Université Concordia University

Building, Civil and Environmental Engineering

CIVI 361

INTRODUCTION TO ENVIRONMENTAL ENGINEERING

LABORATORY MANUAL

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CIVI-361 Introduction to Environmental Engineering

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EXPERIMENT 1 SOLIDS IN WATER AND WASTEWATER

Background: Solids, in the context of water quality, refers to dissolved or suspended matter is surface water, ground water, treated water, or wastewater. Due to the polar nature of water, most dissolved matter is comprised of ions (electrically charged atoms or molecules). Suspended material may be comprised of both settleable and colloidal material. Settleable solids are large enough (> 10^{-3} mm) to eventually settle out of suspension, whereas colloidal material (> 10^{-6} mm and < 10^{-3} mm) will remain in suspension indefinitely. Solids may also be classified as organic or inorganic. Traditionally, environmental engineers determine solids by gravimetric analysis; whereby a known volume of water is evaporated at 105 °C, and the solid residue remaining is weighed. Organic and inorganic content is estimated by volatilizing the dried residue in a furnace at 550 °C and determining the residual weight. The volatilized component is referred to as ***volatile solids,*** and is an estimate of the organic matter content. The remaining residue is referred to ***as fixed solids,*** and is an estimate of the inorganic matter content. Municipal wastewater treatment plants can process large volumes of water, and differentially remove tons of solids on a daily basis; thus, solids inventory is an important part of unit operation design as well as daily operation.

Objective: To determine the solids distribution for a water sample.

Equipment: Analytical balance, gravimetric oven, muffle furnace, desiccator, Imhoff cones, drying dishes, gooch crucibles with glass microfiber filters, vacuum filtration assembly, Conductivity/TDS meter, and measuring cylinders.

EXPERIMENT 1-1 SETTLEABLE SOLIDS

Background: ***Settleable solids*** is the term applied to any solid material settling out of suspension within a definite time period. Settleable solids may be determined by allowing 1L of a water sample to settle in an Imhoff cone for 1 hour. The volume (mL) of settled material is read directly and the result expressed as mL/L. Knowledge of the degree of settling can be used by engineers to forecast possible trouble due to deposition in pipelines wherever flow is restricted. It is also important in the daily operation of settling basins in municipal water treatment and many industrial applications, as well as in the design of sedimentation units in general.

Objective: To determine the volume of settleable solids for a water sample.

Procedure: Pour 1000 mL each of a well-mixed water sample into three Imhoff cones and allow the water to settle for 45 minutes. Then gently stir the contents of each cone with a glass rod to dislodge any solids adhering to the wall of the cones. Continue the settling period for a further 15 minutes. Read the volume of each settled mass and calculate the average. The sample will still contain suspended colloidal material which will not settle out.

Results: Express the average volume (mL) in 1 L of sample as mL/L.

EXPERIMENT 1-2 TOTAL SOLIDS

Background: ***Total solids*** (TS) refers to the residue remaining after a well-mixed water sample of known volume is evaporated in a tarred (pre-weighed) dish to constant weight, in an oven at 105 ±1 °C. The increase in weight (mg), compared to the empty dish, divided by the sample volume (L), represents TS (mg/L).

Objective: To determine the TS for a water sample

Procedure: Measure 25 mL (in triplicate) of a well-mixed water sample into a pre-weighed evaporating dish (which has been previously ignited in a furnace, at 550 °C) and place in an oven set to 105 °C, After the water has been completely evaporated, cool the sample to room temperature in a desiccator and weight 0.0001g constant weight.

Results:

$$\text{TS (mg/L)} = \frac{[\text{wt. of dish after evaporation (mg)}] - [\text{ wt. of empty dish (mg)}]}{\text{sample volume (L)}}$$

EXPERIMENT 1-3 TOTAL SUSPENDED SOLIDS

Background: The ***total suspended solids*** (TSS) is the portion of TS retained on a microfiber filter. It represents the insoluble, particulate solid fraction. We can pre-weigh the filter, filter a known quantity of water, dry, and weigh it again to determine suspended solids.

Objective: To determine the TSS for a water sample.

Procedure: Take a pre-ignited glass microfiber filter, weigh it to 0.0001g. Filter around 10 mL of a well-mixed sample (in triplicate) and dry the filter to constant weight at 105 °C and weigh it.

Results:

$$\text{TSS (mg/L)} = \frac{[\text{wt. of dried crucible with filter + residue (mg)}] - [\text{ wt. of empty crucible with filter (mg)}]}{\text{sample volume (L)}}$$

EXPERIMENT 1-4 TOTAL DISSOLVED SOLIDS

Background: ***Total dissolved solids*** (TDS) refers to the solid content of a filtrate obtained by filtering a water sample through a microfiber glass filter, which removes suspended and colloidal material. The filtrate is then evaporated as in the total solids test. However, since we are determining total solid (TS) and total suspended solids (TSS), we can take advantage of the following relationship to estimate TDS without actual measurement.

$$\text{TS} = \text{TDS} + \text{TSS} \quad \text{or} \quad \text{TDS} = \text{TS} - \text{TSS}$$

Since all the dissolved solids are essentially ionic, many engineers use conductivity meters to estimate TDS. Meters are available which are calibrated for the average ionic species distribution in wastewater. We will use a conductivity meter to estimate TDS on a filtered sample as well. Water high in dissolved solids is generally of inferior palatability as drinking water and may induce unfavorable physiological reactions in the transient consumer. For this reason a limit of 500 mg/L is recommended for drinking water. Highly mineralized water is also unsuited for many industrial applications

Procedure: Use Conductivity/TDS meter to measure TDS.

Results: Calculate result: TDS = TS – TSS. Obtain TDS from direct readout of conductivity meter (mg/L). Then compare with these two TDS results and explain.

EXPERIMENT 1-5 FIXED AND VOLATILE SOLIDS

Background: The residues representing TS and TSS (and TDS by difference) can be ignited in a furnace at 550°C to volatilize the organic fraction (or volatile solids). The residue remaining is the inorganic fraction (or fixed solids). Thus we can determine the fixed and volatile TS fractions (FTS and VTS), as well as the fixed and volatile TSS fractions (FTSS and VTSS). We can also estimate the FTDS and VTDS from

$$\text{FTDS} = \text{FTS} - \text{FTSS} \quad \text{and} \quad \text{VTDS} = \text{VTS} - \text{VTSS}$$

Estimation of the organic solid fraction is important in wastewater treatment operations involving bioreactors, which can biodegrade the organic fraction, as well as in effluent monitoring, where reduction of biodegradable organic material in effluents entering natural water bodies is essential,

Objective: To determine the FTS, FTDS, FTSS, VTS, VTDS, and VTSS for a water sample.

Procedure: Place the already weighed crucible/dish containing the TS, and TSS residues on filters in a muffle furnace set to 550 ± 5°C for 15 minutes. Carefully remove with thongs and place in a desiccator to cool. Weigh each crucible/dish and filter to 0.0001 g.

Results:

$$\text{VTS (mg/L)} = \frac{[\text{wt. of dish (1-2) before ignition (mg)}] - [\text{ wt. of dish after ignition (mg)}]}{\text{sample volume (L)}}$$

$$\text{FTS} = \text{TS} - \text{VTS}$$

$$\text{VTSS (mg/L)} = \frac{[\text{wt. of crucible with filter (1-3) before ignition (mg)}] - [\text{ wt. of crucible with filter after ignition (mg)}]}{\text{sample volume (L)}}$$

$$\text{FTSS} = \text{TSS} - \text{VTSS}$$

$$\text{VTDS} = \text{VTS} - \text{VTSS} \quad \text{and} \quad \text{FTDS} = \text{FTS} - \text{FTSS}$$

Details of report will be discussed in the laboratory session.

EXPERIMENT 2 COLOR, pH AND ALKALINITY OF WATER AND WASTEWATER

BACKGROUND: (pH): The pH of water indicates the activity or molar concentration of hydrogen ions (H^+) in solution, and is given by

$pH = -\log [H^+]$ ..... where $[H^+]$ has units of moles H^+/liter (1)

Pure water reversibly dissociates to a small extent to produce hydrogen ions and hydroxide ions (OH^-). H^+ is essentially the active component of all acids, and OH^- is a strong base or alkaline species.

$H_2O \leftrightarrow H^+ + OH^-$ (2)

The equilibrium constant for the dissociation of water is as follows.

$[H^+]\,[OH^-] = 10^{-14}$ (3)

Since from (2) it follows that $[H^+]$ must equal $[OH^-]$; then using (3), $[H^+] = [OH^-] = 10^{-7}$, which from (1) gives a pH of 7, or neutral pH. Taking the log of each side of (3) we get a relationship which holds fir most water arid wastewater solutions.

$pH + pOH^- = 14$ (4)

Thus, if one measures the pH of a solution, the concentration of OH^- is implicit. For example, water sample having a pH of 5, or 10^{-5} moles $[H^+]$ /liter, has a pOH of 9, or 10^{-9} moles OH^- /liter. Solutions with pH values less than 7 are increasingly acidic, and greater than **7,** increasingly alkaline or basic.

NEUTRAL
↓
pH—> 1 2 3 4 *5* **6 7 8 9 10 11 12 13 14**
STRONG ACID WEAK ACID WEAK BASE STRONG BASE

Natural water bodies can have pH values between 6 and 9. Wastewaters can have pH values anywhere from 0-14, depending on their origin. Determining the pH of natural water bodies is essential for monitoring aquatic ecosystems, and pH adjustment is necessary for the biological and chemical unit operations in water treatment plants.

(Alkalinity): Whereas pH is an *intensity* factor, alkalinity is *a capacity* factor. The alkalinity of a water sample is its capacity to neutralize acid, or H. For the most part the alkaline species in water, in order of increasing alkaline strength, are: bicarbonate ion, HCO_3^-, carbonate ion, $CO_3^{\,2-}$, and hydroxide ion, OH^-. Carbonate and bicarbonate ions derive mainly from atmospheric dissolution of carbon dioxide in water. A water sample's alkalinity is determined by titration with a standard acid solution. If the total alkalinity is required, then a simple titration to pH 4.5 is performed and the total alkalinity is calculated. At pH 4.5 all alkaline species have been neutralized. Standard practice uses a 0.02 N sulfuric acid (H_2SO_4) solution as the titrant. Since 1 ml of this titrant will neutralize 1 mg of $CaCO_3$ (calcium carbonate, is an alkaline mineral), water alkalinity is determined as mg $CaCO_3$ /liter. For example, if it took 250 ml of 0.02 N H_2SO4 to bring the pH of a 1 liter water sample to 4.5, then its standard total alkalinity would be 250 mg $CaCO_3$/liter.

It is also possible to determine the distribution of alkaline species in a water sample as well, using the pH, and titrating to two pH end-points. This method takes advantage of the fact that at pH 8.3 all hydroxide (OH^-) and carbonate ($CO_3^{\,2-}$) have been neutralized. The bicarbonate however (HCO_3^-) is not neutralized at pH 8.3, and is only neutralized at pH 4.5. Figure 2.0 illustrates this.

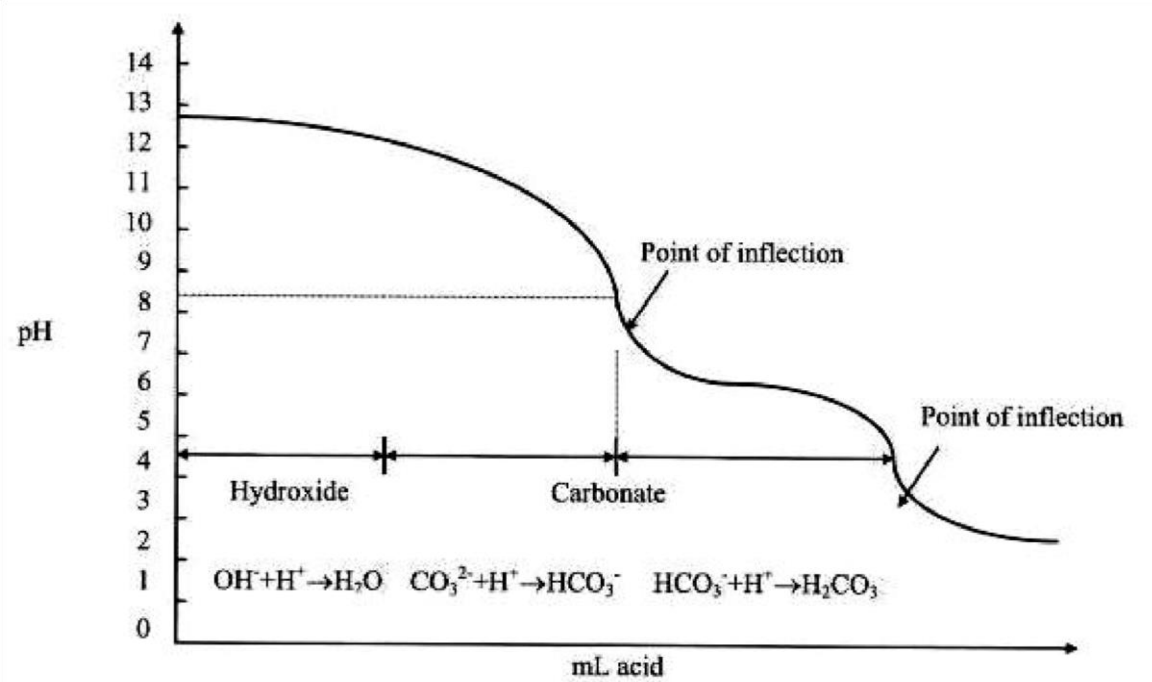


Figure 2.0 Titration curve for a water sample (with a pH> 8.3) showing the first inflection point, or end-point, at pH 8.3, where the hydroxide and carbonate ion are neutralized. Note that the original carbonate is neutralized to bicarbonate. At end-point pH 4.5, the original bicarbonate, and that created from the original carbonate at pH 8.3, is neutralized to carbonic acid.

(Color): Color in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes. Color is removed to make a water suitable for general and industrial applications. Colored industrial wastewaters may require color removal before discharge into watercourses.

The term “color” is used here to mean true color, that is, the color of water from which turbidity has been removed. The term “apparent color” includes not only color due to substances in solution, but also that due to suspended matter. Apparent color is determined on the original sample without filtration or centrifugation. In some highly colored industrial wastewaters color is contributed principally by colloidal or suspended material. In such cases both true color and apparent color should be determined.

OBJECTIVE: To determine the color, total alkalinity and distribution of the alkaline species (OH^-, CO_3^{2-}, and HCO_3^-) in a wastewater sample.

REAGENTS: Standard titrant (**0.025N** H_2SO_4), phenolphthalein indicator solution (for end-point pH 8.3*)*, bromocresol green indicator solution (for endpoint pH 4.5), and series platinum-cobalt (Pt/Co) color standards in different concentration.

EQUIPMENT: Burette with self-zeroing dispenser, 100 ml graduated cylinder, 250 ml flasks, pH meter, and spectrophotometer.

PROCEDURE:

A. Add 100 ml of synthetic wastewater to the flask using the 100 ml graduated cylinder. Put magnetic bar and start stirring. Insert the pH probe into the beaker and wait for the reading to stabilize. Record pH reading. Add 6 drops of phenolphthalein indicator and titrate until the wastewater goes from purple-mauve to colorless. Record the volume of titrant use. Continue add 16 drops of bromocresol green indicator this time, and titrate until the wastewater goes from a blue to a light-green color. Record the volume of titrant used.

B. Filter about 10 ml of sample with ashless paper filter. Turn on the spectrophotometer and select wavelength at 455nm. Use distilled water as blank and measure the provided Pt/Co color standards’ absorbance to build up the calibration curve. Then measure the absorbance of the filtered water sample and non-filtered water sample. Calculate True color and Apparent color (UNITS: Pt/Co COLOR) according to the established calibration curve.

RESULTS: Determining the total alkalinity and the original amounts of OH^-, CO_3^{2-}, and HCO_3^-, as mg $CaCO_3$/liter, is not difficult but it can be confusing at first. The following is a detailed, step by step procedure using example data by 0.02N H2SO4. **Please note that the concentration of standard titrant is different. A calculation factor should be considered.**

Example: A 100 ml wastewater sample has a pH of 11, and it took 20 ml of **0.02N** H_2SO_4 to bring the pH to the pH 8:3 endpoint, and 45 ml to bring it to the pH.4.5 end-point. Determine the total alkalinity and the original amounts of OH^-, CO_3^{2-}, and HCO_3^- in the wastewater as mg $CaCO_3$/liter.

Step 1

From the pH of the water sample determine the $[OH^-]$

pH + pOH = 14

Therefore pOH= 3 and $[OH^-] = 10^{-3}$ *moles* OH^-*/liter.*

Step 2

Change $[OH^-]$ to alkalinity equivalents of mg $CaCO_3$/liter.

$CaCO_3$ equivalent (10^{-3} mole OH^-/liter) x (l Eq/rnole OH^-) x (50,000 mg $CaCO_3$ /Eq) = 50 mg $CaCO_3$/liter

The water sample has hydroxide alkalinity of 50 mg $CaCO_3$*/liter.*

Step 3

Since it took 45 ml to titrate this sample to pH 4.5 there must be an equivalent of 45 mg CaCO3 in the 100 ml sample. Thus it has a total alkalinity of 450 mg $CaCO_3$/liter.

The water sample has a total alkalinity of 450 mg $CaCO_3$*/liter.*

Step 4

Since the water sample has hydroxide alkalinity of 50 mg CaCO3/liter, then there must be 5 mg $CaCO_3$ alka1inity in a 100 ml sample due to the hydroxide. Thus, the hydroxide would consume 5 ml of the 0.02 N sulfuric acid (because 1 ml can neutralize 1 mg $CaCO_3$). Therefore the amount of titrant used to neutralize carbonate to bicarbonate at pH 8.3 must be

20ml – 5 ml = 15 ml

That 15 ml of titrant went to neutralize the original carbonate to bicarbonate.

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$

Thus to bring the original carbonate to carbonic acid (at pH 4 5) would require another 15 ml of titrant (2X)

$2 H^+ + CO_3^{2-} \rightarrow H_2CO_3$

Therefore it took 30 ml of titrant to neutralize all the original carbonate. Thus, there is an equivalent of 30 mg $CaCO_3$ in the 100 ml sample, or 300 mg $CaCO_3$/liter

The water sample has a carbonate alkalinity of 300mg $CaCO_3$*/liter*

Step 5

Since we now know the total, the hydroxide, and the carbonate alkalinity, the bicarbonate alkalinity is easily calculated.

Total alkalinity: 450 mg $CaCO_3$/liter
- Hydroxide alkalinity: 50 mg $CaCO_3$/liter
- Carbonate alkalinity: 300 mg $CaCO_3$/liter

Bicarbonate alkalinity: 100 mg $CaCO_3$/liter

The bicarbonate alkalinity is 100 mg $CaCO_3$*/liter.*

Table 2.0

Titration breakdown

Alkaline Species	ml titrant/100 ml sample	Alkalinity (mg $CaCO_3$/liter)
Hydroxide	5	50
Carbonate	30	300
Bicarbonate	10	100
Total Alkalinity	45	450

* equivalent (Eq) is essentially one mole of neutralizing capacity. Since the hydroxide ion (OH_) can neutralize one mole of H+ per mole hydroxide, it has 1 Eq/mole OH-.

Since the alkaline component of $CaCO_3$, which is CO_3^{2-}, has 2 Eq/mole, and the molecular weight of $CaCO_3$ is 100 g/mole, then $CaCO_3$ has 50 g/Eq, or 50,000 mg/Eq. From this it follows that

$CaCO_3$ equivalent of OH- = (mole OH-/liter)(lEq/mole OH-)(50,000 mg $CaCO_3$ /Eq)

EXPERIMENT 3 SETTLING COLUMN TEST FOR TYPE I SUSPENSIONS

BACKGROUND: Sedimentation or settling is the separation of suspended particles that are denser than water. Sedimentation is widely used in wastewater treatment systems. In this experiment we will investigate discrete, or Type I settling. In discrete settling the particles settle with negligible or no interaction. This will occur under relatively low solids concentration. A typical occurrence of this type of settling is the removal of very fine sand particles from wastewater, as is done in primary settling basin unit operations, for example. The removal efficiencies obtained in sedimentation operation will be a function of the distribution of settling velocities of the particles in suspension. The settling velocity of a particle can be used in the design of settling-basins. The key is to find a lower limit on the settling velocities for particles to settle before they reach the outlet. If we examine the settling of discrete particles in an ideal rectangular settling basin we can model a critical particle settling velocity, V_0, which is the settling velocity of the smallest particle size that is 100% removed. When a particle of this size enters the basin at point 1 (see Figure 3.0**)** it settles with velocity V_0, and travels horizontally with velocity V. It intercepts the sludge zone downstream at point 2.

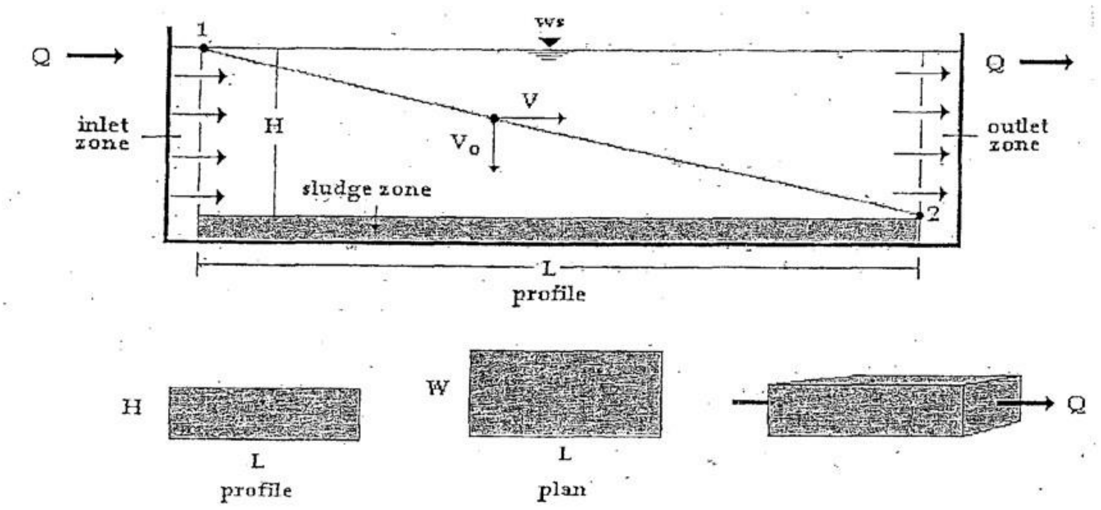


Figure 3.0 Schematic of a profile or section view of an ideal settling basin, which has a flow Q, length, L, water depth, H, and width W.

The detention time in the basin, t, for the particle is given by

$$t = H/V_0 \qquad (1)$$

The detention time is also given by

$$t = L/V \qquad (2)$$

The horizontal velocity is given by flow divided by cross-sectional area HW), or

$$V = Q/HW \qquad (3)$$

Combining (2) and (3) gives

$$t = LWH/Q \qquad (4)$$

Since LWH is the basin volume,∀, then

$$t = \forall/Q \qquad (5)$$

Equating (1) and (4) gives

$$LWH/Q = H/V_0 \qquad (6)$$

Which, upon rearranging yields

$$V_0 = Q/LW = Q/A_p \qquad (7)$$

Where A_p is the plan area of the basin. Flow divided by area has the units of velocity and is termed the *surface loading* or *overflow rate* of basins. Equation (7) shows that the overflow rate is equivalent to the settling velocity of the smallest particle size that is 100% removed. All particles with terminal velocities greater than V_0 will be 100% removed. All particles with terminal velocities $V_t < V_0$, will be partially removed (since they will be distributed at different depths in the water column). For particles with a settling velocity V_t, the fraction of particles removed at a given depth will be the following ratio

$$\text{Fraction of particles removed} = V_t/V_0 \qquad (8)$$

A large variation in particle size will exist in a typical suspension, and one must evaluate the entire range of settling velocities to determine the overall removal for a given design settling velocity or overflow rate. The method used is a settling column test, where the suspension is added to a column and water samples are removed at a given settling depth as a function of time. The samples are analyzed for suspended solids. The mass fraction of particles remaining is then plotted against settling velocity or the surface loading rate, which is the sampling depth divided by sampling time for each fraction (see Figure 3.1). It is from this graph that the overall theoretical removal efficiency for a given surface loading rate is determined.

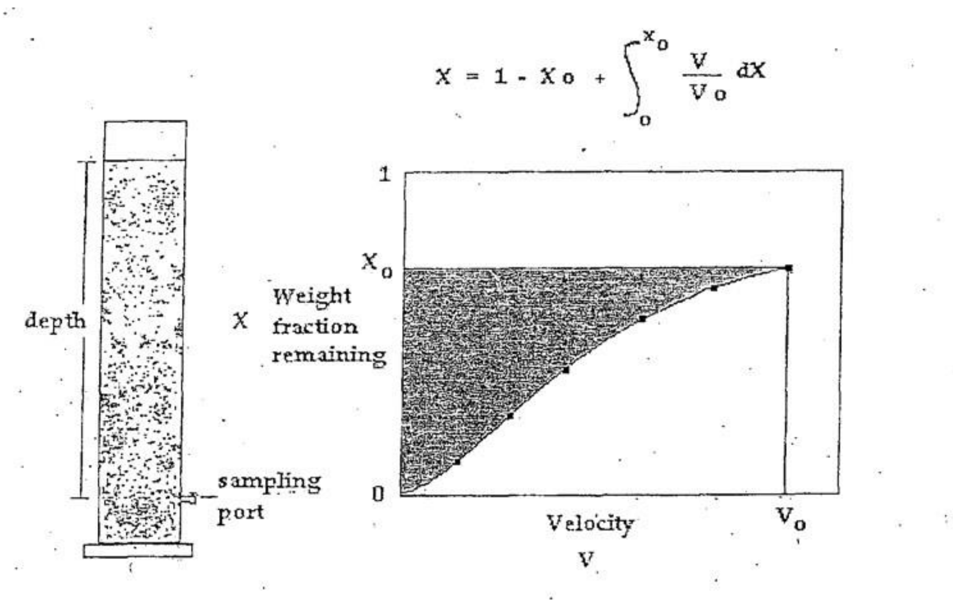


Figure 3.1 A schematic of a settling column. Samples are withdrawn at a given depth over time. The mass fraction of solids remaining is plotted against settling velocity or surface loading rate. The theoretical evolution (by integration) of the cumulative mass fraction of particles removed is shown and corresponds to the shaded area.

OBJECTIVE: To demonstrate the column settling test and to use data obtained to design a primary sedimentation tank.

EQUIPMENT: Settling column with sampling port, 100 ml graduated cylinders, gooch crucible (or aluminum dish) fitted with glass micro-fiber; vacuum filtration set-up, gravimetric oven, and analytical balance (0.0001 g)

PROCEDURE: A model wastewater prepared with very fine sand, silt, and clay, at about *3 g/*liter suspended solids will be added to the column, and samples of about 50ml ~ 100ml each will be taken immediately at the required depth (t = 0). The sample will be collected in a 100 ml graduated cylinder, and the volume of the sample will be accurately noted. At 5 or 10 minutes intervals samples will be removed until a final sampling time of 60 minutes. Suspended solids analysis will be performed on each sample. Samples are filtered with vacuum through a dry, pre-weighed, gooch crucible (or aluminum dish) with a glass micro-fiber filter. Contents of each sample are quantitatively transferred from the cylinder to the crucible with swirling and distilled water washes. The crucible with filter and solids is dried to constant weight in a gravimetric oven at 105℃, and the weight recorded once more. This is performed for each sample.

RESULTS: To determine the suspended solids (SS) in each sample use

$$\frac{\text{weight of crucible (or dish)/filter/SS (g) - weight of empty crucible (or dish)/filter (g)}}{\text{Volume of sample (liter)}}$$

To determine the fraction remaining (X_1) for each sample (i = 10 run to i=60 min) use

$$X = \frac{SS_{t=i}\ (\text{g/liter})}{SS_{t=0}\ (\text{g/liter})}$$

A step by step procedure follows to illustrate how to determine the overall removal of suspended solids from your column test data. Only three velocity points were chosen in the example; **you should choose more points (6 ~ 8) to get satisfy results.** A primary settling tank design problem based on the results will be handed out during the laboratory period.

Protocol for determining the overall removal efficiency

1. **Calculate mass** fraction remaining and **corresponding** settling **velocity:**

$X_i = SS_i / SS_0$, $V_i = Z/T$
Where,
X_i: Mass fraction remaining;
SS_i: Suspended solid concentration at time=i minutes;
SS_0: Suspended solid concentration at time=0 minutes;

V_i: Settling velocity at time=i minutes;
Z: Sampling height of column;
T: Sampling time.

2. **Plot mass** fraction remaining **against** settling velocity. See Figure 3.2

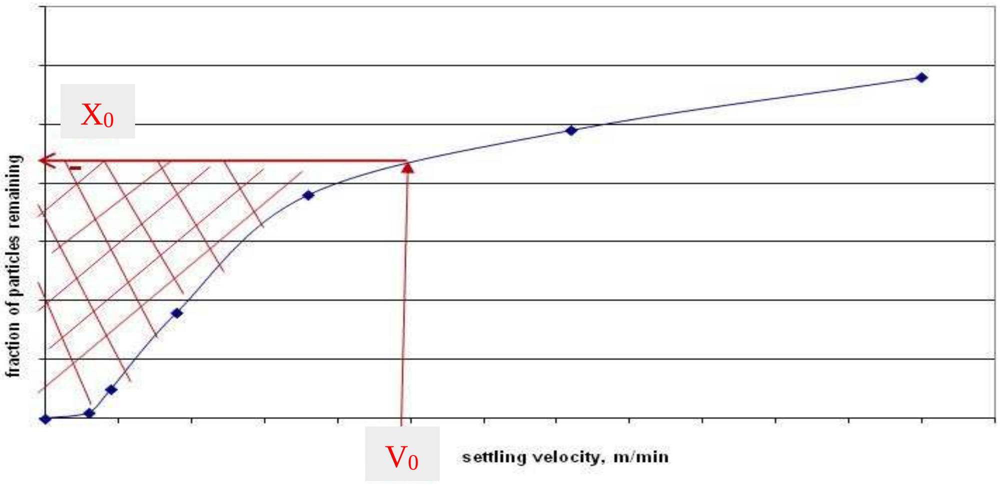


Figure 3.2

3. Determine V_0

4. Determine X_0

5. Integration the shadow area. See Figure 3.3

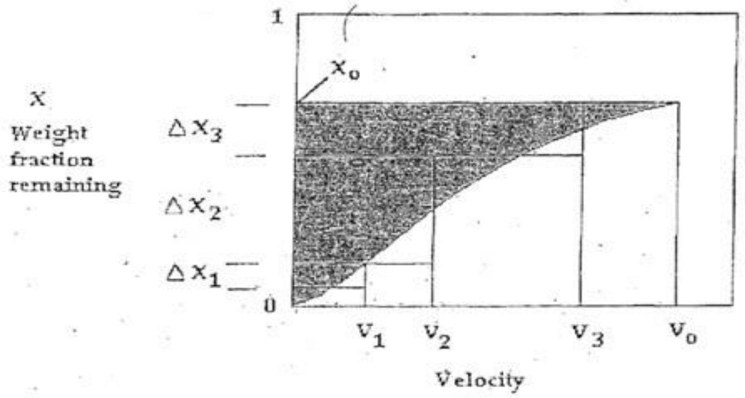
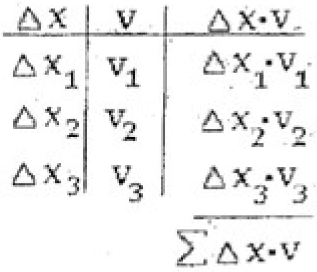


Figure 3.3

6. Determine $\Delta X . V$ by graphical integration. See Figure 3.4



ΔX	V	$\Delta X \cdot V$
ΔX_1	V_1	$\Delta X_1 \cdot V_1$
ΔX_2	V_2	$\Delta X_2 \cdot V_2$
ΔX_3	V_3	$\Delta X_3 \cdot V_3$
		$\sum \Delta X \cdot V$

Figure 3.4

6. Determine overall removed efficiency

$$X = \underbrace{(1 - X0)}_{\substack{\text{Fraction particles} \\ \text{with velocity}>V_0}} + \underbrace{\frac{\sum \Delta X \cdot V}{V0}}_{\substack{\text{Fraction particles} \\ \text{with velocity}<V_0}}$$

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EXPERIMENT 4a JAR TEST FOR OPTIMUM COAGULANT DOSE

Background: Colloids (suspended particles with a diameter between 1μm and 1 nm) occur in virtually all surface water and wastewater**,** and can be comprised of insoluble mineral complexes (such as clays), solid or liquid organic pollutants, proteins, humic acids, or microorganisms such as algae and bacteria. Solid colloids dispersed in water are termed ***sols,*** while liquid colloids dispersed in water are termed ***emulsions.*** Due to their small size they will not settle unless they agglomerate into larger particles. Colloidal suspensions that do not agglomerate naturally are termed ***stable.*** Most colloidal particles have a negative surface charge and stabilization results from an accumulation of a counter positive electrical charge at the particle surface, as dissolved cations arrange themselves in a tightly bound fixed ***layer,*** with a more diffuse layer outside it. The diffuse 'halo' of positive charge creates a repulsive electrostatic energy barrier between colloids, resulting in a stable dispersed system. When two suspended particles approach one another there is also an attractive force, known as van der Waal's force, acting on-them. If two colloids can approach within a critical distance of each other, van der Waal's force can predominate over the electrostatic repulsion, and agglomeration or coagulation can occur, resulting in particle sedimentation.

In water treatment plants, removal of colloids is usually accomplished by adding trivalent metal- salts such as aluminum sulfate or ferric chloride, for example, to coagulate colloids. When a coagulant salt is added to water it dissociates and the metallic ions of $A1^{+3}$ or Fe^{+3} form hydroxo-metallic complexes, such as $A_{13}(OH)_{34}^{+5}$ and $Fe_2(OH)_4^{+5}$. Also, if sufficient alkalinity is present, they will precipitate out in so-called flocs of the hydroxides: $Al(OH)_3$ and $Fe(OH)_3$. For example:

$$Al_2(SO_4)_3.14H_2O + \quad 3Ca(HCO_3)_2 \text{———} \; 2Al(OH)_3\downarrow + \quad 3CaSO_4 + \; 14H_2O + \; 6CO_2$$

Aluminum sulphate Calcium bicarbonate Aluminum hydroxide Calcium sulfate Water Carbon dioxide

(Alum) (Alkalinity) (Floc)

Colloidal dispersions can then be destabilized, agglomerated, and settled by the following mechanisms:

1) adsorption of hydroxo-metallic complexes onto the particles surface, and reduction of the particles effective charge (or zeta potential)

2) inter-particle bridging whereby reactive groups on the destabilized particles-chemically interact

3) by sweep coagulation whereby settling, precipitated hydroxide floes enmesh the particles

Coagulation is not an exact science, and coagulant dosage is determined by the 'jar test', which consists of placing samples of water into beakers, dosing with coagulant, stirring, and allowing them to settle. In the terminology of water treatment procedures, ***coagulation*** refers to the addition and rapid mixing of coagulant to destabilize the colloidal dispersion, while ***flocculation*** refers to the slow stirring, or gentle agitation, to aggregate destabilized colloids and form a rapid settling floc. These same mixing principles are applied to large scale coagulation and flocculation basins in water and wastewater treatment plants. Data obtained from jar tests, such as paddle speeds and area, and mixing times can be employed to develop parameters used to scale-up the operation to plant size facilities.

Objective: To determine the optimum dose and pH of coagulant for the flocculation of a wastewater sample.

Equipment: Six-paddle stirrer/illuminators, 1 L beakers, digital nelphometer, pH papers, timer, pipettes.

Reagents: 10 mg/mL aluminum sulfate and 10 mg/mL ferric chloride green indicator.

Procedure:

1. Determine the optimum dose of coagulant:

Fill six 1-L beakers with 1000 mL each of the synthetic wastewater. Add different doses of stock coagulant solution successively to the beakers. Stir at 80 rpm for 3 minutes (rapid mixing or coagulation), then at 15 rpm for 15 minutes (flocculation). Discontinue stirring and allow the samples to settle for at least 8 minutes (settling). Measure the final turbidity[1] of the settled samples.

2. Determine the optimum pH range:

Every coagulant has an optimum pH range within which the required dose is minimal. For alum it is between 5.0 and 7.5; since $Al(OH)_3$ is insoluble in this pH range and will form a precipitate or floc. For $FeCl_3$ it is between 4.5 and 8.0.

Fill six one liter beakers with 1000 mL each of synthetic wastewater. Add 9 mL alum into each of the first three beakers and 9 mL ferric chloride into each of the remaining three beakers. Add different amounts of 1M HCl or 1M NaOH (as needed) into each beaker to adjust pH to values of around 2, 6 and 12. Stir at 80 rpm for 3 minutes (rapid mixing or coagulation), then at 15 rpm for 15 minutes (flocculation). Discontinue stirring and allow the samples to settle for at least 8 minutes (settling). Measure the final turbidity[2] of the settled samples.

Results: Details on required results and measurements for scaling up this test to a plant size coagulation flocculation system will be discussed during the experiment.

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[1] Turbidity is a measure of the extent to which light is either scattered or absorbed by suspended material in water. We will measure turbidity by light scattering, the units of which are *nephelometric turbidity units* (NTU).

EXPERIMENT 4b ZETA POTENTIAL OF COLLOIDS

Background: Colloidal dispersions are of particular interest to paint and plastic manufacturers, chemical dispersant producers, as well as to environmental engineers. Colloids are extremely small particles (0.001 to 0.000001 mm) that are non-settleable when dispersed in a liquid. From an environmental engineering perspective, many water treatment processes involve gravitational settling as the physical method for removing solids from wastewater or potable water, and due to their small size, gravity has little effect on colloids. Since colloidal size particles dispersed in water make up a considerable portion of the suspended materials in ground water, surface water or wastewater, the study of their properties is essential. Their small size gives them an overall large surface area per unit weight, allowing them to sorb relatively large quantities of toxic materials, organic compounds or waterborne pathogens. In general, suspended colloidal particles with opposite charges will tend to agglomerate into larger particles due to electrostatic attraction (opposite charges attract). Also, neutral suspended particles will tend to agglomerate into larger particles due to van der Waal's forces attractive forces. This agglomeration into larger and larger particles leads to settling of colloidal-size materials. However, when colloids have the same charge they repel each other due to electrostatic repulsion (like charges repel) and a stable dispersed suspension results. Most naturally occurring colloids such as clays and humic substances have a negative charge on their surface and form stable colloidal dispersions. When in water these negatively charged colloids attract positively charged naturally occurring counter ions (cations) to their surfaces resulting in high density fixed cationic layer close to the particle surface and an outer diffuse cationic layer. The zeta potential is a measure of the charge on the colloidal particle operating through a distance, its magnitude is given in millivolts (see Eq.1 and Figure 4b.1). The greater the magnitude of the zeta potential the more stable the dispersion. For colloidal suspensions of particles with negative surface charges zeta potentials between (-50) and (-125) mV form very stable dispersions, those between (-20) and (-40) mV are moderately stable; and those between 0 and (-10) mV are very unstable. In order to destabilize colloidal dispersions environmental engineers reduce the magnitude of the zeta potential by chemical coagulation causing agglomeration. When the effective surface charge or magnitude of the zeta potential is decreased, the particles can approach each other to a point where van der Waals attractive forces are operative (see Figure 4b.2).

Measuring zeta potential. Zeta potentials are measured using a technique called microelectrophoresis. Particles in suspension are placed in an electrophoretic cell and an electric potential is applied across the cell using electrodes. As the charged particles migrate under the influence of the electric field they are viewed by a stereomicroscope to which a video camera is mounted. Their velocity is determined against a tracking line grid which is viewed on a monitor. The particle velocity is related to the magnitude of the zeta potential (their direction is determined by whether the surface charge is positive or negative). The zeta potential is automatically calculated based on the applied voltage, particle velocity, and the viscosity of the liquid and the dielectric constant of the liquid. For environmental engineering considerations the liquid is water.

Equipment: Zeta Meter System 3.0 from Zeta-Meter Inc.

Procedure: The laboratory instructor will first demonstrate the use of the zeta potential meter. Students will measure the zeta potential to see what value they obtain of their samples. An accurate determination as you will see depends upon taking a large number of measurements.

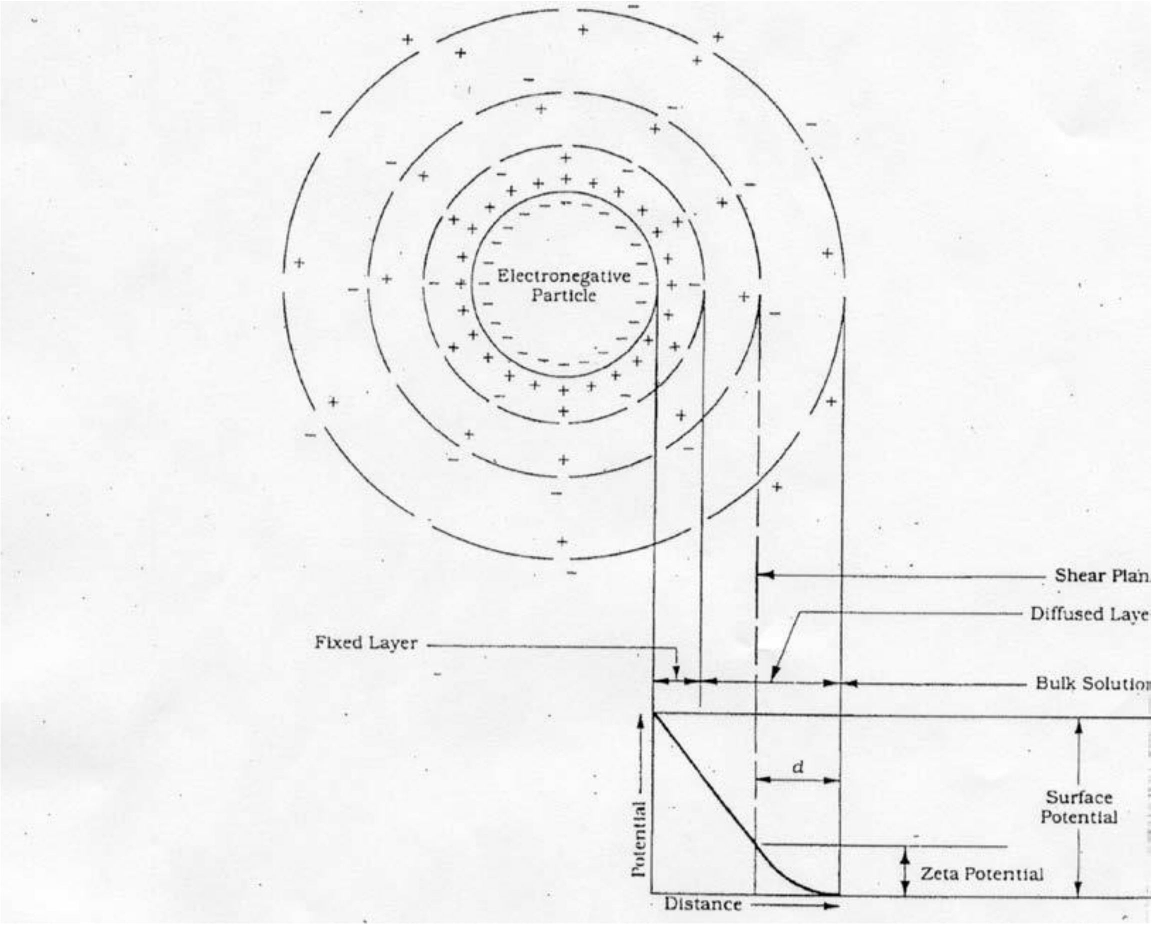

Figure 4b.1. Schematic of a negatively charged colloid particle with its electrostatic field.

The zeta potential is the electrostatic potential at the shear plane. The shear plane can be visualized as a surface where positively charged ions bound in the diffuse layer, closer to the particle surface, move relative to the other ions in the diffuse layer, that are closer to the bulk water, as the particle 'rolls' in the water. Positive ions closer to the negatively charged particle will experience a greater electrostatic attraction and move more in concert with the particle than those further away. The result is described as a shearing of bound ions in the diffuse layer. The zeta potential is the electrostatic potential that is maximum at the shear plan and falls off to zero at the bulk water where positive and negative ions are equally distributed.

$$\zeta=4\pi qd/D \qquad \text{(Equation 1)}$$

where
ζ = zeta potential;
q = charge per unit area;
d = thickness of the layer surrounding the shear surface through which the charge is *effective,* as shown in Figure 4b.1;
D = dielectric constant of the liquid.

Equation 1. The zeta potential measures the charge of the colloid particle, and it is dependent on the distance through which the charge is effective. It follows that the greater the magnitude (the value is –mV for negatively charged colloids and +mV for positively charged colloids) of the zeta potential, the greater are the electrostatic repulsive forces developed and the greater the stability of the colloidal suspension.

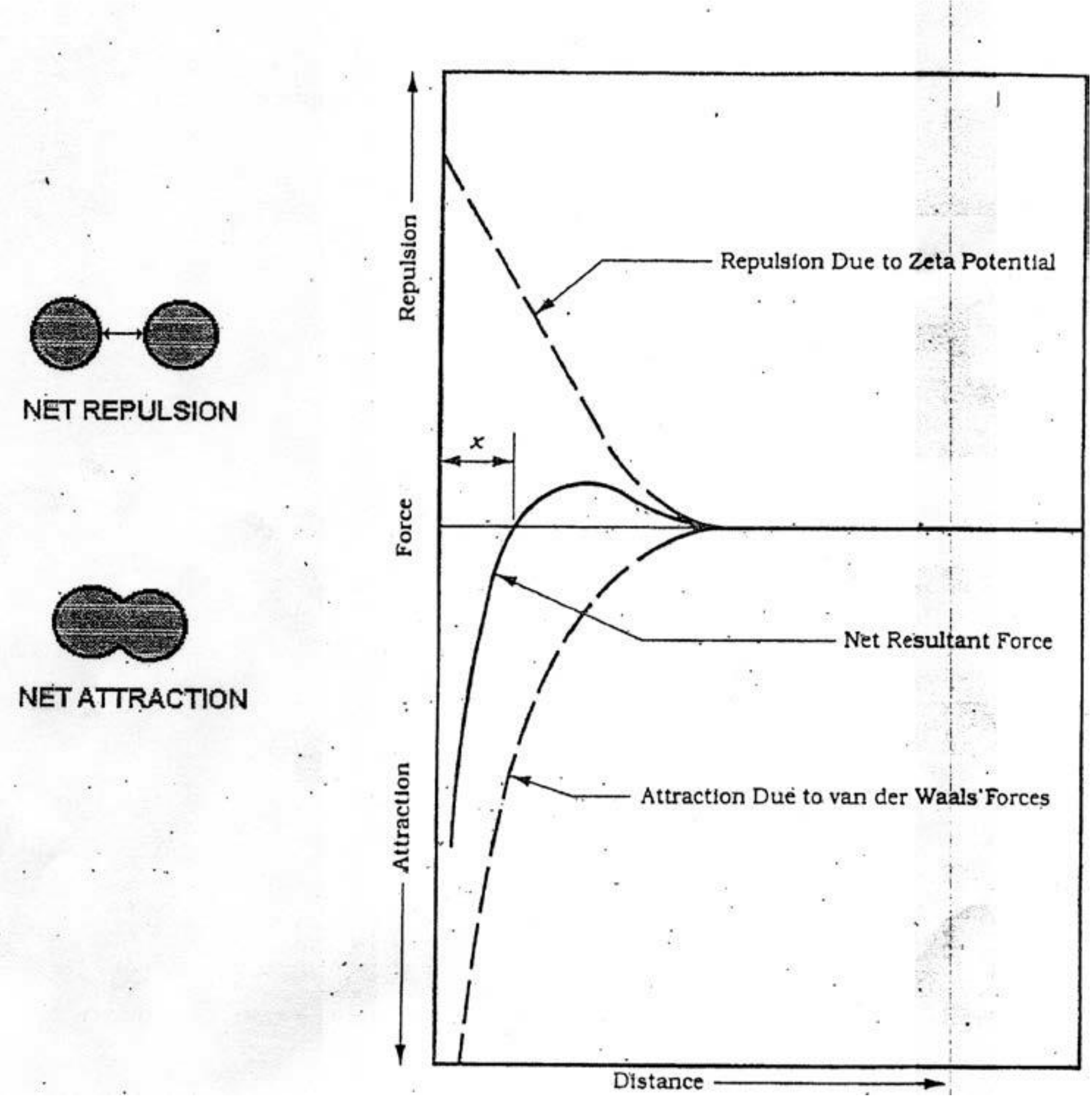

Figure 4b.2 Colloidal interparticles forces vs distance. This figure illustrates the forces acting on two suspended, charged colloidal particles. At greater inter-particle distances the repulsive electrostatic force due to the zeta potential dominates and the net force favors repulsion. At smaller inter-particle distances the attractive van der Waal's dominates and the net force favors particle adherence. Coagulation practice is based on reducing zeta potentials on stable colloidal, dispersions to enhance agglomeration of the smaller particles into larger settleable particles.

EXPERIMENT 5a SPECIFIC OXYGEN CONSUMPTION RATE FOR ACTIVATED SLUDGE

Background: The activated sludge process is a continuous flow, aerobic biological wastewater treatment process for the removal of BOD from domestic and biodegradable industrial wastewater. “Sludge” refers to the microorganisms’ biomass and “activated” refers to the continuous aeration of the wastewater/biomass mixture which is usually referred to as the “mixed liquor”. The biomass is maintained at a relatively constant and homogenous suspension by maintaining sludge levels and mixing (the aeration system accomplishes the mixing). As wastewater enters the aeration basin the microorganisms oxidize soluble and colloidal organic material, in the presence of oxygen, to carbon dioxide and water. Typical detention times are 4-8h. Some of the organic material is recycled into new cells, resulting in an increase in biomass, and the rest of the organic material is used to support existing cell growth and function. The wastewater then flows to a secondary clarifier where biomass or sludge is settled to produce a high quality effluent. Sludge can be recycled back to the aeration basin or wasted to maintain constant levels in the aeration basin (see Figure 1). The efficiency of BOD removal is about 80- 85%. One of the most critical design and operating considerations is maintaining sufficient dissolved oxygen (DO) to maximize BOD removal. Whether an air diffusion or mechanical turbine diffusion system is used, the oxygen consumption rate-for the mixed liquor must be evaluated to design and maintain activated sludge unit operations.

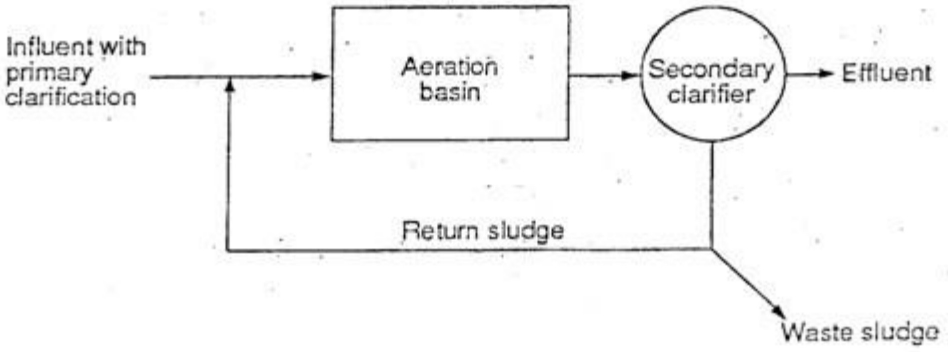

Figure 5.0 Schematic of a continuous flow activated sludge unit operation

In this experiment we will estimate the mixed liquor volatile suspended solids (MLVSS) of an activated sludge (which estimates the suspended biomass in the mixed liquor) by a standard gravimetric method. We will also determine the oxygen consumption rate (OCR) for the mixed liquor and then determine the specific oxygen consumption rate (SOCR), which is simply the OCR divided by the amount of biomass, or the MLVSS. Note: OCR is also called oxygen uptake rate (OUR).

Objective: To determine the oxygen consumption rate for an activated sludge.

Equipment: DO meter with self-stirring DO/BOD probe, gravimetric oven, gravimetric furnace, stopwatch, analytical balance, BOD bottles, gooch crucible with glass micro-fiber filter, desiccator, and vacuum filtration system.

Sludge: Activated sludge was prepared from a commercial mix of naturally occurring aerobic bacteria which are representative of the bacterial population in activated sludge unit operations. The biomass was acclimated on a synthetic wastewater prepared with sucrose (table sugar) as the carbon substrate.

Procedure: MLVSS determination. Filter 5.0 mL (0.005 liters) of a mixed sludge sample through a predried glass micro-fiber filter (fitting in a gooch crucible or an aluminum dish) using vacuum filtration. Place the crucible/dish with filter in a gravimetric oven for 45 minutes at 105°C. Cool the crucible/dish in a desiccator and weigh to 0.0001 g. Then place the crucible/dish in a furnace and ignite for 15 minutes at 550°C. Cool the crucible/dish in a desiccator and weigh. The filter traps suspended solids (SS), which is mostly biomass, and the oven dries the biomass. The furnace burns off or volatizes all the organic matter in the SS. The difference in weight between the dry and ignited SS measures the suspended organic matter content which is a more accurate estimate of the biomass than the dry weight.

OCR determination. Fill a BOD bottle with activated sludge and place a DO probe in the sludge and mix moderately. Then record DO values every 30 seconds until the DO reaches about 3 mg/L.

Results:

$$\mathbf{MLVSS\ (g/L)} = \frac{\boldsymbol{weight\ of\ crucible/dish\ before\ igniton\ (g) - weight\ of\ crucible/dish\ after\ ignition\ (g)}}{\boldsymbol{sample\ volume\ (L)}}$$

OCR (mg O_2/ L / min): Plot DO (mg O_2/L) Vs time and determine the slope. The negative slope indicates DO consumption. This is the OCR. Use the absolute value to calculate the SOCR.

SOCR (mg O_2 consumed/ h/ g MLVSS):

$$\frac{\mathrm{OCR\ (mg\ O2/L\ /min)}}{\mathrm{MLVSS\ (g/L)}} \times \frac{\mathrm{60\ min}}{\mathrm{h}}$$

The SOCR, or specific oxygen consumption rate, is a more useful value than the OCR for operating and maintaining activated sludge units in water treatment facilities, since it takes into account the rate of oxygen consumption per unit weight of biomass in the reactor.

EXPERIMENT 5b BIOCHEMICAL OXYGEN DEMAND (BOD)

Background: The biochemical oxygen demand, or BOD, is an important water quality parameter for environmental engineers. When biodegradable organic matter enters a water body, microorganisms (bacteria, fungi, yeast, and actinomycetes) can oxidize the organic matter, utilizing the dissolved oxygen (DO). This process is the same for all life forms that utilize molecular oxygen to oxidize food, and is termed *respiration*. The bio-oxidation of glucose for example can be illustrated as:

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{MICROORGANISMS} 6CO_2 + 6H_2O + ENERGY$$

It can be calculated from the above reaction that one mole of glucose (180 g/mole) will consume six moles of oxygen (32 g/mole). Since the saturation level of oxygen is about 9 mg/L DO in water at 20°C, it would take a concentration of glucose as low as 8.4375 mg/L to completely remove the DO, if there were no aeration. Many municipal wastes have biodegradable organic equivalents that greatly exceed this level. If the rate of BOD removal is greater than the aeration rate, then the aquatic ecosystem in question is in serious danger. A DO level below 4 mg/ L is fatal to fish and many other aquatic species, and chronically lowered DO values will result in species succession and ecosystem changes: Thus, effluent discharges must be carefully monitored for BOD. In addition many treatment processes for wastewater and sludge involve the use of microorganisms in the presence of dissolved oxygen, to convert dissolved and colloidal organics into biomass which can subsequently be removed by sedimentation. Microorganisms will utilize the organic waste material as a food source, and in the presence of oxygen, respiration will occur, and organic matter such as carbohydrates and proteins, for example, will be oxidized to inorganic compounds such as CO_2, NO3(-), SO4(2-) and PO4(3-). In order to determine aeration rates (to facilitate biological wastewater and sludge treatment processes) some measurement of the capacity of a given sample to consume oxygen is required, such as the BOD test. This BOD assay has been traditionally standardized as a five day test. In this test wastewater (or an appropriate dilution) is placed in a BOD bottle, and the initial DO level is determined. The bottle is stoppered (to avoid aeration) and placed in the dark (to avoid algal growth) for five days at 20°C. At the end of the incubation period the DO is again measured to determine oxygen depletion rate or demand. Since the saturation for DO at 20°C is 9 mg/L, and at levels below 2 mg/L the rate of oxygen utilization drastically falls, the BOD test can only measure a maximum difference in initial and final DO of 7 m/L; or a BOD of 7 mg/L. Since municipal wastewaters have BOD values that average about 200 mg/L, and some wastewaters, especially those derived from the food industry can have BOD values as high as 100,000 mg/L, wastewater samples must be diluted to bring them within the range of this test. Table 1 below lists appropriate dilutions for potential BOD levels.

Table 5.0 Ranges of BOD values covered by various dilution (made to 300 mL)

Sample volume (mL)		Range of BOD
0.02		30,000-105,000
0.05		12,000-42,000
0.10		6,000-21,000
0.20		3,000-10,500
0.50		1,200-4,200
1.0		600-2,100
2.0	Untreated municipal wastewater	300-1,050
5.0		20-420
10.0		60-210
20.0	Treated municipal wastewater	30-105
50.0		12-42
100.0		6-21
300.0		0-7

Objective: To determine the BOD of a wastewater sample.

Equipment: Oxi700 BOD system, magnetic stirrer, incubator, BOD bottles, measuring cylinders and pipets.

Principle of method: Different from traditional method, this respirometric methods provide direct measurements of the oxygen consumed by microorganisms from an air or oxygen-enriched environment in a closed vessel under conditions of constant temperature and agitation. Carbon dioxide produced metabolically by the bacteria is chemically bound by the potassium hydroxide solution contained in the seal cup in the bottle. The result is a pressure drop in the system, which is directly proportional to the BOD value and is measured by the BOD sensor. The BOD level is then displayed directly in mg/l.

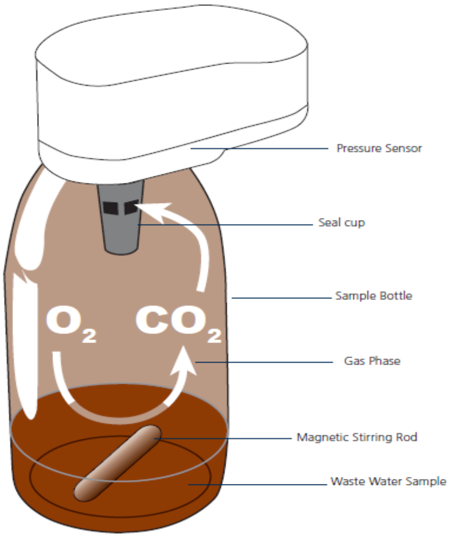

Figure 5.1 The principle of Oxi700 BOD system respirometric methods

The BOD values are stored in the sensor memory and can be viewed on the large-format display at any time without the need for time consuming conversion using factors. This means that test series that end on a weekend can be evaluated during the following week. The measurement period is user-selectable between 1 and 28 days.

Procedure: The BOD level of a sample depends on the quantity of organic matter present, which can vary considerably. The Orbeco-Hellige Oxi700 is calibrated for the various sample volumes and the corresponding measuring ranges listed in the table below.

Range BOD mg/L	Sample volume in mL
0-40	428
0-80	360
0-200	244
0-400	157
0-800	94
0-2000	56
0-4000	21.7

According to COD test result, estimated the BOD measurement range and select the volume for the sample using the above chart: Transfer the measured volume sample into BOD bottle. Insert a magnetic stirring rod. Place 3 drops of KOH solution into the seal gasket. Then insert the gasket in the neck of the bottle. Screw the BOD sensor to the sample bottle and place the bottle in the bottle rack.

Press “Start” key will now start the measurement for this bottle. The unit will display the BOD range and required sample volume. Use “+” or “-” to adjust. Then press “Enter”. The measurement is in room temperature.

Results: Obtained BOD results (mg O_2/L) in 5 days.

EXPERIMENT 5c   CHEMICAL OXYGEN DEMAND) (COD)

Background: Although the BOD test is considered the best estimate of oxygen- consuming capacity for wastewater, this test takes 5 days to perform. The chemical oxygen demand (COD) however is a relatively simple test which can usually be correlated with the BOD. This test measures the oxidizable material in a sample by reacting it with a strong chemical oxidant (such as chromate or permanganate ions). The amount of oxygen (derived from the chemical oxidant) that reacts with the organic matter in the sample is determined by monitoring the reduction of oxidant through a color change that is produced. The intensity of the color change is directly proportional to the degree of oxidation, and is monitored spectrophotometerically. The results are expressed in terms of an equivalent amount of oxygen per liter of sample. The COD has also become a commonly measured parameter for natural water bodies that are suspected of being polluted with organic wastes, and for daily operations in wastewater treatment plants. The method that is currently used in most wastewater treatment plants is the closed reflux colorimetric method. A wastewater sample is oxidized at 150 °C for two hours in a closed vial containing chemical oxidants. Color, or-absorption of light at 600 nm, is determined and compared to a standard chemical (potassium hydrogen phthalate or KHP) with known theoretical oxygen consumption.

Objective: To determine the COD of a wastewater sample by the closed reflux, colorimetric method.

Equipment: Programmable block heater and visible spectrophotometer equipped with cells to hold COD vials.

Reagents: Digestion solution (commercially available pre-measured solution containing a 5mL mixture of sulfuric acid, potassium dichromate, silver sulfate, and sulfuric acid in twist cap digestion vials), and potassium hydrogen phthalate standard or KHP *(*425 KHP mg/L distilled water, having a theoretical COD of 500 mg O_2/L).

Procedure: Add KHP standard solutions (made up to 2.5 mL with distilled water) to the COD vials containing 5 mL of reagent as listed in Table 5.2 below. Recap vials and mix contents by shaking. Heat vials at 150 ± 2°C for 2 hours and cool to room temperature. Zero the spectrophotometer with the standard blank (vial with no KHP) at 600 nm. Read the absorbance for the remaining standards. Use standard concentration vs absorbance to build calibration curve. Similarly prepare wastewater sample. If necessary, dilute with distilled water. For example, add 1.0 mL of wastewater to a COD vial containing 5 mL of reagents, plus 1.5 mL of distilled water, for a final adding sample volume of 2.5 mL.

Table 5.2 Preparation of KHP standards for COD determination

Volume KHP (ml)	Volume water (ml)	COD mg/l
0	2.5	0
0.5	2.0	100
1.0	1.5	200
1.5	1.0	300
2.0	0.5	400
2.5	0	500

Results: Plot Absorbance vs. COD (mg O_2/L) for the standards and draw the best fit straight line through the points, unless you are using a spectrophotometer that automatically generates a standard curve. Read the COD from the curve for the wastewater sample. If you added 1.0 mL of wastewater and diluted it to 2.5 mL with distilled water, we have a 1:2.5 dilution ratio. Thus the samples original COD will be 2.5× the interpolated value.

EXPERIMENT 6 CHLORINE AND CHLORINE DEMAND

BACKGROUND: Most water treatment plants are required to **disinfect** the water, a process used to kill harmful bacteria. The most frequently used method of disinfection is the addition of chlorine. Chlorine disinfectants provide a "residual" level of protection against waterborne pathogens. A chlorine residual is a low level of chlorine remaining in water after its initial application. It constitutes an important safeguard against the risk of subsequent microbial contamination after treatment – a unique and significant benefit for public health.

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + OCl^-$$

The amount of chlorine added to the water is known as the **chlorine dose**. This is a measured quantity chosen by the operator and introduced into the water using a chlorinator or hypochlorinator. When chlorine is added to water, some of the chlorine reacts first with organic materials and metals in the water and is not available for disinfection (this is called the *chlorine demand* of the water). The remaining chlorine concentration after the chlorine demand is accounted for is called *total chlorine residual*. Total chlorine is further divided into: 1) the amount of chlorine that has reacted with ammonia or other nitrogen-containing organic substances in the water is called *combined chlorine* and, 2) the *free chlorine*, which is the chlorine available to inactivate disease-causing organisms, and thus a measure to determine the portability of water.

(Chlorine demand) = (Chlorine dose) - (Total Chlorine residual)

(Total Chlorine residual) = (Free Chlorine) + (Combined Chlorine)

The graph below shows what happens when chlorine (either chlorine gas or a hypochlorite) is added to water. First (between points 1 and 2), the water reacts with reducing compounds in the water, such as hydrogen sulfide, Fe^{2+}. These compounds use up the chlorine, producing no chlorine residual.

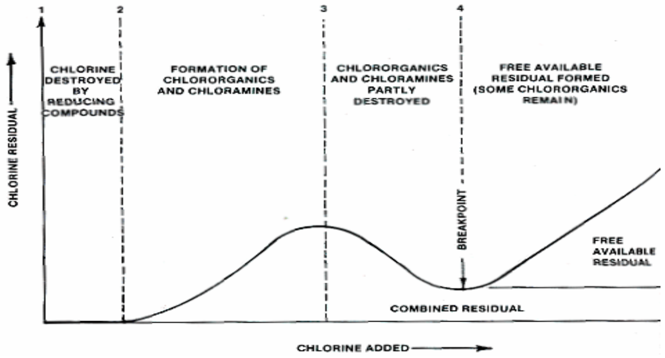

Figure 6.0 The breakpoint (B.P.) of chlorination curve

Next, between points 2 and 3, the chlorine reacts with organics and ammonia naturally found in the water. Some combined chlorine residual is formed - chloramines.

Monochloramine:
$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$
Dichloramine:
$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$
Trichloramine:
$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$

Note that if chloramines were to be used as the disinfecting agent, more ammonia would be added to the water to react with the chlorine. The process would be stopped at point 3. Using chloramine as the disinfecting agent results in little trihalomethane (THM) production but causes taste and odor problems since chloramines typically give a "swimming pool" odor to water.

In contrast, if hypochlorous acid is to be used as the chlorine residual, then chlorine *will* be added past point 3. Between points 3 and 4, the chlorine will break down most of the chloramines in the water, actually lowering the chlorine residual.

Finally, the water reaches the breakpoint, shown at point 4. The **breakpoint** is the point at which the chlorine demand has been totally satisfied - the chlorine has reacted with all reducing agents, organics, and ammonia in the water. When more chlorine is added past the breakpoint, the chlorine reacts with water and forms hypochlorous acid in direct proportion to the amount of chlorine added. This process, known as **breakpoint chlorination**, is the most common form of chlorination, in which enough chlorine is added to the water to bring it past the breakpoint and to create some free chlorine residual. B.P. curve-shape is determined by contact time, temp, chlorine and ammonia concentration, pH, and water quality.

OBJECTIVE: to acquaint you with disinfection of water supplies and to demonstrate techniques for the determination of chlorine residuals; to illustrate the concepts of free and combined chlorine residuals, chlorine demand and break-point chlorination.

EQUIPMENT: Burette with self-zeroing dispenser, sirrer and magnetic bar, 1000 ml beakers, 250 ml beakers, 100 ml graduated cylinder, 250 ml flasks.

REAGENT: bleach or hypochlorite solution, 0.025 N sodium thiosulphate, chlorine free water, (concentrated) glacial acetic acid, potassium iodide (KI) crystals, starch indicator, phosphate buffer solution, N,N-diethyl-p-phenylenediamine (DPD) indicator solution, standard ferrous ammonium sulphate (FAS) solution.

PROCEDURE:

I. PREPARATION OF STOCK CHLORINE SOLUTION

(Iodometric method - total chlorine residual)

1. Prepare a stock solution of strong chlorine water by adding 5 mls of bleach solution (sodium hypochlorite) to about 200 mls of water in a 250 ml volumetric flask. Make up to the 250 ml and invert flask several times to mix.
2. Rinse a burette and fill it with this stock chlorine solution.
3. Take a 250 ml Erlenmeyer flask and add about 1 gram of potassium iodide, about 50 ml of chlorine-free water (distilled water will do), about 5 ml of glacial acetic acid, and exactly 10 ml of 0.025 N sodium thiosulphate solution (use a volumetric pipette).
4. Mix on a stir plate with stir bar.
5. Add 1 ml of starch solution, mix again.
6. Titrate rapidly with the stock chlorine solution until the appearance of a constant purplish-blue colour.
7. From the amount of chlorine solution used, calculate the chlorine concentration in the stock solution.

Cl concentration of stock solution, mg/L Cl as Cl_2 = $\frac{A \times N \times 35{,}450}{B}$

Where:
A: Volume of sodium thiosulphate used, mL
N: Normality of sodium thiosulphate used, N
B: Volume of stock chlorine solution; mL

IIa. Breakpoint Chlorination using Free and Combined Chlorine Residuals Values

We will construct breakpoint chlorination curves for 15 minute and sixty minute contact times.

1. Set up a numbered row of six 600 ml beakers each containing 500 mls of the sample provided (it has been prepared for you, using Ammonium chloride and Acetic acid). See note IIb.1 before proceeding.

2. Chlorine dosing procedure: At time (T) = 0 minutes add the calculated dosage to beaker #1; at T=5 min. add the next dosage to beaker #2; at T=10 min. dose beaker #3; at T=15 min dose beaker #4, and so on. Note that immediately after applying the dose to Beaker # 4 you will have to start titrating a sample of Beaker #1. Coordinate yourselves well for this!

3. At T=15 minutes you will start titrating to determine the free and combined chlorine in sample from beaker #1; at T=20 min titrate beaker #2; etc. At T=60 minutes start titrating at beaker #1 again; T= 65 min beaker #2; and so on.

IIb. Determination of Free and Combined Chlorine by the DPD Method

1. Place 5 ml of phosphate buffer solution and 3 ml of DPD solution in each of six 250 ml beaker and swirl to mix. Prepare these six beakers before starting the dosing process.

2. Add 100 ml of sample or diluted* sample using a 100 ml graduated cylinder and mix again. (*NOTE: If total chlorine is likely to exceed 5 mg/L use a smaller sample and dilute to a total volume of 100 mls with chlorine-free water. It is likely that the top one or two doses could require dilution.). Mix usual volumes of buffer reagent and DPD indicator solution with distilled water before adding sufficient sample to bring total volume to 110ml or the test will not work. (i.e. 5 ml + 5 ml + 50 ml chlorine-free water + 50 mls of sample will give a 1:1 dilution; 5 ml + 5 ml + 75 ml water + 25 ml of sample will give a 1:4 dilution)

    a. Free chlorine: titrate rapidly with standard FAS (Ferrous ammonium sulfate) titrant until the red colour is discharged. Record the burette reading (mls) = Reading A. Note: if no initial red colour do not add FAS, volume =0.
    b. Monochloramine: Add two drops of KI solution (to the same sample) and mix. Continue titrating until red colour (if any) is discharged once again (Reading B). Go to c.
    c. Dichloramine: To the same sample add about 1 g KI and mix to dissolve. Let stir for 2 min (or until completely dissolved) and then continue titrating until red colour (if any) is discharged (Reading C). For dichloramine concentrations greater than 1 mg/L, let stand 2 min more if colour drifts back (indicating incomplete reaction) continue titrating to colourless.

Results: Total chlorine (Free plus Combined) = Reading C
Free residual chlorine = Reading A
Combined residual chlorine (dichloramine plus monochloramine) = Reading C - A
Monochloramine= B-A
Dichloramine= C-B

REFERENCE: Standard Methods for the Examination of Water and Wastewater Methods: 2350 B, C; 4500-Cl F.