Using Spectrophotometers for Water and Wastewater Testing

Kelly Sweazea, Technical Sales Manager
Thermo Scientific Electrochemistry 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.

<table>
<thead>
<tr>
<th>Meter Analysis</th>
<th>10.56am 5Sep12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Name:</td>
<td>ACD001</td>
</tr>
<tr>
<td>Abs 430nm</td>
<td>Result mg/L</td>
</tr>
<tr>
<td>0.001</td>
<td>0.049</td>
</tr>
</tbody>
</table>

Page 1, Sample 1

<table>
<thead>
<tr>
<th>Measure</th>
<th>Blank</th>
<th>Data</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 380 nm.
  - 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
Using Spectrophotometers

• Who uses a spectrophotometer in their facility?
• What are you testing for?
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 many different parameters
• The cost of is less than for an IC or ICP instrument
• No daily equipment prep required
  • other than warm up for tungsten lamp for Vis spec
• Easy 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
Spectrophotometry - Wavelength

• 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
A spectrophotometer uses a light source, a filter (monochromator), a sample vial and a detector.
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

• Who uses DPD for testing chlorine?
Chlorine

- DPD - N,N-diethyl-p-phenylenediamine
  - Reacts with oxidizing substances
  - If chlorine levels are high, the colorless compound dominates
  - DPD color reagents contain a buffer to ~ pH 6.3
Free and Combined Chlorine

- Free chlorine reacts quickly with DPD
  - Reading is usually taken within 1 minute of reaction
  - Reagent has DPD and buffer.

- Combined chlorine usually refers to chloramines
  - Formed on reaction of chlorine with ammonia
  - Have disinfection properties, but not as strong as free chlorine
  - Chloramines react slowly with DPD, so KI is added to the reagent
    - Chloramine oxidizes the iodide to iodine, which then reacts with DPD
Total Chlorine and Combined Chlorine

- Total chlorine = free and combined chlorine
  - If the DPD reagent includes KI (and buffer), the color developed will be due to the total chlorine content

- Free chlorine + combined chlorine = total chlorine

- Combined chlorine = total chlorine – free chlorine
  - Determine combined chlorine by subtracting free chlorine results from the total chlorine results
Interferences with DPD Chemistry

- Other oxidizing substances will react with DPD
  - Iodine
  - Bromine
  - Chlorine dioxide
- Extreme pH can interfere (true for many color reactions)
- Chlorine levels that are too high will be colorless
  - False negatives
  - If it smells like chlorine, dilute and retest
- Strong samples (like seawater) can affect the results
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 ºC
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
Resources

• Contact us for any technical questions!
• Orion Products
  • Technical Service: (800) 225-1480
  • Technical Service fax: (978) 232-6015
  • Local Technical Sales Manager:
    • Kelly Sweazea: (919) 239-9947
• Web site: www.thermoscientific.com/water
• Online library at www.thermoscientific.com/waterlibrary
ISE Easy
What are Ion Selective Electrodes (ISEs)?

- Ion Selective Electrodes are devices which detect specific ion species in solutions.
- ISEs consist of a sensing membrane in a rugged, inert body.
Ion Selective Electrode (ISE) Advantages

- Responsive over a wide concentration range
- Not affected by sample color or turbidity
- Rugged and durable
- Rapid response time
- Real time measurements
- Low purchase and operation cost
- Easy to use
Why Use Ion Selective Electrodes?

- Specific ion detection in solutions
- ISE meters report concentrations
  - No manual calibration curves are required
- ISE meters generate sophisticated curves which are held in the meter’s memory
  - Run standards
  - Run unknowns
  - Read results
- ISE use is endorsed through EPA approved methods
Nutrient Regulations

- **USEPA & NPDES**
  - Govern permits for limits of nutrients
  - Mandate that standard methods must be used for reporting

- **USEPA Approved Methods using an electrode include:**
  - Acidity
  - Alkalinity
  - Ammonia
  - Chloride
  - Chlorine, Total
  - Cyanide
  - Fluoride
  - Total Kjeldahl Nitrogen (TKN)
  - Nitrate
  - Dissolved Oxygen / BOD
  - pH
  - Sulfide
Types Of Sensing Electrodes

• Glass Membrane: pH, sodium

• Plastic Membrane: chloride, nitrate, etc.

• Gas Sensing: ammonia, CO₂, etc.

• Solid State: chlorine, copper, fluoride, etc.
ISE Measurement: Basic Considerations

- Required solutions
- Electrode assembly
- Electrode storage
- Standards: source and preparation
Direct Measurement with ISEs

- Direct measurement is generally preferred:
  - Measure many samples with similar backgrounds
  - Measure high volume of samples
  - Measure wide range of concentrations
  - Easy

- Read measurement by using an ISE meter or by preparing a calibration curve

- Precision is +/- 2%
Direct Measurement with ISEs

- Two-point calibration for linear portion of curve
- Low-level measurements require non-linear multi-point calibration or blank correction. The ISE meter may have an “auto-blank” feature in the settings.
Direct Measurement with ISEs

- Calibrate every 2 hours
- Always calibrate with standards that bracket expected concentration range
- Always use at least two standards that are ten fold apart in concentration
- Slope range for monovalent ions at 20°-25°C: 54-60 mV (includes ammonia, nitrate and fluoride probes)
- Slope range for divalent ions at 20°-25°C: 26-30 mV
Practical Considerations

- Method interferences
- Electrode interferences
- Temperature effects
Practical Considerations

**Method interferences**

Many method interferences are overcome by using an Ionic Strength Adjuster (ISA)

- maintains a constant background when added to samples and standards
- minimizes ionic strength differences
- complexes many interferences
- adjusts pH to proper range
Practical Considerations

- **Electrode interferences**
  - Some ion species cause increased electrode response
  - With some ISEs, there is a maximum allowable ratio
    - Example: not more than 400x as much chloride for the bromide electrode
  - For some ISEs, interferences introduce a gradual error
    - Example: at 10 ppm nitrate, a level of 760 ppm chloride will cause 10% error
  - For some ISEs, interference suppressors are available
    - Example: Sodium ISA removes H+ interferences
Practical Considerations

• **Temperature effects**

  A change in temperature will cause electrode response to shift and change slope

  • On average, a 1°C change in temperature gives rise to a 2% error for monovalent ISEs
    *(this type includes ammonia, nitrate and fluoride probes)*

  • On average, a 1°C change in temperature gives rise to a 4% error for divalent ISEs

  • ISE temperature compensation is generally accomplished by keeping samples and standards at the same temperature, between 20°-25°C.

  • Some, but not all, meters will allow adjustment of the isopotential point for each different ISE electrode, and then the temperature input can be used to adjust the calibration curve
ISE Measurement: Troubleshooting

• Slope Test

• Prepare electrode for measurement
• Add (appropriate volume) ISA to 100 mL DI water, stir
• Pipet 1 mL standard into the beaker, stir. Record the mV reading when stable
• Pipet 10 mL standard into the beaker, stir. Record the mV reading when stable
• For monovalent ISEs, there should be a -54 to -60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C.

  *(includes ammonia, nitrate and fluoride probes)*

• Slope range for divalent ions at 20°-25°C: 26-30 mV
Conductivity Measurement
Properties of Conductivity

Current is carried by electrons

- A wire with 1 ohm resistance allows a current of 1 amp when 1 volt is applied
- Resistance to the flow of electrons = Voltage/Current

*Units of resistance are measured in ohms*

*Conductance is the reciprocal of resistance*

- Conductance of the electrons = Current/Voltage

*Units of conductance are measured in Siemens*

1 Siemen = 1 mho = 1/ohm
1 Siemen = 1000 mS = 1,000,000 µS
Common Units and Symbols

Conductance Units
- S (Siemens)
- mS
- μS

Conductivity Units
- S/cm
- mS/cm
- μS/cm

Resistance Units
- Ω (Ohm)
- kΩ
- MΩ

Resistivity Units
- Ω·cm
- kΩ·cm
- MΩ·cm
Conductivity in Solutions

Conductivity carried by ions is dependent upon:
- Concentration (number of carriers)
- Charge per carrier
- Mobility of carriers

Conductivity = (concentration) x (charge per carrier) x (mobility of the carriers)
Concentration

• The tendency of a salt, acid or base solution to dissociate in water provides more carriers in the form of ions

• More highly ionized species provide more carriers

**Example:**

1% Acetic Acid = 640 µS/cm
1% HCl = 100,000 µS/cm

Conductivity =
(concentration) x (charge per carrier) x (mobility of the carriers)
• In general, as concentration increases, conductivity increases

<table>
<thead>
<tr>
<th>Concentration (M/L)</th>
<th>Conductivity (uS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 M/L</td>
<td>0</td>
</tr>
<tr>
<td>0.0005 M/L</td>
<td>73.9</td>
</tr>
<tr>
<td>0.001 M/L</td>
<td>147</td>
</tr>
<tr>
<td>0.005 M/L</td>
<td>718</td>
</tr>
<tr>
<td>0.01 M/L</td>
<td>1,413</td>
</tr>
<tr>
<td>0.05 M/L</td>
<td>6,667</td>
</tr>
<tr>
<td>0.1 M/L</td>
<td>12,900</td>
</tr>
<tr>
<td>0.5 M/L</td>
<td>8,670</td>
</tr>
<tr>
<td>1.0 M/L</td>
<td>111,900</td>
</tr>
</tbody>
</table>

Conductivity = (concentration) x (charge per carrier) x (mobility of the carriers)
Charge per Carrier

- Divalent ions generally contribute more to conductivity than monovalent ions

\[ \text{Conductivity} = (\text{concentration}) \times (\text{charge per carrier}) \times (\text{mobility of the carriers}) \]
Mobility

- The mobility of each ion species is different. The conductivity of 0.1M NaCl and 0.1M KCl will not be the same.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Relative Mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+</td>
<td>350</td>
</tr>
<tr>
<td>Na+</td>
<td>50</td>
</tr>
<tr>
<td>K=+</td>
<td>74</td>
</tr>
<tr>
<td>Ag+</td>
<td>62</td>
</tr>
<tr>
<td>OH−</td>
<td>200</td>
</tr>
<tr>
<td>F−</td>
<td>55</td>
</tr>
<tr>
<td>Cl−</td>
<td>76</td>
</tr>
<tr>
<td>HCO3−</td>
<td>45</td>
</tr>
</tbody>
</table>

Conductivity = (concentration) x (charge per carrier) x (mobility of the carriers)
Temperature Affects Ion Mobility

• Increasing temperature makes water less viscous, increasing ion mobility.

• Most meters can do a calculation to show all measurements as if the sample were at 20ºC or 25ºC… conductivity temperature compensation / normalization.

<table>
<thead>
<tr>
<th>Example:</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M KCl at 0 ºC = 775 µS/cm</td>
</tr>
<tr>
<td>0.01 M KCl at 25 ºC = 1410 µS/cm</td>
</tr>
</tbody>
</table>

Conductivity =
(concentration) x (charge per carrier) x (mobility of the carriers)
Conductivity Properties

- *Conductivity* and *Resistivity* are inherent properties of a material’s ability to transport electrons

- *Conductance* and *Resistance* depend on both material and geometry

\[
\text{Conductivity} = \frac{d}{A} \times \text{conductance}
\]

(d) distance between the electrodes
(A) electrode area
Conductivity Properties

Conductivity is defined as the reciprocal of the resistance between opposing faces of a 1 cm cube (cm$^3$) at a specific temperature.

Conductivity = $d/A \times$ conductance

$K = 1.0$ cm$^{-1}$
Cell Constant (K) in cm⁻¹

- The cell constant (K) is the value by which you multiply conductance to calculate conductivity.

- The cell constant (K) is the ratio of the distance between the electrodes (d) to the electrode area (A). Fringe field effects is the amount AR.

\[ K = \frac{d}{A + AR} \]

*Conductance = the measured value relative to the specific geometry of the cell*

*Conductivity = the inherent property of the solution being tested*

\[ \text{Conductivity} = \text{Conductance} \times K \]

Conductivity = \( d/A \times \text{conductance} \)

K = 1.0 cm⁻¹
## Cell Constants (K) by Application

<table>
<thead>
<tr>
<th>Cell constant (K)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 0.1 \text{ / cm}$</td>
<td>Pure water</td>
</tr>
<tr>
<td>$K = 0.4 - 1.0 \text{ /cm}$</td>
<td>Environmental water and industrial solutions</td>
</tr>
<tr>
<td>$K = 10 \text{ /cm}$</td>
<td>Very high conductivity samples</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell constant (K)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 0.1$</td>
<td>0.001 uS/cm to 300 uS/cm</td>
</tr>
<tr>
<td>$K = 0.475$</td>
<td>10 uS/cm to 1000 mS/cm</td>
</tr>
<tr>
<td>$K = 1.00$</td>
<td>10 uS/cm to 200 mS/cm</td>
</tr>
<tr>
<td>$K = 10.0$</td>
<td>10 uS/cm to 2000 mS/cm</td>
</tr>
</tbody>
</table>
Temperature Coefficients

- Each ion species has a unique temperature coefficient that can change with changes in concentration.
- Temperature effects vary by ion type.

Some typical temperature coefficients:

<table>
<thead>
<tr>
<th>Sample</th>
<th>% / °C (at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt solution (NaCl)</td>
<td>2.12</td>
</tr>
<tr>
<td>5% NaOH</td>
<td>1.72</td>
</tr>
<tr>
<td>Dilute Ammonia Solution</td>
<td>1.88</td>
</tr>
<tr>
<td>10% HCl</td>
<td>1.32</td>
</tr>
<tr>
<td>5% Sulfuric Acid</td>
<td>0.96</td>
</tr>
<tr>
<td>98% Sulfuric Acid</td>
<td>2.84</td>
</tr>
<tr>
<td>Sugar Syrup</td>
<td>5.64</td>
</tr>
</tbody>
</table>
Non-Linear Temperature Coefficients

• Unlike salt solutions, the temperature coefficient for pure water is not linear

Typical temperature coefficients of pure water:

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>% per °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.1</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
</tr>
<tr>
<td>20</td>
<td>5.5</td>
</tr>
<tr>
<td>30</td>
<td>4.9</td>
</tr>
<tr>
<td>50</td>
<td>3.9</td>
</tr>
<tr>
<td>70</td>
<td>3.1</td>
</tr>
<tr>
<td>90</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Measuring Conductivity

• A meter applies a current to the electrodes in the conductivity cell
Measuring Conductivity

• Reactions can coat the electrode, changing its surface area
  • $2 \text{H}^+ \rightarrow \text{H}_2$ bubbles

• Reactions can deplete all ions in the vicinity, changing the number of carriers

• Instead of using a direct current (DC), the conductivity meter uses an alternating current (AC) to overcome these measurement problems
2-Electrode Cells

• Two electrodes are used to measure current

Benefits:
  – Lower cost than four electrode cells
  – Limited operating range with cell constants geared toward specific applications

Drawbacks:
  – Resistance increases due to polarization
  – Fouling of the electrode surfaces
  – Unable to correct for surface area changes
  – Longer cable lengths will increase resistance
4-Electrode Cells

• A constant current is sent between two outer electrodes and a separate pair of voltage probes measure the voltage drop across part of the solution

• The voltage sensed by the inner two electrodes is proportional to the conductivity and is unaffected by fouling or circuit resistance
Conductivity Measurement

- Most conductivity measurements are made on natural waters

<table>
<thead>
<tr>
<th>WATER</th>
<th>CONDUCTIVITY (µs/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrapure</td>
<td>0.0546</td>
</tr>
<tr>
<td>Good Distilled</td>
<td>0.5</td>
</tr>
<tr>
<td>Good R/O</td>
<td>10</td>
</tr>
<tr>
<td>Typical City</td>
<td>250</td>
</tr>
<tr>
<td>Brackish</td>
<td>10,000</td>
</tr>
</tbody>
</table>
Conductivity Measurement

- In natural waters, conductivity is often expressed as “dissolved solids”
- Measured conductivity is reported as the concentration of NaCl that would have the same conductivity
- Total Dissolved Solids (TDS) assumes all conductivity is due to dissolved NaCl

Comparison of conductivity to TDS:

<table>
<thead>
<tr>
<th>CONDUCTIVITY (μS/cm)</th>
<th>DISSOLVED SOLIDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0210</td>
</tr>
<tr>
<td>1.0</td>
<td>0.44</td>
</tr>
<tr>
<td>10.0</td>
<td>4.6</td>
</tr>
<tr>
<td>100</td>
<td>47</td>
</tr>
<tr>
<td>200</td>
<td>91</td>
</tr>
<tr>
<td>1000</td>
<td>495</td>
</tr>
</tbody>
</table>
Other Measurement Capabilities

• **Salinity** is the measure of the total dissolved salts in a solution and is used to describe seawater, natural and industrial waters. It is based on a relative scale of KCl solution and is measured in parts per thousand (ppt).

• **Resistivity** is equal to the reciprocal of measured conductivity values. It is generally limited to the measurement of ultrapure water where conductivity values would be very low. Measured in MΩ -cm.
Using Turbidimeters for Water and Wastewater Testing
What is Turbidity?

Turbidity is an “expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample.”

*Standard Methods for the Examination of Water and Wastewater, 16th ed.*
What Turbidity Looks Like

The naked eye perceives turbidity at about 10 NTU
What Causes Turbidity?

• **Turbidity** is a measure of the cloudiness of water - the cloudier the water, the greater the turbidity.

• **Turbidity** in water is caused by suspended matter such as clay, silt, and organic matter, and by plankton and other microscopic organisms that interfere with the passage of light through the water (American Public Health Association, 1998).

• **Turbidity** is closely related to total suspended solids (TSS), but also includes plankton, microbes, and other organisms.
Why Measure Turbidity – Drinking Water

• Turbidity itself is not a major health concern, but high turbidity can interfere with disinfection and provide a medium for microbial growth.
  • Contaminants such as bacteria, viruses and parasites can attach themselves to the suspended particles in turbid water.
  • Turbidity must be virtually eliminated for effective disinfection (usually by chlorine) to occur.
• Turbidity, taste, and smell are water quality criteria that are important to drinking water customers.
Why Measure Turbidity – Wastewater

• Turbidity indicates solids remaining in a wastewater effluent, which gives information regarding the efficacy of the treatment process.

• A wastewater discharge shall not cause objectionable odor, taste, turbidity, or discoloration in the receiving water.
Uses for Turbidity Measurements

- Monitor and improve plant efficiency
- Monitor filter breakthrough
- Meet government regulations
Combined Filter and Individual Filter Water Requirements:

- The rules call out on-line turbidity rules in two locations: The combined filter effluent and the individual filter effluents.

- Combined Filter Effluent Requirements:
  - The combined filter effluent must be less than or equal to 0.3 NTU on measurements taken 15 minutes apart.
  - The combined filter effluent must never exceed 1.0 NTU.
  - If these rules are broken, an exceptions report must be filed explaining the deviation.

- Individual Filter Requirements:
  - The turbidity should never be greater than 1.0 NTU based on two measurements taken 15 minutes apart.
  - The turbidity should never be greater than 0.5 NTU at the end of a filter operation based on two consecutive measurements taken 15 minutes apart.
Turbidity—Approved Methods

• USEPA
  • Method 180.1
  • Standard Methods 2130 B
  • Orion Method 4500
  • GLI Method 2
  • Possible acceptance of ISO 7027 in the future?

• International Standards
  • DIN/ EN 27027 - ISO 7027
Units of Measure

NTU: Nephelometric Turbidity Unit
FTU: Formazin Turbidity Unit

Note: A turbidimeter that measures light scattered at 90° is called a Nephelometer.
Particle Effects on Turbidity

- Number of particles
- Color of particles
- Shape of particles
- Refractive Index of particles
- Size of particles
# Particle Scatter Patterns

<table>
<thead>
<tr>
<th>Small Particles</th>
<th>Medium Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Small Particle Diagram" /></td>
<td><img src="image2" alt="Medium Particle Diagram" /></td>
</tr>
<tr>
<td><img src="image3" alt="Large Particle Diagram" /></td>
<td><img src="image4" alt="Large Particle Diagram" /></td>
</tr>
</tbody>
</table>
Evolution of the Turbidimeter

World’s First Turbidimeter

Jackson Candle Turbidimeter
Basic Single-Beam Turbidimeter

Method 180.1
Calibration and Verification – Benchtop/Portable

• Primary Standards – use for calibration or verification
  • Formazin
  • Microspheres of styrene-divinylbenzene (SDVB)
  • Stabilized Formazin

• Secondary Standards – use for verification only
  • Sealed standards
  • Glass or other solids

• Calibration Verification
  • Daily and after every 10th sample
  • Results within 10% of accepted value
  • Analyze a blank with each batch of samples tested
Calibration Standard Pitfalls

- **Formazin**
  - Reproducibility
  - Accuracy
  - Stability – prepare daily for low levels

- **SDVB Microspheres**
  - Instrument specific
  - Must not freeze
Turbidity Measurement Tips

**Measurement Tips**

- Keep turbidity vials scrupulously clean both inside and out.
- Discard vials if they become scratched or etched and silicone oil does not improve their performance.
- Do not handle vials in the light path area.
- Wash vials well with laboratory detergent, rinse repeatedly with deionized water and allow to air dry.
- If condensation forms on the outside of the vial, warm sample to room temperature, wipe off excess moisture and remix sample before analysis.
Tips for Low-Level Turbidity Work

• Observe the cleanliness recommendations listed previously.
• Create a set of matched sample cells.
  • Use dedicated, matched sample cells (vials) for low-level work only.
  • Blank readings should agree within 0.01 NTUs
  • Do not use low-level cells for high turbidity samples.
• Aeration of the sample and bubbles on the interior cell walls can affect low level readings in particular.
  • Perform a visual check of the sample cell before every measurement.
Essentials of pH Measurement

Kelly Sweazea, Technical Sales Manager
Thermo Scientific Electrochemistry Products
Common Questions: What is \( pH \)?

The Theoretical Definition: \[ pH = - \log a_H \]

- \( a_H \) is the hydrogen ion activity.
- In solutions that contain other ions, activity and concentration are not the same.
- The activity is an effective concentration of hydrogen ions, rather than the true concentration; it accounts for the fact that other ions surrounding the hydrogen ions will shield them and affect their ability to participate in chemical reactions.
- These other ions effectively change the hydrogen ion concentration in any process that involves \( H^+ \).
Common Questions: *What is pH?*

- The pH of pure water around room temperature is about 7.
- pH 7 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".

![Diagram showing pH concept]

**LOW pH**: LOTS OF H\(^+\)  
**LOTS OF OH\(^-\)**: HIGH pH
The pH Scale

- \([\text{H}^+]\) activity increases by a factor of 10 for every pH unit.
  - Cola pH is about 2.5. Cola is 10x more acidic than Orange Juice (pH of 3.5)
  - Cola is 100x more acidic than Beer! (pH of 4.5)

### Representative pH values

<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>

Common Questions: What is pH?
Common Questions: *Measuring pH*

**Calibration**

- The Nernst Equation

\[ E = E_0 + s \log a_H \]

- \( E = \) measured potential
- \( E_0 = \) reference potential
- \( s = \) slope = \( \frac{RT}{nF} = 59.2 \) mV at 25 °C
- \( a_H = \) activity
pH Measurement System

- When two solutions containing different concentrations of $H^+$ ions are separated by a permeable glass membrane, a voltage potential is developed across that membrane. (Sensing electrode)
- A voltage potential is also generated from the reference electrode.
- The pH meter measures the voltage potential difference (mV) between the sensing electrode and the outside sample (reference electrode).
- An algorithm in the meter firmware translates the received mV signal into a pH scale.
pH Measurement System

The pH Meter

- Acts as a volt meter
- Translates electrode potential (mV) to pH scale

Meter functions

- Stores calibration curve
- Adjusts for temperature changes
- Adjusts electrode slope
- Signals when reading is stable

Features

- mV and relative mV scales
- Autocalibration /autobuffer recognition
- Number of calibration points
- Display information
- RS232 or recorder outputs
- Datalogging
- GLP/GMP compliant
pH Measurement System

- The pH Electrode
- Sensing Bulb
- Internal Fill Solution (Sensing)
- Reference
- Reference Fill Solution
- Junction
Common Questions: *Electrode Types*

**What is a combination pH electrode?**

- A combination pH electrode is one that has a **sensing half-cell** and **reference half-cell** built into one electrode body instead of existing as two separate electrodes.
What is a triode?

- A triode is a combination electrode (sensing and reference cells) together with an ATC (automatic temperature compensation thermistor) built into one electrode body.
What is meant by a “single junction?”

• There is one junction in the electrode body.

This term applies to Ag/AgCl electrodes that have a silver reference wire and silver ions dispersed in the internal electrolyte fill solution.
What is meant by a “double junction?”

- There are two junctions in the electrode body.

This term applies to any electrode that has a ROSS or calomel electrodes and also to some Ag/AgCl electrodes.
Common Questions: Temperature Compensation

*Why is temperature compensation important when measuring pH?*

- Samples / buffers have different pH values at different temperatures
- *Temperature compensation will contribute to achieving accurate measurements*
The pH electrode slope is the change in mV value divided by the Nernstian theoretical value.

At 25°C, the expected change in mV per pH unit would be 59.2 mV.
Common Questions: *Temperature Compensation*

- Newer meters automatically calculate slope
- Nernstian calculation of slope at 25°C (59.2 mV/pH unit)
  - Example:
    - pH buffer 7 = -10 mV
    - pH buffer 4 = +150 mV
  
  between these 2 buffers there’s a range of 160 mV
  
  59.2 mV x 3 pH units = 177.6 mV

  - Slope = 160 mV / 177.6 mV = 90.1%
Common Questions: *Temperature Compensation*

- Temperature affects calibration slope because it affects the expected change in the mV value per pH unit.
Common Questions: *Temperature Compensation*

- Nernstian calculation of slope at 50°C (64.0 mV/pH unit)
  - Example:
    - pH buffer 7 = -10 mV
    - pH buffer 4 = +150 mV

  between these 2 buffers there’s a range of 160 mV
  
  \[
  64.0 \text{ mV} \times 3 \text{ pH units} = 192.0 \text{ mV}
  \]

  - Slope = 160 mV / 192.0 mV = 83.3%
Common Questions: **Temperature Compensation**

- *Temperature compensation will adjust the calibration slope* across a wide temperature range.

- *It is not possible to normalize pH readings to a specific temperature*, but it is possible to get an accurate pH measurement for any sample temperature.
Common Questions: *Temperature Compensation*

Temperature Compensation Strategies

- *Calibrate and measure at the same temperature*
- *Use automatic temperature compensator (ATC) or 3-in-1 Triode electrode*
- *Manually temperature compensate using temperature control on meter*
- *Use LogR temperature compensation*
- *Record temperature with pH readings*
I have small containers on my bench that are labeled and filled with fresh buffer each week. We re-use these buffers all week. Will this practice affect my calibration?

Cal 1, using fresh 7 and 10 buffer:
• slope between 7-10 = 96.7%

Cal 2, using fresh 7 and old* 10 buffer:
• slope between 7-10 = 93.4%
  * set on shelf uncovered for 8 hours

ALWAYS use fresh buffer for each calibration.
Don’t re-use today’s buffer for tomorrow’s calibration!
Why does it take so long to get a stable reading?

• electrode performance and efficiency

• junction and bulb function  
  (non-clogged and non-coated)

• electrode type  
  (gel effects, open junction, etc.)

• meter stabilization settings (if available)

• resolution settings
Common Questions: Stable Readings… continued

**Why does it take so long to get a stable reading?**

- *inner fill-solution freshness*
- *low ionic strength samples*
  - *use an electrode with an open junction*
  - *stir the samples during measurement*
- *stirred or not?*
- *air bubbles near bulb*
Is there a cleaning routine I can follow to keep my electrode working?

- refresh inner fill solution
- use recommended storage solution
- close fill hole at end of day
- use cleaning remedies if a coated bulb or a clogged junction is the suspected cause of a poor calibration slope