Water Analysis: Some definitions

Reading assignment: Pages 13, 45-50; 289 in Drever, J. I., 1997. The geochemistry of natural waters. Prentice Hall.

Water is seldom pure: it is a good **solvent**, containing many **solutes**

Expressing concentrations of solutes:

- mg/L
- ppm: same as mg/L if the solvent is pure water with density of 1.
- Molarity
- Molality
- gm equivalent weight.
- Normality: Is the number of gm equivalents of compound/ ions/ radicals per liter of solution. Note that the sum of normalities of +ve ions = that of –ve ions.
- Non-ionic dissolved species such as silica cannot be expressed in meq/L.
- Activity vs. concentration

TDS:

Fresh: < 1000 ppm; Slightly saline: 1000 – 3000 ppm; Moderately saline: 3000 – 10000 ppm; Very saline: 10,000 – 35,000 ppm; Brine: > 35,000 ppm
Drinking water: $\leq$ 500 ppm; potable up to 2000 ppm; Sea water: 35,000 ppm; Groundwater: 100 – 300,000 ppm.

Conductivity:

- Conductance is the reciprocal of resistance.
- Conductance is expressed in "Seimens" (formerly known as "mho").
- Conductivity is the "specific conductance" (measured between 2 opposite faces of a 1 cm cube of material).
- Conductivty (μS/cm) = 1/ resistivity (ohms – cm).
- Conductivity is an indirect measure of the TDS. Relationship is given by:

$$\text{ppm TDS} = \text{conductivity } (\mu\text{S/cm}) .\ 0.66$$

Hardness:

Definition: Hardness is the total # of mg/L of "equivalent $CaCO_3$". The term "equivalent $CaCO_3$" = 100/40 Ca^{2+} + 100/24 Mg^{2+} expressed in mg/L.
In other words, hardness is the mgm equivalents of Ca^{2+} + Mg^{2+} per liter of solution "assuming that the solution contains only $CaCO_3$". To understand how this formula was derived, we can express hardness as:

$$(\#\text{ of equivalents of } Ca^{2+} + Mg^{2+}) .\ \text{gm equivalents of } CaCO_3$$

i.e.

$$[\{(\text{mg/L } Ca^{2+}/40) .\ 2\} + \{(\text{mg/L } Mg^{2+}/24) .\ 2\}] .\ 100/2$$

Water types according to hardness:

- 0-60: soft
- 61-120: moderately hard
- 121 – 180: hard
- >180: very hard.

Charge balance, Cation / anion ratio and charge balance error (Table 1b)

- Any solution has to be electrically neutral. This means that the concentration of anions has to be balanced by (i.e. equal to) that of the cations.
- Charge balance: be careful when expressing the concentrations of multivalent ions!!!!
- Cation/anion ratio should be very close to 1.
- Charge balance error should be $\leq$ 5%.

Alkalinity

Alkalinity is the equivalent sum of bases that are titratable with a strong acid. Although all solutions are electrically neutral, the concentration of the strong bases is not necessarily equal to that of strong acids. This is simply because there are many ionic species in solution, and strong bases can be "balanced" by weak acids. Alkalinity is the difference between the concentration of strong basic and acidic radicals. However, note that ions like Na+, Ca+2, K+, Cl^-, ... etc. are considered "conservative" ions as their concentrations are not affected by pH, P, or T. Therefore, another way of defining alkalinity is:

Alkalinity = Σ conservative cations - Σ conservative anions

If Na^+ and Cl^- are the only strong basic and acidic ions in solution, then alkalinity is defined as:

Alkalinity = $[Na^+] – [Cl^-]$.

Applying charge balance constraints and rearranging:

Alkalinity = $[HCO_3^-] + 2[CO_3^{-2}] + [H_3SiO_4^-] + [HS^-] + ... +[OH^-] – [H^+]$

In most natural waters, alkalinity = $[HCO_3^-] + 2[CO_3^{-2}]$, since all other species occur in very low concentrations. This is known as "carbonate alkalinity".

Acidity:

Is the amount of base required to raise the pH of the solution to the bicarbonate end-point.

Acidity = - alkalinity.

III- Chemical constituents of water

- Major constituents: 7 constituents comprising > 99% of the TDS. Their concentrations exceed 5 mg/L.
- Minor constituents: 0.01 – 10 mg/L
- Trace constituents: < 0.1 mg/L.

IV- Graphical representation of water chemistry

- Piper diagrams (see attached figure): meq/L, normalized! Always a good idea to double check results with a CBE calculation.