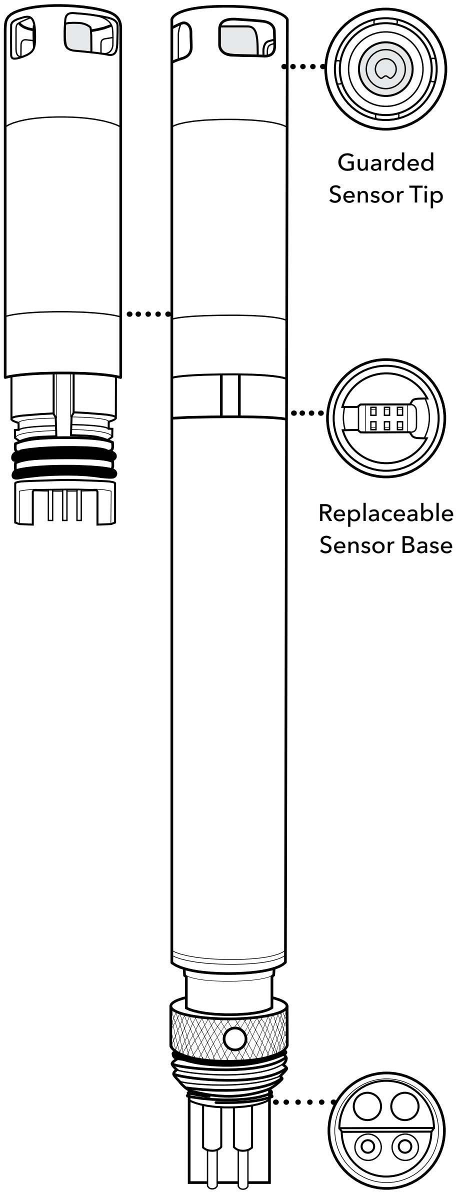
4.16 ISEs: Ammonium, Nitrate, & Chloride

Sensors Overview

NOTE: *Ammonium, nitrate, and chloride ion-selective electrodes (ISEs) should be used in freshwater applications only at depths of less than 55 feet (17 meters) and less than 25 psi.*

The ammonium and nitrate sensors use a silver/silver chloride wire electrode in a custom filling solution. The internal solution is separated from the sample medium by a polymer membrane, which selectively interacts with ammonium or nitrate ions. When the sensor is immersed in water, a potential is established across the membrane that depends on the relative amounts of ions in the sample and the internal solution. This potential is read relative to the Ag/AgCl reference electrode.

(continued)



599709, 599710, 599711;
599743-01, 599744-01, 599745-01 modules

Specifications

Ammonium - NH_4

Units	mg/L-N, millivolts
Temperature	
Operating	0 to 30˚C
Storage	0 to 30°C
Depth	0 to <55 ft (0 to <17 m)
Range	0 to 200 mg/L-N
Accuracy	±10% of reading or ±2 mg/L-N, whichever is greater
Response	T63<30 sec
Resolution	0.01 mg/L
Sensor Type	Ion-selective electrode
Conductivity	<1500 µS/cm

Nitrate - NO_3

Units	mg/L-N, millivolts
Temperature	
Operating	0 to 30˚C
Storage	0 to 30°C
Depth	0 to <55 ft (0 to <17 m)
Range	0 to 200 mg/L-N
Accuracy	±10% of reading or ±2 mg/L-N, whichever is greater
Response	T63<30 sec
Resolution	0.01 mg/L
Sensor Type	Ion-selective electrode
Conductivity	<1500 µS/cm

(Specs. continued)

Specifications *(continued)*

Chloride - Cl

Units	mg/L-Cl, millivolts
Temperature *Operating* *Storage*	 0 to 30˚C 0 to 30°C
Depth	0 to <55 ft (0 to <17 m)
Range	0 to 18000 mg/L-Cl
Accuracy	±15% of reading or ±5 mg/L-Cl, whichever is greater
Response	T63<30 sec
Resolution	0.01 mg/L
Sensor Type	Ion-selective electrode
Salinity	30 psu

NOTE: *Qualification testing for chloride was performed in a stirred calibration solution. Due to the solid state nature of the chloride ISE, the sensor exhibits moderate flow dependence. Mitigation can be achieved by stirring during calibration.*

The chloride sensor uses a solid-state membrane attached to a conductive wire. This sensor operates in a similar fashion to the ammonium and nitrate sensors.

For all ISEs, the linear relationship between the logarithm of the ammonium, nitrate or chloride activity and the observed voltage, as predicted by the Nernst equation, is the basis for the determination.

Ammonium is calculated from the pH, salinity, and temperature readings. If a pH sensor is not in use, the instrument will assume the sample is neutral (pH 7) for the calculation. If a conductivity sensor (salinity) is not in use, the instrument will use the salinity correction value entered in the ammonium sensor calibration screen for the calculation.

> ***NOTE:*** *A pH sensor must be installed in order to receive representative ammonia (NH3) readings (assuming all sensors are calibrated and in good working order).*

Replaceable Sensor Module

The EXO ammonium, chloride, and nitrate sensors have a unique design that incorporates a user-replaceable sensor tip (module) and a reusable sensor base that houses the processing electronics, memory, and wet-mate connector. This allows users to reduce the costs associated with these sensors by only replacing the relatively inexpensive module periodically and not the more costly base.

The connection of the module to the sensor base is designed for one connection only and the procedure must be conducted in an indoor and dry environment. Once installed the module cannot be removed until you are prepared to replace it with a new module.
See Section 5.14 for detailed instructions.

The typical life expectancy of an ISE sensor is three to six months, depending on use.

Precautions

- ISEs are intended for sampling purposes and **must** be calibrated frequently due to sensor drift.
- ISEs can be used in long-term deployments for qualitative trends. Use with an EXO wiper will deform the brush over time and may require more frequent brush replacement. The brush deformation may intensify with the fouling present in the monitored environment.
- ISE sensors only come in guarded configurations. Customers should not remove the plastic guard that protects the ISE membrane.
- For long-term deployments, sensor data should be compared to that of grab samples throughout the monitoring period to note drift.

For a full list of precautions see the end of Section 4.17.

4.17 ISEs: Ammonium, Nitrate, & Chloride

Calibration

This procedure calibrates the EXO ammonium, chloride, or nitrate sensor. The sensors can be calibrated to one, two or three points. The 3-point calibration method assures maximum accuracy when the temperature of the media to be monitored cannot be anticipated; we strongly recommend a 3-point calibration for best performance of ISE sensors. Review the basic calibration description in Section 4.2.

The temperature response of ion-selective electrodes is not as predictable as that of pH sensors. Therefore, be sure to carry out a 3-point calibration the first time you use the sensor. This will provide a default setting for the effect of temperature on your sensor. After this initial calibration, you can use the less time-consuming 2-point and 1-point routines to update the 3-point calibration. However, we strongly recommend a new 3-point calibration after each deployment of 30 days or longer.

Due to the nature of ion-selective electrodes, it is recommended that they be used for sampling purposes for the greatest accuracy. Using an ISE in long-term deployments is possible, but it's important to note that drift occurs over an extended period of time. Collecting grab samples from the site is encouraged to correct for drift. Additionally, sample readings should be taken after sensors have fully stabilized. Calibrating in a continuously stirred solution from 1 to 5 minutes has shown to improve sensor performance. For best performance sensors should be calibrated as close to the expected field conditions as possible.

For more ISE precautions, drift, and accuracy notes please see ISE Precautions at the end of this section.

Calibration Options (Ammonium Example)

1-point

Perform the 1-point option only if you are adjusting a previous calibration. If a 2-point or 3-point calibration has been performed previously, you can adjust the calibration by carrying out a 1-point calibration.

2-point

Perform the 2-point option to calibrate the ammonium sensor using only two calibration standard solutions. In this procedure, the ammonium sensor is calibrated using a 1 mg/L NH_4^+ -N and 100 mg/L NH_4^+ -N calibration standard solutions. A 2-point calibration procedure (as opposed to a 3-point procedure) can save time if the temperature range of the media being monitored is known and stable.

3-point

Perform the 3-point option to calibrate the ammonium sensor using three calibration standard solutions, two at ambient temperature and one at a temperature substantially different from ambient. The 3-point calibration method should be used to assure maximum accuracy when the temperature of the media to be monitored cannot be anticipated. 3-point calibration temperatures should span the range of interest, for example 20°C and 2°C for "cold" and 20°C and 30°C for "hot". The procedure for this calibration is the same as for a 2-point calibration, but the software will prompt you to place the sensor in the additional calibration standard solution to complete the 3-point procedure. Be certain that the calibration standard solution and sensor are thermally equilibrated prior to proceeding with the calibration. The recommended order of calibration standards is (1) 1 mg/L NH_4^+ -N standard at ambient temperature, (2) 100 mg/L NH_4^+ -N standard at ambient temperature, and (3) 1 mg/L NH_4^+ -N standard at a different temperature (usually lower) than ambient, ±10°C minimum.

- To save time during calibration, chill/heat a sufficient amount of 1 mg/L NH_4^+ -N calibration standard solution prior to the start of calibration.

Ammonium Pre-calibration

Soaking

EXO Ammonium Sensors are shipped in a dry container. Before initial use the sensor membrane needs to be soaked in 100 mg/L ammonium standard solution (YSI part #003843). Most users find it useful to soak the sensors overnight; shorter soaking times may be used if the sensor output is monitored and is fully stabilized.

In addition to initially soaking the sensor, users may also see improved performance if the ammonium sensor is soaked in 100 mg/L solution after field deployments. This process helps remove any interfering ions from the sensor membrane.

After the activation process the sensor should be rinsed thoroughly and the following calibration precautions should be observed.

part #003841	1 mg/L
part #003842	10 mg/L
part #003843	100 mg/L

The ammonium sensor should be calibrated using solutions of known total ammonium-nitrogen content or YSI Standards.

If a two point calibration protocol is used, the temperature of the standards should be as close as possible to that of the environmental medium to be monitored. The recommended calibration procedure is one involving three solutions. Two of the solutions should be at ambient temperature while the third should be at least 10˚C different from ambient temperature. This protocol minimizes the effects of taking readings at temperatures that are significantly different from ambient laboratory temperatures.

Calibration Tip

Exposure to the high ionic content of pH buffers can cause a significant, but temporary, drift in the Ammonium, Nitrate, and Chloride sensors. Therefore, when calibrating the pH/ORP probe, YSI recommends that you use one of the following methods to minimize errors in the subsequent readings:

A. When calibrating pH, remove ISE modules from the sonde bulkhead and plug the ports. After pH calibration is complete, replace the ISE sensors and proceed with their calibration with no stabilization delay.

B. Calibrate pH first, immersing all of the probes in the pH buffers. After calibrating pH, place the probes in 100 mg/L nitrate or ammonium standard or 1000 mg/L chloride standard and monitor the reading. Usually, the reading starts low and may take as long as 30 minutes to reach a stable value. When it does, proceed with calibration of the ISE sensor.

Despite the potential problems with interference when using ISEs, it is important to remember that almost all interfering species produce an artificially high ammonium reading. Thus, if the sonde indicates the presence of only small quantities of ammonium, it is unlikely that the reading is erroneously low because of interference. Unusually high ammonium readings (which could be due to interfering ions) should be confirmed by laboratory analysis after collection of water samples.

Ammonium 3-point

> **NOTICE:** Do not expose electrodes to high-conductivity solutions. Exposure will reduce data quality and response of the sensors. During calibration of other sensors, remove the ISEs to avoid exposing them to conductivity standards, Zobell solution, pH buffer, or any solution with significant conductivity.

In the Calibrate menu, select Ammonium, then select Calibrate.

Pour a sufficient amount of 1 mg/L NH_4^+ -N calibration standard solution at ambient temperature in a clean and dry or pre-rinsed calibration cup. Carefully immerse the sensor end of the sonde into the solution, making sure the sensor's tip is in solution by at least 1 cm. Allow at least 1 minute for temperature equilibration before proceeding.

Observe the Pre Calibration Value readings and the Data Stability, and when they are Stable, click Apply to accept this calibration point.

Rinse the sensors in deionized water between changes of the calibration solutions. Pour a sufficient amount of 100 mg/L of NH_4^+ -N calibration standard solution at ambient temperature into a clean, dry or pre-rinsed calibration cup and carefully immerse the sensor end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

Click Add Another Cal Point in the software. Observe the Pre Calibration Value readings and the Data Stability, and when they are Stable, click Apply to accept this calibration point.

Rinse the sensors in deionized water between changes of the calibration solutions. Immerse the sensor end of the sonde in the pre-chilled 1 mg/L NH_4^+ -N calibration standard solution ensuring that the temperature is at least 10°C different than ambient. Allow at least 1 minute for temperature equilibration before proceeding.

Click Add Another Cal Point in the software. Observe the Pre Calibration Value readings and the Data Stability, and when they are Stable, click Apply to accept this calibration point.

Click Complete. View the Calibration Summary screen and QC Score. Click Exit to return to the sensor calibration menu

Rinse the sonde in tap or purified water.

Nitrate 3-point

The calibration procedure for nitrate is identical to the procedure for ammonium, except that the calibration standard solution values are in mg/L NO_3^- -N instead of NH4+ -N.

Chloride 3-point

The calibration procedure for chloride is identical to the procedure for ammonium and nitrate, except that the calibration standard solution values are in mg/L Cl^- instead of NH_4^+ -N or NO_3^- -N. YSI recommends that the user employ standards for chloride that are 10 times greater than for ammonium and nitrate and that span the expected deployment conditions. Typical calibration ranges are 10mg/L Cl^- and 1000mg/L Cl^- or 1000mg/L Cl^- and 18000mg/L Cl^-.

Chloride Standard for Chloride Sensor

⚠ **WARNING:** Read and follow all the safety instructions and MSDS documentation supplied with the chemical before proceeding. Remember that only trained personnel should handle hazardous chemicals.

Preparation

Use the following procedure to prepare 10 and 1000 mg/L chloride reagents for the EXO Chloride sensor. (Nitrate and Ammonium standards can be purchased from YSI or other laboratory supply companies.)

1000 mg/L Standard

1. Purchase solid sodium chloride from a supplier.
2. Accurately weigh 1.655 grams of anhydrous sodium chloride and transfer into a 1000 mL volumetric flask.
3. Add 0.5 grams of anhydrous magnesium sulfate to the flask.
4. Add 500 mL of water to the flask, swirl to dissolve all of the reagents. Dilute to the volumetric mark with water. Mix well by repeated inversion and then transfer the 1000 mg/L standard to a storage bottle.

   Alternatively, simply add 0.5 grams of magnesium sulfate to a liter of a 1000 mg/L chloride standard from a certified supplier.

10 mg/L Standard

1. Accurately measure 10 mL of the above 1000 mg/L standard solution into a 1000 mL volumetric flask.
2. Add 0.5 grams of anhydrous magnesium sulfate to the flask.
3. Add 500 mL of water, swirl to dissolve the solid reagents, and then dilute to the volumetric mark with water. Mix well by repeated inversion and then transfer the 10 mg/L standard to a storage bottle.
4. Rinse the flask extensively with water prior to its use in the preparation of the 1000 mg/L standard.

Sensor Drift

The ion-selective electrodes have the greatest tendency to exhibit calibration drift over time. This drift should not be a major issue for sampling studies where the instrument can be frequently calibrated. However, if the sensor is used in longer-term deployments, drift is almost certain to occur. The extent of the drift will vary depending on the age of the probe, the flow rate at the site, and the quality of the water. For all monitoring studies using ion-selective electrodes, the user should acquire a few grab samples during the deployment for analysis in the laboratory or with another sensor that has been recently calibrated.

Sensor Accuracy Specifications

The typical accuracy specification for the sensors (+/-10% of reading or 2 mg/L which ever is greater for ammonium and nitrate and ±15% of reading or 5 mg/L which ever is greater for chloride) refer to sampling applications where only minimal time has elapsed between calibration and field use.

To maintain accuracy specifications for EXO sensor, we recommend that users calibrate sensors in the lab in standards with temperatures as close to the ambient temperature of the field water as possible.

All ion-selective electrodes are subject to the interaction of species with the sensor membrane, which are similar in nature to the analyte. These interfering species thus include other halide ions (fluoride, bromide, and iodide) as well as other anions.

Despite the potential problems with interference when using ISEs, it is important to remember that almost all interfering species produce an artificially high reading. Thus, if the sensor indicates the presence of only small quantities, it is unlikely that the reading is erroneously low because of interference. Unusually high readings (which could be due to interfering ions) should be confirmed by laboratory analysis after collection of water samples.

ISE Precautions

Ion-selective electrodes may not stabilize as rapidly as pH sensors. Be sure to allow plenty of time for the readings to come to their final values during all calibration routines.

Ion-selective electrodes generally drift more than pH sensors. To check for this drift, read the sensor's value in a calibration standard solution at the end of each deployment.

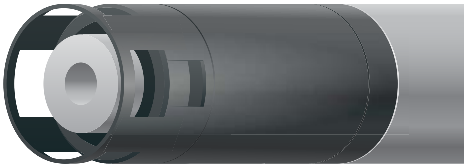
Ammonium and nitrate standards are good growth media for a variety of microorganisms. This growth can significantly reduce the nitrogen content of your standards, an effect that is particularly important for the 1 mg/L solution. It is best to use new standards for each calibration, but if you decide to save your solutions for reuse, we recommend refrigerated storage to minimize the growth of these organisms.

Remember that the ammonium, nitrate, and chloride sensors will take longer to stabilize after exposure to high conductivity solutions such as a pH buffer. To accelerate the recovery process, soak the sensor in 100 mg/L ammonium or nitrate standard solution or 1000 mg/L Cl- standard solution for a few minutes after exposure. In addition, be particularly careful that readings are stable during subsequent calibrations.

Of all the sensors available on the sonde, ion selective electrodes have the greatest tendency to exhibit calibration drift over time. This drift should not be a major problem for sampling studies where the instrument can be frequently calibrated. However, if an ammonium sensor is used in a longer-term deployment study with the sonde, the user should be aware that drift is almost certain to occur. The extent of the drift will vary depending on the age of the probe, the flow rate at the site, and the quality of the water. For all monitoring studies using ion selective electrodes, the user should acquire a few "grab samples" during the course of the deployment for analysis in the laboratory by chemical means or with another ammonium sensor which has been recently calibrated. Remember that the typical accuracy specification for the sensor (+/- 10 % of the reading or 2 mg/L, whichever is larger) refers to sampling applications where only minimal time has elapsed between calibration and field use.

Many users find it useful to swap ISEs after 30 days of deployment with freshly calibrated sensors. On the EXO platform the calibration is retained inside the sensor, so they can be calibrated in the lab and installed in the field.

SmartQC for ISE Sensors



ISE sensor algorithms are derived from three independent coefficients (called J, S, and A) as well as mV, temperature and salinity. J, S, and A are the calibrated coefficients and S specifically is concentration of the analyte being detected by the sensor. S is the coefficient whose gain factor is the basis of SmartQC for these sensors.

Guidance on interpretation of the SmartQC Score for this sensor is as follows:

☑ **Green**: Gain and offset are within acceptable limits. Calibration was performed successfully and results are within factory specified limits.

⚠ **Yellow**: The S gain is near the threshold of calibration limits. If a user calibration results in a yellow QC Score, perform the following actions:

1. Perform a Factory Reset Calibration and re-do the calibration.
2. If the sensor had not been properly stored it may be necessary to rehydrate the reference junction, as described in Section 5.13.
3. Pre-calibration soaking is advisable for ISEs, especially if a non-green SmartQC Score occurs. Pre-soak the ISE tip in its higher concentration calibration solution for at least 12 hours prior to trying another calibration.
4. During calibration, ensure that the standard solutions were thermally equilibrated, meaning that the temperature was stable and not changing during calibration. Sometimes putting the solutions in a water bath can help ensure this.
5. Ensure that the standard value was entered correctly.
6. It is imperative that the sensors, calibration cup, and sonde guard are all very clean when calibrating.
7. Since these modules have a relatively short lifespan, a prior user may have entered an expiration date into the software for when the sensor should be replaced. Check to see if that date is near.
8. Ensure that the sensor is free of debris. Refer to Section 5.13 for additional information on how to properly clean the sensor in order to avoid damage.

If the QC Score remains yellow, the sensor is still able to be used, but ISE’s are the one case where a yellow-scored sensor should not be used for a continuous deployment, because the period of time before it would become red is probably short. It can be used for spot sampling, and should be recalibrated before each day’s use.

☒ **Red**: The S gain is significantly outside of factory specified limits. If a user calibration results in a red QC Score, follow the same steps described above for a yellow QC Score. If the QC Score remains red, it is likely time to replace the sensor module.

If replacement of the module does not return the sensor to a Green QC Score, please contact YSI Technical Support for further assistance.