Alkalinity Workshop: *Basics and Best Practices*

Kelly Sweazea, Specialist
Thermo Scientific Water Analysis & Purification Products
Overview

- Alkalinity Basics
  - What is it and why is it important?
- Alkalinity Chemistry
  - Reactions
  - Carbonate System
- Measuring Alkalinity
  - Methods
- Best Practices
Alkalinity Basics

• According to Standard Methods for the Examination of Water and Wastewater (SM 2320 Alkalinity):

   “Alkalinity of a water is its acid-neutralizing capacity. **It is the sum of all the titratable bases.**”

• It can be also described as the water's capacity to resist changes in pH that would make the water more acidic (“buffering” capacity of water).

• The primary ions that contribute to alkalinity of natural waters are
  • carbonate
  • bicarbonate
  • hydroxide

• Alkalinity may also include contributions from borates, phosphates, silicates, or other bases.
Alkalinity Basics

• Alkalinity is an important measurement in many environmental and industrial applications
  • Water Quality
  • Wastewater Treatment Plants
  • Drinking Water Treatment Plants
Alkalinity: The Chemistry

• Acid / Base Reaction

• Acids
  • Acids release protons (H\(^+\))
  • Strong Acids dissociate almost completely in dilute solutions. The kinetics of these chemical reactions are very fast.

<table>
<thead>
<tr>
<th>Strong Acids:</th>
<th>Weak Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric Acid ( \text{HNO}_3 )</td>
<td>Carbonic Acid ( \text{H}_2\text{CO}_3 )</td>
</tr>
<tr>
<td>Hydrochloric Acid ( \text{HCl} )</td>
<td>Acetic Acid ( \text{H}_3\text{COOH} )</td>
</tr>
<tr>
<td>Sulfuric Acid ( \text{H}_2\text{SO}_4 )</td>
<td>Hydrogen Sulfide ( \text{H}_2\text{S} )</td>
</tr>
<tr>
<td>Water</td>
<td>Water</td>
</tr>
</tbody>
</table>
• Acid / Base Reactions

• Bases
  • A base is a compound that associates protons (or consumes protons H+).
  • Strong bases strongly attract protons, forming weak acids.
  • Weak bases weakly associate with protons, forming strong acids.

Strong Bases
Calcium Hydroxide \( \text{Ca(OH)}_2 \)
Carbonate \( \text{CO}_3^{2-} \)

Weak Bases
Bisulfate \( \text{NaHSO}_4 \)
Alkalinity: The Chemistry

- **Acid, Base & pH**
- **The pH Scale**
- **Each pH unit is a factor 10 in \([H^+]\)**
  - pH of Cola is about 2.5.
  - 10x more acidic than Orange Juice (pH of 3.5).

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid, 10M</td>
<td>-1.0</td>
</tr>
<tr>
<td>Lead-acid battery</td>
<td>0.5</td>
</tr>
<tr>
<td>Gastric acid</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>Lemon juice</td>
<td>2.4</td>
</tr>
<tr>
<td>Cola</td>
<td>2.5</td>
</tr>
<tr>
<td>Vinegar</td>
<td>2.9</td>
</tr>
<tr>
<td>Orange or apple juice</td>
<td>3.5</td>
</tr>
<tr>
<td>Beer</td>
<td>4.5</td>
</tr>
<tr>
<td>Acid Rain</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td>Coffee</td>
<td>5.0</td>
</tr>
<tr>
<td>Tea or healthy skin</td>
<td>5.5</td>
</tr>
<tr>
<td>Milk</td>
<td>6.5</td>
</tr>
<tr>
<td>Pure Water</td>
<td>7.0</td>
</tr>
<tr>
<td>Healthy human saliva</td>
<td>6.5 – 7.4</td>
</tr>
<tr>
<td>Blood</td>
<td>7.34 – 7.45</td>
</tr>
<tr>
<td>Seawater</td>
<td>7.7 – 8.3</td>
</tr>
<tr>
<td>Hand soap</td>
<td>9.0 – 10.0</td>
</tr>
<tr>
<td>Household ammonia</td>
<td>11.5</td>
</tr>
<tr>
<td>Bleach</td>
<td>12.5</td>
</tr>
<tr>
<td>Household lye</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Alkalinity: The Chemistry

• pH = “Potential Hydrogen” or Power of Hydrogen

• The pH of pure water around room temperature is about 7. This is considered "neutral" because the concentration of hydrogen ions (H\(^+\)) is exactly equal to the concentration of hydroxide (OH\(^-\)) ions produced by dissociation of the water.

• Increasing the concentration of H\(^+\) in relation to OH\(^-\) produces a solution with a pH of less than 7, and the solution is considered "acidic".

• Decreasing the concentration H\(^+\) in relation to OH\(^-\) produces a solution with a pH above 7, and the solution is considered "alkaline" or "basic".

LOW pH = LOTS OF H\(^+\)  
LOTS OF OH\(^-\) = HIGH pH
Alkalinity: The Chemistry

- pH measures the activity of the H⁺ ion.
- An increase of H ion activity will increase with pH of a sample, it’s important to know that while pH is related to alkalinity chemistry it’s only one part of the equation.
- pH measurements tell us if the water is acidic, alkaline or neutral. It also provides relative acidity.

  pH does not tell us how much acid or alkali is present.

\[ H_2O \leftrightarrow H^+ + OH^- \]
Alkalinity: The Chemistry

• Buffers or Buffering Capacity
  • A buffer is a solution that resists a change in pH when an acid or base is added to it.

• Natural waters have a large buffing capacity.
  • Example: Rivers/lakes are generally safe for humans because of the alkalinity or buffering capacity that keeps the water at a neutral pH even though an acidic compound might be added.
  • One natural way water’s buffer capacity is increased is through limestone that water naturally passes over through rivers, streams, and lakes. The water dissolves carbonates and bicarbonates from the limestone. This creates the buffering capacity and a safe environment for plants and animals.

• The Carbonate System
  • The key to the carbonate cycle begins with CO2 in the atmosphere and the resulting chemical equation to carbonate in fluctuation.
Carbonate System in Surface Waters

\[ \text{CO}_2 \text{ (aq)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \]

\[ \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+ \]

\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_3^{2-} + 2\text{H}^+ \]

- \( \text{CO}_2 \) from Air
- \( \text{CO}_2 \text{ (aq)} \) and \( \text{H}_2\text{O} \) react to form \( \text{H}_2\text{CO}_3 \) (Carbonic Acid)
- \( \text{H}_2\text{CO}_3 \) dissociates into \( \text{HCO}_3^- \) (Bicarbonate) and \( \text{H}^+ \)
- \( \text{HCO}_3^- \) and \( \text{H}^+ \) form \( \text{CO}_3^{2-} \) (Carbonate) and \( 2\text{H}^+ \)
Carbonate System in Surface Waters

\[ \text{CO}_2 \text{(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \]

Carbonic Acid

\[ \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+ \]

Bicarbonate

\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_3^{2-} + 2\text{H}^+ \]

Carbonate

\[ \text{CO}_3^{2-} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \]

Carbonate
Measuring Alkalinity

- Alkalinity is the buffering capacity of water to maintain the same pH when acid is added.
- Another way to consider it is the ability to neutralize acid.
- Mathematically, alkalinity is shown as:
  \[ \text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \]
- Alkalinity is expressed as mg/L as Calcium Carbonate (CaCO₃)
- Three ions, carbonate / bicarbonate and hydroxide all react with H⁺ to reduce acidity, thus increasing pH and alkalinity.
There are three ways to measure alkalinity:

- Titration (Automatic & Manual)
- Colorimetry
- Test Kit
Measuring Alkalinity

- **Titration:**
  - The traditional, EPA-approved method to measure alkalinity is a titration at room temperature with a standard acid solution to a preselected end point.
  - Results are expressed as mg/L as CaCO₃ (calcium carbonate).
  - The end point can be determined by using a pH electrode or observing a color change with color indicators.
  - Alkalinity is calculated from the volume of standard sulfuric acid or hydrochloric acid required to reach the end point or to change the color.

- **Types:**
  - P-Alkalinity
  - Total Alkalinity
Measuring Alkalinity

- **Titration: P-Alkalinity**
  - P-alkalinity (also known as phenolphthalein alkalinity) – is determined by titration with acid to pH 8.3.
  - It measures the amount of carbonate alkalinity, hydroxyl alkalinity, and a part of bicarbonate alkalinity in a sample.
  - A certain level of the P-alkalinity (causticity) is necessary to protect from corrosion, while excessive P-alkalinity can result in a caustic attack (embrittlement) or caustic water, which causes a burning sensation when it is tasted.
  - P-alkalinity is calculated using the equation below:

\[
P\text{-alkalinity, mg CaCO}_3/L = \left(\frac{(mL \text{ standard acid used to pH 8.3}) \times (\text{normality of standard acid}) \times 50,000}{mL \text{ sample}}\right)
\]
Measuring Alkalinity

- Titration: Total Alkalinity
  - Total Alkalinity also called M-alkalinity (M from methyl orange) is determined by titration with acid to pH 4.5. At this pH, all the hydroxyl, carbonate, and bicarbonate (as well as other basic anions) have been titrated.
  - T-alkalinity (or M-alkalinity) can be calculated as follows:

\[
\text{M-alkalinity, mg CaCO}_3/\text{L} = \left(\frac{\text{mL standard acid used to pH 4.5} \times \text{normality of standard acid}}{\text{mL sample}}\right) \times 50,000
\]
Measuring Alkalinity

• The P- and T-alkalinity results individually and in combination help to determine the properties of water.
• For example;

  • If P-alkalinity is greater than half the T-alkalinity, the water is caustic from contributions of hydroxide alkalinity and carbonate alkalinity.

  • If P-alkalinity is zero, then the water is free of hydroxide and carbonate alkalinity.
Measuring Alkalinity: Manual Titration

• Benefits of Manual Titration:
  • Low cost
  • Minimal lab equipment needed
  • Manual pre-dose for experienced technicians

• Downsides:
  • Repeatability varies between technicians
  • Accuracy (color) dependent on technician
  • Manual calculations
  • Time consuming: overshooting endpoint results in repeated testing
  • Chemical spills (filling burette)
Benefits of Automatic Titration:

- Accuracy
- Repeatability
- Minimal Time to operation (press start & walk away)
- Clear end-point displayed
- Automatic calculations & automatic data logging.
- Easy data transfer with USB Flash Drive
- Ability to save, lock, share methods
- Safety: Draws chemical from bottle

Downsides:

- Initial cost
Measuring Alkalinity

Colorimetric Method

• Colorimetric alkalinity measurement methods are based on a similar principle to the conventional titration, but the acid added is preset while the pH of the endpoint varies.

• In these methods, the reagent(s) is composed of several acids and a pH-sensitive color indicator. Acids react with the alkaline species in the sample and change sample pH; as a result, the color indicator changes its color.

• The change in pH and resulting increase in color is proportional to the alkalinity of the sample and is measured at a specific wavelength (e.g., T-alkalinity at 610 nm and P-alkalinity at 560 nm).
Measuring Alkalinity

- Total Alkalinity Test
- Speaking specifically about the Thermo Scientific Orion Total Alkalinity Test, like the colorimetric method this reagent is also composed of several acids, which react with the titratable bases in a sample.
- As a result, the pH of the sample changes. The resulting pH is measured with pH electrode. The pH reading after the addition of the reagent varies directly with the total alkalinity.
Troubleshooting

**Troubleshooting Alkalinity - Fishbone Diagram**

Fishbone Diagram – potential sources of error in alkalinity testing
Titration: Best Practices

- Colorimetric testing:
  - Filter samples where turbidity may affect results.
Titration: Best Practices

• All Alkalinity Test methods:
  • Clean glassware
    • Use laboratory grade cleaners & at least Type II water for clean glassware
    • Some labs have a laboratory grade dishwater
      – DO NOT USE A COMMERCIAL DISHWASHER
"Now then, when did you say was the last time you checked the expiration dates of these solutions?"
# Titration: Electrode Selection

## pH Electrode Features

### pH Electrode Styles

<table>
<thead>
<tr>
<th>Style</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>12 mm electrode diameter for use in a wide variety of sample sizes</td>
</tr>
<tr>
<td>Semi-micro</td>
<td>6 to 8 mm electrode diameter for sample sizes down to 200 µL</td>
</tr>
<tr>
<td>Micro</td>
<td>1 to 5 mm electrode diameter for samples as small as 0.5 µL and containers as small as 384 well plates</td>
</tr>
<tr>
<td>Rugged Bulb</td>
<td>When glass is required, the extra durable pH bulb prevents breakage</td>
</tr>
<tr>
<td>Spear Tip</td>
<td>For piercing solid or semi solid samples and measuring small volume samples</td>
</tr>
<tr>
<td>Flat Surface Tip</td>
<td>For measuring surfaces of solid or gel samples and measuring small volume samples</td>
</tr>
</tbody>
</table>

### pH Electrode Body Materials

- **Glass Body**
  - Compatible with virtually any sample, including solvents
  - Easy to clean
- **Epoxy Body**
  - Extremely durable and rugged to prevent breakage
  - Value-priced

### pH Electrode Junctions

- **Sure-Flow, Sleeve and Laser-Drilled Hole (Open)**
  - Best junction for dirty, difficult samples
  - Junction is clog-free and easy to clean
  - Ideal for thick or viscous samples, compatible with all sample types
- **Ceramic and Glass Capillary**
  - Better junction for routine lab or field use
  - Junction is high quality and durable
  - Ideal for most applications and samples

### pH Electrode Fill Types

- **Refillable**
  - Easy maintenance, filling solution required
  - Periodic filling and draining needed
  - Long expected life span
  - 0.01 to 0.02 pH precision
  - Best response time
  - 1 to 2 year warranty (6 months for Ag/AgCl micro electrodes)
- **Polymer Filled (Sealed)**
  - Low maintenance, no filling solution needed
  - Sealed reference
  - Easy to use, ideal for most applications
  - 0.02 pH precision
  - Better response time
  - 1 year warranty
- **Gel Filled (Sealed)**
  - Low maintenance, no filling solution needed
  - Sealed reference
  - Easy to use, general purpose
  - 0.05 to 0.1 pH precision
  - Good response time
  - 3 to 6 month warranty

### pH Electrode References

- **ROSS Reference**
  - 0.01 pH precision
  - Best measurement response time
  - Ideal for TRIS, protein and sulfide samples
  - Variety of body styles and types
  - Refillable or gel design
  - Best temperature response
- **Double Junction Ag/AgCl Reference**
  - 0.02 pH precision
  - Better measurement response time
  - Ideal for TRIS, protein and sulfide samples
  - Variety of body styles and types
  - Refillable, polymer or gel design
  - Good temperature response
- **Single Junction Ag/AgCl Reference**
  - 0.02 to 0.1 pH precision
  - Good measurement response time
  - General purpose for everyday use
  - Variety of body styles and types
  - Refillable or gel design
  - Good temperature response
Titration: Electrode Selection

**pH Electrode Features**

**pH Electrode Styles**
- Standard Size: 12 mm electrode diameter for use in a wide variety of sample sizes
- Semi-micro: 6 to 8 mm electrode sample sizes up to 200 µL
- Micro: 1 to 5 mm electrode samples as small as 384 well plate containers

**pH Electrode Body Materials**
- Glass Body: Compatible with virtually any sample, including solvents
- Epoxy Body: Easy to clean

**pH Electrode Fill Types**
- Refillable
  - Easy maintenance, filling solution required
  - Periodic filling and draining needed
  - Long expected life span

**pH Electrode References**
- ROSS Reference
  - 0.01 pH precision
  - Best measurement response time
  - Ideal for TRIS, protein and sulfide samples
  - Variety of body styles and types
  - Refillable or gel design
  - Best temperature response

**pH Electrode Junctions**
- Sure-Flow, Sleeve and Laser-Drilled Hole (Open)
  - Best junction for dirty, difficult samples
  - Junction is clog-free and easy to clean
  - Ideal for thick or viscous samples, compatible with all sample types

**Flat Surface Tip**
- Wick and Glass Fiber
  - Good junction for routine lab or field use
  - Junction used with rugged epoxy electrodes
  - Ideal for aqueous samples

**Spear Tip**
- For piercing solid or semi-solid samples and measuring small volume samples
Titration: Best Practices

- Make sure to use the correct fill solution and storage solution
  - Ross electrodes cannot use silver fill solutions
- Gently stir buffers and samples
- Shake any air bubbles out of the electrode
- Use insulation between stir plate and sample container to minimize heat transfer
- Blot electrodes between samples
- Uncover fill hole during measurement
Titration: Best Practices

- **Sampling and Storage for Alkalinity Samples**
  - In general, sample collection should follow these guidelines:
    - Collect in polyethylene or borosilicate glass bottles and store at a low temperature.
    - Record the sample pH at the source where the sample is collected.
    - Bottles should be completely filled and capped tightly.
    - Do not filter, dilute, concentrate, or alter the sample.
    - Samples should be analyzed as soon as possible; holding time is generally up to 14 days at 4 °C.
  - Consult your local regulations for details.
# Alkalinity Method Overview

<table>
<thead>
<tr>
<th></th>
<th><strong>Automatic Titration</strong></th>
<th><strong>Manual Titration</strong></th>
<th><strong>Colorimetry</strong></th>
<th><strong>Test Kit</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P-alkalinity</strong></td>
<td><strong>Yes</strong></td>
<td><strong>Yes</strong></td>
<td><strong>Yes</strong></td>
<td><strong>No</strong></td>
</tr>
<tr>
<td><strong>M-alkalinity</strong></td>
<td><strong>Yes</strong></td>
<td><strong>Yes</strong></td>
<td><strong>Yes</strong></td>
<td><strong>Yes</strong></td>
</tr>
<tr>
<td><strong>Samples Size</strong></td>
<td>200 mL</td>
<td>200 mL</td>
<td>10 mL</td>
<td>100 mL</td>
</tr>
<tr>
<td><strong>Test Range</strong></td>
<td>All concentration ranges of alkalinity</td>
<td>All concentration ranges of alkalinity</td>
<td>P-alk: 5-200 mg/L M-alk: 5-500 mg/L</td>
<td>0-225 mg/L</td>
</tr>
<tr>
<td><strong>Interferences</strong></td>
<td>Substances that can coat pH electrode</td>
<td>Color method, bias across technicians. Electrode method, substances that can coat pH electrode.</td>
<td>Turbidity or color in the sample</td>
<td>Substances that can coat pH electrode</td>
</tr>
<tr>
<td><strong>EPA Approved</strong></td>
<td>EPA-approved test method</td>
<td>EPA-approved test method</td>
<td>Not EPA approved</td>
<td>Not EPA-approved</td>
</tr>
</tbody>
</table>
**Technical Resources**

- [www.thermofisher.com/water](http://www.thermofisher.com/water)

**Total alkalinity in water by automatic titration**

Water Analyte Instruments, Thermo Fisher Scientific

**Key words**

**Introduction**

Total alkalinity (or m-alkalinity) in a water sample is determined using the preprogrammed method T2 TolAlkalinity. This method is a direct titration to a preset endpoint at pH 4.5 using acids. The method may be edited to perform total alkalinity in other samples as well.

**Recommended equipment**
- Thermo Scientific™ Orion™ Star™ Titror T10 pH, or
  TSM All-In-One, or equivalent with a 20 mL burette
- Thermo Scientific™ Orion™ FOS8™ SurePaw™ BT25/TMK pH electrode, or equivalent
- Thermo Scientific™ Orion™ Automatic Temperature Compensation (ATC) probe
- Analyser balance (for standardisation)
- Volumetric Flasks, 1 L (for standardization)
- Graduated cylinders, 100 mL and 250 mL
- Burettes, 150 mL and 500 mL

**Required reagents and solutions**
- Prepared or prepared hydrochloric acid (HCl) standard
  titrant solution, 0.1 M (0.5N) or 0.02 M (0.02N)
- Reagent grade water (RWW)
- pH buffers, pH 4 and 7

**Optional (for standardization)**
- The U.S. Environmental Protection Agency's (EPA) Primarys (ppm/alkalinity standard), solid
  Use suitable personal protective equipment (PPE) as recommended by the Safety Data Sheets (SDS) for the chemicals used during the procedure.

**Titrator setup**

Connect the Orion pH electrode, ATC, and the stirrer probe to the Titror. If not previously done, input the T2 TolAlkalinity preprogrammed method into the titror from the Methods screen. Place and in the burette with 0.01 M (0.1N) HCl titrant. See the titror user manual for details.

If bubbles are visible in the titrating, disperse them from the burette screen until the bubbles have been expelled. Consider standardizing the titrant before titrating samples. See the following Titrant section.
Using Spectrophotometers for Water and Wastewater Testing

Kelly Sweazea, Specialist
Thermo Scientific Water Analysis & Purification Products
Spectrophotometry is Easy!

• Our eyes can work like spectrophotometers
  • They perceive color
  • They perceive how intense the color is
  • They determine how concentrated a material in a solution is by how intense (dark or light) the color is.

• How many people drink tea?
  • How do you determine when to take the bag out of the tea?
Spectrophotometry is Easy!

The spectroscopy of making tea

• The stronger the tea, the darker the color.
• We use the color of the tea to tell us to concentration of the brewed tea.
• This is an example of a forward color relationship.

• How many people put cream in their coffee?
  • How do you determine how much cream to add?
Spectrophotometry is Easy!

The spectroscopy of making coffee with cream

• The more cream we add, the lighter the color of the coffee.
• We use the lightening of the color of the coffee to tell us the concentration of the cream in the coffee.
• This is an example of a reverse color relationship.
What is a Spectrophotometer?

• An instrument which measures the amount of light of a specified wavelength which passes through (or is absorbed by) a solution.

1. Light source
2. Wavelength selector (grating)
3. Sample (in cell)
4. Detector
Why use a Spectrophotometer?

- A spectrophotometer can be used to tell us how much of a specified material is in a water sample.

- For example, if testing for total nitrogen (TN):
  - Colorless sample → add reagent → yellow color → measure @ 430nm
  - The more nitrogen, the more intense the yellow color.
Spectrophotometry Overview

- UV-Visible spectroscopy measures the absorption of light in the ultraviolet and visible region of the spectrum
  - The UV-Visible region falls between the near-infrared and X-ray regions: 190 to 780 nm
  - UV Spectrum: 190 nm to 380nm
  - Visible (Vis) Spectrum: 325 - 360 nm to 780 nm (near infrared up to 1100 nm)
  - Some tests can only be done with a UV light source, such as:
    - UV254
    - SUVA
    - Chlorophyll_a
Spectrophotometry

• The light absorption wavelength has a direct relationship with the observed color (light absorbed vs. light reflected).

Suppose we shine a beam of white light (all the colors in the spectrum) at a substance that absorbs blue light. Since the blue component of the white light gets absorbed by the substance, the light that is transmitted is mostly yellow, the complementary color of blue. This yellow light reaches our eyes, and we “see” the substance as a yellow colored substance.
Spectrophotometry

- The light absorption wavelength has a direct relationship with the observed color (light absorbed vs. light reflected)
  - Yellow food dye 4 has a maximum absorption wavelength of 430 nm and a wavelength range of 380 to 480 nm – see below
  - Blue food dye 1 has a maximum absorption wavelength of 610 nm and a wavelength range of 570 to 650 nm

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Color Absorbed</th>
<th>Color Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>violet</td>
<td>yellow-green</td>
</tr>
<tr>
<td>435</td>
<td>blue</td>
<td>yellow</td>
</tr>
<tr>
<td>495</td>
<td>green</td>
<td>purple</td>
</tr>
<tr>
<td>560</td>
<td>yellow</td>
<td>blue</td>
</tr>
<tr>
<td>650</td>
<td>orange</td>
<td>greenish blue</td>
</tr>
<tr>
<td>800</td>
<td>red</td>
<td>bluish green</td>
</tr>
</tbody>
</table>
Spectrophotometry Overview

- Sample Chemistry
  - Most ions and compounds in water do not have color. To measure the absorbance of a colorless ion or compound, a reaction is used that produces a measurable color.
  - sample → add reagent → colored sample → measure
Common Applications – Drinking Water

- Alkalinity screening
- Aluminum
- Chloride
- Chlorine – free, total (residual)
- Chlorine Dioxide
- Copper
- Cyanide
- Fluoride
- Iron
- Nitrate
- Nitrite

- Ozone
- Phosphate
- Silica
- Sulfate
- Turbidity (turbidimeter)
- Color
- UV254 or SAC254 (UV-Vis) *
- SUVA (UV-Vis) *
- Chlorophyll-a (<2 nm bandwidth)*

* require UV light source
Common Applications – Wastewater

- Alkalinity
- Aluminum
- Ammonia
- Chloride
- Chlorine – free and total
- Chlorine Dioxide
- Copper
- COD
- Cyanide
- Hardness
- Iron
- Manganese
- Nitrate
- Nitrite
- Total Nitrogen
- Phosphate
- Total Phosphate
- Silica
- Sulfide
- Turbidity (turbidimeter)
- Zinc
- Color
Advantages of a Spectrophotometer

• One instrument can be used to measure for many different parameters
• The cost of a spec is less than for an IC or ICP instrument
• No daily equipment prep required
  • other than warm up for tungsten lamp for Vis spec
• A spec is not complex to use
  • especially when using pre-programmed methods
• The level of training required is minimal
• A number of tests are very simple and quick
  • e.g., chlorine, phosphate, sulfate, total hardness, nitrate
  • Many tests are easy, but may require a wait time or more prep steps
  • Some tests require a digestion, e.g. COD, TN, TP
• Temperature tends not to interfere
• Can test for all nutrients with one instrument
A wavelength is specified by the method – it is chosen to provide the highest sensitivity and selectivity for the resulting color from the reaction (absorbance peak)

For nitrate by chromotropic acid test, a wavelength near 410 to 430 nm is usually used.
Absorbance Measurements

- **Beer’s Law:** \( \text{Absorbance (Abs)} = a \times b \times c \)
  - \( a \) = the ability of a given molecule to absorb a particular wavelength of light, a constant unique to the ion or compound being measured
  - \( b \) = the path length of solution the light passes through – the sample cell
    the longer the path length, the more light gets absorbed
  - \( c \) = the concentration - the more molecules in the solution, the more light is absorbed

![Nitrate by Reaction with Chromotropic Acid](image)
A spectrophotometer uses a light source, a filter (monochromator), a sample vial and a detector.
Dual (Split) Beam UV-Vis Spec – AQ8000

- The dual beam design ensures the most accurate data is measured from each flash of the lamp.
- The signal used for sample determination is a ratio of the reference signal and the sample signal.
Spectrophotometer – Visible Light Source

- Tungsten Halogen Lamp (Orion AquaMate 7000)
  - Measures in the visible region from about 325 to 1100 nm
  - Typical life = 2000 hours (50 weeks at 8 hrs/day, 5 days/week)
  - Warm up time of 10 to 30 minutes
  - Low cost, simple design that allows all the light to pass through the sample
  - Must re-measure the blank regularly to compensate for drift
  - Does not correct for random variations in lamp output
  - Suitable for many applications
Spectrophotometer - UV Light Source

- Xenon Flash Lamp (Orion AquaMate 8000)
  - Measures in the UV and visible UV-Vis regions from 190 to 1100 nm
  - Typical life = 3 to 5 years
  - No warm-up time
  - Can do UV parameters, such as UV254, SUVA, and chlorophyll_a
  - More stable signal
  - Highly accurate design that corrects for any variation caused by lamp fluctuations
  - Blanks need to be measured only when starting a new method
  - More resolution – required for certain measurements such as chlorophyll_a
Zero and Blanks

• Sometimes the terms are used interchangeably
• Follow the reagent use instructions exactly
• Possible zero/blank solutions
  • DI water – clear, colorless
  • Sample – to correct for color or turbidity
  • Reagent blank – DI + reagent
Some Practical Considerations

1. Spectrophotometry works best for more dilute species
   - at the 1 to 2 % level or less
   - often a good technique for low-level work

2. Turbidity & color can often be “blanked (zeroed) out” – if level is not too high

3. Temperature effects are minor ± 5 °C

4. Precision depends on concentration & range – typically 5 - 30 %

5. pH may affect the chemistry of the reaction. Some are buffered.

6. High ionic strength samples (e.g. seawater) may affect the reaction
Best Measurement Techniques

• Low Level Testing
  • Use clean, unblemished sample vial (cell)
  • Use the sample vial for the blank (or zero) and for the sample
    • Wash out the vial well between the tests

• Chemistries
  • Check “Use before” dates
  • Wait recommended time for color development
  • Use appropriate blank as indicated by instructions

• Instrument
  • Wipe clean with soft cloth
  • Prevent dust and liquids from getting into the meter
  • Use pre-programmed methods or user calibration curves
ISE EASY – Ammonia and Fluoride

- Kelly Sweazea, Specialist
- Thermo Scientific Water Analysis & Purification Products
Overview

• Choosing the right electrode and meter

• Preparing your standards

• Performing the measurement

• Optimizing performance

• How to troubleshoot your procedure
Overview

• Choosing the right electrode and meter

• Preparing your standards

• Performing the measurement

• Optimizing performance

• How to troubleshoot your procedure
Why Use Ion Selective Electrodes?

- EPA approved methods: *Ammonia in wastewater*
- Ammonia ISEs detect the species in solutions
- ISE meters report concentrations
  - *No manual calibration curves are required*
Ammonia ISE: 9512 vs. 9512HP

- **Standard (or Classic) 9512BNWP**
  - Reliable and stable performance
  - Best performance at concentrations > 0.1 mg/L

- **High Performance 9512HPBNWP**
  - Better slopes & sensitivity at lowest concentrations
  - Faster response
  - The better performer when analyzing < 0.1 mg/L NH3
Choosing the right electrode

• Good news! There is not a right or wrong choice
• If you are satisfied with your current choice, stick with it.
• If you have the standard electrode, but want faster response or better sensitivity at < 0.1 mg/L NH3, try the 9512HPBNWP
Measuring Fluoride Drinking Water Utilizing ISE

- Direct measurement using an ion selective electrode is the most popular laboratory method for measuring fluoride.
- The SPADNS (colorimetry based) method is also used, but the ISE method is chosen more often due to better accuracy and precision.
- ISE measurement improves laboratory productivity
  - quick, uncomplicated determinations
  - eliminates interferences often associated with colorimetric methods
Why Use Ion Selective Electrodes?

• EPA approved methods: *Fluoride in water*
• Fluoride ISEs detect the species in solutions
• ISE meters report concentrations
  • *No manual calibration curves are required*
Fluoride ISE: Solid State Electrode

Combination electrode: sensing and reference in one electrode body

Half cells: fluoride ISE used with separate reference electrode
ISE Meters

- ISE meters report concentrations
  - *No manual calibration curves are required*
  - *The potentials of known standards are stored in memory to produce a calibration curve*
  - *The potential of the sample is then compared to the calibration curve to determine the concentration*

- ISE meters generate sophisticated curves which are held in the meter’s memory

  Direct Testing =
  1. Run standards
  2. Run unknowns
  3. Read results
Useful Features in ISE Meters

• Rugged and durable
• Large, bright screen - information at a glance
• Easy to learn and use – intuitive, user-friendly interface
• Flexible calibration options
• Ability to create and save methods
• Memory to store test data and multiple calibrations
• Ability to transfer data electronically
• Ability to update meter software
• Stirring options – mechanical stirrer
• Good warranty
Thermo Scientific Orion ISE Meters

• Versa Star pH/ISE Benchtop Meters

  • Single and dual channel systems for one or two pH, ORP or ion selective electrodes; up to four channels by adding modules

  • Large color display with adjustable text sizes and simultaneously or individual channel measurement

  • Numeric keypad for quick and simple data entry

  • Direct concentration measurement or incremental technique options

_Premium option, great for flexibility and performance_
Thermo Scientific Orion ISE Meters

• Orion Dual Star pH/ISE Benchtop Meter
  • Dual channel for two pH, ORP or ion selective electrodes
  • Flexible graphic display with backlight and simultaneously or individual channel measurement
  • Numeric keypad for quick and simple data entry
  • Direct concentration measurement or incremental technique options

Redesigned Orion Dual Star meters are shown

Advanced option, easy-to-use and dependable meter
Thermo Scientific Orion ISE Meters

- Orion Star A214 pH/ISE Benchtop Meter
  - Single channel for one pH, ORP or ion selective electrode
  - Informative graphic display with backlight
  - Comprehensive keypad with dual purpose scroll/shortcut keys
  - Direct concentration measurement

Standard option, economical and simplified meter
Overview

• Choosing the right electrode and meter
• Preparing your standards
• Performing the measurement
• Optimizing performance
• How to troubleshoot your procedure
• Question and answer
Preparing Your Standards

Chemistry Conniptions

They let me play with chemicals

I have no idea what I'm doing
Serial Dilutions - Concept

Serial Dilutions: Easy and Accurate
NH3 Standards, serial dilution: step 1

1. Prepare a 100 ppm ammonia standard by measuring 100 mL of the 1000 ppm ammonia as nitrogen (N) standard (Orion 951007) using a graduated cylinder. Add the 100 mL measured to a 1000 mL volumetric flask. Add 900 mL of distilled/deionized (DI) water, diluting to the mark indicated on the flask. Mix the solution well.

1. Orion 1000 mg/L ammonia stock standard
2. Dilute 1:10 to obtain a 100 mg/L standard
   a) Dilute 100 mL of 1000 mg/L to vol in 1L volumetric.
   b) Or mix 100 mL of 1000 mg/L with 900 mL DI water
3. Makes 1L (1000 mL) of 100 mg/L ammonia standard.
NH3 Standards, serial dilution: step 2

2. Prepare a *10 ppm ammonia standard* by measuring 100 mL of the 100 ppm ammonia standard from Step 1 using a graduated cylinder. Add the 100 mL measured into a 1000 mL volumetric flask. Add 900 mL DI water, diluting to the mark indicated on the flask. Mix the solution well.

1. Orion 100 mg/L ammonia standard – from step 1
2. Dilute 1:10 to obtain a 10 mg/L standard
   a) Dilute 100 mL of 100 mg/L to vol in 1L volumetric
   b) Or mix 100 mL of 100 mg/L with 900 mL DI water
3. Makes 1L (1000 mL) of 10 mg/L ammonia standard.
This App Note is available on the Thermo Scientific website (search on “ammonia standards”, choose “Resources”).

It is also available in the Online Library at thermoscientific.com/waterlibrary.
Overview

• Choosing the electrode and meter

• Preparing your standards

• Performing the measurement

• Optimizing performance

• How to troubleshoot your procedure

• Question and answer
Ammonia ISE Measurement

• Measure from 0.01 ppm to 17,000 ppm ammonia
  • Also use for ammonium and organic nitrogen

• Must adjust sample pH

• The sensor is a pH electrode – it measures change in pH across the membrane

• EPA approved method for waste water – Direct method (SM 4500-NH3 D) or Known Addition method (E)

• Note the manufacturer’s instructions
1. Dissolved NH3 diffuses through the membrane.
2. The pH of the fill solution (FS) changes.
3. The pH change indicates the amount of ammonia-N in the sample.
Gas Sensing Electrode: Ammonia

- Works by measuring the pH change caused by diffusion of ammonia gas through a hydrophobic but porous membrane.

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-
\]
Ammonia and Ammonium Nitrogen

- Ammonia-N = NH$_4^+$ (aq) + NH$_3$(g)
  
  ammonium ion  dissolved ammonia gas

% Ammonia vs. Ammonium @ ~ pH 9

NH$_3$ (g)  NH$_4^+$ (aq)

gas  ion
Ammonia and Ammonium Nitrogen

- Ammonia-N = NH$_4^+$ (aq) + NH$_3$(g)

  - ammonium ion
  - ammonia gas

% Ammonia vs. Ammonium @ ~ pH > 11

NH$_3$ (g)

gas

100%
Using Ion Strength Adjustor (ISA)

1mL to 50 mL

Ammonia pH Adjusting ISA
Contains Sodium Hydroxide and Methanol

Standards

Samples
What the ISA Does – Three Versions

• Blue ISA
  • Adjusts the pH to > pH11, converts NH4+ to NH3
  • Blue color indicates that the pH is sufficiently high
  • Raises the ionic strength to a consistent level.
  • Complexes metals – such as mercury and silver – that could interfere
  • Methanol content may help to keep the membrane clean

• Low Level Blue ISA
  • Same as above but without the metals complexing agent.
  • Formulated for very low level ammonia analysis where metals are not present
What the ISA Does – Three Versions

• Alkaline ISA
  • Adjusts the pH to > pH11, converts NH4+ to NH3
  • Raises the ionic strength to a consistent level.
  • Used at a ratio of 1:100
    • Use 0.5 mL of alkaline reagent for 50 mL of sample, or
    • Use 1 mL of alkaline reagent for 100 mL of sample
Testing Sequence – Direct Method

Make Standards
- Serial Dilutions

Prepare Standards and Samples
- Into beakers, at RT, add ISA just before test

**EPA-approved method**; a good method for large batches, wide range of ammonia, fast

Analyze Samples & QC: Direct Reading

Calibrate and Verify
- If good, proceed.
Direct Method Calibration

Slope -54 to -60 mV at 20-25 deg C

Consider enabling autoblank for low level testing
ISE Incremental Techniques

- Incremental techniques differ from the direct measurement
  - Direct concentration measurement most common
  - Incremental techniques calculate the sample concentration based on the observed response when known changes in concentration are made
    - A separate calibration curve is not required
- Types of ISE Incremental Techniques
  - Known addition
  - Analate addition
  - Known subtraction
  - Analate subtraction
  - Single and double known addition and subtraction
Known Addition

- Known amount of the species being measured is added to the sample
- Eliminates the need for a separate calibration curve for each sample
- Single, double or multiple known additions are possible
- Minimizes effects on results due to complex matrices
- Preferred when:
  - Small number of samples
  - Backgrounds vary, are unknown, or cannot be calibrated out
  - Excess or no complexing agent is present
  - Samples of high ionic strength
Testing Sequence – Known Addition

Make QC Check Standard
- Serial Dilution

Prepare Standards and Samples
- Into beakers, at RT, add ISA just before test

**EPA-approved method**; a good method for small batches, varied or challenging samples

Analyze Samples & QC: Known addition(s)
Single Known Addition (SKA)

**Step 1**
- Test sample (mV)

**Step 2**
- Add known amount of standard

**Step 3***
- Test sample + standard (mV)

**Step 4**
- Read result from meter or calculate

*Step 3: Not specified in the diagram.
How does it work?

- The meter calculates the result based on the sample reading, the sample + standard reading, and the information that we input.
- We input slope, standard concentration, volume, and sample volume.
- The meter calculates ammonia result based on the graph shown here.
Double Known Addition (DKA)

- Like SKA, but two additions of standard are made and three mV readings are taken.
  - Sample,
  - sample + standard,
  - sample + more standard
- The meter calculates the slope and the ammonia result.
- “Calibration in a beaker”
- We only input standard concentration, volumes, and sample volume.
Known Addition - SKA vs. DKA

• Single known addition (SKA)
  • Slope is determined once each day and input to the meter
  • Concentration is determined by a single increment
  • Single incremental techniques are quick and easy
  • Note: the single known addition technique for ammonia is a USEPA-approved method

• Double known addition (DKA)
  • Slope is determined automatically during each sample analysis
  • Concentration is determined by two increments
  • Greater accuracy is achieved for samples with complex matrices
Why use ISE incremental techniques?

- No calibration required
  - Accurate results in less time
- Handles complex matrices or high background interferences
  - No added sample preparation steps
  - More accurate than direct calibration for complex samples
- Works with dilute or concentrated samples
- Sample matrix is not water
Overview

• Choosing the electrode and meter
• Preparing your standards
• Performing the measurement
• Optimizing performance
• How to troubleshoot your procedure
Optimizing Performance

- Electrode Maintenance and Storage
  - Change fill solution and membrane
  - Store in ammonia storage solution (overnight/weekends)
  - Store in standard + ISA, e.g. mid-level (between samples)
  - Rinse thoroughly with deionized or distilled (DI) water before and after each reading and before storage
  - Don’t touch the membrane
Membrane Application

www.youtube.com/watch?v=Sv43b8-LNcw
Inspecting the membrane

Inspect the membrane for damage, wrinkles, drum-tight surface.

In these photos, one is damaged and not smoothed tight. Another has a bit of a wrinkle. The others look good.
Filling the ISE

9512
2-2.5 mL
(~50 drops)

9512 HP
Fill to line

Carefully
shake down,
like a
thermometer

Gently pull
up on the
cable. Soak.
Optimizing Performance

• Ammonia Standards
  • Do it right the first time and save yourself a lot of time
  • Stock standard - not expired.
  • Store properly - tightly closed, out of direct sunlight, at room temperature (or refrigerated)
  • Never put anything into your stock standard bottle – not even a pipet. Never pour any solution back in.
  • Use ammonia-free DI water to prepare standards and rinse glassware.
  • Make sure all glassware and containers (any contact surface) is clean before use.
Optimizing Performance

• Keep it Clean
  • Contamination can be a significant source of error.
  • Clean all labware thoroughly. 1% laboratory detergent solution is useful.
  • Rinse thoroughly with DI water.
  • Store labware away from ammonia sources.
  • Clean up spills and puddles. Spilled ammonia-containing liquids can put ammonia in the air.
  • Use a clean graduated cylinder to measure out each sample
  • Test clean samples first, proceeding to more concentrated samples after.
Optimizing Performance

- Prepare Samples Carefully (including standards)
  - Bring samples & standards to the same temperature
    - Room temperature is good. Keep all +/- 1 or 2 degrees.
    - Use an ATC or thermometer to verify and record.
  - Make sure all glassware and containers are clean before use. Don’t reuse glassware without wash/rinse.
  - Cover samples, esp. if they will be on the bench awhile
- Be accurate:
  - Measure sample volume with graduated cylinder
  - Measure ISA with a pipet
    - Add ISA just before sample testing
  - Measure known addition volumes with a pipet.
Optimizing Performance

• Analyze Samples Consistently (including standards)
  • Add ISA just before making the measurement
  • Rinse electrodes and stirrer (and ATC) thoroughly with DI water before and after each test.
    • best practice – avoid touching the membrane
    • if / when blotting, be careful around the membrane
  • Stir with mechanical or magnetic stirrer to mix thoroughly and speed the response.
    • watch for temperature changes if using a magnetic stirrer
    • stir just fast enough to avoid a vortex
  • Use an electrode holder with an angled position
  • Check for air bubbles on the membrane surface
Optimizing Performance

• Run the Standard Curve
  • Use standards in decade increments – for example, use 0.10, 1.0 and 10 mg/L standards.
  • Consider conditioning the electrode before running the standard curve.
  • Use freshly prepared standards – don’t reuse a standard that has already been tested.
  • Expect a slope of -54 to -60 mV
    • If not, check electrode operation (slope) per User Guide.
    • If Autoblank option is on, slope may be > 60 mV
  • Verify the calibration every two hours or per your SOP.
Tips for low level testing <0.10 mg/L

- Consider using the Orion HP model (9512HPBNWP).
- Try using low-level Blue ISA (951210) or Alkaline reagent (951011).
- Keep all labware and benches clean.
- Use freshly prepared DI water. Gaseous ammonia tends to contaminate water stored in the laboratory.
- Segregate low-level ammonia samples. Test first.
- Consider using the Autoblank function for improved low level results.
- Wait for complete electrode response. Don’t rush.
  - If unsure, wait +1 minute after “ready” to confirm.
- Try immersing in DI+ISA solution or pH 4 between samples.
Autoblock feature at low levels

- Useful for low levels, where ISE response becomes non-linear.
- Autoblock is like drawing a smooth curve.
- More accurate than measuring a zero standard (blank).
- If calibrating and testing NH3 at < 0.1 mg/L, consider enabling the “autoblock” function in Setup.
- Meter only applies autoblock if the calibration mV indicate low-level non-linearity.
- When applied, calculated slope may be higher than typical range.
Tips to improve stability; reduce drift

- Keep your ammonia ISE in “tune” - do the maintenance.
- Pay attention to ISE storage - during testing & overnight
- Pay attention to temperature - measure it, record it
  - Electrode slope, NH3 partial pressure, sample chemistry
- Keep your technique consistent - rinsing, handling, stirring...
- Ensure the electrode is conditioned before calibration
  - e.g., place in a portion of the mid-level std for 15 min
  - e.g., overnight storage in yesterday’s mid-level std
- Use freshly prepared standards. Don’t reuse anything.
- Check for bubbles - on the membrane, inside the ISE
- Check membrane - installed properly, not damaged
- If drifting, try the cord/cable pull. Recalibrate as necessary.
Tips to improve slope

• Keep in ammonia storage solution or mid-level standard overnight.
• Use freshly prepared standards. Don’t reuse anything.
• Check the electrode slope per the procedure in manual.
  • If not good, clean the pH bulb of the inner body. Try Orion 900024 or 1M HCl soak, e.g. 30 minutes. Soak the pH glass only (not the reference wire).
Fluoride ISE Hints

- Always use fresh standards for calibration.
- Stir all standards and samples at a uniform rate. Use insulation material between magnetic stirrer and beaker.
- Between measurements, rinse electrode with DI water. Shake electrode to remove DI water. Do not wipe or rub the fluoride sensing element.
Fluoride ISE Hints

• Flush fill solution weekly.

• Polish electrode when response is sluggish or slope is low. Use fluoridated toothpaste or a one inch piece of polishing strip.
  • Rotate on sensing surface for 30 seconds, rinse with DI water, then soak in 1ppm standard for 10 minutes.

• Store fluoride standards in plastic.

• Capped fluoride standards will be stable for approximately 3 months.
Overview

• Choosing the electrode and meter

• Preparing your standards

• Performing the measurement

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• How to troubleshoot your procedure
Troubleshooting Ammonia - Fishbone Diagram

Fishbone Diagram – potential sources of error in ammonia testing
Troubleshooting

• Solutions – standards, ISA, fill solution
  • Proper storage of all – purchased, prepared
  • Properly prepared standards – volumetric glassware
  • Not expired, not reused, not contaminated
  • Stored at room temperature or refrigerated
  • Water for standards is ammonia-free

• Electrode
  • In-tune:
    • properly stored, maintained, cleaned when required
  • Bubbles: check for bubbles, inside and out
  • Slope check per electrode manual - diagnostic
Electrode Slope Check

1) Put meter in mV mode. Stir.
2) Add 1 ml of 1000 mg/L (or 0.1M) ammonia standard. Read mV, e.g. 48.7 mV
3) Add 10 ml of the same standard. Read mV, e.g. -9.5 mV

**Slope** = 1\textsuperscript{st} mV reading – 2\textsuperscript{nd} mV reading.

In this case,
Slope = 48.7 – (-9.5) = 57.7 mV
Troubleshooting

• Method
  • Follow SOP closely - training, documentation
  • Calibrate carefully and consistently
  • Monitor performance - calibration verification, duplicates, spikes, control samples
  • Pay attention to rinsing, stirring, bubble elimination, electrode angle, and any other factors during testing

• Conditions
  • All samples and standards at room temperature
  • Consistent temperature during testing
  • Manage cross-contamination conditions
Troubleshooting

• Samples
  • Acidified samples - ensure pH is > 11 after adding ISA
  • Read temperature - ensure sample has reached RT
  • Analyze “dirty” and high-level samples after analysis of the “clean” and low-level samples
  • Choose the right ISA
  • Difficult samples – consider matrix-matched standards (e.g. standards in seawater) or known addition method.

• Meter
  • Ensure meter setup parameters have not been changed
  • Consider setting up a pass-word protected method
  • Check calibration log - any significant changes?
Resources

- Contact us for any technical questions!
- Orion Products
  - Technical Service: (800) 225-1480
  - Technical Service: wai.techservbev@thermofisher.com
  - Local Specialist, Water Analysis & Purification Products:
    - Kelly Sweazea: kelly.Sweazea@thermofisher.com (919) 239-9947
  - Web site: www.thermofisher.com/water