically estimates the activity coefficient from the calibration solution's conductivity, and corrects the ISE reading from activity to concentration. That's why the reading just after calibration is higher than the calibration number you just typed in.

For instance, a bottle of 5 mg/liter nitrate concentration has an activity of 4.63 mg/l, and that what it says on the bottle because that's what the nitrate ISE will read. So when you calibrate with that solution, you type in 4.63. When you hit the calibrate button, the Manta knows the ISE reading is low, so it corrects it with the activity coefficient it estimated from the conductivity of the calibration solution, to around 5 mg/l – the true concentration of nitrate ion in the calibration solution. So your reading correctly jumps from 4.63 to 5 when you calibrate.

If you then go to the field to make nitrate measurements, the Manta will continuously correct the nitrate ISE readings with activity coefficients calculated from concurrent conductivity readings.

And while we're talking about ISE's, here's a chart of common electrodes and their interferences:



Ion Name	Range @ 25°C	pH Range	Temperature Range (°C)	Known Interferences
Ammonia	5 x 10^{-7} to 1 M / (0.02 to 17,000 ppm)	Above 11	0 to 50	Volatile Amines
Ammonium	5 x 10^{-6} to 0.1 M / (0.02 to 18,000 ppm)	4 to 10	0 to 50	K^+, Na^+
Bromide	5 x 10^{-7} to 1 M / (0.4 to 79,900 ppm)	1 to 12	0 to 80	I^-, Cl^-, S^{2-}, CN^- and NH_3
Cadmium	1 x 10^{-6} to 0.1M / (0.1 to 11,200 ppm)	2 to 10	0 to 80	Hg^{2+}, Ag^+ & Cu^{2+} must be absent, high levels of
Calcium	5 x 10^{-7} to 1 M / (0.02 to 40,000 ppm)	2.5 to 11	0 to 50	Pb^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}
Carbon Dioxide (carbonate)	1 x 10^{-4} to 0.01 M / (4.4 to 440 ppm)	4.8 to 5.2	0 to 50	Volatile Weak Acids
Chloride	5 x 10^{-5} to 1 M / (1.8 to 35,500 ppm)	2 to 12	0 to 80	CN^-, Br^-, I^-, & S^{2-} must be absent and
Chlorine (Total Residual)	1 x 10^{-7} to 3 x 10^{-4}M / (0.01 to 20 ppm)	3 to 10	0 to 50	- - -
Cupric	1 x 10^{-6} to 0.1 M / (0.064 to 6,400 ppm)	2 to 6	0 to 80	Hg^{2+} & Ag^+ must be absent; high levels Fe^{2+},
Cyanide	8 x 10^{-6} to 0.01 M / (0.2 to 260 ppm)	10 to 14	0 to 80	I^-, Br^-, Cl^-, S^{2-} must be absent
Fluoride	1 x 10^{-6} M to saturation (0.02 ppm to saturation)	5 to 7 @ 10^{-6}M 11 @ >0.1M	0 to 80	OH^-
Fluoroborate	7 x 10^{-6} to 1 M / (0.6 to 87,000 ppm)	2 to 12	0 to 50	I^-, BF^- Br^-, Cl^-, ClO_3^-, ClO_4^-, F^-, HCO_3^-, HPO_4^{-2}, PO_4^{-3},
Iodide	5 x 10^{-8} to 1 M / (0.0064 to 127,000 ppm)	0 to 14	0 to 80	CN^-, $S_2O_3^{2-}$, Cl^-, S^{2-}, NH_3
Lead	1 x 10^{-6} to 0.1 M / (0.2 to 20,700 ppm)	4 to 7	0 to 80	Hg^{2+}, Ag^+, Cu^{2+} must be absent; Fe^{2+} &
Nitrate	7 x 10^{-6} to 1 M / (0.4 to 62,000 ppm)	2.5 to 11	0 to 50	ClO_4^-, I^-, ClO_3^-, F^-
Nitrogen Oxide	5 x 10^{-6} to 0.005 M / (0.2 to 220 ppm)	1 to 2	0 to 50	CO_2, SO_2
Nitrite	3.6 x 10^{-5} to 0.14 M / (1.6 to 6,400 ppm)	2 to 12	0 to 40	- - -
Potassium	1 x 10^{-5} to 1 M / (0.04 to 39,000 ppm)	2 to 12	0 to 50	Cs^+, NH_4^+, Tl^+, H^+, Ag^+, $Tris^+$, Li^+, Na
Silver	1 x 10^{-7} to 1 M / (0.01 to 107,900 ppm)	2 to 12	0 to 80	Hg^{2+}
Sodium	4 x 10^{-6} to 1 M / (0.1 to 23,000 ppm)	Above 9	0 to 80	H^+, K^+
Sulfide	1 x 10^{-7} to 1 M / (0.003 to 32,100 ppm)	7.1 to 12	0 to 80	Hg^{2+}
Surfactant	End Point Indicator	- - -	0 to 40	- - -
Thiocyanate	5 x 10^{-6} to 1 M / (0.29 to 58,100 ppm)	2 to 10	0 to 50	I^-, Br^-, CN^-, NH_3, $S_2O_3^{2-}$, Cl^-, OH^-,

Problems? No problem. E-mail us at wq.support@meas-spec.com or call 512-302-4333, Ext 1111.

EUREKA WATER PROBES

2113 WELLS BRANCH PARKWAY

AUSTIN TX 78728 512-302-4333

WWW.WATERPROBES.COM