

ANION-CATION BALANCES

Introduction

An anion is a negatively charged group eg Cl^- , NO_3^- , SO_4^{2-}

A cation is a positively charged group eg H^+ , NH_4^+ , Ca^{2+}

As an aqueous solution is always electrically neutral, the sum (in milliequivalents/litre) of the anions and the cations should always balance. In addition, the magnitude of the concentration of anions and cations is related to the electrical conductivity (EC, 25°C) of the solution.

Ideally, therefore, we can state:

anions (meq/L) = cations (meq/L) = approx EC/10 (mS/m)

A Basic Anion/Cation Balance Suite

The commonest ions which would need to be included in a minimal ion balance are;

anions HCO_3^- (from pH, alkalinity), Cl^- , SO_4^{2-} possibly NO_3^- , H_2PO_4^- (from DRP), CO_3^{2-} (also from pH, alkalinity)

cations Na, K, Ca, Mg possibly NH_4^+ , Fe, H^+ (from pH)

Units of Measurement

Electrical conductivity is usually reported in “milliSiemens/metre (mS/m)”. Convert from other units as shown in the table below.

To convert from	to mS/m, multiply by
$\mu\text{S/cm}$	0.1
$\mu\text{mho/cm}$	0.1

Laboratories will usually report the **concentration of anions and cations** as “grams per cubic metre ($\text{g}\cdot\text{m}^{-3}$)”. This is the same as milligrams per litre (mg/L) and is an example of a weight per volume unit. For an anion/cation balance we need everything converted to an “electrical charge per volume” basis, the appropriate unit for this being “milliequivalents per litre (meq/L)”.

To carry out this conversion we need to know the relationship between the mass and the charge for each species. Some examples are shown in the following table.

Ion	Charge	Mass	Equivalent Wt	Multiply by (to convert g.m ⁻³ to meq/L)
H ⁺	1	1	1.0	1.0
Na ⁺	1	23.0	23.0	0.0435
K ⁺	1	39.1	39.1	0.0256
Ca ²⁺	2	40.1	20.05	0.0499
Mg ²⁺	2	24.3	12.15	0.0823
Fe ²⁺	2	55.9	28.0	0.0357
Zn ²⁺	2	65.4	32.7	0.0306
NH ₄ ⁺ (as N)	1	14.0	14.0	0.0714
HCO ₃ ⁻	1	61.0	61.0	0.0164
CO ₃ ²⁻	2	60.0	30.0	0.0333
Cl ⁻	1	35.5	35.5	0.0282
F ⁻	1	19.0	19.0	0.0526
SO ₄ ²⁻	2	96	48.0	0.0208
NO ₃ ⁻ (as N)	1	14.0	14.0	0.0714
H ₂ PO ₄	1	97	97	0.0103

To convert from g.m⁻³ to meq/L, the following formula is used.

$$\text{meq/L} = \frac{[\text{g.m}^{-3}] \times \text{charge}}{\text{mass}} = \frac{[\text{g.m}^{-3}]}{\text{equivalent wt}}$$

These factors are shown in the above table.

Once all results are in meq/L, the anions and cations can be summed separately, and compared. Please note that the result reported for the '% Difference in Ion balance' is an absolute difference between the 'Sum of Anions' and 'Sum of Cations' based on the formula taken from APHA. This does not indicate whether the 'Sum of Anions' or the 'Sum of Cations' produced a higher value.

Interpretation of Results

The anions and cations should be totalled as discussed above, and compared to the EC. If all match, then there is no problem.

If only anions and EC match, then there is a problem with cations. If these are low, then are there indications of other cations which could affect this reading (eg NH₄N, Fe, Zn, other metals). If the cations are high then check that any metals, particularly Ca, Mg and Fe were analysed as the 'dissolved', not 'total' fraction. A total digestion will dissolve metals from any suspended solids, elevating the cations.

If only cations and EC match, but anions are low, then check for anions which may be missing from the calculation (eg CN, F, OH, organic acids). High anions may also arise from ions being adsorbed onto suspended solid material.

If EC is much lower than anions and cations, then are the Ca and SO₄ (or DRP) results high? Calcium sulphate and calcium phosphate do not ionise well, so under contribute to EC from what would be expected from their individual concentrations.

A mis-match of anions, cations and EC may also be due to a laboratory error. If this is suspected then please ask the laboratory to check their results.

Criteria for Acceptance (ex APHA)

Calculate the % difference using:

$$\% \text{ Difference} = 100 \frac{\Sigma \text{cations} - \Sigma \text{anions}}{\Sigma \text{cations} + \Sigma \text{anions}}$$

Criteria for acceptance for **clean water** samples are (note that acceptable limits for 'dirty' waters may be much wider);

Anion sum (meq/L)	Acceptable % Difference (Clean waters only)
0-3.0	±0.2 meq/L
3.0-10.0	±2%
10.0-800	±5%

ASTM Standard D 596-83 states "With careful work, the difference will not generally exceed 2% of the total cations or anions for a water containing 250-1000 mg/L (about 4-15 meq/L) of dissolved salts, A somewhat larger percentage can be tolerated if the sum of the cations and anions is less than about 5.00 meq/L."

Total Dissolved Salts (TDS) can be approximated from:

$$\text{Approximate TDS} = 10 \times \text{EC (mS/m)} * 0.67$$

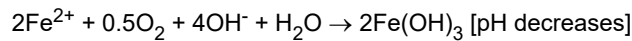
Note that this is **NOT** Total Dissolved **Solids** as any dissolved unionised compounds, eg sugars, will not be included.

Factors which can affect Anion/Cation Balance

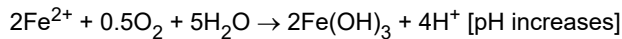
There are a large number of factors which can affect the ion balance, and these should be taken into account when interpreting the results. Factors which we have found from experience include;

1. **Suspended solids.** Bicarbonate is calculated from alkalinity. Alkalinity is determined by titration. If there are carbonates present in the suspended solids they will slowly dissolve during the titration, giving a higher reading for alkalinity, and hence bicarbonate i.e. the anions will be high. Cations adsorbed to the suspended solids may also exchange with the H⁺ titrant, again elevating the apparent alkalinity of the sample.
2. **Filtering the sample.** If the alkalinity and pH are determined off a filtered sample (eg when trying to overcome the problem from 1), some of the volatile CO₂ may have been lost (or some may have been gained) during filtering. This will change the pH (and, to a small degree in most samples, EC) The solution seems to be to take great care when collecting the samples so there is no suspended solids, or, as a final resort, centrifuge the sample to remove SS.
3. **Species not included in the calculation.** For example, the following species which are not usually included in an anion/cation balance calculation because they are not commonly present at significant levels, but which can affect the ion balance.
 - a) **Inorganics**
 - a) fluoride
 - b) lithium (especially geothermal waters)
 - c) soluble Fe
 - d) Silica (present as silicates)
 - e) boron (present as borates, especially geothermal waters)
 - b) **Ionisable organic compounds such as;**
 - a) VFA (Short chain volatile fatty acids. Often found around effluent ponds and landfills)
 - b) Lactic acid (we found from an old dairy company site)
 - c) proteins and small peptides (also found from a dairy company site)

4. Ground Waters high in Fe²⁺ react with Oxygen



or



5. Electric Conductivity (EC)

EC is very temperature dependent (about 2%/°C for groundwaters, but varying with the composition of the water). If field EC is used for the comparison this must be borne in mind. Most EC meters have an integral temperature sensor and correct to 25°C.

6. Different sample containers

pH, EC, alkalinity, NO₃, Cl, SO₄, DRP, Na, K, Ca and Mg are all analysed from an unpreserved sample. This may be filtered for analysis of Na, K, Ca and Mg. NH₄ may be analysed from a sulphuric acid preserved sample and metals from a nitric acid preserved sample. Other ions may have other preservatives (eg NaOH for CN). Subsampling into these different containers can lead to variations which may need to be taken into account eg main sample collected into a large container, then poured into smaller containers which have the preservative. If sediment settles out at a variable rate during this process, the results will be affected.