Alkalinity

CE404 Environmental Analysis
Department of Civil Engineering

Acidity

- Ability to neutralize strong base (e.g. NaOH). If pH<8.5, consider to have acidity
- Same acidity may have different pH: e.g. HCl vs. HAc
- CO_2 acidity vs. mineral acidity
- Concern: little for sanitary/public health
- Acid water: corrosion, acid rains, industrial

Alkalinity

- Acid neutralization capacity (ANC), mostly due to weak acids. e.g. $Ca(HCO_3)_2$
- May also comes from weak and strong bases
- Other salts like borates, silicates, and phosphates may contribute
- Importance:
  - Chemical coagulation
  - Water softening: lime and soda ash
  - Corrosion control
  - Buffer capacity
- Three major forms of alkalinity: OH^-, HCO_3^-, CO_3^{2-}

Alkalinity

- Concern: little for public health
- High alkaline water usually unpalatable
- 8.5 upper bound of secondary standard by EPA
- Alkalinity is the measure of buffer to resist pH drop

Alkalinity

- Measurement: by titration, use 0.020 N H_2SO_4, report as mg/L as $CaCO_3$
- Phenol alkalinity (phenolphthalein indicator)
  - pH 8.3 as end point
  - Phenolphthalein indicator from pink to colorless
  - Measure: all of OH^-, half of CO_3^{2-}
- B.G. alkalinity (bromcresol green indicator)
  - pH 4.5 as end point
  - Measure: all of OH^-, CO_3^{2-} and HCO_3^-
  - Bicarbonate changed to carbonic acid H_2CO_3
  - The amount of acid needed to react with the three forms of alkalinity represents the total alkalinity

Alkalinity

- Fractionating 3 types of alkalinity (OH^-, HCO_3^-, CO_3^{2-})
- Procedure to know the type of alkalinity
  - Measuring alkalinity alone (titration)
  - Measuring alkalinity and pH (pp. 555)
  - Equilibrium equations (pp. 556)

Alkalinity

- Fractionating 3 types of alkalinity (OH^-, HCO_3^-, CO_3^{2-})
- Add P Indicator – if no color → no p alk. and all alk. from bicarbonate
- Add P Indicator – if pink or red→ p alk. present
- Add BG Indicator- yellow (hydroxide)
- After BG Indicator –blue color –titrate form blue to green to yellow
- Compare P Alk to Total Alk to calculate concentrations of alkalinity fractions

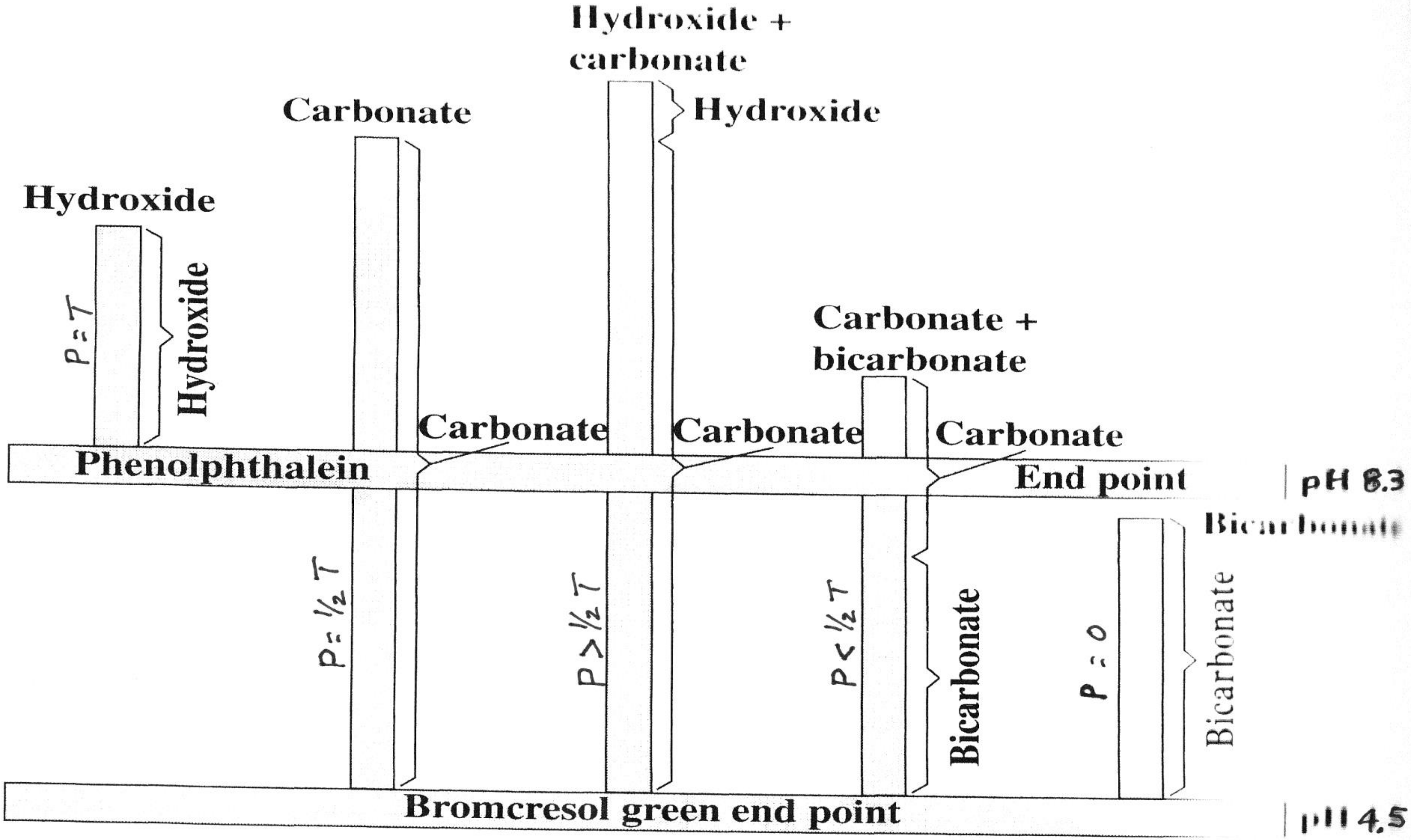
Calculating Alkalinity Fractions

Alkalinity relationships

Result of Titration	Hydroxide-OH^- Alkalinity as $CaCO_3$	Carbonate-CO_3^- Alkalinity as $CaCO_3$	Bicarbonate-HCO_3^- Concentration as $CaCO_3$
$P = 0$	0	0	T
$P < \frac{1}{2} T$	0	2P	T – 2P
$P = \frac{1}{2} T$	0	2P	0
$P > \frac{1}{2} T$	2P – T	2(T – P)	0
$P = T$	T	0	0

Where: P = Phenolphthalein alkalinity; T = Total alkalinity. Sawyer et al. pp. 553-554.

Alkalinity Fractions (Sawyer, p.554)



Alkalinity Fractions

- P=1/2 T – Carbonate = 2P
- P>1/2 T – Carbonate = 2(T-P)

  Hydroxide = 2P-T
- P<1/2 T – Carbonate = 2P

  Bicarbonate = T-2P

Practice problems

- Problem 18.11
- Problem 18.12 sample B

Biochemical Oxygen Demand

CE404

Environmental Analysis

Prof. Isam Alyaseri

Biochemical Oxygen Demand
Definition

- Also known as BOD
- Reported in mg/L
- An estimate of the organic strength of the wastewater
- Measures the amount of oxygen used by microorganisms as they use the nutrients in wastewater when placed in a controlled temperature for five days (in standard conditions)

Biochemical Oxygen Demand
Definition continued

- Water Treatment
  - Not significant
- WasteWater Treatment
  - Environmental agencies or ministries require all secondary wastewater treatment plants to report BOD of effluent
  - Also called BOD_5
  - 5 days set as standard
  - Used on mixed liquor to determine F/M ratio

What is BOD?
Definition continued

It is the rate at which microorganisms use the oxygen in wastewater while digesting organic matter. The BOD test measures the oxygen demand due to both carbon and nitrogen based compounds.

CBOD is carbonaceous BOD. It is a variation of the BOD test that measures the oxygen demand due to carbon based compounds.

Biochemical Oxygen Demand
Definition continued

- Difference between BOD and CBOD test
  - Carbonaceous Biochemical Oxygen Demand is sample with nitrification inhibitor
  - Low strength samples have potential for nitrifiers
  - Nitrifying bacteria are prevented from depleting O_2 in wastewater
  - If nitrifiers allowed to use CO2 as food, test results would inaccurately trend high

Biochemical Oxygen Demand
Regulatory and/or Process Control Levels

- Wastewater – Common ranges in mg/L
  - Raw domestic WW: 200-400 mg/L
  - Secondary WW effluents: < 30 mg/L
- Iraq Ministry regulatory level has to be < 60 mg/L

BOD Use & Theory

- Why?
  - Permit requirements
  - Determine the relative strength of the wastewater
  - Determine waste loadings to wastewater plant
  - Evaluate the efficiency of a plant’s waste removal
- What is the use?
  - Sizing treatment facilities (e.g. bioreactors).
  - Receiving water assimilation capacities.
  - Discharge guidelines.
- Theories
  - Substrate (organics) biodegradation proportional to its remaining concentration.
  - O_2 consumption proportional to substrate biodegradation by bacteria.

BOD Measurements

- Why BOD_5?
  - Organics oxidation 70-80% complete.
  - The time of English rivers to ocean.
  - Absent of nitrification.
  - If too long, no O_2 left in bottle.
- BOD_{ult}:
  - Infinite or > 20 days.
  - Less than ThOD as some substrate not biodegraded or some used for cell tissue mass.
- CBOD:
  - Inhabit nitrification (not to oxidize NH_3)
  - Most permits expect you to measure CBOD in the effluent

Ultimate BOD

$$BOD_t = BOD_u\left(1 - e^{-k_1 t}\right)$$

- BOD_t=BOD exerted in t days
- BOD_u= ultimate BOD
- k_1 = BOD degradation rate constant = deoxygenation constant

BOD Tests & Calculations

- Substrate (sample): biodegradable organics.
- Seed: bacteria capable to oxidize substrate (already in municipal ww. Could be a concern for industrial ww).
- Dilution water: provide growth factors.
- Consumed O_2>2mg/L, remaining O_2> 2mg/L.

Biochemical Oxygen Demand
Sampling Guidelines

- *Standard Methods*, Method 5210
- Flow proportional composite sample or grab
  - 1000 ml
- Plant influent
- Secondary effluent
- Collect before chlorination (otherwise you need to seed)
- Preservatives – None. Store samples at 4^{o}C until time of analysis.
- Hold time – Preferably begin sample analysis within 6 hours of collection. Maximum hold time is 24 hours

BOD Procedure

Equipment

- Dissolved oxygen meter & probe
- Incubator
- BOD bottles & caps
- Graduated cylinders and pipets

Chemicals

- Dilution Water nutrients
- Seed source or polyseed
- Nitrification inhibitor (for CBOD)
- Glucose-glutamic acid quality control solution

Biochemical Oxygen Demand

Biochemical Oxygen Demand

- Line up all your equipment and.....
- Before anything else – start up and calibrate the DO meter

Biochemical Oxygen Demand
Procedures

- Glass bottles should be clean and free from cross-contamination
- Triple rinse and allowed to dry
- Free of toxics which could stress organisms
- Next step – Paperwork/Bench sheet
  - Log sample type and bottle numbers
  - Determine sample volumes…dependent on estimated BOD
    - Calculation (based on valid DO depletion of 4 mg/L)
    - 1200 ÷ Estimated BOD, mg/L

Biochemical Oxygen Demand
Procedures

- Prepare dilution water as needed
  - Add buffer pillow to container
- Add three squirts nitrification inhibitor to all bottles that are used to test CBOD
- Measure samples and add to BOD bottles….
- Start with blanks and go from clean to dirty (Blanks, effluent, influent)
- Add dilution water to samples
- Fill to halfway up the neck of BOD bottle

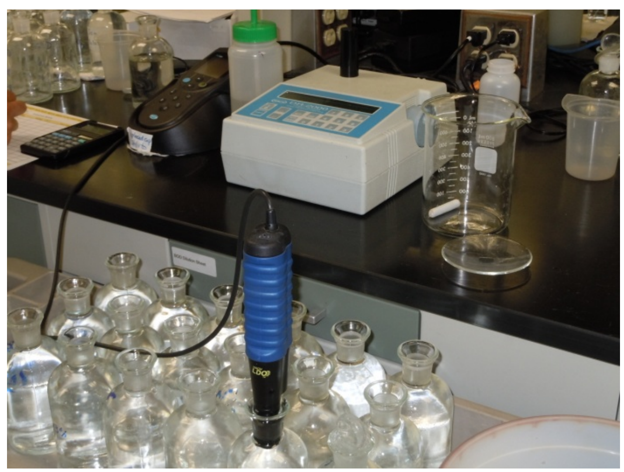
Biochemical Oxygen Demand *Procedures*

Biochemical Oxygen Demand *Procedures*

Biochemical Oxygen Demand *Procedures*

BOD Procedure

- If taken from wastewater plant, you may not need to add seed.
- Measure initial dissolved oxygen.
- Incubate for five days at $20^{o}C$.
- Keep in dark.
- Take bottles out from incubator and measure final dissolved oxygen.

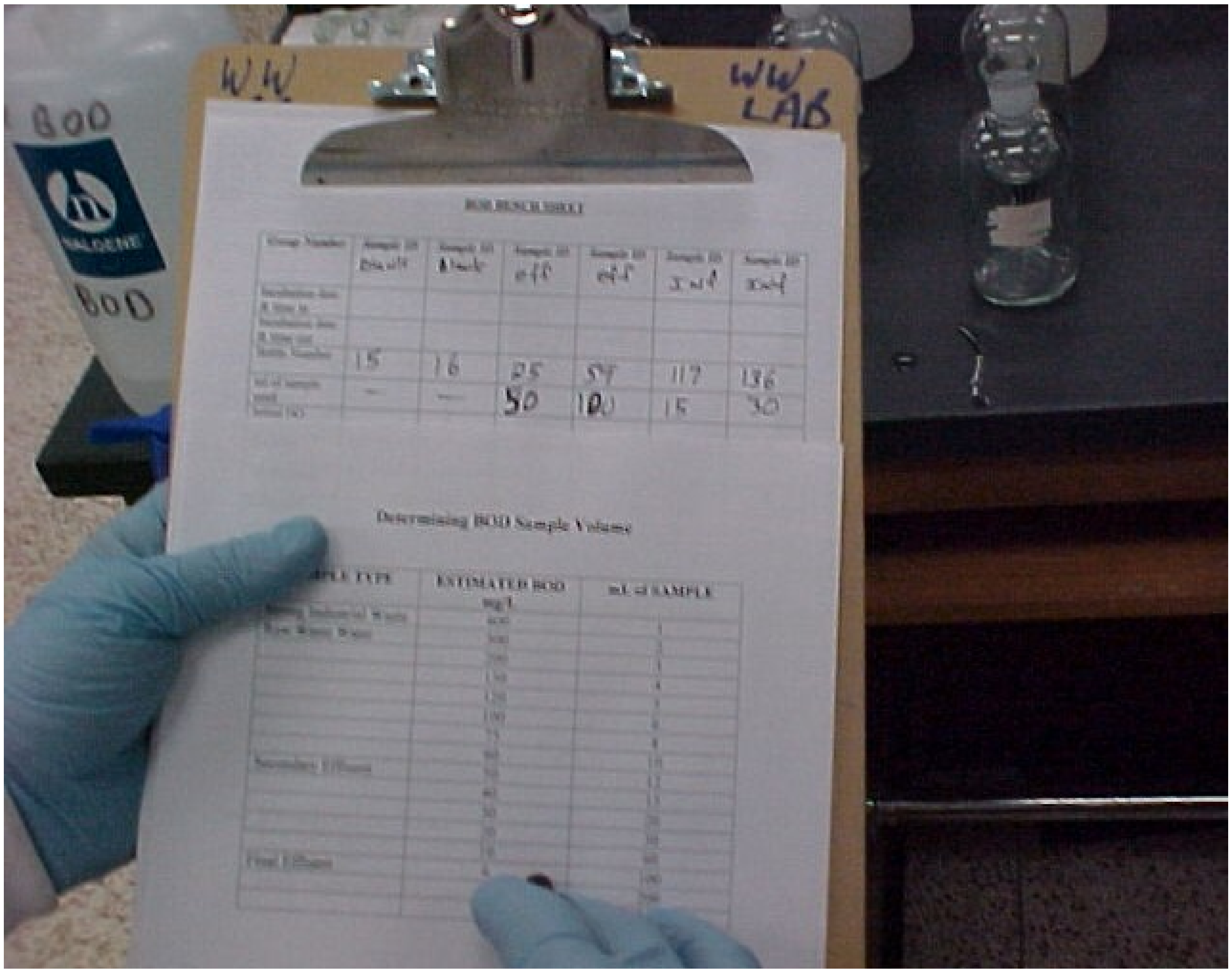


Biochemical Oxygen Demand

- **Hints**
  - Read DO of bottles with BOD probe of DO meter– one at a time
  - Replace spillage with DI water and stopper
  - Ensure you have NO BUBBLES
  - Record results as initial or final DO on bench sheet
  - Rinse probe with DI between readings

Biochemical Oxygen Demand *Procedures*

Biochemical Oxygen Demand *Procedures*



BOD Calculation: Unseeded BOD

$$BOD_t = \frac{DO_i - DO_f}{V_s / V_b} = \left(DO_i - DO_f\right)DF$$

- BOD_t = BOD at t days (mg/L)
- DO_i = initial dissolved oxygen (mg/L)
- DO_f = final dissolved oxygen (mg/L)
- V_s= sample volume (mL)
- V_b = bottle volume (mL) = 300 mL
- DF = dilution factor = V_b/V_s

Example: (8.0 mg/L – 4.0 mg/L) X (300ml) / (5ml) = 240 mg/L

BOD Calculation: Seeded BOD

$$BOD_t = \frac{(DO_{Bf} - DO_{Sf}) - (DO_{Bi} - DO_{Si})}{V_s / V_b} - (DO_{Bi} - DO_{Bf})$$

- BOD_t = BOD at t days (mg/L)
- DO_{Bi} = initial DO of blank (mg/L)
- DO_{Bf} = final DO of blank (mg/L)
- DO_{Si} = initial DO of sample (mg/L)
- DO_{Sf} = final DO of sample (mg/L)

BOD Quality Control

- Dilution Water Blank should not deplete more than 0.2 mg/L
- Each sample should deplete at least 2 mg/L.
- Final DO should not be less than 2.0 mg/L.
- If DO final is less than 2 mg/L or the depletion is less than 2 mg/L, the BOD result is invalid and should not be used for reporting purposes.
- Verify incubator temperature daily.

BOD – Helpful Hints

- Age DI water several days before adding nutrients.
- Store DI water in dark while aging.
- Aerate dilution water for an hour after adding nutrients.
- You can use primary effluent as a seed source.
- Follow manufacturer's directions carefully if you are using polyseed.
- BOD bottles should be scrupulously clean. Acid wash if necessary. Make sure to remove all soap residue.
- Add a DI water seal and cap bottle before incubating.
- Check samples for residual chlorine. Treat with sodium thiosulfite if necessary.
- Samples should be at room temperature.
- Recalibrate the DO meter everyday.

Biochemical Oxygen Demand
Interpreting Readings

- Wastewater
  - Elevated levels in final effluent can indicate
    - High strength input
    - Hydraulic overload
    - Operational control problems
    - Sampling and or analytical error

- Wastewater
  - Determining F/M ratio

BOD, lbs/day ÷ MLVSS lbs

Daily lbs of BOD load (food) per lbs of MLVSS (# of microbes)

Biochemical Oxygen Demand

Plant and/or Chemical Feed Adjustments

- Low F/M – consider increase wasting rate decrease RAS
- High F/M – consider increase RAS lower wasting rate
- Perform other checks prior to making adjustments
  - TSS/VS
  - Ammonia nitrogen
  - Phosphorous
  - DO
  - COD

BOD Limitations

- Limitations
  - 5-day too long for getting results to take action.
  - Nitrification may occur unless CBOD.
  - Poor repeatability due to variations of seeding bacteria.
  - Pretreatment if testing toxic wastes.
  - May need seed: active, well acclimated.
  - Only measure readily biodegradable organics.

Sources of Errors

- Use of different seeds
- Malfunctioning of DO probe
- Unrepresentative sample
- Temp. and pH difference
- Presence of Copper and Cl_2 in dilution water

Chemical Oxygen Demand

CE404

Environmental Analysis

Prof. Isam Alyaseri

Chemical Oxygen Demand (COD)

- Used to measure the organic waste in domestic and industrial wastewaters
- All organic wastes can be oxidized by action of strong oxidizing agents under acidic conditions
- Potassium permanganate historically was used as the strong oxidizer but now replaced with potassium dichromate
- Acidic condition with elevated temperature for the dichromate to work

Chemical Oxygen Demand (COD)

- Chemical to oxidize the organics, calculate as O_2 equivalent.
- Regardless of biodegradability, convert organics to CO_2 and H_2O (some compounds not oxidable e.g. aromatic hydrocarbon).
- COD > BOD. COD includes non-biodegradable and slowly biodegradable
- BOD/COD ratio: biodegradability indicator.

Chemical Oxygen Demand (COD)

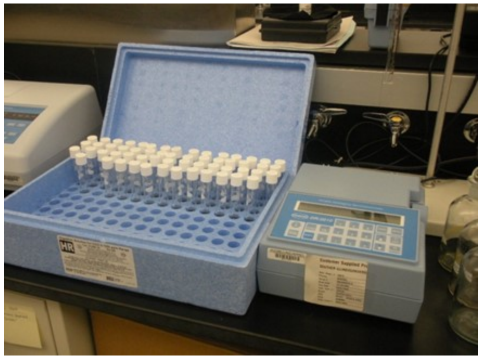
- Reactor Digestion Method

➢ Strong chemical oxidizing agent (potassium dichromate, $K_2Cr_2O_7$) plus a strong acid (H_2SO_4).

➢ Mix with sample and heat for 2 hours in a reactor (150ºC)

➢ Measure consumption of , $K_2Cr_2O_7$ and use a colorimetric or a titrimetric method to convert to oxygen equivalent.

COD Chemicals and Test



- Chemicals
  - $K_2Cr_2O_7$: dichromate ion to oxidize organics.
  - Mercuric sulfate: to inhibit oxidation of Cl^-.
  - Silver sulfate: catalyst.
- Open reflux: to measure remaining $K_2Cr_2O_7$
  - Larger sample size (volumetric method).
  - May lose volatile organics.
  - Use FAS to titrate and ferroin as the indicator.
- **Closed reflux**: to measure consumed.
  - Easier and faster (colorimetric, 600 nm),
  - Smaller sample size.
  - Sampling difficulty if containing visible solids.

COD Chemicals and Test

- Spectrophotometers will be used in this test to detect change in color due to the oxidation process
- Select the proper level of tube concentration (0-150 mg/L) or (0-1500 mg/L)
- Spent solution must be stored and disposed into approved hazardous storage site

COD Advantages and Limitations

- Advantages:
  - Shorter time to get results (total 3 hr.)
  - More precise than BOD.
- Limitations:
  - Can’t provide information on the rate of biodegradation.
  - Can’t tell if the measured is biodegradable or non-biodegradable.
  - Not oxidize all organics to the same degrees.
  - Not like the biodegradation in nature

Jar Test

Dr. Isam Alyaseri
CE404 Lab

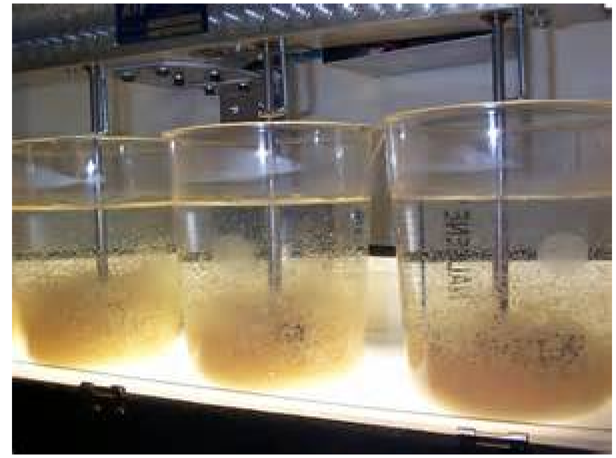
Test Objective

- Jar testing is a pilot-scale test of the treatment chemicals used in a particular water plant.
- It simulates the coagulation/flocculation process in a water treatment plant.
- Helps operators determine if they are using the right amount of treatment chemicals, and, thus, improves the plant's performance.

Test Objective

- Adjusting the amount of treatment chemicals and the sequence in which they are added to samples of raw water held in jars or beakers.
- The sample is then stirred so that the formation, development, and settlement of floc can be watched just as it would be in the full scale treatment plant.
- Floc forms when treatment chemicals react with material in the raw water and clump together.

Jar Test Apparatus



- ***Apparatus:***
- Jar testing apparatus
- Turbidity meter
- Beaker, burette, pipette
- ***Reagents required:***

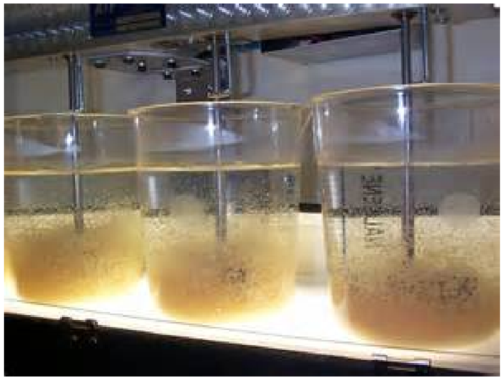
Alum solution (for example: 1 ml containing 10 mg of alum)

Other coagulants

Polymers

Etc.

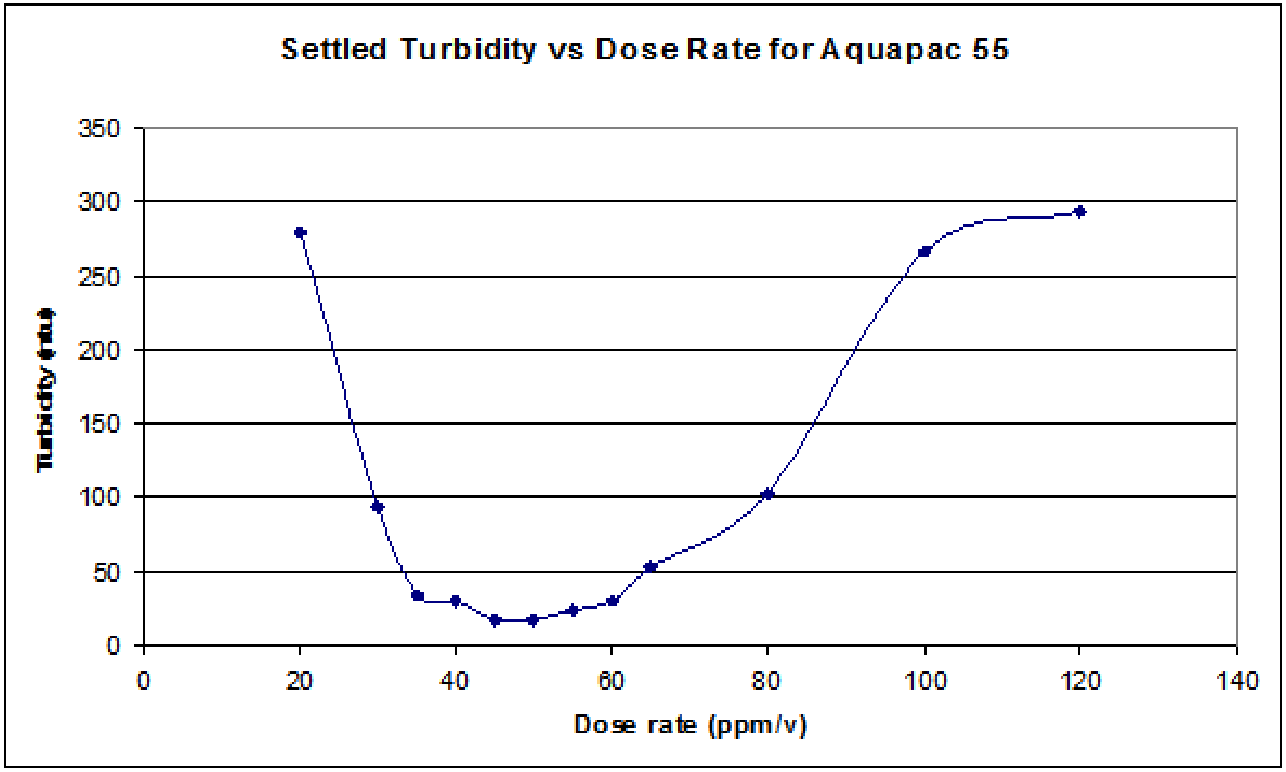
Jar Test Procedure



- Take 1000 ml of given sample in 6 beakers.
- Find the pH of the sample and adjust it to 6 to 8.5.
- Now add 1 ml, 2 ml, 4 ml, 8 ml, 10 ml, 12 ml of alum respectively in each one of the beakers.
- Now insert the paddle of the jar testing apparatus inside the beakers and start it.
- Initially maintain a speed such that the paddles rotate at an angular velocity of 100 rpm for a time of 1 minute.
- Now adjust the speed such that the paddles rotate at 40 rpm/min for a time of 9 minutes.
- Now allow the beakers to settle down for 10 minutes.
- Make an observation as of which of the 6 beakers is most clearer. Also measure the turbidity of each beaker using a turbidity meter and tabulate your results.
- Plot a graph “Settled turbidity” Vs “Coagulant dosage”.

Jar Test Result

- The optimum value of coagulant dosage from the graph should be reported.
- The optimum value of coagulant generally lies between 8 to 10 for normal water from rivers.



Coagulant Aid Dosage Determination

Problem Given the following jar test results, which polymer dose should be used?

Container No.	1	2	3	4	5	6
Alum (mg/L)	6	6	6	6	6	6
Polymer (mg/L)	0.25	0.5	1.0	2.0	3.0	4.0
Turbidity (NTU)	0.9	0.7	0.4	0.3	0.7	1.0

Solution Graph the dose versus the turbidity (Figure 10.25).

While the lowest turbidity is obtained at a dose of 2 mg/L, this turbidity is not much lower than the turbidity obtained at half that dose. In addition, the minimum point on the curve may be between 1 and 2 mg/L. If time permits, it may be useful to run another test. However, since the dose chosen is an estimate, the operator may try 1 mg/L in the plant and adjust the dosage as needed.

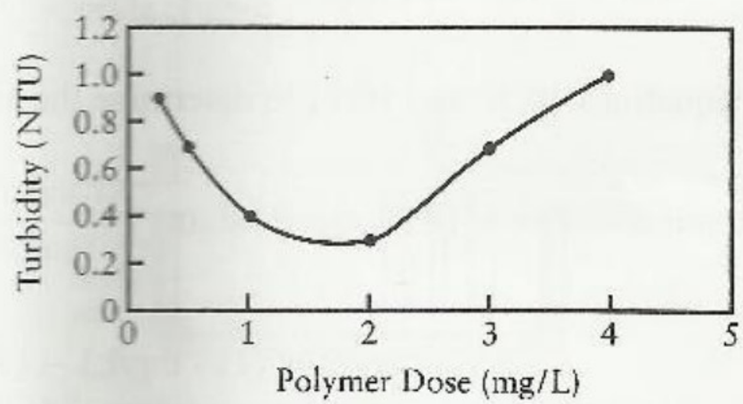


Figure 10.25 Polymer dose versus turbidity.

Work in Lab

- Results from jar test in lab to determine the best alum dose in a DWTP came in as in table below, what is best dose?

Alum dose, mg/L	2	4	6	8	10	12
Turbidity, NTU	19.2	12.6	8.2	7.5	13.8	23.4