



Ion Balance

Data Quality Validation for Metals & Anions in Waters

What is Ion Balance?

An inherent property of all natural waters is that they are electrically neutral. Analytical testing laboratories and their clients can utilize this property as a powerful quality assurance measure and validation tool when test results are available for all of the major dissolved cations and anions commonly found in natural waters.



How is Ion Balance Calculated?

To measure Ion Balance, one compares the overall positive charge with the overall negative charge of all major ionic substances measured in a water sample - understanding that in fact charge balance must exist. To compare anionic and cationic charges, measured ion concentrations are first converted to milliequivalents per litre (meq/L) by dividing measured mg/L concentrations by the equivalent molar mass of each ion (molar mass divided by ionic charge of the most common species). Iron and Manganese are both assumed to have charge of +2, because the ferrous and manganous species of these elements are the primary water soluble forms.

Positively-charged ion concentrations are summed to obtain a Cation Sum, and negatively-charged ions are summed to obtain an Anion Sum. ALS Canada computes Cation and Anion sums using the species shown in Table 1 (optional ions shown are included if test results are available). Calcium,

Primary Cation Sum Components	Primary Anion Sum Components
Calcium	Total Alkalinity
Magnesium	Sulfate
Sodium	Chloride
Potassium	
pH (H ⁺)	
Optional Cations	Optional Anions
Ammonium	Fluoride
Aluminum	Nitrate
Copper	Nitrite
Iron	
Manganese	
Zinc	

Table 1. Ion Balance Calculation Components

Magnesium, Sodium, and Potassium are normally the major cations in most waters (plus pH for acidic samples). Total Alkalinity (as CaCO₃), Sulfate, and Chloride represent the major anions in most waters. Total Alkalinity is a titration test, and includes Bicarbonate (HCO₃⁻), Carbonate (CO₃²⁻), Hydroxide (OH⁻), as well as weak acid radicals such as Silicate, Phosphate, and Borate (Friedman, 1982).

Expression of Ion Balance: Two Conventions

The industry standard convention (based on APHA Method 1030) is to express Ion Balance as Cation - Anion Balance (as shown in Figure 1).

$$\text{Ion Balance (APHA)} = \frac{(\text{Cation Sum} - \text{Anion Sum}) \times 100\%}{(\text{Cation Sum} + \text{Anion Sum})}$$

Figure 1. Cation - Anion Balance as per APHA 1030

For potable drinking waters, anion and cation test results are generally considered to be balanced if the Cation - Anion Balance is between -5% to +5%, but this range is inappropriate for more complex sample types or at trace levels. For general environmental waters including groundwaters, wastewaters, effluents, and surface waters, ALS uses criteria of -10% to +10% for the expected range of Cation - Anion Balance, and samples outside this range are investigated for potential data quality issues or individual test bias.

In Alberta, the historical convention is to calculate Ion Balance as the ratio of Cation Sum to Anion Sum, where 100% represents perfect balance, as shown in Figure 2. ALS recommends the Cation - Anion Balance measure for Ion Balance, which is the industry standard convention published by APHA. Moving forward, ALS will report the APHA convention by default, but both the APHA and Alberta versions may be provided by request (for consistency with historical reports).

For the Alberta Ion Balance (Cations/Anions) convention, measures of 90-110% are considered to be balanced for potable drinking waters, and general environmental water samples can be considered balanced between 80-120%.

Causes of Apparent Imbalance in Waters

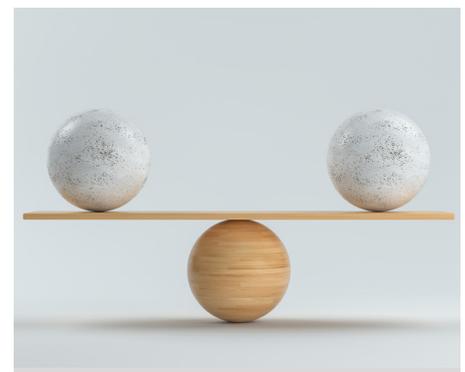
The primary reasons for evaluating Ion Balance are to validate the quality of test results for anions and cations in waters (to identify potential anomalies from sampling or from lab testing), and to recognize where un-tested analytes may be present that contribute significantly to ionic composition. Laboratories use Ion Balance evaluations to flag test results for additional quality reviews or confirmations, which can help to identify rare problems like sample mix-ups or labelling errors (either from field sampling or lab errors), or dilution or calculation errors. End users of laboratory test results can also use Ion Balance to identify whether additional testing is needed for important ionic substances in samples where testing may have been missed.

A common misconception is that Ion Balance measures outside the expected or ideal range are unacceptable because they indicate laboratory errors. This is an entirely false expectation; there are many legitimate reasons for imbalance in measured ion concentrations, many of which cannot be addressed (except sometimes by re-sampling or by additional testing), as explained below:

- Un-Measured Anions or Cations.** A common cause of apparent imbalance is un-measured (or unconsidered) ionic constituents. Only the most common anions and cations are considered in Ion Balance calculations. Significant concentrations of other un-measured or unconsidered ions will cause an apparent imbalance. For best results, analysis of all primary and optional anions and cations listed in Table 1 are recommended, but in some samples, other ions may also be present at significant levels, such as Lithium or Strontium - common in groundwaters in some parts of the world.
- Delayed Filtration &/or Sample Changes over Time.** Water samples for dissolved metals (major cations) must be field filtered and acid preserved (field or lab) to ensure cation test results represent conditions at time of sampling. If field filtration is not done, metals concentrations may be low-biased, and Ion Balance measures are unreliable - especially for anoxic waters, where dissolved Iron and Manganese tend to precipitate as hydroxides after air exposure. Anions are tested as quickly as possible on unpreserved samples, but in some samples (e.g. anoxic waters), concentrations may still change between sampling and analysis. If samples change over time, the earliest measurements are normally the most valid.

$$\text{Ion Balance (Cations/Anions)} = (\text{Cation Sum})/(\text{Anion Sum}) \times 100\%$$

Figure 2. Historical Alberta Ion Balance Calculation



- Suspended Solids / Turbidity.** High levels of Total Suspended Solids (TSS) or turbidity in waters frequently cause apparent imbalance. A common cause of imbalance is where suspended solids contribute to Alkalinity by titration (increasing the Anion Sum) but do not contribute to dissolved cation measurements.
- High TOC/DOC.** Samples with high levels of Total or Dissolved Organic Carbon may contain organic anions (e.g. Fulvic Acids) that are not included in Ion Balance evaluations.
- Use of Total Instead of Dissolved Metals.** Ion Balance is intended to assess only dissolved substances, however some ALS clients ask for Ion Balance to be calculated using Total Metals results, especially for drinking waters, where Dissolved Metals results may not be available. Ion Balance measures using Total Metals results are useful for pristine drinking waters, but Cation Sums may be biased high for samples with turbidity or suspended solids.
- Field Sampling Differences.** Major cations (metals) and anions are tested from independent sample bottles. Differences in the collection of these samples can sometimes be significant and may directly affect and confound Ion Balance measures.
- Samples with Low Ionic Strength.** Samples with low ionic strength may have test results near or below detection limits for some metals or anions, which increases the uncertainty of Ion Balance when measured as a percentage. Where Cation Sum or Anion Sum is < 2 meq/L, ALS advises that their absolute difference should be less than 0.4 meq/L for general environmental waters, or less than 0.2 meq/L for potable waters (unless influenced by other factors highlighted above).

Anions	Concentration		meq/L Calculation	meq/L Ionic Concentration
Chloride	2.4	mg/L	mg/L ÷ 35.5	0.3
Sulfate	628	mg/L	mg/L ÷ 48.0	13.1
Alkalinity	446	mg/L	mg/L ÷ 50.0	8.9
Fluoride	0	mg/L	mg/L ÷ 19.0	0.0
Nitrate-N	0	mg/L	mg/L ÷ 14.0	0.0
Nitrite-N	0	mg/L	mg/L ÷ 14.0	0.0
Anion Sum (AS), meq/L				22.4
Cations	Concentration		meq/L Calculation	meq/L Ionic Concentration
Calcium	108	mg/L	mg/L ÷ 20.0	5.4
Magnesium	38	mg/L	mg/L ÷ 12.2	3.1
Sodium	294	mg/L	mg/L ÷ 23.0	12.8
Potassium	21.2	mg/L	mg/L ÷ 39.1	0.5
Aluminum	0.02	mg/L	mg/L ÷ 8.99	0.0
Copper	0	mg/L	mg/L ÷ 31.8	0.0
Iron	0.84	mg/L	mg/L ÷ 27.9	0.0
Manganese	0.097	mg/L	mg/L ÷ 27.5	0.0
Zinc	0	mg/L	mg/L ÷ 32.7	0.0
Ammonia-N	4.07	mg/L	mg/L ÷ 14.0	0.3
pH	7.92	pH	$10^{-(pH-3)}$	0.0
Cation Sum (CS), meq/L				22.2
Ion Balance (APHA)				-0.4%
Ion Balance (Cations/Anions)				99.2%
Electrical Conductivity (EC, μ S/cm)				1950
Estimated Cation or Anion Sum (EC/100, \pm 20%):				19.5

Table 2. Example Ion Balance Calculations

Reviews of Test Results with Imbalance

Ion Balance is a powerful tool to validate ionic test results, or to identify potential data quality issues. When Ion Balance falls outside normal limits, ALS investigates associated test results, which may include raw data and calculation reviews, physical sample inspections, and re-analyses where possible. If no errors or anomalies are found, Ion Balance results outside normal limits are qualified to provide assurance that associated test results have been fully investigated.

Electrical Conductivity (EC) results can help to identify whether apparent imbalance is more likely due to bias or errors with either Cation or Anion measurements. *Divide Conductivity results (as $\mu\text{S}/\text{cm}$) by 100 to obtain estimates of Cation Sum and Anion Sum in meq/L from EC.* EC is a direct measure of ionic strength (at time of testing), and is less affected than other tests by factors such as TSS, turbidity, or sample matrix effects.

Because of the many valid reasons for apparent imbalance, ALS cannot guarantee that Ion Balance measures will always fall within any pre-defined range. For complex water samples where any of the above-listed causes of imbalance are likely to exist, ALS cannot conduct sample re-tests for the sole purpose of improving Ion Balance

measures, since this practice often detracts from the quality and validity of initial testing. Original test results that passed all associated Quality Control checks can only be revised with defensible evidence that re-test results are more accurate than the originals.

Detailed Ion Balance Calculations

A real-world example of Ion Balance calculations is shown in Table 2, where very good balance between Anion Sum and Cation Sum is illustrated. The most important major ions for most samples are highlighted. Understanding exactly how Ion Balance is calculated together with the confounding factors that can complicate its use provides you with the knowledge needed to interpret Ion Balance results, and to know when laboratory test results should be questioned.

Requesting Ion Balance on ALS Reports

To add Ion Balance calculations to ALS Canada test reports, please request test code EC101D, which requires analysis of Dissolved Metals, Alkalinity, pH, and Anions. Alternatively, request test code EC101T for drinking waters if only Total Metals results are available instead of Dissolved Metals. For best results, ALS recommends testing of all primary and optional ions shown

in Table 1; they will be automatically included in the Ion Balance calculation if analyzed. Please contact your ALS Canada Project Manager for more information.

References

APHA Standard Methods 1030E, Checking Correctness of Analyses, Standard Methods for the Examination of Wastewater, APHA/AWWA/WEF, July 2021.

Friedman, Linda C., Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments (Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, Laboratory Analysis, chapter A6), 1982.