Chloride

HYDROLAB

What is chloride?

Chloride, Cl - , is an ionized form of chlorine. Because most chloride salts are ubiquitous and highly soluble, chloride is one of the most common ions found in natural waters, and is the prevalent ion in seawater. Though not considered a nutrient, chloride is abundant in all living cells.

How is chloride measured?

Chloride ion concentration is measured with a number of traditional, wet-chemistry methods (titration), instrumentally (colorimeters), or by correlation with electrical conductivity measurements.

Chloride ion concentration is also measured with a chloride ion-selective electrode (ISE). The chloride ISE is a pellet of silver chloride in direct contact with the sample water. Because silver chloride has extremely low solubility in water, the silver chloride pellet never reaches chemical equilibrium with the sample water. Instead, a small amount of chloride ion dissolves into the sample. The resulting relative surplus of silver ions at the surface of the pellet creates a measurable electrical potential that varies with the concentration of chloride ions in the sample. This potential is measured with an external reference electrode, and then scaled to chloride ion concentration (provided the ISE has been calibrated with chloride ion calibration solutions).

Notice that ISE's are sensitive only to the ionized form of the chemical in question. Un-ionized forms of the chemical (for instance, insoluble salts or organic compounds), will not be detected by the ISE.

How is chloride measurement useful in water quality monitoring applications?

The chloride ion does not react with, or adsorb to, most components of rocks and soils, and so is easily transported through water columns. Thus chloride is an effective tracer for pollution from chemicals moving from man-made sources into natural water bodies, or for salt water intrusion.

Applications of chloride ion measurement include monitoring landfills for leaks, tracing the movement of point-or non-point source pollutants (for instance, storm water runoff) within a natural water body, monitoring estua-rine waters for changes in salinity, and detection of salt water intrusion into drinking water supplies (ground or surface waters).

How is chloride measurement implemented in Hydrolab instruments?

Hydrolab uses the chloride ISE, and the same external reference electrode used for pH measurement, for chloride measurement. Because the electrical response of the chloride ISE changes with temperature, chloride readings are corrected automatically for temperature effects. However, the temperature response can vary between chloride sensors - so calibration at a second temperature is needed if the temperature of the sample will be different from that of the calibration standards. Three- or four-point calibrations are recommended: two different standards at room temperature, and at least one standard at a temperature close to that expected of the samples.

The chloride ISE response also changes with the ionic strength of the sample, since the chloride ion appears less "active" when surrounded by other ions. Hydrolab corrects for ionic strength by measuring the conductivity of the sample water, calculating the approximate ionic strength of the water (assuming "typical" river water ionic composition at low conductivity, or sea water ionic composition at high conductivity), and then adjusting the chloride reading for any difference between the ionic strengths of the calibration standards and the sample.

For example, suppose you calibrate your chloride ISE with a solution whose chloride concentration is 46 mg/l, and whose conductivity (an approximation of ionic strength) is 500 µmhos.

Suppose then that you made a measurement in a sample whose chloride concentration was also 46 mg/l, but whose conductivity was 5,000 µmhos (due to presence of other ions). The higher ionic strength of the sample would cause the chloride ion to appear less active, meaning the chloride ISE reading would be below 40 mg/l - even though the true concentration is 46 mg/l. The Hydrolab system largely prevents this error by measuring conductivity, calculating an approximate ionic strength, and then correcting the ISE reading.

As a result of Hydrolab's ionic strength correction, the chloride activity, rather than the chloride concentration, of the standard is used for calibration. Hydrolab supplies calibration standards labelled with chloride activity, rather than concentration. For instance, a de-ionized water solution that is:

0.001410 ± 0.000003 molar in potassium chloride,
0.00359 ± 0.00003 molar in potassium nitrate, with
0.055% Glutaraldehyde preservative added

has a chloride concentration of 50 mg/l, but a chloride activity of just 46.2 mg/l. For a higher chloride concentration, Hydrolab supplies a solution that is:

0.0100 ± 0.00005 molar in potassium chloride,

resulting in a 354.5 mg/l chloride concentration, and a 319.3 mg/l activity. (This solution, 0.1 molar potassium chloride, is also used as a 1.413 mS conductivity calibration standard.)

The chloride sensor has a measurement range of 0.5-18,000 mg/l, with a 90% response in less than one minute, at depths to 15 meters. All chloride sensors suffer interference from other ions, working best when the concentrations of bromide, iodide, cyanide, silver, and sulphide ions are much lower than the chloride ion concentration.

Should I consider Hydrolab chloride measurement?

Hydrolab chloride measurement provides these benefits: rugged sensor operating to depths of 15 meters; range of 0.5-18,000 mg/l chloride; field-serviceable reference electrode; automatic correction for temperature; superior automatic compensation for ionic strength effects.

For more information on this or any Hydrolab application please contact Campbell Scientific (Canada) Corp. at (780) 454-2505