

# THE FIVE STEPS OF ANALYSIS



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## The Five Steps

- Sampling and Sample Preservation
- Sample Preparation
- Use of Standards
- Procedure
- Calculations and Interpretation



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## Sample Collection

- The sample must be **representative** of the investigation site.



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## Sample Collection

- Follow the correct sampling protocol for the test and sample type.



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## Sample Collection

- The sample is usually the greatest limiting factor in obtaining a true or representative result.

*The analysis is only as good as the sample*



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## Sample Preservation

- Some tests must be performed on-site
  - Temperature
- Some tests can wait – if this is the case, the sample may need to be preserved
  - pH adjustment
  - Proper temperature
  - Filtration



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**Sample Preparation**

- Filtration
- Dilution
- Distillation
- Digestion
- pH adjustment




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**Use of Standards**

- What is a standard?
  - Solution containing a known amount of a specific substance
  - Example – 1.00mg/L iron standard



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**Use of Standards**

- How are standards used?
  - Accuracy check
  - Instrument calibration



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**Use of Standards**

- Standard Solutions
  - Verify technique, chemistry, and instrumentation
  - Am I running the test correctly?




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**Use of Standards**

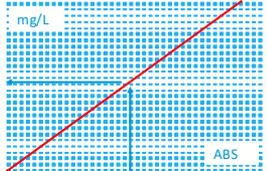
- Standard Additions
  - Identifying interferences and percent recovery
  - Is my sample compatible with the test?




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**Use of Standards**

- Calibration Standards
  - Used to prepare a standard curve




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### Procedure

- Make sure that the procedure is correct for:
  - Analyte
  - Type of sample
  - Concentration range



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### You Have the Answer – Now What?

- What does the answer mean?
  - Interpretation of results is relative to the investigation!



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### You Have the Answer - NowWhat?

- The test was run to ask a question.
- Results of the test help answer the question.



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### What's the Question?

- Regulations or Permits
  - Am I in compliance?
- Process control
  - Is my plant operating correctly?
  - Is it time for preventative maintenance?
- Problems and Troubleshooting
  - What is wrong with my system?
  - How can I fix it?



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## THE FIVE STEPS OF ANALYSIS



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### pH in Wastewater Treatment

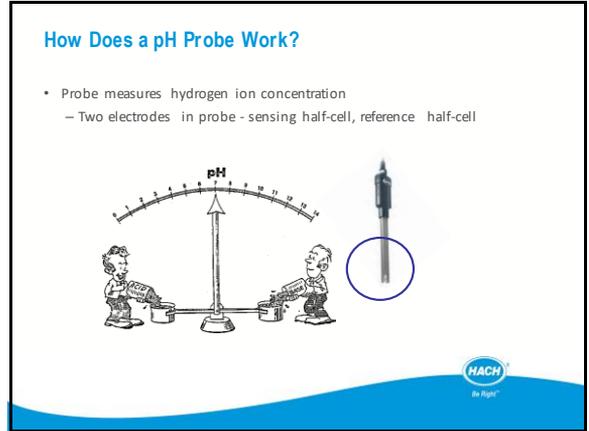
- pH is an electrochemical measurement.
- Can indicate an event/septic conditions/indicator of proper organism environment/NPDES parameter. Nitrification can depress pH
- Requires Frequent calibration/daily with fresh buffers.
- Proper maintenance and storage is essential/ refer to manufacturers recommendations.
- Slope is – 59.16 mv/decade.



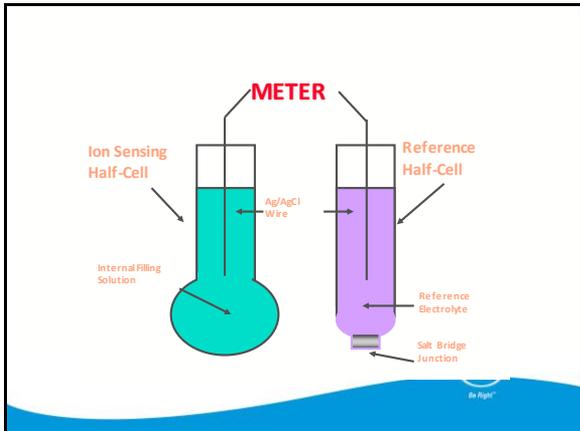
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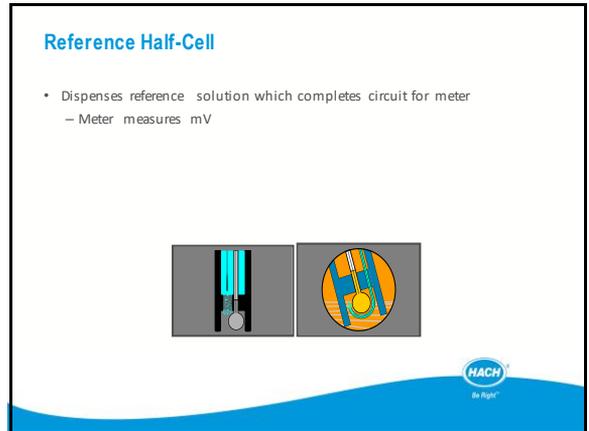
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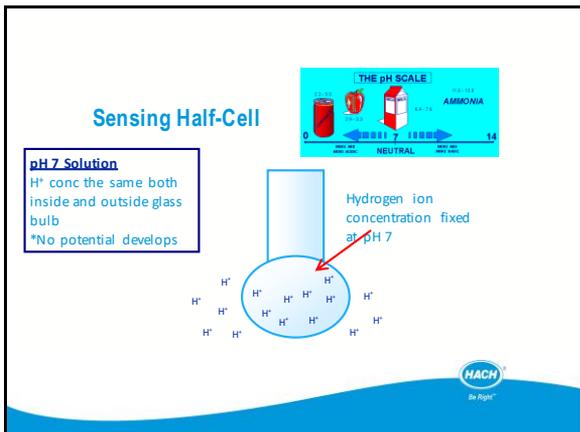
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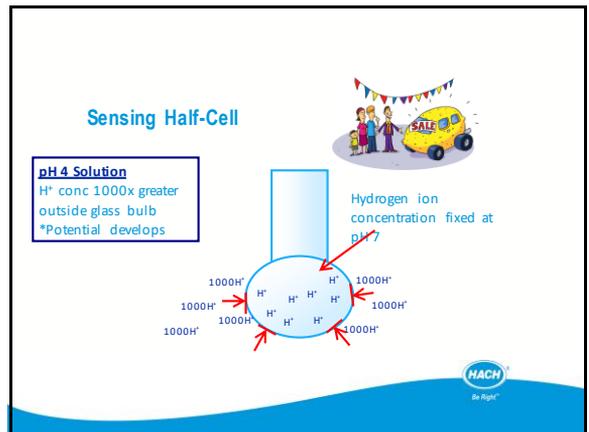
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### Sensing Half-Cell

**pH 10 Solution**  
 H<sup>+</sup> conc 1000x greater  
 inside glass bulb  
 \*Potential develops

Hydrogen ion concentration fixed at pH 7

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### Calibration

- A calibration curve allows the meter to convert a measured millivolt potential into a pH reading.

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### Calibration

- The optimal slope for pH is  $-59.16$  mV/decade.  
 $\pm 1\%$  to  $10\%$

## What does this mean?

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### Calibration

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### Probe Care and Maintenance

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### Maintenance

- New probe
- Calibration
- Measurement/Storage
- Troubleshooting
- Cleaning

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## New Probe

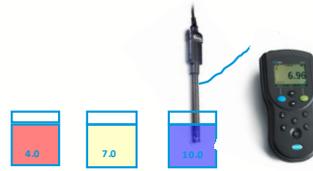
- Condition new pH probe in pH 7 buffer for approximately 30 minutes before initial use



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## Calibrate

- Calibrate pH meters daily using two or three buffer solutions



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## Measurement

- Place probe into sample, stir, and wait for readings to stabilize
- Rinse and dry between measurements
- Storage between measurements
  - Sample or solution of similar ionic strength to sample
  - pH7 buffer



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## Troubleshooting

- mV reading in pH 7 buffer
  - Should read  $0 \pm 30$  mV in pH 7 buffer
- Response time
  - May require cleaning if slow in buffered solution
- Slope
  - Optimal slope is  $-59.16$  mV/decade



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## Cleaning

- Slow response may indicate need for cleaning
  - Alternate soaking in dilute hydrochloric acid and dilute sodium hydroxide
  - Rinse with deionized water
  - Condition in pH 7 buffer before use



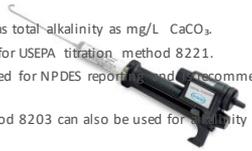
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## Alkalinity

- Alkalinity in Wastewater Treatment
- Measure of a water's capacity to neutralize an acid.
- Alkalinity acts as a buffer resisting changes to the process as a result of Nitrification.
- Typically expressed as total alkalinity as mg/L  $\text{CaCO}_3$ .
- A buret is required for USEPA titration method 8221.
- A pH meter is required for NPDES reporting and is recommended for best results.
- Digital Titrator method 8203 can also be used for alkalinity and is a great process control tool.



Alkalinity

7.14 lb. of alkalinity used to oxidize 1 lb. of  $\text{NH}_3$



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## Dissolved oxygen



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## Dissolved Oxygen

- Basics of DO
- How to Measure DO
- DO probes
  - function and maintenance
- BOD

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## What is Oxygen

Oxygen is a gas composing 20% of the atmosphere.



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## Factors Affecting DO

- Temperature
  - Water at a lower temperature will hold more oxygen than water at a higher temperature
- Pressure
  - The higher the barometric pressure, the more oxygen the water can hold
  - Elevation also affects pressure – the lower the elevation, the higher the pressure
- Salinity
  - The higher the salinity, the less oxygen water can hold
  - High levels of dissolved solids can interfere with the electrochemical measurement of DO (but can be corrected for)



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## Why Measure Dissolved Oxygen?

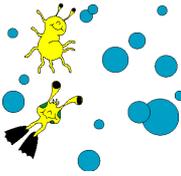
- Important indicator of water quality
  - BOD testing for WW
  - Environmental waters
- Related to:
  - Water pollution
  - Water treatment processes
  - Chemistry of metals
  - Biological activity



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### Why is DO Important?

- Aerobic bacteria must have oxygen to survive.
- Control of DO levels is critical to the operation of a wastewater treatment plant.




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### Why measure DO in WWTP?

- Monitoring O<sub>2</sub> Concentration in Aeration Basins
- Optimizing Nitrification and Denitrification Process
- Optimizing Energy Usage with Plant Blowers
- Monitoring Plant Effluent
- Optimizing Aerobic Digestion




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### DO Meter and Electrode

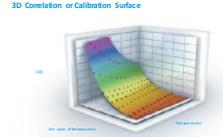
- DO meter and probe are used to measure dissolved oxygen concentration electrochemically.
- Ease of use
- Limits exposure to chemicals
- Safe disposal of samples
- Fast
- Accurate measurement in colored samples or samples containing suspended solids




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### How does Hach LDO™ Work?

- Luminescent technology even though complex, can be easily explained
- LDO measures 'light life span' and temperature
- The probe software correlates these measurements to DO concentration




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### How does Hach LDO™ Work?

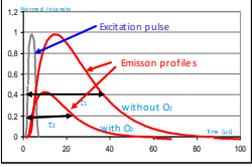
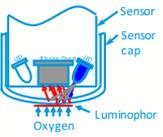
- Blue light is transmitted to the sensor
- The luminescent molecules in the sensor are excited by the blue light
- The molecules relax emitting red light
- The red light is detected by the probe
- A red LED is used as a reference point

The Life Span of Luminescence is the time required for the molecules to relax from their excited state.




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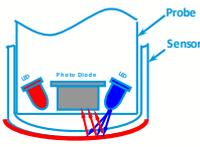
### Hach LDO™ Technology


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### How Does HachLDO™ Work?

- When oxygen contacts the luminescent chemical, the intensity of the red light decreases
- The amount of time it takes for the material to relax is reduced



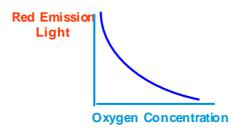
The diagram shows a cross-section of the sensor probe. A red light source is positioned to excite a luminescent material. A photo diode is used to detect the resulting red emission light. The sensor is housed in a cap that allows it to be submerged in water.

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### How Does HachLDO™ Work?

- The higher the oxygen concentration, the less red light that is given off by the sensor



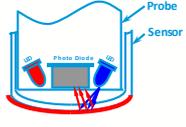
The graph plots Red Emission Light (y-axis) against Oxygen Concentration (x-axis). The curve shows an inverse relationship: as oxygen concentration increases, the intensity of the red emission light decreases.

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### How Does HachLDO™ Work?

- The intensity of the red light is not what's being measured.
- What's being measured is the time it takes after excitation for red light to be given off
  - Lifetime of luminescence

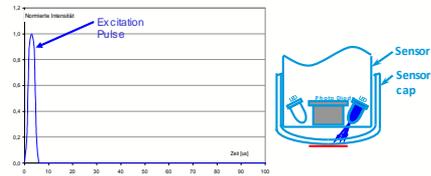


The diagram shows the sensor probe with a photo diode and a sensor cap, similar to slide 51.

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### How does LDO™ work ?

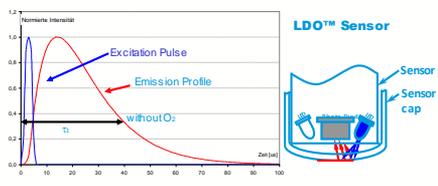


The graph shows a sharp blue excitation pulse at the start of the time axis. The y-axis is labeled 'Normalized Intensity' and the x-axis is 'Time (sec)'. To the right is a diagram of the LDO sensor with its cap.

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### How does LDO™ work ?

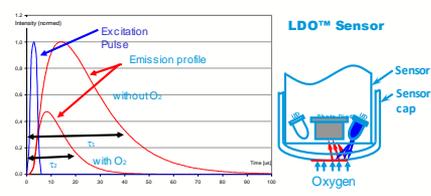


The graph plots Normalized Intensity (y-axis) against Time (sec) (x-axis). It shows a blue excitation pulse and two red emission profiles. The 'without O<sub>2</sub>' profile has a shorter decay time (τ<sub>1</sub>), while the 'with O<sub>2</sub>' profile has a longer decay time (τ<sub>2</sub>).

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### How does LDO™ work ?



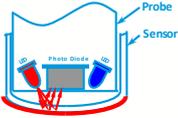
The graph is similar to slide 55, but includes a diagram of the sensor cap with arrows indicating oxygen entering the sensor chamber.

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### How Does HachLDO™ Work?

- A red LED is also present in the probe.
- Between flashes of the blue LED, a red LED of known intensity, is flashed on the sensor.
- The red LED acts as an internal standard (or reference) for a comparison to the red light given off by the luminescent chemical.



The diagram shows a cross-section of the probe sensor. It features a 'Photo Diode' and a 'Red LED' (indicated by a red circle) positioned near the 'Probe' tip. The sensor is labeled 'Sensor'.



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### Why is this a Big Deal?

- Simple Operation and Maintenance**
  - Only one replacement part
  - Inexpensive sensor cap is simple to replace quickly




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### BIOCHEMICAL OXYGEN DEMAND (BOD)




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### BOD

- BOD is an indirect measure of organic content.
- BOD is measured by oxidizing organics using microorganisms (under specific conditions) and directly measuring the amount of oxygen consumed in the process.
- Dilution Method
  - For EPA reporting
- Respirometric Method
  - Not for EPA reporting




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### What is BOD?

**Biochemical Oxygen Demand** is the amount of oxygen, expressed in mg/L or parts per million (ppm), that bacteria take from the water when they oxidize organic matter.

(Hach, Clifford; R. Klein; C. Gibbs. Introduction to Biochemical Oxygen Demand. Hach Company, 1997. Lit# 7022 available on website.)

BOD is a measure of organic pollution. Changes in dissolved oxygen concentration are used as an indirect measure of organic content.



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### Why is BOD Important?

- BOD Removal Efficiency
  - BOD of effluent versus influent



The diagram shows a flow from 'Influent' (300 mg/L) through a 'WWTP' (Wastewater Treatment Plant) to 'Effluent' (30 mg/L). Below the flow, it states '90% Removal'.



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### Why is BOD Important?

- BOD measurements help in monitoring the effect of effluent on the dissolved oxygen concentration of the receiving water body.



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### Calculating BOD

$$\text{BOD}_5, \text{ mg/L} = \frac{(\text{Initial DO} - \text{Final DO}) 300}{S}$$

$$\text{BOD}_5, \text{ mg/L} = \frac{(7.30 - 5.25) 300\text{mL}}{2\text{mL}}$$

$$\text{BOD}_5, \text{ mg/L} = 307.5 \text{ mg/L} \quad S = \text{volume of sample}$$



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### IntelliCAL™ LBOD



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### IntelliCAL™ LBOD Probe

- LDO Technology
- Integrated stirrer
- Designed for the US EPA-Based Method of BOD5 Measurement
  - Critical Bottle Dimension: 0.625 inches (15.875 mm)
  - Can be used in any facility testing for BOD
- For use with the HQ40d Meter



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### COD vs BOD



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### COD vs BOD

- Why compare COD to BOD?
  - Faster process control**
    - Know what you are sending downstream within two hours rather than five days.
  - COD is a more stable measurement method**



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## COD vs BOD

- BOD must still be run to comply with NPDES permit regulations!



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## COD vs BOD

- Why is COD more stable than BOD?
  - The tests use different methods of oxidation
    - BOD - Microorganisms
    - COD - Chemicals (potassium dichromate)



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## COD vs BOD

- Microorganisms are susceptible to pH, temperature, and other variables in the water
  - Oxidation efficiency depends on the condition of the microorganisms



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## COD vs BOD

- Potassium dichromate will oxidize regardless of water conditions.



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## COD vs BOD

- Picky bugs vs Clean Plate Club chemicals
  - COD measurements will always be higher than BOD measurements



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## COD vs BOD

- Can COD be correlated to BOD?
  - **It depends!**
  - Correlation between COD and BOD may or may not exist depending on sample composition, seasonal variation, and other factors.



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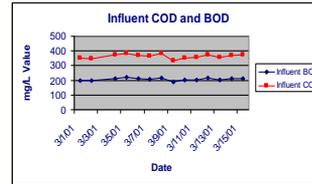
## COD vs BOD

- How can a correlation be determined?
  - **Collect empirical data**
    - COD and BOD data for the same water sample collected over the same period of time
  - **Graph data**
    - Graph COD and BOD data to determine whether or not a correlation exists



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## COD vs BOD



In this example,  
the correlation  
calculates out to  
**COD = 1.75 BOD**



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## COD – Take Home Messages

- COD is an indirect measure of organics.
- COD is measured by oxidizing organics with a strong oxidant (dichromate) and measuring the amount of oxidant consumed in the reaction.
- Correlation between COD and BOD is sample specific and may not always be possible.



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## CHEMICAL OXYGEN DEMAND (COD)



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