Determination of COD of Water

COD

COD is chemical oxygen demand.

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.

What is COD?

COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.

Standard Methods for the Examination of Water and Wastewater

What is COD?

In other words….

➔COD is an indirect measure of the amount of organics in a water sample.

What is COD?

The COD test uses a strong chemical oxidant (potassium dichromate), acid, and heat to oxidize organic carbon to carbon dioxide and water.



What is COD?

COD Reaction

$$2\ KC_8H_3O_4 + 10\ K_2Cr_2O_7 + 41\ H_2SO_4 \rightarrow$$

KHP — Dichromate oxidant — Acid

$$16\ CO_2 + 46\ H_2O + 10\ Cr_2(SO_4)_3 + 11\ K_2SO_4$$

Carbon Dioxide — Water — Chromic Ion

What is COD?

The COD test measures the amount of dichromate (oxidant) consumed in the breakdown of organic matter.

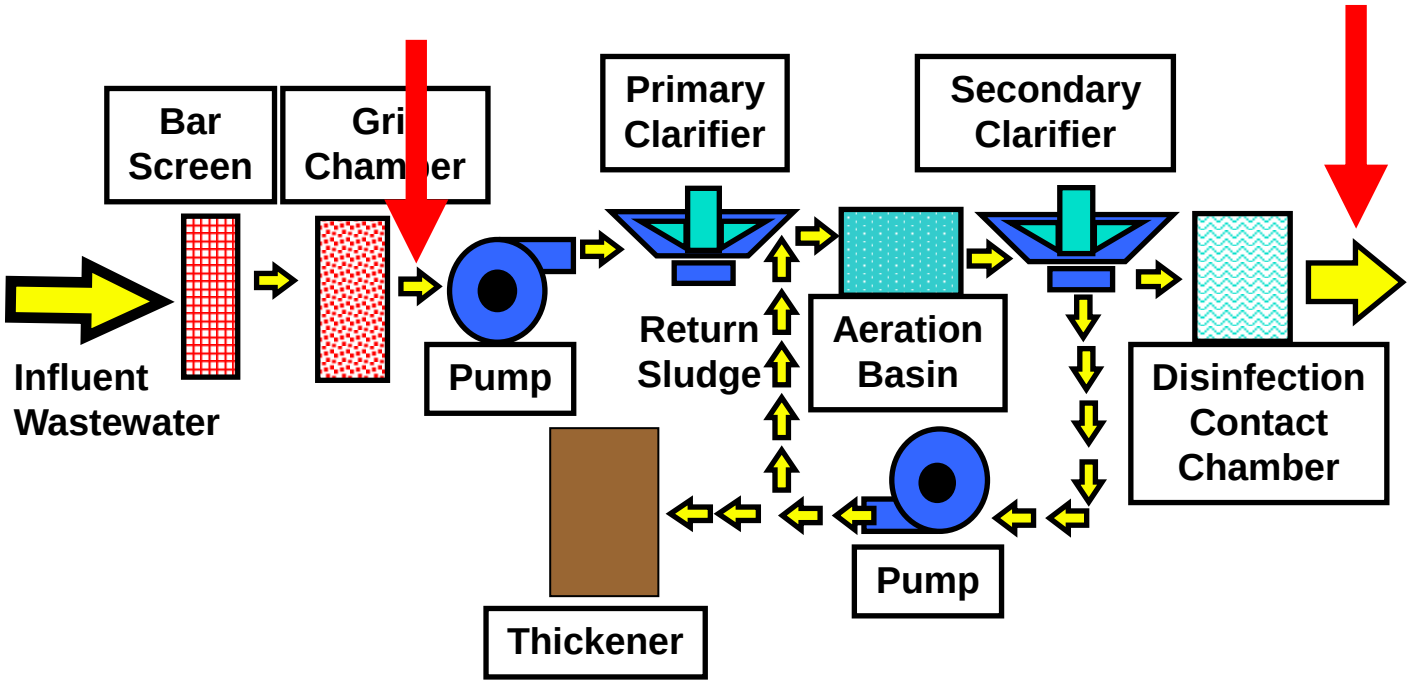
- ➔ More oxidant consumed = High levels of organics
- ➔ Less oxidant consumed = Low levels of organics

What is COD?

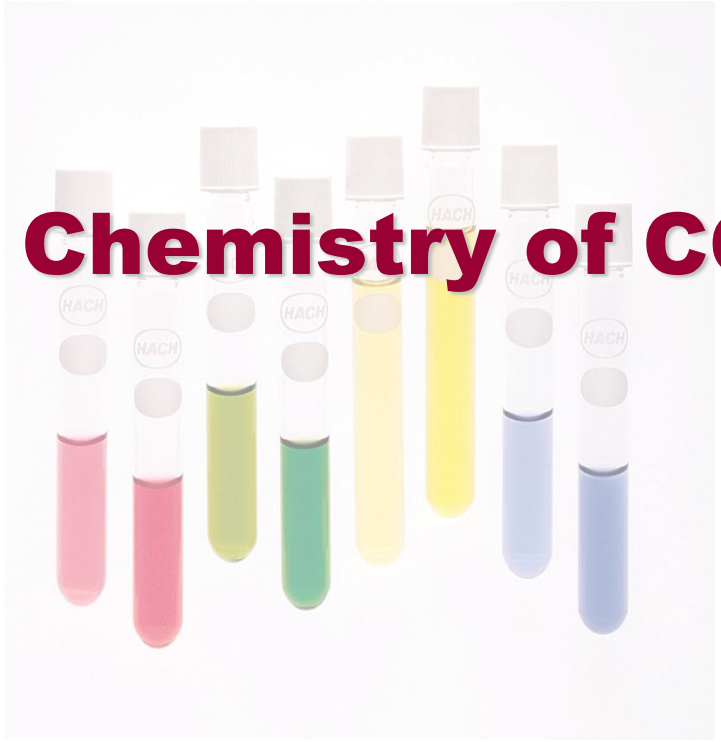
Why measure COD?

- ➔Faster than BOD (2 hours versus 5 days)
- ➔Fewer interferences (chloride)
- ➔Stable methodology yielding repeatable results
- ➔Easy to run!

Where is COD Measured?



The Chemistry of COD



The Chemistry of COD

COD is a two step process

- ➔ Digestion
- ➔ Determination





The Chemistry of COD

Required reagents for COD:

➔Hach COD reagent vials



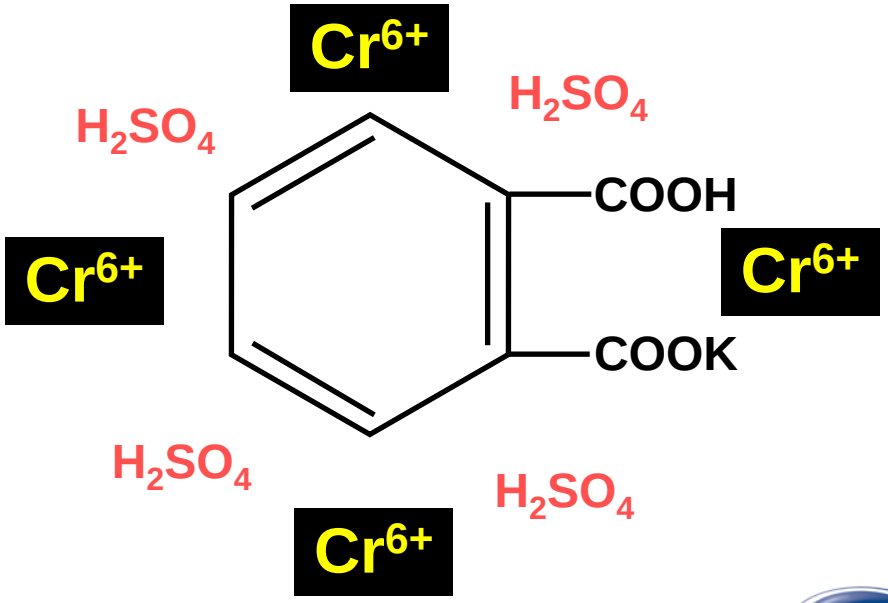
The Chemistry of COD+

Reagent vials contain:

- ➔Potassium dichromate
- ➔50% sulfuric acid
- ➔Silver salt (catalyst)
- ➔Mercuric salt (inhibits chloride interference)

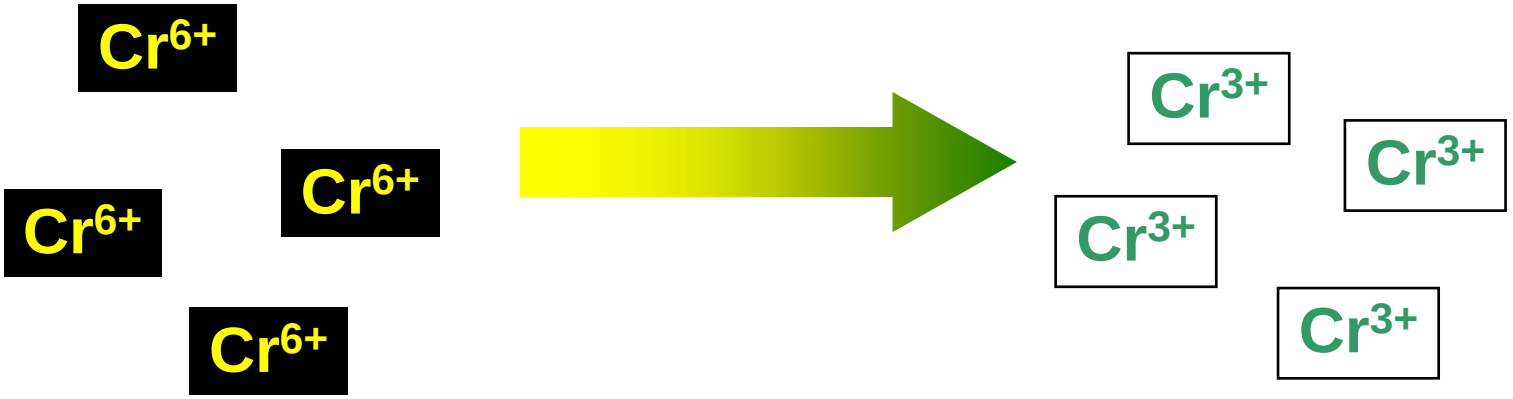
The Chemistry of COD

Organic compounds are oxidized by potassium dichromate and sulfuric acid.



The Chemistry of COD

The oxidation of organics results in the reduction of Cr^{6+} to Cr^{3+}.



The Chemistry of COD

Reduced chromium is the reaction product of interest.

Other products of the reaction include:

- ➔Carbon dioxide
- ➔Water
- ➔Potassium sulfate

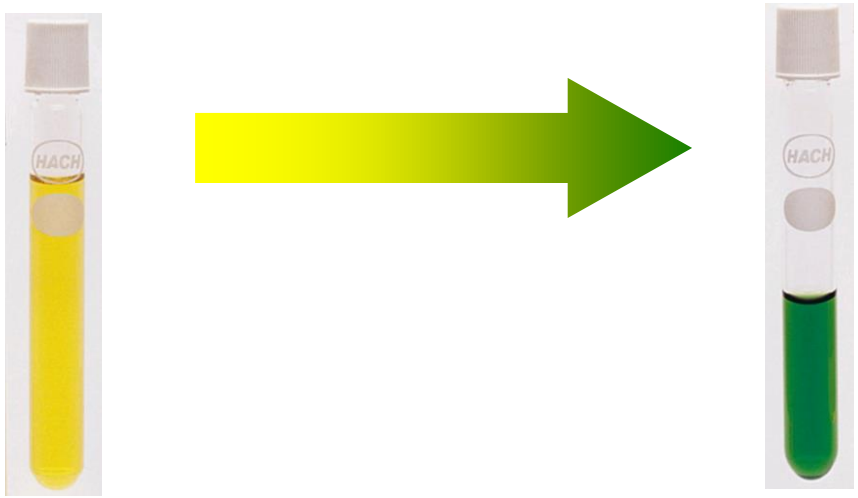
The Chemistry of COD

Why is reduced chromium the reaction product of interest?

- ➔ Cr^{6+} is yellow. Cr^{3+} is green
- ➔ The reduction of Cr^{6+} to Cr^{3+} (and hence the consumption of oxidant) can be monitored colorimetrically.

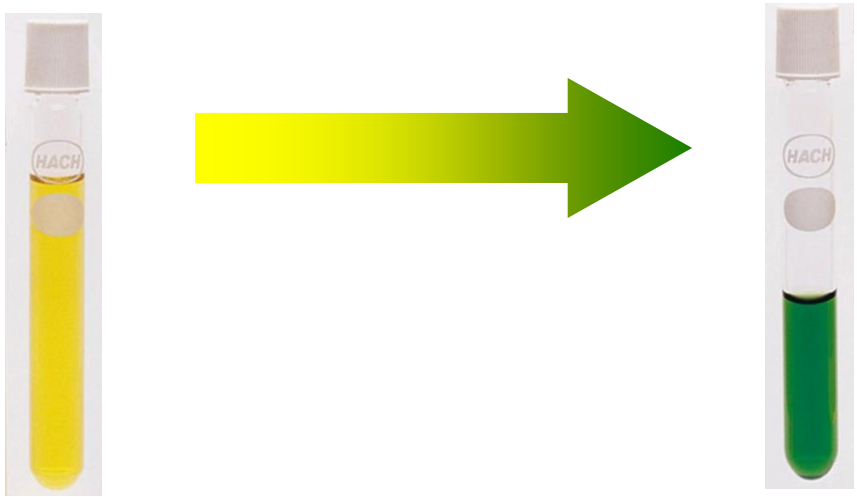
The Chemistry of COD

As organics are oxidized and Cr^{6+} is reduced to Cr^{3+}, the color of the solution changes from yellow to green.



The Chemistry of COD

The amount of green color formed is proportional to the COD of the sample.



The Chemistry of COD

How does chromium relate to COD?

- ➔Each molecule of potassium dichromate has the same oxidizing power as 1.5 molecules of oxygen.
- ➔Oxygen demand is directly related to the percentage of Cr^{6+} that has been reduced to Cr^{3+}.

The Chemistry of COD

Colorimetric measurement

➔Won't solids in sample interfere?

- No! Solids in sample are either digested or settle out of the light path.
- Do not invert vials once they have cooled.



The Chemistry of COD

Colorimetric measurement

➔High Range – measures increase in green color at 620nm

➔Low Range – measures decrease in yellow color at 420nm

The Chemistry of COD

Interferences

- ➔ Chloride is the primary interference
  - ❍ Dichromate will oxidize chloride to chlorine, which results in high readings
  - ❍ Interference controlled up to 2000mg/L Cl^- with mercuric sulfate in Hach COD vials

The Chemistry of COD

Interferences

- ➔ Bromide also interferes
  - ❍ Bromide interference is not controlled by mercuric sulfate
  - ❍ Samples must be diluted to minimize interference



COD vs BOD



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

COD vs BOD

Why is COD more stable than BOD?

- ➔ The tests use different methods of oxidation
  - ❍ BOD - Microorganisms
  - ❍ COD – Chemicals (potassium dichromate)

COD vs BOD

Microorganisms are susceptible to pH, temperature, and other variables in the water.

➔Oxidation efficiency depends on the condition of the microorganisms

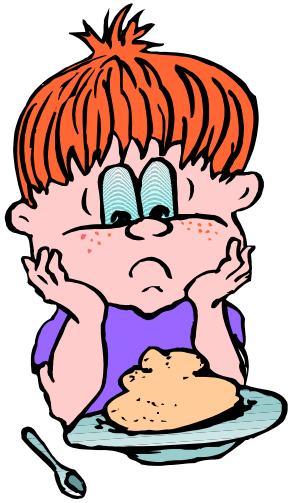
COD vs BOD

Potassium dichromate will oxidize regardless of water conditions.

COD vs BOD

➔COD measurements will always be higher than BOD measurements

BOD





COD

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.

COD vs BOD

How can a correlation be determined?

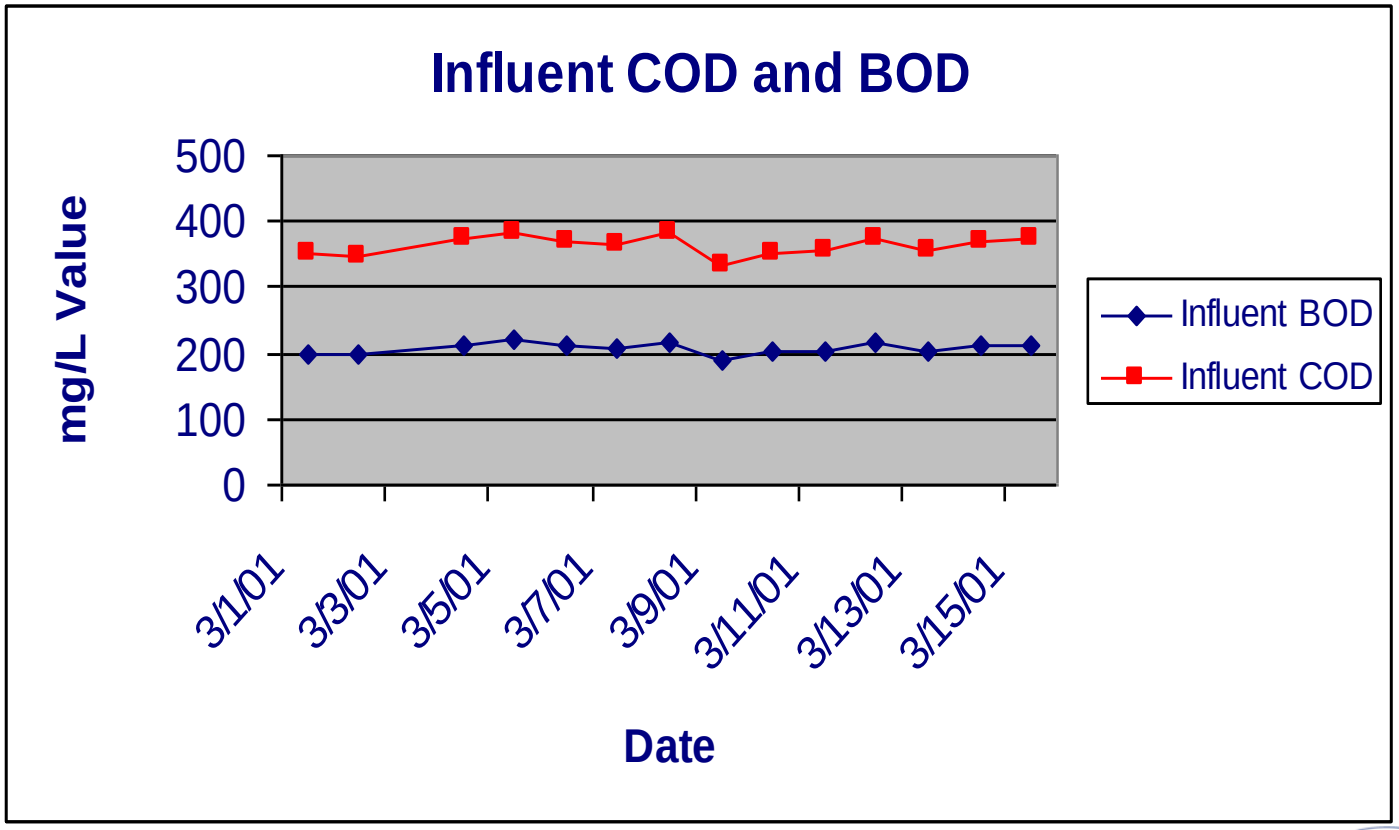
➔Collect empirical data

- 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

COD vs BOD



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

The recovery of organic material is usually >95% (meaning that also most non-biodegradable substances are taken into account).

For various types of (waste)waters, there is usually a more or less constant ratio between BOD and COD:

- domestic wastewater: BOD/COD = 0.65
- surface water: BOD/COD = 0.40

- **Assignment: 1. What are the principal advantages and disadvantages of the COD test over the BOD test?**

- **2. Explain why COD values are greater than BOD values.**