Water Quality

Measures of Water Quality

- What is clean water?
- Is drinking water clean?
  - What are some parameters that determine water quality?
    - Dissolved oxygen – oxygen probe and oxygen meter
    - **Biochemical Oxygen Demand (BOD)**
    - Solids
    - Nitrogen – ammonia
    - Bacteriological quality

- BOD
  - The amount of dissolved oxygen utilized by microbes for the biochemical oxidation of organic material present in a given water sample at certain temperature over specific time period
  - One can calculate the theoretical oxygen demand
    - If you know the chemical formula –
    - for example 1.67 x 10^{-3} M glucose
      - $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
      - 6 x 1.67moles/L x 32 g/mole x 1000 mg/g = 321 mg/L
    - BOD is used because wastewater isn't one organic molecule

Biochemical Oxygen Demand

- Standard BOD Test
  - Run in the absence of light (algae)
  - @ 20°C for 5 days, defined as BOD_5
  - Standard 300 mL volume BOD bottle
- – BOD ultimate, L, BOD greater than 20 days
  - BOD = I –F

    I = initial DO, mg/L

    F = final DO, mg/L

Biochemical Oxygen Demand

- What if the F is =0?
  - Dilution of the sample is required when F = 0. If F = 0 we don't know how much DO would have been used.

BOD = (I – F)D

D = dilution

$$D = \frac{\text{total volume of bottle}}{[\text{total volume of bottle}] - [\text{volume of dilution water}]}$$

Biochemical Oxygen Demand

- Dilution by how much?
  - The proper dilution amount is rarely known before the test.
  - A proper BOD test requires a change of DO of 2 mg/L
  - And more than 2 mg/L remaining at the end of the test
  - The dilution required is calculated as:

$$D = \frac{\text{expected BOD}}{\Delta \text{DO}}$$

Biochemical Oxygen Demand

- Seeding
  - The addition of active microorganisms that take up oxygen
    - May be required in samples that do not have their own
    - If seeding is necessary, any BOD that is contributed by the seed must be subtracted

$$BOD_t = \left[(I - F) - (I' - F')\left(X/Y\right)\right]D$$

Biochemical Oxygen Demand

- BOD with dilution and seed
  - BODt = BOD at time t, mg/L
  - I, F = initial and final DO of sample and seed, mg/L
  - I’, F’ = initial and final DO of seed water, mg/L
  - X = seeded dilution water in sample bottle, mL
  - Y = seeded dilution in bottle with only seed dilution water mL
  - D = dilution of sample

Biochemical Oxygen Demand

- Example
  - Standard BOD test with a 1:30 dilution with seeded dilution water is run. Both bottles begin at saturation, 9.2 mg/L. After five days, the bottle with waste has a DO of 2 mg/L, while the DO of the seed = 8 mg/L. Find the BOD_5.

$$BOD_t = \left[(9.2 - 2) - (9.2 - 8)\left(290/300\right)\right]30$$

$$= 181 \text{ mg/L}$$

Biochemical Oxygen Demand

- Typical BOD values
  - Wastewater $BOD_5 \approx 250$ mg/L
  - Effluent BOD_5 from wastewater < 30 mg/L
  - Industrial wastewater = 30,000 mg/L
  - US Engineers often speak in terms of lbs BOD_5/day
    - Mass rate load of a plant to the receiving stream

Biochemical Oxygen Demand

- The BOD test occurs in a bottle,
  - Thus the mass balance is

Rate of DO accum. = rate of DO consumed

dz/dt = -r

z = dissolved oxygen, mg/L

Assume that it is a first-order reaction

$$\frac{dz}{dt} = -k_1 z \Rightarrow \frac{dz}{z} = -k_1 dt \Rightarrow z = z_o e^{-k_1 t}$$

Biochemical Oxygen Demand

– As O_2 is used, the amount still to be used is z, the amount already used is y

L = y + z

L= ultimate demand

$$z = L - y$$

$$L - y = z_o e^{-k_1 t}, z_o = L$$

$$y = L - Le^{-k_1 t} = L(1 - e^{-k_1 t})$$

Biochemical Oxygen Demand

- Variables
  - y = BOD at any time t
  - L = ultimate BOD
  - k_1 = deoxygenation constant
- – Example
  - Find the BOD5 for a waste with an ultimate BOD = 282 mg/L and a k_1 = 0.348 /day

$$y = L(1 - e^{-k_1 t})$$

$$= 282 \ \text{mg/L} \ (1 - e^{-0.348 \ /day \ *5})$$

$$= 50 \ \text{mg/L}$$

Nitrogenous Oxygen Demand

- Nitrogenous BOD

  Organic matter + O_2 ➔ bacteria + NH_3 + CO_2 + et.al.

  $$2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O$$

  $$2NO_2^- + O_2 \rightarrow 2\ NO_3^-$$

  - Two moles of O_2 per mole of NH_3
  - $BOD_{ult} = a\ (BOD_5) + b(KN)$
    - KN = Kjeldahl nitrogen (measure of organic nitrogen and ammonia)
    - a and b are constants, a = 1.2 & b = 4.0 for example

Chemical Oxygen Demand

Same principle as BOD but different execution.

Rather than biologically decompose/oxidize organic waste, we chemically decompose/oxidize organic waste.

It all begins with…

…a balanced equation!

$$C_nH_aO_bN_c + d\ Cr_2O_7^{2-} + (8d+c)\ H^+ \rightarrow^{\Delta} \rightarrow$$

$$nCO_2 + (a+8d-3c)/2\ H_2O\ \ + c\ NH_4^+ + 2\ dCr^{3+}$$

Ignoring the stoichiometry for the moment

$$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \xrightarrow{\Delta} CO_2 + H_2O + NH_4^+ + Cr^{3+}$$

$$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$$

You can’t help but notice the similarities!

The differences

$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \longrightarrow^{\Delta} \longrightarrow$

$CO_2 + H_2O + NH_4^+ + Cr^{3+}$

$C_nH_aO_bN_c + O_2 \longrightarrow CO_2 + H_2O + NH_3$

NH_4^+ instead of NH_3. Why?

It's in acid. NH_3 is a base. In acid, it gets protonated.

The differences

$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \rightarrow^{\Delta} \rightarrow$

$CO_2 + H_2O + NH_4^+ + Cr^{3+}$

$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$

$Cr_2O_7^{2-}$ and acid with heat instead of bacteria and oxygen in a warm, dark place.

Other than that, they are really the identical process.

Where's the O in C-D?

$$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \longrightarrow^{\Delta} \longrightarrow$$
$$CO_2 + H_2O + NH_4^+ + Cr^{3+}$$

It's in the dichromate ($Cr_2O_7^{2-}$).

How to test for COD…

How would you test for COD?

You need to monitor either the disappearance of dichromate or the appearance of Cr^{3+}

Excess dichromate

Dichromate can be reduced inorganically to Cr^{3+} using Fe^{2+}

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

To Conduct the test:

Take x mL of the waste water sample to be tested. Add an equal amount of $K_2Cr_2O_7$ solution to the sample and a sample of distilled water (the blank).

After digestion, you titrate both the blank and the waste water sample with an $Fe(NH_4)_2(SO_4)_2$ standard solution.

The difference between the 2 titrations is the amount of $Cr_2O_7^{2-}$ used in the digestion.

Sample COD problem

A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and to 50 mL of distilled water. Both samples are heated to 50°C for 30 minutes. The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

What’s going on?

You add dichromate to distilled water AND to your water sample.

What does dichromate do in distilled water?

NOTHING! There’s nothing for it to oxidize.

You can't avoid the stoichiometry

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

The titration reaction has 6:1 stoichiometry of the Fe^{2+} titrant to the $Cr_2O_7^{2-}$.

Titrating the solutions with Fe^{2+} is telling us how much dichromate is left over!

We have different amounts of dichromate in the 2 different samples, does this make sense?

Yes, we reduced some dichromate in the “dirty” sample while the distilled water should have all the dichromate it started with!

The difference between the two samples is the amount of dichromate reduced and, therefore, the amount of organic material oxidized!

Normality

You can express solution concentrations (like the Fe^{2+}) in "normality" instead of "molarity".

Do we remember what "normality" is?

$$\text{Normality} = \frac{\text{equivalent moles of solute}}{\text{L solution}}$$

Normality

This is a redox titration – equivalence is about electrons.

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

Each iron atom transfers 1 electron.

Each dichromate molecule involves 6 electrons.

This means that 1 M Fe^{2+} = 1 N Fe^{2+}

1 M $Cr_2O_7^{2-}$ = 6 N $Cr_2O_7^{2-}$

Just a titration!

The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint.

How do we start?

Balanced equation

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow$$
$$6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

And then….?

$$i_2 M_1 V_1 = i_1 M_2 V_2$$

$$i_{Fe} M_{Cr} V_{Cr} = i_{Cr} M_{Fe} V_{Fe}$$

$$6 * M_{Cr} * 50 \text{ mL} = 1 * 0.1015 \text{ M} * 15.36 \text{ mL}$$

$$M_{Cr} = 5.20 \text{x} 10^{-3} \text{ M } \; Cr_2O_7^{2-}$$

Using Normality

$N_1V_1 = N_2V_2$

$N_{Cr}V_{Cr} = N_{Fe}V_{Fe}$

N_{Cr}* 50 mL = 0.1015 N * 15.36 mL

N_{Cr} = $3.12x10^{-2}$ N $Cr_2O_7^{2-}$

For the reference water:

$N_1V_1 = N_2V_2$

$N_{Cr}V_{Cr} = N_{Fe}V_{Fe}$

N_{Cr}* 50 mL = 0.1015 N * 23.65 mL

$N_{Cr} = 4.80\text{x}10^{-2}$ N $Cr_2O_7^{2-}$

What does this mean?

Pure water:

$N_{Cr} = 4.80 \times 10^{-2}$ N $Cr_2O_7^{2-}$

"Dirty" water:

$N_{Cr} = 3.12 \times 10^{-2}$ N $Cr_2O_7^{2-}$

The difference between the two is the amount reduced! Since the volume is the same, you can just subtract:

4.80×10^{-2} N - 3.12×10^{-2} N = 1.68×10^{-2} N $Cr_2O_7^{2-}$ reduced

Still no “O” in C-D!

We could express the impurity based strictly on the dichromate used: the more dichromate required, the more organic material that must have been there.

Then there would be no “O” in C-D which would now simply be DD – dichromate demand.

Equivalent oxygen

Instead of reporting the dichromate used, the dichromate is converted into equivalent amount of oxygen, as if you were again "burning" the organic waste as in the BOD process:

$$C_nH_aO_bN_c + O_2 \longrightarrow CO_2 + H_2O + NH_3$$

(unbalanced)

It's the oxygen, dummy!

So, we convert Normality of dichromate used into mg/L of oxygen demand!

It is very easy to do.

How would you convert Molarity to g/L?

Use the molar mass!!!

Molarity to g/L

$$\frac{\text{Moles oxygen}}{\text{L oxygen}} * \frac{\text{32 g oxygen}}{\text{mole oxygen}}$$

How would you convert Molarity of dichromate to g/L of equivalent oxygen?

Throw in the stoichiometry!

Molarity dichromate to g O/L

$$\frac{\text{Moles } Cr_2O_7^{2-}}{\text{L } Cr_2O_7^{2-}} * \frac{x \text{ moles } O_2}{y \text{ mol } Cr_2O_7^{2-}} * \frac{32 \text{ g } O_2}{\text{mole } O_2}$$

You'd need to compare the 2 balanced equations to get the overall stoichiometry

But Normality makes your life easier.

Normality to g/L

How would you convert Normality to g/L?

Include the “equivalent molar mass”!

What the he** is “equivalent molar mass”?

It’s the molar mass of 1 reactive unit.

It's a redox reaction

An equivalent is…

…an electron

How many electrons does O_2 transfer?

FOUR! $O_2 \rightarrow 2\ O^{2-}$

So, the "equivalent mass of oxygen" is…

… 8 g/mol $\left[\dfrac{32\text{ g }O_2}{\text{mol }O_2} * \dfrac{1\text{ mol }O_2}{4\text{ equiv moles}}\right]$

Convert Normality O_2 to g O_2/L

$$N\ O_2 = \frac{\text{equiv moles } O_2}{\text{L solution}} * \frac{8 \text{ g } O_2}{\text{equiv mole } O_2}$$

Convert Normality $Cr_2O_7^{2-}$ to g O_2/L

1.68×10^{-2} N $Cr_2O_7^{2-}$ reduced = 1.68×10^{-2} N O_2

Normality is always 1:1 stoichiometry

$$\frac{1.68\times10^{-2} \text{ equiv moles } O_2}{\text{L solution}} * \frac{8 \text{ g } O_2}{\text{equiv mole } O_2} * \frac{1000 \text{ mg}}{1 \text{ g}} =$$

= 134 mg O_2 /L

This is the COD of the original sample.

The Formula in the Book

You could calculate the COD using the scheme I just outlined. Your book reduces this to a single formula that is often usable:

$$\text{COD (mg/L)} = \frac{8000\ (\text{mL blank} - \text{mL sample})\ [Fe^{2+}]}{\text{mL sample}}$$

Sample COD problem

A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and 50 mL of distilled water. Both samples are heated to 50°C for 30 minutes. The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

Short and Sweet

$$\text{COD (mg/L)} = \frac{8000\ (\text{mL blank} - \text{mL sample})\ [Fe^{2+}]}{\text{mL sample}}$$

$$\text{COD (mg/L)} = \frac{8000\ (23.65 - 15.36\ \text{mL})\ [0.1015\ \text{M}]}{50\ \text{mL}}$$

COD = 135 mg/L

(Bit of a rounding error)

COD errors

The most common COD errors are due to oxidation of inorganic species.

Dichromate is a powerful oxidant – it will oxidize not only almost all organics but many metals and non-metal ions:

$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$

$6\ Cl^- + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 3\ Cl_2 + 2\ Cr^{3+} + 7\ H_2O$

COD errors

As a result, contaminated water will tend to test higher than it should based strictly on the organic contamination.

COD vs. BOD

They purport to measure the same thing – but they will never agree.

Biggest error in BOD?

BOD tends to err on the low side due to humus ("inedible" organic waste).

Biggest error in COD?

COD tends to err on the high side due to oxidation of inorganic species.

Using COD

COD is again a relative measure: higher COD = dirtier water.

COD can be used with BOD – they are not a replacement for each other.

COD must be viewed in context of all other tests.

Comparing all of our "oxygens"

Dissolved oxygen ( ) – amount of actual oxygen dissolved in a water sample. Higher number = purer water

BOD_5 – Actual amount of dissolved oxygen metabolised over 5 days. Higher number = dirtier

BOD – Extrapolated amount of theoretical oxygen that would be needed to completely metabolise organic waste. Higher number = dirtier

COD – Actual amount of oxygen required to completely oxidize organic waste CHEMICALLY. Higher number = dirtier.