Ammonium

What is Ammonium?

Ammonium, NH_4^+, is an ionized form of nitrogen. There are many naturally occurring forms of nitrogen, including the nitrogen gas that comprises nearly 80% of the atmosphere. Nitrogen compounds dissolved in water are usually classified as organic or inorganic. Soluble inorganic nitrogen compounds include ammonia, nitrite, and nitrate. Nitrate is related to ammonia in that nitrifying bacteria convert ammonia to nitrate, which is less toxic to animal life.

Ammonia has two forms – the ammonium ion and un-ionized, dissolved ammonia gas (NH_3). The form depends on pH, with ammonium predominating when the pH is below 8.75, and ammonia predominating above pH 9.75. The forms are freely interconverted during a change in pH. Total ammonia is the sum of ammonium and ammonia concentrations.

How is Ammonium measured?

Ammonium ion concentration is measured with a number of wet-chemistry or instrumental methods.

Ammonium ion concentration is also measured with an ammonium ion-selective electrode (ISE). Inside the ammonium ISE is a reference electrode immersed in a solution of fixed ammonium ion concentration. This solution is separated from the sample by a polymer membrane containing a chemical compound that reacts, selectively, with ammonium ions. Ammonium ions on each side of the membrane equilibrate with the reactive compound at the inner and outer membrane surfaces. A result of the passing of ammonium ions across the membrane surface from the sample is a measurable electrical potential that varies with the concentration of ammonium ions in the sample. This potential is measured with an external reference electrode (which is not the same reference electrode immersed in the sealed solution), and then scaled to ammonium ion concentration (provided the ISE has been calibrated with ammonium ion calibration solutions).

Because the relationship between ammonium ion concentration and dissolved ammonia gas concentration is controlled by pH, total ammonia can be calculated if the ammonium ion concentration and the pH of the water are known. However, if the pH of the sample is above 10, most of the total ammonia is in the form of dissolved ammonia gas (which is not measured by the ammonium sensor). Accurate measurements become difficult as the ammonium ion formed becomes very small compared to total ammonia.

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 Ammonium measurement useful in water quality monitoring applications?

Nitrogen is an essential nutrient for all forms of life, including all levels of aquatic organisms. Biologically available nitrogen is found in both suspended solids and dissolved compounds in natural waters. Many natural waters are nitrogen-limited, meaning that nitrogen compounds are the limiting nutrients. Thus even small changes in biologically available nitrogen levels can dramatically affect the levels of microbiological, plant, and eventually, animal life. High levels of accessible nitrogen, of which total ammonia is one form, can lead to an over abundance of micro-organisms, a situation which often results in mortality to higher organisms (such as fish and shrimp) because of depleted dissolved oxygen.

Excessive total ammonia can also result in mortality to the higher organisms, especially when high pH levels favour dissolved ammonia gas, which is more toxic than the ammonium form.

Applications of ammonium ion measurement include tracing the movement of point- or non-point source pollutants (for instance, runoff from agricultural operations), monitoring aquaculture projects for excessive waste concentrations, and surveying nutrient levels in natural water bodies.

How is Ammonium measurement implemented in Hydrolab instruments?

Hydrolab uses the ammonium ISE and the same external reference electrode used for pH measurement, for ammonium measurement. Because the electrical response of the ammonium ISE changes with temperature, ammonium readings are corrected automatically for temperature effects. However, the temperature response can vary between ammonium sensors – so calibration at a second temperature is needed if the temperature of the sample will be different from that of the calibration standards. Threeor 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 ammonium ISE response also changes with the ionic strength of the sample, since the ammonium 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) and then adjusting the ammonium reading for any difference between the ionic strengths of the calibration standards and the sample.

For example, suppose you calibrate your ammonium ISE with a solution whose ammonium concentration is 5 mg/1-N, and whose conductivity (an approximation of ionic strength) is 100 µmhos. Suppose then that you made a measurement in a sample whose ammonium concentration was also 5 mg/1-N, but whose conductivity was 1000 µmhos. The higher ionic strength of the sample would cause the ammonium ion to appear less active, meaning the ammonium ISE reading would be approximately 0.4 mg/1-N lower than the calibration standard – even though the true concentrations are both 5mg/1-N. 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 ammonium activity, rather than the ammonium concentration, of the standard is used for calibration. Hydrolab supplies calibration standards labelled with ammonium activity, rather than concentration. For instance, a de-ionized water solution that is:

> 0.00357 ± 0.00001 molar in ammonium chloride,
> 0.000477 ± 0.000004 molar in magnesium acetate,
> 0.000954 ± 0.000004 molar in acetic acid, with
> 0.055% glutaraldehyde preservative added,

has an ammonium concentration of 50 mg/1-N, but an ammonium activity of just 46.2 mg/1-N. For a lower ammonium concentration, Hydrolab supplies a solution that is:

> 0.000357 ± 0.000001 molar in ammonium chloride,
> 0.001548 ± 0.00001 molar in magnesium acetate,
> 0.003095 ± 0.00001 molar in acetic acid, with
> 0.055% glutaraldehyde preservative added,

resulting in a 5 mg/1-N ammonium concentration, and a 4.62 mg/1-N activity.

The ammonium sensor has a measurement range of 0.1 – 50 mg/1-N (mg/1-N means mg/1 of nitrogen, present, in this case, in the ammonium form), with a 90% response in less than one minute, at depths to 15 meters. Leaching of chemicals from the membrane, coating of the membrane with surfactants or biological growth, or damage to the membrane can lead to a decreased sensitivity of the sensor. Eventually, the sensor will no longer calibrate or operate properly. The lifetime of the sensor depends greatly on deployment conditions. The ammonium sensor will last longer in clean waters than in severely contaminated waters.

All ammonium ISE's suffer interference from other ions, especially sodium and potassium. Even though the sensor is most selective to ammonium, other ions, when found in high concentrations, can dominate the sensor response. For example, concentrations of 23 mg/1 of potassium ion, 821 mg/1 of sodium ion, or 4,340 mg/1 of magnesium ion all "look like" about 1 mg/1-N of ammonium ion to an ammonium ISE. Significant interference are not likely to be encountered in water with conductivity below 1,000 µS, but in sea water, which contains over 10,000 mg/1 of sodium ion, an ammonium sensor would read over 12 mg/1-N for ammonium concentration, even in the absence of ammonium, because of the sodium interference. Because of the sodium ion interference, the ammonium sensor performs poorly in salt water.

Should I consider Hydrolab Ammonium measurement?

Hydrolab ammonium measurement provides these benefits:

- Rugged sensor operating to depths of 15 meters;
- range of 0.1 – 50 mg/1-N ammonium;
- automatic calculation of ammonia and total ammonia concentrations;
- 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.