MODULE 4 WATERCHEMISTRY AND ANALYSIS

UNIT1 PHYSICAL PARAMETERS RELEVANT TO WATER ANALYSIS

CONTENTS

1.0 INTRODUCTION

Water appears to be the most essential of the three indispensable matters (air, water and food) to man. Although there is a common observation that without air, man can barely survive for a very few minutes (that is, between threetofive minutes) and without food, he may survive for up to fifty days. However, it is also a common knowledge that without water on the wet surfaces of alveoli in humans or gills in fish for instance, intercellular oxygen exchange is impossible. Several other biochemical reactions that are vital to life are water-dependent. Water is also needed for day-to-day running of vital domestic, industrial and agricultural activities.

Water needless to say, is so important for both the sustenance and continuity of life,hence, having a good understanding of chemistry and analysis of water is vital to sustainability of man and his various activities (in the face of the fact that less than 2percent of the total water available on the surface of the earth is suitable for drinking). Apart from the seeming “localization” of the two percent good water, technological advancement and rapid industrialization with their concurrent pollution tendencies have placed the limited good water under serious stress.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- name the physical parameters that are relevant to the chemistry and analysis of water
- explain how the parameters (turbidity, colour, taste andodour, solids) are measured
- interprete and apply the data obtainable from the measured parameters in solving practicalproblems related to water analysis.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
   Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Notable Physical Parameters of Water

4.1.1 Turbidity

The term “turbid” is applied to waters containing suspended matter that interferes with the passage of light through the water or in which visual depth is restricted.

Turbidity may be caused by a wide variety of suspended materials ranging in sizes from colloidal to coarse dispersions, depending upon the degree of turbulence. In lakes or other water existing under relatively quiescent conditions, most of the turbidity is due to colloidal and extremely fine dispersions;in river under flood conditions, the turbidity is as a result of to relatively coarse dispersion,while glacier–fed rivers and lakes, turbidity is due to colloidal coarse particles produced by the grinding action of the glacier. As rivers descend from mountainous areas to the plains, they receive contributions of turbidity from farming and other operations that disturb the soil. Under flood conditions, great amounts of topsoil are washed to receiving streams. Much of these materials is inorganic in nature and includes clay and silt, but considerable amounts of organic matter are included. As the rivers progress toward the ocean, they pass through urban areas where domestic and industrial treated and untreated wastewaters may be added. These wastewaters often contain large quantities of both organic and inorganic substances that produce turbidity. Street washings contribute much turbidity as well.

Organic materials reaching rivers serve as food for bacteria. The resulting bacterial growth and other microorganisms that feed upon the bacteria produce additional turbidity. Inorganic nutrients such as nitrogen and phosphorus present in wastewater discharges and agricultural runoff stimulate the growth of algae which also contribute to turbidity.

Significance of Turbidity in Public Water Supplies

- **Aesthetics**: Any turbidity in a sample of drinking water is automatically associated withpossible wastewater pollution and the health hazards occasioned by it.
- **Filterability**: Filtration of water is rendered more difficult and costlywith increasing turbidity.
- **Disinfection**: To be effective, there must be direct contact between a given disinfectant (e.g. chlorine, ozone, chlorine dioxide or UVradiation) and the organisms it has to kill. In cases where turbidity is caused by municipal wastewater suspended solids or runoff from animal feed lots, many of the pathogenic organisms may be encased in the particles and remain protected from the action of the disinfectant.
- **Method of Turbidity Determination**
  Instrumental method that employs the principle of nephelometry is used. A light source illuminates the sample and one or more photoelectric detectors are used with a readout device to indicate the intensity of scattered light. A particular formation polymer suspension is used as a standard. Turbidity in treated drinking water must never exceed onenephelometric turbidity unit (NTU).
  1 NTU = 1mg S_iO_2/L.

Applications of Turbidity Data

- ***Water Supply***: Knowledge of the turbidity variation in raw-water supplies is of primeimportance to water treatment plant operations. Such measurements are used in conjunction with other information to determine whether a supply requires special treatment by chemical coagulation and filtration before it may be used for a public water supply.
- ***Determination of Effectiveness of Coagulants*****:** Water supplies obtained from rivers usually require chemicalflocculation because of high turbidity.Turbidity measurements are used to determine the most effective and economical chemical to use.
- ***Gauging the Amount of Chemicals*****:** Turbidity measurements help to gauge the amount of chemicals needed from day to day in the operation of treatment works. This is particularly important on “flashy” rivers where no impoundment is provided. Measurements of turbidity in settled water prior to filtration is useful in controlling chemical dosages so as to prevent excessive loading of rapid sand filters.
- ***Checking Faulty Filter Operation*****:** Turbidity measurements of the filtered water are neededtocheck on faulty filter operation and to ensure conformity to regulatory requirements.
- ***Effluent Control*****:** Turbidity measurements offer a quick means of determining the levels of suspended solids in an effluent so as to know the minimum amount of coagulants needed to produce high-quality effluent.

4.1.2 Colour

Many surface waters, particularly those emanating from swampy areas, are often coloured to the extent that they are not suitable for domestic or some industrial uses without being treated to remove the colour. The colouring materials, many of which are humic substances, result from contact of water with organic debris, such as leaves, needles of conifers and woods, all in various stages of decomposition. Iron is sometimes present as ferric humate and produces a colour of high potency. Natural colour exists in water primarily as negatively charged colloidal particles and its removal can readily be accomplished by a coagulant having a trivalent metallic ion such as aluminum or iron.

Surface waters may appear highly coloured because of coloured suspended matter when in reality they are not. Rivers that drain areas of red clay soils become highly coloured during times of flood. Colour caused by suspended matter is referred to as **apparent colour**while colour caused by vegetable or organic extracts that are colloidal is called **true colour**. At times, surface waters may become coloured by the presence of dyes from textile industries and pulping operations in the paper industry which leads to production of liquors containing lignin derivatives and other materials in dissolved form.

Significance of colour in public water supplies

- **Disinfection problem:** Waters containing colouring matter derived from natural Substancesundergoing decay in swamps and forests are not considered to possess toxic properties. However, disinfection by chlorination results in the formation of chloroform, other trihalomethanes and a range of other chlorinated organics, leading to problems of much current concern.
- **Problem of aestheticunacceptability:** The natural colouring materials impart a yellow-brownish appearance somewhat like that of urine to water. This makes consumers to seekother sources of drinking water if the public water supply is not aesthetically acceptable no matter how safe it may be from the hygienic viewpoint. The alternative sources sought by consumers may be springs or wells with uncertain levels of pathogenic organism. Waters intended for human use should not exceed 15 colour units.

Standard colour solutions

This is done by preparing a stock solution of potassium chloroplatinate (K_2PtCl_6) that contains 500mg/L of platinum. Cobalt chloride is added to provide the proper tint. The colour produced by 1mg/L of platinum (in the form of K_2PtCl_6) is taken as the standard unit of colour. The stock solution has a colour of 500 units, and a series of working standard is prepared from it by dilution. A matched set of colour-comparism tubes, called **Nessler tubes** are usually used to contain the standard. A series ranging from 0 to 70 colour units is employed. Samples with colour less than 70 units are tested by direct comparison with the prepared standards. For samples with a colour greater than 70 units, a dilution is made with demineralised water and colour calculation is made, using a correction factor for the dilution employed.

Suspended matter in samples must be removed to enable determination of true colour. This is usually accomplished by centrifuging; filtration is not recommended because of possible adsorption of colour on the filtering medium.

Applications of Colour Data

- **Consumption Specifications:** The decision about whether to treat a water sample further to meet the World Health

Organization (WHO) guideline of 15 colour units for drinking water can be taken from the colour data obtained.

- **Indicator of Possible Formation of Toxins:** Colour in natural waters is an indirect indicator of the potential for trihalomethane formation during disinfection with chlorine. A water supply is generally desired with a colour low enough so that chemical treatment will not be required and trihalomethane formation will not constitute a burdensome treatment problem.
- **Designs of Treatment Plant:** Before a chemical treatment plant is designed, research is conducted to ascertain the best chemicals to use and amounts required. Colour determinations serve as the basis of the decisions. Such data are necessary for proper selection of chemical feeding machinery and the design of storage space.
- **Means of Ensuring Economical Operations:** Colour determinations on the raw and treated water or wastewater govern the dosages of chemicals used, to ensure economical operation and to produce a low-colour water that is well within accepted limits.

4.1.3 Taste and Odour

The sensations of taste and smell are closely related and often confused. Hence, a wide variety of tastes and odours may be attributed to water by consumers. Substances that produce an odour in water will almost invariably import a taste as well. The converse is not true, as there are many mineral substances that produce taste but no odour.

Significance of Taste and Odour in Water Supply

Consumers find taste and odour aesthetically displeasing for obvious reasons. Because water is thought of as tasteless and odourless, the consumer associates taste and odour with contamination and may prefer to use a tasteless, odourless water that might actually pose more of a health threat. Odours produced by organic substances may pose more than just aesthetic problem since some of those substances are carcinogenic.

Sources of Taste and Odour

Many substances with which water comes into contact in nature or during human use may lead to perceptible taste and odour. These include minerals, metals and salts from the constituents of wastewater. Inorganic substances are more likely to produce tastes unaccompanied by odour. Alkaline materials impart a bitter taste to water, while metallic salts may give a salty or bitter taste.

Organic materials, on the other hand, are likely to produce both taste and odour. A multitude of organic chemicals may cause taste and odour problems in water, with petroleum –based products being prime offenders. Biological decomposition of organics may result in both taste and odour producing liquids and gases in water. Principal among them are the reduced products of sulphure that impart a “rotten egg” taste and odour. Also, certain species of algae secrete an oily substance that may result in both odour and taste. The combination of two or more substances, neither of which would produce taste or odour by itself, may sometimes result in taste and odour problems e.g. organics and chlorine may exhibit this synergistic effect.

Measurement of Taste and Odour

Direct measurement of materials that produce tastes and odours can be made if the causative agents are known. Several types of analysis are available for measuring taste-producing inorganic. Measurement of taste and odour-causing organics can be made using **gas or liquid chromatography.** Because chromatographic analysis is time-consuming and require expensive equipment, it is not routinely performed on water samples, but should be done it problem organics are suspected.

However, because of possible synergistic effects, quantifying the sources of organics does not necessarily quantify the nature or intensity of taste and odour. Quantitative tastes that employ the human senses of taste and smell can be used e.g. the “threshold odour number” (TON). Various amounts of odourous water are poured into containers and diluted with enough odour-free distilled water to make a 200 mL mixture. An assembled panel of five to ten “noses” is used to determine the mixture in which the odour is just barely perceptible to the sense of smell. The TON of that sample is then calculated using the formula

$$TON = \frac{A + B}{A}$$

whereA = the volume (ml) of odourous water and B = the volume of odour –free water required to produce a 200 ml mixture.

Application of TON Data

Potable water is expected to be taste and odour free. However, United States Environmental Protection Agency (USEPA) does not have a maximum standard for TON. A TON of three has been recommended by the Public Health Service and serves as a guideline rather than a legal standard.

4.1.4 Temperature

Temperature is not used to evaluate directly either potable water or wastewater. It is, however, one of the most important parameters in natural surface-water systems. The temperature of surface waters governs to a large extent the biological species present and their rates of activity. Temperature has an effect on most chemical reactions that occur in natural water system. Temperature also has a pronounced effect on the solubilities of gases in water.

Sources of Temperature

The temperature of natural water systems responds to many factors, the ambient temperature (temperature of the surrounding atmosphere) being the most universal. Generally, shallow bodies of water are more affected by ambient temperatures than the deeper bodies. The use of water for dissipation of waste heat in industry and the subsequent discharge of the heated water may result in dramatic, though perhaps localised, temperature changes in receiving streams. Removal of forest canopies and irrigation return flows can also result in increased stream temperature.

Impacts of Temperature

Cooler waters usually have a wider diversity of biological species. At lower temperatures, the rate of biological activity such as food supplies utilisations, growth, reproduction, etc, is slower. An increase of 10^0C is usually sufficient to double the biological activity, if essential nutrients are present.

At elevated temperature and increased metabolic rates, organisms that are more efficient at food utilisation and reproduction flourish, while other species decline and are perhaps eliminated altogether. Accelerated growth of algae often recurs in warm water and can become a problem when cells cluster into algae mats. Natural secretion of oils by algae into the mats and the decay products of dead algae cells can result in taste and odour problems. Higher-order species, such as fish, are affected dramatically by temperature and by dissolved oxygen levels, which are a function of temperature. Game fish generally require cooler temperatures and higher dissolved-oxygen levels.

Temperature changes affect the reaction rates and solubility levels of chemicals; most chemical reactions involving dissolution of solids are accelerated by increased temperatures, while the solubility of gases, on the other hand, decreases at elevated temperatures.

4.1.5 Solids in Water Supplies

The total solids in a liquid sample consist of total dissolved solids and total suspended solids. Total dissolved solids are materials in the water that will pass through a filter with a 2.0 µm or smaller nominal average pore size. The material retained by the filter is the total suspended solids.

The amount and nature of dissolved and suspended matter occurring in liquid material vary greatly. In potable waters, most of the matter is in dissolved form and consists mainly of inorganic salts, small amounts of organic matter and dissolved gases. The total dissolved solids content of potable waters usually ranges from 20 to 1,000 mg/L, and as a rule, hardness increases with total dissolved solids.

Unlike the measurement of total suspended solids where sample drying is conducted at 103 to 105^{0}C, total dissolved solid analysis for water supplies is conducted at 180^{0}C. The reason for the higher temperature used in the latter is to remove all mechanically occluded water. Here, organic matter is generally very low in concentration and losses due to the higher drying temperature will be negligible.

Significance of Solids Determination

- Water with a total solid content of less than 500 mg/L is most desirable for domestic use.Ahigher total solid content imparts taste to the water and often has a laxative and sometimesthereverse effect upon people whose bodies are not used to the higher levels.
- Water with a high dissolved solid content tends to stain glassware and has adverseimpacts on irrigated crops, plants and grasses. The suspended solids analysis is used to ensure that an important wastewater discharge requirement is met.
- In cases in which water softening is needed, the type of softening procedure may be dictated by the dissolved solid content, since precipitation methods decrease the solidsand exchange methods increase the solids.
- Corrosion control is frequently accomplished by the production Of stabilised waters through pH adjustment. The pH stabilisation depends, to an extent, upon the totalsolids present as well as the alkalinity and temperature.

Determination of Solids in Water Supplies

Dissolved solids are the major concern in water supplies; therefore, the total solids determination and the specific conductance measurement are of greatest interest. Suspended solids tests are seldom made because of the small amounts present. They are more easily evaluated by measurement of turbidity.

Total Solids

The determination of total solids is easily made by evaporation and drying of a measured sample in a tarred container. The use of platinum dishes is highly recommended because of the ease with which they can be brought to constant weight before use. Vycor ware is a good substitute, but the use of porcelain dishes has to be avoided because of their tendency to change weight.

Specific Conductance

A rapid estimation of the dissolved solids content of a water supply can be obtained by specific conductance measurements. Such measurements indicate the capacity of a sample to carry an electric current, which in turn is related to the concentration of ionised substances in the water. Most dissolved inorganic substances in water supplies are in the ionised form and so contribute to the specific conductance. Although this measurement is affected by the nature of the various ions, their relative concentrations and the ionic strength of the water, such measurements can give a practical estimate of the variations in dissolved mineral content of a given water supply. Also, by the use of an empirical factor, specific conductance can allow a rough estimate to be made of the dissolved mineral content of water samples.

Dissolved and Suspended Matter

In cases where turbidity measurements are not adequate to provide the necessary information, the suspended solids may be determined by filtration through a glass-fibre filter. Another technique is to filter a sample of water through filter paper and determine total solids in the filtrate. The difference between total solids in unfiltered and filtered samples is a measure of the suspended solids present.

5.0 ACTIVITY

i. Discuss the nature of materials causing turbidity in (a) river water during a fresh flood, (b) polluted river water and (c) domestic wastewater.
ii. Discuss briefly the causes of colour in water.
iii. Differentiate between “apparent” and “true” colour
iv. What is the purpose of adding cobalt chloride to colour standards?
v. Suggest one method by which colour can be removed from water.

6.0 SUMMARY

In this study, you have learnt that:

- Turbidity, colour, pH and solid content of water are important prerequisite determinants as to whether a water sample will be suitable for municipal water supply purposes.
- Such parameters (turbidity, colour, pH and solid content) of a water supply affect other water characteristics of water tremendously.

7.0 ASSIGNMENT

i. For a given water sample, exactly 80mL of it was needed to make its odour just detectable. Determine the TON for this water sample and state, with reason, whether the water is safe for domestic purposes or not based on its TON value calculated given that TON < 3 is adjudged safe.

ii. What significant information is furnished by the determination of solids in a water supply sample?

iii. Why is 103 to 105^{0}C the drying temperature generally used fortotal solids analysis? Under what conditions and why is 180^{0}C sometimes used as the drying temperature?

8.0 REFERENCES

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UNIT 2 IMPORTANT CHEMICAL PARAMETERS IN WATER CHEMISTRY AND ANALYSIS

CONTENTS

1.0 INTRODUCTION

Like physical parameters, several chemical parameters are paramount to crucial decision making concerning the quality of public water supplies. Among these are pH, acidity, alkalinity and hardness.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define pH, acidity, alkalinity and water hardness
- explain how to determine acidity, alkalinity, water hardness and residual chlorine of a water sample
- interprete and apply the data obtained with respect to acidity, alkalinity, water hardness and residual chlorine/chlorine demand to practical decision making about water quality.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.

4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Some Relevant Chemical Parameters of Water

4.1.1 pH

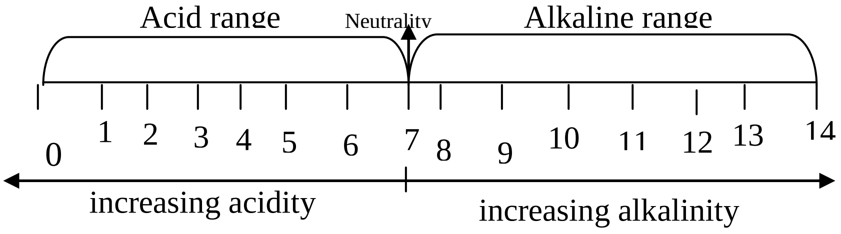
PH is a term used to express the intensity of the acid or alkaline condition of a solution. It is a way of expressing the hydrogen-ion concentration or more precisely, the hydrogen-ion activity. It is important in almost every phase of environmental science and engineering. In the field of water supplies, it is a factor that must be considered in chemical coagulation, disinfection, water softening and correction control. In wastewater treatment employing biological processes, pH must be controlled within a range favourable to the particular organisms involved. Chemical processes used to coagulate wastewaters, dewater sludges or oxidise certain substance, such as cyanide ion, require that the pH be controlled within rather narrow limits.

pH and the Ionic Product of Water (K_W)

The pH of a solution is defined as the negative logarithm to base ten of the hydrogen ion concentration of that solution. That is,

$$pH = -\log_{10}[H^+] \text{ or } pH = \log_{10}\frac{1}{[H^+]}$$

The pH scale ranges from O to 14, with pH 7 at 25^0C representing absolute neutrality.



At 250^0C, pure water dissociates as follows:

$$H_2O \longrightarrow H^+ + OH^-$$

The $[H^+]$, using the hydrogen electrode, of pure water at 25^0C has been found to be 10^{-7}? This implies that the $[OH^-]$ will also be 10^{-7}. The equilibrium equation gives:

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Since the ionisation degree is so small and the concentration is so large, it is considered that the concentration of water is constant. Hence,

$K_w = [H^+]\ [OH^-)$

For pure water at 25^0C, $K_w = 10^{-7} \text{ x } 10^{-7} = 10^{-14}$

By implication, pH = 7 and pOH =7

So, pH + pOH = 14

4.1.2 Acidity

Acidity is a measure of the ability of a given water sample to neutralise strong bases to an indicator end point. Most natural waters, domestic wastewaters and many industrial wastes are buffered principally by a carbon dioxide-bicarbonate system.

Sources and Nature of Acidity

Carbonic and species are formed when CO_2 enters surface waters. This happens when the concentration of CO_2 in water is less than that in equilibrium with CO_2 in the atmosphere. Through biological oxidation of organic matter particularly in polluted water, CO_2 produced can also be absorbed by water.

Ground waters and waters from the hypolimnion of stratified lakes and reservoirs often contain considerable amounts of CO_2 resulting from bacterial oxidation of organic matter with which the water has been in contact. Under these conditions, the CO_2 is not free to escape to the atmosphere. Carbon dioxide is an end product of both aerobic and anaerobic bacterial oxidation; therefore, its concentration is not limited by the amount of dissolved oxygen originally present. It is not uncommon to encounter ground waters with 30 to 50 mg/L of CO_2.

Mineral acidity is present in many industrial wastes particularly those of the metallurgical industry and some from the production of synthetic organic materials. The drainage from abandoned mines and iron ore dumps will contain significant amounts of sulphuric acid or salts of sulphuric acid if sulphure, sulphide or iron pyrite are present. Conversion of these materials to sulphuric acid and sulphate is brought about by sulphure-oxidizing bacteria under aerobic conditions.

$$2S + 3O_2 + 2H_2O \xrightarrow[\text{bact}]{} 4H^+ + 2SO_4^{2-}$$

$$FeS_2 + 3\tfrac{1}{2}\, O_2 + H_2O \xrightarrow[\text{bact}]{} Fe^{2+} + 2H^+ + 2SO_4^{2-}$$

Salts of trivalent heavy metals particularly e.g. Fe^{3+} and Al^{3+}hydrolyse in water to release mineral acidity.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + 3Cl^-$$

Many industrial wastes contain organic acids. Combination of fossil fuels in power plants and automobiles leads to the formation of oxides of nitrogen and sulphure, which when mixed with rain, hydrolyse to form sulphuric and nitric acids.

Significance of Acidity

Acid waters are of concern because of their corrosive characteristics and the expenses involved in removing or controlling the corrosion-producing substances. The corrosive factor in most waters is CO_2, but in many industrial wastes, it is mineral acidity. Acid rain can lower the pH in poorly buffered lakes thereby adversely affecting aquatic life, and can increase the amount of chemical, such as aluminum, leached from soil into surface.

Methods of Acidity Measurement

Both CO_2 and mineral acidity can be measured by means of standard solutions of alkaline reagents. Mineral acids are measured by titration to a pH of about 3.7, the methyl orange end point. For this reason, mineral acidity is also called **methyl orange acidity**. Titration of a sample to the phenolphthalein end point of pH 8.3 measures both mineral acidity plus acidity due to weak acids. This total acidity is also termed phenolphthalein acidity.

Determination of Acidity in Natural and Waste Waters

(a) Methyl Orange Acidity: While methyl orange was formerly used for this purpose, bromophenol blue is now recommended as it has a sharper colour change at pH 3.7. The titration is carried out using 0.02M NaOH. Results are reported in terms of methyl orange acidity expressed as $CaCO_3$. That is,

$$\text{Acidity (as mg/L } CaCO_3\text{)} = \frac{VxMx100000}{mLsample}$$

where V = mL sodium hydroxide titrant.
M = molarity of sodium hydroxide

The molecular weight of $CaCO_3$ = 100g (=100,000mg)

(b) Phenolphthalein Acidity: This measures the total acidity resulting from both mineral acids and weak acids in the sample. Either phenolphthalein or metacresol purple indicator can be used for this titration. When heavy-metal salts are present, it is usually desirable to heat the sample to boiling and then carry out the titration. The heat speeds the hydrolysis of the metal salts, allowing the titration to be completed more readily. Again, 0.02M NaOH is used as the titrating agent. Result are reported in terms of phenolphthalein acidity expressed as $CaCO_3$ as before.

Determination of Total Acidity by Mixed Indicators Method

The mixed indicator is prepared by mixing 10mL of 0.1percentthymol blue (in 50percent ethanol) with 30mL of 0.1percent phenolphthalein (in 50percent ethanol). Measure accurately 50 or 100mL of water sample into a titration flask. Add one drop of the mixed indicator. Titrate with 0.0125M barium hydroxide solution to the end point yellow (acid) to violet detected with a pH meter rather than by indicator.

$$\text{Acidity (as mg/L CaCO2)} = \frac{VxMx100000}{mLsample}$$

where V = Ml barium hydroxide

M = molarity of barium hydroxide

100000 = molar weight of $CaCO_3$ (i.e. 100g).

4.1.3 Alkalinity

The alkalinity of a water sample is a measure of its capacity, to neutralize acids. Constituents of alkalinity in natural water systems include CO_3^{2-}, HCO_3^-, OH^-, $HSiO_3^-$, $H_2BO_3^-$, HPO_4^-, HS^- and NH_3^0. These compounds result from the dissolution of mineral substances in the soil and atmosphere. Phosphates may also originate from detergents in waste water discharges and from fertilizers and insecticides from agricultural land. Hydrogen sulphide and ammonia may be products of microbial decomposition of organic material.

By far, the most common constituents of alkalinity are bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydroxide (OH^-). In addition to their mineral origin, these substances can originate from CO_2, a constituent of the atmosphere and a product of microbial decomposition of organic material, according to the following reactions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (dissolved } CO_2 \text{ and carbonic acid)}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \text{ (bicarbonate)}$$

$$HCO^-_3H^+ \rightleftharpoons HCO_3^{2-} \text{ (carbonate)}$$

$$CO^{2-}_3\ H_2O \rightleftharpoons HCO_3^- + OH^- \text{ (hydroxide).}$$

The last reaction is a weak reaction chemically. However, utilisation of the bicarbonate ion as a carbon source by algae can drive the reaction to the right and result in substantial accumulation of OH^-. Water with heavy algal growths often has pH values as high as 9 to 10.

Significance and Application of Alkalinity Data

The principal objection to alkalinewater is the reactions that can occur between alkalinity and certain actions in the water. The resultant precipitate can foul pipes and other water-system appurtenances. Alkalinity is an important consideration in calculating the lime and soda-ash requirements in softening of water by precipitation methods. It is also a means of evaluating the buffering capacity of waste waters and sludges.

Determination of Alkalinity in Natural and Treated Waters (Titration Method)

In the natural and treated waters alkalinity determination, four quantities are commonly reported. These are phenolphthalein alkalinity, total alkalinity, carbonate alkalinity and total carbon dioxide.

Determination of Phenolphthalein Alkilinity (PA)

Put 50 mL or 100 mL of water sample into a clean conical flask. Add one drop of 0.05M sodium throsulphate contents
solution to remove free residual chlorine if present. Add 2 drops of phenolphthalein indicator. If the solution remains coloured, then PA = 0. If the solution turns red, PA is present. Then titrate the solution with 0.02M HCl until the colour disappears.

The conversion obtained in this titration corresponds to:

$$OH^- + CO^{2-}_3 + 2H^+ \longrightarrow H_2O + HCO_3^-$$

Now,

$$\text{PA (as mg/L } CaCO_3) = \frac{V_P xMx100000}{mLsample}$$

whereV$_p$ = volume (mL) of the acid used
M = molarity of the acid

Determination of Total Alkalinity (TA)

Add two drops of mixed indicator (bromocresol green + methyl red solution) or of methyl orange indicator into 50 or 100 mL of water sample in a clean conical flask. Shake and titrate with 0.02M HCl acid until, at pH 4.6, the colour changes to pink (for mixed indicator) or from yellow to orange (for methyl orange indicator).

The conversion for this titration corresponds to

$OH^- + CO^{2-}{}_3 + HCO_3^- + 4H^+ \quad \rightarrow \qquad 3H_2O + 2CO_2$

Now,

TA (as mg/L $CaCO_3$) = $\frac{V_T x M x 100000}{mL sample}$

Where V_T = volume (mL) of acid used
M = molarity of acid used.

Determination of Hydroxide, Hydrogen Carbonate and Carbonate

To 50 or 100 mL of the water sample in a clean volumetric flask, add a slight excess of $BaCl_2$ solution to precipitate the carbonate. The HCO_3^- and OH^- are not affected; the $HCO^-{}_3$ is not also affected by phenolphthalein indicator. Add two drops of phenolphthalein indicator and titrate the OH^- in the water sample against 0.02M HCl until the solution is colourless. Let the volume of the acid used be V_HmL. Add two drops of the mixed indicator or methyl orange to the solution of the hydroxide/ acid titration. Shake and titrate the HCO_3^- to the end point with 0.02M HCl. Let the volume of acid used be V_{HC}mL.

To a fresh 50 or 100 mL water sample, add 2 drops of mixed indicator or methyl orange and shake. Titrate to the end point with 0.02M HCl. The volume of the acid used, V_T, is for the three species OH^-, HCO_3^- and CO_3^{2-}. Hence, the volume of acid used for CO_3^{2-} only, $V_C = [V_T-(V_H + V_{HC})]$ mL. The alkalinities can now be calculated as usual.

Determination of Total CO_2

Collect the water sample into a 500 mL flask leaving no air space. Take to the laboratory as soon as possible and siphon into a 100 mL graduated cylinder allowing overflow to occur. Add five to ten drops of phenolphthalein indicator. If the water sample turns red, the free-CO_2 is absent, but if the water remains colourless, titrate rapidly with a standard Na_2CO_3 or NaOH solution until pink colour persists for about 30 seconds.

Alkalinity as mg/L CO_2 = $\frac{V x M x 44000}{mL water sample}$

where V = volume (mL) of Na_2CO_3 OR NaOH used
M = molarity of the alkali (Na_2CO_3 or NaOH)
44000 = molar weight of CO_2 in mg.

4.1.4 Hardness

Hardness is defined as the concentration of multivalent metallic cations in water which determine the capacity of the water to precipitate soap. Depending on the anion with whichit associates, hardness is classified ascalcium and magnesium hardness, carbonate hardness and noncarbonate hardness and pseudo-hardness. Carbonate hardness is sensitive to heat and precipitates readily at high temperatures, e.g.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

Water hardness is due mainly to the presence of $Ca^{2+}$and Mg^{2+} in water. Other ions that may cause hardness include Fe^{2+}, Mn^{2+}, Sr^{2+} and Al^{3+}. The latter are found in much smaller quantities than Ca^{2+} and Mg^{2+}, and for all practical purposes, hardness may be represented by the sum of the Ca^{2+} and Mg^{2+} ions in a given water sample.

Impacts of Water Hardness

Soap consumption by hard waters represents an economic loss to the water user. Sodium soaps react with multivalent metallic cations to form a precipitate, thereby losing their surfactant properties.

$$2NaCO_2C_{17}H_{35} + Ca^{2+} \longrightarrow Ca^{2+}(CO_2C_{17}H_{35})_2 + 2Na^+$$

soapprecipitate

Lathering does not occur until all of the hardness ions are precipitated. The precipitate formed adheres to surfaces of tubs, sinks, dishwashers and may stain clothing, dishes and other items. Residues of the precipitate may remain in the pores so that skin may feel rough and uncomfortable. Boiler scale, resulting from carbonate hardness, may cause considerable economic loss through fouling of water heaters and hot-water pipes. Changes in pH of the water distribution systems may also result in deposits of precipitates. Bicarbonates begin to convert to the less soluble carbonates at pH values above 9.0.

Magnesium hardness, particularly associated with the sulphate ion, has a laxative effect on persons unaccustomed to it. Magnesium concentrations of less than 50 mg/L are desirable in potable waters although many public water supplies exceed this amount.

Determination of Hardness

Hardness can be measured by using spectrophotometric techniques or chemical titration to determine the quantity of calcium and magnesium ions in a given water sample. Hardness can be measured directly by titration with ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T (EBT) as an indicator. The EBT reacts with the divalent metallic cations, forming a complex that is red in colour. The EDTA replaces the EBT in the complex, and when the replacement is complete, the solution changes from red to blue.

$$M^{n+} + EBT \longrightarrow M-EBT$$

$$\underset{\text{red}}{M-EBT} + EDTA \longrightarrow \underset{\text{blue}}{M-EDTA} + EBT$$

If 0.01M EDTA is used, 1.0 mL of the titrant measures 1.0 mg of hardness as $CaCO_3$.

Application of Hardness Data

Hardness of water is an important consideration in determining the suitability of a given water source for domestic and industrial uses. The environmental engineer uses it as a basis for recommending the need for softening processes and design types. Hardness may range from practically zero to several hundred or thousand parts per million. Although acceptability levels vary according to a consumer's acclimation to hardness, a generally accepted classification is as follows:

Soft water < 50 mg/L as $CaCO_3$
Moderately hard water 50 – 150 mg/L as $CaCO_3$
Hard water 150 – 300 mg/L as $CaCO_3$
Very hard water > 300 mg/L as $CaCO_3$

The Public Health Service Standards recommend a maximum of 500 mg/L of hardness in drinking water.

5.0 ACTIVITY

i. What is the pH and pOH of a solution containing (a) 1.008g of H^+ and (b) 0.1008g of H^+, per litre?

ii. a. What causes acidity in natural waters?
   b. What pH range is used to measure
      (1) Mineral Acidity and (2) Total Acidity, in water?
   c. Why are we concerned with acidity in water?

iii. a. Briefly discuss the presence of alkalinity in natural waters.
   b. Of what benefits is alkalinity in natural water?

6.0 SUMMARY

In this unit, you have learnt that:

- pH of a given natural water sample may generally range from acidic to alkaline region.
- Different organisms and chemical species respond to pH variations differently.
- Acidity and alkalinity come from both natural and anthropogenic sources.
- Chemical parameters of water determine, to a large extent, the purposes a given water supply may serve.

7.0 ASSIGNMENT

i. Discuss the principles involved in the EDTA titrimetric method of measuring hardness of water.
ii. Calculate the phenolphthalein and total alkalinities of a 50 mL water sample that required 5.3 mL 0.02M HCl to reach the phenolphthalein end point and a total of 15.2 mL to reach the methyl orange end point.

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UNIT3 BIOCHEMICAL PARAMETERS IN WATER CHEMISTRY AND ANALYSIS

1.0 INTRODUCTION

Natural watercourses contain many dissolved minerals and gases that interact chemically with one another in complex and varied ways. The interaction may alternately aid or obstruct natural purification processes of natural water systems. Strictly speaking, most of the chemical interactions that play a part in self-purification of watercourses are biologically mediated. These chemical reactions are not spontaneous, but require an external source of energy for initiation.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD)
- discuss the procedures of measuring DO, BOD and COD
- state the environmental significance of DO, BOD and COD data.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.

4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Biochemical Parameters Crucial to Water Chemistry and Analysis

4.1.1 Dissolved Oxygen (DO)

All the gases of the atmosphere are soluble in water to some degree. Both nitrogen and oxygen are classified as poorly soluble. Since they do not react with water chemically, their solubility is directly proportional to their partial pressures.

The solubility of oxygen in saline water is less than in fresh water. The solubility of atmospheric oxygen, in fresh waters ranges from 14.6 mg/L at 0^0C to about 7 mg/L at 35^0C under oneatm of pressure. Dissolved oxygen is one of the most important constituents of natural water system. A stream must have a minimum of about two mg/L of dissolved oxygen to maintain higher life forms such as fish and other aquatic animal species. At least, four mg/L of dissolved oxygen is required for game fish and some species may require more.

The amount of oxygen found by determination in a sample of water at the time of collection is the dissolved oxygen.

Methods of DO Determination

The Winkler of iodometric method and its modifications are the standard volumetric procedures for determining dissolved oxygen. The test depends upon the fact that oxygen oxidises Mn^{2+} to a higher state of valence under alkaline conditions and that Mn in higher states of valence is capable of oxidising I^- to I_2 under acidic conditions. Thus, the amount of I_2 released is equivalent to the dissolved oxygen originally present. The iodine is measured with standard sodium thiosulphate solution and interpreted in terms of dissolved oxygen.

The Winkler Method (Unmodified)

The unmodified Winkler method is applicable only to relatively pure waters since the method is subject to interference from a great many substances. Certain oxidising agents such as nitrite (NO_2^-) and Fe^{3+} are capable of oxidising I^- to I_2 and produce results that are too high. Reducing agents such as Fe^{2+}, SO_3^{2-}, S^{2-} and polythionate, reduce I_2 to I^- and produce results that are too low.

The reactions involved are:

$Mn^{2+} + 20H^- \longrightarrow Mn(OH)_2(s)$ (white precipitate)

$Mn^{2+} + 20H^- + ½O_2 \longrightarrow MnO_2(s) + H_2O$

or $Mn\ (OH)_2 + ½O_2 \longrightarrow MnO_2(s) + H_2O$

If no oxygen is present, a white precipitate of $Mn(OH)_2$ forms when $MnSO_4$ and the alkali-iodide reagent (NaOH + KI) are added to the sample. But if oxygen is present, some of the Mn^{2+} is thenoxidised to Mn^4 andprecipitates as a brown hydrated oxide.

After shaking the sample for a time sufficient (at least 20 seconds) to allow all oxygen to react, the floc is allowed to settle; then H_2SO_4 is added. Under the low pH conditions, the MnO_2OXIDISEs I^- to I_2.

$$MnO_2 + 2I^- + 4H^+ \longrightarrow Mn^{2+} + I_2 + 2H_2O$$

I_2 is rather insoluble in water, but forms a complex with the excess I^- present to reversibly form the more soluble tri-iodate, thus preventing the escape of I_2 from solution

$$I_2 + I^- \rightleftharpoons I_3^-$$

Stopper the sample and shake for 10 seconds or more. Titrate the samples (200 mL) with 0.0125M or 0.025N thiosulphate to the end point. The mL of thiosulphate used is interpreted directly in terms of mg/L of dissolved oxygen.

The Azide Modification of the Winkler Method

The nitrite ion is one of the most frequent interferences encountered in the DO determination of wastewaters, river waters and incubated biochemical oxygen demand (BOD) samples. It does not oxidise Mn^{2+} but does oxidise I^- to I_2 under acidic conditions. It is particularly troublesome because its reduced form, N_2O_2, is oxidised by oxygen, which enters the sample during the titration procedure and is converted to NO_2^- again, establishing a cyclic reaction that can lead to erroneously high results. The reactions involved are:

$$2NO_2^- + 2I^- + 4H^+ \longrightarrow I_3 + N_2O_2 + 2H_2O$$

$$N_2O_2 + ½O_2 + H_2O \longrightarrow 2NO_2^- + 2H^+$$

When interference from nitrite is present, it is impossible to obtain a permanent end point. As soon as the blue colour of the starch indicator is discharged, the nitrite formed will react with more I^- to produce I_2 and the blue colour of the starch indicator will return. To overcome this interference, sodium azide (NaN_3) in alkali-KI reagent is used. When

H_2SO_4 acid is added, the following reactions occur and the NO_2^- is destroyed

$$NaN_3 + H^+ \longrightarrow HN_3 + Na^+$$

$$HN_3 + NO^-_2 + H^+ \longrightarrow N_2 + N_2O + H_2O$$

By this procedure, nitrite interference is eliminated and the method of determination retains the simplicity of the original Winkler procedure.

$$\text{mg/L DO} = \frac{16000xMxV}{\frac{V_2}{V_1}(V_2 - 2.0)}$$

where M = molarity of thiosulphate solution

V = Volume of thiosulphate (mL) used for titration

V_1 = Volume of the bottle with stopper in place

V_2 = Volume of aliquot taken for titration

If all the contents of the bottle are titrated, then mg/L DO = $\frac{16000xMxV}{(V_1 - 2.0)}$

4.1.2 Biochemical Oxygen Demand (BOD)

The amount of oxygen consumed during microbial utilisation of organics in a water sample is called the BOD. The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD value.

Measuring the BOD

The BOD is measured by determining the oxygen consumed from a water sample placed in an air-tight container and kept in a controlled environment for a preselected period of time. In the standard test, a 300 mL BOD bottle is used and the sample is incubated for five days at 20^0C. Light must be excluded from the incubator to prevent algal growth that may produce oxygen in the bottle. Because the saturation concentration for oxygen in water at 20^0C is approximately nine mg/L, dilution of the sample with BOD-free, oxygen-saturated water is necessary to measure BOD values greater than just a few mg/L.

The BOD of a diluted sample is calculated by

$$BOD = \frac{DO_i - DO_f}{P}$$

whereDO$_i$ = the initial dissolved oxygen concentration (mg/L)

DO$_f$ = the final dissolved oxygen concentration (mg/L).

P = the decimal fraction of the sample in the 300mL bottle.

Most natural waters and municipal wastewaters will have a population of microorganisms that will consume the organics. In sterile waters, microorganism must be added and the BOD of the material containing the organisms must be determined and subtracted from the total BOD of the mixture. The presence of toxic materials (such as residual chlorine, chloramines and copper) will invalidate the BOD results.

Determining BOD_5

The BOD of a wastewater was suspected to range from 50 to 200 mg/L. Three dilutions (5, 10 and 20 mL) of the wastewater were prepared to cover this range of 50 to 200 mg/L. First, the samples (5, 10 and 20 mL wastewater) were placed in three respective 300 mL standard BOD bottles. Each was then diluted to 300 mL with organic free, oxygen-saturated water. The initial dissolved oxygen was determined and the bottles tightly stoppered and placed in the incubator at 20^0C for five days, after which the dissolved oxygen was again determined. The values obtained are as computed in the table below.

Wastewater (mL)	**DO_i mg/L**	**DO_5 mg/L**	**O_2 used mg/L**	**P**	**BOD_5 mg/L**
5	9.2	6.9	2.3	$\frac{5}{300} = 0.0167$	138
10	9.1	4.4	4.7	$\frac{10}{300} = 0.033$	142
20	8.9	1.5	7.4	$\frac{20}{300} = 0.067$	110

Since the final DO is less than 2.0 mg/L, the third BOD_5 value of 110 mg/L can be disregarded. Thus, the average BOD_5 of the waste water is ½ (138+142) mg/L i.e. 140 mg/L.

Application of BOD Data

BOD is the major criterion used in stream pollution control where organic loading must be restricted to maintain desired dissolved-oxygen levels. The determination is used in studies to measure the purification capacity of streams. It helps regulatory authorities in checking the quality of effluent discharged to streams. Information concerning the BOD of wastes is an important consideration in the design of treatment facilities. After treatment plants are placed in operation, the test is used to evaluate the efficiency of various processes.

4.1.3 Chemical Oxygen Demand

COD is a measure of the total amount of oxygen required for complete oxidation to CO_2 and H_2O of organic matter present in a sample of wastewater or effluent. COD is a rapidly measured parameter used to determine the pollution strength of domestic and industrial waste.

The determination is achieved by using strong oxidising agents under acidic conditions. Excess amount of the oxidising agent is used. Oxygen is released, some is used to oxidisean equivalent amount of the waste to CO_2 and the unused is determined by titration with a reducing agent of known strength. The amount used for the oxidation of the wastes is known by difference. Potassium dichromate, $K_2Cr_2O_7$, is the most suitable oxidising agent. The reaction is:

$$Cr_2O^{2-}{}_7 + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

or $$Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 4H_2O + 3(O).$$

Ferrous ion is an excellent reducing agent for dichromate. The reaction is:

$$Cr_2O^{2-}{}_7 + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$$

Ferroin (1, 10 – Phenanthroline monohydrate + iron (II) sulphateheptahydrate) is an excellent indicator for this purpose. It gives a very sharp brown colour change that is easily detected. Calculation of COD is made from the formula:

$$\text{COD (mg/L)} = \frac{(V_b - V_s)xMx16000}{mLsample}$$

or $$\text{COD (mg/L)} = \frac{(V_b - V_s)xNx16000}{mLsample}$$

whereV_b = mL ferrous ammonium sulphate used for blank
V_s = mL ferrous ammonium sulphate used for sample
M = molarity of ferrous ammonium sulphate
N = normality of ferrous ammonium sulphate

Inorganic Interferences

Among the reduced inorganic ions that can be oxidised under the conditions of COD test, Cl^- causes the most serious problems because it is usually present in high concentrations in most wastewaters. Its presence can cause erroneously high results to be obtained.

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

However, this interference can be eliminated by the addition of mercuric sulphate to the sample prior to the addition of other reagents. The mercuric ion combines with the chloride ion to form a poorly ionised mercuric chloride complex.

$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2$$

Nitrite ion, NO_2^-, is another source of interference capable of being oxidised to nitrate in the pressure of dichromate. This interference can be overcomes by the additioin of sulfamic acid to the dichromate solution. Nitrite ion, with other ones such as ferrous and sulphide ions that can also cause interference, seldom occur to any significant amounts in waste or natural waters.

Applications of COD Data

In conjunction with the BOD test, the COD test is helpful in indicating toxic conditions and the presence of biologically resistant organic substances. The test is widely used in the operation of treatment facilities because of the speed with which results can be obtained.

5.0 ACTIVITY

i. How does azide eliminate the nitrite interference in the iodometric method for determining dissolved oxygen?
ii. List two requirements that must be complied with in order to obtain reliable BOD data.
iii. List two different applications of COD data.

6.0 SUMMARY

In this unit, you have learnt that:

- all the atmosphere gases can dissolve in water to some extent;
- DO, BOD AND COD are informative parameters when determined to have an understanding of wastewater quality;
- there can be chemical or organic species that are capable of interfering with the results obtained in DO, BOD and COD determinations.

7.0 ASSIGNMENT

i. List four inorganic species that interfere with COD analysis.
ii. Which of the species is the most prevalent and how do you handle the interference caused by this particular species?

8.0 REFERENCES

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UNIT 4 ANIONS AND OTHER CONSTITUENTS OF CONCERN IN WATER CHEMISTRY AND ANALYSIS

1.0 INTRODUCTION

Depending on their levels in a given water source and the use for which the water is intended, anions like chloride (Cl^-), fluoride (F^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) and residual chlorine, nitrogen, iron and manganese, oil and grease, and volatile acids, can all constitute sources of worries. It is true that some of them occur naturally in the environmental compartments, but they can pose stressful conditions on humans and the biota whenever their natural background levels are exceeded in water bodies.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- name some common anions usually found in water bodies and state their health and environmental implications in water supplies
- discuss the basic relevant chemistry of the anions and other water contaminants such as nitrogen and residual chlorine in water
- list relevant methods that can be used to determine the presence of Cl^-, F^-, SO_4^{2-} and PO_4^{3-} in a waste water sample.

3.0 HOW TO STUDY THIS UNIT

1. You are expected to read carefully, through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments.
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers.
3. Share your difficulties with your course mates, facilitators and by consulting other relevant materials particularly the internet.
4. Note that if you follow the instructions you will feel self fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

4.0 MAIN CONTENT

4.1 Common Anions in Natural and Wastewaters

4.1.1 Chloride (Cl^-)

Chloride occurs in all natural waters in varying concentrations. The chloride content normally increases as the mineral content increases. Upland and mountain supplies are usually quite low in chloride, whereas river and ground waters usually have a considerable amount. Chloride levels in sea and ocean waters are very high.

Chloride content in a water sample can be determined by Mohr Method, Mercuric Nitrate Method and Ferricyanide Method.
In reasonable concentrations, chloride is not harmful to humans. At concentrations above 250 mg/L, it gives a salty taste to water, which is objectionable to many people. The USEPA Secondary Standard for chloride in drinking water is 250 mg/L, the same value contained in the WHO guidelines. Evapotransportation tends to increase the chloride and salinity at the root zone of irrigated plants, making it difficult for crops to take up water due to osmotic pressure differences. As such, chloride and total salinity concentrations at or below the drinking water standards are normally specified for waters used to irrigate salt-sensitive crops.

4.1.2 Fluoride (F^-)

The monitoring of the presence and level of fluoride ion in water requires greater vigilant efforts than is given to chloride ion. This is because of the health implications of fluoride ion especially in humans. Approximately one mg/L of fluoride ion is desirable in public waters for optimal dental health. At decreasing levels, dental caries becomes a serious problem, and at increasing levels, dental fluorosis (mottled enamel) becomes a problem. In the recent times, a higher level of fluoride is being implicated for liver problems as well.

The principal forms in which fluoride is added to public water supplies are sodium fluoride (NaF), calcium fluoride (CaF_2), hydrogen fluoride (HF), sodium silicofluoride (Na_2SiF_6), hydrofluosilicic acid (H_2SiF_6) and ammonium silicofluoride [$(NH_4)_2SiF_6$]. All these compounds dissociate in water to yield fluoride ion. At the concentrations of about one mg/L involved in water treatment, hydrolysis of the fluosilicate ion is essentially complete.

$$SiF_6^{2-} + 3H_2O \rightleftarrows 6F^- + 6H^+ + SiO_3^{2-}$$

On this basis, the fluoride in silicofluorides can be determined by any method that is sensitive to fluoride ion e.g. the electrode method, colorimetric procedures and ion chromatography. Excess fluoride in water can be removed by passing of water through various types of defluoridation media such as tricalcium phosphate, bone char and bone meal. Activated alumina was found to accomplish fluoride removal by a combination of ion exchange and sorption. Fluoride can also be removed during lime softening through co-precipitation with magnesium hydroxide or by alum coagulation.

4.1.3 Sulphate (SO_4^{2-})

Sulphate ion is one of the major anions occurring in natural waters. It has a cathartic effect upon humans when it is presents in excessive amounts in public water supplies. The USEPA Secondary Standard for sulphate is 250 mg/L in waters intended for human consumption. Sulphate is important in both public and industrial water supplies because of the tendency of waters containing appreciable amounts to form hard scales in boilers and heat exchangers.

Sulphate is of considerable concern because it is indirectly responsible for serious problems of odour and sewer-corrosion resulting from the reduction of SO_4^{2-} to H_2S under anaerobic conditions.

$$SO_4^{2-} + \text{organic matter} \xrightarrow{\text{bacteria}} S^{2-} + H_2O + CO_2$$
$$S^{2-} + H^+ \rightleftarrows HS^-$$
$$HS^- + H^+ \rightleftarrows H_2S$$

Bacteria of the genus *Thiobacillus*are ubiquitous in nature and are capable of sulphide oxidation to sulphuric acid at a pH as low as 2 under the aerobic conditions normally prevailing in sewers.

$$H_2S + 2O_2 \xrightarrow[\text{bacteria}]{} H_2SO_4$$

Being a strong acid, H_2SO_4 attacks the concrete in the sewer. H_2SO_4 formation in this way is particularly serious in the crown, where drainage is at a minimum. Drainage running through abandoned coal mines and other exploited mineral-bearing deposits can be a source of high sulphate concentrations as well as low pH conditions in the streams within the vicinity. The sulphide minerals are oxidised through bacterial and chemical actions to produce sulphuric acid

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow[\text{bacteria}]{} 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

The lowered pH and high iron content procedure added harm to water quality. Combustion of fossil fuels leads to formation of gaseous oxides of sulphure which hydrolyse when dissolved in rainwater to form sulphuric acid. Analysis of SO_4^{2-}in a sample of wastewater can be carried out using gravimetric, turbidimetric and automated methylthymol blue analysis.

4.1.4 Phosphate (PO_4^{3-}).

The inorganic compounds of phosphorus of significance in environmental chemistry are the phosphates or their molecularly dehydrated forms (polyphosphates) or condensed phosphates. Organically bound phosphorus is usually a minor consideration. Phosphorus compounds commonly encountered in environmental science generally are **orthophosphates** such as trisodium phosphate (Na_3PO_4), disodium phosphate (Na_2HPO_4), monosodium phosphate ((NaH_2PO_4) and diammonium phosphate ($(NH_4)_2HPO_4$), and **polyphosphates** such as sodium hexametaphosphate ($Na_3(PO_3)_6$), sodium tripolyphosphate ($Na_5P_3O_{10}$) and tetrasodium pyrophosphate ($Na_4P_2O_7$).

Polyphosphates are used in some public water supplies as a means of controlling corrosion. They are also used in some softened waters for stabilisation of calcium carbonate to eliminate the need for recarbonation. Both nitrogen and phosphorus are essential for the growth of algae and cyanobacteria. Limitation in amounts of these elements is usually the factor that controls their rate of growth. Where both nitrogen and phosphorus are plenty, algal blooms occur, which may produce a variety of nuisance conditions. The critical level for inorganic phosphorus in water has been put at approximately 0.005mg/L (5 µg/L).

Phosphorus occurring as orthophosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-},

PO_4^{3-}) can be measured quantitatively by gravimetric, volumetric or colorimetric methods. Polyphosphates are first converted to orthophosphates by boiling acidified sample for 90 minutes or more. Organic phosphorus is first digested before the phosphorus measurement is carried out.

4.1.5 Residual Chlorine

The prime purpose of disinfecting public water supplies and wastewater effluents is to prevent the spread of waterborne diseases. The practice of disinfection with chlorine has become so widespread and generally accepted as if no problem is associated with the practice.

In more recent years, chlorination has been found to produce trichalomethanes and other organics of health concern. Thus, the use of alternative disinfectants, such as chloromines, chlorine dioxide, UV radiation and ozone, which do not cause this particular problem, is increasing. One important limitation is that chlorination alone is not sufficiently protective against some disease-causing protozoa such as *Giardia lamblia*and *Cryptosporidium paevum;* good filteration is also required. Chlorine is used to disinfect water in the form of free chlorine or as hypochlorite. In either form, it acts as a potent oxidizing agent. Chlorine combines with water to form hypchlorous and hydrochloric acids. The hydrochlorous acid formed is a weak acid and is very poorly dissociated at pH< 6.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

The nature of the reactions is dominated by the free Cl_2 with the resultant development of obnoxious compounds such as tri-chloramine, NCl_3. to minimise these effects, high-quality water is often used as chlorinator feed water. Hypochlorite is used in the form of solutions of sodium hypochlorites and the dry form of calcium hypochlorite. Solution of Na hypochlorite is popular where large amounts are necessary such as in wastewater disinfection, while Ca hypochlorite is popular where limited amounts are required or intermittent usage is dictated. Both compounds ionise in water to yield hypochlorite ion, OCl^-. Free chlorine tends to decrease the pH, whereas hypochlorite tends to increase the pH.

$$NaOCl \rightarrow Na^+ + OCl^-$$
$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^-$$

Reactions of Chlorine and Hypochlorous acid with Substances in Water

- **Reactions with NH_3**: Ammonia reacts with chlorine or hypochlorous acid to form monochoramine, dichloramine and trichloromaine depending on the relative amounts of each, and to some extent, on the pH.

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

In water chemistry, chlorine, hypochlorous acid and hypochlorite ion are called free chlorine residuals while chloramines are called combined chlorine residuals.

- **Reactions with reducing agents:** Chlorine combines with a wide variety of reducing agents such as H_2S, Fe^{2+}, Mn^{2+} and NO_2^-. Their demand for chlorine must be satisfied beforechlorine becomes available to accomplish disinfection.

$Cl_2 + H_2S \rightarrow 2HCl + S$

- **Reactions with unsaturated organic compounds:** Organic compounds that possess unsaturated linkages will add hypochlorous acid and increase the chlorine demand

$H_2C{=}CH_2 + HOCl \rightarrow H_2C(OH)CH_2(Cl)$

- **Reactions with other halogens:** Chlorine also reacts with other halogens in water e.g. hypochlorous acid reacts with bromide to form hypobromous acid.

$HOCl + Br^- \rightarrow HOBr + Cl^-$

- **Reactions with phenols:** Chlorine reacts with phenols to produce mono-, di-, or trichlorophenols, which can impart tastes and odours to waters.

- **Reactions with humic substances:** Chlorine and hypobromous acid react with humic substances present in most halogenated products including **trihalomethanes** (THMs) such as chloroform, bromodichloromethane, dibromochloromethane and bromoform, and **haloacetic acids**. The THMs are suspectedhuman carcinogens which are regulated in drinking water with a sum total maximum contaminant level (MCL) of 80 µg/L.

4.1.6 Nitrogen

The compounds of nitrogen are of great importance in water resources, in the atmosphere and in the life processes of all plants and animals. Nitrogen can exist in seven oxidation states, and all of them are of environmental interest: NH_3 (-3); N_2 (0); N_2O (+1); NO (+2); N_2O_3 (+3); NO_2 (+4) and N_2O_5 (+5). Three of these (NH_3, N_2O_3 and N_2O_5) combine with water to form inorganic ionised species (NH_4^+, NO_2^- and NO_3^-) that can reach high concentrations,

$$\begin{aligned} NH_2 + H_2O &\rightarrow NH_4^+ + OH^- \\ N_2O_3 + H_2O &\rightarrow 2H^+ + 2NO_2^- \\ N_2O_5 + H_2O &\rightarrow 2H^+ + 2NO_3^- \end{aligned}$$

The respective water-soluble species formed: ammonium, nitrite and nitrate ions, are of historical environmental concern in water. Their concentrations in drinking water supplies and surface waters have been regulated for decades.

In water, most of the nitrogen is originally present in the form of organic (protein) nitrogen and ammonia. As time progresses, the organic nitrogen is gradually converted to ammonia nitrogen, and later on, if aerobic conditions are present, oxidation of ammonia to nitrite and nitrate occurs. Thus, waters that contained mostly organics and ammonia nitrogen were considered to have been recently polluted and therefore of great potential danger. Waters in which most of the nitrogen was in the form of nitrate were considered to have been polluted a long time previously and therefore offered little threat to the public health. Waters with appreciable amounts of nitrite were of highly questionable character.

Waters with high nitrate content often caused methaemoglobinaemia in infants as a result of the interaction of nitrite with haemoglobin; the nitrite being formed from nitrate reduction in the digestive system. The USEPA has set a MCL requiring that the nitrate-nitrogen concentration not exceed 10 mg/L and the nitrite-nitrogen concentration not exceed 1 mg/L in public water supplies. Nitrite can also interact with amines enzymatically or chemically, especially when chlorinating for disinfection, to form nitrosamines, which are strong carcinogens.

The formation of N- nitrosodimethylamine (NDMA) by these processes has been found to result during wastewater treatment and has become an issue recently in wastewater reuse projects and contaminated groundwater supplies.

4.1.7 Iron and Manganese in Water

Both iron and manganese create serious problems in public water supplies. The problems are most extensive and critical with underground waters, but difficulties are encountered at certain seasons of the year in waters drawn from some rivers and some impounded surface supplies. Why some underground supplies are relatively free of iron and manganese and others contain so much has been a difficult explanation when viewed solely from the view point of inorganic chemistry alone. Changes in environmental conditions brought about by biological reactions, are major considerations.

It is important to consider how iron and manganese are converted to soluble forms and gain access into water since both of them are present in insoluble forms in significant amounts in nearly all soils. Iron exists in soil and minerals mainly as insoluble ferric oxides and iron sulphide (pyrite). It occurs in some areas also as ferrous carbonate (siderite) which is only very slightly soluble. Since ground waters usually contain significant amounts of CO_2, appreciable amounts of ferrous carbonate may be dissolved in a manner similar to that of calcium and magnesium carbonates dissolution.

$$FeCO_3(s) + CO_2 + H_2O \rightarrow Fe^{2+} + 2HCO_3^-.$$

Dissolution of measurable amounts of iron from insoluble solid ferric compounds does not occur, even in the presence of appreciate amounts of CO_2, as long as dissolved oxygen is present. Under reducing (anaerobic) conditions, however, the ferric iron is reduced to ferrous iron, and solution occurs without difficulty.

Manganese exists in the soil principally as manganese dioxide, which is very insoluble in water containing carbon dioxide. Under anaerobic conditions, Mn in the dioxide form is reduced from an oxidation state of IV to II, and solution occurs, as with ferric oxides.

When oxygen-bearing water is injected into the ground for recharge of the groundwater aquifer, it is sometimes noted that the soluble iron content of the water increases. This observation seems to contradict the need for anaerobic conditions. The explanation is that the oxygen is consumed through the oxidation of insoluble pyrite (FeS_2), leading to anaerobic conditions and the formation of soluble iron sulphate. Only under anaerobic conditions are the soluble forms of iron and manganese (Fe(II) and Mn(II)) thermodynamically stable.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO^{2-}_4 + 4H^+$$

As far as it is known, humans suffer no harmful effects from drinking waters containing iron and manganese. Such waters, when exposed to the air become turbid and highly unacceptable from an aesthetic viewpoint, owing to the oxidation of Fe(II) and Mn(II) to Fe(III) and Mn(IV) respectively. Both iron and manganese interfere with laundering operations, impart objectionable stains to plumbing fixtures and cause difficulties in distribution systems by supporting of iron bacteria. Iron also imparts a taste to water which is detectable at very low concentrations. For these reasons, the USEPA secondary standards for iron and manganese in public water supplies are 0.3 mg/L and 0.05 mg/L respectively.

4.1.8 Oil and Grease in Water

The oil and grease content of domestic and certain industrial wastes, and sludges, is an important consideration in the handling and treatment of these materials for ultimate disposal. Oil and grease have poor solubility in water and do separate from the aqueous phase. This characteristic of oil and grease complicates the transportation of wastes though pipeline, their destruction in biological treatment units and their eventual disposal into the receiving streams.

Very few processing plants have provisions for the separate disposal of waters from meat-packing industry and restaurants to scavengers or by incineration. As a result, the oil and grease which separate as scum, in primary settling tanks are normally transferred with the settled solids to disposal units. In sludge digestion tanks, oil and grease tend to separate and float on the surface to form dense scum layers. Scum problems have been particularly severe where high-grease-content wastes have been admitted to public sewer systems. The vacuum filtration of sludge is also complicated by high grease content.

Not all the oil and grease is removed from the sewage by primary settling units. Appreciable amounts remain in the clarified wastewater in a finely divided emulsified form. During subsequent biological attack in secondary treatment units or in the receiving stream, the emulsifying agents are usually destroyed, and the finely divided oil and grease particles become free to coalesce into grease particles that separate from the water. In activated-sludge plants, the grease often accumulates into “grease balls” that give an unsightly appearance to the surface of final settling tanks. Both trickling filters and the activated sludge process are adversely affected by unreasonable amounts of grease that seems to coat the biological solids sufficiently to interfere with oxygen transfer from the liquid to the interior of the living cells. This is sometimes described as a “smothering” action.

Spills of crude and refined petroleum from ships used for their transport have resulted in loss of fish, mammals and waterfowl, and the fouling of beaches. Also, oil and grease leaking from automobiles result in high concentrations in storm runoff from streets, contaminating water ways into which storm water drains.

4.1.9 Volatile Acids in Water

The volatile-acids determination is widely used in the control of anaerobic waste treatment processes. In the biochemical decomposition of organic matter that occurs, facultative and anaerobic bacteria of wide variety hydrolyse and convert the complex materials to low-molecular-weight compounds. Among the low-molecular-weight compounds formed are the short-chain fatty acids such as acetic, propionic, butyric, and to a less extent, isobutyric, valeric, isovaleric and caproic, are important components. These low-molecular-weight fatty acids are termed **volatile acids** because they can be distilled at atmospheric pressure.

An accumulation of volatile acids can have a disastrous effect upon anaerobic treatment if the buffering capacity of the system is exceeded and the pH falls to unfavourable levels.

In anaerobic digestion, units that are operating in a stabilised condition, three groups of bacteria work in harmony to accomplish the destruction of organic matter. Following hydrolysis and fermentation to complex acids, the acidogenic and dehydrogenating organisms carry the degradation to acetic acid and hydrogen. Then the methanogenic bacteria complete the conversion into methane and carbon dioxide. When a sufficient population of methanogenic bacteria is present and environmental conditions are favourable, they utilise the end products produced by acidogenic bacteria as fast as they are formed. As a result, acids do not accumulate beyond the neutralising abilities of the natural buffers present, and the pH remains in a favourable range for the methane bacteria. Under such conditions, the volatile acid content of digesting sludges, or anaerobically treated wastewaters usually runs in the range of 50 to 250 mg/L.

Untreated municipal wastewater sludges and many industrial wastewaters have a relatively low buffering capacity, and when they are allowed to ferment anaerobically, volatile acids are produced so much faster than the few methanogenetic bacteria present can consume them that the buffers are soon spent and free acids exist to depress the pH. At pH values below 6.5, methanogenetic bacteria are seriously inhibited, but many fermentative and acidogenic bacteria are not until pH levels fall to about five. Under such unbalanced conditions, the volatile-acids concentration continues to increase to levels of 2000 to 6000mg/L or more, depending upon the solids content of the sludge.

5.0 ACTIVITY

Activity1

1. Discuss briefly the effects of excess amounts of chloride fluoride, sulphate and phosphate ions in a water supply intended for domestics use.

Activity2

Explain the observation: "Free chlorine, used as a water supply disinfectant, tends to decrease the pH, whereas hypochlorite tends to increase the pH". Equations of the chemical reactions involved are important.

Activity3

1. (a) In what forms does nitrogen normally occur in natural water?
   (b) What is the importance of nitrogen analysis in water pollution control?
2. What is the environmental significance of iron and manganese in water supplies?
3. Discus briefly how iron and manganese get into underground water supplies.

Activity4

1. List four important sources that contribute oil and grease to municipal wastewaters.
2. Name five difficulties that could arise in the process of treating wastewaters with high levels of oil and grease.
3. (a) What is meant by "volatile acids"?
   (b) Indicate (i) what are the most prevalent volatile acids formed during anaerobic treatment, (ii) the general classes of organic compounds from which each of the most prevalent volatile acids result.

6.0 SUMMARY

In this unit, you have learnt that:

- the levels of Cl^-, F^-, SO^{2-}_4 and PO^{2-}_4 in a given water sample can be part of the indicesused toassess the quality of the water.
- residual chlorine in water can lead to the formation such compounds known to be human carcinogens e.g. chloroform.
- the presence of nitrogenous compound can directly or indirectly affect a water quality and the uses to which the water can be put.
- metals like Fe and Mn can still find their ways into the groundwater even when the metals were not originally found in soluble forms.
- oil and grease and volatile acids can constitute very serious problems at various stages of waste water treatment particularly.

7.0 ASSIGNMENT

1. Discuss one analytical method in each case for measuring the concentration of (i) Mn and(ii) Fe, in water supplies.

8.0 REFERENCES

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