

Ion-Selective Electrodes: What's the Difference Between Activity and Concentration?

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 lower than the ion's actual 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 designed to give a concentration number. Then the Solinst Eureka Manta Multiprobe 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 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:

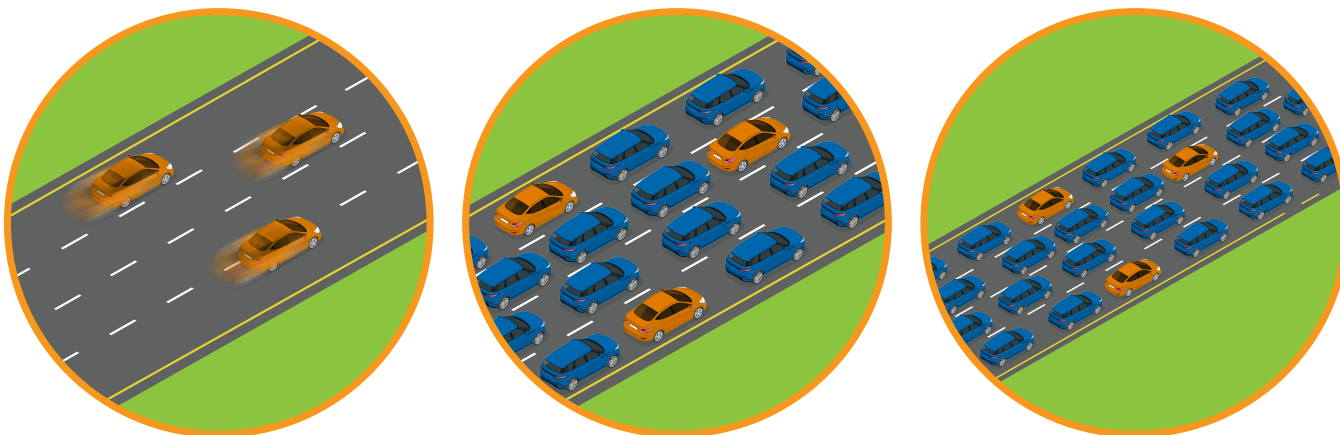
- $17 / (11 + 17) = 61\%$, meaning that the chloride ion makes up 61% of the weight of NaCl
- $61\% (0.05 \text{ mg/l}) = 0.03 \text{ mg/l}$, meaning that the chloride ion concentration in your solution is 0.03 mg/l (and we can assume that the sodium ion makes up 0.02 mg/l)

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

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Chemical Activity

Suppose three orange cars are driving on an otherwise empty highway. There is plenty of room so they can drive fast and change lanes easily. But suppose it's rush hour and 2000 blue cars show up suddenly on the same highway. Now, the orange cars must move a lot slower and be much more careful not to hit any other cars.



Notice that the concentration of orange cars remained constant at three on the highway. But their activity decreased markedly when the concentration of blue cars jumped to 2000 on the highway. It's the same way with ions. If you dump a double handful of calcium carbonate (CaCO_3) into that solution with the 0.03 mg/l chloride ion concentration, the chloride ion concentration does not change. But, like the orange cars on the highway, the chlorides just can't move around like they used to – the congestion causes a reduction in their activity. That reduction in activity changes how an ISE "sees" the ion.

Even after adding the CaCO_3 , 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 CaCO_3 you dump in, the more the activity of the chloride ion drops and the more the reading from the chloride ISE falls away from the concentration value. Fortunately, the Manta fixes that problem.

What to do?

If you know how much CaCO_3 you dumped into the water containing 0.03 mg/l chloride ion, you can 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 and the gap between the activity and the concentration widens. (If you're interested, look up Debye-Hückel to see how activity coefficients are calculated.)

Suppose you have a solution for which you calculate an activity coefficient of 0.85, and your chloride ISE gives 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 what to do:

$$2 \text{ mg/l} / 0.85 = 2.35 \text{ mg/l}$$

So the actual concentration is 2.35 mg/l, not 2 mg/l that the ISE read.

What if it is not known how much of what chemicals are in the water sample?

If you have a Manta with an ISE, it should also include a conductivity sensor. The Manta uses the conductivity reading, which is a gross indicator of ionic activity in the water, to estimate the solution's activity coefficient and then corrects the ISE's reading as described above. This correction is not perfect, because some ions have a greater effect on the activity coefficient than others – but it's a decent fix, especially since it is not known what is actually in the water.

The “activity-reducing” 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 they would with any other ion. But that's taken care of using the Manta's conductivity estimation of activity coefficient.

So how does the difference in between activity and concentration affect the calibration of an ISE?

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 certain bottle of 5 mg/liter nitrate solution has an activity of 4.63 mg/l, and that's what it says on the bottle because that's what a 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 readings with activity coefficients calculated from concurrent conductivity readings. Your data will be in terms of concentration.

Common Electrodes and Their Interferences

ISE's – Ion-Selective Electrodes – are often not quite as selective as their name might imply. They often have trouble distinguishing between the ion they are supposed to be measuring and ions of similar size and charge. For instance, a nitrate ISE is designed to be selective for NO_3^- but it is also, to a lesser extent, sensitive to Cl^- (chloride). The extent to which similar ions interfere with the measurement of an ISE's intended analyte is called the Selectivity Coefficient (SC).

For example, chloride's selectivity coefficient for a nitrate sensor is 0.006. Multiply that by 100 to get 0.6% tells you that the nitrate sensor's reading is increased by 0.6% of the chloride present. That may not seem like much, but if you are using the nitrate sensor in sea water, the sea water's high concentration of chloride swamps normal nitrate concentration and your nitrate ISE reading is worthless. Other ISE's have interferences with higher SC's. For instance, the potassium (K^+) SC for an ammonium (NH_4^+) sensor is 0.1, meaning that 10% of any potassium present in a water sample shows up in the ammonium sensor's reading.

*This list of selectivity coefficients (SC) will help you decide whether or not your analysis is being compromised by the presence of other ions that you do not wish to measure.

Ammonium: Potassium (0.1), Sodium (0.002), Magnesium (0.0002), Calcium (0.00006), Lithium (0.00003).

Bromide: Chloride (0.002), Hydroxyl (0.00003). Silver, Cyanide, Sulphide and Iodide must be absent.

Cadmium: Iron (10) or Lead (10) these should be less than 1 /100th of the Cadmium concentration. Silver, Sulphide, copper and Mercury must be absent.

Calcium: Iron Fe^{+2} (0.02) Strontium (0.008), Barium (0.005) Copper (0.002), Sodium, (0.0005), Mg (0.0006), K (0.00005), NH_4^+ (0.00003), Lithium (0.00001), Al^{+3} (5) Only tolerated in low concentrations.

Chloride: Iodide, Bromide, Cyanide, Sulphide, Silver must be absent, or only present in insignificant amounts compared to the Chloride ion.

Copper: Bromide (>1), Chloride (>1). Silver, Sulphide and Mercury must be absent.

Cyanide: Silver, Sulphide and Iodide should not be present

Fluoride: Hydroxyl (0.1)

Iodide: Bromide (0.0004), Chloride (0.000001). Silver Sulphide and Iodide should be absent.

Lead: Cadmium (>1) . Silver Sulphide, Copper, Iron II, Iron III and Mercury Should be absent.

Mercury: Silver and Sulphide must be absent

Nitrate: Chloride (0.006) Bicarbonate (0.005), Nitrite (0.001), Acetate (0.0005), Fluoride (0.0001), Sulphate (0.00001).

Nitrite: Acetate (0.001), Fluoride (0.0008), Chloride (0.00005), Nitrate (0.00001), Sulphate (0.00001). Cyanide must be absent

Perchlorate: Thiocyanate (0.03), Iodide (0.02), Nitrate (0.02), Chloride (0.0003), Phosphate (0.0002), Acetate (0.0001).

Potassium: Rubidium (2), Caesium (0.4), Ammonium (0.01), Sodium (0.0004), Calcium (0.0003), Magnesium (0.0003), Lithium (0.0001).

Silver: Sulphide and Mercury should be absent or in very low concentrations relative to Silver

Sodium PVC: Potassium (0.6), Ammonium (0.2), Calcium (0.02), Magnesium (0.03).

Sulphide: Silver and mercury should be absent

Thiocyanate: Silver, Sulphide, Chloride and Iodide must be absent. Small interference from Bromide and Thiosulphate.

*source: <https://edt.co.uk/ise-selectivity>