Indian Institute of Technology Delhi (India)
Department of Civil Engineering
CVL212 Environmental Engineering (3-0-2)/Second Semester 2023-24
Lecture: Monday and Thursday (9:30am-11:00am; LH316)
Laboratory: (Group-wise) (Block 4, Room 313: Environmental Engineering Lab)
Course Email: 2302-cvl212@courses.iitd.ac.in

Course Outline

Course Coordinator: Dr. Arun Kumar (Block 4, Room 215;arunku@civil.iitd.ac.in)
Course Overview (Pre-requisites: CVL100): Water and wastewater treatment overview; Unit processes: systems of water purification, processes (sedimentation, coagulation-flocculation, softening, disinfection, adsorption, ion exchange, filtration) and kinetics in unit operation of water purification-theory and design aspects; distribution of water layout systems: design aspects; Wastewater engineering: systems of sanitation, wastewater collection systems design and flows, Characteristics and microbiology of wastewater, BOD kinetics; Unit processes for wastewater treatment (screening, sedimentation; biological aerobic and anaerobic process)-theory and design aspects; Biological processes (Nutrient and phosphorous removal); advanced wastewater treatment-theory and design aspects; Air pollution (health effects, regulatory standards, dispersion; stacks,

Course Policy
Distribution of Marks (total =100):
1. Lecture portion :60%*(75% Institute rule applies)*

Minor Examinations	*35 % (1 minor exam)*
Attendance	*(75% Institute rule applies; TIMBLE only)*
Major Examination	*50%*
Lecture quiz	*15%*

2. Laboratory portion :40% *(75% Institute rule applies)*

Lab Quiz	*30%*
Lab Report	*60% **(No late submission)***
Lab attendance	*10%*

Homework/Classwork: Read the assigned sections/problems before the class and always come prepared for doing class problems. Bring calculator daily in the class.
Attendance Rule: If a student's attendance is **less than 75%**, the student may be awarded **one grade less than the actual grade** that he (she) has earned as per the institute policy.
Students needing special accommodations for exams on medical grounds (with IITD certificate) must submit applications in accordance with institute's policy **within one week of absence.** Students are responsible for checking IIT Delhi course email list daily for getting course information. **All medical reports should be submitted within one week of absence. Outside medical certificate need to be verified at IITD hospital before submission.**

Study Materials:
Peavy, HS, Rowe D.R., Tchobanoglous G., 2000, "Environmental Engineering", McGraw Hill Int.
(note: Some additional power point slides and handouts will be available on the website. Class is the primary place for delivery of materials. ***Check Teaching Activity Section of http://web.iitd.ac.in/~arunku/ daily for course information)***

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2)

Laboratory Manual

Laboratory Guidelines

1. The class will be divided into groups of 4-5 students that will be working together in the lab and in writing the laboratory reports. Each group will submit only one lab report.
2. Always bring lab manual, calculator and lab note book.
3. **All lab data will be entered on a sheet of a paper and checked with a Teaching Assistant before attaching it with the lab report. The lab report will be submitted in laboratory itself.**
4. All reports should **strictly follow** this outline (Name/Entry no./Group no.)**:**
   - Title: Include course title, experiment title, date of experiment, date of report submission, and names of group members
   - Summary: A one paragraph statement covering the important objectives, background materials, procedures, results, and conclusions. It is considered to be the most influential parts of reports and it need to be written clearly and concisely.
   - Objectives: Make a clear statement of experimental objectives**.**
   - Background: In one paragraph explain the importance of the experiment in environmental engineering
   - Methods: Briefly explain the methodology used.
   - Results and Discussion: This section should include a presentation of reduced data (i.e. quantities calculated from raw data) in tabular or graphical format. Refer Tables and Graphs in text and include a title (Table 1, Table 2 or so; Figure 1, Figure 2, or so). Graph axes should **be labeled always with units.**
   - Conclusions and Recommendations: Briefly list the results and recommendations for improving the experiments**.**
   - References: Any citations should be documented here**.**
   - Appendices: Raw data and statistical methods should be included here**.**

Grading: All lab reports will be **due on the day of lab and graded in 50 points.**

Attendance: Attendance is **compulsory in all labs**. IIT Delhi 75% rule applies to laboratory attendance also. Only in the case of emergency, the make-up lab will be scheduled well in advance with the consent of the faculty. **No lab will be re-scheduled for early train reservations.**

Lab Safety:

Students **without shoes will not be allowed in the lab**. **Bring lab coat and a permanent marker to lab.** Always wear full sleeves clothes. Wear safety glasses and gloves when recommended. Leave bags and coats in designated areas. Bring only the essentials to the lab bench. No eating, drinking, playing, or applying cosmetics (including hand lotion, etc.). Never use broken or chipped glassware. Place broken glassware in specially marked containers. Mouth pipetting is forbidden. Hands should be washed after contact with hazardous materials and before leaving the lab.

Lab Etiquette:

Return all chemicals and supplies to the proper location after use. It is necessary to take chemicals from reagent bottles, pour out slightly more than the amount of chemical needed into a clean beaker. Never pour a chemical back into a reagent bottle. Clean up for the next person. At the conclusion of each work period, all used **glassware must be cleaned and set to drain**. Remove label tape, scrub inside of glassware with water and laboratory detergent, rinse with tap water, rinse with distilled water, and place cleaned glassware on a rack to dry. No experiment is complete until the laboratory is cleaned.

Procedure for cleaning of glassware in laboratory

Glassware Cleaners

1. Clean the equipment thoroughly with soap and water for basic cleaning. You may need to use a wire brush to remove some residue. Detergent using bottle brushes and scouring pads can be used as needed.

2. After cleaning, rinse the glassware with running tap water. When test tubes, graduates, flasks and similar containers are rinsed with tap water, allow the water to run into and over them for a short time, then partly fill each piece with water.

3. Thoroughly shake and empty at least six times and ensure that all soap residue is removed.

Note:

- Do not use cleaning brushes that are so worn that the spine hits the glass. Serious scratches may result. Scratched glass is more prone to break during experiments. Any mark in the uniform surface of glassware is a potential breaking point, especially when the piece is heated. Do not allow acid to come into contact with a piece of glassware before the detergent (or soap) is thoroughly removed. If this happens, a film of grease may be formed.

- To prevent breakage when rinsing or washing pipets, cylinders or burets, be careful not to let tips hit the sink or the water tap.

Sterilizing Contaminated Glassware

- Autoclave glassware or sterilize it in large steam ovens or similar apparatus. If viruses or spore-bearing bacteria are present, autoclaving is absolutely necessary.

Handling and Storing

- Protect clean glassware from dust. This is done best by plugging with cotton, corking, taping a heavy piece of paper over the mouth or placing the glassware in a dust-free cabinet.

- Store glassware in specially designed racks. Avoid breakage by keeping pieces separated.

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory 1.
Experiment 1A: pH

Objective: Measure sample pH

Background: The pH is one of the basic water and wastewater characteristics. It expresses the intensity of acid or alkaline conditions by indicating the hydrogen ion activity. Some of the processes in water quality engineering that require pH monitoring and control are the following: disinfection, coagulation, softening, biological treatment etc. Natural waters usually have pH values close to neutral. Figure 1 shows pH values of commonly used household products.

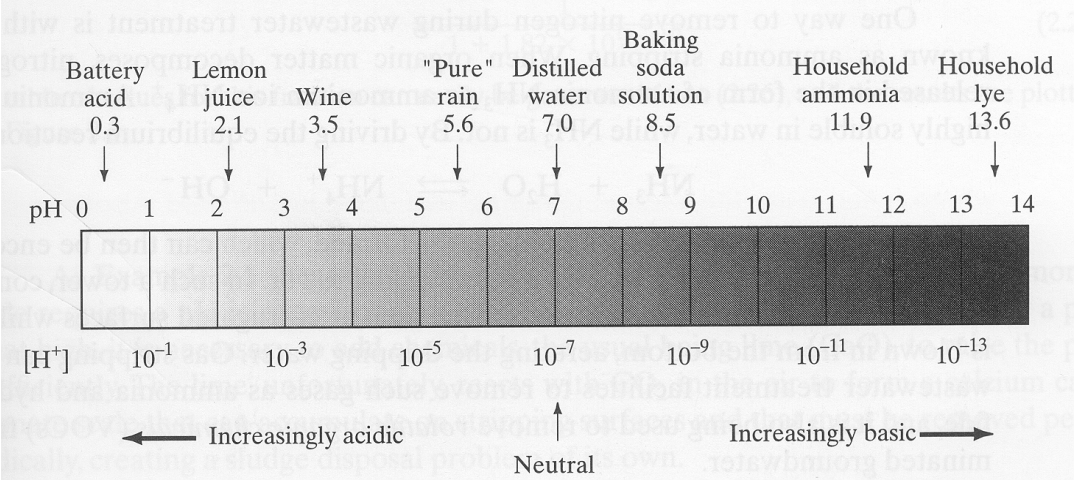

Figure 1. pH Scale

Procedure

Samples will be provided. Calibrate pH and record pH values of both samples

Sample Questions to Answer:

1. Why pH is an important parameter in environmental engineering? Did you find any different in pH of two samples? Why or why not?

Reference Material:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater

Experiment 1B: Solids Analysis

(2540 D. Total Suspended Solids Dried at 103-105ºC; 2540 E. Fixed and Volatile Solids Ignited at 550ºC)

Objective:

To illustrate the various operations involved in gravimetric analysis and to determine the various categories of solids that are commonly defined in water and wastewater.

Background:

Solids analysis provides one of the fundamental measurements used for control of the activated sludge process and for the regulation of wastewater discharges. *Gravimetric analysis* is based on the determination of constituents or categories of materials by measurement of their weight. The experiment illustrates the principles of weighing and demonstrates separation and categorization techniques used to define the various types of solids in waters and wastewaters. These techniques involve three analytic operations in addition to weighing. These are: filtration, evaporation, and combustion. *Filtration* is used to separate suspended or particulate (non-filterable) fraction from dissolved or soluble (filterable) fractions. *Evaporation* separates water from material dissolved or suspended in it. *Combustion* differentiates between organic and inorganic matter. Organic matter will be destroyed completely by burning at 550ºC for 30 min.

Procedure:

Samples: (1) A turbid water

1. Weigh filters (mass=B g). Filter samples (50 ml).
2. Run each sample in duplicates. You will have a total of 4 samples.
3. Oven dry at 103ºC for 30 min (please note that standard methods recommend 1 hour). At this stage all water will be evaporated and only suspended solids will be retained on filter. Weigh filters now (mass =A g).
4. **Calculate concentration of total suspended solids**

   mg total suspended solids =1000*(A-B)/(sample volume in mL) (1)
5. Weight crucibles (mass=C) and then weight crucible and filter (total mass=E).
6. Put crucibles with filter paper in muffle furnace and Ignite at 550ºC for 15 min. At this stage all volatile components of solids will be volatilized and only fixed inert solid materials will be left in crucible. Weigh crucible after proper cooling (mass=D g).
7. **Calculate concentration of volatile suspended solids (F) :**

   mg volatile suspended solids/L =1000*(E-D)/(sample volume in mL) (2)
8. **Calculate concentration of fixed suspended solids (G) :**

   mg volatile suspended solids/L =1000*(D-C)/(sample volume in mL)

Sample Questions to Answer:

1. Why solid determination is important?
2. What do you expect about volatile and fixed suspended solids in drinking water and in raw wastewater? Discuss using their solid characteristics.

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (2540 D. Total Suspended Solids Dried at 103-105ºC; 2540 E. Fixed and Volatile Solids Ignited at 550ºC)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 2A: Aciditiy

(Methods: 4500 B. Electrometric Method; 2320 B. Titration Method)

Objective: Measure mineral and phenolphthalein acidity

Background:

Acids contribute to corrosiveness and influence chemical reaction rates, chemical speciation and biological processes. Acidity of water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end point pH used in the determination. When the chemical composition of the sample is known study mineral acids, weak acids such as carbonic and acetic and hydrolyzing salts such as iron or aluminum sulfate may contribute to the measured acidity according to the method of determination.

Mineral acidity: It is measured by titration to a pH of about 3.5, the methyl orange end point (also known as methyl orange acidity). **Total acidity:** Titration of a sample to the phenolphthalein end point of pH 8.3 measures mineral acidity plus acidity due to weak acids, thus this is called as total acidity (or phenolphthalein acidity). In water analysis, this test does not bear significant importance because methyl orange acidity invariably remains absent in the raw water and even phenolphthalein acidity (that too principally due to the excessive-prevalence of dissolved carbon dioxide and carbonic acids) normally does not exist to a significant extent in the raw water.

Importance: As for as water analysis is concerned, acidity test does not bear significant importance because methyl orange acidity invariably remains absent in the raw water and even phenolphthalein acidity (that too principally due to the excessive-prevalence of dissolved carbon dioxide and carbonic acids) normally does not exist to a significant extent in the raw water.

Procedure:

pH meter; Reagents: Sodium hydroxide titrant (0.02 N); Phenolphthalein Indicator; Methyl Orange Indicator

Steps:

1. Take 50 ml sample in a conical flask and add 2-3 drops of methyl orange indicator solution.
2. Fill the burette with 0.02 N NaOH solution and titrate till the colour of solution just changes to faint **orange** colour, indicating the end point. Record the volume of titrant consumed as V_1 in ml. Calculate the methyl orange acidity using Eq (1a):

Methyl orange acidity (or Mineral Acidity) = (V_1×1000)/(Sample volume) **(1a)**

When the 0.02 N NaOH solution, used in titration is not standardized, mineral acidity is calculated using following Eq (1b):

Methyl orange acidity= (V1×N×50×1000)/ (Sample vol.) **(1b)**

3. For phenolphthalein acidity test, add 2-3 drops of phenolphthalein indicator solution to water sample from step 2 and continue the titration till the faint **pink** colour develops in the solution (i.e., the end point of titration). Record the volume of titration consumed as V_2 (mL) and calculate total acidity or phenolphthalein acidity using Eq.(2):

Total acidity (or Phenolphthalein Acidity)= (V_2×N×50×1000)/ (Sample vol.) **(2)**

Sample Questions to Answer:

A water sample has a methyl orange acidity of 60 mg/L. Calculate the quantity of lime in mg/L of $Ca(OH)_2$ required to raise the pH to 3.7?

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Methods: 4500 B. Electrometric Method; 2320 B. Titration Method)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

Experiment 2B: Alkalinity

(Methods: 4500 B. Electrometric Method; 2320 B. Titration Method)

Objective:

Using dye indicators measure phenolphthalein alkalinity and total alkalinity. Calculate hydroxide, carbonate and bicarbonate alkalinity.

Background:

The alkalinity of the water is a measure of its capacity to neutralize acids. The alkalinity of natural waters is due primarily to the salts of week acids. Bicarbonates represent the major form of alkalinity. Alkalinity can be expressed as follows:

$$\textbf{Alkalinity (mol/L)} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (1)$$

Figure 1 presents the carbonate speciation diagram at different pH values. Waters rich in bicarbonates (HCO_3^-) have high acid neutralizing capacity (high alkalinity).

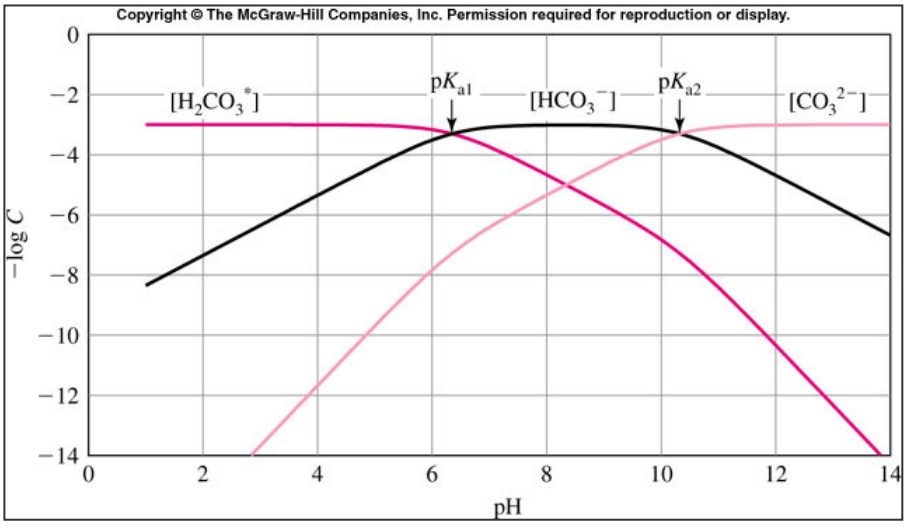

Figure 1. Carbonate Species

Alkalinity is measured by titrating a sample with acid. A titration curve of a bicarbonate containing water is presented in Figure 2.

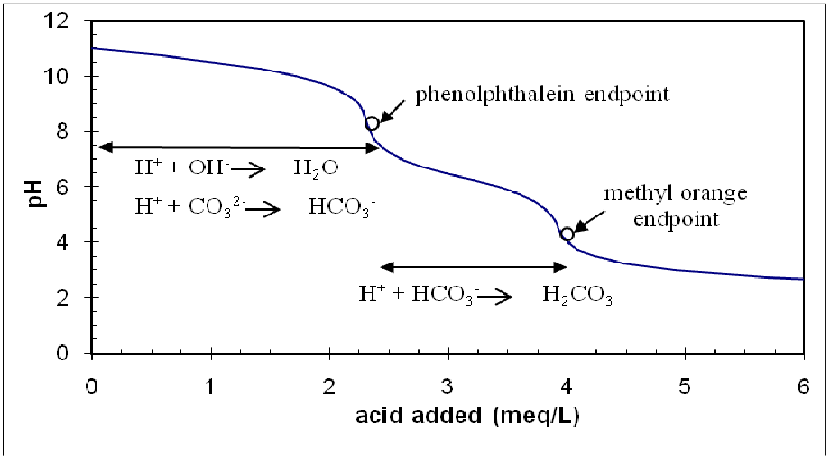

Figure 2. Alkalinity Titration Curve

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. As alkalinity of many surface waters constitute of carbonates, bicarbonate and hydroxide contents, it is assumed to be an indicator of these constituents as well. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than or only slightly greater than that of the water supply.

Procedure:

pH meter; Reagents for alkalinity (H_2SO_4 (0.02N); Methyl Orange Indicator; Phenolphthalein Indicator)

1. Collect 50 mL water sample, add 3 drops of phenolphthalein indicator, titrate the 50 mL sample with 0.02N sulfuric acid to pH 8.3 and estimate phenolphthalein alkalinity (Eq. 2a) (phenolphthalein indicator will change color, from pink to clear, at pH 8.3).

   Phenolphthalein Alkalinity (in mg/L as $CaCO_3$) = (A1×N ×50,000) / V (2a)

   Where: A1 = volume of sulfuric acid used in mL; N = normality of acid used to titrate; V= volume of sample used in mL

2. Use the same sample. Add 3 drops of bromcresol green indicator. Titrate the 50 mL sample with 0.02N sulfuric acid to pH 4.5 and estimate total alkalinity (bromcresol green indicator will change color, from blue to yellow, at pH 4.5). Amount of acid used at this moment starting from step1 (i.e., A2) is used to react with the hydroxide, carbonate, and bicarbonate and it constitutes of total alkalinity (Eq. 2b):

   Total Alkalinity (in mg/L as $CaCO_3$) = (A×N ×50,000) / V (2b)

   Where: A2 = volume of acid used in mL starting from step 1 (i.e., A2>A1); All other parameters are defined in Eq. 2a.

(Note: If after adding phenolphthalein indicator no colour develops, it means no phenolphthalein alkalinity and it can be reported as "Phenolphthalein alkalinity absent".)

Calculation from Alkalinity and pH measurements:

Hydroxide alk. (mg/L as $CaCO_3$)= $50{,}000 \times 10^{[pH-pK_w]}$; pK_w= 15 at 24°C (3a)

Carbonate alk. (mg/L as $CaCO_3$)= 2 × [Phenolphthalein alk.-hydroxide alk.] (3b)

Bicarbonate alk. (mg/L as $CaCO_3$)= Total alk.-[Carbonate alk.+ hydroxide alk.] (3c)

Sample Questions to Answer:

1. Calculate the phenolphthalein and total alkalinities of following sample: A 50-ml sample required 5.3 ml N/50 sulfuric acid to reach the phenolphthalein end point, and total of 15.2 ml to reach the bromcresol green end point.
2. How does pH play a role in affecting alkalinity and acidity of a given water sample?

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Methods: 4500 B. Electrometric Method; 2320 B. Titration Method)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

++

Practice Problems (<u>Not for submission</u>)

2. A sample of water collected in the field had a pH of 6.8, which changed to 7.5 by the time the sample was brought to the laboratory. Give a possible explanation for this change.
3. How does carbon dioxide dissolution in lake water affect algal bloom?
4. For the following samples, calculate hydroxide, carbonate, and bicarbonate alkalinity by the procedure (Alkalinity and pH measurements). The sample size is 100 mL, N/50 sulfuric acid is used as the titrant and the water temperature is 25°C.

Sample	**pH**	**Total mL titrant to reach end point**	
		Phenolphthalein	**Bromcresol green**
A	11	10	15.5
D	7	0	12.7
C	11.2	8.2	8.3

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 3: Sulfate Ions

Objective: To determine sulfate ion concentration in a water sample using method: 4500-SO_4^{2-} E. Turbidimetric Method)

Background:

Sulfate are found in appreciable quantity in all natural waters, particularly high in arid and semi arid regions where natural waters in general have high salt content. Sulfate salts are mostly soluble in water and impart hardness. Water with high concentrations has a bitter test. Sulfate may cause intestinal disorders. These ions can produce hydrogen sulfides as per following equation (1):

SO_4^{2-}+organic matter →S^{2-}+H_2O+CO_2 (1a) ***(in the presence of anaerobic bacteria)***

S^{2-}+ H^+ ↔ HS^- (1b)

HS^-+ H^+ ↔ H_2S (1c)

The sulfate data is used in determining applicability of different water types for their public and industrial applications. It indirectly indicates extent of problems that can arise due to reduction of sulfates to hydrogen sulfides. In addition, sulfate content of organic matter fed to anaerobic digester is important information as it gives idea of generation of hydrogen sulfides, which needs to be removed.

Procedure:

The turbidimetric method depends on the fact that barium sulfate formed following barium chloride addition to a sample (Equation 2) tends to precipitate in a colloidal form and this tendency is enhanced in the presence of an acidic buffer (consists of magnesium chloride, potassium nitrate, sodium acetate, and acetic acid). These precipitates need to be separated through filtration (using a filter) before sample is analyzed for sulfate concentration. This is a very rapid method and can be used for samples with sulfate concentration greater than 10 mg/L (samples can be diluted and then it can be analyzed).

Ba^{2+} + SO_4^{2-} →$BaSO_4$ (precipitate; poorly soluble) (2)

Reagents:

1. Buffer Solution A: Dissolve 30 g magnesium chloride ($MgCl_2.6H_2O$), 5 g sodium acetate ($CH_3COONa.3H_2O$), 1.0 g potassium nitrate (KNO_3), and 20 mL acetic acid (CH_3COOH; 99%) in 500 mL distilled water and make up to 1000 mL.
2. Buffer Solution B(**required when the sample SO_4^{2-} <10 mg/L**): Dissolve 30 g magnesium chloride, 5 g sodium acetate, 0.111 g sodium sulfate, and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.
3. Dry Barium Chloride ($BaCl_2$) crystals
4. Standard Sulfate Solution: Dissolve 0.1479 g of anhydrous sodium sulfate in distilled water to make the volume 1 L. This solution contains 100 mg sulfate/L (i.e., 1 mL=100µg SO_4^{2-}). Prepare standards of various strengths (preferably from 0.0 to 40.0mg/L at the intervals of 5 mg/L by diluting this stock solution). Above 40 mg/L accuracy decreases and $BaSO_4$ suspensions lose stability.

Apparatus: Whatman No. 1 filter paper; Spectrophotometer; Magnetic stirrer

Steps:

1. Filter the sample though filter paper (Whatman No. 1) and take 50 mL of filtrate in an Erlenmeyer flask.
2. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add 0.15 g of barium chloride to the sample and stir the sample with the help of magnetic stirrer for about an hour.

3. Measure the absorbance against a distilled water blank **(DO NOT ADD BARIUM CHLORIDE TO IT.)** at 420 nm using spectrophotometer. Absorbance for the blank sample is taken to correct for sample color and turbidity.

Sample Name	***Turbidity (NTU)***	***Sample Name***	***Turbidity (NTU)***
Distilled water blank		Standard 1 (5ppm)	30
Sample 1		10ppm	60
Sample 2		15	89
		20	101
		25	129
		30	157
		35	191
		40	205

4. Process the standard solution of different strengths in similar way and record the absorbance for each solution. Plot a standard sulfate calibration curve on a graph paper from these absorbance values putting strengths (mg/L) on X-axis and absorbance @ 420 nm on Y-axis. Fit a best-fit linear model to the data. Express equation as:

Absorbance value= A+B× Sulfate concentration (in mg/L) (3)

5. Using the standard sulfate calibration curve (a linear-model; Equation 3), find out sulfate concentration in the given unknown sample in mg/L.

Sulfate concentration (mg SO_4^{2-}/L) = (1000×mg SO_4^{2-})/(mL sample) (4)

Sample Questions to Answer:

Explain relevance of preparing standard sulfate solutions in determining sulfate concentration for unknown samples.

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Methods: 4500-SO_4^{2-} E. Turbidimetric Method)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 4a: Dissolved Oxygen

Objective: Determine DO content of a given sample

Background:

Dissolved oxygen (DO) levels in environmental water depend on the physiochemical and biochemical activities in water body and it is an important useful in pollution and waste treatment process control. Two methods are commonly used to determine DO concentration: (1) The iodometric method which is a titration-based method and depends on oxidizing property of DO and (2) The membrane electrode procedure, which works based on the rate of diffusion of molecular oxygen across a membrane.

In the Iodometric method, divalent manganese solution is added to the solution, followed by addition of strong alkali in a glass-stopper bottle. DO rapidly oxidize an equivalent amount of the dispersed divalent manganese hydroxide precipitates to hydroxides of higher valence states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent of the original DO content. The iodine is then titrated with a stranded solution of thiosulfate. The titration end point can be detected visually with a starch indicator. Some oxidizing and reducing agents present in solution can interfere with the iodometric method. Oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Also, organic matter present in solution can be oxidized partially in the presence of oxidized manganese precipitate, thus causing negative errors. Thus some modification of procedure is required.

Standardization of thiosulfate solution

$2Na_2S_2O_3.5H_2O+I_2 \Leftrightarrow Na_2S_4O_6 +2NaI+10H_2O$ (1a)

$2S_2O_3^{2-}+I_2 \Leftrightarrow S_4O_6^{2-}+2I^-$ (1b)

$Cr_2O_7^{2-}+6I^-+14H^+ \Leftrightarrow 2Cr^{3+}+3I_2+7H_2O$ (1c)

$2IO_3^-+10I^-+12H^+ \Leftrightarrow 6I_2+6H_2O$ (1d)

The Winkler Method for DO Determination

If no oxygen is present, a pure white precipitate is formed when MnSO4 and alkali-iodide reagent (NaOH+KI) are added to the sample.

$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$ (white precipitate) (2a)

If sample has some oxygen, Mn2+ is oxidized to Mn4+ and precipitates brown hydrated oxide.

$Mn^{2+} + 2OH^- +0.5O_2 \rightarrow MnO_2$ (brown hydrated precipitate) + H_2O (2b)

The oxidation of Mn2+ to MnO2 is called fixation of the oxygen, occurs slowly at low temperature.

$Mn(OH)_2 +0.5O_2 \rightarrow MnO_2 +H_2O$ (2c)

After shaking the sample for a time sufficient to allow all oxygen to react, the floc is allowed to settle so to leave 5 cm of clear liquid below the stopper; then sulfuric acid is added. Under the low pH conditions, MnO2 oxidizes to produce I_2. I2 is insoluble in water and forms complex is excess iodide ion is present in solution, thus preventing escape of iodine ions from solution.

$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$ (2d)
$I_2 + I^- \Leftrightarrow I_3^-$ (2e)
Now the sample is ready for titration with thiosufate solution.

The Azide Modification with the Winkler Method for DO Determination
This modification is used because of presence of nitrite ions. This occurs in effluents from wastewater treatment plants employing biological processes, in river water and in incubated BOD samples. It does not oxidize Mn2+ but doses oxidize I^- to I2 under acidic conditions. When the reduced form of nitrite (N2O2) is oxidized by oxygen, it is converted to NO_2^- again, establishing the cycle again that can result in erroneous results, far in excess of amounts that would be expected.
$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O$ (3a)
$N_2O_2 + 0.5O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$ (3b)

When interference from nitrites is present, it is impossible to obtain a permanent end point. As soon as the blue color of the starch indicator has been discharged, the nitrites formed by the reaction (3b) reacts with more iodide ions to produce I_2 and the blue color of the starch indicator will return. The nitrite interference is easily overcome with use of sodium azide (NaN_3), which is incorporated in the alkali-KI reagent. When sulfuric acid is added, following reactions happen:
$NaN_3 + H^+ \rightarrow HN_3 + Na^+$ (3c)
$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O$ (3d)

Lab Procedure

Method: The Azide Modification (For nitrite-N < 0.05 mg/L and Ferrous iron<1 mg/L)

The azide modification is used to minimize the effect of interfering materials. It removes interference caused by nitrite which is most commonly found interference in biologically treated effluents and in incubated BOD samples.

Collection of Samples for DO Determination

Samplers are designed to ensure that air cannot enter into the sample. Most samplers are designed to retain 3-4 times the volume of samples which is required for analysis purposes. As oxygen values change with time due to any biological activity, it is important to fix it in field immediately after collection. This is done using reagents using in DO test and then the titration is done in laboratory. This method gives low results for samples with high iodine demand and in this case it is better to preserve sample using 0.7 mL concentrated sulfuric acid and 0.02 g sodium azide. When this is doe it is necessary to add 3 mL of alkali-iodide reagent rather than the usual 2 mL because of the extra acid the sample contains. Better results are also obtained if the sample is fixed and stored in the dark and on the ice until the analyses are conducted. The final titration should not be delayed more than 6 hours.

Reagents:

5. Manganese sulfate solution: Dissolve 480 g $MnSO_4.4H_2O$, 400 g $MnSO_4.2H_2O$ or 364 g $MnSO_4.H_2O$ in distilled water, filter, and dilute to 1L. The $MnSO_4$ solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.
6. Alkali-iodide-azide reagent
7. Sulfuric acid: One mL is equivalent to ~ 3mL alkali-iodide-azide reagent.
8. Starch solution: Dissolve 2 g laboratory-grade soluble starch and 0.2 g salicyclic acid as preservative in 100 mL hot distilled water.
9. Standard sodium thiosulfate titrant: Dissolve 6.205 g $Na_2S_2O_3 .5H_2O$ in distiller water and add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution.
10. Standard potassium bi-iodate solution (0.0021M): Dissolve 812.4 mg $KH(IO_3)$ in distilled water and dilute to 1000 mL.
11. Standardization: Dissolve e ~ 2 g KI, free from iodate in an Erlenmeyer flask with 100 to 150 mL distilled water; add 1 mL 6N H_2SO_4 or a few drops of conc. H_2SO_4 and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate librated iodine with thiosulfate titrant, adding starch toward end of titration, when a pale straw color is reached. When the solution is of equal, 20.00 mL 0.025M $Na_2S_2O_3$ should be required. If not, adjust the $Na_2S_2O_3$ solution to 0.025M.

Apparatus: Incubation bottle 300mL volume; Air compressor

Steps:

6. Make dilution water by adding 2mL/L of following reagents in distilled water:
    a. Phosphate buffer solution
    b. Magnesium sulfate solution
    c. Calcium chloride solution
    d. Ferric chloride solution
    e. Sodium Sulfite solution
7. Take 300 mL sample in BOD bottle. Prepare two sets of this sample. Keep one set for DO analysis for day 0 (i.e., Sample0Day) and another sample in BOD incubator for 5 days at 20°C (Sample5Day) (*this is how 5-day BOD experiment is done)*. **Here you will prepare duplicate samples and analyze at Day 0 (i.e., Sample0Day_A and Sample0Day_B).**
8. For a given sample bottle, add 1 mL of alkali azide and then 1 mL manganous sulfate solution. Shake well the bottle and keep it open for 5 minutes to settle the precipitate. Add 2 mL concentrated H_2SO_4 and place the cap on the bottle. Shake well the bottle till all the precipitate is dissolved.
9. Take 203 mL of sample in conical flask and titrate with standard sodium thiosulfate solution (0.025N) till the colour changes from dark yellow to light yellow. Then add few drops of starch indicator and continue to titrate till the color of the solution becomes either colorless or changes to its original sample colour. Note down volume of 0.025N sodium thiosulfate consumed.
10. Calculate DO value of the sample. ***Remember that in 200 mL sample, 1 mL of sodium thiosulfate of 0.025N equals to 1 mg/L dissolved oxygen***:
    =>Dissolved oxygen (DO) (in mg/L) = mL of sodium thiosulfate (0.025N) consumed.

Notes: Dilution of Sample

1. 0.1, 0.5, and 1% for strong waste water
2. 1.0, 2.5, and 5% for raw and settled sewage
3. 5.0, 12.5 and 25% for oxidized effluent
4. 25, 50 and 100% for polluted river water

Questions

Q1. What precautions do you need to take during DO measurement in raw wastewater sample? Hint: This sample can have both oxidizing and reducing agents.

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Method: 4500-O. C. Azide Modification)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

++++++++Additional Question+++++++

QA1. Compute ultimate BOD and oxygen consumption rate constant using the following data for a stream receiving treated effluent.

Time (days)	BOD exerted at time t (Y_t)
2	11
4	18
6	22
8	24
10	26

Q2. To determine BOD of a sample, three dilutions of the samples are made (BOD bottle volume=300mL). In the BOD dilution water (without sample), initial DO=0 (blank). All samples are incubated at 20°C for 5 days. Look at the following data and calculate 5-day BOD value of the sample at 15°C?

$$\textbf{t-day BOD} = [DO_t - DO_0]/(P) \quad (1)$$

where P= Dilution factor = 300mL/(sample volume in mL)

Bottle no.	Wastewater sample (mL)	Initial DO (mg/L) (DO_0)	DO at 5-day (mL) (DO_5)
1	20	8.9	1.5
2	10	9.1	2.5
3	5	9.2	5.8
4	2	9.2	7.5

Laboratory Experiment 4b: Chlorides

Reference Material:

- AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater
- Sawyer, C. N., McCarty, P. L., and Parkin, G. F. 2000. Chemistry for Environmental Engineering. Fourth Edition, McGraw-Hill, Inc., New York.

Methods: Mohr Method (4500 B-Cl^-; Argentometric Method)

Objectives: Determine chloride ion concentration in a water sample.

Background:

Chloride in the form of chloride (Cl^-) ion is one of the major inorganic anions in water and wastewater. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system (Average estimate of excretion: 6 g of chlorides/person/day; additional chloride burden due to human consumption on wastewater: 15 mg/L). Along the sea coast chloride may be present in high concentration because of leakage of salt water into the sewage system. It also may be increased by industrial process. In potable water, the salty taste produced by chloride concentration is variable and depends on the chemical composition of water. Some waters containing 250 mg/L Cl^- may have a detectable salty taste if sodium cation is present. On the other hand, the typical salty taste may be absent in waters containing as much as 1000 mg/L when the predominant cations are calcium and magnesium. In addition, a high chloride contents may harm metallic pipes and structures as well as growing plants.

The measured chloride ions can be used to know salinity of different water sources. For brackish water (or sea water or industrial brine solution), it is an important parameter and indicates the extent of desalting of apparatus required. It also interferes with COD determination and thus it requires a correction to be made on the basis of amount present or else a complexing agent, such as $HgSO_4$ can be added. Further, chloride ions are used as tracer ions in column studies to model fate of different contaminants in soil and liquid media.

Lab Procedure

Method:

The Mohr Method uses silver nitrate for titration (normality: 0.0141) *(method applicability: 0.15 to 10 mg/L chloride ions)*. This corresponds to **1 mL of 0.0141 equals to 1 mg chloride in solution.** The silver nitrate solution is standardized against standard chloride solution, prepared from sodium chloride (NaCl). During the titration, chloride ion is precipitated as white silver chloride (Eq.1):

$$Ag^+ + Cl^- \leftrightarrows AgCl \qquad (\text{Solubility product constant, } K_{sp}=3\times10^{-10}) \quad (1)$$

The indicator (potassium chromate) is added to visualize the endpoint, demonstrating presence of excess silver ions. In the presence of excess silver ions, solubility product of silver chromate exceeded and it forms a reddish-brown precipitate (Eq.2). This stage is taken as evidence that all chloride ions have been consumed and only excess silver ions have reacted with chromate ions:

$$2Ag^+ + CrO_4^{2-} \leftrightarrows Ag_2CrO_4 \qquad (K_{sp}=5\times10^{-12}) \quad (1)$$

Apparatus: Burette, conical flask, pipette, measuring cylinder

Reagents: Potassium chromate indicator solution, standard silver nitrate titrant.

Steps:

1. Take 25 ml sample in a conical flask. Measure sample pH.
2. Add 1.0ml indicator solution,
3. Titrate with standard silver nitrate solution to pinkish yellow end point and note down volume of titrant used. Also measure sample pH.
4. Calculate chloride ion concentration using Eq.(3):

Chloride Ion Concentration (mg/L) = (A×N ×35.45)*1000 / V_{sample} (3)

Where: A = volume of titrant used, N is normality of silver nitrate (here we used N/71 or 0.0141 N), and V_{sample} is volume of sample used (mL).

Precautions:

1. A uniform sample size must be used, preferably 100 mL, so that ionic concentrations needed to indicate the end point will be constant.
2. The pH must be in the range of 7 to 8 as silver ions are precipitated as AgOH at high pH levels and the chromate ions are converted to $Cr_2O_7^{2-}$ at low pH values.
3. A definite amount of indicator must be used to provide a certain concentration of chromate ions, otherwise silver chromate may form too soon or not soon enough.
4. Caution should be made to notice indicator color change as it can varies person-to-person. The usual range is 0.2 to 0.4 mL of titrant.

Answer these questions also (for Submission with Lab report):

5. Does the measured chloride ion concentration exceed the receiving body (i.e., river in this case) maximum concentration criteria? Look at the CPCB website for getting allowable concentration information. Comment on it.

++

Practice Problems (Not for submission)

1. What is the role of chromate ions in chloride determination?
2. As potassium chromate is an oxidizing agent, what would happen to chloride determination if the sample were consists of organic matter (say 100 mg/L glucose) as well.
3. Why pH range is important in chloride determination?
4. Would the analytical results by the Mohr method for chlorides be higher, lower or the same as the true color value if any excess of indicator were accidentally added to the sample? Why?

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 5: Hardness

Objective: Measure (1) Total hardness and (2) Calcium hardness using dye indicators

Background:

Hard Water:

Hard waters are generally considered to be those waters that require considerable amounts of soap to produce foam and that also produce scale in water pipes, heaters, boilers and other units in which the temperature of water is increased. Hard water are appropriate for human consumption similar to that as soft waters, however it produces adverse actions with soap and thus their use for cleaning purposes is unsatisfactory and thus their removal from water is required. Hardness of waters varies from place to place. In general, surface waters are softer than ground waters. Waters are commonly classified based on degree of hardness (Table 1):

Table 1. Classification of hardness types

Hardness (mg/L)	Degree of hardness
0-75	Soft
75-100	Moderately hard
150-300	Hard
>300	Very hard

Hardness:

Hardness is caused by polyvalent metallic cations, though the divalent cations, such as calcium and magnesium cations are usually the predominant cause of hardness. In addition, hardness is also caused by Fe^{2+} and Mn^{2+} ions. For example, when hard water is heated, Ca^{2+} ions react with bicarbonate (HCO_3^-) ions to form insoluble calcium carbonate ($CaCO_3$) (Eq. 1). This precipitate, known as *scale,* coats the vessels in which the water is heated, producing the mineral deposits on your cooking dishes. Equation 2 presents magnesium hardness.

$$Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} \longrightarrow CaCO_{3(s)} + H_2O + CO_2 \quad (1a)$$

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Mg(OH)_{2(s)} \quad (1b)$$

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in mg/L. When hardness (numerically) is greater than the sum of carbonate and bicarbonate alkalinity, amount of hardness equivalent to the total alkalinity is called **"Carbonate hardness".**

Carbonate hardness (mg/L) = Alkalinity (2a)

When alkalinity > Total hardness:

Carbonate hardness (mg/L) = Total hardness (2b)

The amount of hardness in excess of this is called **"Non-carbonate hardness (NCH)"**. These are associated with sulfate chloride, and nitrate ions. It is calculated using Eq (2c):

NCH (mg/L) = Total hardness-Carbonate hardness (2c)

Determination of Hardness:
Hardness is expressed as mg/L $CaCO_3$. The first method is calculation based method and the second method is titration method using EDTA.

(i) Calculation method

For this method, concentration of cations should be known and then all concentrations are expressed in terms of $CaCO_3$ using **Eq. 3:**

$$\text{Hardness (in mg/L as } CaCO_3) = [M^{2+} \text{ (in mg/L)} \times 50]/ \text{ (E.Wt. of } M^{2+}) \quad (3)$$

Where: M^{2+} = mass of divalent ions (mg/L) and E.Wt. = Equivalent weight of divalent ions (g/mole)

Example: If in a sample, 15 mg/L $Ca^{2+}$are present (, hardness is given by

$$\text{Hardness (in mg/L as } CaCO_3) = [\text{mass of } Ca^{2+} \text{ (in mg/L)} \times 50]/ \text{ (E.Wt. of } Ca^{2+})$$

Here, E.Wt. of Ca^{2+} = (40g/mole)/2=20 g/mole

So, Hardness due to calcium ions = [15 mg/L × 50]/ (20) = 37.5 mg/L $CaCO_3$

(ii) EDTA Titrimetric Method

This method uses ethylenediaminetetracetic acid (EDTA), chelating agents, which forms complex ions with $Ca^{2+}$and Mg^{2+} and other divalent ions causing hardness (Eq. 4a):

$$M^{2+} + \text{EDTA} \rightarrow [\text{M.EDTA}]_{\text{complex}} \quad (4a)$$

The successful use of EDTA for determining hardness depends on presence of an indicator which can show presence of excess EDTA in solution or when all the ions present in solution have been complexed. Eriochrome Black T (EBT) (blue color solution) serves as an excellent indicator to show when all hardness ions have been consumed. When small amount of EBT is added to hard water with pH>10, it combines with Ca^{2+} and Mg^{2+} ions to form weak complex ions (wine-red color solution) (Eq. 4b):

$$M^{2+} + \text{Eriochrome Black T} \rightarrow [\text{M.Ericochrome Black T}]_{\text{complex}} \quad (4b)$$

During the titration with EDTA, all free hardness ions are complexed as per Eq. 4a and subsequently, EDTA disrupts the wine red complex as it can form a stable complex with the hardness ions. At this stage, solution color changes from red wine color to blue color, indicating the end of the titration.

Lab Procedure:

Reagents: Buffer solution; EDTA Titrant; EBT

1. Measure Ca-Hardness and Total Hardness by titration as described below. **Use a different sample for each measurement.**
2. **Total Hardness**: Take 100 ml of the sample and add 2 ml buffer solution in it and add 2-3 drops of Black T. Titrate it with standard EDTA solution (with continuous stirring) until the last reddish colour disappears. At the end point the solution turns blue. Note down the volume used. Calculate Hardness as follows:

   Hardness (in mg/L as $CaCO_3$) = (V× N × 50 ×1000) / (SV) (5)

   Where: V = volume of titrant (mL); N = normality of EDTA; 50 = equivalent weight of $CaCO_3$; SV = sample volume (mL)
3. **Ca-Hardness:** Take 50 ml of the sample and add 1 ml Sodium Hydroxide solution (8%) in it and add pinch of Mercurex Powder. Titrate with standard EDTA solution until the light pink colour of solution converts into light blue color.

Answer these questions also:

1. Among finished drinking water, raw wastewater and de-ionized water, which water is expected to have the highest carbonate hardness and why?
2. A sample has 50mg/L Ca^{2+},150mg/L Mg^{2+} 50 mg/L Na^{+}, 20 mg/L Cl^{-} and 100 mg/L glucose. Calculate its total hardness, carbonate and non-carbonate hardness?

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Methods: 2340 C. EDTA Titrimetric Method)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 6: Standard Curve, Synthetic Solution Preparation and Glassware Washing and Microbial Decontamination Procedure

Objective 1: To develop standard curve for sulfate ions

Procedure:

Reagents & Apparatus: Whatman No. 1 filter paper; Spectrophotometer; Magnetic stirrer

Steps:

Each group will be provided 100 mg/L sulfate ion standard stock solution (prepared by dissolving 0.1479 g of anhydrous sodium sulfate in 1 liter distilled water).

Using this solution, each subgroup needs to prepare standard sulfate ion solution of given concentration and measure its absorbance @ 420 nm using spectrophotometer. Finally absorbance values of all concentrations will be shared to al subgroup.

concentration	C1	C2		C5
absorbance	A1			A5

Using these values, a linear model need to be fit as following using the method given in file ("Linear model fitting"):

Absorbance value= A+B× Sulfate concentration (in mg/L) (1)

Sample Questions to Answer:

Using developed standard curve (Eq1), determine concentration values in surface water samples with following absorbance values and compare determined sulfate ion values with allowable sulfate ion values in drinking water

Sample	1	2	3	4	5
absorbance	0.02	0.2	0.3	0.7	0.8

Reference Materials:

CEL212 Sulfate ions handout

CEL212 Linear Model Fitting Handout

Objective 2: To Prepare synthetic solution with given composition

Procedure:

Solution volume: 250 mL

Assignment of Sample composition for different subgroups

subgroup	ions (moles/L)				
	SO_4^{2-}	Cl^-	Ba^+	Ca^+	HCO_3^-
1	0.01	0.01	0.01		
2		0.01	0.01	0.01	
3			0.01	0.01	0.01
4		0.01		0.01	0.01
5	0.01		0.01		0.01

Objective 3: To learn washing of glassware and autoclaving for microbial decontamination

Procedure

Material: Glassware used in making synthetic solution and standard solution and unused media plates

Steps:

Glassware Cleaners

4. Clean the equipment thoroughly with soap and water for basic cleaning. You may need to use a wire brush to remove some residue. Detergent using bottle brushes and scouring pads can be used as needed.
5. After cleaning, rinse the glassware with running tap water. When test tubes, graduates, flasks and similar containers are rinsed with tap water, allow the water to run into and over them for a short time, then partly fill each piece with water.
6. Thoroughly shake and empty at least six times and ensure that all soap residue is removed.

Note:

- Do not use cleaning brushes that are so worn that the spine hits the glass. Serious scratches may result. Scratched glass is more prone to break during experiments. Any mark in the uniform surface of glassware is a potential breaking point, especially when the piece is heated. Do not allow acid to come into contact with a piece of glassware before the detergent (or soap) is thoroughly removed. If this happens, a film of grease may be formed.
- To prevent breakage when rinsing or washing pipets, cylinders or burets, be careful not to let tips hit the sink or the water tap.

Sterilizing Contaminated Glassware

- Autoclave glassware or sterilize it in large steam ovens or similar apparatus. If viruses or spore-bearing bacteria are present, autoclaving is absolutely necessary.

Handling and Storing

- Protect clean glassware from dust. This is done best by plugging with cotton, corking, taping a heavy piece of paper over the mouth or placing the glassware in a dust-free cabinet.
- Store glassware in specially designed racks. Avoid breakage by keeping pieces separated.

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 7: Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

7A: Biochemical Oxygen Demand (BOD)

Objective : To determine BOD value for determining biodegradability of solution.

Background:

The most widely used test indicating organic pollution of both wastewater and surface water is the 5-day BOD (BOD_5). This determination involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. BOD_5 is the total amount of oxygen consumed by microorganisms during the first five days of biodegradation. Oxygen demand is associated with the biodegradation of the carbonaceous portion of wastes and oxidation of nitrogen compounds such as ammonia. The following equations simplify the process of biodegradation:

Organic matter + O_2 + microorganisms → CO_2 + H_2O + new microbial cells

Ammonia + O_2 + microorganisms → NO_3 + H_2O + new microbial cells

Procedure:

Apparatus: Incubation bottle 300mL volume; Air compressor, 20°C incubator

Reagents for DO measurement:

12. Manganese sulfate solution: Dissolve 480 g $MnSO_4.4H_2O$, 400 g $MnSO_4.2H_2O$ or 364 g $MnSO_4.H_2O$ in distilled water, filter, and dilute to 1L. The $MnSO_4$ solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.
13. Alkali-iodide-azide reagent
14. Sulfuric acid: One mL is equivalent to ~ 3mL alkali-iodide-azide reagent.
15. Starch solution: Dissolve 2 g laboratory-grade soluble starch and 0.2 g salicyclic acid as preservative in 100 mL hot distilled water.
16. Standard sodium thiosulfate titrant: Dissolve 6.205 g $Na_2S_2O_3 .5H_2O$ in distiller water and add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution.
17. Standard potassium bi-iodate solution (0.0021M): Dissolve 812.4 mg $KH(IO_3)$ in distilled water and dilute to 1000 mL.
18. Standardization: Dissolve e ~ 2 g KI, free from iodate in an Erlenmeyer flask with 100 to 150 mL distilled water; add 1 mL 6N H_2SO_4 or a few drops of conc. H_2SO_4 and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate librated iodine with thiosulfate titrant, adding starch toward end of titration, when a pale straw color is reached. When the solution is of equal, 20.00 mL 0.025M $Na_2S_2O_3$ should be required. If not, adjust the $Na_2S_2O_3$ solution to 0.025M.

Steps:

DO measurement:

11. Make dilution water by adding 2mL/L of following reagents in distilled water:
    a. Phosphate buffer solution
    b. Magnesium sulfate solution
    c. Calcium chloride solution
    d. Ferric chloride solution
    e. Sodium Sulfite solution
12. For a given sample bottle, add 1 mL of alkali azide and then 1 mL manganous sulfate solution. Shake well the bottle and keep it open for 5 minutes to settle the precipitate. Add 2 mL concentrated H_2SO_4 and place the cap on the bottle. Shake well the bottle till all the precipitate is dissolved.
13. Take 203 mL of sample in conical flask and titrate with standard sodium thiosulfate solution (0.025N) till the colour changes from dark yellow to light yellow. Then add few drops of starch indicator and continue to titrate till the color of the solution becomes either colorless or changes to its original sample colour. Note down volume of 0.025N sodium thiosulfate consumed.
14. Calculate DO value of the sample. *Remember that in 200 mL sample, 1 mL of sodium thiosulfate of 0.025N equals to 1 mg/L dissolved oxygen*:
    =>Dissolved oxygen (DO) (in mg/L) = mL of sodium thiosulfate (0.025N) consumed.

BOD:

1. Prepare BOD dilutions. Use dilution water (it contains nutrients, the exact contents are described in Standard Methods):Blank (only dilution water);5 mL sample in 300 mL BOD bottle, fill up with dilution water;15 mL sample in 300 mL BOD bottle, fill up with dilution water;20 mL sample in 300 mL BOD bottle, fill up with dilution water
2. Take 300 mL sample in BOD bottle. Prepare two sets of this sample. Keep one set for DO analysis for day 0 (i.e., Sample0Day) and another sample in BOD incubator for 5 days at 20°C (Sample5Day).
3. Measure DO in different samples at t=0.
4. Incubate samples in 20°C for 5 days.
5. Come back in the lab after 5 days and record dissolved oxygen.
6. Record data in following manner.

Bottle no.	Wastewater sample (mL)	Initial DO (mg/L) (DO_0)	DO at 5-day (mL) (DO_5)
1			
2			
3			
4			

Calculate 5-day BOD value of the sample at 20°C:

$$\textbf{t-day BOD} = [DO_t - DO_0]/(P) \qquad (1)$$

where P= Dilution factor = 300mL/(sample volume in mL)

Sample Questions to Answer:

1. If 5-day BOD at 20°C=150mg/L (k=0.23/day), calculate 5-day BOD at 15°C and 22°C? Use following dependence of (k) with temperature: $k_T = k_{20}\{\theta\}^{(T-20)}$

Reference:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Method: 4500-O. C. Azide Modification)

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater

(Method: 5210B,5-day BOD)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

++++++++++++Additional questions (not to submit)++++++++++++

Q: Calculate oxygen consumption rates of samples with given data and comment on biodegradability

time(d)	sample 1(BOD(mg/L) at 20degC)	sample 2(BOD(mg/L) at 20degC)
1	5	10
4	10	20
5	70	40
8	90	50
30	120	80

7B:Chemical Oxygen Demand (COD) (closed reflux method)

Objective 2: To determine COD value for determining organic strength of solution **(Closed Reflux Method)**

Background:

Chemical oxygen demand (COD) is termed as the amount of a specific oxidizing agent that reacts with sample under controlled conditions and it is expressed as oxygen equivalence. This parameter indicates the extent of organic matter contamination of water and is always higher than the biochemical oxygen demand (BOD). It is used to indicate organic matter contamination and it helps in knowing overall organic load to the receiving body.

Selection of Method

There are two methods for COD determination. The first method: open reflux method is suitable for a wide range of wastes where large volume of sample is required (for samples with COD= 50 mg O_2/L). In the second method: closed reflux methods, small quantities of metallic salt reagents are required and small quantities of hazardous waste is produced (for samples with COD= 5 to 50 mg O_2/L). In the closed reflux method, ampules and culture tubes with premeasured reagents are used and then samples is placed in the tube and COD is determined. In this experiment, closed reflux method is used and samples with COD < 50 mg O_2/L are tested.

Reaction with dichromate solution of sample:

Potassium dichromate is a strong oxidizing agent and it can be used to prepare solution of exact normality.

$$\mathbf{C_nH_aO_bN_c + d\ Cr_2O_7^{2-} + (8d+c)\ H^+ \Rightarrow nCO_2 + [(a+8d-3c)/2]H_2O + c\ NH_4^+ + 2dCr^{3+}} \quad \mathbf{(1)}$$

Here d=(2n/3)+(a/6)-(b/3)-(c/2)

During experiment, excess dichromate concentration is determined by titrating it with ferrous ammonium sulfate (FAS). The reaction is given by:

$$\mathbf{6Fe^{2+}\ Cr_2O_7^{2-} + 14\ H^+ \Rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O} \quad \mathbf{(2)}$$

Here d=(2n/3)+(a/6)-(b/3)-(c/2)

Ferroin (ferrous 1,10-phenanthroline sulfate): It is used to indicate change in oxidation-reduction potential of the solution and it indicates the condition when all dichromate has been reduced by ferrous ion. It gives a very sharp brown color change which can be seen in spite of blue color generated by the Cr^{3+} ions formed on reduction of the dichromate.

Procedure:

*Apparatus: D*igestion vessels; block heater; microburet; ampule sealer. Borosilicate culture tubes (16mm*100 mm or 20 mm*150mm) with TFE lined-screw caps are used. The block heater is required to operate at 150±2°C with holes to accommodated digestion vessels. **Do not use an oven because of the possibility of leaking samples generating corrosive and explosive atmosphere.**

Reagents:

a. Standard potassium dichromate digestion solution, 0.01667M: Add to about 500 mL distilled water 4.903 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150°C for 2 h, 167 mL conc. H_2SO_4, and 33.3 g $HgSO_4$. Dissolve, cool to room temperature, and dilute to 1000 mL.

b. Sulfuric acid reagent:

c. Ferroin indicator solution: Dilute it by a factor of 5 as required. This indicator is used to indicate change in oxidation-reduction potential of the solution.
d. Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10M: Dissolve 39.2 g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 mL conc H2SO4, cool, and dilute to 1000 mL. Standardize solution daily against standard K2Cr2O7 digestion solution as follows: Pipet 5.00 mL digestion solution into a small beaker. Add 10 mL reagent water to substitute for sample. Cool to room temperature. Add 1 to 2 drops diluted ferroin indicator and titrate with FAS titrant.

$$\textbf{Molarity of FAS solution} = [V_{K2Cr2O7} \times 0.1] / (V_{FAS}) \quad (3)$$

Where: $V_{K2Cr2O7}$ = volume of K2Cr2O7 (mL); V_{FAS} = volume of FAS (mL)

e. Sulfamic acid:
f. Potassium hydrogen phthalate standard:

Steps:

4. Wash culture tubes and caps with 20% H2SO4 before using to prevent contamination.
5. Place sample in culture tube or ampule and add digestion solution. Carefully run sulfuric acid reagent down inside of vessel so an acid layer is formed under the sample-digestion solution layer and tightly cap tubes or seal ampules, and invert each several times to mix completely.
6. Place tubes or ampules in block digester preheated to 150°C and reflux for 2 h behind a protective shield. CAUTION: *These sealed vessels may be under pressure from gases generated during digestion. Wear face and hand protection when handling* and dangerous pressures will be generated at 150°C.
7. Cool to room temperature and place vessels in test tube rack. Some mercuric sulfate may precipitate out but this will not affect the analysis.
8. Remove culture tube caps and add small TFE-covered magnetic stirring bar. If ampules are used, transfer contents to a larger container for titrating.
9. Add 0.05 to 0.10 mL (1 to 2 drops) ferroin indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10M FAS. The end point is a sharp color change from blue-green to reddish brown, although the bluegreen may reappear within minutes. In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.
10. COD is given by

$$\textbf{COD as mg/L } O_2\textbf{/L} = [(A-B) \times M \times 8000) / (V_{sample}) \quad (4)$$

Where: A = volume of FAS used for blank (mL);
B= volume of FAS used for sample (mL);
M=molarity of FAS; 8000= miliquivalent weight of oxygen ×1000 mL/L

Analyze samples in duplicates because of small sample size.

Sample Questions to Answer:

3. Why do the COD analysis and BOD analysis give different results for the same waste?
4. What could be inferred from the following samples concerning the relative ease of biodegradability: Sample A (5-d BOD/COD=24/30) and Sample B (5-d BOD/COD=10/50)?

Reference:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Methods: 5220 C. Closed Reflux Titrimetric Method)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 8: Total Coliforms using MULTIPLE-TUBE FERMENTATION TECHNIQUE (Points: 20)

Objective: To introduce concepts of total coliforms using the MULTIPLE-TUBE FERMENTATION TECHNIQUE

Background:

Read Handout Standard Methods 9221 MULTIPLE-TUBE FERMENTATION TECHNIQUE FOR MEMBERS OF THE COLIFORM GROUP (section 9221A to 9221C). In summary, coliforms group of bacteria ferment lactose and produce gas. a broth containing lactose and other substances which inhibit noncoliform organisms is placed in series of test tubers which are then inoculated with a decimal fraction of 1 mL(100,10,1,0.1,0.01, etc.). These tubes are incubated at the appropriate temperature and inspected for development of gas. The first stage is called the presumptive test and tubes with gas developed are presumed to have coliforms present (we will do till this stage).

A similar is test, called as confirmed test, is set up to confirm the presence of coliforms organisms. See following schematic of all test involved.

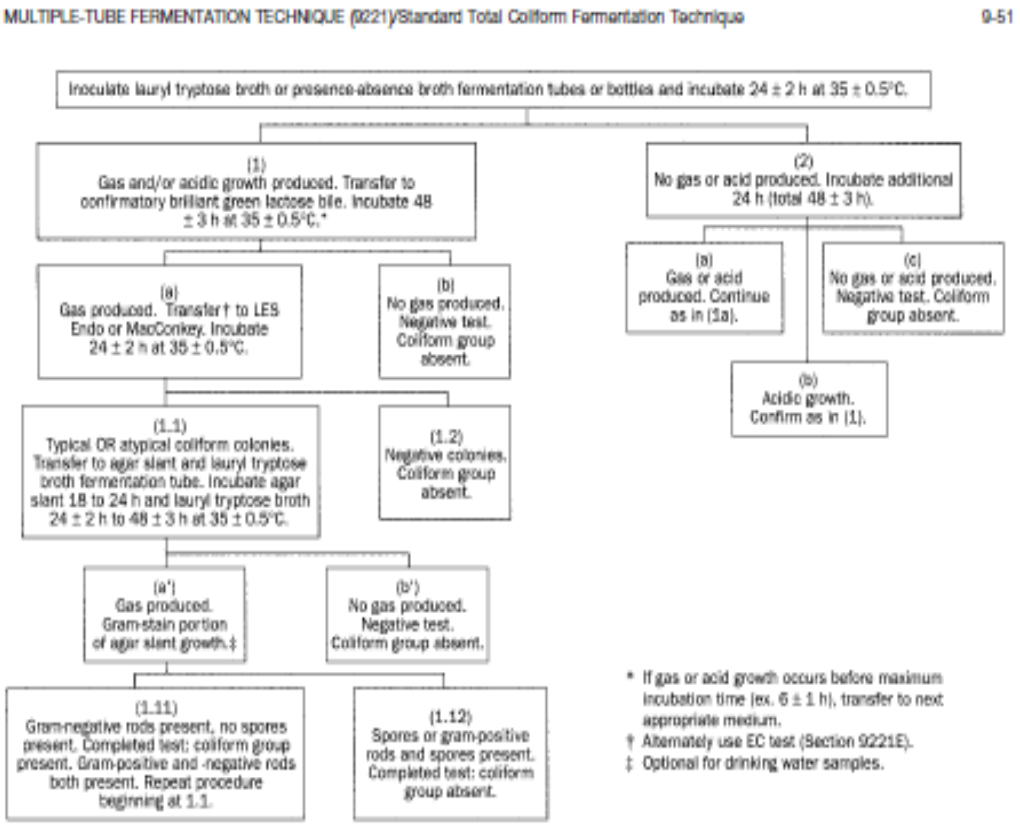

Figure 9221:1. Schematic outline of presumptive, confirmed, and completed phases for total coliform detection.

A statistical method in conjunction of following table is used to determine the most probable number of coliform bacteria in 100 mL of sample. When more than 3 dilutions are used in decimal series of dilution, select the three most appropriate dilutions refer following table.

TABLE 9221:IV. MPN INDEX AND 95% CONFIDENCE LIMITS FOR VARIOUS COMBINATIONS OF POSITIVE RESULTS WHEN FIVE TUBES ARE USED PER DILUTION (10 mL, 1.0 mL, 0.1 mL)*

Combination of Positives	MPN Index/ 100 mL	Confidence Limits	
		Low	High
0-0-0	<1.8	—	6.8
0-0-1	1.8	0.090	6.8
0-1-0	1.8	0.090	6.9
0-1-1	3.6	0.70	10
0-2-0	3.7	0.70	10
0-2-1	5.5	1.8	15
0-3-0	5.6	1.8	15
1-0-0	2.0	0.10	10
1-0-1	4.0	0.70	10
1-0-2	6.0	1.8	15
1-1-0	4.0	0.71	12
1-1-1	6.1	1.8	15
1-1-2	8.1	3.4	22
1-2-0	6.1	1.8	15
1-2-1	8.2	3.4	22
1-3-0	8.3	3.4	22
1-3-1	10	3.5	22
1-4-0	10	3.5	22
2-0-0	4.5	0.79	15
2-0-1	6.8	1.8	15
2-0-2	9.1	3.4	22
2-1-0	6.8	1.8	17
2-1-1	9.2	3.4	22
2-1-2	12	4.1	26
2-2-0	9.3	3.4	22
2-2-1	12	4.1	26
2-2-2	14	5.9	36
2-3-0	12	4.1	26
2-3-1	14	5.9	36
2-4-0	15	5.9	36
3-0-0	7.8	2.1	22
3-0-1	11	3.5	23
3-0-2	13	5.6	35
3-1-0	11	3.5	26
3-1-1	14	5.6	36
3-1-2	17	6.0	36
3-2-0	14	5.7	36
3-2-1	17	6.8	40
3-2-2	20	6.8	40
3-3-0	17	6.8	40
3-3-1	21	6.8	40
3-3-2	24	9.8	70
3-4-0	21	6.8	40
3-4-1	24	9.8	70
3-5-0	25	9.8	70
4-0-0	13	4.1	35
4-0-1	17	5.9	36
4-0-2	21	6.8	40

* Results to two significant figures.

Combination of Positives	MPN Index/ 100 ml.	Confidence Limits	
		Low	High
4-0-3	25	9.8	70
4-1-0	17	6.0	40
4-1-1	21	6.8	42
4-1-2	26	9.8	70
4-1-3	31	10	70
4-2-0	22	6.8	50
4-2-1	26	9.8	70
4-2-2	32	10	70
4-2-3	38	14	100
4-3-0	27	9.9	70
4-3-1	33	10	70
4-3-2	39	14	100
4-4-0	34	14	100
4-4-1	40	14	100
4-4-2	47	15	120
4-5-0	41	14	100
4-5-1	48	15	120
5-0-0	23	6.8	70
5-0-1	31	10	70
5-0-2	43	14	100
5-0-3	58	22	150
5-1-0	33	10	100
5-1-1	46	14	120
5-1-2	63	22	150
5-1-3	84	34	220
5-2-0	49	15	150
5-2-1	70	22	170
5-2-2	94	34	230
5-2-3	120	36	250
5-2-4	150	58	400
5-3-0	79	22	220
5-3-1	110	34	250
5-3-2	140	52	400
5-3-3	170	70	400
5-3-4	210	70	400
5-4-0	130	36	400
5-4-1	170	58	400
5-4-2	220	70	440
5-4-3	280	100	710
5-4-4	350	100	710
5-4-5	430	150	1100
5-5-0	240	70	710
5-5-1	350	100	1100
5-5-2	540	150	1700
5-5-3	920	220	2600
5-5-4	1600	400	4600
5-5-5	>1600	700	—

When the series of decimal dilutions is different from that in above table, select the MPN value from above table and calculate according following formula:

MPN/100 mL = (Table MPN/100 mL)*(10/V)

Where V=volume of one sample portion at the lowest selected dilution

Example calculation: Determine MPN of coliform organisms

example	sample volume (mL)					combination of positives selected	MPN index no./100 mL
	10	1	0.1	0.01	0.001		
no. positive	4	2	1	1	0		
no. negative	1	3	4	4	5		

Select a series where tubes each have positive results. Use sample size 10, 1, 0.1 ml (with combination of positives: 4-2-1).

From table, MPN/100 mL comes out to be 26 (range: 9-78 organisms/100 mL possible at 95% confidence level).

Report Writing:

Sample: Vasant Kunj Wastewater Sample

Write steps for measuring total coliforms in laboratory (2-page maximum)

Sample Questions to Answer:

Solve following question for determining total coliforms in unknown sample.

example	sample volume (mL)					combination of positives selected	MPN index no./100 mL
	10	1	0.1	0.01	0.001		
no. positive	0	0	1	0	0		
no. negative							

Reference:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater
(Method: 9221 B, 9221C and 9222D)

Indian Institute of Technology Delhi (India)
Department of Civil Engineering

CVL212 Environmental Engineering (3-0-2) Laboratory

Laboratory Experiment 9: Air Quality Monitoring

(Prepared by Praveen and Prof. Mukesh Khare)

Objective: To understand operation of air quality monitor and compare air quality (CO, CO_2, temperature, relative humidity) of indoor and outdoor air environments

Background:

Indoor Air Quality monitoring

With 90% of our time spent indoors, determining the quality of the air we breathe indoors is essential for good health and productivity. The IAQ monitor key indoor air quality indicators including CO_2, humidity, temperature and CO. Should these measurements fall outside recognized guidelines; further tests can be made to suggest an appropriate course of action. For example, ventilation studies show that as room temperatures rise above 75°F(24°C) the ability of occupants to concentrate can drop by up to 50% and high levels of carbon dioxide will indicate poor ventilation that results in drowsiness and perceived stuffiness. Both situations are very common and seriously affect productivity. Over-ventilation wastes energy and results in increased building running costs. The Surveyor range has been designed with the user in mind. Minimal training is required to use the instruments as the intuitive menu system and display provide step-by-step guides for each operation that are updated when smart probes are plugged in.

Description of the instrument

The ambient air conditions measuring instrument, for assessing Indoor Air Quality and tuning and testing VAC systems, stands out on account of its efficient measurement process. The user-friendly measuring instrument has the right measurement engineering for every application and different flow speeds; for example, thermal probes, vane or Pitot tube measurement. Probe-controlled menus and selectable user profiles, e.g. for duct measurement or long-term measurement, ensure the user-friendliest operation possible. The new IAQ probe measures Indoor Air Quality by measuring the CO_2 level, air moisture and air temperature. In addition, lux and comfort level probes can be connected to measure draught air. Clear analysis and archiving ensure convenient documentation. Temperature and humidity measurement is built-in in the new thermal probe. The special flow protocol professionally documents duct measurements. It is also possible to connect additional temperature and humidity probes. Readings from up to 3 temperature or humidity probes can be displayed in the measuring instrument; data transmission is by radio, i.e. wireless.

- Instrument memory for 10,000 readings
- PC software for analysis, filing and documentation of measurement data
- Thermal probes, vane measurement and built-in differential pressure probe probe for Pitot tube measurement
- IAQ probe, lux probe and comfort level probe

Procedure:

Measure air quality of three indoor locations and one outdoor location and compare their air quality parameters.

Apparatus: Indoor air quality monitor (automatic sampler) for carbon monoxide (CO), carbon dioxide (CO_2), temperature, humidity and pressure.

Steps:

For a given location:

7. Prepare a sampling assembly.
8. Set the time constant depending upon the required averaging period (Instrument can be switch on and it will display concentration).
9. Simultaneously instrument will start recording the concentration values in the memory card. Using data transfer cable (i.e. RS232 cable) can download data from instrument to personal computers.

Compile data for all locations in following manner and compare air quality of different locations. Also comment on air quality parameters with regards to CPCB and USEPA guidelines.

location	carbon monoxide	carbon dioxide	relative humidity	temperature
indoor 1				
indoor 2				
indoor 3				
outdoor				

Reference:

AQ-5000, indoor air quality monitor manual, QUEST technology, USA.

Testo 435, Indoor air quality manual, testo, Inc., USA.

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.