**Electrodes** Ammonium Ion-Selective Electrode Calcium Ion-Selective Electrode Chloride Ion-Selective Electrode Nitrate Ion-Selective Electrode

**Ion Selective** 

(Order Code NH4-BTA) (Order Code CA-BTA) (Order Code CL-BTA) (Order Code NO3-BTA)

Vernier Ion-Selective Electrodes can be used to measure the concentration of a specific ion in aqueous samples. The species available include Nitrate  $(NO_3^-)$ , Chloride  $(CI^-)$ , Calcium  $(Ca^{2^+})$ , and Ammonium  $(NH_4^+)$ . These electrodes can be used to perform a wide variety of tests or planned experiments.

- Water Hardness (Calcium ISE): Calcium is very useful as an indicator of hardness of water in freshwater samples. Even though water hardness is also due to other ions (Mg<sup>2+</sup> and Fe<sup>3+</sup>), because Ca<sup>2+</sup> is normally the predominate hardness ion, hardness as Ca<sup>2+</sup> is a reliable indicator of water hardness.
- Nitrate Monitoring (Nitrate ISE): Use this ISE to qualitatively determine the concentration of the nitrate ion, NO<sub>3</sub><sup>-</sup>, in freshwater samples. This ion may appear in samples due to waste or fertilizer runoff. Increased levels of nitrate may also be present in waste from plants or in water samples with animal decay.
- Salinity and Chloride Monitoring in Seawater (Chloride ISE): Use this ISE to determine the concentration of chloride ion, Cl<sup>-</sup>, or salinity levels in saltwater samples. The wide range of this electrode allows you to measure salinity (as sodium chloride), chloride concentration, seawater, or brackish water samples.
- Monitoring Streams for Ammonium (Ammonium ISE): Ammonium (NH<sub>4</sub><sup>+</sup>) is often present as a result of water runoff from fertilized fields. This ISE gives you an easy way to check for this environmentally important ion.

## Inventory of Items Included with the ISE

- Ion-Selective Electrode (Nitrate, Calcium, Chloride, or Ammonium)
- bottle of High Standard solution with MSDS sheet (1000 mg/L for Ca<sup>2+</sup> and Cl<sup>-</sup>, or 100 mg/L for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>)
- bottle of Low Standard solution with MSDS sheet (10 mg/L for Ca<sup>2+</sup> and Cl<sup>-</sup>, or 1 mg/L for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>)
- ISE Soaking Bottle (empty bottle with insertion cap)

This sensor is equipped with circuitry that supports auto-ID. When used with LabQuest 2, LabQuest, LabQuest Mini, LabPro, Go! Link, SensorDAQ, TI-Nspire Lab Cradle, EasyLink, or CBL 2, the data-collection software identifies the sensor and uses pre-defined parameters to configure an experiment appropriate to the recognized sensor.

## **Data Collection Interfaces**

This sensor can be used with the following interfaces to collect data.

- Vernier LabQuest<sup>®</sup> 2 or original LabQuest<sup>®</sup> as a standalone device or with a computer
- Vernier LabQuest<sup>®</sup> Mini with a computer
- Vernier LabPro<sup>®</sup> with a computer or TI graphing calculator
- Vernier Go!<sup>®</sup>Link
- Vernier EasyLink<sup>®</sup>
- Vernier SensorDAQ<sup>®</sup>
- CBL 2<sup>тм</sup>
- TI-Nspire<sup>™</sup> Lab Cradle

## **Data-Collection Software**

This sensor can be used with an interface and the following data-collection software.

- Logger *Pro* **3** This computer program is used with LabQuest 2, LabQuest, LabQuest Mini, LabPro, or Go!Link.
- Logger Pro 2 This computer program is used with ULI or Serial Box Interface.
- Logger Lite This computer program is used with LabQuest 2, LabQuest, LabQuest Mini, LabPro, or Go!Link.
- LabQuest App This program is used when LabQuest 2 or LabQuest is used as a standalone device.
- EasyData App This calculator application for the TI-83 Plus and TI-84 Plus can be used with CBL 2, LabPro, and Vernier EasyLink. We recommend version 2.0 or newer, which can be downloaded from the Vernier web site, www.vernier.com/easy/easydata.html, and then transferred to the calculator. See the Vernier web site, www.vernier.com/calc/software/index.html for more information on the App and Program Transfer Guidebook.
- **DataMate program** Use DataMate with LabPro or CBL 2 and TI-73, TI-83, TI-84, TI-86, TI-89, and Voyage 200 calculators. See the LabPro and CBL 2 Guidebooks for instructions on transferring DataMate to the calculator.
- DataQuest<sup>™</sup> Software for TI-Nspire This calculator application for the TI-Nspire can be used with the EasyLink or TI-Nspire Lab Cradle.
- LabVIEW National Instruments LabVIEW<sup>TM</sup> software is a graphical programming language sold by National Instruments. It is used with SensorDAQ and can be used with a number of other Vernier interfaces. See www.vernier.com/labview for more information.

## Collecting Data with the ISE

Here is the general procedure to follow when using the ISE.

- 1. The Ion-Selective Electrode (ISE) must be soaked in the High Standard solution (included with the ISE) for approximately 30 minutes. Important: Make sure the ISE is not resting on the bottom of the container, and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE.
- 2. If the ISE needs to be transported to the field during the soaking process, use the Short-Term ISE Soaking Bottle. Remove the cap from the bottle and fill it 3/4-full

with High Standard. Slide the bottle's cap onto the ISE, insert it into the bottle, and tighten. Important: Do not leave the ISE soaking for more than 24 hours. Long-term storage should be in the Long-Term ISE Storage Bottle.

- 3. Connect the ISE to the interface.
- 4. Start the data-collection software.<sup>1</sup>
- 5. The software will identify the ISE. See below for calibration instructions.

## Calibrating the ISE with a Computer

- 1. Choose Calibrate from the Experiment menu and then click Calibrate Now.
- 2. High Standard Calibration Point The ISE should still be soaking in the High Standard. Enter the concentration value of the High Standard (e.g., 100 for 100 mg/L or 1000 for 1000 mg/L) in the edit box.
- 3. When the voltage reading for Reading 1 stabilizes (~1 minute), click SKeep.
- 4. Low Standard Calibration Point Remove the ISE from the High Standard, rinse well with distilled water from a wash bottle, and gently blot dry with a paper towel or lab wipe. Place the electrode into the Low Standard (included with your ISE). Important: Make sure the ISE is not resting on the bottom of the container, and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE.
- 5. Enter the concentration value of the Low Standard (e.g., 1 for 1 mg/L or 10 for 10 mg/L).
- 6. After 60 seconds, click SKeep and then Done. To collect data, continue with the steps in the Collecting Data section, below.

## Calibrating the ISE with a LabQuest App

- 1. Choose Calibrate from the Sensors menu and select Calibrate Now.
- 2. **High Standard Calibration Point** The ISE should still be soaking in the High Standard. Enter **1000** as the concentration in mg/L Ca<sup>2+</sup> for Reading 1.
- 3. When the voltage reading stabilizes, tap Keep.
- 4. Low Standard Calibration Point Rinse the ISE thoroughly with distilled water and gently blot it dry with a tissue. Important: Failure to carefully rinse and dry the ISE will contaminate the standard.
- 5. Place the tip of the ISE into the Low Standard ( $10 \text{ mg/L Ca}^{2+}$ ). Be sure that the ISE is not resting on the bottom of the bottle and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE.
- 6. Enter 10 as the concentration of the standard in mg/L  $Ca^{2+}$  for Reading 2.
- 7. After briefly swirling the solution, hold the ISE still and wait approximately 30 seconds for the voltage reading to stabilize. When the voltage reading stabilizes, tap Keep.
- 8. Select OK. To collect data, continue with the steps in the Collecting Data section, below.

## Calibrating the ISE with TI Graphing Calculators

Enter the calibration routine for your data-collection program. Consult the reference material for the software on your handheld to get specific information concerning the calibration steps.

- High Standard Calibration Point The ISE should still be soaking in the High Standard. Enter the concentration value of the High Standard (e.g., 100 for 100 mg/L or 1000 for 1000 mg/L).
- Low Standard Calibration Point Remove the ISE from the High Standard, rinse well with distilled water from a wash bottle, and gently blot dry with a paper towel or lab wipe. Place the electrode into the Low Standard (included with your ISE). Important: Make sure the ISE is not resting on the bottom of the container, and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE. After 60 seconds, enter the concentration value of the Low Standard (e.g., 1 for 1 mg/L or 10 for 10 mg/L). To collect data, continue with the steps below.

## **Collecting Data**

- 1. Rinse off the end of the ISE, and blot it dry with a lab wipe.
- 2. Insert the tip of the ISE into the sample to be tested. Important: Make sure the ISE is not resting on the bottom of the container, and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE. **Note**: Do not completely submerge the sensor. The handle is not waterproof.
- **Note:** Do not completely submerge the sensor. The handle is not waterproc
- 3. Hold the ISE still for 60 seconds and record the displayed reading.

## **Using ISEs with Other Vernier Sensors**

Some combinations of sensors interfere with each other when placed in the same solution. The degree of interference depends on many factors, including which combination of sensors is being used, which interface is being used, and others. For more information, see www.vernier.com/til/638/

## Storing Ion-Selective Electrodes

Proper care and storage is important to consideration for optimal longevity, especially with the PVC membrane ISEs (Ammonium, Calcium, and Nitrate).

- Long-term storage of ISEs (longer than 24 hours) should be done in the Long-Term ISE Storage Bottle, which is included. The sponge in the bottom of the bottle should be kept moist with distilled water. When you finish using the ISE, simply rinse it off with distilled water and blot it dry using a paper towel or lab wipe. Loosen the lid of the bottle and insert the ISE. **NOTE**: The tip of the ISE should NOT be touching the sponge. Check to be sure the white ceramic junctions are inside, rather than outside the bottle or under the grommet. Tighten the lid. This storage system keeps the electrode in a humid environment, which prevents the reference junctions from completely drying out.
- Short-term, wet storage (less than 24 hours) can be done by using the Short-Term ISE Soaking Bottle included with the electrode. Fill the bottle 3/4 full with High Standard. Loosen the cap, insert the electrode into the bottle, and tighten.

<sup>&</sup>lt;sup>1</sup> If you are using Logger *Pro* 2 with either a ULI or SBI, the sensor will not auto-ID. Open an experiment file for the Colorimeter in the Probes & Sensors folder.

### Specifications

| Range of ISE Electrodes                               |  |  |
|---|--|--|
| Ammonium (NH <sub>4</sub> <sup>+</sup> )              | $0.10-18,000 \text{ mg/L}$ or ppm ( $5.5 \times 10^{-6} \text{ M}$ to $1.0 \text{ M}$ )  |  |
| Calcium ( $Ca^{2+}$ )                                 | 0.20-40,000  mg/L or ppm (5 × 10-6 M to 1.0 M)   |  |
| Chloride (Cl <sup>-</sup> )                           | $1.8-35,500 \text{ mg/L or ppm} (5 \times 10^{-5} \text{ M to } 1.0 \text{ M})$  |  |
|   |  |  |
| Nitrate $(NO_3^-)$                                    | 0.10–14,000 mg/L or ppm (7 × 10 <sup>-6</sup> M to 1.0 M)  |  |
| Resolution  |  |  |
| 13-bit (SensorDAQ)                                    | The resolution values for each range will be half as large as those shown for 12-bit interfaces.   |  |
| 12-bit (LabQuest 2,                                   | large as those shown for 12-oft interfaces.  |  |
| LabQuest, LabQuest                                    |  |  |
| Mini, LabPro, Go! Link,                               |  |  |
| ULI, or SBI)  | (% of high-scale reading)  |  |
| Ammonium $(NH_4^+)$                                   | 0.7% of reading (0.10 ±0.0007 or 18,000 ±130 mg/L)   |  |
| Calcium ( $Ca^{2+}$ )                                 | 1.4% of reading $(0.20 \pm 0.0028 \text{ or } 40,000 \pm 560 \text{ mg/L})$  |  |
| Chloride (Cl <sup>-</sup> )                           | 0.7% of reading (1.8 ±0.013 or 35,500 ±250 mg/L  |  |
| Nitrate $(NO_3^{-})$                                  | 0.7% of reading (0.10 ±0.0007 or 14,000 ±98 mg/L   |  |
| 10-bit (CBL 2)  | The resolution values for each range will be four  |  |
|   | times as large as those shown for 12-bit interfaces.   |  |
| Interfering Ions                                      | $K^+$  |  |
| Ammonium $(NH_4^+)$                                   |  |  |
| Calcium (Ca <sup>2+</sup> )                           | $Pb^{2+}, Hg^{2+}, Sr^{2+}, Cu^{2+}, Ni^{2+}$  |  |
| Chloride (Cl <sup>-</sup> )                           | $CN^{-}, Br^{-}, I^{-}, S^{2-}$  |  |
| Nitrate $(NO_3^{-})$                                  | $ClO_4^-$ , $\Gamma^-$ , $ClO_3^-$ , $CN^-$ , $BF_4^-$   |  |
| pH Range  | 4.75   |  |
| Ammonium $(NH_4^+)$                                   | 4-7.5  |  |
| Calcium (Ca <sup>2+</sup> )                           | 3-10   |  |
| Chloride (Cl <sup>-</sup> )                           | 2–12   |  |
| Nitrate $(NO_3^-)$                                    | 2.5–11   |  |
| Electrode Slope (log voltage i                        |  |  |
| Ammonium $(NH_4^+)$                                   | +56 mV/decade  |  |
| Calcium (Ca <sup>2+</sup> )                           | 56 mV/decade   |  |
| Chloride (Cl <sup>-</sup> )                           | +28 mV/decade  |  |
| Nitrate (NO <sub>3</sub> <sup>-</sup> ) -56 mV/decade |  |  |
| Approximate Calibration Volt                          |  |  |
| Ammonium $(NH_4^+)$                                   | High $(100 \text{ mg/L})=2.1 \text{ V}$ , Low $(1 \text{ mg/L})=1.3 \text{ V}$<br>High $(1000 \text{ mg/L})=1.0 \text{ V}$ , Low $(10 \text{ mg/L})=1.5 \text{ V}$ |  |
| Calcium (Ca <sup>2+</sup> )                           | High $(1000 \text{ mg/L})=1.9 \text{ V}$ , Low $(10 \text{ mg/L})=1.5 \text{ V}$   |  |
| Chloride (Cl <sup><math>-</math></sup> )              | High $(1000 \text{ mg/L})=2.0 \text{V}$ , Low $(10 \text{ mg/L})=2.8 \text{V}$<br>High $(100 \text{ mg/L})=1.6 \text{V}$ , Low $(1 \text{ mg/L})=2.4 \text{V}$     |  |
| Nitrate $(NO_3^-)$                                    | High (100 mg/L)=1.6 V, Low (1 mg/L)=2.4 V  |  |
| Electrode resistance                                  | 1 to 4 M $\Omega$  |  |
| Reproducibility                                       | $\pm$ 5% of reading  |  |
| Temperature range (can be placed in)                  | 0 to 50°C (no temperature compensation)  |  |
|   |  |  |
| Minimum immersion                                     | 1 inch   |  |

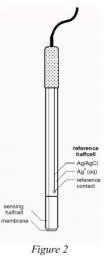
**NOTE**: Vernier products are designed for educational use. Our products are not designed nor recommended for any industrial, medical, or commercial process such as life support, patient diagnosis, control of a manufacturing process, or industrial testing of any kind.

### How Your Ion-Selective Electrode Works

Vernier Ion-Selective Electrodes (ISEs) are membrane-based electrodes that measure a specific ion (e.g.,  $Ca^{2+}$ ) in an aqueous solution. When the membrane of the electrode is in contact with a solution containing the specific ion, a voltage, dependent on the level of that ion in solution, develops at the membrane. All of our ISEs are combination style; that is, the voltage develops in relation to an internal Ag/AgCl reference electrode. The ISEs measure for the specific ion concentrations directly. Samples need to be aqueous to avoid contaminating or dissolving the membrane. Vernier Ion-Selective Electrodes (ISEs) have two types of membranes:

- Solid Polymer Membrane This type of PVC membrane is used in our Nitrate, Calcium, and Ammonium ISEs. The membrane is a porous plastic disk, permeable to the ion exchanger, but impermeable to water. It allows the sensing cell to contact the sample solution and separates the internal filling solution from the sample. Our PVC membrane electrodes have replaceable membrane modules.
- Solid State Membrane This thin crystal disk, used in our Chloride ISE, is an ionic conductor. It separates the internal reference solution from the sample solution. The Chloride ISE does not have replaceable membrane modules.

The voltage developed between the sensing and reference electrodes is a measure of the concentration of the reactive ion being measured. As the concentration of the ion reacting at the sensing electrode varies, so does the voltage measured between the two electrodes.



As described in the Nernst equation, ISE response is a linear equation:

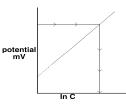
E = Eo + m(ln a)

where E is the measured voltage, Eo is the standard potential for the combination of the two half cells, m is the slope, ln is natural log, and a is the activity of the measured ion species.

Assuming the ionic strength is fairly constant, the Nernst equation may be rewritten to describe the electrode response to the concentration, C, of the measured ionic species:

E = Eo + m(lnC)

A graph of the natural log of concentration (lnC) *vs.* potential (V) can be plotted (see Figure 3).





The method for determining the concentration of  $Ca^{2+}$ ,  $NH_4^+$ ,  $NO_3^-$ , or  $Cl^-$  ions using one of our ISEs is based on the following:

- The interface reads a voltage that is related to ion concentration.
- Using the voltage reading and the principle described in Figure 3, the natural log of concentration of the specific ion can be determined.
- The ion concentration can be determined from the natural log of concentration.

## Maintaining and Replacing the ISE Standard Calibration Solutions

Having accurate standard solutions is essential for performing good calibrations. The two standard solutions that were included with your ISE can last a long time if you take care not to contaminate them with a wet or dirty probe. At some point, you will need to replenish your supply of standard solutions.

Vernier sells replacement standards in 500 mL bottles. Order codes are:

| Ammonium Low Standard: NH4-LST | Α |
|--------------------------------|---|
| Calcium Low Standard: CA-LST   | С |
| Chloride Low Standard: CL-LST  | С |
| Nitrate Low Standard: NO3-LST  | Ν |

Ammonium High Standard: NH4-HST Calcium High Standard: CA-HST Chloride High Standard: CL-HST Nitrate High Standard: NO3-HST

To prepare your own standard solutions, use the information in the table below. **Note**: Use glassware designed for accurate volume measurements, such as volumetric flasks or graduated cylinders. All glassware must be very clean.

| Standard Solution   | Concentration (mg/L<br>or ppm) | Preparation Method using High<br>Quality Distilled Water   |
|---|--------------------------------|--|
| $\begin{array}{c} Ammonium \\ (NH_4^+) \text{ ISE High} \\ \text{Standard} \end{array}$ | $100 \text{ mg/L NH}_4^+$ as N | 0.382 g NH <sub>4</sub> Cl / 1 L solution  |
| Ammonium<br>$(NH_4^+)$ ISE Low<br>Standard  | $1 \text{ mg/L NH}_4^+$ as N   | Dilute the High Standard by a factor of 100 (from 100 mg/L to 1 mg/L).*                                    |
| Calcium (Ca <sup>2+</sup> )<br>ISE High<br>Standard                                     | 1000 mg/L as Ca                | 2.771 g CaCl <sub>2</sub> / 1 L solution or<br>3.669 g CaCl <sub>2</sub> •2H <sub>2</sub> 0 / 1 L solution |
| Calcium (Ca <sup>2+</sup> )<br>ISE Low Standard   | 10 mg/L as Ca                  | Dilute the High Standard by a factor<br>of 100 (from 1000 mg/L to 10<br>mg/L).*                            |
| Chloride (Cl <sup>-</sup> ) ISE<br>High Standard  | 1000 mg/L as Cl                | 1.648 g NaCl / 1 L solution  |
| Chloride (Cl <sup>-</sup> ) ISE<br>Low Standard   | 10 mg/L as Cl                  | Dilute the High Standard by a factor<br>of 100 (from 1000 mg/L to 10<br>mg/L).*                            |
| Nitrate (NO <sub>3</sub> <sup>-</sup> ) ISE<br>High Standard                            | 100 mg/L NO3 as N              | 0.607 g Na NO <sub>3</sub> / 1 L solution  |
| Nitrate (NO <sub>3</sub> <sup>-</sup> ) ISE<br>Low Standard                             | 1 mg/L NO3 as N                | Dilute the High Standard by a factor<br>of 100 (from 100 mg/L to 1 mg/L).*                                 |

\*Perform two serial dilutions as described below.

- a. Combine 100 mL of the High Standard with 900 mL of distilled water. Mix well.
- b. Combine 100 mL of the solution made in Step a with 900 mL of distilled water. Mix well.

# Replacement Membrane Modules (Ammonium, Nitrate, and Calcium only)

The Nitrate, Calcium, and Ammonium ISEs each have a PVC membrane with a limited life expectancy. They are warranted to be free from defects for a period of twelve (12) months from the date of purchase; it is possible, however, that you may get somewhat longer use than the warranty period. If you start to notice a reduced response (e.g., distinctly different voltages or voltage ranges during calibration), it is probably time to replace the membrane module. **Important**: Do not order membrane modules far in advance of the time you will be using them; the process of degradation takes place even when they are stored on the shelf. Note that the Chloride ISE has a solid-state membrane, with a longer membrane life, and does not need a replacement module.

## Using Ionic Strength Adjuster (ISA) Solutions to Improve Accuracy

For optimal results at low concentrations of calcium, chloride, and nitrate ions, a standard method for making measurements with ion-selective electrodes is to add ionic strength adjuster (ISA) solutions to each of your standard solutions and samples. **Note**: Do not use an ISA for low concentrations of ammonium.

Adding an ISA ensures that the total ion activity in each solution being measured is nearly equal, regardless of the specific ion concentration. This is especially important when measuring very low concentrations of specific ions. The ISA contains no ions common to the Ion-Selective Electrode itself. **Note**: The additions of ISA to samples or standards described below do not need to have a high level of accuracy— combining the ISA solution and sample solution counting drops using a disposable Beral pipet works fine. The following are instructions for using ISA solutions with Vernier Ion-Selective Electrodes.

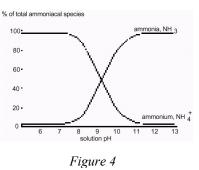
- **Calcium ISA** Add the 1.0 M KCl ISA solution (7.46 g KCl / 100 mL solution) to the Ca<sup>2+</sup> standard or to the solution being measured, in a ratio of 1 part of ISA (by volume) to 50 parts of total solution (e.g., 1 mL of ISA to 50 mL of total solution, or 2 drops of ISA to 5 mL of total solution).
- Chloride ISA Add the 5.0 M NaNO<sub>3</sub> ISA solution (42.50 g NaNO<sub>3</sub> / 100 mL solution) to the Cl<sup>-</sup> standard or to the solution being measured, in a ratio of 1 part of ISA (by volume) to 50 parts of the total solution (e.g., 1 mL of ISA to 50 mL of total solution, or 2 drops of ISA to 5 mL of total solution).
- Nitrate ISA Add the 2.0 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ISA solution (26.42 g (NH<sub>4</sub>) 2SO<sub>4</sub> / 100 mL solution) to the NO<sub>3</sub><sup>-</sup> standard or to the solution being measured, in a ratio of 1 part of ISA (by volume) to 50 parts of total solution (e.g., 1 mL of ISA to 50 mL of total solution, or 2 drops of ISA to 5 mL of total solution).

## Using the Ammonium Ion-Selective Electrode

The Ammonium ISE can be used to determine concentrations of  $NH_4^+$  ions in aqueous solutions, in units of mg/L, ppm, or mol/L. Concentrations of aqueous ammonium ions should not be mistaken for concentration of aqueous ammonia, or  $NH_3(aq)$ . The concentrations of these two species, though different, are often involved in the same equilibrium reaction:

Reaction 1:  $NH_3(aq) + H^+(aq) \longleftrightarrow NH_4^+(aq)$ 

In a more acidic environment, higher concentrations of H+ ions will cause this reaction to shift toward the right, resulting in higher concentrations of  $NH_4^+$ . In a more basic (alkaline) environment, the concentration of  $NH_4^+$  will be lower, causing the reaction to shift toward the reactants, producing higher concentrations of  $NH_3$ . At pH values greater than 10 (see Figure 4), most of the ammonium ions will be converted to ammonia. At pH values less than 7.5, most of the aqueous ammonia will be converted to ammonium ions.



#### Sampling Freshwater Samples for Ammonium Concentration

While permissible levels of ammonium in drinking water should not exceed 0.5 mg/L, streams or ponds near heavily fertilized fields may have higher concentrations of this ion. Fertilizers containing ammonium sulfate,  $(NH_4)_2SO_4$ , or ammonium nitrate,  $NH_4NH_3$ , may result in runoff from fields containing higher levels of the ammonium ion,  $NH_4^+$ . Monitoring ammonium levels on a stream that borders fertilized fields may show significant seasonal differences in  $NH_4^+$  concentrations. In this kind of study, you may also take pH measurements in your water samples; as indicated in the previous paragraph, higher or lower pH values can greatly affect the ratio of  $NH_4^+$ /  $NH_3$  in a sample. Since the Ammonium ISE measures only  $NH_4^+$  levels, you may want to adjust your samples to the same pH value each time you make measurements; this may not be necessary if you have relatively "hard" water. Hard water is naturally buffered against changes in pH.

## Using the Ammonium ISE at Low Concentration Levels (0.1–0.5 mg/L $NH_4^+$ -N)

If the concentration of your sample is less than 0.5 mg/L  $NH_4^+$ - N, you will obtain better results if you calibrate the electrode with 0.1 mg/L and 1.0 mg/L  $NH_4^+$ - N. This is because the slope of the calibration changes at these low levels. You can make up the 0.1 mg/L Ammonium Standard by following the directions in Table 1 to make the 1.0 mg/L  $NH_4^+$ - N Standard, then diluting one more time using 100 mL of the 1.0 mg/L with 900 mL of high quality distilled water.

#### **Expressing Ammonium Concentration**

Concentrations of ammonium are often expressed in units of mg/L  $NH_4^+$  as N. Here is a calculation for a 100 mg/L  $NH_4^+$  as N standard solution that is prepared by adding solid NH4Cl to distilled water:

$$\frac{100 \text{ mg NH}_4^+}{1 \text{ L}} \times \frac{1 \text{ g NH}_4^+}{1000 \text{ mg NH}_4^+} \times \frac{53.5 \text{ g NH}_4\text{Cl}}{14.0 \text{ g NH}_4^+ - \text{N}} = 0.382 \text{ g NH}_4\text{Cl/Lsolution}$$

#### Using the Calcium Ion-Selective Electrode

Your Calcium Ion-Selective Electrode can be used to determine the concentration of aqueous  $Ca^{2+}$  ions, in the range of 1.8 to 40,100 mg/L. It can be especially useful in determining "hardness of water." Calcium ions are often found in freshwater samples as a result of water flowing over soil and mineral deposits containing limestone, chalk, magnesite, or dolomite. In one common reaction, limestone is dissolved according to the reaction

$$CaCO_3(s) + H+(aq) \longleftrightarrow Ca^{2+}(aq) + HCO_3^{-}(aq)$$

This reaction and others similar to it produce water with a relatively high concentration of  $Ca^{2+}$  ions, and lesser concentrations of  $Mg^{2+}$  and  $Fe^{3+}$  ions—known as hard water.

#### Using the Calcium ISE to Determine Water Hardness as Ca<sup>2+</sup>

Many methods of determining water hardness use "total hardness," or the sum of hardness due to  $Mg^{2+}$  and  $Ca^{2+}$ . Since the  $Ca^{2+}$  concentration of freshwater usually exceeds that of  $Mg^{2+}$ , determining the  $Ca^{2+}$  concentration alone is a good indicator of water hardness—we will refer to this measurement as "calcium hardness." For best results, calibrate the Calcium ISE using the 10 mg/L and 1000 mg/L standards.

Using the standard solutions described here, your results will be in units of mg/L of  $Ca^{2+}$ . Units of calcium hardness are usually expressed as "calcium hardness as  $CaCO_3$ ". To convert from units of mg/L of  $Ca^{2+}$  (150 mg/L is used in this example) to units of calcium hardness as  $CaCO_3$ , in mg/L, you would use this expression:

$$\frac{150 \text{ mg Ca}^{2+}}{1 \text{ L}} \times \frac{100 \text{ g CaCO}_3}{40 \text{ g Ca}^{2+}} = 374 \text{ mg/ L (hardness as CaCO}_3)$$

It is important to remember that total hardness, taking into account both the Ca and Mg levels, will be about 1.5 times higher than your calcium hardness value. Water hardness varies considerably in different parts of the United States, from levels of less than 60 mg/L (total hardness as CaCO<sub>3</sub>) in Washington, Oregon, Louisiana, Mississippi, Tennessee, and New England, to levels exceeding 250 mg/L or higher in Midwestern states (Ohio, Indiana, Illinois, Iowa, Nebraska, South Dakota, and Oklahoma). Water with a hardness as CaCO<sub>3</sub> level greater than 120 mg/L is considered to be "hard," while levels exceeding 180 mg/L are referred to as "very hard."equivalence point occurs first, with the Mg<sup>2+</sup> equivalence point following; therefore Ca<sup>2+</sup> can be determined as well as total hardness (as Ca<sup>2+</sup> and Mg<sup>2+</sup>). A plot of ln [Ca<sup>2+</sup>] (natural log of calcium ion concentration) vs. volume is used to determine the equivalence point. The second derivative can be used to calculate the point of maximum inflection at the equivalence point of the titration.

#### Using the Chloride Ion-Selective Electrode

Chloride ions are found in freshwater samples as a result of water flowing over saltcontaining minerals. These salts might include either sodium chloride (NaCl) or potassium chloride (KCl). The EPA maximum contamination level for chloride concentration in drinking water is 250 mg/L. The chloride ion concentration in seawater is approximately 19,400 mg/L—well below the upper limit of the Chloride ISE of 35,500 mg/L. When the response of the Chloride ISE begins to slow, the membrane may need polishing. Cut a small piece (about 1 inch square) from a polishing strip. Wet the end of the electrode and the dull side of the polishing strip thoroughly with distilled water. Using only moderate pressure, polish the end of the electrode by gently rubbing in a circular motion. This will remove the inactive layer of the membrane which impedes measurement. Rinse thoroughly with distilled water and recalibrate in the usual manner.

#### Sampling Freshwater Samples for Chloride Concentration

For best results, calibrate the Chloride ISE using the 10 mg/L and 1000 mg/L standards.

#### Measuring Chloride Concentration of Saltwater or Brackish Water

When measuring chloride concentration in seawater or brackish water, calibrate the Chloride ISE using the 1000 mg/L standard included with your Chloride ISE for one calibration point (or 1.806 parts per thousand, or ppt). For the second calibration point, prepare a standard that is 20,000 mg/L Cl<sup>-</sup> by adding 32.96 g of solid NaCl to enough distilled water to prepare 1 L of solution:

 $\frac{20000 \text{ mg Cl}^-}{1 \text{ L}} \times \frac{1 \text{ g Cl}^-}{1000 \text{ mg Cl}^-} \times \frac{58.5 \text{ g NaCl}}{355 \text{ g Cl}^-} = 32.96 \text{ g NaCl} / \text{ L solution}$ 

If you are calibrating in ppt, call this solution 36.13 ppt.

### Determining Salinity of Saltwater or Brackish Water

Salinity is the total of all salts dissolved in water, expressed either as mg/L (equal to parts per million, ppm) or in parts per thousand (ppt). Seawater contains a fairly constant quantity of chloride ions. From your measurement of chloride ion concentration (in the previous section), salinity can be calculated using the following formula:

Salinity (mg/L or ppm) =  $1.8066 \times [Cl^{-} \text{ concentration, mg/L}]$ 

Using this formula, the salinity of saltwater is calculated to be:

Salinity (mg/L or ppm) = 1.8066 × (19400 mg/L) = 35,000 mg/L

The level of salinity of seawater in parts per thousand, or ppt, would be: Salinity (ppt) = 35000 / 1000 = 35 ppt

## Using the Nitrate Ion-Selective Electrode

Nitrate ions,  $NO_3^-$ , may be found in freshwater samples from a variety of sources. Sewage is often the primary source. Sometimes nitrates are present due to runoff from fertilized fields. Nitrates can also result from the runoff from cattle feedlots and barnyards. In all of these cases, as plant and animal organisms die, bacterial action breaks down the protein into ammonia,  $NH_3$ . Some ammonia is converted into ammonium ions,  $NH_4^+$ . Other bacterial action converts some of the ammonia and ammonium ions into nitrite ions,  $NO_2^-$ , and then into nitrate ions,  $NO_3^-$ .

#### **Units of Nitrate Concentration**

Nitrate ion concentration is usually expressed in units of mg/L of  $NO_3^-$  as N, also known as "nitrate-nitrogen." This means that the concentration of nitrate is expressed as if the nitrate were only in the form of nitrogen itself. The standards that are included with your Nitrate ISE have concentrations of 1 and 100 mg/L of  $NO_3^-$  as N.

Here is the calculation for making a 100 mg/L  $NO_3^-$  as N standard starting with solid NaNO<sub>3</sub> (as shown in Table 1). Notice that the atomic weight of N, 14.0, is used instead of the atomic weight of  $NO_3^-$ , 62.0.

$$\frac{100 \text{ mg N}}{1 \text{ L}} \times \frac{1 \text{ g N}}{1000 \text{ mg N}} \times \frac{85.0 \text{ g NaNO}_3}{14.0 \text{ g N}} = 0.607 \text{ g NaNO}_3 / \text{ L solution}$$

Unpolluted waters usually have nitrate-nitrogen (NO<sub>3</sub><sup>-</sup> as N) levels below 1 mg/L. Nitrate-nitrogen levels above 10 mg/L are considered unsafe for drinking water.

Test results are sometimes published in units of  $mg/L NO_3^-$  instead of  $NO_3^-$  as N. To convert 100 mg/L  $NO_3^-$  as N to mg/L  $NO_3^-$ , you would perform this conversion:

$$\frac{100 \text{ mg N}}{1 \text{ L}} \times \frac{62.0 \text{ g NO}_3}{14.0 \text{ g N}} = 443 \text{ mg}/\text{ L NO}_3$$

### Sampling Freshwater Samples for Nitrate Concentration

For best results, calibrate the Nitrate ISE, using the 1 mg/L and 100 mg/L standards.

## How Can I Have My ISE Read mV Output Instead of mg/L?

The amplification equation is: V = 0.00727 \* mV + 1.223

Therefore, the reverse amplification equation, solving for mV, would be: mV = 137.55\*V - 0.1682

#### Warranty

Vernier warrants this product to be free from defects in materials and workmanship for a period of five years from the date of shipment to the customer. This warranty does not cover damage to the product caused by abuse or improper use. ISE modules are covered by a one-year warranty.



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#### Rev. 5/3/12

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