Thermo SCIENTIFIC

Application Note

Tip Log #126

Applications Tip of the Week
Determination of Ammonia in Seawater

Total ammonia nitrogen (TAN) plays an important role in marine systems. In one form, it is a nutrient - a source of nitrogen for phytoplankton. However, in another form, it is a waste product and is toxic to fish, even at low levels. This Tip provides an overview on TAN, including test methods and hints on how to overcome the challenges of testing for TAN in seawater samples.

The concentration of TAN in the ocean varies substantially, from less than 0.002 ppm to as much as 0.7 ppm TAN, but is usually very low in surface seawater (<0.02 ppm TAN)[1] . For aquariums and marine aquaculture, some experts suggest it is prudent to keep the TAN concentration <0.1 ppm to maintain healthy fish, and at 0.25 ppm TAN, immediate treatment may be required[1].

In water and seawater, ammonia exists in two forms:
1) as NH_3, un-ionized ammonia (UIA) gas dissolved in water – toxic to fish.
2) as NH_4^+, ionized ammonium – relatively non-toxic.

The two forms are measured and reported together as TAN. The toxic UIA form can be calculated from the measured TAN value when pH, temperature, and salinity are measured, too. Therefore, a complete testing system for TAN in seawater will include test equipment for TAN, pH, temperature, and salinity (by conductivity).

The proportion of UIA in water increases when pH increases and when temperature increases. In seawater, the proportion of UIA will be lower than in fresh water. To calculate the concentration of UIA in a seawater sample, enter the measured TAN, pH, temperature, and salinity into the ammonia calculator that was developed by the American Fisheries Society (http://fisheries.org/hatchery, table 10).

Test methods for TAN in Seawater
The following Orion methods and their modifications are usually used for TAN analysis in seawater[2]:

- The Ion Selective Electrode (ISE) Method
- The Colorimetric Salicylate Method

Some Recommended Orion Equipment for Ammonia Testing of Seawater Samples*

Ammonia (TAN) by ISE **pH and temperature by pH Triode™** **Salinity by conductivity**	**Ammonia (TAN) by Colorimetry, Salicylate** **pH and temperature by pH Triode™** **Salinity by conductivity**
Orion 9512HPBNWP NH3 ISE (for TAN) Orion VERSA STAR VSTAR52 benchtop meter kit (pH/conductivity/ temperature) Orion VSTAR-ISE module (for TAN)	Orion AQ4000 portable colorimeter (for TAN) Orion AC4P12 NH_3 (TAN) Salicylate powder reagent Orion STARA3255 portable meter kit (pH/conductivity/temperature)

*Contact an Orion technical sales representative or the Orion Technical Service phone line for options and additional assistance.

Tips for Testing TAN in Seawater

There are some challenges when testing TAN, especially in seawater. See below for challenges and recommendations to optimize for seawater testing.

Challenge	Test Method	Recommendation
Water stored in the laboratory can become contaminated with ammonia.	All	Use ammonia free water for the preparation of all standards. If ammonia contamination is a problem, pass water through a column with an acidic cation-exchange resin.
Ammonia electrode response becomes non-linear at very low concentrations	ISE	Enable the Auto-blank function on the Orion meter – it produces accurate results when measuring in the non-linear range.
The high ionic strength of seawater can affect ammonia activity and therefore ISE response	ISE	Option A: Match the ionic strength (IS) of standards and seawater samples by making standards with a matrix similar to the samples, but not containing ammonia. For example, the calibration standards can be prepared using artificial seawater or from a low-nutrient seawater by the removal of background ammonium.[3] Option B: Use the known addition method for ISE – this method accounts for the true ISE response in seawater and requires no matrix matching of standards.
Magnesium hydroxide and calcium carbonate can build up on the electrode sensing membrane after repeated use in seawater.	ISE	Clean these precipitates periodically by dipping the electrode sensing tip into 1 M hydrochloric acid and rinsing with ammonia free water.
Calcium and magnesium from seawater can precipitate as hydroxide during the analysis and interfere with the measurement results.	Colorimetric - Salicylate	Per E. Kingsley et. al.[4]: Add 1 mL of a solution containing 110 g/L sodium citrate and 40 g/L sodium hydroxide into each 25 mL of seawater sample before or after the addition of salicylate chemistries to the sample. It helps prevent calcium and magnesium precipitation and keeps the pH at ~ 13, where the salicylate reaction is most sensitive.
Ammonia binders and formalin interfere with some colorimetric tests.	Colorimetric	According to the University of Florida IFAS[5], ammonia binders and formalin do not interfere with the salicylate method.

References

1. Ammonia and the Reef Aquarium with Randy Holmes-Farley, http://reefkeeping.com/issues/2007-02/rhf/index.php .
2. See our Application Tip, Log #125, Ammonia in Freshwater Aquaculture for details on ISE and colorimetry testing.
3. Continuous colorimetric determination of trace ammonium in seawater with a long-path liquid waveguide capillary cell. Qian Perry Li, Jia-Zhong Zhang, Frank J. Millero, Dennis A. Hansell. Marine Chemistry, Volume 96, Issues 1–2, 11 August 2005, Pages 73-8. http://yyy.rsmas.miami.edu/groups/biogeochem/Hansell%20pdfs/53%20Hansell.pdf.
4. New Nitrate and Total Ammonia Testing Procedures in use at the Monterey Bay Aquarium. Eric Kingsley, Nicholas Modisette, Roger Phillips, Monterey Bay Aquarium, Monterey, Ca 93940. http://www.slideserve.com/mattox/new-nitrate-and-total-ammonia-testing-procedures-in-use-at-the-monterey-bay-aquarium.
5. Ammonia in Aquatic Systems, R. Francis-Floyd, et. el., University of Florida IFAS Extension, 2005. http://edis.ifas.ufl.edu/fa031 .