ENVIORNMENTAL CHEMISTRY

(DCHE24)

(MSC CHEMISTRY)

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PAPER – VIII : ENVIRONMENTAL CHEMISTRY

SYLLABUS

Unit – I
BASIC SEGMENTS OF ENVIRONMENT & LITHOSPHERE

Environmental Chemistry – Significance of basic segments of environment – Nomenclature in the study of environmental chemistry.

Lithosphere – Principles of weathering – effect of temperature, water, air, plants and animals on weathering., Soil formation / development – factors affecting soil development – functions of soils – soil colloids – ion exchange properties.

Analysis of soil: Sampling, determination of moisture, total nitrogen, phosphorous, silicon, lime, humus, nitrogen, alkali salts

Unit – II
AIR POLLUTION

Atmospheric sources and emission of air pollutants – carbon monoxide-sulphur, oxides-oxides of nitrogen, organic pollutants and photo chemical smog-particulates – acid rain., and control with special reference to particulate and radioactive substances.

Analysis of carbon mono oxide – carbon dioxide – sulphur dioxide – hydrogen sulfide, oxides of nitrogen, ammonia, ozone, hydrocarbons, aromatic hydrocarbons.

Unit – III
HYDROSPHERE AND WATER POLLUTION

Hydrosphere – water resources – hydrological cycle – unique properties of water – composition of sea water – water quality parameters – domestic water pollution – industrial, agricultural, solid waste, thermal, shipping water pollution and radio active waste pollution.

Effects of soaps, detergents, pesticides, hydrocarbon with regard to water pollution.

Effect of specific pollutants like mercury, lead, arsenic, selenium, nitrites, oil.

Unit – IV
ANALYSIS AND TREATMENT METHODS IN CASE OF WATER POLLUTION

Continuous monitoring of water pollutants – principles, monitoring instruments, monitoring of sulphur dioxide, hydrogen sulphide, oxides of nitrogen, oxides of carbon, hydrocarbons, ozone and suspended particulate matter. Determination of DO, COD, BOD, phosphates, nitrogen compounds.

Techniques of water treatment – primary, secondary and territory methods – use, of coagulants – flash distillation – solar stills, ion exchange reverse osmosis, electro dialysis, disinfection methods.

Books suggested:

1. A.K.DE, Environmental Chemistry – New Age International Publishers.
2. J.A.DAJI, A Text Book of Soil Science – Media Promoters and Publishers.
3. Dr.V.P.Kudesia, Water Pollution – Pragati Prakashan.
4. S.S.DARA, A Text Book of Environmental Chemistry and Pollution Control – S.Chand and Company Ltd.
5. P.S.Sindhu, Environmental Chemistry – New Age International Publishers.
6. O.D.Tyagi and M.Mehra, A Text Book of Environmental Chemistry – Anmol Publications Pvt. Ltd.
7. N.F.Voznaya, Chemistry of water and Microbiology – Mir Publishers Moscow.
8. S.L.Chopra and J.S.Kanwar Analytical Agricultural Chemistry – Kalyani Publishers.
9. A.K.Babko and A.T.Pilipenko, Photometric Analysis – Mir Publishers Moscow.
10. N.N.Ushakova Analytical Chemistry for Soil Scientists – Mir Publishers Moscow.
11. N.Manivasakam, Physico Chemical Examination of Water, Sewage and Industrial Effluents – Pragati Prakashan, Meerut.
12. M.L.Jackson, Soil Chemical Analysis – Prentice Hall of India Private Limited.
13. R.M.Upadhyay and N.L.Sharma, Manual of Soil, Plant, Water and Fertilizer Analysis – Kalyani Publishers.
14. C.S.Rao, Environmental Pollution Control Engineering – Wiley Eastern Limited.
15. S.M.Khopkar, Environmental Pollution Analysis – Wiley Eastern Limited.
16. S.K.Banerji, Environmental Chemistry – Prentice Hall of India Private Limited.
17. N.C.Brady, The Nature and Properties of Soils – S.Chand and Company Limited.
18. B.K.Sharma, Environmental Chemistry – Pragathi Prakasan.

Acknowledgements

The authors wish to thank with gratitude the various authors and publishers of the above mentioned books as they have used the figures, diagrams and data at times directly or in a modified form. They also wish to thank the services of Ms.B.Jyothirmai in the preparation of this study material in several ways.

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UNIT 1

BASIC SEGMENTS OF ENVIRONMENT

Lesson 1

Objectives of the lesson: This lesson introduces the student to the study of environment.

Environment consists of four basic segments, they are

1. Atmosphere
2. Hydrosphere
3. Lithosphere
4. Biosphere

Atmosphere:

It is generally known as protective blanket of gases surrounding the earth, which sustains life on earth and saves it from hostile environment.

Major Functions:

1. It transmits only near ultraviolet (UV), visible, radio waves and near infra red (IR) radiation (i.e., between 300-2500 nm) while filtering out tissue damaging UV radiation below 300 nm.
2. The atmosphere plays a vital role in maintaining the heat balance of the earth. It absorbs IR radiation emitted from the sun and reemitted from the earth.
3. Atmosphere is a major source of oxygen that is essential for life on earth and carbon dioxide (CO_2) which is essential for plant photosynthesis. It also supplies nitrogen, which will be through by nitrogen fixing bacteria and ammonia manufacturing plants to yield chemically bound nitrogen essential for life.
4. Atmosphere serves as carrier of water from oceans to land.

Hydrosphere:

It includes all types of water sources like oceans, seas, rivers, lakes, streams, reservoirs, glaciers polar ice caps and ground water (i.e., water beneath the earth's surface). 97% of water is in the oceans containing high salt content, which does not permit human consumption. 2% of water resource is locked in polar ice caps and glaciers. Remaining 1% is available as fresh water as surface water i.e., rivers, lakes, streams for human consumption and also for industrial purposes which includes agriculture etc.

Major uses of Water:

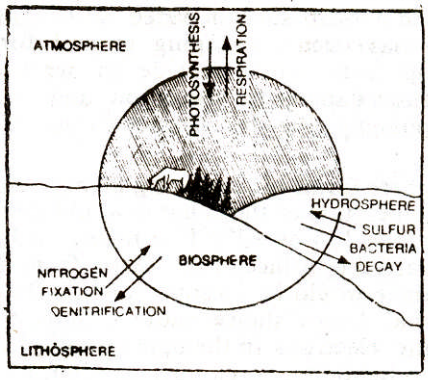
Major uses of water are for irrigation 30%, for thermal power plants 50%, besides for other purposes like domestic use (7%) and about 12% for industrial consumption. Pesticides, fertilizers, agricultural runoff, human and animal wastes contaminate surface water as sewage and in the form of industrial wastes.

Lithosphere:

It is the outer mantle consisting of minerals occurring in the earth's crust and the soil. Soil is the most important component of lithosphere.

Biosphere:

This denotes the realm of living organisms and their interactions with the environment. Ex: atmosphere, hydrosphere and lithosphere. Both biosphere and environment influence each other considerably. Thus oxygen and carbon dioxide levels are based entirely on the plant kingdom. As a matter of fact green plants are alone responsible for accumulation of oxygen in the atmosphere, through photosynthesis and decay, the original atmosphere has been devoid of oxygen.



Environmental segments

NOMENCLATURE IN THE STUDY OF ENVIRONMENTAL CHEMISTRY:

Environmental Chemistry may be defined as the study of chemical phenomenon in the environment. It is a multidisciplinary science involving chemistry, physics, life science, agriculture, medical science, public health and sanitary engineering etc. In a broader sense it is a study of sources, reactions, transport, effect and fate of chemical species in air, water, soil and the effect of human activities upon these. The basic understanding of fundamental chemistry is not only essential for all chemists but also for all non-chemists, who were engaged in environmental science. One of the main objectives of study of environmental chemistry is to understand the nature and quality of specific pollutants in the environment and the determination of their levels. The difficulty of analysing for many environmental pollutants is that their amount in the natural samples is appreciably small.

Ex: The levels of air pollutants may be less than a μg per cubic cm of air and the levels of many water pollutants may be parts per million by weight or even less than this.

Contaminant:

The material which does not occur in nature but is introduced by human activity into the environment affecting its composition. A contaminant is classified as a pollutant when it exerts detrimental effect.

Pollutant:

A substance present in nature in greater than natural abundance due to human activity, which ultimately has a detrimental effect on the environment and there from on living organisms and mankind. Examples: Lead, mercury, sulphur dioxide, carbondioxide etc.

Definition of a pollutant:

As per The Indian Environment Protection Act 1986- " A pollutant has been defined as any solid, liquid, or gaseous substance present in such concentration as may be or tend to be injurious to environment."

Units of Pollution: Generally they may be expressed as one part per million- means one part per million parts of gas, liquid or solid mixture in which the pollutant is found. In case of gaseous mixture, the reference is generally to ppm by volume which in case of liquids and solids the reference has been generally to ppm / weight.

Symbol	**Definition**	**Fraction**
ppm	parts per million	10^{-6}
pphm	parts per hundred million	10^{-8}
ppb	parts per billion	10^{-9}
ppt	parts per trillion	10^{-12}

Environmental pollution:

It can be defined as the unfavourable alternation of our surroundings wholly or largely or as a by-product of man’s actions through direct or indirect effects of changes in energy pattern, radiation levels, chemical and physical constitution and abundance of organisms. These changes may affect man directly or through his supplies of water and of agriculture and other biological products, his belongings or possessions or his opportunities for recreation and appreciation of nature. The most vital and controversial question left unanswered by this definition of environmental pollution has been the question of what constitutes an unfavourable alternation. In the opinion of some people it is unfavourable and in opinion of others it may be favourable. The determination of the extent of the favourable verses unfavourable effects or of benefits verses costs is difficult because it will be ultimately subjective.

Major classification

***NATURAL* (substantial)**	***MAN MADE (Artificial)* (or) Man generated pollutants**
1. Hydro carbons in atmosphere	1. Completely man generated like chlorinated hydrocarbons (DDT, BHC, etc.)
2. Radiation	2. Lead aerosols
3. Sulphur oxides in atmosphere	3. Substantially man generated oil on oceans
	4. Phosphates in running water

Types of pollution:

The following types have been noticed

1. Air Pollution
2. Water Pollution
3. Solid- waste Pollution
4. Land Pollution
5. Marine Pollution
6. Noise Pollution
7. Radiation Pollution
8. Thermal Pollution

The other important terms that are to be learnt before going to the study of environmental chemistry are:
- source
- receptor
- sink
- pathways of a pollutant
- speciation.

Source:

It is a place from which a pollutant originally originates. Identification of source is important in contemplating pollution elimination and / or control.

Receptor:

The medium which is affected by a pollutant .Man is the receptor of photo chemical smog causing irritation to eyes and respiratory tract. Trout finger lings are the receptors which may die from exposure to dieldrin in water.

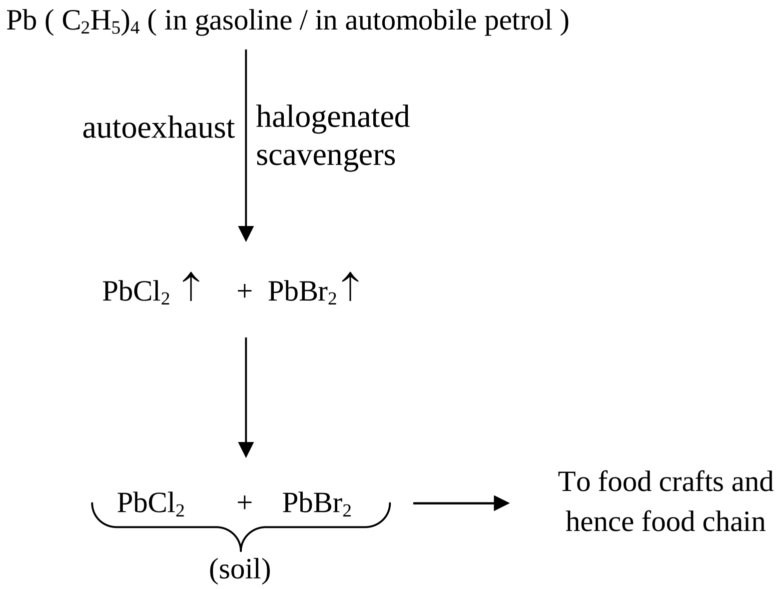
Sink:

Sink is a medium which retains and interacts with a long lived pollutant. The oceans are the sinks for atmospheric CO_2, a lime stone wall or a marble wall may act as a sink for atmospheric sulphuric acid and ultimately gets damaged.

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2$$

Path ways of Pollution:

The mechanism by which the pollutant is distributed by its source to the environmental segments:



Speciation:

Different chemical forms or species of inorganic, organic, organo-metallic compounds are present in the environment. It is highly essential to identify the chemical species of a pollutant since some species are more toxic than the others. Thus methyl mercury $(CH_3Hg)^+$, and dimethyl mercury $(CH_3)_2Hg$ are deadly poisonous compared to other species of mercury.

Dissolved Oxygen (DO):

Oxygen is an essentially important species in water. It is consumed due to oxidation of organic matter or by reducing agents etc: It is an important water quality parameter. The optimum value for good water quality is 4–6 mg / L of DO (dissolved oxygen), which ensures healthy aquatic life in a water body. Depletion in DO levels indicates water pollution.

Chemical Oxygen Demand (COD):

This is an index of the organic content of water (oxygen demanding substances in water) and is an important water quality parameter. The test is based upon the chemical oxidation of material in water by $K_2Cr_2O_7$ in 50% H_2SO_4.

Biological Oxygen Demand (BOD):

This is also a water quality parameter for organic matter in water, which is empirical in nature. It is measured by the quantity of oxygen utilised by suitable aquatic micro-organisms during a five day incubation period.

Threshold Limit Value (TLV):

This indicates the permissible level of the toxic pollutant in atmosphere to which a healthy industrial worker is exposed during an eight - hour day with out any adverse effect. TLV values for Be and Zn are 0.002 and 1.000 mg / m^3 respectively.

UNIT 1

LITHOSPHERE - A

Lesson 2

Objectives of the lesson: This lesson deals about the structure of earth, composition of earth crust, minerals and rocks.

LITHOSPHERE

STRUCTURE OF THE EARTH:

Earth Crust: The soil which covers the surface of the earth is composed of inorganic matter consisting of vegetable and animal remains. The mineral matter of the earth's crust is derived from disintegration of rocks by atmospheric and other agencies. In order to know about the earths crust it is better to know about the origin of earth.

Earth's Origin:

Basis for the knowledge of earth formation is based on the old theory of *Nebular hypothesis*.

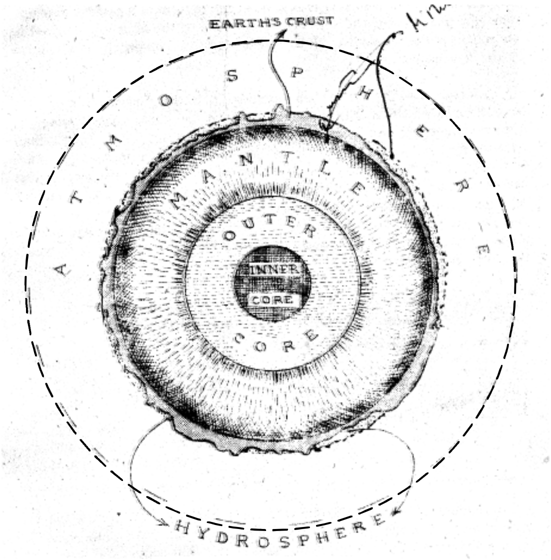
According to this it is believed that the solar system is existed to be as *Nebula* or a cloudy mass of matter in the form of vapour or gases. Nebula was intensely hot and incandescent. It was also supposed to be perpetually revolving. With the lapse of time the nebula began to cool. As a result the outer layers of vapours condensed and were thrown out in the form of rings.

Several rings might have been thrown away with time. These rings on further condensation and disruption became the planets. These planets on further cooling threw their rings i.e., as seen in the case of Saturn. In some cases the planet rings broke into pieces known as satellites like moon. The central mass which is still incandescent and not yet condensed is the Sun.

STRUCTURE OF EARTH:

The earth is also formed in similar fashion. When it first formed it might be hot and plastic. The earth which consists of inner globe, lithosphere is surrounded by hydrosphere and atmosphere. The outside of the earth is quite cool and solid but the interior is still very hot and in a fluid condition. The outer layer of earth which we know lies over a denser molten mass in which various gases are dissolved at high pressures. This outer layer is known as Earth's Crust.

Atmosphere is the outer most layer and exists in the form of gaseous envelop round the planet. Next to it is the hydrosphere or the layer of water. The lithosphere is the innermost globe which is almost completely surround by the hydrosphere.



Structure of earth

Earth's Crust:

The earth's crust is 20 to 40 miles thick and consists of different kinds of rocks. Below this crust lies the mantle (layer of dense rocks) which extends to a depth of about 1800 miles and the upper portion to a depth of about 150 miles. There after it is solid rigid mass of rocks. The outer core which lies below the mantle is composed of some heavy metals like iron and nickel in molten or semi fluid condition for about 1300 miles thickness.

The pressure at surface of outer core is about 1.5 million atmospheres. In spite of its extremely high temperature 4000°c the inner core is believed to be in solid state in view of enormous pressure. The density of different layers gradually increases from the outer crust to the inner core.

The earth's crust mainly composed of mineral matter. The mineral matter is made up of various elements. Only a few inert gases are present as such.

Atmosphere:

Atmosphere extends from surface of earth to 200 miles lighter than hydrosphere. It exerts a pressure of 14.6 lb / Sq inch at sea level. It contains mixture of gases: N_2, O_2, CO_2 and water vapour. Besides it also contains small quantities of hydrogen, ammonia, sulphonated hydrogen, sulphurous acid gas, ozone, nitrogen oxides. Also consists of inert gases like helium, argon, neon, krypton and xenon.

Composition:

The amount of carbondioxide in urban areas is higher than in rural areas. Also sulphur containing gases are present in air. Ozone and nitrogen oxides are formed due to electrical discharges during thunderstorms. Amount of aqueous vapour is variable. Average amount is less than 1% but in humid climates it will be about 4%.

Average composition of atmospheric air

Compound	By volume %	By weight %
Nitrogen	78	75.5
Oxygen	21	23.1
Carbon dioxide	0.03	0.04
Other Gases	0.97	1.36

Hydrosphere:

The hydrosphere is the layer of water surrounding the lithosphere present in the form of seas and oceans which covers nearly about 70% of the surface of earth above sea level. The surface of waters of various seas is in one level. This is known as sea level. Depth of water in the ocean varies. The average depth is about 2 ½ miles. It is 6 miles at its greatest depth and occupies 139,440,000sq.miles. The total volume of water is about 15 times the volume of land above sea level. If all the land on the earth is leveled the water will stand to about a height of two miles. It contains mineral matter. It is due to the flow of surface waters from the earth to the seas. Average mineral matter content is 3.5%. The seawater has higher specific gravity than terrestrial water due to the salts present in it. The average density is 1.026. It varies from place to place. It is least dense at estuarine areas and lies average at places where evaporation is high.

COMPOSITION OF SEA WATER

Average Composition of mineral matter in sea water (Percent)

Calcium Carbonate	0.012
Calcium Sulphate	0.126
Magnesium Sulphate	0.116
Magnesium Chloride	0.381
Magnesium Bromide	0.007
Potassium Sulphate	0.086
Sodium Chloride	2.721

Chemical contents present in seawater as a whole:

Element	Percent
Oxygen	85.79
Hydrogen	10.67
Chlorine	2.67
Sodium	1.14
Magnesium	0.14
Calcium	0.05
Potassium	0.05
Sulphur	0.09
Bromine	0.008
Carbon	0.002

LITHOSPHERE:

It is innermost body with in the gaseous and watery envelops. Land is one which rises above seawater and visible to us. Land forms about 1/4 of the total surface of earth. Most of the land is situated in the northern hemisphere.

Lithosphere consists of two portions:

1. Upper or outer cool solid surface
2. Inner hot or molten mass.

Lithosphere is heavier than both hydrosphere and atmosphere. Mean density is 5.5 compared to that of water as one. The outer crust has a density of about 2.5–3.0. The outer solid layer or earth crust is about 10-20 miles thick. It consists of various rocks enveloped by a thin mantle of soil. The inner mass is in molten condition.

There are two opinions about the inner mass

1. According to one the entire mass is in molten condition up to the center.
2. Molten mass will be there up to 50-100 miles surrounding the gaseous center.

However it is very hot and it is under enormous pressure. As we go inside the earth there is increase in temperature i.e., is for every 64ft average rise in temperature is 1^0F. At this rate the temperature at about 25-50 miles will be quite sufficient to melt all the substances known to us. Hence this supports the idea that entire inner mass is in molten condition. Further support to this is provided during eruption of volcanoes. Volcanoes erupt large quantities of very hot molten material known as *Lava*. The existence of hot springs at some places also shows that the interior of earth is very hot.

Composition of Earth's Crust:

The earth's crust principally composed of mineral matter. The mineral matter is made up of various elements and only a few inert gases are present as such. The elements do not exist as such in earth's crust. They will be in the form of chemical compounds known as m*inerals* which consists of one or more elements. While many of these minerals in turn combine together to form aggregates which are known as rocks.

Percentage of Elements present in the Earth's Crust

Element	**Percent (%)**
Oxygen	47.02
Calcium	3.50
Titanium	0.41
Phosphorous	0.09
Strontium	0.02
Silicon	28.06
Magnesium	2.62

Percentage of Elements present in the Earth's Crust (Contd.)

Element	**Percent (%)**
Hydrogen	0.17
Sulphur	0.07
Fluorine	0.01
Chlorine	0.01
Aluminium	8.16
Potassium	2.33
Carbon	0.12
Manganese	0.07
Iron	4.64
Sodium	2.63
Barium	0.05
Chromium	0.01
Nickel	0.01
Lithium	0.01

MINERALS

Minerals are naturally occurring substances with definite chemical composition and with distinct physical characteristics. They will be having two or more elements in chemical combination and in certain definite proportion. Mineral that forms original component of a rock is known as *Primary mineral* **(**Ex: Feldspar, Hornblende, Mica etc). *Secondary minerals* are those which are formed, deposited or introduced as a result of subsequent changes in rocks. Limonite, gibbsite and some clay minerals (like kaolinite, mantomorillonite etc.,) are secondary minerals. Quartz is obtained as primary and secondary mineral.

Essential minerals are those which form as chief constituent of a rock and characteristic component of the rock. The presence or absences of minerals of which there are no consequences are called *accessory minerals.*

The important physical characteristics of minerals are crystal form, colour, streak, luster, opacity, hardness, specific gravity, cleavage and fracture. About 1000 minerals are known to present in earth's crust. The most abundant minerals present in *igneous rocks* are feldspars which constitute 60% pyrooxines and amphiboles 18%, quartz 12%, mica 4%, and all others 6%. Soil nature and character will be influenced by the mineralogical make up of the parent materials. The deficiency or excess of certain elements in soil in the minerals may have profound effect on the growth and development of animals and plants. Some minerals decompose more quickly than others and thus liberate plant nutrients more readily.

Quartz:

It is one of the four silica minerals occurring in nature. Quartz, cristobalite, tridymite (crystaline) and opal (amorphous). Some of the important varieties are:

Mineral	**Characteristics**
Rock Crystal	colourless
Amethyst	purple
Chal cedony	unite
Carnelian	red
Blood stone	green with red spot
Rose quartz	pink
Citrine	yellow
Agate	bounded
Smoky quartz	brown or black
Flint and chest	massive

Quartz is the dominant mineral in granite, rhyolite, sand stone and conglomerate.

Feldspar: It is divided into two types

ORTHOCLASE	***PLAGLIOCLASE***
Potash feldspars present in granite, syenite and similar other igneous rocks.	Soda feldspar eg., albite or calcium feldspar eg., anthonite or sodium feldspar eg., oligoclase labrodorite

Other important primary minerals are apatite, magnetite and limonite. Secondary minerals are clay minerals apatite, calcite, dolomite, gypsum, gibbsite, hematite, limonite etc:

Rocks:

It may be defined as a mass of mineral matter. They are composed of one or more minerals. Some rocks are hard and feebly aggregated such as sand stone and loose sand. Rocks possess characters like structure, colour, specific gravity, cleavage or fracture. Rocks are divided into three main classes according to their origin or mode of formation.

1. Igneous rocks	(due to action of heat)
2. Aqueous rocks	(due to action of water)
3. Metamorphic rocks	(by the interaction of igneous and aqueous rocks)

Igneous rocks:

These are rocks formed due to the action of heat. These will be formed when molten mass cooled and consolidated into solid rock. (The other rocks aqueous and metamorphic rocks are formed consequently). They constitute 95% of earth’s crust. They are about 10 miles thick. They are mostly crystalline and hence known as crystalline rocks. They are also called massive rocks because they occur in big masses. They contain mainly primary minerals like quartz, feldspar, amphiboles, pyroxenes and mica etc:

Igneous rocks were classified into three groups according to their formation / occurrence, viz: extrusive, intrusive and plutonic.

Extrusive:

When the molten mass comes on to the earth and solidifies on cooling we say they are *extrusive rocks.* Ex: Rhyolite, Obsidian, Trachyte, Dolerite and Basalt.

Intrusive:

When the molten mass solidifies beneath the surface we say they are *intrusive rocks.* While rocks formed in vertical cracks are known as d*ykes* and with horizontal cracks are called *sills.*

Plutonic:

Among intrusive rocks which consolidate at a much greater depth are known as *Plutonic.*
Ex: Granite, Syenite, Diorite and Gabbro.

The matter that consolidates in irregular cracks is known as *Vein.*

Vesicular rocks:

Igneous rocks because of volcanic origin contain water under great pressure and when molten mass comes out, the pressure is released and water turns into steam. When that steam cannot escape a globular cavity forms, which is known as vesicule and the rock that contain such vesicule is known as vesicular rocks.

The igneous rocks are classified into four groups according to their chemical composition.

1. Acid rocks which contain more than 65% silica.
2. Sub acid rocks contain 60-65% silica.
3. Sub basic rocks which contain 55-60% silica.
4. Basic rocks which contain 45-55% silica.

Acid rocks : Granite, Rhyolite, Obsidian, Pitch stone.
Sub acid rocks : Syenite, Trachyte.
Sub basic rocks : Diorite, Andesite.
Basic rocks : Gabbro, Dolerite, Basalt.

Aqueous rocks:

They are formed from sediments brought by water and hence also known as sedimentary rocks. They are also known as stratified rocks. These rocks mainly contain secondary minerals. They are divided into six groups.

1. Arenaceous
2. Argillaceous
3. Calcareous
4. Carbonaceous
5. Siliceous
6. Precipitated salts.

Arenaceous Rocks : Coarse grained particles. Disintegrated from old rocks.
Argillaceous Rocks : Small size particles known as clay, kaolin or china clay.
Calcarious Rocks : Carbonate of lime and magnesium.
Carbaneous Rocks : These are formed due to decomposition of vegetation under anaerobic condition.
Siliceous Rocks : They have organic origin having formed from plants and animals.
Precipitated Rocks : Deposits formed as rock masses either by cooling, evaporation or by direct chemical precipitation.

Metamorphic rocks:

The igneous rocks and aqueous rocks after they are first formed undergo changes. Consequent on the changes, rocks so formed are known as metamorphic rocks. The metamorphosis may be brought by the action of water, heat, and pressure.

Thus changes brought by
water are known as hydro metamorphism,
heat are known as thermo metamorphism,
pressure are known as dynamo metamorphism.

UNIT 1

LITHOSPHERE - B

Lesson 3

Objectives of the lesson: This lesson deals with principles of weathering, soil formation / development, and properties.

PRINCIPLES OF WEATHERING:

This naturally occurs on the surface of the rocks and hence susceptible for continuous changes. These changes are brought about by climatic conditions. By virtue of these changes new substances are formed as a consequence of breaking up of old compounds. During this process rocks are subjected to constant stress and strain and finally lead to the formation of soil.

The process of transformation of solid rocks into soil is known as *weathering*. Weathering is a process by which earth's crust or lithosphere is broken down by the activities of atmosphere with the aid of hydrosphere and biosphere. Generally physical weathering is brought about by mechanical action of various weathering agents and the process is known as *disintegration*. The chemical weathering leads to *decomposition***.** The principle agents that take part in process of weathering are temperature, water, air, plants and animals. Each of these agents act on rocks both mechanically as well as chemically. Some processes are simple while others are complex. Most of the changes take place simultaneously and helps the transformation of solid rock into soil as a synergistic process.

Effect of temperature:

The effect of temperature is mainly mechanical. The rock gets heated up due to Sun's heat and expands. In nights the temperature falls and rock gets cooled and contract. These alternate actions of expansion and contraction day by day and night by night lead to the development of cracks in rock and gets broken into big pieces first, then small pieces and finally into small particles. The other way of action is, the rocks do not conduct heat easily. There will be temperature gradient between the upper surface and the inner portion and this differential heating leads to unequal expansion and contraction of rocks since the minerals of rocks have a variety of rates of expansion and contraction. For example, the cubical expansion of quartz is twice that of feldspar. The surface of rock is broken up in the form of layers.

Effect of water:

Water acts on rocks both mechanically as well as chemically and it is a most potent agent responsible for weathering of rocks. Part of the rainwater that falls on the earth is carried underground through cracks and fissure (deep cleft or deep crack) and part flows over the ground in the form of streams and rivers. In cold regions the temperatures are low and water freezes at times. Similarly water present in chinks and crevices also freezes. On freezing water expand in volume. The increase in volume exerts pressure in rock. Due to tremendous pressure the rocks break down and transform into soil. On the other hand the water that flows over the ground exerts erosive action and results in transportation of the eroded material and hence there will be grinding action on the materials that are being carried away. This grinding action depends on two factors (1) speed with which it flows and (2) amount of material it carries in suspension.

Another way in which ground water is responsible for disintegration of rocks is due to the formation of glaciers. When ice is formed in mountainous regions on slopes and hillsides and it begins to move, such block of ice in motion is known as glacier. Like rivers the glaciers also excavate the sides along the path of their movement. Chemical action of water on rocks is due to the presence of substances dissolved in it. Some of the important reactions taking place by the action of water are hydrolysis, oxidation, reduction, carbonation, hydration and solution.

Hydrolysis:

It brings about most important change during weathering of minerals.

$$\underset{\text{orthoclase}}{K_2OAl_2O_36SiO_2} + 3H_2O \rightarrow \underset{\text{new silicate}}{Al_2O_3.\ 2SiO_2.2H_2O} + 2KOH + 4SiO_2$$

The KOH that is formed there may combine with carbonates and potassium carbonates and other new substances so formed are collectively known as weathering complexes.

Oxidation:

Oxygen in presence of water is capable of converting many minerals into oxides. These oxides are further converted to hydroxides. Generally oxides are restricted to surface of rock.

$$4FeO + O_2 \rightarrow 2FeO$$

This phenomenon is similar to rusting of iron. Another system is conversion of sulphides to sulphates. This leads to increase in volume and helps in disintegration of material. Sulphates are highly soluble and removed in solution and help to loosen the mass.

$$FeS + 2O_2 \rightarrow FeSO_4$$

Reduction:

This occurs in places which are not properly drained or where there is accumulation of organic matter and as such some higher oxides are reduced to lower oxides.

$$2Fe_2O_3 - O_2 \rightarrow 4FeO$$

Carbonation:

The moisture present combines with carbon dioxide in atmosphere.

$$H_2O + CO_2 \rightarrow H_2CO_3$$

The carbonic acid or carbonated water attacks many rocks and minerals and brings them into solution. Lime stone which is insoluble in water is dissolved readily by carbonated water and thus it is removed from parent rock.

$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$

It also attacks insoluble silicate materials like feldspar, mica, hornblende etc..

$K_2OAl_2O_36SiO_2 + 4H_2O + CO_2 \rightarrow Al_2O_3\,2SiO_2.2H_2O + K_2CO_3 + 4SiO_2$
(Felspar) (Kaolin)

$K_2O.3Al_2O_36SiO_2\,2H_2O + H_2O + CO_2 \rightarrow 3(Al_2O_3.2SiO_2.2H_2O) + K_2CO_3$
(muscovite) (Kaolin)

Water may also contain nitric acid brought about by rainwater from atmosphere. It may also contain some organic acids obtained by decomposition of plant materials. These acids in water may produce a similar sort of action (decomposition) like carbonic acid.

Hydration:

Water itself combines with certain materials and produce new compounds.

$2Fe_2O_3 + 3H_2O \rightarrow 2Fe_2O_3.3H_2O$
(hematite) (limonite)

$3(MgO.FeO.SiO_2) + 2H_2O \rightarrow 3\,MgO.2SiO_2.\,2H_2O + SiO_2 + 3FeO$

Solution:

Some substances present in rocks are directly soluble in water and removed continuously by flowing or percolating water and hence the rock no longer remains solid but falls to pieces. The solvent action of water increases when it is acidulated by dissolution of organic and inorganic acids and hence they can remove silica also.

Effect of air:

It is partly mechanical and chemical. Moving air and wind has great destructive effects on rocks. And further wind carrying particles in suspension, like those of sands and rock fragments and exert a grinding action where by the rock get disintegrated and this process of weathering is more pronounced in dry regions. The chemical effect of air is due to various gases especially carbon dioxide and oxygen in the atmosphere. The carbon dioxide brought to earth's surface by rain exerts the effect of carbonated water.

Effect of plants:

The effect of vegetation on rocks is both physical and chemical. Simple plants like mosses and lichens grow upon exposed rock, which depend on moisture for sustenance and hence the surface of rock moistened continuously. The moisture acts in various ways in decomposing and disintegrating processes. In some cases, roots of trees gain entrance into small cracks and crevices of rocks. They continue to grow and hence exert great pressure on sides and hence bring about disintegration and this is more pronounced when water enters such system. Other type of action is due to organic compounds formed during decay.

Plant roots respire carbon dioxide, the carbon dioxide so liberated gets dissolved in soil water and the carbonic acid so formed attacks the rocks and minerals and brings about the decomposition. Some very minute forms of life like bacteria, fungi produce acids like nitric acid also bring about decomposition.

Effect of animals:

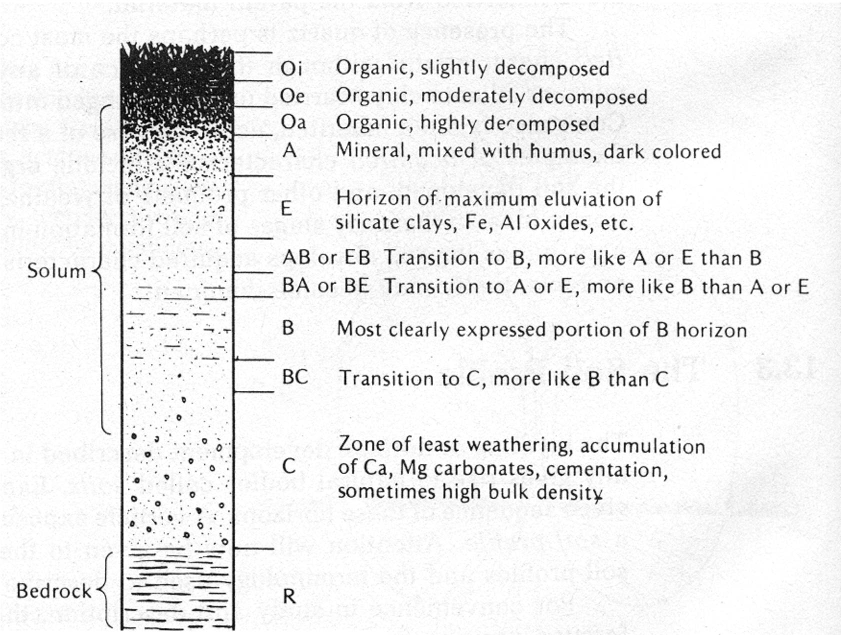
Animals like rats and rabbits which burrow the ground dig out large quantities of primary decomposed rock. The burrows opened by these animals serve as tunnels or passages through which water and air enter and thus bring about decomposition and disintegration of rocky material in the interior. Similarly, the animal remains decompose to give acidic substances and these substances attack the rock. The smaller animals like insects and worms also posses great destructive powers Ex: earthworms etc..

Quantity of soil passed by these creatures may amount to 10 tonnes per acre yearly and certain types of ants and burrowing insects carry leaves and other organic materials down their burrows and weathering is achieved on decay of these materials.

Development of soil profile:

The vertical section of soil showing the various layers from the surface to the unaffected parent material is known as soil profile. The various layers are known as horizons. The soil profile contains mainly three horizons named as horizon A, horizon B and horizon C. The surface soil or that layer of soil at the top, which is liable to leaching and from which some soil constituents have been removed is known as horizon A, or the horizon of eluviation (removal of material in solution or in suspension from upper layer to lower layer by runoff percolation). The intermediate layer in which the materials leached from horizon A have been re-deposited is known as horizon B, or the horizon of illuviation.

Pictorial depiction of mineral soil profile, showing the major horizons that may be present in a well-drained soil in the temperate humid regions. Any particular profile may exhibit only some of these horizons and the relative depths may vary. There may be more detailed subhorizons than depicted here. The solum includes the A, E and B plus some fragipans and duripans of C horizon.



Soil Formation / Development:

Pedogenic Process:

Soil body or soil column is the formation of new body as a result of various weathering processes which are known to be destructive in nature where in several agents will play a key role in the formation of soil.

Weathering and soil development are not two separate processes. Soil body is the final product of these events. Soil development or soil genesis is the result of various factors known collectively as soil formers.

Factors of soil development:

Five important factors which are responsible for this activity are

1) parent material
2) climate
3) biosphere
4) topography and
5) time

The above factors can be classified into two types namely 1. *passive* and 2. *active.*

Parent material, topography and time are *passive* factors. Climate and biosphere are *active* factors. The other processes are *endodynamo morphic* in which parent material plays important role e.g., young soils or soils formed on mountains while *ectodynamomorphic* in which climatic influence will be more; they obliterate the effects of parent material.

Topography or the relief of the land:

This is an important passive factor. Affects the movement of soil moisture and water and also affects ground water table.

Slope Exposure: Southern exposure is warmer than northern exposure and hence differs.

Time or age controls the maturity of the soil body. If a soil body is acted upon by soil formers for a longer time and when the process of soil formation is complete - it is known as mature soil. There will be two horizons, young or mature soil. In course of time young soils become mature and mature soil sometimes become degraded.

Effect of Rainfall:

Of all the climatic elements rainfall or precipitation is the most important. Due to its percolation and movement it carries parent material as substances as solution or as suspension.

Effect of Temperature:

Another climatic agent, where high temperature hinders the process of leaching, causes an upward movement of soluble salts.

Effect of Vegetation:

Biosphere is another active soil forming agent which includes elements like vegetation, micro organisms and animals including rodents, insects, worms etc. The activities of vegetation are more pronounced. The roots of plants penetrate into parent material where they act both mechanically and chemically. More percolation and drainage will be there. Greater dissolution of minerals through the action of carbon dioxide and other acidic substances will be excreted by them. Decomposition and humifications increase solubilisation of minerals.

The indirect effects of vegetation are:

- influences climate in lowering of temperature of air and increases its humidity
- reduces evaporation and increase precipitation
- grasses reduce run-off and greater quantities of rainwater penetrate into parent material.

Effect of Organisms:

It is related to humification and mineralisation of vegetation. Action of animals particularly burrowing animals dig and mix up the soil mass and thus disturb the parent material. Earthworms, ants and other insects carry matter from one depth to another whose total influence is very great.

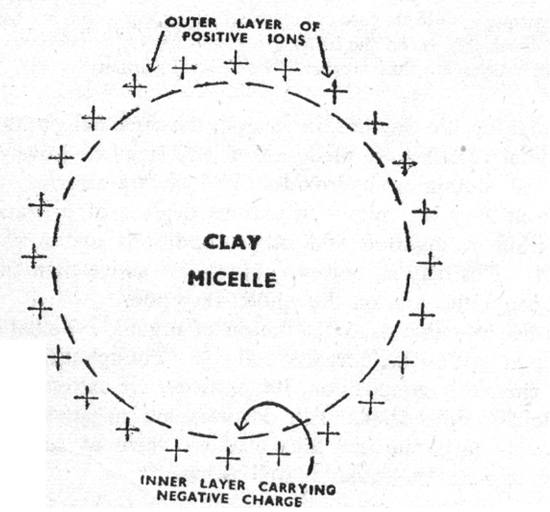
Soil colloids

Nature of soil colloids:

The clay fraction of soil contains less than 0.002mm in size. Most of these particles are smaller than 0.001mm and hence posses the properties like those of typical colloidal substance viz. gelatin, starch, silicic acid, ferric hydroxide etc: Hence particles are known as soil colloids.

Soil colloids are of two kinds: 1. inorganic and 2. organic

The inorganic colloid or colloidal clay as it is called, is derived from weathering of rocks and parent materials and consists of minerals of secondary origin. The organic colloid is derived from decomposition of plant and animal remains. These two together form the colloidal complex of the soil. However inorganic colloids form a major portion.



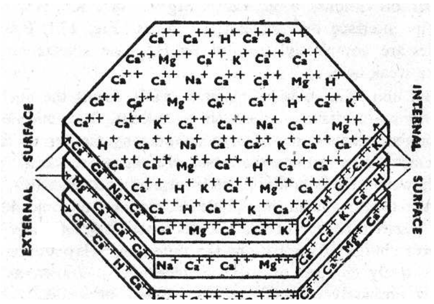
Diagrammatic representation of colloidal clay crystals

Constitution:

The inorganic colloid of soil consists mainly of crystalline clay minerals of which hydrated alumino-silicates is a salt of weak alumino-or ferro-alumino -silicic acid in loose combination with a number of cations, eg.Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, H^{+} etc.. The crystal unit of colloidal particles which form nucleus and to which the cations are attached is known as *micelle.*

The micelle which is negatively charged behaves like a large anion, very similar to negative radical of an acid and attracts positively charged cations. Thus electrical double layer of which negative charge of micelle constitutes the inner ionic layer and positive charge of cations the outer ionic layer. On the other hand when suspended in water the clay micelle as well as cations is surrounded by water molecules, which are also held electrostatically. Each clay or colloid particle thus carries a large number of cations, each surrounded by a swarm of water molecules, on its external as well as internal surfaces.

It is believed that the constitution of organic colloidal material is same as that of inorganic colloids. Though it has a very complex and variable composition, its particles are extremely small in size i.e., of true colloidal dimensions. The particles are negatively charged and their tremendously large surface area enables them to adsorb extremely large quantities of water molecules as well as ions.



Diagrammatic representation of colloidal clay crystals

Properties of Soil Colloids:

Soil colloids possess the same properties that of ordinary colloidal materials. They show Brownian movement, do not pass through semi-permeable membrane, and carry an electrical charge. When suspended in water, imbibe large quantities of water, swell and increase in volume when they absorb water and shrink when they are dried. They also possess the properties of cohesion, adhesion, adsorption, flocculation and de-flocculation.

Brownian Movement:

It is mainly responsible for coagulation or flocculation of colloidal particles because during their movement they collide with each other. The smaller the particles, the more rapid are its movement and more often it collide. When particles in suspension collide with each other they adhere together, under circumstances and form a loose aggregate or floc.

Non-Permeability:

Colloids, as opposed to crystalloids, are unable to pass through semi-permeable membrane. The membrane allows the passage of water and dissolved substance, but retains the colloidal particles. Hence colloidal materials can be separated from crystalloids in this way by dialysis or by ultra-filtration.

Electric Charge:

All colloids carry a definite electric charge. When suspended in water, soil colloids carry a negative charge. Colloidal clay develops negative electrical charge in two ways. Dissociation of hydrogen from hydroxyl groups attached to silicon in silica sheets of the clay minerals leaves residual oxygen carrying a negative charge. Another way in which negative charge is developed is due to isomorphous replacement of ions in silica and alumina sheets of clay material.

Adsorption:

The phenomenon of adsorption is confined to the surface of colloidal particles. The soil colloids exert a selective adsorption of ions. At the same time all ions are not adsorbed to the same degree.

Ammonium, potassium, magnesium and phosphate ions are more readily adsorbed than calcium, sodium and sulphate. While nitrite, chloride and bicarbonate ions are not adsorbed or very little if at all. The property of adsorption plays an important role in soil fertility. It is due to this property of soil it is able to hold water and plant nutrients and keeps them available for use of the growing plants. It enables the soil colloids to function as a reservoir of nutrients for plant use.

Flocculation:

As long as colloidal particles remain charged, they repel each other and suspension remains stable. If on any account they loose their charge or if the magnitude of charge is reduced, the particles coalesce, from flocs or loose aggregates and settle out. This phenomenon of *coalescence* and formation of flocs is known as *flocculation.* The reverse process of breaking up of flocs into individual particles is known as deflocculation or dispersion. The phenomenon of flocculation plays an important role in cultivation of soils.

Swelling:

A colloidal substance undergoes a preliminary swelling when it is brought in contact with water. This phenomenon is known as imbibition is accompanied by the disappearance of certain amount of water. The water so disappeared is known as *water of imbibition*. Though the colloidal material increases in volume on swelling there is an actual contraction of total volume. Soil colloidal presents the same phenomenon.

Heat of Wetting:

During the imbibition of water by soil colloidal material, a certain amount of heat is evolved which is known as heat of wetting. Heat is also evolved when soil clay is wetted with liquid other than water such as alcohol, benzene etc., but heat evolved due to water is more. The amount of heat evolved varies with the amount and nature of colloidal material and the type of adsorbed cations.

Cohesion and Adhesion:

Unlike sand and silt, clay particle possess the properties of cohesion and adhesion. Cohesion is phenomenon of sticking together of colloidal particles, while adhesion refers to phenomenon of sticking the colloidal particles to other substances.

Plasticity:

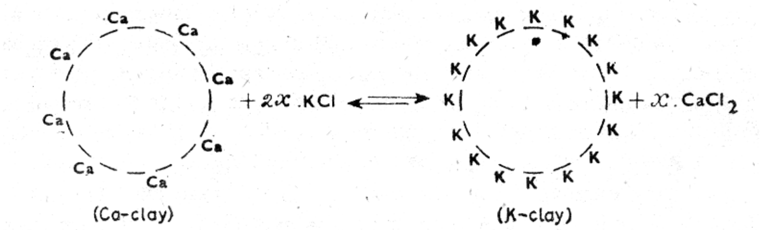
In fields (soil), the colloidal particles are present in a gel condition. Like other gels, soil colloids posses the property of plasticity that is they can be molded into any form or shape.

Ion exchange

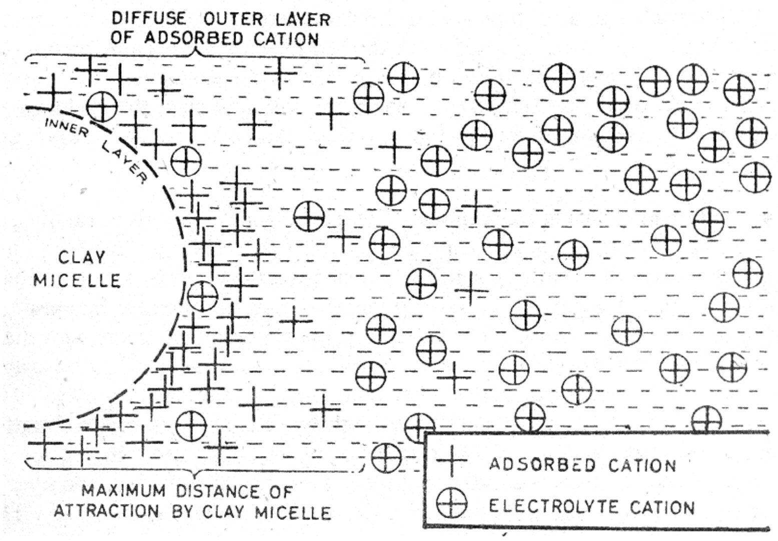
The fine particles of clay and humus, which are collectively known as complex, are very reactive and it is in this colloidal complex that most of the reactivity of the soil resides. The most important activity of colloidal complex is exchange of ions that take place when it is brought in contact with a solution of electrolyte. Both cation and anion take part in this exchange. Though reaction is chemical in nature, it is located in surface of colloid particles. The phenomenon of ion exchange is of great importance in agriculture since it has considerable influence on the retention and liberation of plant nutrients such as calcium, magnesium, potassium and phosphorous etc. It plays an important role in reclamation of acid and alkali soils. It also influences the effect of fertilizers and fertilizer particles.

Surface Reaction:

When an ordinary soil is brought in contact with solution of electrolyte like potassium chloride, a part of the potassium is adsorbed by soil and at the same time an equivalent quantity of cations liberated into solution. This phenomenon of exchange of cations between soil and salt solution is known as cation or base exchange. Cations that take part in this reaction are called exchangeable or replaceable cations or bases.



The exchange of cations has been explained on the basis of the electro kinetic theory of ion exchange. According to this theory the adsorbed cations forming the outer shell of ionic double layer are supposed to be in a state of oscillation, when suspended in water form a diffused double layer. Due to these oscillations, some of cations move away from surface of clay micelle. In the presence of solution of electrolyte, a cation of the added electrolyte slips in between inner positive layer and outer oscillating positive ion. The electrolyte cation is now adsorbed on the micelle and surface cation remains in solution as an exchanged ion. Thus exchange of cations takes place.



Schematic presentation of diffuse double layer and exchange of ions

The rapidity of exchange depends upon zeta potential because zeta potential varies with the nature of adsorbed cation and its size and hydration.

Nature of Exchangeable Cation:

The exchangeable cations normally present in agricultural soils are Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+ and NH_4^+. In processes of weathering and clay formation the water in immediate vicinity of decomposing primary mineral is rich in calcium, magnesium, potassium and sodium ions. The newly formed clay mineral reacts with these ions and adsorbs them on its surface. Ordinarily, calcium ions adsorb to much greater extent.

Cation Exchangeable Capacity:

Cation exchangeable capacity of soil represents the capacity of colloidal complex to exchange all its cations with the cations of the electrolyte solution or the surrounding liquid.

Base saturation:

Base saturation represents the total exchangeable bases (Ca, Mg, K, Na) expressed as a percentage of total cation adsorbing or cation exchange capacity of soil, can be calculated from the formula.

$$V = \frac{100S}{T}$$

where V - percentage of base saturation
S - total exchangeable bases
T - cation exchangeable capacity

The difference between cation exchange capacity and total exchangeable bases (T – S) gives the extent of unsaturation or the amount of exchangeable hydrogen present in soil.

Replacing Power of Cations:

The replacing power of cations varies with type of ion, size, degree of hydration, its valence and concentration and kind of clay mineral involved.

The replacing power of monovalent cation increases in the following order:
Li< Na < K < Rb < Cs < H and for divalent ions the order is Mg < Ca< Sr < Ba

In case of mixture of monovalent and divalent system

$$Na < K < NH_4 < Mg < Ca < H$$

Thus we can understand that sodium is more easily replaced than potassium, potassium than ammonium and so on.

Anion Exchange:

The process of anion exchange is similar to that of cation exchange and is governed by some factors that influence the later process. In case of silicate clay the exchange takes place between OH ions of clay minerals and anions like NO_3^-, Cl^-, SO_4^{2-}, $H_2PO_4^-$ etc., in soil solution. The OH ion originates from broken bonds of the clay lattice. The capacity for holding anion increases with increase in acidity.

The lower the pH the greater is the adsorption. All anions are not adsorbed equally and readily. Some anions such as $H_2PO_4^-$ are adsorbed very readily at all pH values in the acid as well as alkaline range. Cl^- and SO_4^{2-} ions are adsorbed at slightly low pH but none at neutrality, while NO_3^- ions are not adsorbed at all. The affinity for adsorption is of the order $NO_3^- < Cl^- < SO_4^{2-} < PO_4^{3-}$ for the use of plants. The phenomenon of anion exchange can be demonstrated by exchange of hydroxyl ion clay.

$$\text{OH-clay} + H_2PO_4^- \rightleftharpoons H_2PO_4^- \text{- clay} + OH^-$$

The adsorption of phosphate ions by clay particles from soil solution reduces its availability to plants. This is known as phosphate fixation. As reaction is reversible the phosphate ion again become available when they are replaced by OH^- ions which are released by substances like lime applied to soil to correct soil acidity. The other anions for example bicarbonates, silicates may replace adsorbed phosphate. Hence the fixation is only temporary. The OH^- ions originate not only from silicate clay but also from sesquioxide clay that is hydrous oxides of iron and aluminium present in the soil. The phosphate ions react with the hydrous oxides also and get fixed as in the case of silicate clay, forming insoluble hydrous phosphates of

$$Al(OH)_3 + H_2PO_4^- \rightleftharpoons Al(OH)_2\ H_2PO_4 + OH^-$$

If the reaction takes place at low pH under strongly acidic conditions, the phosphate ions are irreversibly fixed and totally unavailable for the use of plants.

UNIT
1

SOIL ANALYSIS

Lesson
4

Objectives of the lesson: This lesson deals with sampling and chemical analysis of soils.

SOIL SAMPLING

The collection of a proper sample plays a vital role in the success and / or failure of soil analysis which helps as an aid to guide for the use of fertilizers or for any other treatments for greater productivity. Apart from this subsequent handling operations are equally important. Several steps are involved in obtaining the final sample: They are

1. Taking and mixing a series of cores from the area to be sampled;
2. Further sub sampling this original sample in one or more operations;
3. It will be then subjected for air drying, grinding, sieving, mixing and storing. The greatest possibility for error in securing a representative sample can be avoided by careful operations at every stage besides selection of location of sampling at the beginning.

The following steps are the out come of the practical considerations in obtaining the desired sample.

1. A series of cores taken based on some systematic grid lay out of the areas of equal diameter. A reasonable depth should be considered in order to get composite sample.
2. Independent separate soil cores should be analysed or replicate sets of composites made to determine statistical significance of results on the final composite.
3. The total number of soil cores to be composited will depend on the variability of the soil, the degree of accuracy desired, the particular element or elements to be determined.
4. Cultivated soils are generally more variable when compared with virgin soils. However, saline and alkali soils are extremely variable.
5. Separate composite samples representing different segments of the soil profile or root zone should be taken into consideration.
6. The sample must be free from contamination from soil surface materials (crop residues, manure, fertilizers, etc).
7. It is appropriate to make a map depicting initial sampling.

The importance of soil analysis, to know the nature of soil, cannot be over emphasized because the production of crop in any region depends on the nature and the properties of soil as well on the crop variety and the cultural practices. When and how much of the fertilizer should be applied can only be determined from the results of the carefully conducted soil analysis.

Operating techniques in soil sampling:

i) From a clean face of the profile dig a pit and remove soil
ii) With help of an auger or soil sampler a soil sample is taken.

The different types of augers like

a) Cylindrical auger,
b) Screw auger or Carpenter auger, and
c) Post hole auger are used:

Test borings are made to determine the nature of the soil profile, and then from a fresh site, samples are collected by means of the auger. The representative samples so obtained are transferred to receptacles for transport. If the soil is to be kept in moist condition as for moisture determination, bacterial count and nitrate estimation etc: air tight containers are preferred. If however the soil is to be air dried, cloth bags subsequently numbered are very convenient for the purpose. The method of sampling to be used and the amount of soil retained will depend upon the purpose for which the sample is required, the nature of soil, the time available and other conditions

To obtain a true representative sample of an area, it is necessary to take large number of samples spread over the area and then sub-sampling is done. For soil survey work a type sample only is required that is sample taken from one particular spot is typical of the surrounding area. This area may be large or small and its boundaries are determined by putting down test bores at intervals. These boundaries are then drawn on the map. For this kind of survey work, the post hole auger is the most suitable.

Method of taking composite:

By means of 4” post hole auger, number of samples are collected from the sites representative of the plot or area to be examined. It is preferable to take a sample from the upper six inches. The remaining sample representatives can be obtained from in between 6” - 9”, 9”-12”, 12”-18” layers. The soil samples taken from the same layers of different bores combined. Any lumps present are crushed into smaller pieces and mixed thoroughly on a piece of canvas. From this material a grab sample is taken, that is the material is spread into a thin layer and then small portions of soil sample at random are taken, so that the sample taken is about 1Kg and is representative of the original material. The sample is placed in a numbered calico bag or in a tin with a tightly fitting lid and labeled carefully with the location, besides depth of soil. One label containing detailed notes of the sample is put inside the bag or container and transported to the soil testing laboratory.

Method for collection of samples of soil:

The site of the pit is carefully chosen, taking into consideration ground cover, micro relief, degree of erosion, surface drainage, proximity to trees and all other factors likely to affect the soil in comparison with the normal type it is intended to represent. By means of suitable bearings the position of the pit are fixed on the map.

As far as possible, the location of the pit must be in such a way that there is maximum sunshine on one end at the time of sampling. This will help in differentiating between the colour, texture and consistence of soil in various horizons. If possible the pit must be dug to the depth such that it is sufficient to expose the horizon of the soil. In deep soils use an arbitrary depth of 3.5 feet. It is preferable to collect samples from the layers deeper than the bottom of the pit by means of auger.

One face of the pit is carefully cleaned with a spade and the succession and depth of each horizon is noted. The surface is pricked with the knife or edge of the spade to show up structure, colour and compactness. Before sampling the litter and plant material is cleared from the surface, with out removing grass roots or organic matter embedded in the horizon. First sample is obtained in such a manner that it should represent the whole of the surface horizon up to the depth of the first distinct change in colour or texture. Sample from horizon below this are taken by cutting steps in the pit face and removing a portion of the layer typical of horizon with out attempting to include its full depth. Sample is placed together with a slip of paper identifying the soil, in a numbered calico bag for transport to the laboratory.

The soil samples are generally obtained for the following purposes:

a) To study the fertility status of soils
b) To study the alkalinity and salinity problems
c) To determine the suitability of the soil for laying gardens.
d) Soil survey
e) To obtain the data on Acidity and lime problems
f) To study the probable effect of canal irrigation on the soil, especially with respect to likelihood of kallar problems.

DETERMINATION OF SOIL MOISTURE:

A common method of expressing soil moisture percentage is in terms of wet weight percentage or the kilograms of water associated with 1 kg of dry soil. For example, if 1 kg of moist soil (soil and water) loses of 0.2 kg of water when dried, the 0.8 kg of dry matter is used as the base for the percentage calculation, 0.2/0.8 x 100 = 25%. The weight of the wet soil is an unsatisfactory basis for calculation since it changes with every moisture fluctuation.

Moisture content is also commonly expressed in volume percentage, that is, the volume of soil water as a percentage of the volume of the soil sample. Other volume measures, such as cubic miters of H_2O per cubic meter of soil, are employed. These measures have the advantage of giving a better picture of the moisture available to roots in a given volume of soil.

A known weight of a sample of moist soil, usually taken in cores from the field, is dried in an oven at a temperature of 100–110^{0}C and weighed again. The moisture lost by heating represents the soil moisture in the moist sample.

DETERMINATION OF TOTAL NITROGEN IN SOILS:

Total nitrogen in soils will vary from as low as 0.01 percent to 0.03 percent. In plants it ranges from 0.2 to 0.4 percent, depending upon species, the plant part and age.

KJELDAHL METHOD MODIFIED TO INCLUDE NITRATES:

Principle:

Organic and nitrate nitrogen is converted to ammonium sulphate and the ammonia gas is distilled into boric acid and titrated with sulphuric acid.

Reagents:

1. Sulphuric salicylic acid: One g of salicylic acid is dissolved in 30 ml of concentrated sulphuric acid.
2. Sodium thiosulphate, 24 mesh dried powder.
3. Sulphate mixture: 10 parts of potassium sulphate, 1 part of ferrous sulphate, and 1/2 part of copper sulphate are mixed and made to pass a 40 mesh sieve by grinding.
4. Sodium hydroxide: 450 g in litre of water.
5. Mossy zinc; large pieces.
6. Boric acid: 2 percent aqueous solution.
7. Standard sulphuric acid 0.1 N.
8. Bromo cresol green-methyl red indicator: 0.1 percent solution of bromo cresol green is prepared by adding 2ml of 0.1N sodium hydoxide per 0.8g of indicator; and 0.1percent methyl red is prepared in 95 percent ethanol. 25ml of methyl red is mixed with bromo cresol green indicator and dilute to 200 ml with ethyl alcohol.

Procedure:

Take 10g of soil or one g of plant tissue, or 0.5g of seed material which should pass through a 20 mesh sieve.

Add to it 50 ml of the sulphuric-salicylic acid mixture and shake to get intimate contact of the soil with the reagent. Add 5g of sodium thiosulphate and heat gently for about 5minutes, taking care to avoid frothing. Cool, add 10g of the sulphate mixture, and seed material, then digest in kjeldahl flask at full heat. With soils, plant and seed material, the digestion is continued for 1 hour after the solution has cleared.

Cool and add 300ml of distilled water and fit in the distillation apparatus. Add 100ml of concentrated sodium hydroxide and a large piece of zinc. For the soils add 2 large teaspoons of glass beads (5 mm in diameter). Connect to distillation head, and distil off 150ml onto 50 ml of 2 percent boric acid solution. Add 10 drops of the bromo cresol green-methyl red indicator and titrate to the first faint pink colour green-methyl standard sulphuric acid. Blanks should be run and the titration carried to the same end point in exactly the same manner.

Calculations:

Weight of soil taken = 10g
Volume 0.1 N H_2SO_4 used in titration = x ml
Weight of nitrogen in 10g soil = x x 0.1 x 0.014 = 0.0014 x
% Nitrogen = 0.0014 x 100/10 = 0.014 x%
me of nitrogen in 10 g soil = x x 0.1
= 0.1 x

me percent of nitrogen in soil = $0.1\,x \times 100/10$

= x

ppm of nitrogen in soil = % nitrogen 1000000/100

= $0.14\,x \times 10^4 = 140\,x$

where me is milli equivalents

DETERMINATION OF PHOSPHORUS

Preparation of extract:

Take 20-50ml of the HCl or sodium carbonate extract in a 50ml porcelain glazed dish. Evaporate on a water bath and ignite at a dull red heat. Rub with a pestle and ignite again. Extract the well-ignited mass with hot water and filter free from chlorides. Keep the residue on the filter paper for the estimation of P_2O_5 and the extract for potash.

Determination of P_2O_5 :

Digest the residue from which the potassium is removed for half an hour on a water bath with 30 ml of 10% sulphuric acid and filter free from acid. Transfer the filtrate to a 400 ml beaker. Add 5-10 ml of nitric acid and then add ammonia until a precipitate that forms dissolves on shaking. Dilute to about 100 ml and warm to about $25^0 – 30^0$C and put a piece of red litmus paper which should turn blue. Now add drop-by-drop HNO_3 (1:10) till it just turns red again. Add sufficient amount (30 ml) of molybdate solution to ensure complete precipitation. Shake vigorously for five minutes; allow for standing for at least half an hour. Filter by decantation using No 44 Whatman filter paper. Wash the precipitate with 2% solution of sodium nitrate or ice cold water. The washing should be continued till the filtrate is free from acid. It can be tested by adding a drop of standard alkali and a few drops of phenolphthalein.

The filtrate should have pink colour. Spread the filter paper on the sides of the beaker in which the precipitation was done. Wash it with a jet of distilled water. Dissolve in a known amount of N/10 NaOH. Titrate with N/10 sulphuric acid, using phenolphthalein indicator till the pink colour of phenolphthalein just disappears. Introduce the filter paper in the beaker and add more acid till the pinkish colour, which reappeared on the addition of the filter paper, disappears. Calculate results assuming

$$1\text{ml N/10 NaOH} = 0.000309 \text{ g } P_2O_5$$

1. The solution in which the phosphate is estimated by this method should not contain more than 10mg P_2O_5.
2. Assuming that soil contains about 0.2% P_2O_5 then 20 ml N/10 NaOH will be enough to dissolve the precipitate of phosphomolybadate formed from 50ml of the HCl extract.

DETERMINATION OF SILICON IN SOIL SAMPLE:

The silicon from the sodium carbonate fusion is dehydrated with $HClO_4$ washed free from metallic cations with 6N HCl, and then is brought into solution in NaOH and determined colorimetrically by the molybdosilicic yellow colour method.

The molybdo silicic acid yellow colour is very sensitive to salt concentration. However the large amount of molybdate added serves as an excellent buffer so that a 0.25ml error in measurement of the 6N HCl does not produce a significant change of pH or colour intensity.

Standard Silicon solution:

Clear quartz crystals are digested for an hour in concentrated HCl to remove surface impurities then washed and grinded to fine powder that will pass a 0.5-mm sieve. The powder is ignited briefly in a crucible, and then cooled placed in a vial and tightly stoppered. A 0.01070g sample is a placed in a platinum crucible and fused with Na_2CO_3. The melt is dissolved in water and diluted to a volume of 1 litre in a volume flask. This solution contains 50□g of elemental silicon per ml. Aliquots (1,2,3,4,.....and 10 ml) of this solution are taken for the standard curves, and the colour is developed . The percentage light transmission for each of these solutions is plotted against µ g of Si per 50ml on semilog paper.

<u>*Procedure:*</u>

A soil sample is taken in a crucible and fused with $Na_2CO_{3.}$ When the crucible from the Na_2CO_3 fusion has cooled, the cover is placed on the crucible, and 8ml of 60% $HClO_4$ is added drop wise under the slightly raised lid. When effervescence has ceased, the lid and sides of the crucible are washed with water and crucible with lid covering three fourth of the top, is placed in a sand bath on an electric plate, and the suspension is evaporated to fumes of $HClO_4$, when dense fumes appear, the crucible is covered, and the suspension is boiled gently for 10 minutes at a temperature a little above 200^{o}c.

When the crucible has cooled, approximately 5ml of distilled water is added, and the suspension is carefully mixed and heated almost to boiling to dissolve the salts that have solidified on cooling. The suspension is then transferred to a 60ml pointed centrifuge tube, and the crucible is rinsed with a wash bottle, the washings being added to the tube. All the silica does not have to be removed from the crucible at this time. Approximately 2ml of 6N HCl is added, and the suspension is diluted to exactly 60ml with water, thoroughly mixed with the air-jet stirrer, and centrifuged at 1800 rpm for 5minutes to throw down the silica. The suspension adhering to the air-jet stirrer is washed back into the crucible.

A 50-ml aliquot is pipetted with a lowry pipette from the supernatant liquid in the centrifuge and transferred to another 60ml pointed centrifuge tube. This solution is used for the determination of aluminium which is designated as A.

To wash the silica in the tube into a 50ml of 1.2N HCl is added and stirred, and the suspension is centrifuged at 1800 rpm for about 5minutes. The supernatant liquid is then decanted by suction and subsequently discarded, since an aliquot for analysis of the solute has already been taken.

The silica is then washed from the tube into 250-500ml nickel or platinum beaker with a stream from the wash bottle, and the silica adhering to the sides of the crucible in which the dehydration was carried out is also transferred. The final washing of both the centrifuge and the crucible was made with 5% NaOH to make sure that all the SiO_2 is removed. Approximately 2.5g of NaOH pellets are added to suspension in the nickel / platinum beaker, and the volume is adjusted to 100ml.The solution is then boiled for 5 minutes to dissolve SiO_2. When cool, this solution is transferred to a 500ml volumetric flask and diluted to the mark with distilled water. This solution is used to determine silicon which is designated as B.

A 10ml solution of ammonium molybdate is placed in a 50ml volumetric flask, and the volume is adjusted to about 30ml with distilled water. Then 5ml of 6N HCl is added, and the flask is swirled to dissolve the white precipitate that forms. Finally a solution B aliquot containing 50 to 500 μ g of Si is added, and then solution is diluted to the mark with distilled water.A5-ml aliquot of the solution B is desirable for samples containing from 5 to 50% elemental Si. The solution is mixed well transferred to the colorimetric tube, and allowed to stand for 30 minutes before the percentage light transmission is read with a 400 mμ light maximum. Reference to the standard curve gives the μ g of Si / 50ml.

$$\%\mathrm{Si} = \frac{\mu\mathrm{g\ of\ Si\ 50ml}}{\mathrm{ml\ in\ aliquot}} \times \frac{0.05}{\mathrm{Wt.of\ sample\ in\ g}}$$

DETERMINATION OF LIME

Calcium carbonate of the soil can be determined by titrating the soil suspension with N/2 sulphuric acid in the presence of a mixture of indicators, bromomethyl blue and bromocresol green. Calcium sulphate and aluminium chloride are also added to make the appearance of colour very distinct. Calcium sulphate provides a uniform condition through out the reaction and the final colour change occurs in its presence irrespective of the amount of calcium carbonate present in the soil. Aluminium chloride lowers the pH of the soil suspension, and brings the colour change just at the point, when no carbonates are present.

Reagents:

1. N/2 sulphuric acid
2. 0.1N $AlCl_3.6H_2O$: Dissolve 8.05g of aluminium chloride in a small quantity of water and transfer it to1 litre measuring flask. Dilute to 1 litre.
3. Bromothymol blue 1% alcoholic solution: Grind 1g of bromothymol blue in an agate pestle and mortar. Dissolve it in 100ml alcohol and stock in a pyrex bottle.
4. Bromocresol green (1% alcoholic solution): Prepare the solution in the same way as in bromothymol blue.

Procedure:

Weight out 10g of soil and stir it with 100ml of distilled water in a titration flask. Add an excess of calcium sulphate (0.2-0.5g). Bring the soil suspension well and 10ml of 0.1N $AlCl_3.6H_2O$ solution. Shake the suspension well and add 10 drops of bromothymol blue and 10 drops of bromocresol green and note the colour. Green colour shows the amount of $CaCO_3$ over 1% and a golden yellow colour is indicative of the absence of $CaCO_3$ .If the carbonates are present the procedure is as follows:

Bring the contents of the flask to the boiling point and titrate against 0.5N sulphuric acid. Boil for a minute or two after each addition and allow to settle for a couple of minutes. This however is only necessary in the later stage of titration as it is easy to see the green colour edge in the beginning. The titration is complete, when the colour of the suspending liquid is golden yellow, which persists on boiling for a couple of minutes and allowing it to settle for a minute or two. The amount of sulphuric acid used is equivalent to the total carbonate in the soil.

1ml of 0.5N sulphuric acid = 1ml of 0.5N $CaCO_3$ = 0.5me of $CaCO_3$
= 50/2 1/1000 = 0.25g $CaCO_3$

Calculations:

Amount of soil taken = 10g

Amount of 0.5N H_2SO_4 used = X ml

Percentage of $CaCO_3$ in the soil = $\frac{0.025 \times X \times 100}{10}$ (or)

$$= \frac{\text{volume of } 0.5N\ H_2SO_4}{4}$$

= Percentage of $CaCO_3$ in the soil.

DETERMINATION OF HUMUS (ORGANIC CARBON):

Principle:

For the determination of organic matter or organic carbon of the soil, dry combustion and wet digestion methods are used. The dry combustion method gives absolute values and is useful for very accurate work. For ordinary routine work Walkalay and Black's rapid titration method is useful. In this method the soil is digested with chromic and sulphuric acid. The excess of chromic acid, not reduced by the organic matter of the soil, is determined by sulphate solution. Nitrates interfere with the estimation only when present in more than 1/20th of the carbon. The chlorides also interfere, but a correction factor equal to 1/12 of the chloride can be applied. It must however be admitted that the values obtained by the Walklay-Black method are only approximate, because all the carbon which is oxidised is 60-90 percent with a mean value between 75-80 percent.

Reagents:

1. Potassium dichromate (1N): Dissolve 49.0g 0f $K_2Cr_2O_7$ in water and make it to one litre.
2. Sulphuric acid not less than 96%
3. Phosphoric acid (85 percent).
4. Diphenylamine indicator solution: Dissolve 0.5g of diphenylamine in a mixture of 100ml sulphuric acid and 20ml water and store in a coloured bottle.
5. Ferrous ammonium sulphate (N/2): Dissolve 392.0 g of analytical reagent grade $FeSO_4$ $(NH)_2SO_4$ $6H_2O$ in water. Add 15 ml sulphuric acid and dilute to 2 litres.

Procedure:

Take 2- 10 g of soil (0.5mm) in a 500ml conical flask. Add 10ml of 1N potassium dichromate solution and 200ml of concentrated sulphuric acid. Shake well for a minute or two and allow it to stand on an asbestos mat for about 30 minutes. Add 200ml of water, 10ml of phosphoric acid and 1ml of diphenyl amine indicator solution. A deep violet colour will appear. Titrate it with N/2 ferrous ammonium sulphate solution, till the violet colour change to purple and finally to green.

Add 0.5ml of potassium dichromate solution accurately with a burette or a pipette and titrate with ferrous ammonium sulphate solution, until the colour changes to green. If more than 8ml of the potassium dichromate solution has been reduced during the digestion, then the determination should be repeated using a smaller quantity of soil.

In the same way carry out a blank determination also and calculate the results as follows:

Calculations:

Weight of soil taken = w g
Volume of 0.5N ferrous ammonium sulphate required for reducing 10.0ml $K_2Cr_2O_7$ solution = x ml
Volume of 0.5N ferrous ammonium sulphate required for reducing the excess of dichromate = y ml
Difference = (x-y) ml
1ml of 1N $K_2Cr_2O_7$ = 0.003g of carbon

$$\text{Percentage of carbon in soil (z)} = \frac{(x-y)\times 0.003\times 100}{2\times w}$$

$$\text{Percentage of organic carbon in the soil} = \frac{z\times 100}{58} \quad \text{(or)} \quad = \quad z \times 1.724.$$

DETERMINATION OF NITRATE NITROGEN IN SOIL:

Nitrate nitrogen in soils will vary from less than 1.0 to several hundred parts per million.

Principle:

The soil extract is clarified by use of copper sulphate, calcium hydroxide, and magnesium carbonate. Nitrate is determined in the extract by phenol disulphonic acid method of Harper (1924).

Reagents:

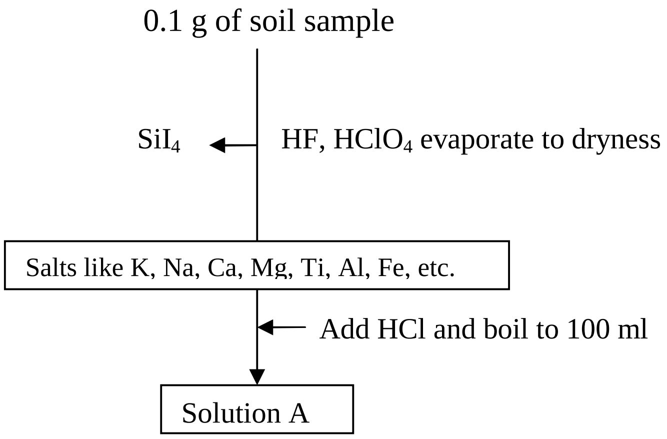
1. Copper solution, 1 N.
2. Calcium hydroxide powder.
3. Magnesium carbonate powder.
4. Phenoldisulphonic acid.
   Dissolve 25g of pure white phenol in 50 ml of pure concentrated sulphuric acid. Add 75 ml of fuming sulphuric acid and heat in a boiling water bath for 2 hours. Store in brown bottle.
5. Ammonium hydroxide: Dilute 1 part of strong ammonium hydroxide with 2 parts of water.
6. Standard nitrate solution: Dissolve 0.7216g of pure potassium nitrate in 1 litre of water. This solution contains 100 ppm nitrogen as nitrate.
7. Silver sulphate: 0.02N (nitrate free).
8. Carbon black.

Procedure:

Place the soil sample as brought from the field in an oven at 70°C for 41 hours. Grind and pass it through a 2mm sieve. Weigh out 50g of soil and place it in a 500 ml flask. Add 250 ml of distilled water containing 5ml of 1N copper sulphate solution and shake, for 10 minutes.

If the soil is not very acidic and does not give a coloured extract, add 0.4g of calcium hydroxide and 1g of magnesium carbonate to the soil suspension and shake for 5 minutes more to precipitate the copper. Filter on a dry filter paper and discard the first 20 ml of filtrate. If the soil gives a coloured extract allow it to settle. Decant about 125ml of the supernatant liquid in to a flask. Add 0.2g of calcium hydroxide and 0.5g of magnesium carbonate. Shake for 5 minutes, and filter as before. Transfer 10 ml of it with a pipette to an evaporating dish. Heat it to dryness. Cool and add rapidly 2 ml of phenoldisulphonic acid directly to the center of the evaporating dish, and rotate the dish in such a way that the reagent comes in contact with the entire residue. Let it stand for 10 minutes. Add about 15 ml of cold water, and stir with a short glass rod until the residue is in solution. Cool slowly and add ammonium hydroxide until it becomes slightly alkaline. Transfer this yellow solution to a Nessler's tube, dilute and compare with standard solution containing 1 ppm nitrogen as nitrate using a colorimeter or Nessler tubes. A convenient and satisfactory standard can be made by evaporating to dryness 25 ml of a solution containing 22 ppm nitrogen as potassium nitrate. When cool add 4ml of phenoldisuphonic acid, allow to standing for 10 minutes, and making up the volume to 500ml. This solution contains 1ppm of nitrogen (0.001 mg nitrogen per ml). Develop the colour by adding just enough ammonium hydroxide to make it alkaline. The yellow colour develops at this stage. Compare the standards with the unknown whose content of nitrate is then calculated.

DETERMINATION OF ALKALI SALTS:



A separate aliquot is taken for different elements and individual methods are used for determination of alkali salts. For example, potassium by cobalt nitrate method, for calcium, magnesium, and aluminium by complexometric method using EDTA, iron by volumetric or potentiometric titration method using dichromate.

UNIT 2

AIR POLLUTION

Lesson 1

Objectives of the lesson: This lesson deals with sources and classification of atmospheric pollutants besides the role of carbonmonoxide and carbondioxide in the atmosphere.

Excessive release of air pollutants in air by anthropogenic activities disturb the dynamic equilibrium in the atmosphere and there by effect the man and his environment.

According to World Health Organisation (WHO), "*Substances put into air by the activity of mankind in concentrations sufficient to cause harmful effect to his health, vegetables, property or to interfere with the enjoyment of his properties*".

Thus the atmosphere is a dynamic system, which steadily absorbs various pollutants from natural as well as man made sources thus acting as a natural sink. Gases such as CO, CO_2, H_2S, SO_2 and oxides of nitrogen (NO_x) as well as particulate matter such as sand and dust are continuously released into the atmosphere through natural activities as forest fires, volcanic eruption, decay of vegetation, winds and sand or dust storms.

Man made pollutants (Ex: CO, CO_2, H_2S, SO_2 and nitrogen oxides (NO_x), hydrocarbons (HCN), particulates etc., are also released into the atmosphere. These activities surpassed the release of pollutants by nature thousand fold. The magnitude of problem of air pollution has increased alarmingly due to population explosion, urbanisation, industralisation, increase of automobiles and other human tendencies for greater comforts. The pollutants travel through air disperse and may interact with each other and on the other hand if the sink absorb these pollutants in a slower rate than they were dispersed or enter into the atmosphere, there is a danger of their being accumulated in the air. Such disturbances in the dynamic equilibrium may affect the very life on the earth and its environment. The dilution and dispersion of the gaseous pollutants in the atmosphere depends upon the meteorological conditions prevailing at that time.

Study of air pollution:

Study of air pollution involves 1. Sources and Effects
2. Behaviour and fate of air pollutants
3. Analysis of air pollutants.

Definition: Air pollution may be defined as “Any atmospheric condition in which certain substances are present in such concentration that can/may produce undesirable effects on man and his environment”.

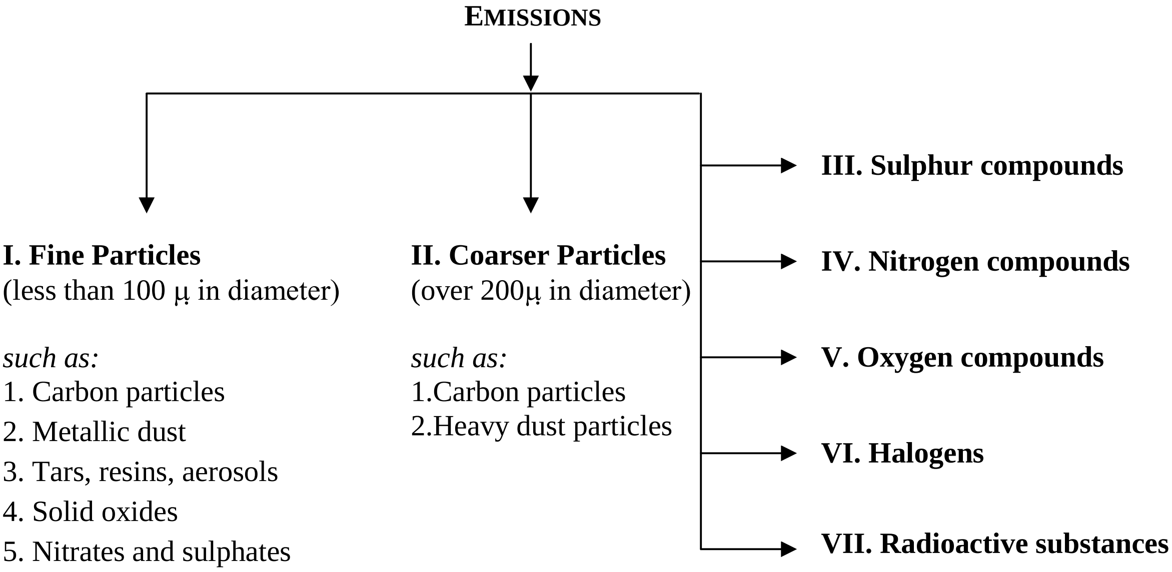
Sources and effects:

They may be

1. Gases like : Oxides of Sulphur SO_2, CO, CO_2, H_2S, oxides of nitrogen (NO_x) and hydro carbons(HC)
2. Particulate matter like: Smoke, dust, snooze, aerosols etc.
3. Radioactive materials and others

SOURCES AND EMISSIONS:

The major sources of air pollutants have been particulates and gaseous matter, which get released by the burning of fossil fuels such as coal and petroleum etc. Out of this a variety of emissions are



EMISSIONS

I. Fine Particles
(less than 100 µ in diameter)

such as:
1. Carbon particles
2. Metallic dust
3. Tars, resins, aerosols
4. Solid oxides
5. Nitrates and sulphates

II. Coarser Particles
(over 200µ in diameter)

such as:
1.Carbon particles
2.Heavy dust particles

III. Sulphur compounds

IV. Nitrogen compounds

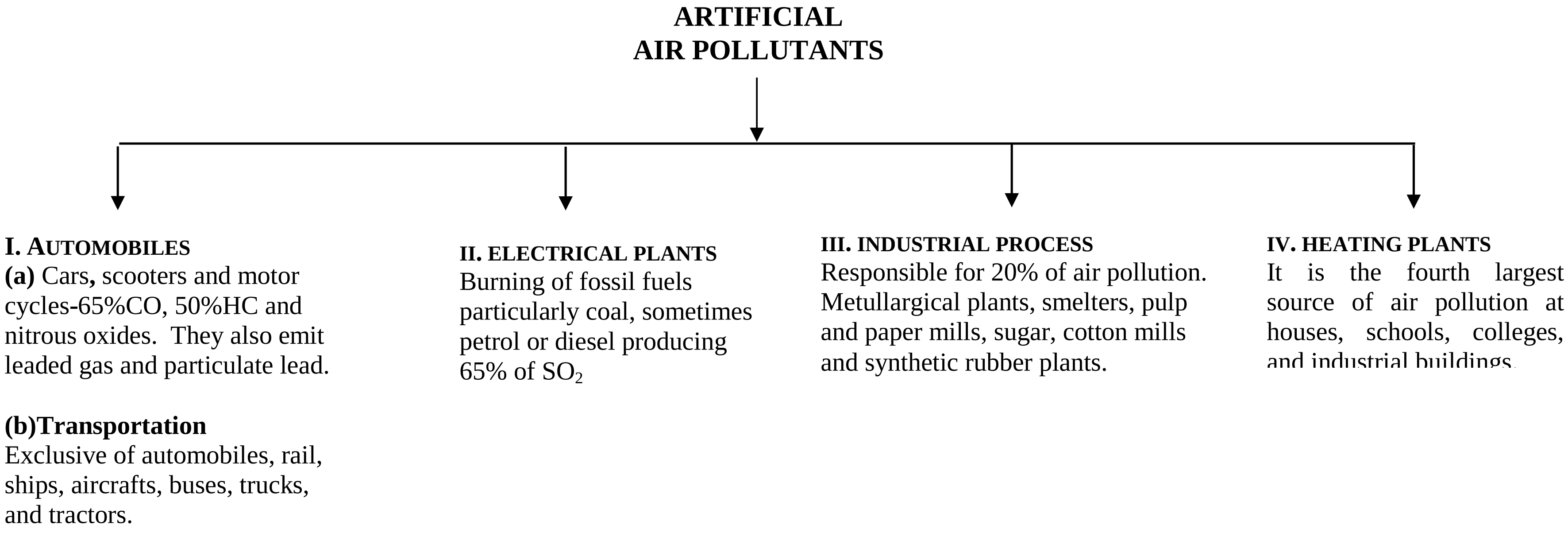
V. Oxygen compounds

VI. Halogens

VII. Radioactive substances

Artificial pollutants:

Artificial pollutants are poured into the air mainly by at least through four major fuel-burning sources.



ARTIFICIAL AIR POLLUTANTS

I. AUTOMOBILES

(a) Cars**,** scooters and motor cycles-65%CO, 50%HC and nitrous oxides. They also emit leaded gas and particulate lead.

(b)Transportation

Exclusive of automobiles, rail, ships, aircrafts, buses, trucks, and tractors.

II. ELECTRICAL PLANTS

Burning of fossil fuels particularly coal, sometimes petrol or diesel producing 65% of SO_2

III. INDUSTRIAL PROCESS

Responsible for 20% of air pollution. Metullargical plants, smelters, pulp and paper mills, sugar, cotton mills and synthetic rubber plants.

IV. HEATING PLANTS

It is the fourth largest source of air pollution at houses, schools, colleges, and industrial buildings.

Flow chart for artificial air pollutants

Other sources of air pollutants:

Other sources of air pollutants are minor in quantities but they bear their significance due to their harmful effects.

Agricultural: Pesticides, agricultural field burning, and other practices from construction industries, seed dressing and chemicals used for it.

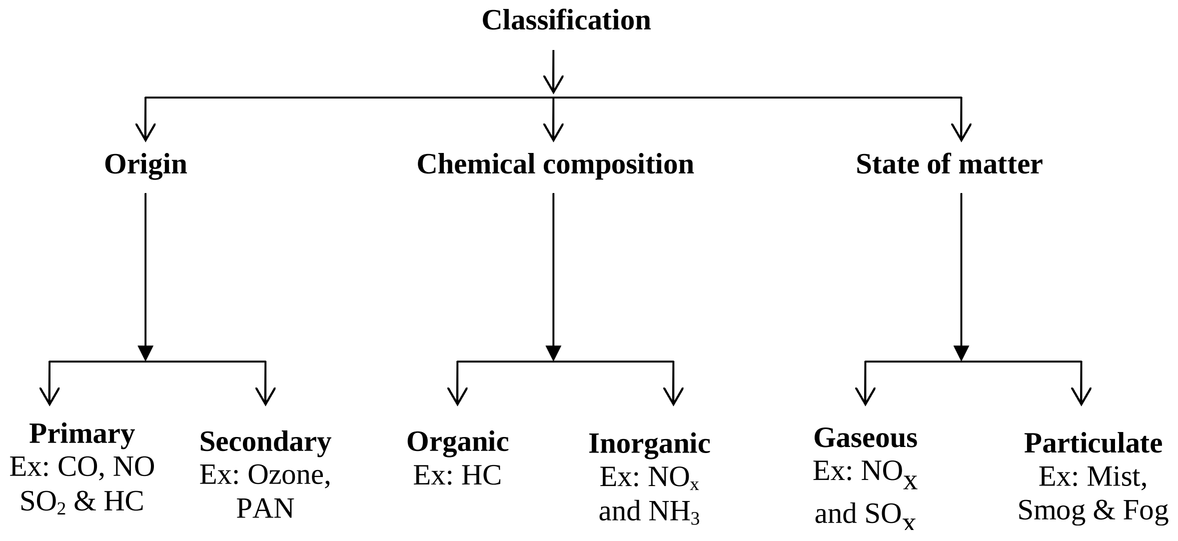
Remaining sources: Include natural sources like pollen, hydro carbons from vegetation, dust from deserts, storms and volcanic activities.

The typical composition of unpolluted air has been given under

Source	**CO**	**PM**	**SO**	**HC**	**NO**
Mortar vehicles					
Gasoline	53.5	0.5	0.2	13.8	6.0
Diesel	0.2	0.3	0.1	0.4	0.5
Air crafts	2.4	0.0	0.0	0.3	0.0
Rail roads& others	2.0	0.4	0.5	0.6	0.8
Total transportation	51.5	1.1	0.7	15.1	7.3
Coal	0.7	7.4	18.3	0.2	3.6
Fuel oil	0.1	0.3	3.9	0.1	0.9
Natural gas	0.0	0.2	0.0	0.0	4.1
Structural fires	0.2	0.5	0.0	0.1	0.0
Total miscellaneous	15.3	8.7	0.5	7.7	1.5
TOTAL	**91.0**	**25.7**	**30.2**	**29.1**	**18.7**

CLASSIFICATION OF AIR POLLUTANTS:

These can be classified based on their origin, chemical composition and states of matter.



I. Study of air pollutants with regard to origin:

Primary pollutants : Ex. CO, NO_2, SO_2 and hydrocarbons
Secondary Pollutants : Ex. Ozone, PAN compounds

(a) Primary:

Pollutants which are directly emitted into the atmosphere and found as such in the Atmosphere.

Examples: CO, NO_2, SO_2 and hydro carbons

(b) Secondary:

These are derived from primary pollutants due to smog.

Examples: O_3, photo chemical and photochemical reactions in atmosphere.

II. Based on chemical composition:

(a)Organic - Hydro carbons, aldehydes, amines and alcohols

(b) Inorganic:
1. Carbon compounds – CO and carbonates
2. Nitrogen compounds – NO_x, NH_3
3. Sulphur compounds – H_2S, SO_2, H_2SO_4, SO_3
4. Halogen compounds – HF, HCl, metallic fluorides
5. Oxidising agent – O_3
6. Other inorganic pollutants like fly ash, silica, asbestos, dust from metallurgical industries.

III. Based on state of matter:

(a) *Gaseous* – They get mixed up with air and do not normally settle out. CO, NO_x and SO_2

(b) *Particulates* – They exist in colloidal state as aerosols, smoke, fumes, dust, mist, fog, smog and spray.

Types of air pollution:

Constituent	**Molecular formula**	**Volume / Fraction**	**Total mass (millions of metric tonnes)**
Nitrogen	N_2	78.09%	3,850,000,000
Oxgen	O_2	20.94%	1,180,000,000
Argon	Ar	0.93%	65,000,000
Carbon dioxide	CO_2	0.032%	2,500,000
Neon	Ne	18 ppm	64,000
Helium	He	5.2 ppm	3,700
Methane	CH_4	1.3 ppm	3,700
Krypton	Kr	1 ppm	15,000
Hydrogen	H_2	0.5 ppm	180
Nitrous oxide	N_2O	0.25 ppm	1,900
Carbon monoxide	CO	0.1 ppm	500
Ozone	O_3	0.02 ppm	200
Sulphur dioxide	SO_2	0.001 ppm	11
Nitrogen dioxide	NO_2	0.001ppm	8

Man made air pollution in urban areas is often referred to as smog. The word smog is coined first by Dr.H.A.Devoeum is an organiser of British smoke abatement societies to describe the smoke-fog of the London peasoupers referred as *Classical smog*. While smog in Los Angeles, which is different, is referred as *Photochemical smog* formed through chemical reactions involving Sunlight.

Characteristics of classical and photochemical smog:

Characteristics	**Classical smog**	**Photochemical smog**
1. First occurrence noted	at London	at Los Angles
2. Principal pollutants	SO_x, particulate matter	CO, free radicals, HC
3. Principal sources	Industrial and house hold fuel	Motor vehicle fuel consumption
4. Effect on human	Lung and throat irritation	Eye irritation
5. Effect on compounds, time of occurrence	Reducing, winter months	Oxidising, around midday of summer

Units of measurement of air pollution:

Concentration of air pollutant is expressed as ppm based on volume measurement represent the volume of pollutant contained in one million volume of air. Volumes of pollutant and air determined at STP 25^0 C (77^0 F) and 760nm of Hg. Second way of expressing concentrations is based on mass of pollutants to volume of air containing it. Unit often used is $\mu g/m^3$, in case of heavy pollutants mg/m^3.

SOURCES AND EMISSIONS OF CARBONMONOXIDE:

It is a colourless, odourless, tasteless gas above – 192^0C. It is 96.5% as heavy as air and is not appreciably soluble in water. The basic chemical processes that yield CO is as follows.

1. In complete combustion of fuel and carbon compounds. This happens when available oxygen is less than the amount required for combustion.

$$2C + O_2 \rightarrow 2CO \qquad \text{--------------} (1)$$
$$2CO + O_2 \rightarrow 2CO_2 \qquad \text{--------------} (2)$$

The reaction (1) goes 10 times faster than the other one, such that CO will be the end product if insufficient oxygen is present in the process. On the other hand CO will be the end product although sufficient oxygen is present when the mixture of fuel and air are poorly mixed.

2. In industrial processes at elevated temperatures (ex: Blast furnace) the reaction between CO_2 and carbon containing material will result in the production of carbonmonoxide.

$$CO_2 + C \rightarrow 2CO$$

The CO produced is beneficial where it acts as a reducing agent in the production of iron from iron oxide ores. However, some CO may escape into the atmosphere and act as a pollutant.

3. In this process dissociation of carbondioxide occurs at high temperatures

$$CO_2 \rightleftharpoons CO + O_2$$

Thus CO_2 and CO exists in equilibrium at high temperatures. High temperature favours the production of CO_2 and oxygen. For example 1% dissociation of CO_2 occurs at 1745^0C and 5% at 1940^0 C.

Sources and sinks of CO pollution:

Natural processes e.g. volcanic eruption, natural gas emission, and electric discharge during storms, seed germination, marsh gas production etc., contribute to a little extent in atmosphere. About 80% of CO as pollutant is from automobiles. Maximum levels of this toxic gas tend to occur in congested urban areas at times where in maximum number of people is exposed such as during rush hours. The levels of CO may be between 50 – 100ppm.

In urban areas the atmospheric levels of CO exhibit a positive correlation with density of heavy traffic and a negative correlation with the wind speed. Forest debris, forest fires and deliberate agricultural and waste coal burning also contribute CO to the considerable level. Next class of contributors of CO is iron and steel industries and to certain extent from petroleum and paper industry.

Statistical Data:

The emission on a global scale is 350 million tonnes. (Human activities 275 million tonnes per year and natural 75 million tonnes /year), of which U.S.A., alone accounts for 100 million tonnes of CO into atmosphere.

(a) Transportation - contributes about 64% of CO
   Motor vehicles- 55.3%
   Air crafts -2.4%
   Rail, roads - 0.1%

(b) Miscellaneous sources- 16.9%
   Forest fires - 7.5%
   Agricultural burning -8.2%
   Agricultural burning implies controlled burning of forest debris, crop residues, bush, weeds and other vegetation.

(c) Industrial processes, mainly iron and steel industries and to certain extent from petroleum and paper industries constitutes the third largest contributor of CO (9.6%) to the air. The atmospheric background of CO is 0.1ppm.

Sinks:

The actual input of CO into the atmosphere by human activities is expected to double its concentration in the ambient atmosphere for every five years. But the actual increase in ambient global concentration is much less. Soil micro organisms found to be more effective in the removal of CO. The appropriate explanation for CO sink anomaly is the removal of CO by micro organisms. About 2.8 Kg of soil is able to remove 120ppm of CO in about 3 hours contact. The same sample when sterilized failed to remove CO from air. A total of 16 kinds of fungi, which are able to remove CO are isolated. While 200 micro organisms were isolated from soil and cultured. On the other hand CO is being oxidised to CO_2 in the atmosphere by OH^* radical, atomic oxygen, NO_2 and HO_2 (hydro-peroxide radical) N_2O, O_3 and excited molecules.

$$OH^* + CO \rightarrow CO_2 + H^*$$

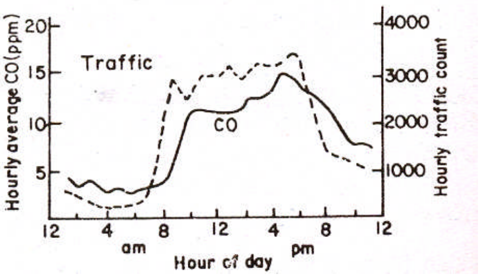
$$H^* + O_2 + M \rightarrow HO_2^* + M$$

$$HO_2^* + NO \rightarrow HO^* + NO_2$$

Where in HO^* radical will be regenerated, M is a rigid body.

Concentration profile of CO:

Although soil sink has the capacity to remove 5 times the annual discharge of CO per year significant contribution of CO exist because of neither CO nor the soil sinks are distributed uniformly. In fact the largest CO producing area often has the least amount of soil sink available. As said earlier it has been found that a positive correlation between traffic volume and CO production exists in a busy street of Manhattan of U.S.A which is depicted in figure.



CO Build-up in Manhattan Air from Heavy Traffic

Effect of CO on plants:

No detrimental effects have been detected in higher plants subjected to exposures of CO for 1–3 weeks at concentration levels up to 100ppm. Nitrogen fixation ability of free-living bacteria was inhibited by a 35hour exposure to CO levels of 2000ppm.The nitrogen fixation ability of free living bacteria in clover roots was inhibited after a 1- month exposure to 100ppm CO concentration. As CO levels rarely reach 100ppm, even for short periods of time; significant impact on vegetation and associated micro organisms seems unlikely at present.

Effect of CO on human health:

Carbon monoxide displaces oxygen from hemoglobin to produce carboxyhaemoglobin:

$$O_2Hb + CO \rightarrow COHb + O_2$$

The result is reduction in the blood's capacity for carrying oxygen. The level of COHb in the blood increases with the level of exposure to atmospheric CO and with increasing physical activity. Hence people become unconscious. However the effect can be reversed by exposure to O_2. Progressively higher exposures cause impairment of central nervous system (CNS) functions, change in cardiac and pulmonary functions, drowsiness, coma, respiratory failure, and finally death.

Effect of continuous exposure to various levels of CO:

COHb blood level (%)	Demonstrated Effects
<1%	Negligible effect
1-2%	Effect on behavior in performance
2-5%	CNS will be effected
>5%	Cardiac pulmonary functional changes
10-80%	Head ache, Fatigue, drowsiness, coma, respiratory failure and death.

The level of COHb in the blood is directly related to the CO concentration of the inhaled air. For a given ambient air CO concentration, the COHb level in the blood will reach an equilibrium concentration after a sufficient time period. This equilibrium COHb level will be maintained in the long as the ambient air CO level remains unchanged. However, the COHb level will slowly change in the same direction as the CO concentration of the ambient air as a new equibrilium is established. The normal or background level of blood COHb is about 0.5%. The equilibrium percentage of COHb in the blood stream of a person continuously exposed to the ambient air CO concentration of less than 100ppm can be estimated by the following equation;

$$\%\ \text{COHb in blood} = 0.16 \times (\text{CO conc. of air in ppm}) + 0.5$$

Blood COHb air equilibrium data

Ambient CO concentration(ppm)	Equilibrium concentration of blood COHb(%)
10	2.1
20	3.7
30	5.3
50	8.5
70	11.7

Smoking can be considered as causing pollution by individuals themselves. Cigarette smoke contains a CO concentration greater than 20,000ppm, during inhalation this is diluted to a level of about 400-500ppm.This high level of CO in the inhaled air results in higher COHb level in the blood of smokers as compared to non-smokers. The following table illustrates the observations

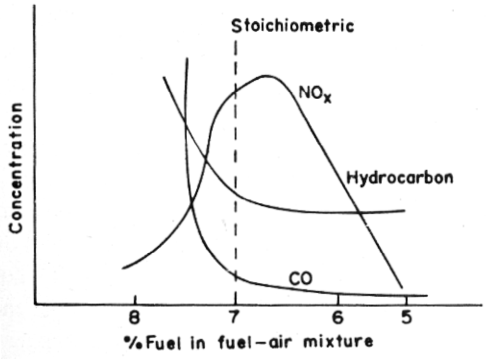
BLOOD - COHb LEVELS OF SMOKERS

Category of smokers	Median equilibrium Blood level of COHb (%)
Never smoked	1.3
Excess smoker	1.4
Pipe and / or cigar smoker only	1.7
Light cigar smoker (1/2 packet or less / day) non inhaler	2.3
Light cigar smoker (1/2 packet or less / day) inhaler	3.8
Moderate (1/2 pack or 2 packets / day) inhaler	5.9
Heavy cigarette smoker (2 or more packets /day)	6.9

Control of CO pollution:

The concentration sources are responsible for 74% of all CO emissions and gasoline-fed internal combustion processes are primarily accountable for it. The internal combustion engine emission consists of CO, NO_x, hydrocarbons and particulate matter. When one of these pollutants is subjected to control measures, the amounts of other pollutants are affected at the same rate. The relation ship between CO, NO_x, and hydrocarbons is illustrated in the following graph.

It follows that a low air fuel ratio reduces NO_x remarkably to the least, but increases CO and hydrocarbon emissions. Stoichiometric ratio indicates the right portion of oxygen on fuel for complete oxidation of carbon and hydrogen into CO_2 and H_2O. CO emission may be lowered by using relatively lean air /fuel mixture that is one in which the weight ratio of air to fuel is relatively high. At air / fuel ratios of 16/1, the internal combustion engine virtually emits no CO.



Effect of % fuel in air-fuel mixture on auto exhaust composition

Extensive investigations have been contemplated to control automotive emissions.

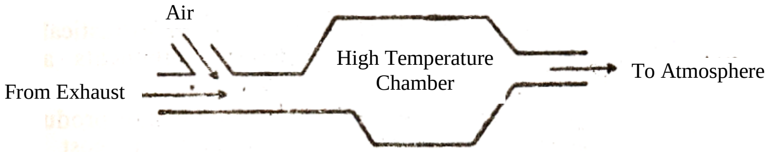
1. Modification of internal combustion engine to reduce the amounts of pollutants formed during the fuel consumption.
2. Development of exhaust system reactors, which will complete the combustion process and change potential pollutants into more acceptable forms.
3. Development of substitute fuels for gasoline, which will yield low concentrations of pollutants upon combustion.
4. Development of pollution- free power sources to replace the internal combustion engine.

Two types of exhaust reactors are developed

1. Thermal exhaust reactor
2. Catalytic reactor

1. Thermal exhaust reactor:

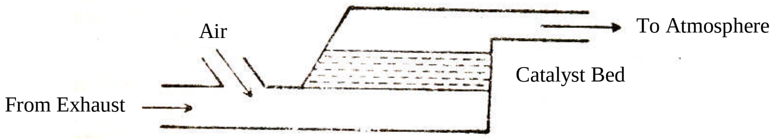
This contains a high temperature chamber, which is attached to exhaust engine, which has a provision of supplying oxygen for complete combustion process. But it is not economical since the material cost will be very high because it has to with stand high temperature and pressure.



Thermal Exhaust Reactor

2. Catalytic reactor

It has a bed of granular catalyst gets activated at moderate temperatures when compared to the others. The main difficulty is the cost of durable catalyst.

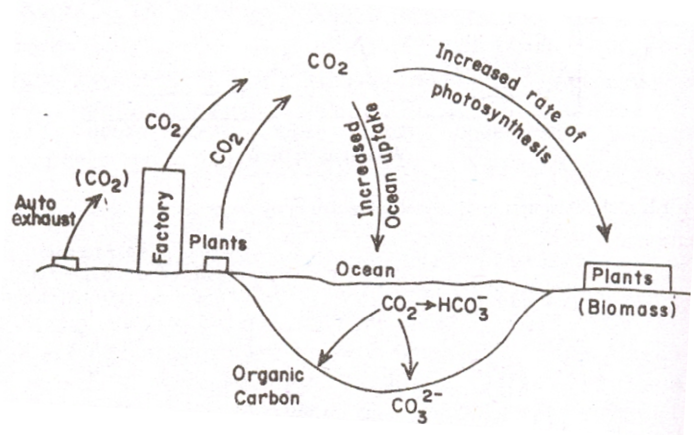


Catalytic Exhaust Reactor

SOURCES AND EMISSIONS OF CARBONDIOXIDE:

The atmosphere consists of 0.0314% by volume of carbon dioxide (CO_2). It is a non-pollutant species in the atmosphere. CO_2 along with water vapour is mainly responsible for absorption of IR radiations from the sun, re-radiation of this energy back to the earth surface. In terms of strictly chemical reactions in atmosphere CO_2 is relatively insignificant species. It is present in relatively low concentration it does not participate significantly in photochemical reactions. The IR radiation which absorbs is not sufficiently energetic to cause chemical reactions.

CO_2 is released by volcanoes, oceans, decaying plants as well as human activities, such as deforestation and combustion of fossil fuels. Automobile exhausts account for 30% of CO_2 emissions in developed countries. Methane is released from coal mines, decomposition of organic matter in swamps, rice paddy cultivation, guts of termites, in forest debris and stomachs of ruminants.



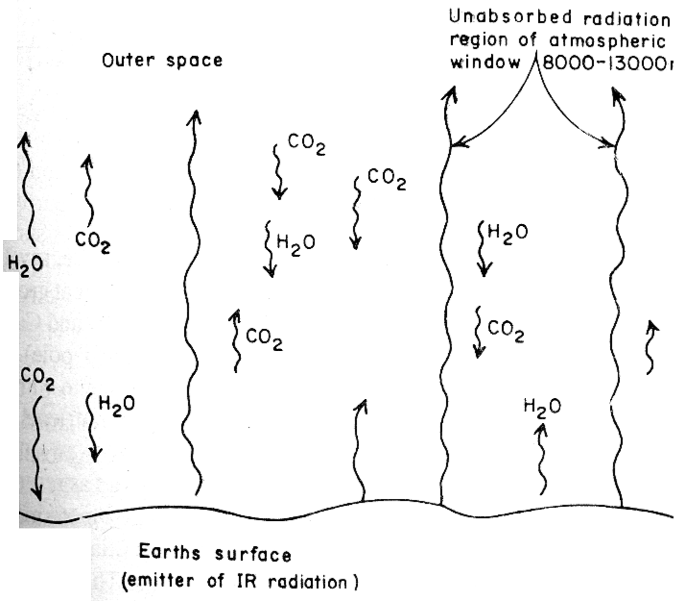
Sources and sinks of carbon dioxide

Chlorofluoro carbons (CFCs) are used as coolants in refrigerators, propellants, in aerosol sprays, plastic foam materials like “thermocoles” or “styrofoam” and in automobile air-conditioners.

Oceans and biomass are the major sinks for the atmospheric CO_2; Oceans convert CO_2 into soluble bicarbonates. The photosynthetic activity in the green plants increases the CO_2 level in the atmosphere. Forest is the places where lot of photosynthetic activity occurs. They also act as vast reservoirs of fixed but readily oxidisable carbon in the form of vegetation, wood and humus. Hence, forests maintain a balance in the atmospheric CO_2 level. Therefore deforestation definitely upsets this balance and increases the atmospheric CO_2 level. It is estimated that atmospheric CO_2content has increased by 25% during the last two centuries.

Green House Effect:

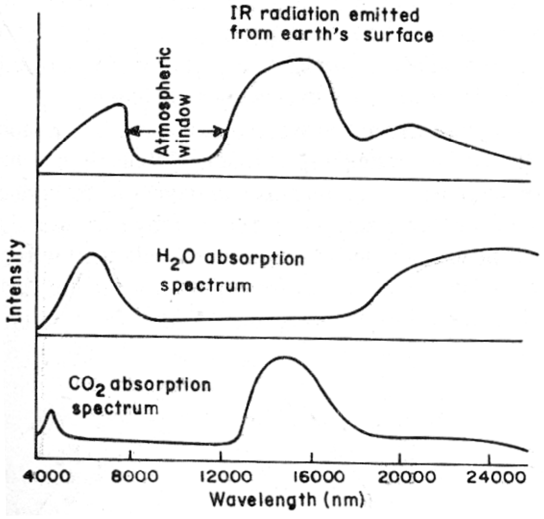
Carbondioxide (present level 325ppm), although a relatively insignificant non-pollutant species in the atmosphere, it is of a serious environmental concern. It has a potential to rival of nuclear wars in terms of massive irreversible damage to the environment.



The greenhouse effect

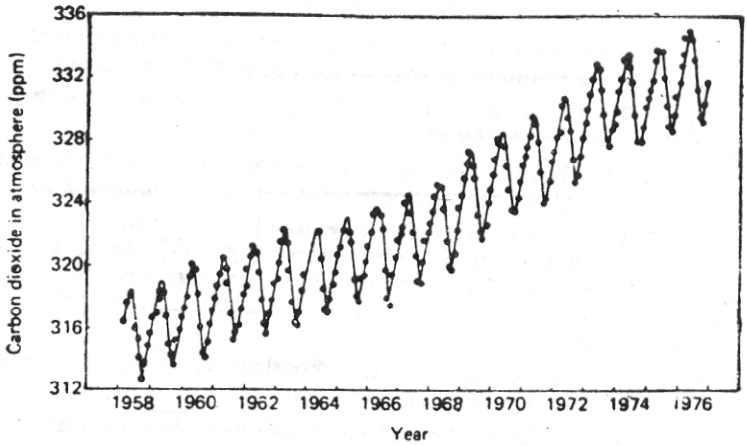
Among the constituents of the atmosphere, only carbondioxide and water vapour strongly absorb IR radiation (14000-25000nm) and effectively block a large fraction of earth's emitted radiation

The radiation thus absorbed by CO_2 and water vapour is partly reemitted to the earth's surface. The net result is that the earth surface gets heated up by the phenomenon called *Green House Effect.* The current global trend in deforestation, along with increased combustion of fossil fuels, has a cumulative effect on the net increase in CO_2 content. Forest is the area where a great deal of photosynthesis occurs. Moreover they maintain reservoirs of fixed but readily oxidisable carbon in the form of wood and humus. The over all result is that they serve to maintain a balance in the atmospheric CO_2 level. The combustion of fossil fuels have a little effect on the oxygen stock of the atmosphere which is relatively large but has considerable impact on the CO_2 content, which is only about 325ppm at present. Records of CO_2 over the last centaury have revealed that there has been a gradual



Absorption of terrestrial radiation by water and carbon dioxide

increase from about 290ppm before 1890 to the present value.

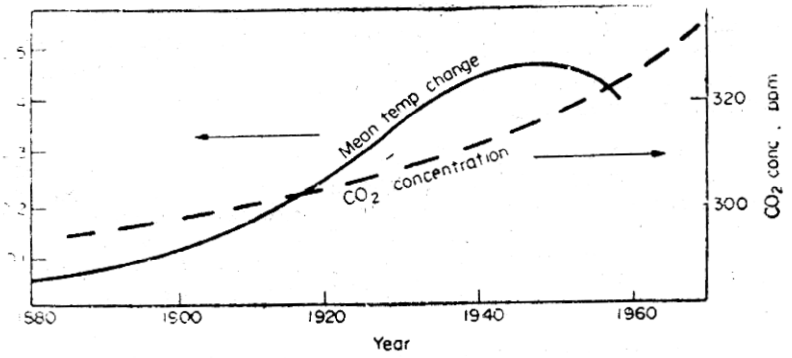


The trends of carbon dioxide concentration at the Mauna Loa Observatory

CO_2 under goes photochemical reaction to give CO

$$CO_2 + h\nu \rightarrow CO + O$$

The world's climate is dependent on the global heat balance; a mean temperature change of 2–3K would have a marked effect. Of the 8.4×10^4 Jm^{-2} min^{-1} (1400 Watt m^{-2}) energy that enters the earth's atmosphere, approximately 45% reaches the earth's surface and adjacent atmosphere directly or after being scattered. The incoming U.V, Visible, and IR energy has a maximum intensity; at earth's surface around 480nm, while energy reemitted from the earth is only in the IR region (2000 – 40,000nm) with a maximum intensity around 10,000nm.If this energy was lost to the atmosphere the temperature of the earth's surface would be around -20^0C to -40^0C. However some of the IR is absorbed by water vapour and carbon dioxide in the air and reemitted in all directions, some of which returns to the earth producing an average temperature of around 14^0C.The earth's mean temperature rose by 0.4^0C from 1880 to 1940, and from 1945 has dropped around 0.1^0C. The initial rise has been correlated with an increase in atmospheric concentration of CO_2.

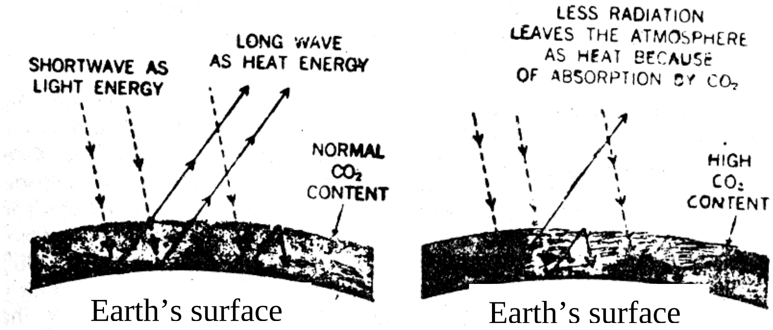


Changes in mean world temperature and CO_2 levels in the atmosphere

A large concentration of CO_2 gets introduced into atmosphere from fossil fuel burning furnaces and breathing of animals. From fossil fuels alone, more than 2.5×10^{13} tonnes of CO_2 is being emitted into the atmosphere from earth's surface. CO_2 that is injected into the atmosphere will not remain there; about half of it get utilized by the plant life or absorbed by the water of the ocean. Part of CO_2 dissolved in the ocean may get precipitated or incorporated in the marine organisms.

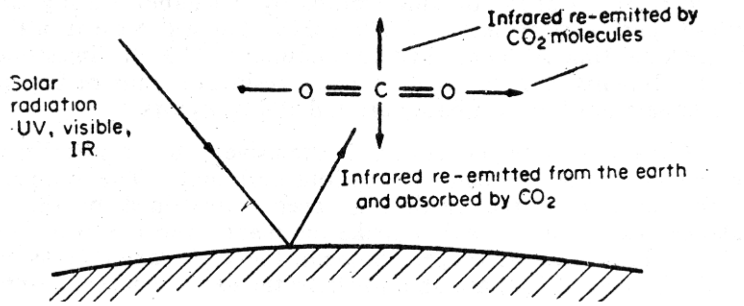
In this respect aquatic plants of ocean play an important role in maintaining the concentration of CO_2 equilibrium between the atmosphere and the surface layers of the ocean. CO_2 emitted by volcanoes during several billion years was at least 40,000 times that still present in the air. The normal resident time of CO_2 in atmosphere has been probably around one lakh years. CO_2 gets confined exclusively to troposphere. In dense concentration it can act as a serious pollutant.

The temperature at the surface of the earth has been maintained at the energy balance of the Sun rays that strike the planet and heat that gets radiated back into the space. Some of the Sun's rays that penetrate into the thick layer of CO_2 are able to strike the earth and get converted into heat; the heated earth is able to reradiate this absorbed energy as radiation of longer wavelength. Much of this does not pass through CO_2 layer to outer space but gets absorbed by the CO_2 and water in the atmosphere and adds to the heat that has been already present. Thus the atmosphere on earth heats up and this phenomenon is termed as *Green House Effect*.



Shortwave radiation (light) strikes the earth and is transformed into longwave radiation (Heat). Since carbon dioxide absorbs longwave radiation, the more carbon dioxide contained in the atmosphere, the more heat is retained and the warmer the atmosphere becomes

CO_2 thus acts as the glass of green house and on global scale tends to warm the air in the lower levels of the atmosphere. In the green house effect increase in CO_2 concentration means more IR radiation is trapped and reemitted back to the earth, producing a build up of IR radiation in the atmosphere and a mean global temperature rise. Estimates of the rise in temperature with the increase in CO_2 concentration range from 0.1 to 4.9^0C with a mean around 2^0C for doubling the CO_2 concentration to 600ppm.



A schematic drawing illustrating the greenhouse effect.
Infrared radiation from the earth absorbed by CO_2 molecules is re-emitted in all directions returning some back to the earth's surface.

UNIT
2

STUDY OF AIR POLLUTANTS - A

Lesson
2

Objectives of the lesson: This lesson deals with the role of oxides of sulphur and nitrogen in atmosphere.

SOURCES AND EMISSIONS OF OXIDES OF SULPHUR

Basic chemical reactions:

Pollution from sulphur oxides consists primarily of two colourless gaseous compounds, sulphur dioxide (SO_2) and sulphur trioxide (SO_3). Collectively the two are designated as SO_x. The combustion of any sulphur containing compounds will produce both sulphur oxides. A simplified mechanism for the formation of SO_x may be represented by a two-step process.

$$S + O_2 \rightleftharpoons SO_2$$

$$2SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

The existence of SO_3 in the air as a gas is possible only if the concentration of water vapour is very low.

Sulphur dioxide:

Sulphur dioxide is a colourless gas with pungent odour. It is produced from combustion of any sulphur bearing material. It is always accompanied with SO_3.

$$S + O_2 \rightleftharpoons SO_2$$

$$2SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

Under normal conditions of atmosphere SO_3 reacts with water vapour to give H_2SO_4.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Most probably SO_2 is practically oxidised to SO_3 in air by the photolytic and catalytic process in the presence of ozone and NO_x and photochemical smog. NO_x exerts the catalytic effect, which is the basis for industrial production of H_2SO_4 by lead chamber process. Catalytic oxidation takes place in presence of metal oxides.

$$SO_2 + O_3 \longrightarrow SO_3 + O_2 \xrightarrow{H_2O} H_2SO_4 \longrightarrow \underset{\text{Aerosol droplets}}{(H_2SO_4)_n} \qquad \text{(OR)}$$

$$SO_2 + \tfrac{1}{2}\,O_2 \xrightarrow[\text{Metal oxide}]{\text{Soot dust}} SO_3 \xrightarrow{H_2O} H_2SO_4 \longrightarrow \underset{\text{Aerosol droplets}}{(H_2SO_4)_n}$$

This phenomenon gives *acid rain.*

Sources: Natural process of volcanoes cause 67% (SO_x) pollution, which is evenly, distributed all over the globe. Man made sources contribute to about 33%. Annual worldwide emissions are 146 and 145 x 10^6 tonnes respectively from man made and natural process respectively. Among man made sources

Fuel consumption	74%
Industrial	22%
Transportation	2%

Sulphur aerosols in urban areas are generally smaller than 2 microns and are especially capable of penetrating inner most parts of lungs that is pulmonary region. They are becoming responsible for respiratory troubles particularly among older people of 70 + years age. The defects are not known.

The following chemical reactions may be considered as the factors for sulphur oxides contribution into the atmosphere.

$$H_2S + 3/2\,O_2 \rightarrow SO_2 + H_2O$$

$$H_2S + O \rightarrow OH^* + HS \xrightarrow{\text{oxygen}} SO_2 + H_2O$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$ZnS / PbS + 3O_2 \rightarrow 2PbO / 2ZnO + 2SO_2$$

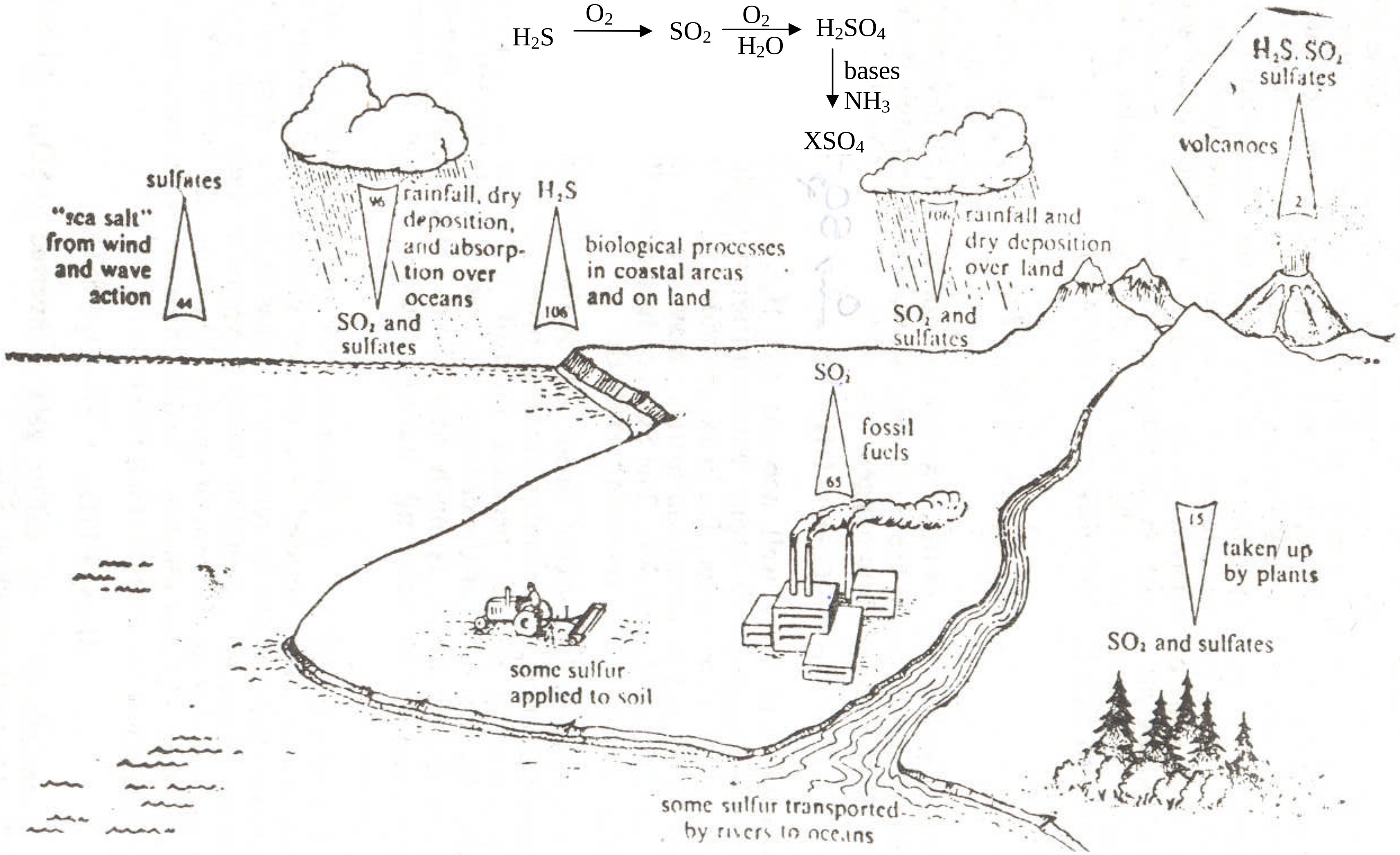
$$CuS + 3O_2 \rightarrow 2Cu + SO_2$$

$$H_2S + O \rightarrow OH^* + HS \rightarrow SO_2 + H_2S$$

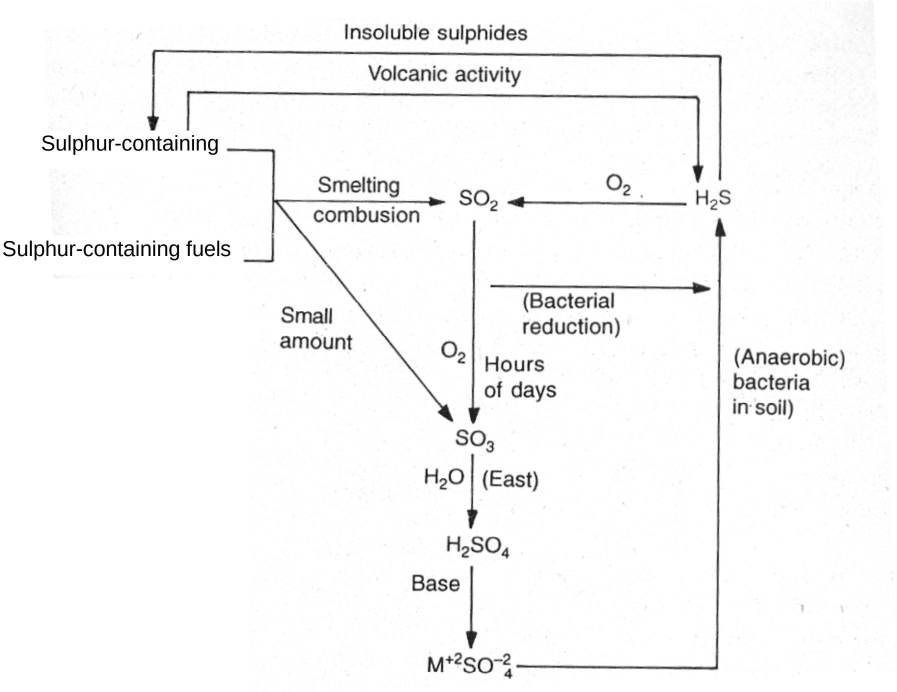
Sulphur oxides of zinc and lead give rise to metallic oxides where as copper sulphides form metallic copper. Most of the sulphur oxides are converted to H_2SO_4 and the ratio of H_2SO_4 to SO_2 is dependent upon number of factors

1. Amount of moisture in the atmosphere
2. The residence time of sulphur contaminant in air.
3. The amount of catalytic matter in air
4. Amount of Sunlight
5. Amount of precipitation

$$\begin{tikzcd}
H_2S \arrow[r, "O_2"] & SO_2 \arrow[r, "O_2", "H_2O"'] & H_2SO_4 \arrow[d, "bases" right, "NH_3"' right] \\
 & & XSO_4
\end{tikzcd}$$



Atmospheric sulfur cycle. Values are in millions of tons (teregrams) of S as estimated by James P. Friend, "The Golbal Sulfur Cycle," in *Chemistry of the Lower Atmosphere.*



The Sulphur Cycle

Effect on plants:

Atmospheric SO_2 is harmful to plants. Acute exposure yields to leaf necrosis (death of cells in leaf). The edges of the leaf, areas between leaf veins are damaged. Chronic exposure of plants to SO_2 causes chlorosis (a bleaching or yellowing of normal green portion of leaf). Apart from SO_2 plants will be effected by H_2SO_4 aerosols. There is some evidence that SO_2 might have suppressed the growth and yield of plants with out causing visible injuries.

Effect on humans:

The effect of SO_x in animals and healthy humans are much higher, their levels causing plant damage. The main effect of SO_x appears to be irritation to respiratory system, although high levels of SO_x are needed. It is more potent to produce injurious effects in the healthy adults. So sulphur dioxide can be considered as the single air pollutant health hazard. Exposure to air contaminated by SO_2 also stimulates mucous secretion. Although SO_2 causes death in humans at 500ppm, it has been found that it has number of harmful effects on laboratory animals even at 5ppm.

Effect on materials:

1. Much of damage to materials from SO_x pollution is caused by highly reactive H_2SO_4 that is produced by SO_3 reacts with atmospheric water vapour.
2. The drying and hardening of some paints gets increased upon exposure to SO_2. Such changes in paint films are likely to influence their subsequent durability.

3. The corrosive rates of most of the metals especially Fe, Zn, steel are accelerated by SO_2 polluted environment. Particulate matter, high humidity, temperature also play an important role in this corrosion.
4. High concentration of sulphuric acid from atmospheric pollutants is capable of attacking a wide variety of building materials. Especially carbonate containing materials such as marble, lime stone, roofing slate and mortar are susceptible.

   Carbonates are converted to sulphides which are water soluble

   $$CaCO_3 \text{ (lime stone)} + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

   The material becomes pitted and weakened mechanically as the soluble sulphates are bleached away by rainwater. The $CaSO_4$ formed on the surface of masonry is about twice as bulky as carbonate of the same from which it is formed. Such stones appear as leprous or deceased.
5. Some textile fibers particularly those from vegetable sources loose some strength when exposed to acids.
6. Animal fibers such as wool are more resistant.
7. Leather has a strong affinity for SO_2 which causes its strength to loose and finally disintegrate.
8. Paper also absorbs SO_2 which is then decolourised and become brittle and fragile.

Reactions in atmosphere:

There are four ways in which SO_2 may reacts, which are

1. Photochemical reactions
2. Photochemical / chemical reactions in presence of NO_x and / or hydrocarbons.
3. Chemical process in water dropping (moisture) consists of metal salts and NH_3.
4. Reactions of solid particles in atmosphere

In lower atmosphere SO_2 absorbs solar radiations on regions 300 – 400nm, to produce excited states.

$$SO_2 + h\nu \rightarrow SO_2^*$$

Several reactions follow with its interaction with molecular oxygen and complete the oxidation of SO_2 to SO_3.

$$SO^{*}2 + O_2 \rightarrow SO_4^{2-}$$

$$SO_4^{2-} + O_2 \rightarrow SO_3 + O_3$$

$$SO_2 + O_3 + h\nu \rightarrow SO_3 + O_2$$

The third body 'M' is also required to carry off excess of energy of the reaction. 5 – 30ppm of SO_2 absorbs at a relative humidity of 30-90% and the presence of natural Sunlight will lead to the following reactions.

$$SO_2 + 1/2\ O_2 + H_2O \rightarrow H_2SO_4$$

The above reaction is prompted by presence of hydrocarbons and NO_x, which are key components of photochemical smog.

Another free radical OH^* present in photochemical smog reacts with SO_2.

$$HO^* + SO_2 \rightarrow HOSO^*{}_2$$

$$HOSO^*{}_2 + O_2 \rightarrow HOSO_2O^*{}_2$$

$$HOSO_2O_2{}^* + NO \quad HOSO_2O^* + NO_2$$

In relatively humid atmosphere SO_2 is probably oxidized by reactions occurring inside water air droplet which proceed faster in presence of NH_3 and catalyst such as Mn(II), Fe(II), Ni(II), Cu(II)

$$NH_3 + SO_2{}^* + H_2O \rightarrow NH_4 + HSO_3{}^-$$

$$NH_3 + HSO^-{}_3 \rightarrow NH_4^+ + SO_3^{2-}$$

Solid particles such as soot provide heterogeneous phases for catalytic oxidation of SO_2.

Soot particles are common features of polluted atmosphere. It has been made clear from Photo Electron Spectroscopy (PES) studies that SO_4^{2-} is there in soot particles. SO_2 is a serious air pollutant responsible for smog resulting in several incidents of loss of human life besides it contributes to acid rain.

Control of SO_X :

Four possible factors are encountered for the control of SO_x .

1. The removal of SO_x from fuel gases.
2. Removal of sulphur from fuel before burning.
3. Use of low sulphur fuel.
4. Substitution of some other energy sources from fuel consumption.

SO_x from fuel gases can be conveniently eliminated by using chemical scrubbers. The flue stake gases are passed through calcium carbonate.

$$2CaCO_3 + 2SO_2 + O_2 \longrightarrow 2CaSO_4 + CO_2$$

The method appears economical but it is not favoured for the problem of disposal of calcium sulphate. An alternative process is based on the reaction between HSO_3^- (bisulphate) ions and citrate ions. The flue gas is cooled to 15^0C and freed from particulates and traces of H_2SO_4. It is then led into an absorption tower and brought into contact with a solution containing citrate ions.

$$SO_2 + H_2O \rightarrow HSO_{3^-} + H^+$$

$$HSO_{3^-} + H_2Cit^- \rightarrow (HSO_3 H_2 Cit)^{2-}$$

The solution is next fed into closed vessel into which H_2S is bubbled. Normally the factory is build with tall smoke stacks to disperse the plume over a wide area; this reduces the local problems but create problems to areas of certain distance.

OXIDES OF NITROGEN

The oxides of nitrogen in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO) and red brown nitrogen dioxide (NO_2). Nitrous oxide originates from microbiological processes and occurs in unpolluted air at a level of about 0.25ppm. In lower atmosphere it has particularly no influence on chemical reactions but at higher altitudes it leads to depletion of ozone layer. Nitric oxide (NO) and pungent red brown nitrogen dioxide (NO_2) are important constituents of polluted air. Generally they are designated as NO_x enter the atmosphere mainly from anthropogenic sources that is combustion of fossil fuels in both stationery and mobile sources. The annual global input of the NO_x is of the order 86 million tonnes.

$$N_2O + h\gamma \rightarrow N_2 + O \quad \text{------------ (1)}$$
$$N_2O + O \rightarrow NO + NO \quad \text{------------ (2)}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{------------ (3)}$$

The bulk of NO_x global basically originates from microbiological action (bacterial decay of organic matter) on the earth’s surface, which yields N_2O. This N_2O is inert in the troposphere but it reacts with atomic oxygen in the stratosphere to form NO and then enters ozone elimination process (or) destruction cycle. This cycle is disrupted when NO_2 reacts with OH* radical to give HNO_3.

$$NO_2 + OH \rightarrow HNO_3 \quad \text{------------ (4)}$$

At the next step NO reacts with OH to produce HNO_2

$$NO + OH \rightarrow HNO_2 \quad \text{------------ (5)}$$

These acids being soluble in water are quickly rained out into the troposphere.

The sources and sinks of NO_x are summarised as follows.

The over all process of elimination of NO probably consists of its reaction with molecular oxygen (O_2), ozone, or atomic oxygen (O) (in the presence of third body, M) to yield NO_2

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad \text{------------ (6)}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{------------ (7)}$$
$$NO + O + M \rightarrow NO_2 + M \quad \text{------------ (8)}$$

where M is the third body.

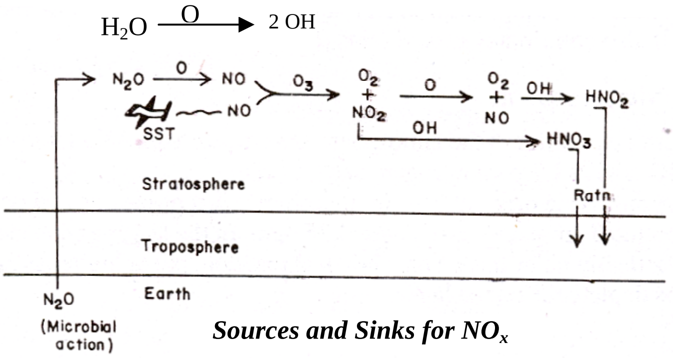
The estimated value of 3.5×10^9 molecules / cm^3 of NO_x is present in stratosphere. The sources and sinks of NO_x in troposphere are not identified. There is a large reserve of ambient NO_2 concentration (1300 MT approximately) with annual fluctuations indicating a residence time of about 10 years. So the heat produced rate is 130 metric tonnes / year. The stratosphere N_2O flux is however about 35 metric tonnes / year. The oceans and water are also supersaturated with N_2O which is released with a global production rate of 100 metric tonnes / year.

NITROGEN DIOXIDE (NO_2)

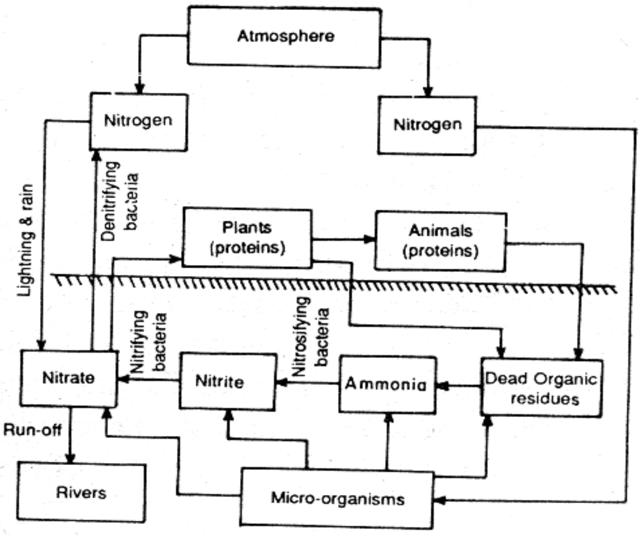
It is an important species in the atmosphere. It absorbs sunlight below 398nm undergoing photochemical decomposition and above 430nm forming excited molecule.

$$NO_2 + h\nu \rightarrow NO_2^* \quad \text{----------------- (9)}$$

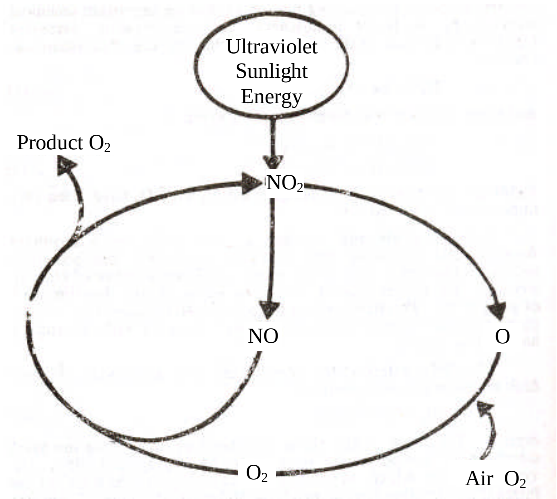
$$NO_2^* \rightarrow NO + O \quad \text{----------------- (10)}$$



Sources and Sinks for NO_x



Nitrogen pathways in soil



Photolytic NO_2 Cycle

The photo dissociation of NO_2 can yield a series of inorganic reactions besides a number of reactions involving organic species.

$$O + O_2 + (M) \rightarrow O_3 + M \qquad \text{-------------------11}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{------------------12}$$

$$NO_2 + O_3 \rightarrow NO_3^- + O_2 \qquad \text{-------------------13}$$

$$O + NO_2 \rightarrow NO + O_2 \qquad \text{-------------------14}$$

$$O + NO_2 + M \rightarrow NO_{3^-} + M \qquad \text{-------------------15}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad \text{-------------------16}$$

$$NO + NO_3 \rightarrow 2NO_2 \qquad \text{-------------------17}$$

$$O + NO + M \rightarrow NO_2 + M \qquad \text{-------------------18}$$

Nitrogen dioxide finally ends up as nitric acid. Nitrates (or) organic nitrogen compounds under the conditions of photochemical smog lead to

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad \text{-------------------19}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad \text{-------------------20}$$

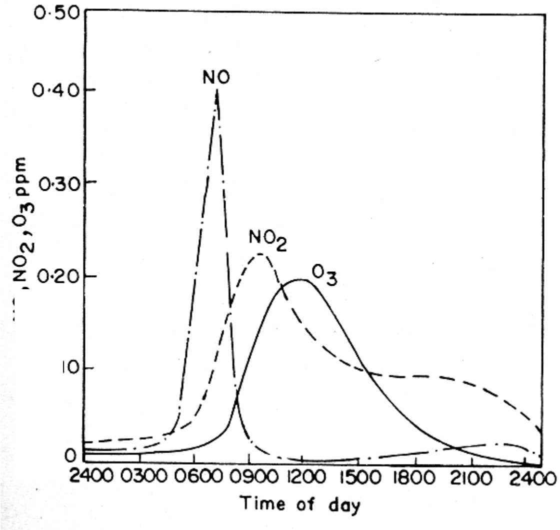
In the stratosphere NO_2 also reacts with the hydroxy radical HO^* to form HNO_3

$$NO_2 + HO^* \rightarrow HNO_3 \qquad \text{-------------------21}$$

It appears that HNO_3 is the temporary sink for NO_2 in the stratosphere. Nitric acid produced from NO_2 is removed as acid rain. Alternatively it reacts with gases (ammonia, particulate lime) for producing particulate nitrates. Thus the NO_x pool is consumed by the conversion to HNO_3 and HNO_2 and balanced by the activation but supplemented by the NO_2 from the earth below due to microbial action. Human activities also play a significant role in the matter of NO_x load in the stratosphere. The supersonic air crafts (SSTX) fly in the stratosphere because of low air resistance, which helps in maintaining supersonic speed because these discharge large quantities of NO_x into the stratosphere. It is calculated that a fleet of 500 supersonic aircrafts flying 7 hours each day will contribute annually the existing concentration of NO_x into the stratosphere.

The residence time of these gases in the stratosphere is of order of a year or so. Hence there is a possibility of doubling of stratospheric concentration $NO_{x,}$ which in turn tend to reduce ozone concentration by about 40%. Recently it has been found that NO_x from stratosphere can be removed very efficiently by hydroxyl radical HO*. Besides these things by man made contributions for the additional load of NO_x should be considered. Nuclear explosions produce large quantities of $NO_{x,}$ which are injected directly into the stratosphere. Nuclear tests conducted by both U.S.A. and U.S.S.R. in early 60's reduced the concentration of ozone by about 4% which may arise to 50% if the bulk nuclear arsenals of are released. This will lead to extensive radiation in the ozone shield, which in turn will spell disaster for mankind in terms of large-scale damage to food production with increased exposure to U.V. radiation.

Concentration profile of NO_x:



Average daily 1-hour concentration of selected pollutants in Los Angels, USA

In urban areas, NO_X levels follow a regular pattern depending on sunlight and traffic density.

1. Before day light, NO and NO_2 levels remain fairly stable at concentrations slightly higher than the daily minimum.
2. As the traffic rush begins and increases (6–8 A.M.), the level of NO increases and becomes maximum.
3. At mid-morning with increased ultra violet light the NO_2 level increases (8 – 10A.M.) due to conversion of NO into NO_2.
4. Ozone begins to accumulate as the NO concentration drops to a level of 0.1ppm.
5. As solar energy decreases automobile traffic increases in the evening (5-8ppm) the concentration again goes up.
6. The solar energy is unavailable to convert NO to NO_2 (through hydro carbon interaction) but ozone accumulated during the day reacts with NO. The result is an increase in NO_2 and a decrease in ozone levels.

Harmful effects of Nitrogen oxide:

Both oxides of nitrogen i.e., NO and NO_2 are potential health hazards. Animal mortality studies indicate that NO_2 is about 4 times toxic than NO. NO is not an irritant and is considered as a health hazard at a concentration found in atmosphere.

Effect of NO_X on Human beings:

1. Acute exposure to NO_2 can be quite harmful to human health. The health effects due to NO_2 vary with the degree of exposure.
2. Death generally results from 2-10 days after exposure to 500ppm or more of NO_2.
3. Deaths have caused from the inhalation of NO_2 containing gases from burning celluloid and nitro cellulose films.

Effect of NO_X on Plants:

Although excessive damage to plants has been noticed to heavy NO_X exposure, this has been attributed to secondary products of nitrogen oxide such as PAN formed in smog.

Effect of NO_X on Materials:

Some textile dyes will fade upon exposure to NO_X . A combination of unfavorable weather and NO_2 produced acid aerosols, which damaged the nylon. High levels of particulate nitrates have brought about stress-corrosion, failures of nickel- brass wire spring in relays used by telephone companies.

Control of oxides of nitrogen:

1. Approaches have been postulated for the catalytic reduction of NO in stock gas involves methane.

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O$$

and also by ammonia

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

by carbon monoxide

$$2CO + 2NO \rightarrow N_2 + 2CO_2$$

2. Production of undesirable by- products is a major concern in this process.

For example : SO_2 reacts with CO for producing toxic carbonyl sulphide

$$SO_2 + 3CO \rightarrow 2CO_2 + COS$$

Most sorption processes are aimed at simultaneous removal of both nitrogen and sulphur oxides. Sulphuric acid solutions or alkaline scrubbing solutions having $Ca(OH)_2$ or $Mg(OH)_2$ may be used. The species N_2O_3 is produced by the reaction.

$$NO + NO_2 \rightleftharpoons N_2O_3$$

The modified sulphuric acid scrubbing process has following steps

Oxidiser: Flue gas and NO_2 are put into an oxidiser in which the following reaction takes place

$$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$$

Scrubber: Here the gases come in contact with H_2SO_4 which is introduced into a scrubber.

$$NO + NO_2 \rightarrow N_2O_3$$

$$N_2O_3 + 2H_2SO_4 \rightarrow 2NOHSO_4 + H_2O$$

The cleansed flue gas gets released into the atmosphere.

Decomposer: Sulphuric acid is formed in a decomposer and NO_2 is again regenerated. Some of the sulphuric acid is recycled to the scrubber.

$$2NOHSO_4 + H_2O + 1/2\,O_2 \rightarrow 2\,NO_2 + 2H_2SO_4$$

HNO_3 Reactor: Nitric acid is formed in the HNO_3 reactor

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

and excess of NO_2 and NO are recirculated through the oxidizer.

ACID RAINS:

Much of the NO_x and SO_x entering the atmosphere are converted into HNO_3 and H_2SO_4 respectively. The detailed photochemical reactions in the atmosphere are summarized.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \ldots\ldots\ldots\ldots (1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \ldots\ldots\ldots\ldots (2)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad \ldots\ldots\ldots\ldots (3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad \ldots\ldots\ldots\ldots (4)$$

HNO_3 removed as a precipitate or as particulate nitrates after reaction with bases (NH_3, particulate lime).

$$SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow[\text{soot particles (metal oxide)}]{\text{(HC, NO)}} H_2SO_4 \quad \ldots\ldots\ldots\ldots (5)$$

The presence of hydrocarbons and NO_x accelerates the oxidation rate of the reaction. In water droplets, ions such as Mn(II), Fe(II), Ni(II) and Cu(II) catalyze the oxidation reaction. Soot particles are also known to be strongly involved in catalyzing the oxidation of SO_2.

HNO_3 and H_2SO_4 combine with HCl from HCl emission (both by natural and anthropogenic sources) to generate acidic precipitation which is widely known as acid rain. Acid rain is now a major pollution threat in some areas.

Acid rain causes extensive damage to building and sculptural materials of marble, limestone, slate, mortar, etc. These materials become pitted and weakened mechanically as the soluble sulphates are leached out by rain water.

$$\underset{\text{lime stone}}{CaCO_3} + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \quad \ldots\ldots\ldots\ldots (6)$$

UNIT 2

STUDY OF AIR POLLUTANTS - B

Lesson 3

Objectives of the lesson: This lesson deals with behaviour of organic pollutants and particulates in the atmosphere.

ORGANIC POLLUTANTS AND PHOTO CHEMICAL SMOG

Natural sources particularly trees emits large quantities of hydrocarbons into the atmosphere. Methane is the major naturally occurring hydrocarbon. It is produced in large quantities by bacteria in anaerobic decompositions of organic matter in water, sediments and soil.

$$2(CH_2O) \xrightarrow{\text{bacteria}} CO_2 + CH_4$$

Domesticated animals contribute about 85 million tonnes of CH_4 to atmosphere every year. It has a mean residence time of about 3 – 7 years in atmosphere. Anthropogenic activities contribute about 15% of hydrocarbons. Automobiles are major contributors among them. The global hydrocarbon emission is 570 x 10^6 tonnes per year.

SOURCE	**EMISSIONS**
Petroleum	*%*
Refining	7.2
Oils and Distillates	0.4
Gasoline	38.5
Evaporation in transfer and storage	8.8
Coal	
Heating	2.3
Power generation	0.2
Industrial uses	0.8
Wood (fuel and forest fires)	2.2
Incinerators and refuse burning	28.3
Solvent evaporation	11.3

A number of different specific hydrocarbon compounds are found in regions heavily polluted by such substances. Over 20 different compounds were identified and analyzed. Of these, methane was present at by far the highest concentration, an average of 2400 parts per billion (ppb) by volume in downtown Los Angles.

Hydro carbons	% (ppb)
Ethane & Ethylene	102
Acetylene & Propane	76
n-butane	46
Iso pentane	35
Toluene	30
n-pentane	21
m-Xylene	12
Iso-butane	12

It was observed that as the day progresses, the concentration of unsaturated hydrocarbons (butenes) decreases to a greater extent than that of the paraffin’s. The decrease in the paraffin’s was attributed entirely to mixing and consequent dilution.

Industrial processes constitute the next large source. Hydrocarbons get lost to the atmosphere during production, processing, storage, and transfer of products containing them. Gasoline hydrocarbons are lost in vapour from during the loading of tank truck, the filling of service station storage tanks, and the filling of automobile fuel tanks. The evaporation of organic solvents, most of which contain hydrocarbons, account for nearly 10% of all industrial emissions. These solvents are important ingredients of paints, varnishes, lacquers, under coatings and similar products. These products consist of 40 – 80% solvent, which usually evaporate during or after application. The process involved in the manufacture of these products also comprises potential hydrocarbon source.

Production and control of pollutant hydrocarbon from automobiles:

Pollution from hydrocarbons is mainly caused from automobile engines. This is due to chemical reactions that will occur as a result of incomplete burning of gasoline (petrol) at high temperature. Several hundreds of components will be produced, some of them are highly reactive while others like benzopyrene are carcinogenic (cancer causing). The exhaust from automobile engine will be refracted by obstacles like pedestrians and travel upwards in the atmosphere and then encounter with solar radiation and deliver photo chemical oxidation products in the atmosphere. Apart from exhaust, automobiles have several potential sources of pollutant hydrocarbons, some of them are listed below

1. Crank case: (20% of hydro carbons are produced)

Mist composed of lubricating oil, and receives “blow by” consisting of exhaust gas and unoxidised carburated mixture from around the piston. Blow by is recirculated through the engine, intake many fold by way of the PCV (positive crank case ventilation) valve.

2. Fuel system: (15% of hydro carbons are produced)

Pollution may originate from fuel tank and carburetor. During rest they emit gasoline vapour.

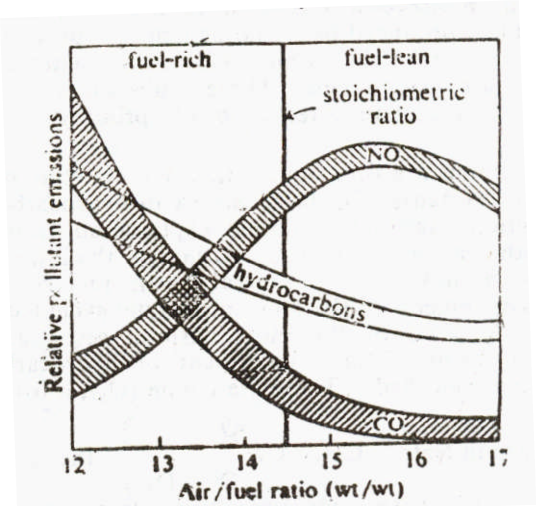
3. Exhaust system: (65% of hydro carbons are produced)

The automobile exhaust is the greatest source of hydrocarbons. The air/fuel ratio in internal combustion engine has marked effect on the emission of hydrocarbons.

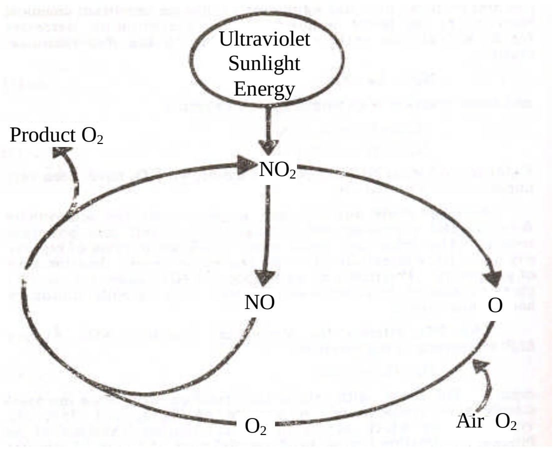
As the air fuel ratio becomes richer in fuel than the stoichiometric ratio, the emission of hydrocarbon increases sharply. Modified exhaust engines are highly helpful in controlling them.

Photochemical oxidants:

The term photochemical oxidant is used to describe an atmospheric substance produced by photochemical process (a chemical process which requires Sunlight which will oxidise materials not readily oxidised by gaseous oxygen). These substances are secondary pollutants produced by interaction of primary pollutants with light. The involvement of NO_2 in photolytic cycle is well established.

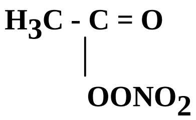


Effect of air / fuel ratio on pollutant emissions from an internal combustion piston engine



Photolytic NO_2 Cycle

Two harmful secondary pollutants namely ozone and peroxy acyl nitrates (PAN)



$$\begin{array}{l} H_3C - \underset{\displaystyle OONO_2}{\underset{|}{C}} = O \end{array}$$

are produced as a result of hydrocarbon in the above cycle. Generally the later are groped as PAN compounds. The simplest member is peroxy acyl nitrates. Ozone is obviously not a hydrocarbon but its concentration increases as a consequence of hydrocarbon reactions.

Formation of Photochemical Reaction:

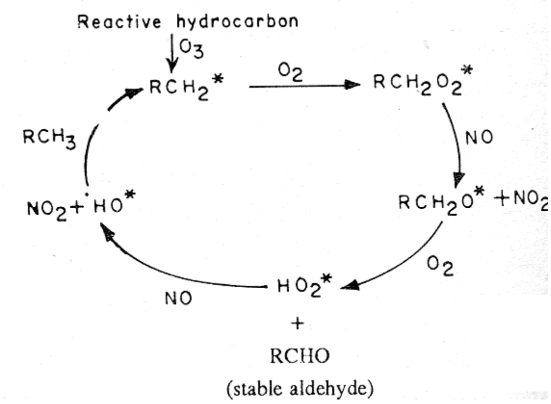
Harmful Effect of Hydrocarbon:

Pollution was not caused by hydrocarbons themselves but as byproducts of photochemical reactions in which hydrocarbons participate. Hydrocarbons are not directly reactive with light. But they are highly reactive with substances produced photo chemically. The formation of oxidants in the atmosphere gives rise to a phenomenon known as *Photochemical smog***.**

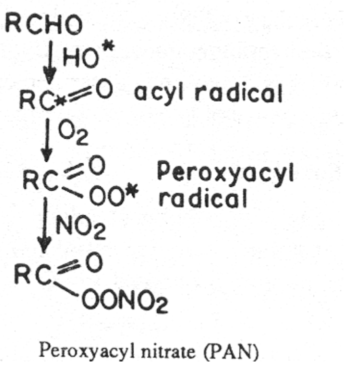
Smog is an odd combination of smoke and fog. However this is chemically reduced smog where as photochemical smog is an oxidizing smog having high concentration of oxidants. Photochemical smog, is characterized by brown hazy fumes, which irritates the eyes and lungs. It also leads to cracking of rubber and expensive damage to plant life.

Probable Mechanism for Smog forming Reactions:

Reactive Hydrocarbon



Smog forming reactions



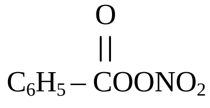
PAN formation reactions

ROOT FOR PAN FORMING REACTIONS:

1. Reactive hydrocarbons (those with C=C groups) from auto exhaust interact with ozone to form hydrocarbon free radical RCH_2^*
2. RCH_2^* rapidly reacts with O_2 to form another free radical form $RCH_2O_2^*$
3. $RCH_2O_2^*$ reacts rapidly with NO and give RCH_2O^* and NO_2
4. This new free radical interacts with O_2 to yield a stable aldehyde (RCHO) and hydro peroxy radical HO_2^*
5. HO_2^* reacts with another NO molecule to give NO_2 and HO^*
6. HO^* is extremely reactive and rapidly reacts with stable hydro carbon RCH_3 to yield H_2O and regenerates the hydro carbon free radical RCH_2^* and completes the cycle. This is a chain reaction. One complete cycle yields two molecules of NO_2 and one molecule of aldehyde (RCHO) and regenerates the free radical RCH_2, so there will be rapid build up of small products.
7. The aldehyde RCHO may initiate another route by interaction with HO radical leading to the formation of (RC^*= O) acyl radical; peroxy acyl radical (by reaction with O_2) and finally peroxy acyl nitrate $(R\underset{\underset{O}{\|}}{C}OONO_2)$ by reaction with NO_2.

PAN is the most potent eye irritant found in smog. Photochemical smog shows characteristic variations of small ingredients with the time of the day.

1. Hydro carbon level will be maximum between early morning traffic rush hours 8 and 10 am then decrease because of consumption due to smog formation reactions.
2. NO concentration has a peak value at the same time and then falls as NO_2 concentration increases.
3. Subsequently there will be rise in concentration of oxidants. (The oxidants are nothing but aldehydes and PAN containing irritating ingredients of smog).
4. The other related compounds are peroxy benzoyl nitrate (PBN)



$$C_6H_5-\overset{\overset{O}{\|}}{C}OONO_2$$

A powerful eye irritant and lachrymator (tear producing).

The other family members are

Peroxy propionyl nitrate	(PPN)
Per acetic acid	$CH_3(CO)\ OOH$
Acetyl peroxide	$CH_3(CO)\ OO(CO)\ CH_3$
Ethyl hydroxy peroxide	$CH_3\ CH_2OOH$
Tertiary butyl hydroxide	$(CH_3)_3\ (CO)OH$
N-butylhydro peroxide	$CH_3\ CH_2\ CH_2\ CH_2OOH$

The time variations in levels of hydrocarbons, ozone, NO and NO_2 are explained in a group of over all reactions proposed first by Friedlander and Seinfeld

1. Primary photochemical reactions

$$NO_2 + h\nu \rightarrow NO + O \qquad \text{---------------1}$$

2. Reactions involving two O_2 species

$$O_2 + O + M \rightarrow O_3 + M \qquad \text{---------------2}$$

where M is the third body.

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad \text{---------------3}$$

3. Production of organic free radicals from hydrocarbons, RH

$$O + RH \rightarrow R^{*} + \text{other products} \qquad \text{---------------4}$$

$$O_3 + RH \rightarrow R^{*} + \text{other products} \qquad \text{---------------5}$$

R^{*} is a free radical which may or may not have oxygen.

4. Chain propagation, branching and termination

$$NO + R^{*} \rightarrow NO_2 + R \qquad \text{---------------6}$$

In this case R^{*} contains oxygen and oxidises NO. It is one of many chain propagation reactions some of which involve NO.

$$NO + R \rightarrow \text{Products} \quad (\text{ex}: PAN)$$

This is the most common chain terminating reaction, which occurs because NO_2 is a stable free radical present at high concentration in a smoggy atmosphere.

Concentration and Distribution of Hydro carbons and Photochemical Oxidants:

The average concentration of hydrocarbon in air will be between 0.03 and 0.1ppm (except methane because of its lack of reactivity). Ozone has been identified as the most concentrated component of pollutant air. With high pollutant oxidation level PAN concentrations are of the order 0.01ppm.Visible effects of ozone are injury to plants and leaves are therefore bleached.

Secondary Pollutants:

The major secondary photo chemical pollutant is peroxy acyl nitrate, and other common pollutants are perxoy propionyl nitrate (PPN), peroxy butyl nitrate (PBN) and Peroxy isobutyl nitrate ($P_{iso}BN$). Plant injury from PAN shows glazing and bronzing of the lower leaf (coat with shiny structure). General attack on younger leaves, eventually leaf tissue dies. It has been found to be toxic to citrus, salad crops and coniferous trees.

Hydrocarbon	**Concentration**	**Exposure time**	**Effect**
PAN	0.2-0.3ppm	few hours	Injury to vegetation
PAN	0.1ppm	5 hours	Injury to sensitive plants
Ethylene	1ppm	-	Adverse effects on vegetation (Inhibition of growth, brings about colour changes in leaves, death of flowering plants)
Acetylene and propylene	60-500ppm	-	Shows toxicity on plants

Effect on Humans:

Hydrocarbons won't exert any undesirable effect on humans, but photochemical oxidants enter body directly through inhalation and respiratory process cause eye irritation.

With regard to ozone

Concentration (ppm)	**Time**	**Effect**
0.2	-	No ill effects
0.3	-	No throat irritation begins
1.0 – 3.0	2 hours	Extreme fatigue
9ppm	2 hours	Several pulmonary edema

Toxicity of Aromatic Hydrocarbons

Compound	**Concentration (ppm)**	**Effect**
Benzene	100	Mucous membrane irritation
	3,000	Endurable ½ - 1 hour
	7,500	Dangerous after 1/2 -1 hour
	20,000	Fatal after 5-10 minutes
Toluene	200	Mild, fatigue, weakness and confusion after 8
	600	Loss of coordination, pupils dilated after 8 hours

Effect of hydrocarbons and photochemical oxidants on materials:

Weathering is the result of attack of air pollutants particularly photo chemical oxidants. It is revealed that ozone exerts effects on rubber and textile. Many organic polymers including rubber and natural synthetic textiles are effected by small amounts of ozone. Susceptibility to attack increases with increasing number of carbon to CO_2, double bond is the site of attack.

Two different effects are produced by these reactions, Carbon-chain breaking and carbon-chain cross-linking. In the first, long chains of carbon atoms that make up the polymer are broken, and the second effect results in formation of new links between two parallel carbon chains. This causes the material to become less elastic and more brittle.

Rubber in the relaxed state can be exposed to ozone for long periods of time with out forming any characteristic cracks. However exposure to ambient concentrations of 0.01–0.02 ppm ozone will result in the formation of cracks if the rubber is under a strain of as little as 2 or 3%. Apparently a coating consisting of a compound of rubber and ozone (ozonide), which forms on the surface and protects against further penetration and attack by ozone. This protective film (surface) cracks when rubber is stretched and fresh rubber surfaces are exposed to the atmospheric ozone.

Concentration of ozone (ppm)	**Time for first crack to appear** (minutes)
0.02	65
0.26	5
0.45	3
20,000 (2%)	1 second (cracks form immediately)

Ozone also attacks cellulose in textile factory, order of causing effect is cotton, nylon, polyester.

Chemicals and photochemical reactions in the atmosphere:

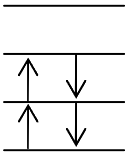
The main difficulty in studying the atmospheric chemistry is that one has to deal with unusually low concentrations, many chemical reactions needs a third body to absorb excess energy. Chemical reactions occur slowly in the upper atmosphere due to the sparse concentration (thinly spread not dense or scattered) of third body to absorb excess energy but readily takes place in a container in laboratory whose walls effectively absorbs energy. Container walls may serve as catalyst for some important reactions or they may absorb important species and react chemically with the more reactive ones. Absorption of light by chemical species can cause reactions.

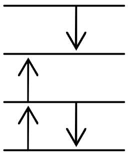
The photochemical reactions may occur even at low temperatures and in the absence of catalysts. Such photochemical reactions induced by intense solar radiations, play a very important role in deciding the nature and ultimate fate of chemical species in the atmosphere.

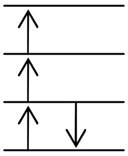
The three relatively reactive and unstable species, which are involved in chemical process, are
1. Electronically excited molecules
2. Atoms or molecular fragments with shared electrons called free radicals
3. Ionised atoms or molecular fragments.

Electronically excited molecules are produced when stable molecules absorb electromagnetic radiation in the U.V. or visible region of the spectrum. Generally U.V. or visible radiations are energetic to excite molecules to certain lower energy levels although a molecule may posses several possible excited species. The nature of excited state may be understood considering the disposition of electrons in a molecule. Most molecules have an even number of electrons.

The electrons occupy orbital with a maximum number of two electrons having opposite spin occupying the same orbital. One of these electrons is promoted to vacant orbital of higher energy, after the absorption of light. If the electrons thus promoted is still of opposite spin from its former partner, the excited state is called *singlet state* and if the electrons are spins are the same, the excited state is called *triplet state.*


Ground state


Singlet state


Triplet state

These excited states are energized compared to the ground state and are chemically reactive species. There are two conditions to occur photochemical reactions.

I-Law: The reacting species must absorb light, if the absorbed light is in the visible region the species will be coloured.

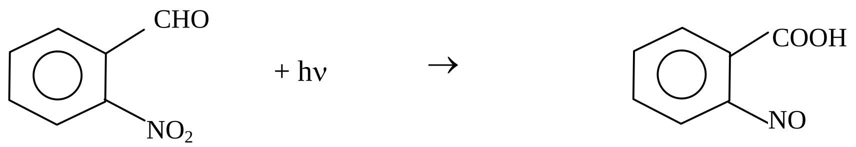
II-Law: Photo chemical process involves activation of molecules by the absorption of one quantum of light that is h γ ergs/ second. γ is the frequency of light; h is the Planck's constant (6.62 x 10^{-7} erg/sec). An energy transfer may take place in which an excited species may transfer energy to another species. A subsequent reaction by the second molecule is termed as a photosensitized reaction. The air glow arises from luminescence of excited sodium atoms (Na*) formed in atmosphere by an intermolecular energy transfer forming reaction.

$$O_2^* + Na \rightarrow O_2 + Na^*$$

In some cases only energy transfer with in the molecule occurs.

$$XY^* \text{ (excited)} \rightarrow XY^{\dagger} \text{ (†-shown as superscript)}$$

This process is called intramolecular transfer, where the dagger (†) denotes an excited state different from the initial one. Finally the exciting species undergoes spontaneous isomerisation as in the conversion of



o- nitro benzaldehyde to o- nitroso benzoic acid, a reaction used in chemical actinometers to measure exposure to electromagnetic radiation. The absorption of very energetic radiation may result in the detachment of an electron. This process is called *Photoionisation.*

$$\mathbf{N_2 + h\nu \longrightarrow N_2^+ + e^-}$$

Photosensitization is considered as a sub category of photo dissociation in which one of the dissociation product is an electron. Light absorbed in IR region is not sufficiently energetic to break chemical bonds. The receptor molecules gain vibrational and rotational energy. The energy absorbed as IR radiation ultimately is dissipated as heat and raises the temperature of the atmosphere. The absorption of IR is very important in the earth's acquiring heat from the Sun and in the retention of energy radiated from earth's surface. The atmosphere is a tremendous dynamic system with wide fluctuations of the parameters i.e., composition, temperature and intensity of sunlight. Obviously different processes will be observed under varying atmospheric conditions, while oxygen plays an important role in the atmosphere and ozone in the stratosphere.

PARTICULATES

Definition: Small solid particles and liquid droplets are collectively called particulates. These are present in atmosphere in fairly large amounts and some times pose serious air pollution problems. Many different chemical substances present can enter the atmosphere in particulate form. The wide range in chemical substances which can enter the atmosphere in products form originating from a single source, coal combustion, is shown in the table below.

Table: Fly ash composition (Coal Combustion)

Component (% calculated AS)	% of fly ash
Carbon	0.37 – 36.2
Iron (as FeO or Fe_2O_3)	2.00 – 26.8
Magnesium (as MgO)	0.06 – 4.77
Calcium (as CaO)	0.12 – 14.73
Aluminium (as Al_2O_3)	9.81 – 58.4
Sulphur (as SO_2)	0.12 – 24.33
Titanium (as TiO_2)	000 – 2.80
Carbonate (as CO_3^-)	0.00 – 2.60
Silicon (as SiO_2)	17.3 – 63.6
Phosphorus (as P_2O_5)	0.07 – 47.2
Potassium (as K_2O)	2.80 – 3.00
Sodium (as Na_2O)	0.20 – 0.90

Physical properties:

Size: The size is an important physical property. Particulates range in size from a diameter of 0.0002 microns (about the size of molecule) to a diameter of 500 microns.

Life Time: Their lifetime may vary from a few seconds to 12 months. This lifetime however depends on the settling time rate, which again depends upon the size and density of the particles and turbulence of air. *Population:* The number of particles in the atmosphere varies from several hundred / cm^3 in clear air to more than one lakh in cm^3 in highly polluted air.

Weight or mass: In urban area the particulate mass level may range from 60 micro grams / m^3 to 200 micro grams / m^3. The size and composition of particulate matter may vary with daytime and with weather conditions. Further elemental composition may differ markedly with particle size and this may affect strong influence on toxological effects of particulate matter. Calcium tends to occur in large particles, which are produced, from wind erosion, rock quarries, cement etc. Similarly common soil components like Fe, Mn, K, Ti occur in large particles while Pb and Br occur to a large extent in smaller particles around 0.5 microns.

A particulate toxological hazard is presented in the range 0.05–1 micron have been found to be retained in the respiratory system. But the total particulate matter of air is less important than the chemical nature and size of the particles. The particulates rather have generally large surface areas and hence present good sites of adsorption of various organic and inorganic matters. Their optical properties, which are ability to scatter light and reduced visibility, are important in determining the effects on solar radiation. Very small solid particles are carbon black, silver iodide, combustion nuclei, sea salt nuclei and large particles are cement dust, wind blown soil dust and foundry dust. Pulverised coal, liquid particulate matter is generally categorised as *mist* this includes rain drop, fog and sulphuric acid mist.

Particulate matter of Biological origin:

Origin: Particulates originate through wide variety of processes. They may be from simple grinding of bulk matter to complicated chemical or bio chemical synthesis. There are numerous natural processes which inject particulate matter into the atmosphere which amounts for about 80-2000 million tonnes / year.

Natural processes: Volcanic eruptions, blowing of dust and soil by wind, spraying of salt and other solid particles by seas, oceans etc.

Man made processes: Fly ash from power plants, smelters and mining operations, smoke from incomplete combustion process. Statistics reveal that fuel combustion from stationary sources (coal, natural gas, wood), industrial process and miscellaneous sources to forest fuels, structural fire, coal refuse burning and agricultural burning share almost equally (1/3 each) which amount between 200-450 million tonnes / year. In countries like USA the annual particulate emission is about 20 x 10^6 tonnes including 5 x 10^6 fine particles (less than 3 microns).

Physical processes for particulate formation:

The particulates about approximately one-micron size are formed by disintegration process of large particles. This is called dispersion process and the product is termed as dispersion aerosol.

Dust or solid dispersion aerosols:

They generally originate from natural sources, sea spray, wind blown dust, volcanic dust. On the other hand cultivation of land has made it much easier for the wind to pick up topsoil and blow it over great distance. High energies are required to break material down to small particles than to synthesise particles through chemical process. Hence most dispersion processes are relatively large as a result these large particles have less harmful effects.

Chemical process for formation of Inorganic particulate matter:

Metal oxides form a major group of inorganic particles in the atmosphere. They originate from the combustion of fuels. Thus particulate iron oxide originates in the combustion of pyrite containing coal.

$$3\,FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2$$

Part of the $CaCO_3$ in the ash fraction of coal is converted to CaO and discharged through the stack.

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

Automobiles are sources of lead particles in the atmosphere. Combustion of leaded gasoline discharge lead halides through the exhaust system.

$$Pb\,(C_2H_5)_4 + O_2 + (\text{ halogenated scavengers }) \rightarrow PbCl_2 + PbBr_2 + PbBrCl + CO_2 + H_2O$$

The halogenated scavengers are dichloroethane and dibromoethane. In USA more than 2×10^5 tonnes of lead are dumped into the atmosphere every year. In recent years, however this quantity is decreasing with the use of unleaded gasoline. Aerosol mist arises from sulphuric acid, obtained by oxidation sulphur dioxide which collects water vapour to form small liquid droplets:

$$2\,SO_2 + O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4$$

In the presence of basic air pollutants such as ammonia or calcium oxide, salts are formed, by loosing water and under low humid conditions. Solid aerosols are left behind.

$$\underset{\text{(droplet)}}{H_2SO_4} + \underset{\text{(gas)}}{2NH_3} \rightarrow \underset{\text{(droplet)}}{(NH_4)_2SO_4}$$

$$\underset{\text{(droplet)}}{H_2SO_4} + \underset{\text{(particle)}}{CaO} \rightarrow \underset{\text{(droplet)}}{CaSO_4} + H_2O$$

Composition of Inorganic particulate matter:

The proportion of elements in atmospheric particulate matter reflects the relative abundance of elements in the parent material, which provides a good idea about the source of the particulate matter.

Eg: Particulate matter largely from ocean spray origin in a coastal area receiving sulphurdioxide pollution may show anomalously high sulphate and corresponding low chloride. The sulphate comes from atmospheric oxidation of sulphurdioxide to form nonvolatile ionic sulphate, whereas some chloride may get lost from the solid aerosol as volatile HCl.

$$2\ SO_2 + O_2 + 2\ H_2O \rightarrow 2\ H_2SO_4$$

$$H_2SO_4 + 2\ NaCl\ (\text{Particulate}) \rightarrow Na_2SO_4\ (\text{particulate}) + 2\ HCl\ (\text{gas})$$

Chemical composition:

Atmospheric particulate matter has an extremely wide diversity of chemical composition. In polluted urban atmosphere, the particulate matter may contain organic matter, nitrogen compounds, sulphur compounds, metals and radionuclides. An extensive analysis of particulate matter collected from large number of sampling stations in urban locations as the following average composition expressed in micro grams / m^3. The sampling was done biweekly.

Total suspended particulates	- 105
Ammonium	1.3
Nitrate	2.6
Sulphate	10.6
Benzene soluble organics	6.8
Antimony	0.01
Arsenic	0.02
Cadmium	0.002
Chromium	0.015
Copper	0.09
Iron	1.58
Lead	0.79
Manganese	0.034
Nickel	0.79
Tin	0.02
Titanium	0.04
Vanadium	0.05
Zinc	0.67
Molybdeum	<0.005

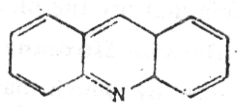
The average levels of berylium, bismuth, and cobalt found were all less than 0.0005 μg/ m^3, although maximum values of 0.010, 0.064, and 0.060 μg/ m^3, respectively were observed.

Organic Particulate Matter:

Organic particulate matter originates from a wide variety of sources. e.g. Emissions from automobiles, combustion from fuel, etc. Typical organic particulate matter, as obtained in the form of a benzene- extractable fraction from 200 air samples in USA showed an average formula,
$C_{32.4}H_{48}O_{3.8}S_{0.083}\ (\text{halogen}_{0.065})\ (\text{alkoxy}_{0.12})$.

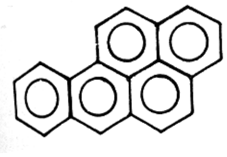
It is found to occur in the range of 1 micron. The aliphatic fraction of neutral group is always having a high percentage of long chain hydrocarbon, especially containing 16–28 carbon atoms. They are not significant in the point of view of health hazard. On the other hand hydrocarbons present in aromatic fraction are poly nuclear aromatics and some are proved to be carcinogens. Aldehydes, ketones, epoxides, peroxides, esters, quinones and lactones are found among oxygenated neutral organic compounds.

A few of them may be mutagenic or carcinogenic. Acidic fractions contain long chain fatty acids and non-volatile phenols. Other acids that are recovered include: lauric acid, myristic acid, palmetic acid, stearic acid, olic acid, linoleic acid. The basic fraction consists of alkaline-N-hetero cyclic hydrocarbons such as *acridine.*

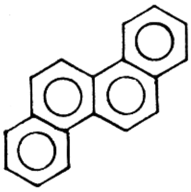


Acridine

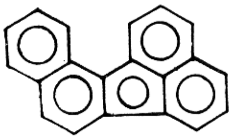
Besides these things PAH (polycyclic aromatic hydro carbons) are important organic particulate matter benzo - α - pyrene, chrysene and benzofluoranthrene.



benzo (α–) pyrene



chrysene



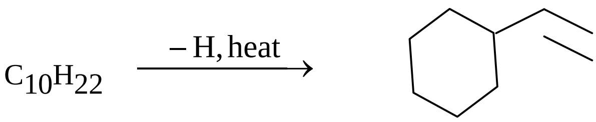
benzofluoranthene

The PAH compounds occur in the urban atmospheres at levels of about 20 µg / m^3. They are found mostly in solid state. They will be sorted onto soot particle. A soot particle contains both organic and inorganic particulates.

Soot Particulate Matter:

Origin:

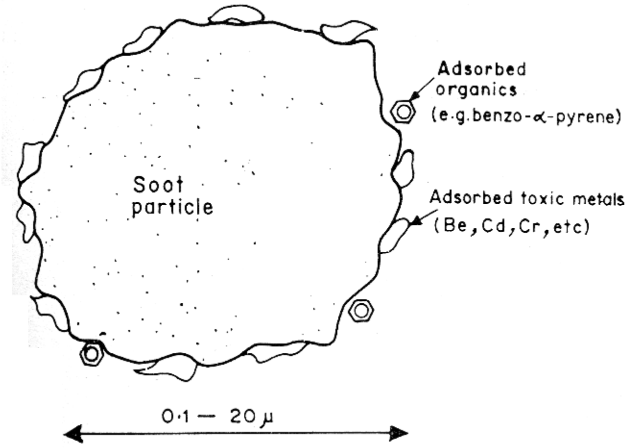
They originate from the pyrolysis of higher paraffins present in fuels and plant material. High molecular weight paraffins are pyrolysed to yield $C_{10}H_{22}$, which undergoes further pyrolysis (which is a technique where in chemical decomposition is brought by heating).



$C_{10}H_{22} \xrightarrow{-\text{H, heat}}$

Poly cyclic aromatic hydro carbons

Most of the PAH compounds remain adsorbed on the soot particles. Soot is formed on a residue on the combustion of fuel in power plants and automobiles. It accounts for 50% of the particulate load in urban areas. Chemically it is a highly condensed product of poly nuclear aromatic hydro carbon consisting of several thousand interconnected crystallites which are made up of graphite platelets, each platelet is having about 100 condensed aromatic rings. The hydrogen content of soot is 1–3% and oxygen content is 5–10% due to partial surface oxidation.



Soot particle from the combustion of fossils fuels

Because of its large surface area, soot acts as a carrier of toxic organics e.g., benzo -α - pyrene and toxic trace metals like: Mn, Cd, Cr, Ni, V, Be etc.

Role of seasonal variations in particulate pollution:

The extent of particulate pollution vary with season in autumn and winter, increased heating of houses, buildings creates demand for more power and hence more particulates. Particulates in atmosphere may influence the formation of clouds, rain, and snow by acting as nuclei on which water condensation can takes place. Universal climate changes can also be related to particulate pollution. The reduction in the amount of solar radiation reaching the earth's surface may upset the earth's atmosphere, heat balance, which is a delicate thing. Although with increase of CO_2 content atmospheric temperature should increase but actual studies reveal that it has been decreasing since 1940. This is because of increased reflection of solar radiation by particulates compensating the climate effect of increased compensation of CO_2.

RADIONUCLIEDS:

Atmospheric radiation originates from both natural and man-made sources.

Natural Sources:

- Cosmic rays from outer space enter the atmosphere and their quantum depends on the altitude and latitude of a location. People living at 1.5Km.altitude in the higher altitude receive double the quantity of cosmic radiation compared to a community living at sea level on the equator.
- Some radioactive nuclides in the earth's crust also emit radiations continuously, which are present in rocks, U_{238}, Th_{234}, Ra236, soils and building materials.
- Some radioactive nuclides present in soil and drinking water enter human body through food chain such as food / drink. Example: K_{40}, C-14, Rn_{222}.

The annual average background radiation is 105 mrem (one thousand part of Roentgen equivalent man). This unit is derived from X-ray dosage or roentgen(r) -it provides biological measurement of human exposure to radiation dosage. The annual dosage of 105 mrem is apparently harmless for man but it may have long-term effect causing genetic damage.

Man made sources:

i) X-rays used in medicine and dentistry.
ii) Radio active fall out resulting from testing of nuclear weapons.
iii) Industrial emissions from nuclear reactions and processing installation.

Explanation:

1) X-rays penetrate through human body average dosage / person / year is about 50 mrem. Though they are beneficial for diagnostic purpose and radiotherapy but proper shielding of reproductive organs is necessary. X-ray has cumulative effect in the body.

2) Explosions of nuclear weapons in air, on ground, under ground and undersea have major contribution to man-made radiation: considerable fission products (with the exception of under ground tests) - C-14, Sr-90, I-131, Cs-137 etc., are dried in the atmosphere. From high -yield mega tonne weapons these fission products also enter the stratosphere where they stay for about 10 years. The nuclides may under go further disintegration in the atmosphere where they may spread all over the globe. Ultimately they settle on the earth's surface as radioactive fall out and then contaminate the food chain.

3) Third source is from increasing use of radioisotopes in industry, research, and medicine and from nuclear reactors used from power generations. The largest contribution is from nuclear reactors and nuclear fuel processing plants. Gaseous waste consisting of Ar-41, Xe-133, I-131, Kr-85, C-14, H-3 are discharged during the operation of the reactor, while the liquid wastes consists of Fe-59, Co-60, H-3 along with corrosion products. The reactors require periodic discharging with a new fuel and removal of spent fuel. These are highly radioactive and must be stored under water for several months. The reprocessing of spent fuel involves significant gaseous wastes I-131, Kr-85, H-3 liquid and solid wastes of high activity.

Average man-made and background radiation is about 155 m rem / year, out of which 25% is of man made radiations. Another source is from leakage of radiation from nuclear reactors.

Toxic Metals in Atmosphere:

Mercury in atmosphere:

Mercury in the atmosphere is of great concern due to its toxicity. Elemental mercury is volatile and enters into atmosphere in atomic form. It enters atmosphere in elemental form from coal combustion and volcanoes. Most of the coal is having appreciable levels of mercury. Some of the mercury in the atmosphere gets associated with particulate matter. Volatile organo mercury compounds such as dimethyl mercury $(CH_3)_2Hg$ are also present in atmosphere besides monomethyl mercury salts such as CH_3HgBr.

Lead in atmosphere:

There are conflicting opinions about atmospheric reactions of lead and ultimate fate of lead. This is a most serious atmospheric heavy metal pollutant .The lead halides from automobiles exhaust are the common forms of atmospheric lead.

Ex: Lead bromochloride ($PbBrCl$) and Ammonium chloride lead bromo chloride ($NH_4Cl.2PbBrCl$)

Beryllium in atmosphere:

It is a component of special type of alloys. It is mostly used in electrical, electronic components space gear and nuclear equipment.

Asbestos:

Asbestos is a fibrous silicate, the fibres are separable yielding fine filaments. Small fibers of asbestos irrigate lung tissue causing a condition called *Asbestosis***,** which is caused by *lung fibrosis.*

Mineral Particulate Matter from Combustion- Fly ash:

Much of mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high ash fossil fuel. Although precautions were taken by stack system for collecting these particles at the chimneys of furnaces etc., smaller particles will be escaping and causing most of the damage to human health, plants and visibility.

EFFECTS OF PARTICULATE MATTER:

Effect of Particulate on plants:

Dust when it rest or reside on the leaves of the plant form a coat on them causing a hindrance to sunlight reaching the leaves for photosynthesis process upsetting the process of CO_2 exchange. The other indirect effect of particulate deposited on plants has a chance of having harmful chemical components to animals that use the plants as food.

Effect of particulate on Humans:

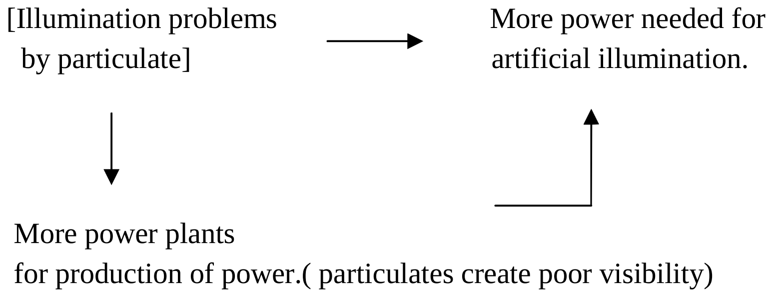
The only major route through which particles enter the body is the respiratory track. Generally large particles are likely to be retained in the nasal cavity and in the pharynx. Hence only very small particulates are likely to reach the lung and retained there. The respiratory system may get damaged directly by particulate material. In addition particulate matter and its soluble components may get transported to organs far away from lungs and create a detrimental effect on these organs. Particles cleared from the respiratory tract largely enter the gastrointestinal track. Material may also enter blood after it is transported into gastrointestinal tract. Particles over 5.0microns in diameter are stopped and deposited in the nose and the throat. Mostly they will be removed by ciliary action. Particles between 0.5μ- 5.0μ may get deposited in lungs. Particles less than 0.5 μ in diameter reach and may settle in the alveoli. Some of the particles retain in the alveoli and some gets adsorbed into the blood.

Particulate matter, which enter and remain in the lung, can exert a toxic effect in three different ways.

1. The particles may be intrinsically toxic because of physical or chemical characteristics.
2. The particles may insert themselves but once they enter the respiratory tract, they may interfere with the removal of other more harmful material.
3. The particles may carry adsorbed or absorbed irradiant gas molecules and thus enable such molecules to reach and retain in sensitive areas of lungs.

Effect of Particulate on Solar radiation and Climate:

Due to scattering of light and absorption by the particles the type and extent of solar radiation reaching the surface of the earth will be changing. As a result there will be reduction in the visibility, which creates dangerous problems particularly for automobile and aircraft operations. A viscous cycle of increasing particulate pollution happens as shown below



DEVICES FOR REDUCING PARTICULATE EMISSIONS:

(Control of Air Pollutants):

In the earlier methods of removal of undesirable emissions, problems were tackled at final stages. Current designs were made to incorporate the idea of controlling the undesirable emissions at their source itself. This kind of preventive measure is known as *Source Control Measure.*

The two major advantages of this measure are

1. The volume of gaseous emissions to be handled becomes considerably less
2. The gaseous emissions can be more easily controlled and useful products may be isolated as benefits.

Mention may be made of the following technique used in industry for removing particulate matter from gaseous effluents.

1. Electro static precipitation
2. Gravitational settling
3. Cyclone collector
4. Wet scrubbers

1. Electro static precipitation:

This is the most commonly used method to control or remove particulate matter from gaseous emissions because it has the capacity to handle large volumes of gaseous emissions.

Plate like electrostatic precipitators:

The plate type is having a series of parallel metal plates with large electrical potentials that are of opposite sign on every other plate. This technique is generally useful for the removal of fly ash in power plants, chemical and metallurgical process, industries and collection of particulates in chemical units.

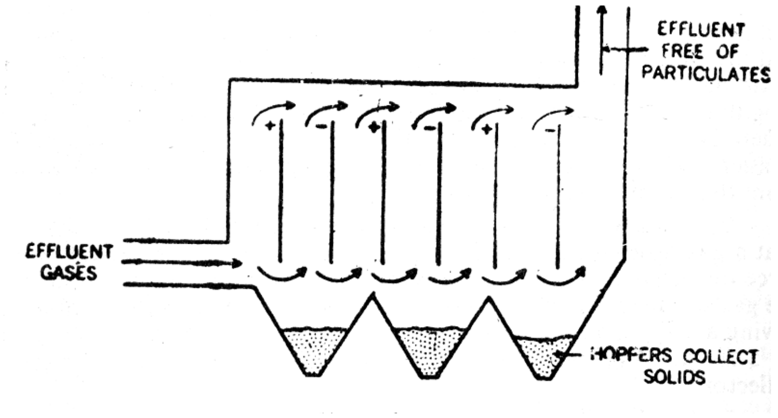


Plate – Type Electrostatic Precipitator

<u>*Tube like electrostatic precipitator:*</u>

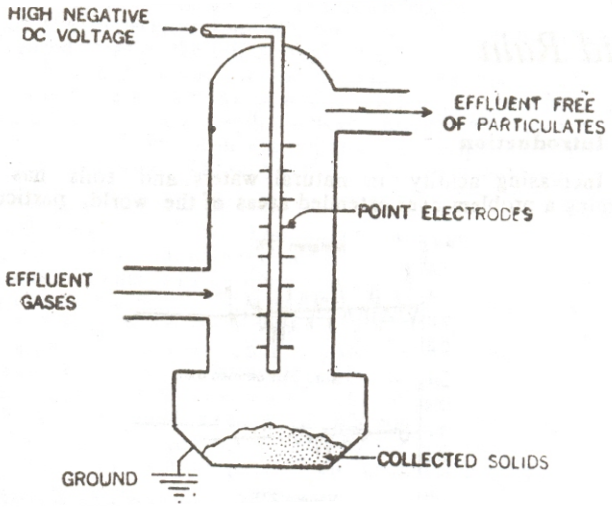
Tube like electrostatic precipitator is based on the principle that aerosol particles acquire electrical charges when subjected to electrical field. The particles acquire a charge when a gas stream is led through a high- voltage dc- corona. The charged particles are attracted to a grounded surface from which they are removed.

$F = E q$

where F is force in dynes

E = voltage gradient (volt/ cm)

q = electrostatic charge on particles (esu)



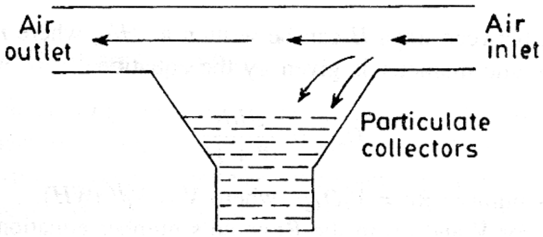
Tube-Type Electrostatic Precipitator

2. Gravitational settling chamber:

Gravitational settling chamber can be used only when the particle size is large measuring above 50microns. The most common use of these settling chambers is to pre clean the pollutants and hence known as p*re cleaners.* The diagrammatic representation for the simplest form of settling chambers useful for handling large volumes of particulates is as follows.

Large volume of polluted air is passed at low velocity. The heavier particles will settle down by gravitational pull into the particulate collectors.

The Tray settling chamber is more efficient device. This is generally used when the particulates have a commercial value, which needs their



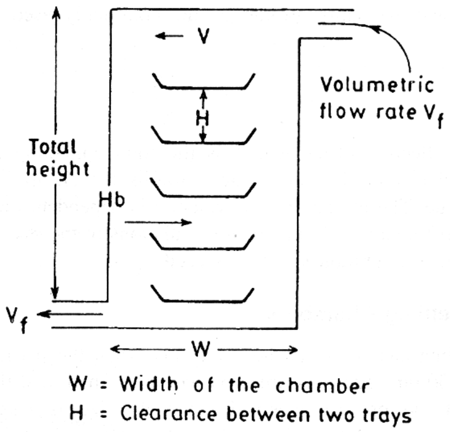
A simple particle setting chamber

recovery. In this method the particulates move in a laminar flow fashion .The efficiency of the device is due to

1. The travel distance of each particle is much shorter before falling into tray.
2. The flow velocity of particles remains substantially the same over the entire period of their flight.
3. The particulate gets several opportunities to fall in the collector. The collection efficiency can be further improved by using turbulent flow type.

Use of Laminar Flow Chamber:

The laminar flow chamber is very much used due to simplicity of design and operation, requirement of minimal supervision and perfect theoretical collection efficiency. However, it is disadvantageous because of its large size and the necessity for large number of trays.



Tray-type chamber

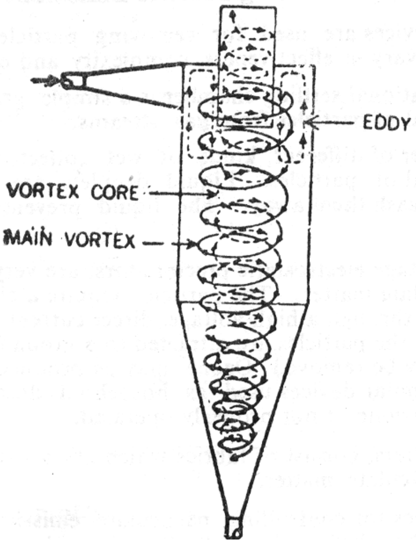
Turbulent Flow Settling Chamber:

The method overcomes many of disadvantages of the laminar flow collectors. In this technique gas containing the particulates is allowed to spin. The centrifugal force generated by the spinning gas help in the separation of particulate matter. There are different types of turbulent flow chambers as given below:

1. Straight through flow type.
2. Reverse flow type collector
3. Impeller type collector.

Cyclone Scrubber:

This device is an application of the fact that a gas flowing in a tight circular spiral gives rise to a centrifugal force on suspended particles, forcing them to move outward through the gas stream to a wall where they are collected. Such units are having a 95% removal efficiency for particles in the diameter range of 5–20 microns.



Typical Cyclone Collector

3. Wet Scrubbers:

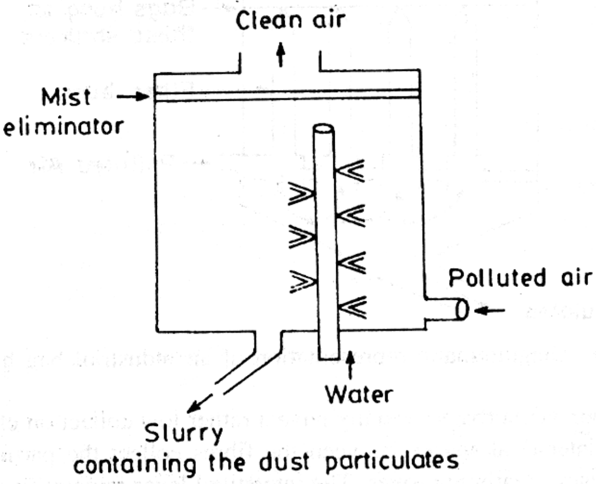
Cleaning using a liquid (usually water) to assist in removing solid, liquid, or gaseous contaminant is termed as wet scrubber. The effectiveness of devices of type has been found to depend upon the degree of contact and interaction between the liquid phase and the contaminate to be removed. The amount of contact and interaction get increased by using spray chambers or towers, where the liquid is introduced into the gas stream as a fine spray. Another approach frequently used is to make the liquid to percolate downward through a packed bed of material while the gas stream moves upward through the packed bed and liquid in a counter- current fashion.

Three principle wet scrubbers are used in industry

1. Cyclone scrubber
2. Spray chambers
3. Venturi scrubbers

1. Cyclone Scrubber:

The simplest Cyclone scrubber is obtained when a battery of nossils is fitted inside the conventional dry cyclone. The water spray acts on the particles in the outer vortex and the dust- laden liquid particle are thrown out ward against the wet inner wall of the cyclone.



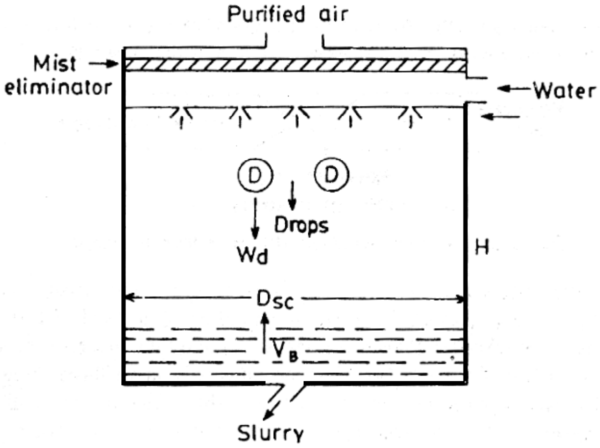
Cyclone scrubber

The polluted air is inserted at the bottom of the vertical cylinders in which sprays are located along the central area of scrubber. The water jets give a tangential acceleration radically and during this acceleration the drops sweep up the particulates, which then flow down and form slurry (containing dust particles)

2. Spray Chambers:

Spray chambers are the simplest type of wet collectors. Generally water is sprayed from top. The drop removes the particulate by scrubbing action, consisting of intersection, impaction and diffusion.

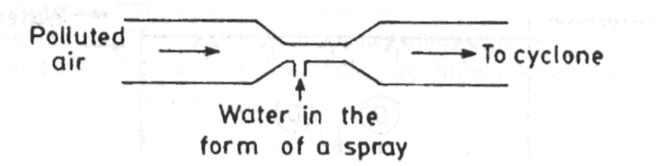
The effectiveness of the conventional form of the spray tower ranges from 94% for 50µm size particle to 99% for 25µm .



Slurry spray chamber

3. *Venturi Scrubbers:*

These are cleaning devices where the water drops are injected into the air stream near the point of entry to the section of maximum velocity in order to accelerate the air speed. The acceleration however does not stop at the end of the throat out but continues into the diverging section of the collector or a cyclone situated at the down stream of the scrubber to collect the drops.



Venturi scrubber (throat injection model)

The crucial factor in the entire set up is the length of the throat, which should be long enough so that most of the particles get collected at the throat. If the throat is too short a few particles get collected at the throat and thus much of the efficiency of the process is lost. On the other hand unusually large throat length causes a considerable drop in pressure. This process is highly efficient for smaller particles.

UNIT 2

AIR POLLUTION ANALYSIS

Lesson 4

Objectives of the lesson: This lesson exclusively deals with the monitoring and analysis of various air pollutants.

CONTINUOUS MONITORING OF AIR POLLUTANTS:

Introduction:

Several of the laboratory methods fail to furnish the reliable information, when the pollutant is emitted ceaselessly and especially when it is necessary to measure it at site such as in a field, or in any out door location. At a time it is difficult to collect the sample and bring it to the laboratory for further analysis. In addition there is a good possibility that we have to take several measurements on regular basis at constant and regular intervals. In such a case we adopt rapid methods by which we can analyse air pollutants on continuous basis. Fortunately, few of the laboratory methods can be on the out door locations, some times it is always possible to use basic principles underlying laboratory methods for testing of pollutants to device a novel method for continuous measurement. Such continuous measurement is termed as '*monitoring*'. Rapid or continuous analysis of air pollutants on regular basis at constant and regular intervals is called '*continuous monitoring*'.

Principles of monitoring methods:

Since it is necessary to measure the air pollution on a regular basis, there is a need to identify some physical property of the pollutant for such measurements. The component of the instrument, which measures such parameter is called a transducer. A specific property, characteristic of a particular pollutant such as light transmittance or absorbance, electrical conductivity, change in potential, generation of material by passing of electricity, nucleation of fog formation or radioactivity is usually measured. Such properties are summarised in the following table and examples of gaseous pollutants, which can be measured, are cited.

Physical principles involved in various monitoring methods.

S.No.	Physical principles of measurements	Examples
1.	Molecular absorbance (UV/Visible/IR)	SO_2 , NO_2, H_2S, CO
2.	Atomic absorption (AAS)	SO_2, Hg
3.	Atomic emission (ICP–AAS)	SO_2, meal pollutant
4.	Molecular luminescence (Florescence)	SO_2 , NO_2
5.	Light scattering (Nephelometry and Turbidimetry)	Particulates
6.	Magnetic resonance/ Electron spin resonance (NMR/ESR)	Organics
7.	Polarography, Amperometry	Pesticides

S.No.	Physical principles of measurements	Examples
8.	Conductance, High frequency	SO_2
9.	Potential - pH measurement	NO-NO_x
10.	Coulometry – Anodic stripping voltametry (ASV)	SO_2
11.	Radio analytical (NAA / IDM)	Radio active pollutants
12.	Gas Chromatography (GC)	Organics, HCl

The monitoring instrument is usually composed of three components, viz., air remover, transducer and recorder. The air remover component consists of a flow meter and a pressure gauge. They measure rate of flow of air passing and the pressure under which gas pollutants exist. Transducer in fact is the heart of the instrument, which measures a physical property while the recorder notes the change in physical property of the gaseous pollutant; example spectrophotometres are used to measure the concentration of the pollutant.

Monitoring instruments:

The common air pollution instruments for measurement are summarised in the following tables. The limits of measurements are given in first table and while the technique of measurement of measurement is given in the column of the second table.

Air pollution monitoring instrument and limit

S. No	Instrument	Pollutant to be measured	Limit of analysis (ppm)
1.	IR gas analyser	Hydro carbons, CO, CH_4	10 – 100
	NDIR analysis	CO, CO_2	Non dispersive
	Car exhaust meter	Auto exhaust analysis	–
	CO-monitor	Catalytic oxidation	0 – 50
2.	SO_2 monitor	Conductivity	0 – 100
	SO_2 monitor	Coulometric titration	0 – 40
3.	O_3 monitor	Chemiluminescence	0 – 0.1
4.	NO-NO_x monitor	Chemiluminescence	0.05
5.	H_2S analyzer	Colorimetry	0.40

Air monitoring instrument and technique

S.No.	Instrument	Pollutant Measured	Technique of analysis
1.	Conductometric analyzer	SO_2	Conductometric measurement
2.	Continuous SO_2 monitor	SO_2	Coulometric measurement
3.	Gas Liquid chromatograph	CO, NO	Gas chromatography
		Hydrocarbon	With different detectors
4.	Nitric oxide monitor	NO_2	Florescence technique

S.No.	Instrument	Pollutant Measured	Technique of analysis
5.	Ozone monitor	Ozone	Chemiluminiscence technique
6.	Infra red gas analyzer	CO, CH_4 and HC	Infared absorption
7.	Fluorescence spectroscope	Organic pollutant	Florescence & Phosphorescence
8.	Smoke meter	Smoke, Smog	Light scattering technique
9.	Atomic absorption spectrophotometer (AAS)	Trace metal analysis	Atomic absorption spectroscopy
10.	Spectrograph	Metal pollutants at tracer level	UV Visible spectroscopy

MONITORING OF AIR POLLUTANTS

ANALYSIS OF OXIDES OF CARBON

Carbon monoxide:

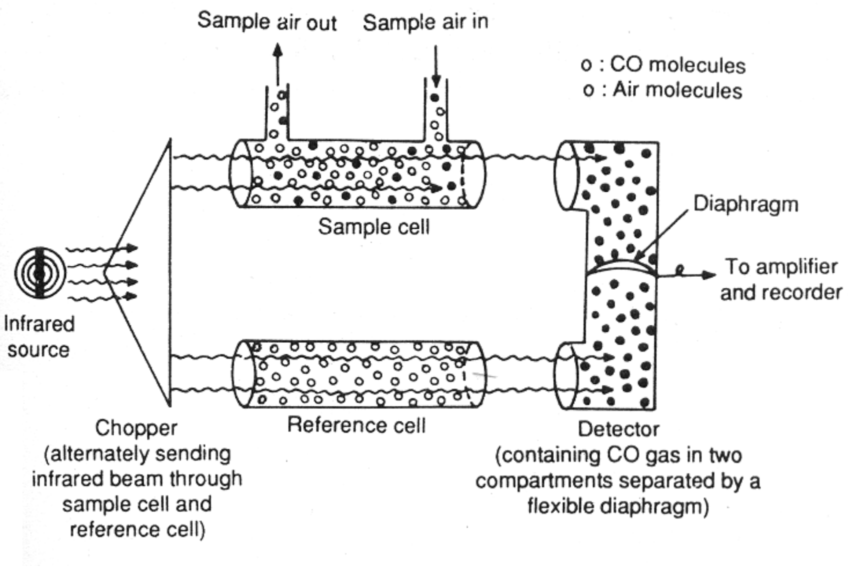
The various methods for monitoring carbon monoxide are as follows

S.No.	Method	Remarks
1.	Non-Dispersive IR	H_2O vapour interferes
2.	NDIR spectrometry	Specific, sensitive, reliable method
3.	IR Fluorescence method	No interference by H_2O vapour
4.	AAS (reduction of HgO –Hg)	Need a charcoal filter
5.	Electro catalytic method	Need selective scrubbing of SO_2, NO_2
6.	Electo chemical transducer	Ethylene and acetylene interfere
7.	FID (after CH_4 formation)	Sensitive method compared to NDIR
8.	Hopcalite based CO-monitor	Temperature rise for converting to CO_2 is measured

Method -1: *Non-dispersive infra red spectroscopy:*

The standard method for analysis of carbon monoxide (CO) is non dispersive IR spectrophotometry. It is based on the principle that CO strongly absorbs IR radiations at certain wavelength. When IR radiation is led through a long cell (100cm) containing CO, part of energy of radiation is absorbed by CO, which can be correlated with concentration of CO.

In the non-dispersive IR spectrometer, the IR radiation from the source is not dispersed according to wavelength by a prism or grating as in a standard IR spectrometer. It is made very specific for a given compound or type of compound by using the material under investigation as a part of the detector. Radiation from an IR source is ‘chopped’ by a rotating device so that it alternatively passes through a sample cell and a reference cell.



Non-dispersive infrared spectroscopy

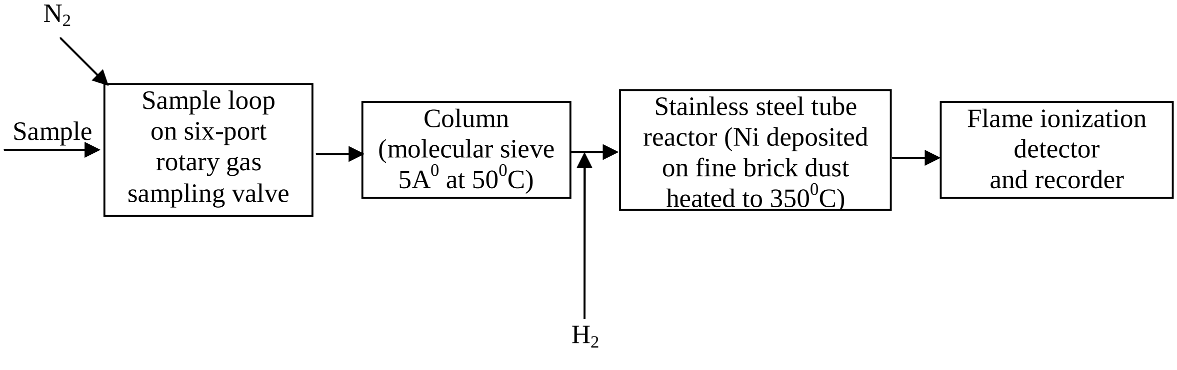
Both the beams of light are incident on the detector, which is filled with CO gas and divided into two compartments by a flexible diaphragm. The relative amount of IR radiations absorbed by CO in two sections of a detector is determined by CO levels in the sample. The differences in the amounts of IR radiations absorbed in two compartments give rise to temperature difference so that the diaphragm bulges slightly towards one side. Such a movement of diaphragm even to a slight extent can be detected and recorded. By this method upto 150ppm of CO can be measured with a relative accuracy of ±5% in the optimum concentration range.

Method-2: *Gas chromatographic determination of carbonmonoxide:*

Low levels of CO (<10ppm) can be conveniently measured after catalytic reduction by hyrogen over a nickel catalyst at 360^{o}C by gas chromatography with a flame ionization detector.

$$CO + 3H_2 = CH_4 + H_2O$$

The sample is fed into the sample loop on a six port-rotary gas sample valve. The column contains a molecular sieve, $5A^0$ at 50^0C. The catalytic reduction is conducted in a small tubular reactor, made of stainless steel and heated to 360^0C. Nickel is deposited on fine brick dust in this tube. With temperature programming to 250^0C, CO_2 can also be determined.



Gas Chromatographic determination of CO

However, CO monitoring methods are many

1. Iodine vapour visual colorimetry

$$I_2O_2 \quad + \longrightarrow \quad CO \quad I_2 + CO_2$$

2. Atomic absorption spectroscopy

It measures the Hg, after reduction of HgO to Hg by cold vapour

$$HgO + CO \longrightarrow Hg + CO_2$$

3. Reflectance spectroscopy

$$PdCl_2 \quad \longrightarrow \quad + CO \quad COCl_2 + Pd$$

4. Hopcalite based CO – monitor

A novel method for CO- monitor is Hopcalite based CO monitor. Here the temperature raised is measured. Such rise is due to heat generated in the exothermic conversion of CO to CO_2 in the presence of Hopcalite catalyst. Oxides of Mn or Cu serve the purpose of such catalyst. Humidity will effect measurement. Hence it is necessary to maintain catalyst at a temperature of 100^0 C.

Analysis of carbondioxide:

The analysis of CO_2 is simple. It is bubbled through a solution of NaOH or KOH to form carbonates. The unreacted alkali is titrated against a standard solution of some acid. The measurement of CO_2 is the index of human and plant activity, as a significant portion of CO_2 in the air is anthropogenic.

MONITORING OF SULPHUR DIOXIDE:

The various methods used for monitoring of sulphur dioxide are summarised in the following table.

S.No.	Method	Remarks
1.	$Ba(ClO_4)_2$ Titration	Valid till 500ppm
2.	West-Gaeke method	–
3.	Conductometric method	Commonly used
4.	Coulometric method	KBr reduction with the use of three electrodes
5.	GLC-flame photo detector	Specific for SO_2

1. $Ba(ClO_4)_2$Titration:

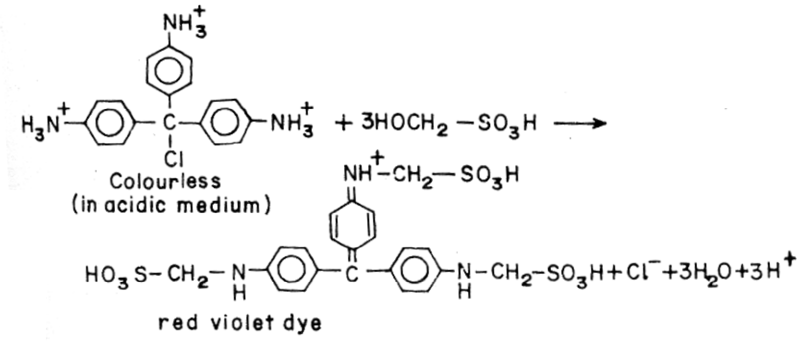
In simple barium per chlorate titration sulphur dioxide is reacted with hydrogen peroxide or water to form sulphuric acid, which in turn is reacted to form $BaSO_4$. The method is valid when high concentrations of SO_2 are encountered but many metals like lead show strong interference.

2. West – Gaeke spectrophotometric method:

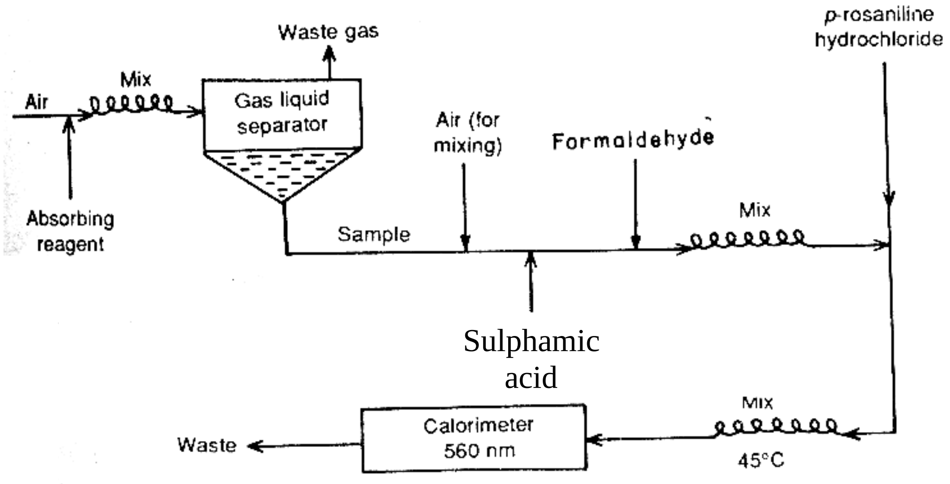
This is a standard method for monitoring 0.0005 to 5ppm SO_2 in ambient air. SO_2 is collected in a scrubbing solution containing $HgCl_4^{2-}$ ($HgCl_2$ + KCl) whose efficiency is 95%. The solution is allowed to react with HCHO and then with p-rosaniline hydrochloride.

$$HgCl_4^{2-} + SO_2 + H_2O = HgCl_2.SO_3^{2-} + 2H^+ + 2Cl^-$$

$$SO_2 + H_2O + HCHO = HOCH_2 - SO_3H$$



The absorbance of the product (red violet dye) is measured at 548nm. (Na_2SO_3 is used as check iodometrically as the standard). A block diagram of a continuous SO_2 monitor, based upon the West-Gaeke method and developed by Technicon is given below.



SO_2 monitor using a modified West-Gaeke method

The major interference from NO_2 (>2ppm) is eliminated by the addition of sulphamic acid (NH_2SO_3H). This reagent acts as a reducing agent for the conversion of NO_2 to nitrogen gas.

Procedure:

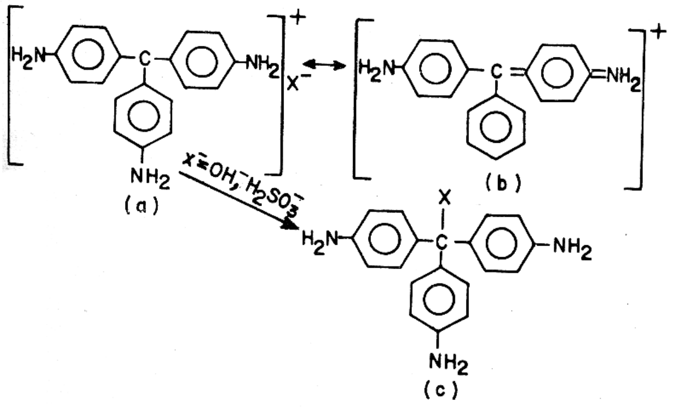
1. About 30–60L of air is pumped through 10ml of the scrubbing solution (13.6g of $HgCl_2$ and 7.5g of KCl in one litre water) in a small impenger at 1-2 L/Minute.
2. Then 1ml of dilute p-rosaniline solution (4ml of 1% aqueous solution acidified with 6ml of concentrated HCl and diluted to 100ml with water) and 1ml of 0.2% HCHO solution (5ml of commercial 40% solution diluted to 1L with water) are added. The absorbance of the solution is measured at 560nm after 20–30 minutes. Dilute solution of Na_2SO_3 is used and checked iodometrically as standard. The main disadvantage with the above method is handling high concentrations of toxic and costly $HgCl_2$.

Das Gupta et al developed a method based on absorption of SO_2 into HCHO buffered a pH 4.0. Sulphite liberated from the compound by base is added to acidic p-rosaniline and the absorbance is measured at 580nm. Interference from oxygen, nitrogen dioxide and transition metal ions is negligible (nil).

The reaction mechanism has been suggested to be as follows

$$\begin{tikzcd}
(NH_2Ph)_3C^+ + HCHO \arrow[r] & (NH_2Ph)_2\,C^+Ph\,.NHCH_2OH \arrow[d, "HSO_3^-"', "OH^-"] \\
& (NH_2Ph)_2\,C^+Ph\,.NHCH_2SO_3H \arrow[d, "HCHO"] \\
& \text{etc.}
\end{tikzcd}$$

An amino carbinol appears to be the first intermediate, which undergoes nucleophilic substitution by bisulphite. The same can be represented as follows



The method is less susceptible to NO_2 interference than the West-Gaeke method. However, with fairly high levels of NO_x or O_3, sulphamic acid or sodium sulphonate addition is necessary as in case of West-Gaeke method. Interference from Mn(II) can be eliminated by adding 0.1 milli mole of CDTA (Trans 1,2-Cyclo hexane dinitrio tetra acetic acid) to the absorber solution.

3. Conductometric method:

This method is the basis for commercial continuous SO_2 analyser since 1929. SO_2 is collected into H_2O_2 solution and increased conductance of H_2SO_4 solution is measured.

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

4. Amperometric method:

Some SO_2 monitors are based on amperometry in which an electric current is measured which is proportional to SO_2 in the collecting solution. SO_2 is allowed to react with in solution causing changes in the measuring electrode potential.

$$SO_2 + Br_2 + 2\,H_2O \longrightarrow H_2SO_4 + 2HBr$$

The potential is restored to original value by regenerating bromine electro chemically and measuring the current required for regeneration.

ANALYSIS OF HYDROGEN SULPHIDE:

Generally H_2S co-exists with SO_2 in the atmosphere. H_2S is produced by the reduction of sulphates and organo sulphur compounds by the bacterium Desulpho vibrio de sulphuricans and associated with methane thiol (CH_3SH) dimethyl sulphide (CH_3SCH_3), dimethyl disulphide (CH_3SSCH_3) and carboxyl sulphide (COS). The odours of all these species are objectionable even at very low concentrations. The TLV of H_2S is 10 ppm. As H_2S readily oxidised in air, it is trapped as the insoluble metal sulphide (CdS, HgS, ZnS, Ag_2S) in the absorption reagent.

The most simple and reliable method for monitoring of hydrogen sulphide (H_2S) is of flow colorimetry. Instead of using any kind of chromogenic ligands, it would be worth to explore simple chemistry of second group of qualitative analysis. Among metals tested ex: Cu, Cd, As, Sb, Bi, Sn, it was found that Arsenic gives reproducible results by formation of As_2S_3, which conforms to Beer's Law.

The tape coated with $AsCl_3$ is slowly moved, K_2CO_3 is impregnated on glass fibre filters to remove SO_2 contamination; a sponge containing dilute HCl wets the tape before its interaction with H_2S, to under go reaction as

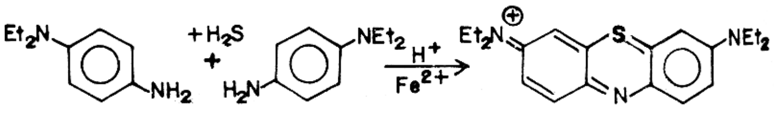
$$2\,AsCl_3 + HCl + 3H_2S \longrightarrow As_2S_3 + 8H^+ + 8Cl^- \text{ (yellow colouration)}$$

The lowest detection limit is 5ppm, with working range of monitoring of 1 – 800ppm.

Procedure:

50ml of 1% solution of $3CdSO_4 .8H_2O$ and 50ml of 0.01M NaOH are taken in a standard glass wash bottle with a fritted glass disperser. 100–500L of air is pumped through the wash bottle at a rate of 10 –15 L/minute. 2ml of 1M $NaClO_4$ is added and the contents are shaken well.

Then 1ml of 2% w/v N,N-Diethyl– p – phenylene diamine in 50% (w/v) H_2SO_4 and 1ml of filtered 10% (w/v) solution of iron(III) ammonium sulphate dissolved in the 1M H_2SO_4 are added. The contents are transferred into a separating funnel after 10 mints and extracted with 10ml of $CHCl_3$ twice. The extracts are collected into 25ml standard volumetric flasks and made upto the mark and the absorbance is measured at 670nm in a 1cm cell. A calibration curve is drawn using a stock solution (1–10 micro grams range) which is prepared by washing the crystals (Na_2S) with ethanol and drying on filter paper.



Ethylene Blue

ANALYSIS OF OXIDES OF NITROGEN (NO_x)

Chemiluminescence method:

It is the standard method for NO_x analysis, based on interaction with ozone to yield electronically excited NO_2^* molecule, which emits radiation in the range 600–3000 nm.

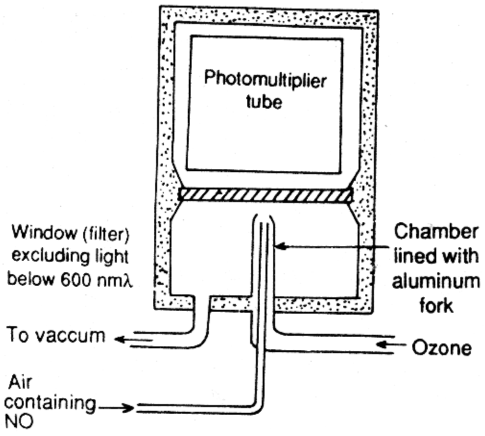
$$NO + O_3 \longrightarrow NO_2^* + O_2$$
$$NO_2^* \longrightarrow NO_2 + h\nu$$

The emitted light is measured by photo multiplier. The intensity of emitted light proportional to the concentration of NO_2.

<u>Apparatus:</u>

The apparatus consists of a chamber into which there is a scope for providing ozone and to allow air enriched with NO. The chamber is evacuated by using a vacuum pump. The chamber is separated with a window (filter), which can exclude light below 600nm.

Since NO_2 may invariably associated along with NO in air sample, it is necessary to convert NO_2 to NO before analysis. This can be done by passing the air sample over a thermal converter before actually entering this process. Analysis of this sample gives total NO_2 (i,e., NO and NO_2).



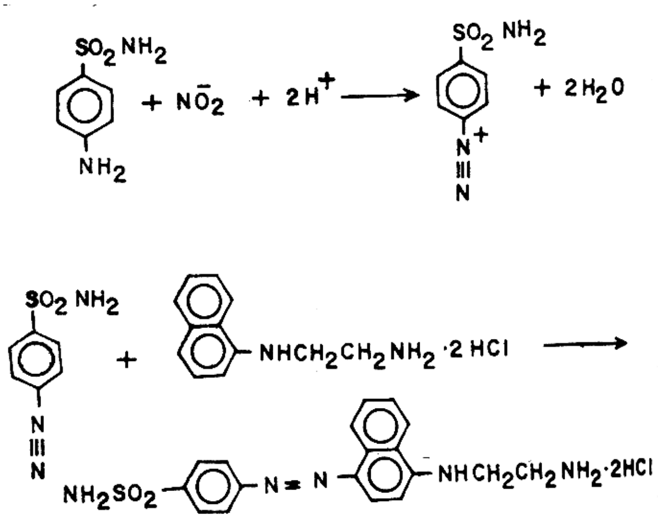
Chemiluminescence detector for NO

On the other hand if we allow the air sample (with out pretreatment) i.e., not passing through thermal converter, then we get only NO. Thus the concentration of NO_2 can be calculated from difference of these two measurements. If other nitrogen compounds are present in large excess besides NO and NO_2, they interfere with this determination. Although particulates are bound to interfere, the interference can be eliminated by using membrane filters at the inlet of air.

This method is also applicable for the analysis of ozone by interaction of ozone with NO.

Spectrophotometric method:

NO_x is collected over sodium hydroxide solution. The NO_2 produced is allowed to react with phosphoric acid, sulphanilamide and N(1-napthyl) ethylene diamine dihydrochloride. The resulting reddish purple azodye is measured at 543nm.



Azodye

Another method involves the absorption of sodium arsenite gas on H_2O_2 in the presence of sulphanilamide, H_2SO_4 and N-naphthl ethylene diamine hydrochloride (NEDA). A red coloured complex formed is measured at 550nm. SO_2 does not interfere; the only limitation is that $NaAsO_3$ is toxic in nature.

DETERMINATION OF OZONE IN AIR:

Chemiluminescence method: The method is same as given above for the analysis of **oxides of nitrogen**.

ANALYSIS OF AMMONIA

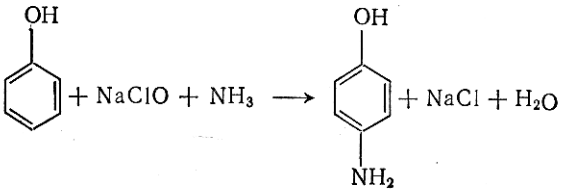
A 100-1000 litre sample of air containing from 1 to 100 μg NH_3 / m^3 is passed through 23 ml of 0.01N sulphuric acid at a rate of 3–30l/min. If the air contains much hydrogen sulphide, it is removed by heating the acid solution. The solution is transferred into a 25 ml measuring flask, water is added to the mark, and the solution is mixed. Ammonium is determined in an aliquot either by Nessler's method or indophenol method.

Determining ammonia by indophenol method:

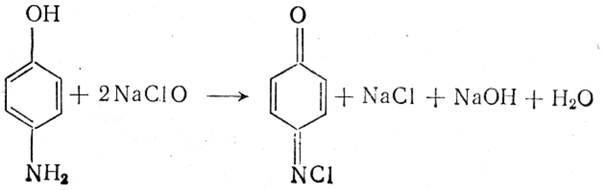
The reagents used in the indophenol method are various phenols, mostly phenol itself and thymol. In addition to sodium hypo chlorite, hypobromite and chloramine are also used. As a rule sodium hypochlorite reacts with NH_3 to oxidise it to nitrogen.

$$3NaOCl + 2NH_3 \longrightarrow 3NaCl + 3H_2O + N_2$$

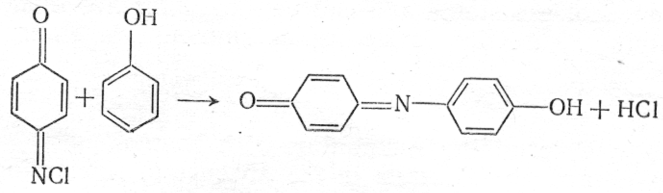
A dye is however formed in presence of excess of phenol. The chemistry of this process is supposed to be the formation p-amino phenol.



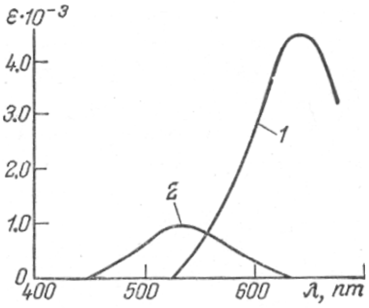
At the second step, p-amino phenol reacts with sodium hypochlorite to form quino chloroimine.



Quino chloroimine reacts with second molecule of phenol to form indophenol dye.



Indo phenol is red (λ_{max}= 530 nm) in acid medium and blue (λ_{max}= 680nm) in alkaline medium. The dye is obtained from phenol is extracted poorly, but if thymol is used as the initial substance, the obtained colour compound can be extracted with various organic solvents. The colour of the solution varies depending on the particular solvent; with amyl alcohol it is bluish green, with isoamyl acetate – violet and red with benzene. The colour intensity also differs greatly.

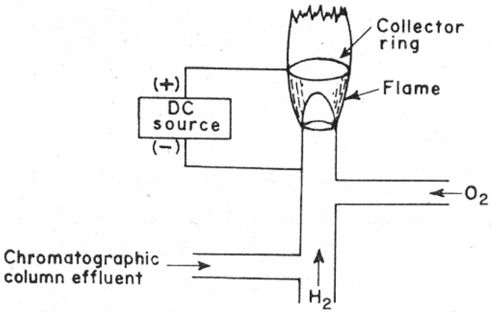


Absorption spectra of product of reaction of thymol and sodium hyhobromite in n-butyl alcohol (1) and in isoamyl acetate (2)

Analysis of hydrocarbons:

Atmospheric hydrocarbons are easily sampled. Methane, a non pollutant constituent is usually separated from the sample before analysis. Preconcentration is necessary in the case of hydrocarbons before analysis. Straw, a highly boiling petroleum distillate is used as a liquid absorber selective for hydrocarbons. Cryogenic low temperature techniques are employed to freeze hydrocarbons and other gaseous pollutants. The drawback in the case of cryogenic collectors is the collection of water along with gaseous sample from atmosphere. This problem can be eliminated using desiccators, freeze thaw cycles etc.

Hydrocarbons can be conveniently collected in an absorption column packed with a very porous styrene divinyl benzene polymer. Air is sampled at the rate of 4 litres per minute. Since only 10 lit sample is necessary, it takes short time for the collector of the total sample. The sample collector is heated subsequently to desorb the sample for gas chromatographic analysis. As little as 0.1 μg of hydrocarbon / m^3 of air can be estimated using flame ionisation detector for the gas chromatograph.



Flame ionization detector for the analysis of hydrocarbons

The gas chromatograph in conjunction with a mass spectrometer (GCMS) is highly suitable for identification of low levels of hydrocarbons

Flame ionization detector (FID) is extremely sensitive for detecting organic compounds. In flame, organic compounds form highly conducting fragments, such as C^+. On applying a potential gradient across the flame, a small current is generated which is readily measured. The response of flame ionization detector is roughly proportional to the number of carbon atoms in the compound. Halogen, nitrogen or oxygen if present in the organic compounds, decrease the sensitivity of the detector. It is sensitive to very low levels of hydrocarbons ranging down to 10^{-3} μg.

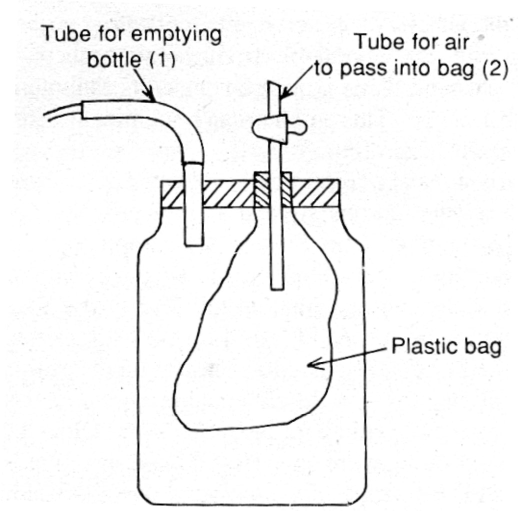
Aromatic hydrocarbons in exhaust petrol and air:

Benzene and toluene and other aromatic hydrocarbons occur in petrol (5% and 10% v/v respectively) and also at low levels in automobile exhaust along with other unburnt gases. The threshold limiting value (TLV) for benzene is only 10 ppm v/v (30 mg/m^3). Exhaust gases contain a few hundred mg/m^3 of unburnt aromatics where as the air near petrol pump in operation is likely to have benzene levels close to the TLV.

The aromatics mentioned above can easily be estimated by GLC with FID and a polyethylene glycol stationary phase (carbowax 1540) run at 90^0C. The standards are prepared as 0.1% v/v solutions in CS_2.

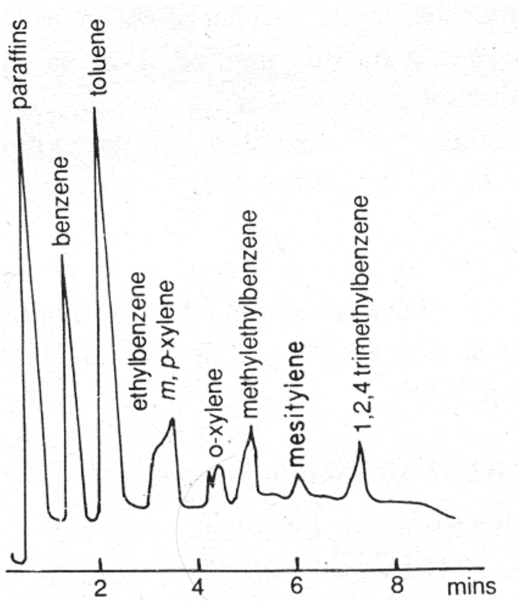
Procedure for exhaust gas:

Flush out and fill a one litre bag in bottle sampler with exhaust gas through a $CaCl_2$ drying tube, by placing the tap tube inside the exhaust pipe of the automobile. The samples are collected at different engine speeds.



Bag in bottle for air sampling, 1, tube with mouth piece for emptying bottle; 2, tube for air to pass into bag

Plastic bags are commonly used which may be polyethylene or polyester. Blowing into the space between the bag and 1 lit jar through tube (1) expels the contents of the bag through tap and tube (2). This is followed by sucking on (1) which will fill the bag. The bag fills itself if the flow of the gas being sampled is fast.



Gas chromatogram of aromatics in 5-star petrol. Carbowax 1540 column at 90^{0}C, sample 1% v/v in CS$_2$

UNIT 3

HYDROSPHERE - A

Lesson 1

Objectives of the lesson: This lesson deals with basic understanding of hydrosphere and unique properties of water.

Water is very complicated and vitally important substance. It is the medium which gave birth to first primitive living molecule and with out it no life can exist. The history of human civilisation reveals that civilisation and water supply are almost synonymous. Several cities and civilisations have disappeared due to shortage of water originating from climatic changes. Several millions of people all over the world particularly in developing countries are loosing their lives due to water–borne diseases. An understanding of water chemistry is basis of knowledge of the multidimensional aspects of aquatic environmental chemistry, which involve the sources, composition, reactions and transportation of water.

WATER SOURCES*:*

About 97% of water is in the oceans, which is unfit for human consumption and other uses because of its high salt content. 2% is in the form of glaciers and ice caps. Only 1% is available as fresh water in the form of rivers, lakes, streams, reservoirs and ground water, which is suitable for human consumption. Ground water has mineral enrichment by virtue of its passage through soil, which is rich in minerals. The groundwater percolates through seepage into the water levels and hence it will assume the properties of the salts that are present in the under ground. Surface water contains lot of organic matter and mineral nutrient, which feed algae and large bacteria population.

Mass balance of annual rainfall:

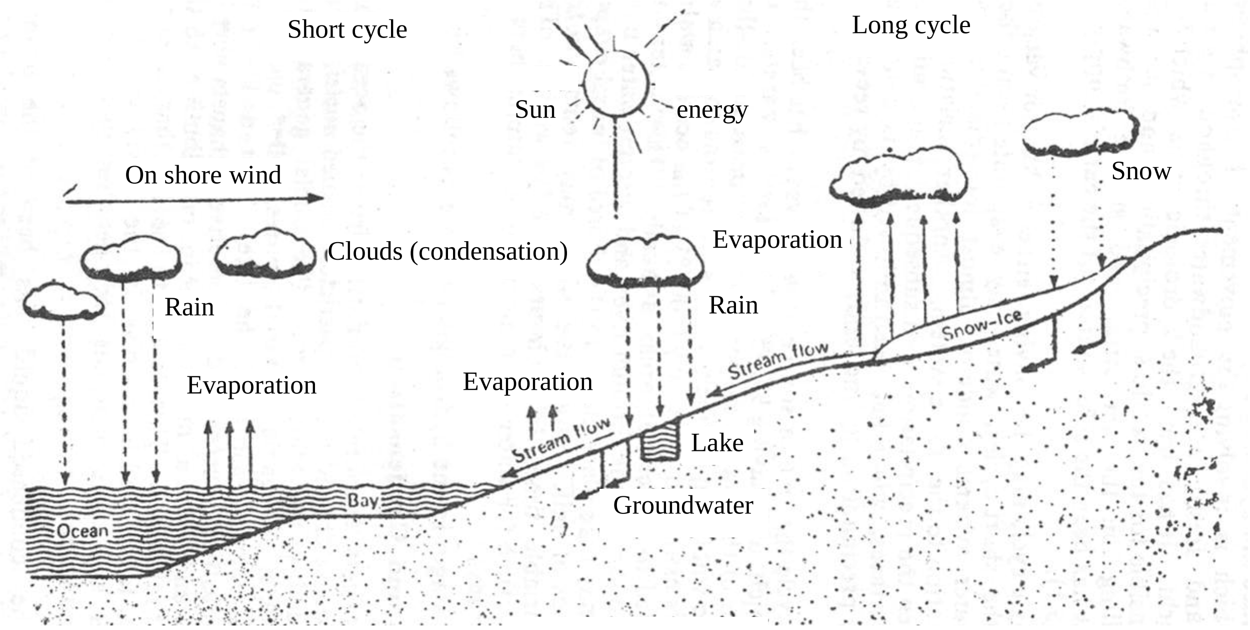
The mass balance of annual rainfall shows that about 70% of water is lost by direct evaporation and transpiration by plants, while the remaining 30% goes in the form of streams. The approximate breakup of this stream flow as consumed by man is 8% for irrigation, 2% for domestic use, 4% for industries, 12% for electrical utilities.

Irrigation for agricultural purposes and electrical power plants are the major consumers of water. The surface water resources continue to get contaminated with run off water from agricultural fields, containing pesticides, fertilizers, soil particles and waste chemicals from industries and sewage from cities and rural areas.

HYDROLOGICAL CYCLE:

Hydrological cycle involves several stages

1. Evaporation and condensation
2. Run off, Stream flow, infiltration
3. Evapotranspiration
4. Ground water



The Hydrological Cycle

Evaporation and condensation:

Water gets evaporated primarily from oceans and tends to condense around minute particles termed as nuclei, which have been in suspension in atmosphere. Nuclei generally are small particles of organic material (like spores, pollen), fine mineral particles and volcanic ash. All solid particles will tend to have a system of nuclei. Anthropogenic inputs like dust and smoke particles from industries and automobile exhaust will also serve as nuclei, which help in contributing themselves for the contamination of rainwater.

Initially the condensed liquid is in the form of extremely small droplets. Due to small size, the rate of fall is negligible hence get retained in the atmosphere as clouds. Then the precipitation process occurs when the masses of warm, moist air move towards the regions of air.

The other mechanism involved in condensation takes place with the cooling of air masses as they move towards high mountains. In all cases cooling of warm, moist air has been responsible for condensation and precipitation of rain water.

Runoff, stream flow and infiltration:

Out of rainfall on terrestrial area a portion is captured by vegetation. This process is known as *interception*. As there is large surface area, this water readily exposed to wind action and gets evaporated. The remainder of the water falls to the earth and portion of it sinks into the soil surface, by a process is known as *infiltration*. The remaining portion of water (not filtered into soil) is called *surface runoff*, which flows over a surface and gets discharged into streams. The water entering a stream by surface run off plus the water entering via ground water flow is known as *runoff*. The terms '*run off*' and '*surface run off*' are different and distinct.

Surface runoff = precipitation – water lost by interception and infiltration

Runoff, on the other hand has been generally synonymous with stream flow, which is equal to sum of the surface water and ground water that enters the stream.

Evapotranspiration:

A large amount of the precipitated water is converted into vapour by evaporation and / or transpiration. Evaporation refers to the process whereby molecules of liquid water (at the surface of a water body or in moist soil) absorb sufficient energy to leave the liquid state and enter the vapour state. The energy absorbed by the water in this process gets stored within the vapour – hence some what large amount of heat contained in the moist air. Transpiration refers to the process where by terrestrial and emergent aquatic vegetation release a water vapour to the atmosphere. In the process of photosynthesis all plants have been taking in liquid water and carbondioxide and, by a complex series of reactions convert these materials to carbohydrate, oxygen gas and water vapour. Submergent aquatic vegetation also liberates water and oxygen as vapour and will be dissolved into surrounding liquid water. The water vapour may get converted into liquid form where as oxygen remains in water column as dissolved oxygen. In most of the regions water lost by evaporation cannot be measured separately from the water lost by transpiration. Consequently two processes are together called *Evapotranspiration.*

Ground water:

The lengthiest portion of the hydrological cycle would get completed when ground water gets returned to earth’s surface. The return may take place by springs, transpiration, or by artificial means.

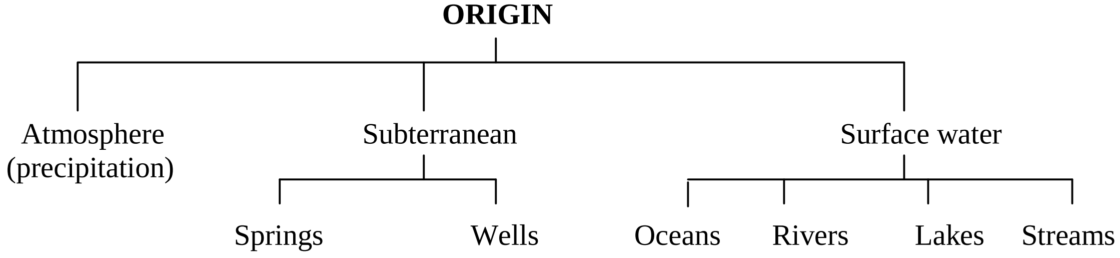
Any natural surface discharge of sufficient water that will flow as a small rivulet is known as a spring, while a smaller discharge is known as surface seepage. Ground water may also be discharged as sub aqueous springs below the surface of lakes, rivers, and marine systems. Three major factors affecting the magnitude of a spring have been the land area accepting the rainfall and thus contributing water to the sub surface system, the permeability of the soil and subsoil, and the quantity of water entering the system (the amount of recharge). The use of water, in the developed areas, prior to recharge has been known to alter the quality and quantity of the water entering the sub- surface system.

CLASSIFICATION OF NATURAL WATERS:

Classification of natural waters is based on different approaches to the problem

1. Origin
2. Amount and character of impurities
3. By virtue of their uses

1. *Classification based on origin is given below:*



2. Amount and character of impurities:

a. Fresh water
b. Salt water
c. Soft water
d. Hard water
e. Clear water
f. Coloured water
g. Colourless water
h. Turbid water
i. Opalescent water.

3. By virtue of their uses:

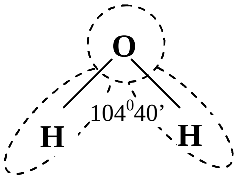
Potable
Domestic
Industrial (in manufacturing textile, paper and leather)
Irrigational
Cooling (cooling of machinery, liquid and gaseous products in condensers and coolers)
Medicinal water

Composition of natural water usually may vary with time; mineral and organic suspended matter gradually settles by gravity, part of the organic matter is consumed as food by living organisms. The chemical and biological processes occurring in natural water destroy the readily oxidisable organic substances by the formation of hydroxides with Fe, Mn, Al, by binding as colloidal mixtures in water by these hydroxides which ultimately affect the composition of natural water. Bulk of organic matter is *humin* (vitamins, fats, proteins, hydrocarbons, organic acids). They occur in natural water but their presence is insignificant with that compared to organic matter.

UNIQUE PROPERTIES OF WATER (OR)

[(UNIQUE CHARACTERISTICS OF WATER SUBSTANCES (OR) PHYSICO CHEMICAL PROPERTIES OF WATER (OR) PHYSICAL CHEMISTRY OF WATER)]

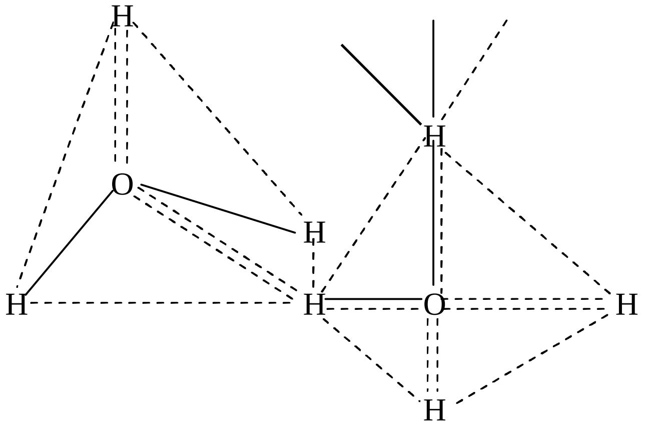
Water substance has a number of abnormal properties that have important ocenographic and meteorological significance. Water possesses unique physical properties compared to H_2S, tellurite and selenite. The indifferent / unusual properties of water are a direct consequence of structure of water and nature of component elements. The gaseous water molecule is angular and bond angle is 104^0 40^1.



The structure of the water molecule and the hydrogen bond

Dotted line indicates the effective sizes of individual atoms. The electrons are distributed unequally in the molecule hence to assign a partial positive charge (+δ) to hydrogen ion and partial negative charge (–δ) to oxygen. Each positive centre (or the hydrogen atom) in a given molecule, hydrogen is attracted to and forms a weak link with negative centre / or oxygen atom. The weak link in hydrogen ions, joins two oxygen atoms is hydrogen bond. The strength of this is about 10% that of a covalent hydrogen – oxygen bond. Water behaves as it does because of consequences of the hydrogen bonding. These include of the following

1. The hydrogen bond causes large irregular aggregates of molecules ultimately in ice, each oxygen is involved in two hydrogen bonds and thus surround with four hydrogen atoms giving a tetrahedral geometry.
2. The bond angle is distorted from $104^0 40^1$ to $109^0 28^1$. Typical of the molecule having tetrahedral geometry and a large open structure results for solid water substance.



Tetrahedral geometry of water showing hydrogen bonds (dotted lines) and covalent bonds (solid lines)

3. Because of extensive aggregation, liquid water substance, behaves as if it were a large molecule than would be expected from the formula H_2O. As a result typical properties of water appear surprisingly abnormal when compared with those of non polar substances such as methane.

Comparison of physical properties of water and methane:

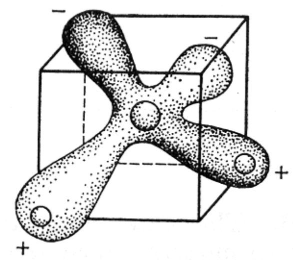
Physical properties	**Water**	**Methane**
Molecular weight	n x 18	16
Melting point	0^0C	-182.5^0C
Heat of fusion	79.63	14.5
Heat capacity (cal / gm / ^{0}C)	1.0	0.5
Boiling point	100^0C	-161.5^0C
Heat of vapourisation (cal / g)	536	122
Electrical conductivity at 18 ^{0}C	4.3×10^{-8} ohm^{-1}cm^{-1}	–
Dielectric constant at 0^0C	88.3	–
Dielectric constant at 18^0C	81.0	–
Thermal conductivity	0.00143 cal cm^{-1} sec^{-1}deg^{-1}	–

For example the boiling point of water is about 100^0C higher than might be expected

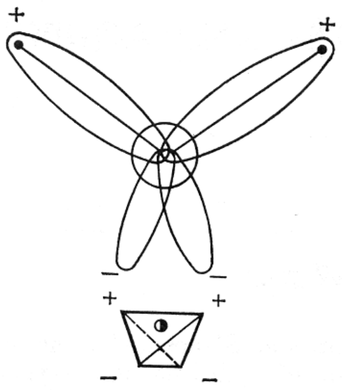
1. If hydrogen bonding suddenly ceases, then ocean vapourize instantly. The heats of fusion and vapourisation are abnormally high which makes water substance useful for refrigeration and air conditioning purposes respectively.
2. Heat of fusion is responsible for the temperature controlling effect during freezing of ice and melting of ice into water.
3. Heat of vapourisation is extremely important in heat and water transfer to and from the atmosphere. The abnormality of many of these properties can be rationalised in terms of extra energy needed to over come the effects of hydrogen bonding.
4. Because of the open structure of ice, ice floats and water has a maximum density above the melting point. As water is heated from 0^0 C to 4^0 C. Its volume does not increase but on the contrary, contracts and water does retain its maximum density not at its freezing point 0^0 C but at 4^0 C, (more accurately at 3.98^0 C).
5. As water is frozen, it expands instead of being contracted as with all other substances and its density decreases.
6. The freezing point of water decreases with increasing pressure (instead of increase as might be expected).
7. The specific heat of water is extraordinarily high compared with that of other substances.
8. Due to high dielectric constant water is a better solvent and dissociating agent than other liquids.
9. Water is characteristic of having highest surface tension than all the liquids, i.e., 75 ergs/cm^2 (glycerol-65, ammonia-42, Hg - 436, others below 30). Surface tension and density are decisive for the height to which a liquid can rise in a capillary system as if filters through a porous obstacle.

Structure of Liquid Water:

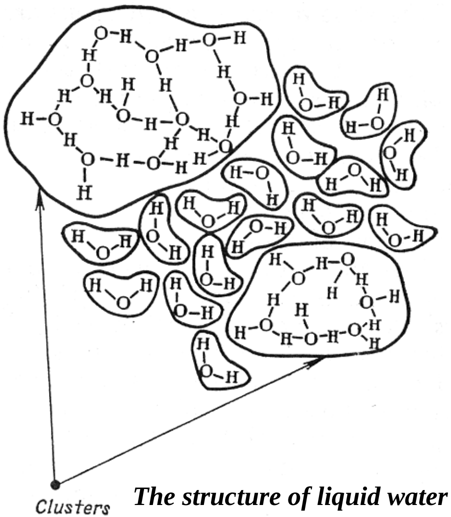
Various models have been proposed to explain the abnormal properties of water in the liquid state. Most of these show liquid water as a crystalline substance. The ordered crystalline (liquid crystals) arrangement of particles in liquid water has been proved experimentally. As ice melts, its lattice is partly disrupted and the voids and the open structures of ice are filled with liberated water molecules. Thus the density of liquid water increases.



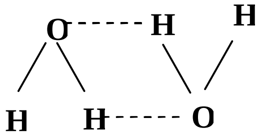
The electron cloud of the water molecule



The electron orbitals of the water molecule



The structure of liquid water in Frank-Wen flickering clusters



The greatest stability is found in this twin molecule $(H_2O)_2$ with two hydrodgen bonds

UNIT 3

HYDROSPHERE - B

Lesson 2

Objectives of the lesson: This lesson deals with composition of sea water and water quality parameters.

COMPOSITION OF SEA WATER:

The seas and oceans might be the products of gigantic acid-base titrations during the early stages of formation of earth. Acids like HCl , H_2SO_4, along with CO_2 which leaked out through volcanoes might have been titrated with bases liberated by the weathering of primary rock. The surface water courses namely ponds, lakes, streams and rivers are not linked with one another like the oceans. Thus they retain their separate chemical entities which are not however, vastly distinct. While in seas / oceans major anionic constituents are carbonates, sulphates and silicates. Chloride is the major species in seawater.

In surface water calcium is the major cation while sodium is the major constituent of seawater. Seawater contains about 2000 times more dissolved salts than fresh water, the average chemicals composition (world mean) of river and lake water is expressed in % weight as follows

Cations	Anions
Calcium – 20.4%	Carbonate – 35.2%
Sodium – 5.8%	Chloride – 5.7%
Magnesium – 3.4%	Sulphate – 12.1%
$(Fe, Al)_2 O_3$ – 2.7%	Silicate – 11.7%
Potassium – 2.1%	Nitrate – 0.9%

Chemically, seawater is a solution of 0.5M NaCl and 0.05M $MgSO_4$ containing traces of all conceivable matter in the universe. The oceans and seas are ultimate sinks for many geo chemical and human activities. The ratio of the major constituents of sea water is almost the same all over the globe although salt content is variable from place to place.

Abundant elements in sea water are

Sodium, Chloride and Magnesium -90%
Potassium, Calcium and Sulphates -3%
Other elements- 7%

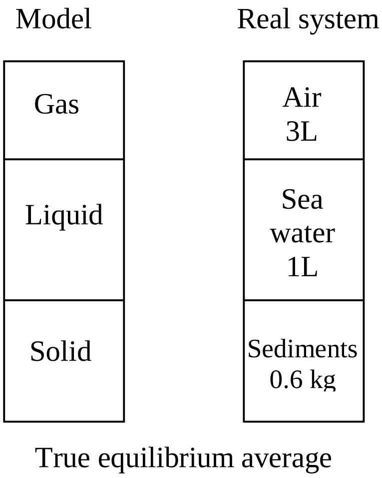
The salt content of sea water in various seas / oceans

Statistical Data of Salt Content:

Baltic Sea - 7.5%
Black Sea - 18.5%
North Sea - 32.8%
Pacific Ocean - 33.36%
Atlantic ocean - 36%
Mediterranean Sea - 39.4%
Red Sea - 43%

Sea water model:

It is an empirical model giving consideration for all the substances that may contribute for seawater. Goldschmidt proposed composition of sea water that for each Kg seas / ocean water 600 grams of primary igneous rock has been decomposed. It is estimated that one litre of seawater is in equilibrium with 0.6Kg of sediment and three litres of air.



Sea water model compared with real system

Preparation:

Start with one litre or 54.9 mole of water, and add the elements as hydroxides or oxides, in order of their abundance. Shake thoroughly after each addition till equilibrium is reached. Then analyze the solid and solution phases. The step - wise additions and reactions are shown below:

1. First add 6.06 mole SiO_2. At equilibrium, the solid phase consists of solid quartz SiO_2, an important constituent of marine sediments. In solution, the species are mainly $Si(OH)_4$ and $SiO(OH)_3^-$ (~ 5%).

2. Next add 1.85M $Al(OH)_3$ to the mixture. At equilibrium two solid phases are formed; quartz, SiO_2 and kaolinite, $Al_2O_5(OH)_4$, while the solution contains species like $Al(OH)_2^+$, $Al(OH)_3$ and polyion which play an important role in the building up of various silicate minerals.

3. Then, 0.55M HCl, 0.76M NaOH, 0.41M KOH, 0.44M MgO and 0.1M CaO are added. This will lead to rearrangement of the solid phase: part of the quartz and all the kaolinite is rearranged to

aluminosilicates with a charged aluminosilicate frame work in which Mg replaces some Al, and Na^+, K^+, Ca^{2+}, Mg^{2+} may enter the holes of the frame work. The resulting mica group of clay minerals ex. phillipste, (M^1Si, $M^{11}Al$) Si_2O_3 (H_2O) where M^1 = Na or K, M^{11} = Ca or Ba and gluconite dominate the marine sediments. The solution contains Cl^- and cations which take part in the ion exchange equilibrium between the solution and silicate phases.

$$3Al_2Si_2O_5(OH)_4(S) + 4SiO_2(S) + 2K^+ + 2Ca^{2+} + 9H_2O \rightleftharpoons 2KCaAl_3Si_5O_{16}(H_2O)_6(S) + 6H^+$$

Moreover, there will be ionexchange equilibria between the solution and each separate phase. Such ion exchange equilibria remain the main buffering factor in the sea. It is experimentally observed that K^+ is bound more strongly than Na^+ to layer silicate.

$$(Na / K)_{solid} = 10^{-0.14} ; \qquad (Na / K)_{solution} = 10^{-0.67}$$

Similarly Ca^{2+} is bound more strongly than Mg^{2+} so that the concentrations of Na^+ and Mg^{2+} will exceed those of Ca^{2+} and K^+ in seawater.

4. In fourth stage add 0.46M $CaCO_3$ and 0.09M $MgCO_3$. At equilibrium the fresh solid phases consists of 0.09M dolomite, $MgCa(CO_3)_2$ and 0.37M calcite, $CaCO_3$. Some $MgCO_3$ would go into solid solution in the calacite phase.

5. The next constituent to be added is 0.027mole oxygen, which remains mainly in the gas phase. In water, dissolved oxygen is in the order of 0.002M which is responsible for maintaining the oxidation potential, expressed as pE.

$$\tfrac{1}{2} O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O \quad \log K = 41.55$$

$$pE = 12.5$$

6. In the next step, 0.55M Fe is added as FeOOH to the mixture. At equilibrium, some Fe will react with the silicate phases but considerable part remains as FeOOH. The amount of the silicate phases may increase and they contain Fe^{3+} in Al^{3+} positions and probably some Fe^{2+} in Mg^{2+} positions. The average concentration of the dissolved $Fe(OH)_2^+$ in sea water is $10^{-7.2}$ M.

7. The next addition to the equilibrium mixture is 0.06M TiO_2. At equilibrium, some Ti enters the silicate phase by substitution, and the rest remain as rutile, TiO_2 in the solid phase. The Ti species in the solid water is probably $Ti(OH)_4$ ($\sim 10^{-6.7}$ M).

8. Addition of 0.03 M HF in the next step leads to rearrangement of silicate phases through substitution of the O^{2-} or OH^- group by F, probably some CaF_2, fluorspar, may also precipitate.

9. 0.03M H_2SO_4 added in the next stage will permit large amount ions in the solution and cause some rearrangement in the silicate phase. Equilibrium pH remains unaffected due to the presence of a large bulk of silicates. The sulphates, found in some marine sediment are probably adsorbed to the phases already mentioned. The seawater presumably contains some complexes with divalent metal ions.

10. Phosphate is added as 0.02M phosphoric acid or Na_2HPO_4. This leads to some rearrangement in silicate phases. The only stable solid phosphate phase is presumably hydroxyapatite, $Ca_5(PO_4)_3OH$. Phosphate ions are also adsorbed on FeOOH and, to some extent, on the silicate phase. The total phosphorous concentration found in the sea water is about $10^{-5.5}$ to 10^{-6} M.

11. The last addition of the major elements is 0.01M Mn as MnO_2. The stable Mn solid phase is MnO_2 and dissolved species are Mn^{2+}, MnO_4^- in trace concentrations. (10^{-7} to 10^{-8}M).

12. In equilibrium mixture there is about 0.1M N_2 in the air. This is a case of non equilibrium since N_2 is chemically inert and the impact of lightening to form NO_2^- and NO_3^- is counter balanced by biological activities in seas / ocean water.

13. After addition of major constituents in the above order next we have to add minor element in one lot, as hydroxides, oxides, or chlorides (Li, B, V, Cr, Zn, Rb, Sr, Zr, Ba, Be, Co, Ni, Cu, Ga, Br, Y, Sn, Ce, Se, Ge, Mo, As, Cs, Th, Sb, I, W, Hg, Ag, Cd, Bi, Au, Pa and La). At pH of seawater, hydroxide complexing is important for all ions having charge greater than 2. The chloride complexing competes with the hydroxide. Besides these, sulphate and carbonate complexes exist for several cations. Finally, organic compounds (10^{-4} to 10^{-5}M) also form complexes with metal ions, also at trace levels. Some anion redox equilibria are significant in sea water examples are ClO_3^- / Cl^-, IO_3^- / I^- , BrO_3^- / Br^-

Thus the above seawater model gives useful information about solid phases and species in solution in sea / ocean water.

WATER QUALITY PARAMETERS:

Drinking Water:

It should be harmless to man and it must have organoleptic properties. It should fit for domestic use.

Toxic chemicals in water: The following are the allowed concentrations of chemicals in water.

Berylium and Selenium	0.01-0.07 mg / lit
Molybdenum and Fluorine	0.05 - 0.7 mg / lit
Arsenic	0.05 mg / lit
Lead	0.1mg / lit
Polyaryl amine	2mg / lit
Nitrates	10mg / lit

Organo leptic Characteristics:

They lead to odour, smack, colour and turbidity. pH of water 6.8 – 8.5, water should be colourless, odourless and tasteless.

Dissolved oxygen	4 – 6ppm
Fluoride	1.5ppm
pH	6 – 8.5
Chemical oxygen demand	4.0
Biological oxygen demand	1ppm

Bacteriological parameters:

Total amount of bacteria in 1ml of non diluted water should not exceed 100.
Coliform cells / 100ml – 100 in numbers
Total bacterial cell count / 100ml - 1 x 10^6

Radioactivity

Grossbeta 1000 pica curies / L - 10^{-12}

Surface Water:

The permissible limits for the surface water will be 3 – 5 times more / higher than the domestic. The general requirements for recreation, aesthetics, swimming, navigation, aquatic life, fish, wild life are as follows

Recreation and aesthetic:

Surface water should be free from

1. Materials which impart colour, taste, and turbidity (ex: phenols, oils, grease).
2. Substances tend to form objectionable deposits or float on the surface debris, oil, and scum.
3. Toxic substances including radio nuclides, physiologically harmful to man, fish and other aquatic plants and animals.
4. Substances which are likely to result in promoting growth of the undesirable aquatic life.

Aquatic Life, Fish and Wild life:

The general surface water should be free from

1. Settleable matter which limits the growth of flora and biota.
2. Floating matter like oil and grease which form colour films on the surface, which coats banks and the bottoms of the water courses, taints aquatic biota and causes toxic effects to fish and man.
3. Temperature should not be raised by 3^0 - 5^0 by hot sewage water.
4. pH 6.5 to 8.5.
5. D.O.: 4 to 6 ppm.

Irrigational Water:

Salinity or total dissolved solids is the most important parameter for the irrigation, since it controls the availability of water to plants through osmotic pressure (regulatory mechanism). It should not contain salts greater than 1.5g / L. Excess salts are determinate to crops. Large quantities of Na^+ are especially harmful to plants.

Cooling Water:

Untreated natural water is normally used for cooling purposes. The requirements for cooling water are

1. As low temperature as possible.
2. The lowest possible temporary hardness.
3. Least possible suspended matter particularly of organic origin.
4. Insignificant permanent hardness.
5. It should not corrode the equipment.

Water for Boilers:

It should have

1. Lowest possible total hardness and permanent hardness.
2. The lowest possible silicic acid content.
3. It should not contain dissolved gases like carbondioxide and hydrogen.

Technical Water:

The requirement depends on purpose for which it is being used

1. For cinema film and textile paper - it should be free from Fe, Mn and silicic acid.

Manufacture of man made fibres:

It should not contain more than 2 mg /L of oxygen for its oxidation.

It should be soft; its iron content should not exceed 0.03 mg / L.

Silk and Drying Industries:

It should be totally free from Fe, not even in traces and organic matter.

Tannery:

Water should be soft water free from putrefaction bacteria and fungi as they impair the strength of the tanned leather.

Manufacture of strach:

Foliage water weeds should be absent.

WATER QUALITY PARAMETERS AND STANDARDS:

The parameters for water quality characterisation are listed in the table below. The permissible limits are laid down by the United States Public Health, Drinking Water standards (USPH) and Indian Standard Institution (ISI) are listed for comparison these refer to domestic water supplies for drinking water.

Parameters	USPH standards	ISI standards
Colour	colourless	-
Odour	odourLess	-
Taste	tasteless	-

Parameters	USPH standards	ISI standards
Inorganic chemicals		
pH	6 – 8.5	6.0 – 9.0
Specific conductance		300 μmho / cm
Dissolved oxygen	4-6ppm	3ppm
Total dissolved solid	500	-
Suspended solid	5.0	-
Chloride	250	600
Sulphate	250	1000
Cyanide	0.05	0.01
Nitrate and nitrite	<10	-
Fluoride	1.5	3
Phosphate	0.1	-
Sulphide	0.1μg /L (ppb)	-
Ammonia	0.5	-
Boran	1	-
Phenol	0.01	-

UNIT 3

WATER POLLUTION - A

Lesson 3

Objectives of the lesson: This lesson deals with study of types of water pollution besides effects of domestic and agricultural pollutants.

TYPES OF WATER POLLUTION:

Domestic water pollution:

It includes wastewater from homes and commercial establishments. Domestic wastewater arises from many small sources spread over fairly wide area that is through residential and commercial cleaning operations, laundry, food preparation, body cleaning functions and body excretions.

The composition of domestic waste water is relatively constant when compared to industrial wastewater and all these things are transmitted by sewage to municipal waste treatment plants. Some impurities in domestic waste gets diluted and generally to the 0.1% of total mass. This is generally organic in nature and gets oxidised by bacteria decomposition to nitrate, phosphate, carbondioxide. As the decomposition needs dissolved oxygen it depletes oxygen which in turn as an indicator for BOD.

Industrial wastewater pollution:

It occurs only at specific locations and hence collection and treatment is sparingly simple. There are water using factories which discharge waste with a total BOD load about 3–4 times greater than the sewered population.

Textile manufacturing units:

Waste from textile manufacturing processes will be from washing out of the impurities in fibres, as well as in the discarding chemicals used in processing of fibres. Generally these wastes are organic, having a high BOD and extremely alkaline.

Food processing:

Food processing wastes from meat, dairy and sugar-beat processing as well as brewing, distilling and canning operations, generate large amount of organic byproducts that are disposed in wastewater. When wastewater is discarded, along with these byproducts it leads to high BOD and consequent oxygen depletion in the receiving water.

Pulp and paper industries:

The effluent released from pulp and paper processing operations has been a mixture of chemicals which would be used in the digestion of raw wood chips, cellulose fibres and dissolved lignin. The wastewater also includes paper and wood preservatives like penta chloro phenol and sodium penta chloro phenate as well as methyl mercapton, all of which are toxic to fish. The effluent is generally brownish in colour and lowers the photo synthetic rate of aquatic communities by hindering the sunlight penetration into the water column. As a consequence there is increase in BOD of the receiving water while colour imparted to the water interferes with sunlight penetration reduces photosynthesis and hence further depletion of oxygen levels.

Steel mills:

The water is contaminated in coking of coal and pickling of steel and washing of flue gases from blast furnace. After use they tend to be acidic having deleterious substances like phenol, cyanogen, ore, coke and fine suspended solids. Other industries release traces of metals produced or plated in their wastewater. Metals commonly found in this wastewater have been chromium, mercury, nickel, lead, copper and cadmium.

A variety of contaminants enter marine and fresh water environment in the effluents released from the various chemicals manufacturing plants. The release of acids results not only from acid manufacturing processes but from practically all other chemical manufacturing processes as well.

Most of the Indian rivers and fresh water streams are seriously polluted by industrial wastes or effluents which come along waste waters of different industries such as petro-chemical complexes; fertilizer factories; oil refineries; pulp, paper textile, sugar and steel mills, tanneries, distilleries, coal washeries etc.

Agricultural water pollution:

They include sediments, fertilizers and farm animal waste. They can enter water ways as run off from agricultural lands and farm animal waste are from the large feedlots.

Agricultural waste include pesticides that are sprayed on crops, as well as sediments, fertilizers and plants and animal debris which are carried into water ways through runoff during rainfall. Inorganic fertilizers, being plant nutrients lead to over fertilization of the wastewater ways the addition of excess plant nutrients may lead to a disturbance of phosphorous and nitrogen balance. When plants die they settle to the bottom and since they are organic, in turn there will be increase in BOD during decomposition. Soil erosion posses four fold problem. It increases a normal rate of filling of water ways into which it washes, decreases the amount of fertile land for crop production, carries pesticide coated soil particles into the water, and decreases the transparency of the water which limits photosynthesis. In addition the sediment carried in to fresh water system tends to clog the gills of the fish and settles out over incubating eggs causing suffocation.

A large number of pesticides have come into wide spread use in recent years. They are not only non biodegradable but also sparingly soluble in water. Hence when sprayed they remain in soil for longer periods, they tend to be carried by a runoff as suspended particles through rainfall into surface, marine or ground water system. In surface, fresh and ground water systems. They may also enter the drinking water supplies of various communities.

Solid waste system pollution:

It varies with the socio economic status of the generating community.

a) Garbage, which include all decomposable waste from household as well as from food, canning, freezing, and meat processing operations.

b) Rubbish includes non-decomposable waste they may be combustible or non combustible. The combustible materials include garden waste, cloth and paper where as non combustible materials include masonry stationary, chemicals.

c) Sewage sludge is generated from settling process from primary, secondary and tertiary methods as well as solid from cesspools which must be removed periodically.

d) Miscellaneous materials include industrial waste by chemicals, plants and explosives as well as mining wastes, such as slag heaps and mine tailings.

The majority of wastes classified as combustible –rubbish, garbage and sewage sludge – has been disposed off by one of the three major methods: incineration, using it as landfill, or disposal by ocean dumping. Incineration generally leads to air pollution, land fill operations and ocean dumping leads to water contamination. If land fill disposal is used the material as it decomposes will dissolves in or become suspended in the rain water percolating into the ground water and then into subsurface aquifers. This tends to contaminate not only ground water but also surface water. Because of its highly organic nature they help in increase of BOD in the receiving water and the sediment becomes coated with highly organic ooze. Non combustible materials are generally disposed of in land fill site or by ocean dumping.

Thermal pollution:

Thermal pollution takes place because of many electric generating companies use water in the process of cooling their generators. This heated water is then released into the system from which it was drawn, causing a warming trend of the surface water. Thermal pollution results when the heated effluent released into poorly flushed systems. In these cases permanent temperature increase often result, which tend to decrease the solubility of dissolved oxygen. In lakes it also becomes possible to bring about nutrient redistributions and prolong summer stagnation periods.

Increase in water temperature decreases the oxygen saturation, percentage and at the same time accelerates the depletion of DO levels. The DO levels fall rapidly due to normal biological functions in the lower layers and may lead to anaerobic conditions. In addition to the low DO levels metabolic activity of micro organisms increases with temperature at a rate of double for every 10^0C rise in temperature. Thus an increase in temperature produces simultaneously a decrease in the availability in oxygen and an increase in the rate at which it is consumed.

When heated water gets released into the large well flushed marine systems where there is a little if any permanent temperature rises. There are, however, problems related to the operation of plants utilising marine waters in the cooling process. Evidence reveals that seawater tends to corrode the cooling pipes, which are generally constructed of a copper nickel alloy termed Monel. These metals readily dissolve in the heated seawater and are then released into the marine environment together with the heated effluent.

An increase in temperature also increases the toxicity of some chemical pollutants and therefore more toxic in summer months.

Shipping water pollution:

It includes both human sewage and other wastes, the most important of which has been oil.

Oil pollution results from accidents involving oil tankers and from spills at offshore oil drilling sites. A more persistent source of oil pollution results from the practice of oil tankers, after they deliver the oil, to fill the empty tanks with sea water to act as ballast for the return trip. Prior to docking, the seawater ballast, contaminated with the oil that remains in the tank is discharged. Although this practice is illegal, it is difficult to prevent. The alternative is to pump the contaminated seawater into tanks at port. This is not only inconvenient but also uneconomical. In addition, there will remain the problem of disposal when the disposal tanks are full.

Radioactive waste pollution:

Very little is known about the threshold of the radiation damage to aquatic environments from wastes of uranium and thorium, mining and refining from nuclear power plants and from industrial use of radio active materials. Radium is the most significant waste product and is considered to be hazard in drinking water. Sr^{90} which emanates from testing of nuclear weapons accumulating in bones and teeth and cause serious disorder in human beings. The maximum permissible levels per litre are Ra^{226} - 3 pica curies, Sr^{90} 10 pica curies.

Certain marine organisms have capacity to accumulate radioactive nuclides from water. This biomagnifications may cause objectionable radioactivity in living organisms although radiation level in water may be low enough to be considered safe. Phyto plankton to fish may concentrate metal radionuclides by factors of $10^2 – 10^5$. Radioactive substances can enter human along with food and water and gets accumulated in blood and certain organs like thyroid gland, liver and bone and muscular tissues. At present some low and medium level radio active wastes are sealed in containers and dumped into ocean as disposed mechanism. If there is any damage to this leading to leakage from the containers the nuclear waste could escape and enter the marine system. Then streams and ocean currents and eventually reach coastal water could circulate them.

EFFECT OF SOAPS, DETERGENTS, PESTICIDES, HYDROCARBONS WITH REGARD TO WATER POLLUTION

Soaps, detergents and pesticides are grouped under synthetic organic chemicals or compounds. In contrast to organic waste, they are not biodegradable and may persist for longer periods. They are of great concern in the present context because most of the synthetic organic compounds are accumulative toxic poisons.

Effect of soaps and detergents:

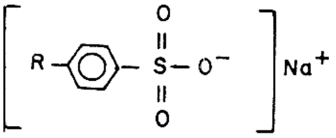
Soaps and detergents are having similar structure and their mechanism of cleansing actions is similar. Both are having a hydrophobic portion (usually a long hydro carbon chain) to which a hydrophilic (polar group) is attached. Such materials are surface active that is they concentrate on the surface of the aqueous solution. This decreases the surface tension of water so that it penetrates the surface and interstices of the object being cleaned.

Laundry detergents constitute a waste which is another potential organic contaminant. They are two components. Surfactants and builders and out of these surfactants become a problem as it is very difficult in breaking down the bacterial action besides having a long residence time. Most of the detergents will be using sodium tripoly phosphate as builders, which ultimately promotes eutrophication because of its nutritional value.

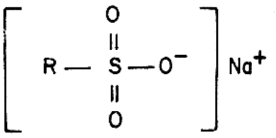
The basic active ingredient is the surfactant or surface-active agent besides a builder. It lowers the surface tension and allows dirt particles to become linked to water. The dirt is subsequently lifted or floated from the soiled garment during washing process. The builders added to detergents complex with Ca^{2+} or Mg^{2+} are reactive towards water to form alkaline solution which provides optimum medium for the function of surfactants. Both the surfactants and builders of detergents cause water pollution problem.

The typical surfactants and Builders

Anionic Surfactants:



Alkyl benzene Sulphonate (ABS)

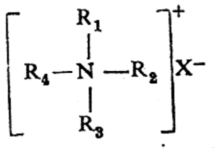


$$\left[R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-\right]Na^+$$

Linear alkyl Sulphonate (LAS)

R = Hydrocarbon chain with 12-19 carbons

Cationic Surfactants:

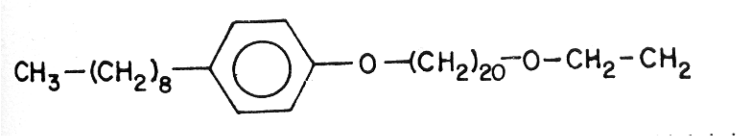


$$\left[R_4-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{N}}-R_2\right]^+X^-$$

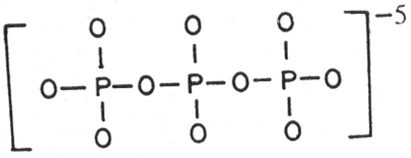
Quaternary ammonium salt

R_1, R_2, R_3 are short hydrocarbon chains and R_4 is aromatic;
X= halogen or acid group

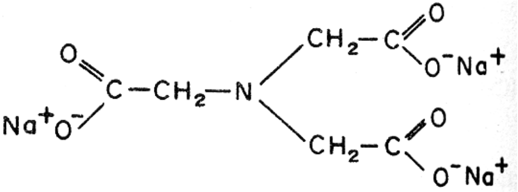
Non ionic Surfactants:



Builders:



These hydrolysis products do not pose any threat to aquatic animal life. However eutrophication by excessive growth in ponds is another problem since phosphate act as a nutrient for plants.



It is relatively biodegradable and relatively cheap. But it is hygroscopic and converts to cake in open package.

Eutrophication:

Eutrophication means well nourished. When sewage and agricultural run-off containing phosphates or other nutrients enter natural water bodies, they cause over nutrition, leading to the process of *eutrophication*. It provides nutrients for a water body which supports aquatic life. A lake starts its life cycle as oligotrophic i.e., a clear body of water. With the introduction of nutrients through land run-off and growth and decay of aquatic life, the lake collects a good amount of organic substances. Eventually there is algal bloom when the lake becomes marsh and debris. Thus the lake is filled with sediments while aquatic animal life will perish. It will then turn into dry land.

Generally the most likely plant nutrient is phosphorus, and it has been generally named as the culprit in excessive eutrophication. Household detergents constitute a common source of phosphate in wastewater, and eutrophication control has to be concentrated upon eliminating phosphates from detergents, removing phosphate at the sewage treatment plant, from entering bodies of water. In some cases nitrogen or even carbon constitute limiting nutrients. Particularly in sea water nitrogen may be a limiting nutrient.

The rate of eutrophication strikes a balance between the production of aquatic life and its destruction by bacterial decomposition. With large inputs of nutrients from human sources, bacterial decomposition cannot keep pace with productivity and sedimentation is accelerated whereby eutrophication is favoured. Lakes can be protected from eutrophication only by providing measures for sewage treatment and preventing the sewage from entering the water bodies.

Effect of pesticide with regard to water pollution:

Pesticides come under synthetic organic chemicals in contrast to the organic waste they are not biodegradable and may persist for longer periods. They are of great concern in the present context because most of the synthetic organic compounds are accumulative toxic poisons.

Pesticides can be classified into three types

1. Insecticides
2. Herbicides
3. Fungicides

Others include rodenticides (pesticides to kill rats, mice and bears), molluscides (to kill invertebrate animals like snails, squids etc.,) and acaricides (to kill ticks and mites).

Sources:

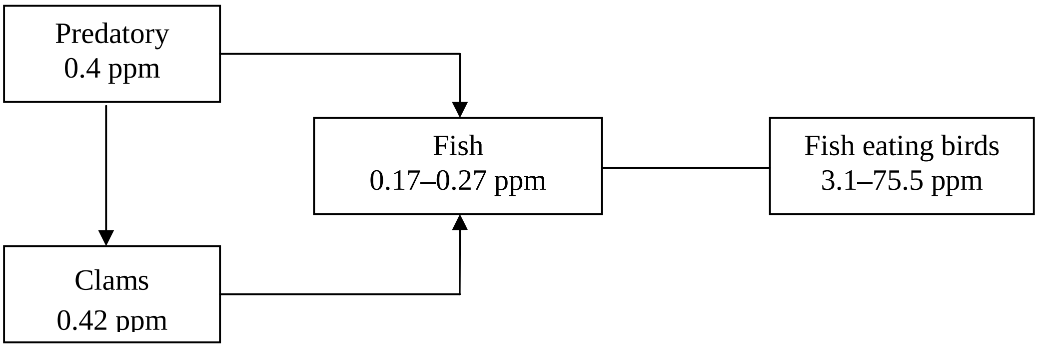
Pollution from pesticides result primarily from surface runoff from agricultural lands, waste discharged by pesticides manufacturing units. Because of their worldwide usage nearly all the rivers and oceans of the world contain pesticides residues.

Four major structural classes are:

1. Chlorinated hydrocarbons
2. Organo phosphates
3. Carbomates
4. Chlorophenoxy acids

Among them 1,2 and 3 serve mainly as insecticides and 4 as herbicides. The chlorinated organo pesticides like dichloro diphenyl trichloro ethane (DDT), dieldrine, aldrine are hazardous mainly due to their concentration in food chain. They have high stability, low vapour pressure, very low solubility in water but have substantial solubility in oils and fats.

For example, the concentration of DDT in fresh water is 0.00001ppm but is being amplified by biological magnification. Typical food chain for the amplification of concentration of DDT is shown below:

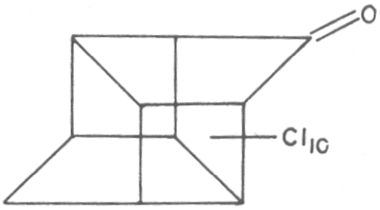


Accumulation of DDT in aquatic food chain (in ppm)

Several water pollution and health problems have been associated with the manufacture of pesticides.

Kepone Case:

A serious disaster occurred in mid 1970 in Hope Well, Virginia USA, during production of kepone. kepone is used for the control of tobacco wire worm, ants and cockroaches. It shows cumulative toxicity to birds, rodents, humans and also causes cancer to rodents. Every year 50,000Kg of kepone was dumped into sewage system, which was ultimately discharged into Chesapeake Bay. Fish and shellfish in the river and estuary showed 1ppm which was above the permissible limit. Workers in plant also suffered from various diseases (inhaled upto 3g / m^3 of kepone).



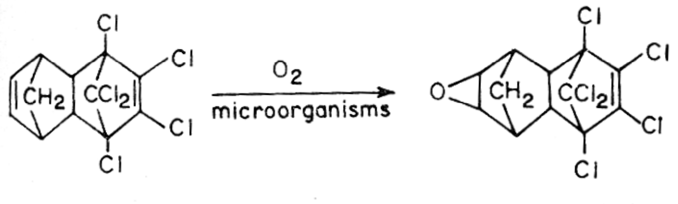
Persistent pesticides:

Pesticides are found wide spread in various parts of the environment. Their impact on the environment is based on their properties.

1. Tendency to vapourise
2. Tendency to dissolve in water and other solvents
3. Resistant to various degradation processes

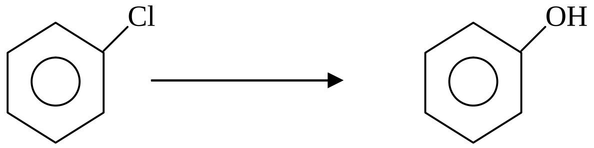
Biodegradation of Pesticides:

1. The biodegradability varies from pesticide to pesticide aldrin undergoes oxidation to dieldrin (epoxide form)



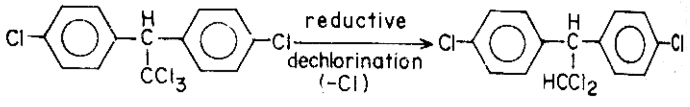
Aldrin Dieldrin

2. Oxidation may also occur by introduction OH groups in aromatic rings.



Chloro benzene Phenol

3. It may be noted that the degradation intermediates be more toxic to some microorganisms than are the original pesticides. Thus DDD is more toxic than DDT.



DDT TDE (DDD)

Hydrocarbons:

Hydrocarbons (like benzene, toluene, xylene etc.,) have in general narcotic effect on human beings. Butadiene isoprene affects bone marrow. Benzene causes respiratory disorder and narcosis. It causes blood dyscrasia and blood anemia. Toluene in comparison to benzene is less toxic. It causes lymphocytosis. It has bad effect, if the dose exceeds 200 ppm. It causes drowsiness, mild headache, and impaired coordination. Fortunately, it cannot penetrate through the skin. It is usually excreted through urine as hippuric acid. Amongst aromatic hydrocarbons, xylene has least toxicity. A high dose can produce liver and kidney damage and hyperplasia of bone marrow. It is a narcotic.

Carbon tetrachloride is harmful, as it has depressing action on central nervous system, it causes gastrointestinal disturbance and causes liver, kidney and lungs problems. It causes loss of appetite, vomiting. Certain of the compounds which are used as refrigerants may cause cardiac and pulmonary problems.

UNIT
3

WATER POLLUTION - B

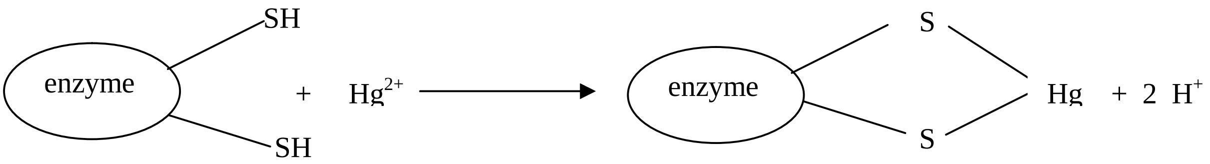
Lesson
4

Objectives of the lesson: This lesson deals with effect of specific pollutants like mercury, lead, arsenic, selenium, nitrates and oil

EFFECTS OF SPECIFIC POLLUTANTS

Interferences of toxic metals with biochemical processes:

Toxic metals attack the active sites of enzymes, inhibiting essential enzyme functions. Heavy metal ions such as Pb^{2+}, Hg^{2+}, Cd^{2+} act as enzyme inhibitors. They attract –SH, $-SCH_3$ in methionine and cysteine amino acids, which are part of the enzyme structures:



Heavy metal ion can replace the light metal ion of similar charge and size from metallo enzymes and inhibit its normal activity or induce toxicity. Thus Cd^{2+} can replace Zn^{2+} and can lead to cadmium toxicity. Cadmium (Cd^{2+}) can inhibit the activity of enzyme such as amylase, carbonic anhydrase, ATP(adenosine tri phosphate), alcohol dehydrogenase and carboxylic peptidase. Pb^{2+} can inhibit the activity of enzymes like carbonic anhydrase, cytochrome oxidase, alkaline phosphotase, ATP and some important enzymes in the synthesis of haeme.

MERCURY:

Introduction:

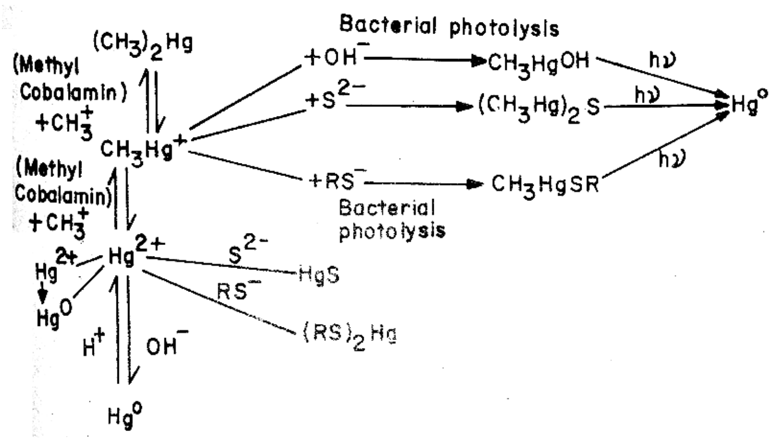
Mercury is a non-essential trace metal constituting 0.00003% by weight of the earth's crust. It is extracted mainly from its sulfide ore, cinnabar (HgS). Mercury, both in the metallic form (quick silver) and as the sulphide (HgS) played prominent role in therapeutics, alchemy and folklore. Mercury chloride or calomel enjoyed popularity as a laxative. Mercuric oxide, salicylate and chloride salts were used as antiseptics. Red mercuric sulfide, mercuric benzoate, mercurous acetate and mercurous iodide were used for treating syphillis. Organic mercurials such as metaphen and mercurochrome exert a weak bacteristatic action and are used as local antiseptics. Mercury is still used as diuretic to a limited extent. Mercury is now mostly used as filling material for dental cavities as silver amalgam. Mercury was used in the past in felt-hat manufacture and for processing but its use for this purpose is minimal.

Environmental levels:

Information regarding environmental levels of mercury came only after the discovery of flameless atomic absorption analysis technique. On the basis of mean concentrations of mercury in cereals, vegetables, pulses, milk, and fish, the average intake of mercury through the normal diet of adult is estimated to be 7.3 µg /day. The mean mercury concentration in water varies from 2µg to 33µg / L. The US EPA limit of mercury in drinking water is 2µg / L.

Fate of mercury in the environment:

Extensive research has been carried out on the aquatic chemistry of mercury and its biotransformation, toxicity to biota and its monitoring and analysis techniques. The fate of 'Hg' in environment is described as follows



Environmental chemistry of mercury

Biochemical effects of Mercury:

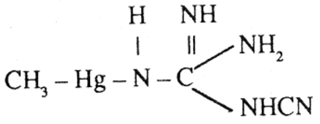
Mercury enters into the environment mainly though human activities. The sources of entry of mercury into the environment apart from natural sources are

1. Chlor alkali industries
2. Production of electrical apparatus like mercury batteries, mercury vapour lamps etc.
3. Agricultural industry through fungicides for seed dressing.

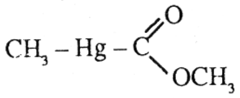
The typical components of mercury that are used in seed dressing are

$CH_3 - Hg - C \equiv N$

Methylmercurynitrile



Methylmercurydicyandiamide



Methylmercuryacetate

$C_2H_5 - Hg - Cl$

Ethylmercurychloride

Toxicity:

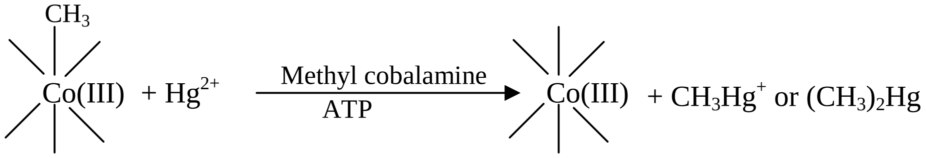
The toxicity of mercury depends on its chemical species as shown in the following table.

Chemical Species of Mercury	Chemical and bio chemical properties
Elemental mercury (Hg)	Relatively inert and non toxic, vapour is highly toxic when inhaled.
Mercurous ion (Hg_2^{2+})	Insoluble as chloride and low toxicity
Mercuric ion (Hg^{2+})	Toxic but not easily transported across biological membranes
Organo mercurials (RHg^+)	Highly toxic, particularly CH_3Hg+ (methyl mercury) causes irreversible nerve and brain damage and easily transported across biological membranes, stored in fat tissues.
Diorgano mercurials (R_2Hg)	Low toxicity but are converted to RHg+ in acidic medium.
Mercuric sulphide (Hg S)	Highly insoluble and non toxic, trapped in soils in this form.

Elementary mercury is fairly inert and non-toxic, if swallowed it is excreted with out serious damage. Due to its high vapour pressure, the vapour if inhaled it enters brain through blood stream leading to severe damage of central nervous system (CNS). The most toxic species of mercury are the organo mercurials particularly mono methyl mercury CH_3Hg^+ which is soluble in fat, the lipid fraction of membranes and brain tissue.

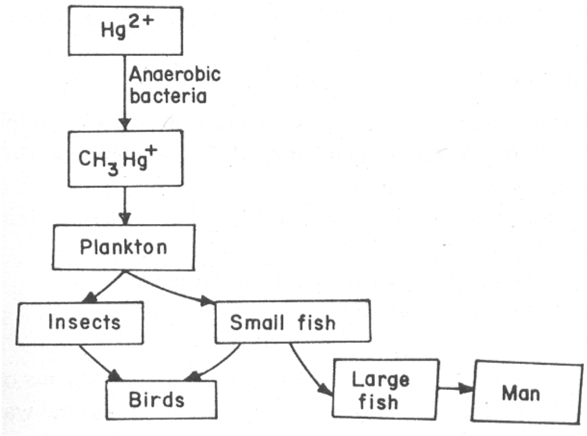
Species of mercury in food chain and propagation of Hg:

In Minimata, incident mercury was discharged in Minamata Bay which was swallowed by fish Monomethyl mercury (CH_3Hg^+) is the species found in the fish and subsequent research revealed that mercury or its salt can be converted to methyl mercury by anaerobic methane synthesising bacteria in water.

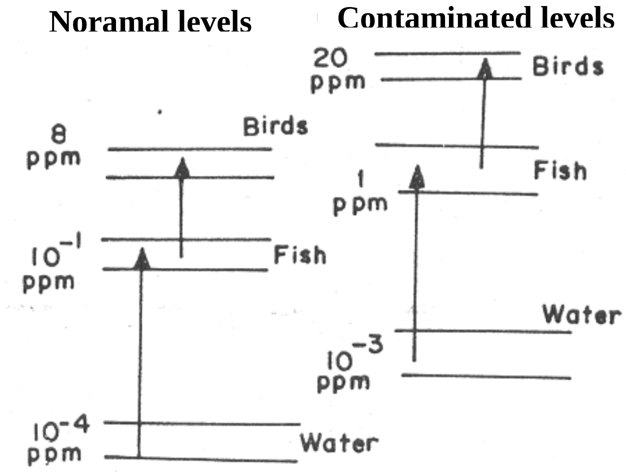


$$CH_3\text{-}Co(III) + Hg^{2+} \xrightarrow[\text{ATP}]{\text{Methyl cobalamine}} Co(III) + CH_3Hg^+ \text{ or } (CH_3)_2Hg$$

An acidic medium promotes the conversion of dimethyl mercury to methyl mercury which is soluble in water and thus enters the food chain through plankton and is concentrated in fish by a factor of 10^3 or more as it passes up through food chain as shown below.



Mechanism of propagation



Propagation of mercury in food chain

LEAD:

Effect of specific pollutants - Lead :

Lead is a relative abundant metal in nature, occurring in lead minerals. In the atmosphere it is relatively more abundant than other heavy metals. The main source of surplus lead in the environment originating from anthropogenic activities like combustion of gases of petroleum products and gasoline and hence its concentration is relatively more in atmosphere and thus enters the water and plant life and finally food chain.

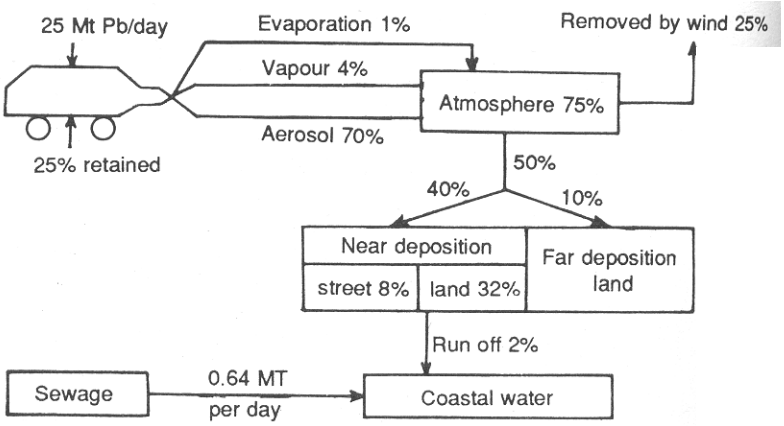
Pathways of lead in environment:

A survey with regard to fate of lead contributed from automobile fleet in Los Angles basin, USA in the environment reveals that out of about 25 MT lead input over day. 25% is retained in car body and 75% goes to the atmosphere and out of which 1% is lost by evaporation, through vapour 4%, and aerosol 70%.

From the atmosphere 25% of lead is removed by wind and 50% is gradually deposited on land from which it is partly washed in to coastal waters (2%). Input of lead from sewage is 0.64MT / day.

Organo lead compounds are more toxic than inorganic lead salts. Commercially five *tetra alkyl lead compounds* (TAL) are important, they are

1. Tetra methyl lead (TML)
2. Tri methyl lead (TMEL)
3. Di methyl di ethyl lead (DMEL)
4. Methyl tri ethyl lead (MTEL)
5. Tetra ethyl lead (TEL)



Pathways of lead in environment

Most organic lead enters into atmosphere during the process of making gasoline into leaded gasoline and use in vehicles. There are also indications of natural methylation of inorganic lead in the environment. The ionic alkyl lead compounds are considered as highly toxic to mammals. TAL (Tetra alkyl lead) compounds in the environment decompose to form highly soluble ionic alkyl lead. The degradation appears to follow the path way

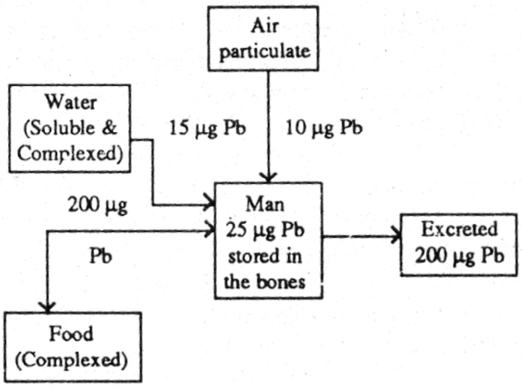
$PbR_4 \rightarrow PbR_3^+ \rightarrow PbR_2^{2+} \rightarrow PbR^{3+} \rightarrow Pb^{+2}$ where R is the alkyl group.

Flow chart of Lead balance in Human body:

The lead in gasoline is discharged as lead halides through exhaust system. It may be noted that most of the Pb intake by a typical city dweller is from diet (about 200–300 µg / day) air and water added a further 10–15 µg / day, of the total intake 200µg is excreted and 25µg is stored in bones each day.

$$Pb(C_2H_5)_4 + O_2 \xrightarrow{\text{halogenated scavengers}} PbCl_2 + PbBr_2 + PbBrCl + CO_2 + H_2O$$

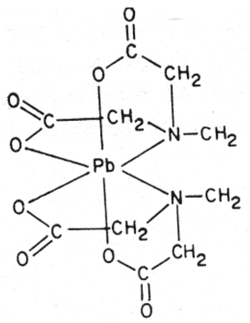
The halogenated scavengers are dichloroethane and dibromoethane.



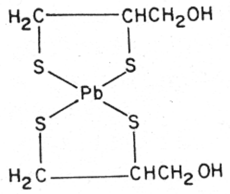
Daily lead balance for a city resident

Biochemical effects of lead:

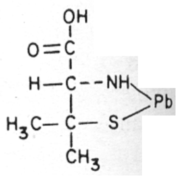
Lead interferes with haeme synthesis, which leads to haematological damage. Thus lead also does not permit the utilisation of oxygen and glucose. At higher levels of lead in the blood, symptoms of anaemia appear due to haemoglobin deficiency and other effects are disfunction of kidney and finally brain damage. Due to chemical analogy of Pb^{2+} and Ca^{2+} bones act as repositories of lead in the body. How ever the Pb poisoning can be cured with chelating agents, which strongly bind with Pb^{2+}. For this calcium chelate in solution is fed to victim of Pb poisoning. Pb^{2+} displaces Ca^{2+} from chelate resulting in Pb – chelate formation which is rapidly excreted in urine. The typical lead chelates are



Pb-EDTA chelate



Pb-BAL chelate
(BAL=2, 3-dimercaptopropanol)
BAL, abbrev of British anti-lewisite



Pb-d-pencillamine chelate

ARSENIC:

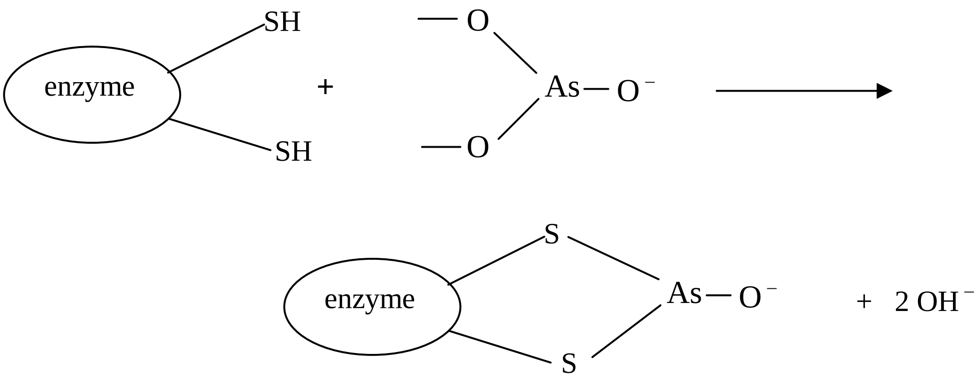
Effect of arsenic:

Arsenic commonly occurs in insecticides, fungicides and herbicides. Among its compounds those of arsenic (III) are compounds most toxic. Bio methylation of arsenic has been studied in detail. Ambient air appears to contain arsenic mostly as the inorganic species some in $(CH_3)_3As$ in vapour form and some methyl arsenic compounds as particulates.

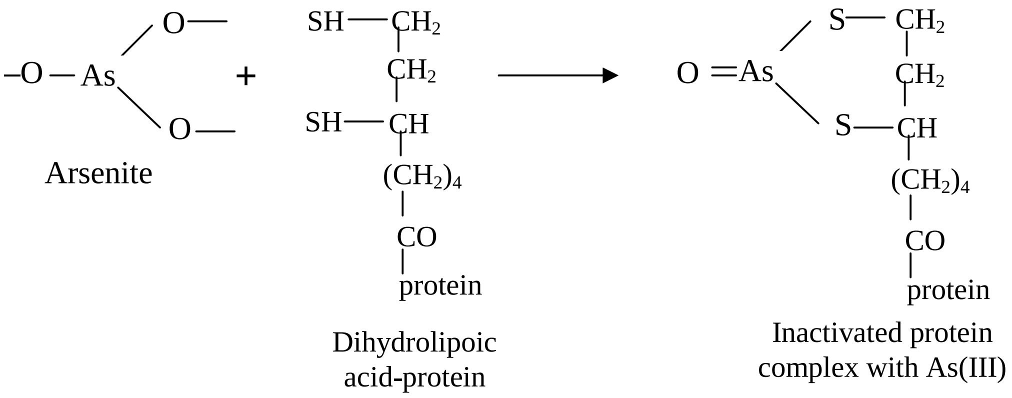
Speciation of arsenic in water, urine and biological samples has been conducted by iodide (I^-) reduction instead of $NaBH_4$ reduction. Arsenic (V) compounds are converted to iodides in presence of I^- which are then allowed to react with diethyl ammonium diethyl dithiocarbomate to form arsenic complexes of diethyl dithiocarbomate.

Biochemical effects of arsenic:

Arsenic(III) exerts its toxic action by attacking groups - SH- of an enzyme there by inhibiting enzyme action.

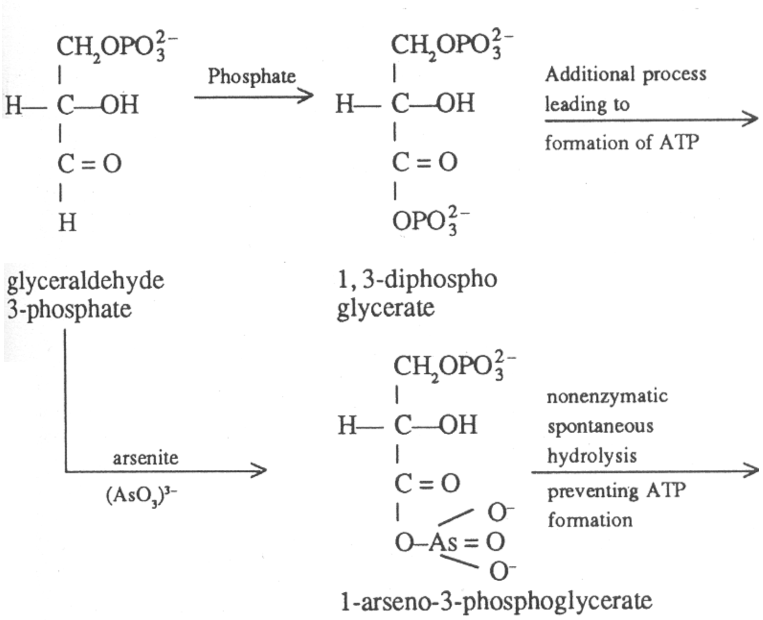


The enzymes which generate cellular energy in citric acid cycle are adversely effected. The inhibitory action is based on inactivation of pyruvate dehydrogenase by complexation with As (III), where by generation of ATP is prevented.



Biochemical effects of arsenic

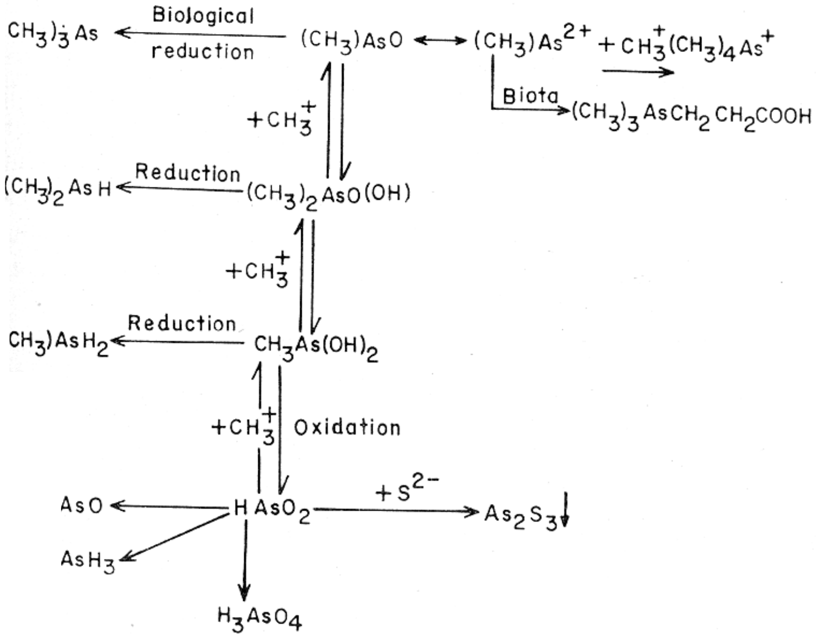
By virtue of its chemical similarity to phosphorus, arsenic interferes with some biochemical processes involving phosphorus. An important step in ATP generation is the enzymatic synthesis of 1,3 di phospho glycerate from glyceraldehyde 3- phosphate. Arsenite interferes by producing 1-arseno 3-phospho glycerate instad of 1,3- di phospho glycerate. Phosphrylation is replaced by arsenolysis which consists of spontaneous hydrolysis to 3-phospho glycerate and arsenate.



Arsenic (III) compounds at high concentrations coagulate proteins possibly by attacking the sulphur bonds and three major biochemical actions of arsenic are

1. Coagulation of proteins
2. Complexation with coenzymes
3. Uncoupling of phosphorylation

The general antidotes for arsenic poisoning are chemicals having –SH groups which are capable of bounding to As(III).



Environmental chemistry of Arsenic

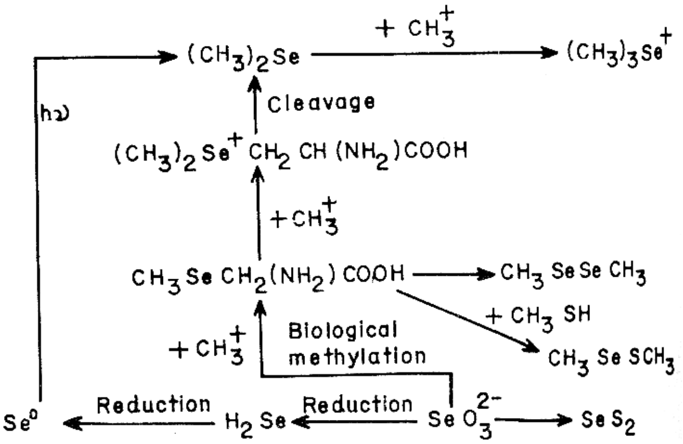
SELENIUM:

Selenium is a chalcophile element. It is a non metal similar in properties to those of sulphur and often found in association with one another. It is an essential trace element and is a natural component of an enzyme glutathione peroxidase. Although selenium is an essential element excessive amounts of it are extremely toxic. It is considered to be more toxic than arsenic. Owing to its extreme volatility it easily dissipates into the atmosphere, which accounts for 50% of its emissions through atmosphere. It exhibits variable valencies such as -2, 0, +2, +4, +6.

Ex: Hydrogen selenide (-2)	Elemental selenide (0)
Selenium dioxide (+2)	Selenites (+4)
Selenates (+6)	

Selenous acid (H_2SeO_3) and its salts are the major water soluble selenium species. H_2SeO_3 is very mobile in the aqueous environment and readily available to plants. SeO_4^{2-} is fairly strong oxidising agent and readily reducible to SeO_3^{2-} under most environmental conditions.

Manifestation of Selenium in Environment:



Environmental chemistry of selenium

Biochemical Effects:

Animals dwelling or grazing in selenoferous areas suffer from chronic diseases like alkali disease which is characterised by hair loss, soreness of joints, dullness, sloughing of hooves (separation of layers) and sometimes cirrhosis and anemia. Acute selenosis may lead to blind staggers characterised by impairment of vision, paralysis leading to death, owing to respiratory failure. Chronic selenium poisoning may be attributed for symptoms like dermatitis and staining of fingers, teeth and hair. Selenium is mutagenic, teratogenic.

Selenium toxicity occurs mainly in neutral and alkaline soils. Selenium concentration in human body ranges from 0.10–0.34 µg/ml.

NITRATES:

The danger of drinking water containing high nitrate content has long been recognized. Livestock has been affected by well waters containing 75 to 150 ppm of nitrate nitrogen. The primary source of excessive nitrates in well water has been the leaching of nitrate salts into the underground water supply from agricultural fertilization and the seepage of sewage.

Biochemical effects of nitrogen oxides (Nitrates):

One of the symptoms of nitrate poison has been described as cyanosis, in which there has been a bluish discolouration of the skin and mucous membranes. The red blood cells lose their capacity to carry oxygen, causing the blood to turn dark and resulting in death from asphyxiation. The failure of the red blood cells has been due to the conversion of their haemoglobin to a closely related substance, mathemoglobin, which cannot combine with oxygen. The conversion is brought about by the action of nitrite on the iron (Fe) in the hemoglobin molecule, which oxidizes it from divalent to trivalent iron. The condition produced by nitrate (or nitrite) poisoning has been termed as *methemoglobinemia.*

$$\begin{array}{l}\text{Hemoglobin (Fe}^{2+}\text{)}\\ \text{can combine with}\\ \text{oxygen}\end{array} \xrightarrow{\text{nitrite}} \begin{array}{l}\text{Methemoglobin (Fe}^{3+}\text{)}\\ \text{cannot combine with}\\ \text{oxygen}\end{array}$$

For a nitrate to be highly toxic it must first get converted to nitrite. In cattle it has been believed to be brought about by action of certain microorganisms prevalent in the rumen the first pouch of the stomach.

$$\underset{\text{Nitrate}}{NO_3^-} \xrightarrow[\text{reduction}]{\text{microbial}} \underset{\text{Nitrite}}{NO_2^-}$$

Nitrate poisoning takes place in many animals including cattle, sheep, horses, turkeys and man. Human infants are highly susceptible to nitrate poisoning. It is believed to get caused by the lower gastric acidity (i.e., high gastric pH) which favours nitrate–reduction. Nitrate poisoning of infants has been reported from drinking water having nitrate in the range of 15 to 250 ppm of nitrate nitrogen equal to 67, to 1,100 ppm nitrate ion (NO_3^-).

Effect of nitrates through plants:

Nitrates have been normally present in many plants, often at levels that cause poisoning of livestock. Plants having 1% of nitrates have been toxic to cattle and 0.5% has been found to be the maximum that can be tolerated.

On the other hand high concentration of nitrate in drinking water may lead to reduction to nitrite by bacterial action in intestine. It enters blood stream and forms a complex known as methemoglobin, when it encounters haemoglobin. As a result oxygen carrying capacity of the blood is reduced producing a condition called metemoglobin anaemia or *blue baby disease*. In young babies it is frequently fatal. The nitrates further converted to amines and nitrasoamines in human body leading to possible cause called gastric cancer.

OIL:

Biochemical effects of oil:

Oil pollution results from accidents involving oil tankers and from spills at off shore oil drilling sites. A major persistent source of oil pollution results from the practice of oil tankers, after they deliver the oil, to fill the empty tanks with sea water to act as ballast for the return trip. Prior to docking, the seawater ballast contaminated with oil present in the tankers is discharged. Although this practice is illegal, it is difficult to prevent.

However spillage also cause marine pollution and shore contamination since oil is virtually insoluble in water it floats and spread rapidly into a thin layer. The lighter, low components, which are toxic to organisms, are soon evaporated and others are degraded biologically at a slow rate. At sea oil spills are responsible for death of sea birds. The oil penetrates the bird feathers there by affecting their insulation and buoyancy. Thus the birds become older and more susceptible to diseases and experience difficulty in floating and flying. The birds ingest oil when they dive, to catch food and also when they preen their contaminated plumage. This ingestion of oil produces toxic effects. Very little is known about toxic effects of oil on marine and fresh water organisms.

This slim layer reduces light penetration and reduces atmospheric reoxygenation of water. Then dense algal growth eventually dies and the subsequent biodegradable produce an oxygen deficient situation resulting in foul smelling. Organisms which either flow near or on the surface and those which they come on to surface for air are most likely to be affected. In oil spills on surface of water prevent oxygen transfer from atmosphere and lead to low DO level in water due to microbial oxidation attack on hydrocarbon molecule. It also endangers water birds, coastal plants and animals.

Films of oils on the surface may be driven inshore through the action of winds and tides and may accumulate along the shore alike where they cause aesthetic problems.

UNIT 4

WATER POLLUTION ANALYSIS

Lesson 1

Objectives of the lesson: This lesson deals with study of types of water pollutants, sampling and analysis.

STUDY OF WATER POLLUTION AND WATER POLLUTION ANALYSIS:

Categories of water pollution:

Water pollution can be classified as follows:

1. Oxygen demanding wastes
2. Disease causing agents
3. Synthetic organic compounds
4. Plant nutrients
5. Inorganic Chemicals and minerals
6. Sediments
7. Radioactive Substances
8. Thermal Discharges
9. Oil wastes

Pollution of the waterways is often caused by a combination of the above categories, which are responsible for the problem.

Classification of water pollutants and their influence:

Oxygen Demanding Wastes:

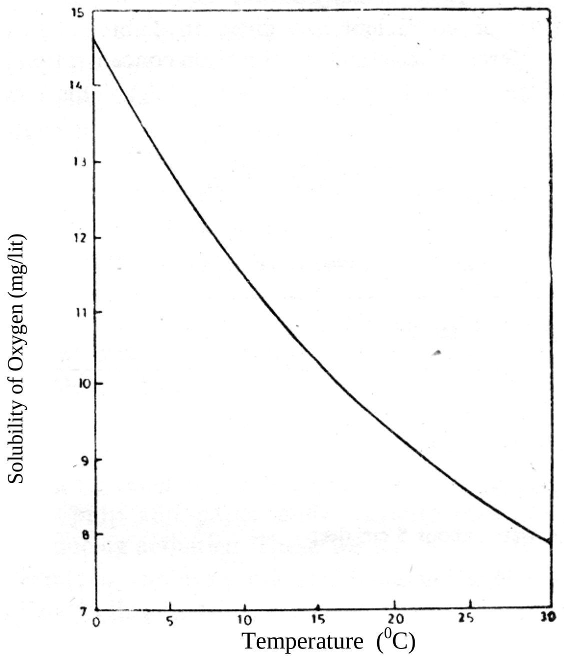
***1. Dissolved Oxygen (DO)*:**

Dissolved oxygen is essential for sustenance of the plant and animal life in any aquatic system. The minimum dissolved oxygen level that is required by warm water fish is 5mg/l. If dissolved oxygen level drops below this concentration the water can be classified as polluted. The main causes which can effect dissolved oxygen concentration are:

- Reaeration
- Photosynthesis
- Respiration
- Oxidation of wastes

<u>Reaeration:</u>

It is a process where oxygen transfer takes place from atmosphere to water. The solubility of oxygen in fresh water at saturation point decreases with an increase in temperature. eg: 15% at 4^0C, 7% at 35^0C.



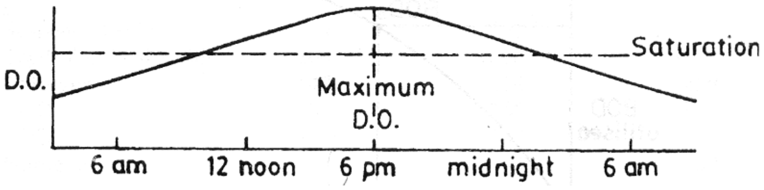
Saturation concentrations of dissolved oxygen in fresh water

Photosynthesis:

During the process of photosynthesis, the liberated oxygen cause an increase in dissolved oxygen level of water. This is a process of addition or regeneration of oxygen in water.

Respiration:

Contains removal of oxygen takes place during respiration. The process of photosynthesis, respiration and reaeration lead to variation of dissolved oxygen as shown below.



Diuranal variation

Water gets deoxygenated due to the presence of substances, collectively known as oxygen demanding Wastes. There is another process by which dissolved oxygen levels gets affected i.e.,

$$\text{Organic matter + microorganisms + D.O.}$$

$$\downarrow$$

$$CO_2 + H_2O + \text{New bacterial cells}$$

The only problem here is the depletion of oxygen.

2. Biochemical / Biological Oxygen Demand (BOD):

BOD is the measure of oxygen utilized by micro organisms during the oxidation of organic materials. It is an important index which gives a measure of sewage strength. BOD is proportional to the amount of organic matter oxidized.

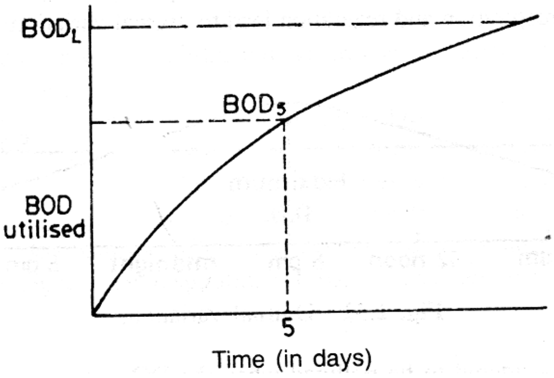


Illustration of BOD vs time

where BOD_L is the ultimate oxygen demand or the total oxygen demand for a given water sample polluted by sewage or otherwise.

A mathematical relation can be established i.e.,

$$BOD_{(utilised)} = BOD_L (1 - e^{-kt})$$

Where k is the reaction rate constant, t is the time in days

BOD of very pure water is around 1ppm. However water can be considered pure at a BOD level upto 3ppm. Storm runoffs, treatment plant effluents tend to introduce more oxygen than necessary for growth of micro organisms. Niltrosomonas and nitrobacter carryout the conversion of ammonia to nitrate.

$$NH_3 \xrightarrow[\text{Nitrosomonas}]{O_2} NO_2 \xrightarrow[\text{Nitrobacter}]{O_2} NO_3$$

The waste discharged into water body like river or pond cause depletion of D.O. due to consumption of oxygen by microbes. As a part of natural in built mechanism, simultaneously a process of reaeration takes place. This process replaces the depleted oxygen through surface absorption process. Deoxygenation and regeneration takes place simultaneously which is a dynamic process.

Disease Causing Agents:

Water is a potential carrier of pathogenic micro-organisms. These pathogens are carried out into water bodies by sewage and waste from farms and various industries specially tanning and meat packaging industries. Some bacteria are responsible for water borne diseases include those responsible for cholera, typhoid, dysentery, gastro enterities, viruses, are also found in water including strains (an injury to a muscle or a tendon caused by stretching or over exertion) responsible for polio, infections, hepatitis and coxsackie fever. Water also contains some animal parasites like roundworm and the pork tapeworm.

Domestic water Pollution:

It includes wastewater from houses and commercial establishments. Domestic waste water arises from many small sources over the fairly wide area that is through residential and commercial cleaning operations, laundry, food preparation, body cleaning functions and body excretions.

The composition of domestic waste water is relatively constant when compared to industrial waste water and all these things are transmitted by sewage to municipal waste treatment plants. Some impurities in domestic wastes get diluted and generally to the 0.1% of total mass. This is generally organic in nature and gets oxidized by bacterial decomposition to nitrate, phosphate, CO_2. As the decomposition needs O_2, it depletes oxygen which in turn as an indicator for BOD.

The origin and nature of rest of the pollutants were discussed in detail in the study of hydrosphere.

COLLECTION OF SAMPLES FOR WATER ANALYSIS:

The collection of the sample should be done with utmost care since all interpretations are based on the report of the analyst. The sample water about 2 litres should be collected in a clean plastic container and it should be sealed at the mouth. Floating material should not be allowed to enter the bottle. If possible sample should be collected below the surface of water.

Immediate attention is required with regard to analysis for certain constituents because the composition of water may change before it is brought to the laboratory.

The maximum limits of storage are:

(1) Highly polluted waters : 10-12 hours
(2) Slightly polluted waters : 48 hours

Sometimes the change in temperature also changes the pH value as the dissolved gases (O_2, CO_2, H_2S) may be lost. For biological examinations the sample should be collected in sterilised neutral glass stoppered 250 ml bottles. The stopper should be wrapped by a parchment paper. If sample contains traces of residual chlorine, an amount equal to 3 mg of sodium thiosulphate is added to neutralise it before sterilisation. The sample should be examined within one hour. For testing the suitability of water, the following three types of examinations are performed:

(A) Physical Examination:

(i) Colour, (ii) Odour and taste and (iii) Turbidity.

(B) Chemical Examination:

(i) Total solids, (ii) Organic matter, (iii) Alkalinity, (iv) Hardness, (v) pH, (vi) Acidity,
(vii) Nitrogen as (a) nitrites; (b) nitrates; (c) free ammonia and (d) albuminoid ammonia,
(viii) Sulphates, (ix) Chlorides, (x) Dissolved oxygen(D.O.), (xi) Biochemical oxygen demand (BO.D.), (xii) Chemical oxygen demand (C.O.D.)(xiii) free CO_2, (xiv) Free and combined available chlorine, (xv) Chlorine demand and (xvi) Chlorine dosage.

(C) Microbiological Examination: (i) Total count and coliform MPN.

For physico-chemical and biological examination of water, a proper sampling procedure must be adopted.

There are two types of samples: (1) Grab sample and (2) Composite sample.

1) Grab sample:

A grab sample is a manually collected in a single operation in case of water or waste water.

2) Composite sample:

When a grab sample is collected at regular intervals for a certain period for example 12 hrs or 18 hrs and when this is mixed with water or waste water sample is called composite sample.

Quantity of sample:

In general, about 2 litres of sample is taken for physical and chemical examination of water.

Sample container:

Ordmarily stoppered Winchester Quartz bottle of 2.5 litres capacity is sufficient. Generally glass containers are preferred over polythene materials. All sample containers before use must be cleaned thoroughly to remove all extraneous matter. Soda lime glass bottles are not recommended as sample containers. Glass stoppers or new cork stoppers that have been thoroughly washed or plastic caps with suitable liners are recommended.

Frequency of sampling:

For water having sewage contamination, individual samples at frequent intervals such as biweekly or monthly are to be taken for analysis work. If samples are taken from river then they may be taken at short intervals, for instance daily. If there are greater variations, samples should be taken at hourly intervals.

Sampling of potable waters:

The sample should be taken from the tap directly. Before collecting the sample, the inside and outside of tap should thoroughly be cleaned.

Sampling for water analysis:

Sampling of well water:

If water from a well is collected, then water has to be pumped for a longer time so that sample represents ground water that feeds the well.

Sampling in larger rivers and streams:

Three or four samples are taken at mid point of equal cross sectional areas of such rivers and streams. The samples are then combined together to obtain a composite sample. If only a grab sample is taken, it is better to collect in the middle of the stream and at mid depth. When a river is mixing with a sewage then sample is taken down stream sufficiently away to allow thorough mixing. Generally a distance of 1 to 3 or 4 Km below the tributary is advisable.

Sampling of sewage:

For collection of sewage samples, a composite sample over 24 hrs period has been suggested. The different grab samples should be combined in a container of 2-3 litres.

Sampling industrial effluent:

As industrial samples are subject to rapid change within a few minutes due to breakdowns, spillovers floor washing etc. hence it is necessary to collect individual samples at uniform intervals, say 10 or 20 minutes. In fact the degree of variation in rate of flow will determine the time interval for sampling.

Polythene containers are used for collecting raw sewage, activated sludge etc. Cleaning procedure of these containers was to soak the jars in 2% HNO_3 solution for 24 hours, followed by multiple rinses with doubly distilled water. The collected samples should be stored at 4°C in the freeze after adding 5 ml of conc. HNO_3 to each litre of raw sewage to avoid absorption on the surface of polythene. Samples should be collected from different points after different treatments.

Preservation of samples:

Generally samples should be kept in dark at low temperature however some specific preservation methods are as follows:

(I) Oxygen demand: Samples should be preserved at 4^0C.

(II) Total organic carbon: Conc. HCl is added to lower down the pH below 2.

(III) Nitrogen balance: 1 ml conc. H_2SO_4 is added per litre and refrigerated.

(IV) C OD: Add conc. H_2SO_4 is added to bring pH about 3.

(V) Sulphide: 0.2 ml zinc acetate solution is added per 100 ml sample.

ANALYSIS AND TREATMENT METHODS OF WATER POLLUTANTS:

The determination of sulphurdioxide, hydrogen sulphide, oxides of nitrogen, oxides of carbon, hydrocarbon can be done by the methods that are already discussed in the second unit with regard to air pollution analysis.

SOLIDS

Solid is a general term irrespective of their chemical nature and hence it can be referred as residue after evaporation of the water sample. The analysis of solids in water samples includes total solids, dissolved solids, suspended solids and settleable solids.

Total solids:

These can be determined by taking the water sample into a clean dry platinum dish or glass dish. For sewage and effluent samples a porcelain dish is to be used. The sample in the dish is evaporated to dry ness taking precaution that the water sample is previously dried. The sample is evaporated to the required temperature and kept in desiccators and the dish is weighed. From the difference in weights of the crucible before and after the amount of total solids can be reported as follows:

$$\text{mg/l total solids} = \frac{\text{mg total solids} \times 1000}{\text{mg of sample}}$$

Dissolved solids: The different types are :
total dissolved solids
fixed dissolved solids and
volatile dissolved solids

Suspended solids: There are two approaches for estimating the total suspended solids.

1. Filatraion method and centrifugation method.

Filtration can be achieved by means of a gooch crucible in which an asbestos mat is placed which is treated for this purpose. Then allow to flow the sample water and then place the crucible after the filtration is over in a muffle furnace at 550^0 C. Cooled and weighed.

2. Centrifugation method:

The sample is centrifugated and the supernatant solution is decanted and the contents are dried in a muffle furnace at 550^0 C. Cooled and weighed.

The calculations are similar to the above method.

AMMONIA:

Ammonia is present in surface water, ground water and domestic sewage. Generally it is produced due to deamination of organic nitrogen containing compounds and hydrolysis of urea. In water bodies it is naturally produced by the reduction of nitrates under anaerobic conditions. Nessler’s method is quite useful for the determination of ammonia nitrogen upto 5 ppm while the titration methods will be useful when the level of ammonia exceeds 5 ppm. Distillation is essential when the sample is coloured and when the titrimetric method is followed:

Nessler's method for the determination of ammonia:

Basically the method is based on the reaction between NH_3 and HgI_4^{2-} (tetraiodo mercury (II) anion) in alkaline solution:

$$NH_3 + 2HgI_4^{2-} + 3OH^- \rightarrow \underset{\text{orange brown}}{NH_2Hg_2IO} + 7I^- + 2H_2O$$

The orange brown reaction product tends to precipitate at higher concentrations and hence the colour is measured at lower concentrations at 420nm spectro photometrically.

Procedure I:

1. To a 100ml sample a little NaOH is added to neutralize the acid used for storage and then 1ml of 10% $ZnSO_4$ $7H_2O$ besides 1ml of 10% NaOH are added. The solution is thoroughly stirred and filtered.
2. The colourless middle fraction is collected. To it 1drop of 50% disodium salt of EDTA is added mixed well and 2ml of Nessler's agent [70g KI + 160g HgI_2 + 160g NaOH (ice cool) diluted to 1 liter]. The contents are thoroughly mixed.
3. The resulting yellow coloured solution is measured at 420nm.

Procedure II:

When the sample is coloured distill sample of 500 ml with dilute NaOH and the distillate is collected into 200ml of 0.1 N H_2SO_4. The contents are made upto 250ml in a volumetric flask. An aliquot is taken and neutralized with 0.1N NaOH. This is treated with 2ml of Nessler's agent and measurement is done as described in procedure I.

HYDROGEN SULPHIDE:

Zinc acetate solution is added to the sample, and zinc sulphide is co-precipitated with zinc hydroxide. Sulphide is finally determined by ethylene blue method.

Procedure:

A measured volume of test water is placed in a beaker and to it zinc acetate (2% solution) and sodium carbonate (1M) are added. If the test water contains small quantities of sulphide a little amount of sodium hydroxide is added (0.5 to 1ml) per each 250ml sample of water. If the water reacts alkaline the quantity of sodium carbonate are alkali can be decreased. The contents are stirred until a precipitate appears, which is allowed to settle and the solution is decanted. The sulphur content of the decanted solution is determined by ethylene blue method as described in air pollution analysis.

DISSOLVED OXYGEN (DO):

In natural and wastewaters, dissolved oxygen levels depend on the physical, chemical and biological activities of the water body. The analysis of dissolved oxygen plays a key role in water pollution control activities and waste treatment process control. Three methods are in use

1. Winkler's method or Iodometric method
2. Polarographic method
3. Electrometric method

Winkler's method:

Dissolved oxygen is allowed to react with I^- to form I_2 which is then allowed to react with standard $Na_2S_2O_3$ solution. A fast quantitative reaction is ensured by addition of Mn(II) salts in strongly alkaline medium.

$$Mn^{+2} + \frac{1}{2} O_2 + 2OH^- \rightarrow MnO_2 \downarrow + H_2$$

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

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Interference due to oxidising agents such as NO_2^- and SO_3^{2-} present in wastewater may be eliminated by the addition of NaN_3 (sodium azide) to alkaline I^- solution. On acidification NO_2 is decomposed.

$$N_3H + HNO_2 \rightarrow N_2 + N_2O + H_2O$$

Procedure:

1. To a 100ml sample in a 250ml bottle, add 2ml of 40% KF (to mask Fe^{+3}), 2ml of 36% $MnSO_4$ and 2ml of alkaline iodide - azide solution (50g of NaOH +13.5g of NaI +1g NaN_3 diluted to 1L).
2. Shake well, allow the precipitate to settle and then add 6ml of 12N H_2SO_4.
3. Shake the mixture until the precipitate dissolves and then titrate the liberated iodine with 0.025M $Na_2S_2O_3$ solution. The amount of hypo consumed by iodine gives the amount of dissolved oxygen present in water.

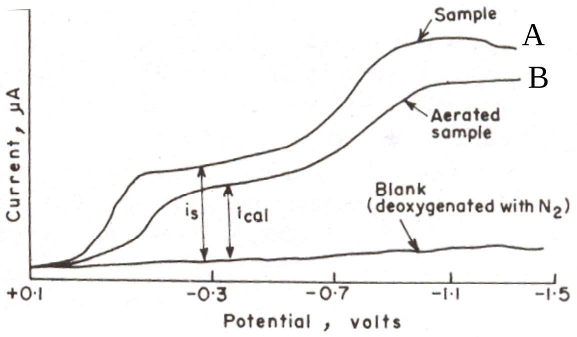
5ml of 0.025M $Na_2S_2O_3$ = 1mg / L of DO

Polarographic method:

Oxygen can be reduced at various electrodes in aqueous solutions if a small negative voltage is applied. The magnitude of the current which flows is determined by the rate at which oxygen can diffuse to the electrode.

Procedure:

1. Transfer 10ml of the sample to the polarographic cell, add 0.1ml of 1M KCl and little Hg.
2. Insert the DME (Dropping Mercury Electrode) with a head of 50 cm of Hg and take readings of current at potentials increasing –0.1 to –1.5V. The height of the wave, 'i_s' for the sample is proportional to the level of DO.
3. Allow an air stream to bubble through the solution for 5minutes, note the temperature and plot a second polarogram. The wave height, 'i_{cal}' gives the DO in air saturated water.
4. Remove all DO by bubbling N_2 (oxygen free) for 10 minutes and plot again.
5. Measure 'i_s' against the blank plot and obtain the DO value from the calibration curve.



Polarographic waves for dissolved oxygen in a sample (upper wave A), aerated sample (middle wave B) and a blank (deoxygenated with N_2)

Electrometric method (or) Membrane electrode method (Mackereth oxygen cell)**:**

The polarographic method is not desirable for DO analysis in industrial or domestic wastewaters as the Hg electrode gets poisoned by impurities in the test solutions. This problem is solved by using the membrane electrode method. Two metal electrodes, one of Ag and other of lead (Pb) are immersed in a saturated $KHCO_3$ solution separated from the test solution by a polyethylne membrane, around 0.06mm thick. Thus a galvonic cell can be plugged to a pH meter to give a direct reading of DO in mg/L (the scale of 0-14 pH becomes 0–14mg/L DO). The current is measured for the sample, for a standard (sample with air saturation) and for a blank (sample after treatment with a little Na_2SO_3 to expel oxygen).

The Mackereth oxygen cell:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (\text{Ag electrode})$$

$$Pb + 4OH^- \rightarrow PbO_2 + 2H_2O + 4e^-$$

$$2Pb + 4OH^- \rightarrow 2Pb(OH)_2 + 4e^- \quad (\text{Pb electrode})$$

CHEMICAL OXYGEN DEMAND (COD):

This is a satisfactory method for determining the organic load of a water body. It is a rapidly measurable parameter for stream and industrial waste studies and control of water treatment plants. The method is based on the chemical oxidation of organic material in the presence of a catalyst by $Cr_2O_7^{2-}$ in 50% sulphuric acid.

$$3(CH_2O) + 16H^+ + 2\,Cr_2O_7^{2-} \longrightarrow 4Cr^{3+} + 3CO_2 + 11H_2O$$

The amount of unreacted $Cr_2O_7^{2-}$ is then determined by titration with a standard Mohr's salt solution. Ag_2SO_4 catalyses the oxidation of straight chain aliphatic compounds, aromatic hydrocarbons and pyridine. $HgSO_4$ ties up Cl^- as soluble complex and prevents its interference.

Procedure:

1. Take 5–50ml of sample in a conical flask with ground glass joint of 250ml capacity; add 10–20 ml of 0.25N $K_2Cr_2O_7^{2-}$ in 18N H_2SO_4, 1g Ag_2SO_4, and 1g $HgSO_4$.
2. Reflux for 6 hours, cool and titrate excess $Cr_2O_7^{2-}$ with 0.1N Mohr's salt solution in 8N H_2SO_4 using 8–10 drops of ferroin.

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

BIOCHEMICAL OXYGEN DEMAND (BOD) :

This is an empirical semi quantitative method based on oxidation of organic matter by suitable micro organisms during a five day period. There is nothing specialty about 5 days but the test originated in England where the maximum streams flow is 5 days.

The degree of microbial mediated oxygen consumption by organic pollutants in water is known as the biochemical oxygen demand. This parameter is commonly measured by the quantity O_2 utilised by suitable aquatic micro organisms during 5 day period.

$$(CH_2O) + O_2 \longrightarrow CO_2 + H_2O \quad \text{(in presence of micro organisms)}$$

The selection of micro organisms (seed) is crucial and the results are obviously not reproducible. The purpose of seeding is to introduce into the sample a biological population capable of oxidising the organic matter in the wastewater, where such micro organisms are already present, i.e., in domestic waste water or surface waters seedling is unnecessary. But when the sample is deficient in micro organisms the dilution water needs seedling. The standard seed material is settled domestic wastewater which has been stored for 24-36 hours at 20^0C.

1.Preparation of dilution water:

Take desired volume of distilled water in a suitable bottle and add 1ml of phosphate buffer (pH 7.2), 1ml of $MgSO_4$ (22.5g/L), 1ml of $CaCl_2$ (27.5g/L), and 1ml of $FeCl_3$ (0.25g/L).

2. Dilution techniquie:

The dilution technique depends on the nature of the sample: 0.1–1% for industrial wastes, 1–5% for raw and settled sewage, 25–100% for polluted river water and 5-25% for oxidised effluents.

3. Procedure:

Aerate the water sample thoroughly by bubbling air through the diffusion tube into the sample for 5 minutes or until the DO is 7 ppm, make a measured dilution with dilution water if BOD is greater than DO level. Seed with a little diluted domestic wastewater (1.2 ml/L). Measure DO on a suitable aliquot (D_1)

Fill a screw topped incubation bottle (250–300ml) to the brim with the remaining diluted sample. Seal the bottle and incubate in dark for 5 days at 20^0C. Measure DO on an aliquot of the sample (D_2).

$$\text{mg/L BOD} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

Where D_1 = DO of diluted sample

D_2 = DO of diluted sample after incubation

B_1 = DO of dilution water containing seed before incubation

B_2 = DO of dilution water containing seed after incubation.

f = Ratio of seed in sample to seed in control and

P = Decimal fraction of sample used

BOD of 80mg/l means that biodegradation of organic matter in a liter of sample consumes 80 mg of oxygen.

DETERMINATION OF PHOSPHATE:

It occurs in natural and wastewaters as inorganic and organically bound phosphate. Phosphates are largely used for laundry purposes, treatment of boiler waters and agriculture. The run-offs from all these sources find their way into water bodies. Organic phosphates are formed primarily by biological processes, but are also contributed by domestic sewage. Phosphates also occur in bottom sediments and in biological sludges, both in precipitated inorganic forms and incorporated into organic compounds.

Procedure:

The total phosphate content of the sample includes all of the o-phosphates and condensed phosphates, both soluble and insoluble and organic and inorganic species. A digestion method is necessary to oxidise organic–bound phosphorus for rupturing both C–P and C–O–P bonds and releasing phosphorus as soluble PO_4^{3-}.

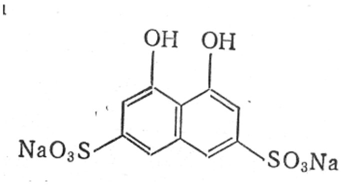
$HNO_3 - H_2SO_4$ digestion method is usually recommended for most of the samples.

In a dilute o-phosphate solution, ammonium molybdate reacts in acidic medium to form molybdo phosphoric acid. The latter reacts with vanadium to form yellow vanado molybdo phosphoric acid, which is measured at 460nm.

1. Take 100ml sample (50–1000micro grams of phosphorus) in a beaker. Digest with 1ml concentrated H_2SO_4 + 5ml of HNO_3 and evaporate to dryness. Repeat digestion and evaporation.
2. Leach the residue with 5ml of 5N HNO_3 and transfer to a 50ml volumetric flask.
3. Add 5ml of 10% ammonium molybdate and then 5ml of 0.25% ammonium vanadate (in 6N HCl)
4. Dilute to the mark with distilled water. Wait for 10 minutes.
5. Measure the absorbance of the yellow reaction product, vanado molybdo phosphate at 460nm. Measure a blank carried through the same steps.
6. Prepare a calibration curve using a series of standard solutions of phosphate (220g KH_2PO_4 /L) (1ml ≡ 50μg PO_4^{3-}).

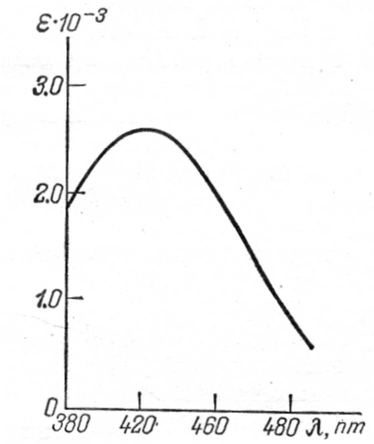
DETERMINATION OF NITROGEN COMPOUNDS (NITRATE and NITRITE)

Determining nitrate with chromotropic acid:

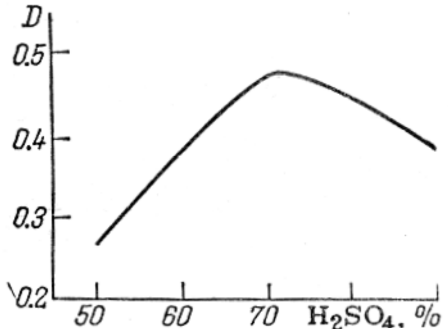


Chromotropic acid (A)

Disodium salt of chromotropic acid (1,8 dihydroxy naphthalene 3,6-di sulphonic acid) (**A**) reacts in sulphuric acid with nitrate and nitrite to form a coloured compound having the absorption maximum at 440nm (I). The reaction is employed in photometric determination of nitrate. According to Basargin and Charnova, optimal acidity is 70% as sulphuric acid (II).



I. Absorption spectrum of product of reaction of chromotropic acid nitrate in sulphuric acid



II. Effect of sulphuric acid concentration on reaction of chromotropic acid with nitrate. Conditions for plotting the curve: NO_3^-; b = 3.0 cm; optical filter (λ_{eff} = 440nm)

The composition of the product of reaction between chromotropic acid and nitrite depends on the concentration of sulphuric acid. For example in 70% H_2SO_4 the components react in the ratio 1:1, and in 10% acid – 1:5 (one mole of chromotropic acid reacts with five moles of nitrite). Sensitivity of reaction can be increased by using 2-bromo chromotropic acid

Interfering substances:

Since nitrite ion reacts similarly, it interferes with the determination of nitrate ion and other oxidisers (Cl_2, dichromate etc.,) also interferes with the determination. Their effect can be removed by adding to the test sample 1–2 drops of urea sulphite solution (containing 5g of urea and 4g of sodium sulphite in 100ml) or 2ml of antimonous sulphate (0.5g of metallic antimony dissolved in 80ml of concentrated sulpuhuric acid cooled and diluted with 20ml of ice cold water). Chlorides do not react with chromotropic acid but the chloride ion increases the absorbance of the solutions in the presence of nitrates. This phenomenon is often used to increase the sensitivity of the reaction. It should be remembered that chloride content should be equal in test sample and in solutions used to plot a calibration curve.

Determination of 50µg of NO_3^- in 10ml is not affected by 50–fold quantity of Zn^{2+}, Ni^{2+}, Mn^{2+}, V(IV), Mo(VI), 20 fold quantity of Cu^{2+}, 5 fold quantity of Fe^{2+} and Fe^{3+}. However determination of nitrate is not adversely effected by the presence of 10 fold quantity of Fe^{3+} and 50 fold quantity of Fe^{2+}. Greater quantities of iron can be separated by cation exchanging.

Cobalt and boron strongly interfere with the determination and their quantities should not exceed that of nitrate.
Measurement of absorbance: Absorbance is measured at 440 nm.

Determination of nitrites:

Discussion:

When dilute acid solutions of sulphanilic acid and alpha–naphthyl amine are acted upon by nitrous acid, a red coloration is produced, which may be used for the colorimetric determination of nitrites. The sulphanilic acid is converted into the corresponding diazo compound, which couples with the $\tilde{\alpha}$-naphthyl amine to form $\tilde{\alpha}$-naphthyl amine-p-azo benzene-p-sulphonic acid, a red azo dye. The full colour does not appear at once, a satisfactory colour comparison can be made after 10-15mins, provided the sample and the standard are treated in the same way.

Reagents:

Sulphanilic acid reagent (Solution-1)

Dissolve 0.6g of A.R. sulphanilic acid in 100ml of 20% hydrochloric acid.*α-naphthyl amine reagent (solution-2)*

Dissolve 0.48g of A.R. α-naphthyl amine in 100ml of 1.3% v/v hydrochloric acid.

Standard Nitrite solution:

Dissolve 4.93g of A.R. sodium nitrite in water and dilute with deionised water to one litre. Dilute 10.0ml of this standard solution to one litre with boiled out water or deionised water. 1.0ml of this solution corresponds to 0.01mg of nitrite nitrogen.

Sodium acetate (2M):

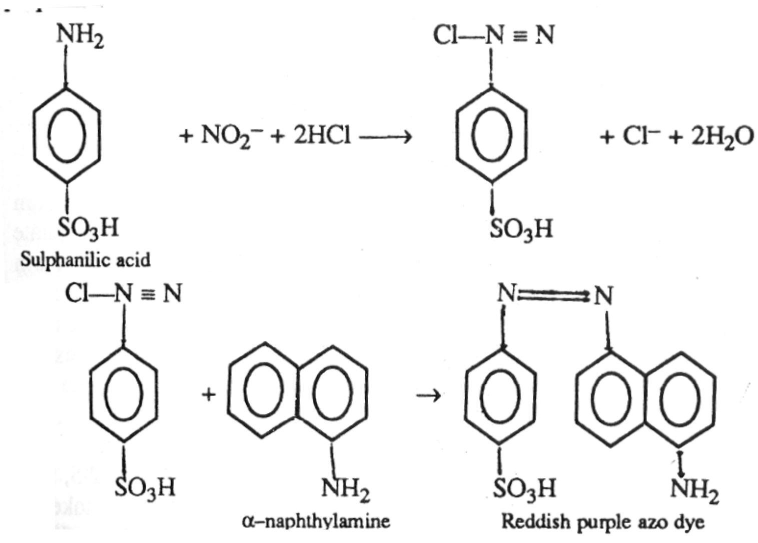
Dissolve 16.4g of anhydrous sodium acetate in water and dilute to 100ml with distilled water.

Procedure:

Dilute the sample to give a nitrite concentration of about 0.5mg/L. Prepare a series of Nessler's tubes containing the following volumes of standards nitrite solution dilute to 50.0ml :- 0.0, 0.2, 0.4, 0.6, 0.8, 1.0ml. Place 50ml of the unknown solution in a Nessler's tube. To each tube add 1.0ml of solution-1 and stir with a special glass rod with flattened end, check that the pH of the solution is 1.4–1.7. After 5–10 mints add 1ml of α-naphthylamine reagent, 1ml of 2M sodium acetate solution and mix well. The pH should be 2 – 2.5. After 10 minutes, compare the colours of the tubes. If a closer approximation is required prepare a fresh series of standards on either side of the first value and repeat the comparison, starting all the tests at the same time.

To obtain more accurate results, proceed as follows. Place a quantity of the sample containing 0.03mg or less of the nitrite in a 50ml volumetric flask, add 1.0ml of the sulphanilic acid reagent, mix well and allow to stand for at least 3 minutes and not more than 10minutes at room temperature in a diffused light. Then introduce 1.0ml of the α- naphthyl amine reagent and 1.0ml of 2M sodium acetate solution to act as a buffer (pH 2.0–2.5). Dilute to volume and mix well. After 10 minutes but not later than 30 minutes, measure the intensity of the reddish purple colour by any suitable means. Measure the optical density at 520mμ against reagent blank distilled water. Alternatively, use a photoelectric colorimetre with a green filter. Construct a calibration curve using known nitrite standards, preferably in the nitrite nitrogen range of the samples.

MECHANISM



UNIT 4

TECHNIQUES OF WATER TREATMENT

Lesson 2

Objectives of the lesson: This lesson deals with basic techniques in treatment of water.

TECHNIQUES OF WATER TREATMENT (OR) PURIFICATION OF WASTEWATER

The treatment process can be basically divided into two types:

1. Treatment of wastewater or effluent or polluted water
2. Treatment of water for drinking purpose

The treatment of effluent or polluted water is rather complicated and needs a special device for the treatment of an effluent / polluted water depending upon the contents. On the other hand treatment of waters for drinking water supplies attracts more importance in view of the public health.

TREATMENT OF WASTE WATER / EFFLUENT / POLLUTED WATER

METHODS AND EQUIPMENT USED IN WASTEWATER TREATMENT:

Wastewater treatment is a process which contemplates the process of purification of polluted water or discharged water to be let of into the environment in a safe condition or to reuse it in the safe condition. However purification is the process, which aims at making the raw water suitable to our needs. The purpose of water treatment is to remove the contaminants from water, so that the treated water can meet the acceptable quality standards. The quality standards again depend on the point whether the water will be reused or discharged in the receiving stream.

The various methods used in sewage and industrial water treatment are as follows

I. PRELIMINARY TREATMENT

The principal objectives of preliminary treatment are the removal of gross solids (i.e., large floating and suspended solid matter), grit, oil and grease if they are present in considerable quantities.

Large quantities of floating rubbish such as cans, cloth, wood and other larger objects present in wastewaters are usually removed by metal bars, acting like strainers as the wastewater moves beneath them in an open channel. The velocity of the channels is then reduced in grit –settling chamber of a large size than the previous channel. Removal of gross solids is generally accomplished by passing wastewater through mixed or moving screens.

Grit (or detritus) is removed in the early stages of treatment in grit channels or tanks to safe guard against any damage to pumps and other equipment by abrasion and also to avoid settling in pipe bends and channels. Grit, being heavier than organic solids, can be separated from organic solids by careful regulation of the flow velocity in the grit tanks.

The grit settling chambers are periodically disconnected from the main system to remove the grit manually, for the possible use in land filling, road making, and on sludge drying beds. If the wastewater contains appreciable quantities of oil and grease, then it is advisable to remove as much of these as possible in the preliminary treatment it self to avoid adverse effect on the rest of the plant. This is achieved by passing the wastewater through skimming tanks where oil and grease are skimmed off. This process can be rendered more efficient by aeration, chlorination or vacuum flotation.

II. PRIMARY TREATMENT:

After the removal of gross solids, gritty materials and excessive quantities of oil and grease, the next step is to remove the remaining suspended solids as much as possible. This step is aimed at reducing the strength of wastewater and also to facilitate secondary treatment.

Primary treatment involves the following methods for water treatment

a. Sedimentation
b. Mechanical flocculation
c. Chemical coagulation
d. Equilisation
e. Neutralisation

a. Sedimentation:

The suspended matter can be removed efficiently and economically by sedimentation.

The Sedimentation tanks are designed to enable smaller and lighter particles to settle under gravity. The most common equipment used includes horizontal flow sedimentation tanks and center–feed circular clarifiers. The settled sludge is removed from the sedimentation tanks by mechanical scrapping into hoppers and pumping it out subsequently. In a well designed continuous flow sedimentation tank, about 50% of the suspended solid matter is settled out with in two hours of detention time. An efficient sedimentation system is expected to remove about 90% of the suspended solids and 40% of organic matter (thus reducing the BOD).

Finely divided suspended solids and colloidal particles cannot be efficiently removed by simple sedimentation that is through gravity. In such cases, mechanical flocculation or chemical coagulation is employed.

b. *Mechanical flocculation:* The wastewater is passed through a tank with a detention time of 30 minutes and fitted with paddles rotating at an optimum peripheral speed of 0.43m/s. Under this gentle stirring, the finely divided suspended solids coalesce into large particles and settle out. Specialised equipment such as clariflocculator is also available, where in flocculating chamber is a part of a sedimentation tank.

b. *Chemical coagulation:* It involves the application of certain chemicals, which form a floc (flocculating precipitate) that absorbs and entrains the suspended and colloidal particles present.
The coagulants in common use are

1. Hydrated Lime
2. Alum $Al_2 (SO_4)_3. 18H_2O$
3. Copperas Fe $SO_4. 7H_2O$
4. Ferric Chloride
5. Chlorinated Copperas Fe SO_4.Cl (mixture of ferric sulphate and chloride)

Alum is the most popular coagulant used both in water and wastewater treatment. For best results the chemicals used for coagulation are well mixed with wastewater in baffled channels followed by mechanical flocculation before sedimentation. Pre-aeration for about 10 minutes before sedimentation is also found to help in the removal of entrained gases like CO_2 and H_2S and improved flocculation and separation of oil and grease.

c. *Equalisation:* Some industries produce different types of wastes having different characteristics at different intervals of time. Hence uniform treatment is not possible. In order to overcome this problem different streams of effluents are held in big holding tanks for specified periods of time.

Each unit volume of waste is mixed thoroughly with other unit volumes of other wastes to produce a homogenous and equalized effluent. Aeration or mechanical agitation with paddles usually gives better mixing of different volumes of effluents. Basically this is a process of homogenising the heterogenous types of effluents released from different segments of a chemical industry.

d. *Neutralisation:* Highly acidic or highly alkaline wastes should be properly neutralised before being discharged. Acidic waters are normally neutralised by treatment with limestone or lime slurry or caustic soda depending upon the type and quantity of the waste. Alkaline wastes may be neutralised by treatment with sulphuric acid or CO_2 or waste boiler flue gas. If both acidic and alkaline wastes are produced in the same plant or at nearby plants, storing them in separate holding tanks and mutual neutralisation by mixing them in appropriate proportion is the cheapest method.

III. SECONDARY TREATMENT:

The secondary treatment contemplates the removal of dissolved and colloidal organic matter present in wastewaters by biological processes involving bacteria and other micro-organisms. These processes may be aerobic/ anaerobic.

In aerobic process, bacteria and other micro-organisms consume organic matter as food and they bring about following sequential changes.

(a) Coagulation or flocculation of colloidal matter
(b) Oxidation of dissolved organic matter to CO_2 , and
(c) Degradation of nitrogenous organic wastes to NH_3 which were later converted to NO_2^- (nitrite) and eventually to nitrate.

Thus secondary treatment reduces BOD and also removes appreciable amounts of oil and phenol. These processes are generally expensive in both commissioning and maintenance.

Certain micro-organisms, in presence of dissolved oxygen and in proper environmental conditions, utilise organic waste as their food, and convert into simple compounds such as CO_2, H_2O, nitrates and sulphates, which are non-pollutants. This process therefore can be used to remove organic substances from wastes. Almost all organic substances with a few exceptions, such as hydrocarbons and ethers can be oxidised by aerobic biological treatment. Complex cell tissues and protein materials are also synthesised during this process, which are then agglomerated and removed from the waste by settling. Germicidal and resistant organics, such as cyanides and phenols also can be destroyed by special types of micro-organisms, after prolonged acclimatization periods.

Under anaerobic conditions (i.e., in the absence of dissolved oxygen or gaseous oxygen), certain groups of micro-organisms (ex., hydrolyte and methane forming organisms) can carry out the digestion of complex organic wastes. The hydrolyte organisms convert complex organic compounds to simple and low-molecular weight organic acids and alcohols. They are further converted to CO_2 and CH_4 by methane bacteria.

Anaerobic treatment is employed for the digestion of sludges. This method is most economical and effective for organic liquid wastes from diary and slaughterhouses etc., were treated by this method effectively. The efficiency of this process depends upon pH, temperature, waste loading, absence of oxygen and toxic materials.

The broad classification of secondary treatment is given below:

SECONDARY TREATMENT

AEROBIC DIGESITION

1. Aerated lagoons
2. Trickling filters
3. Activated sludge
4. Oxidation ditches
5. Oxidation ponds

ANAEROBIC DIGESTION

AEROBIC TECHNIQUES:

1. Aerated Lagoons:

These are large holding tanks having a depth of 3–5m and are lined with cement or rubber. The effluents collected from primary treatment are fed into these tanks and re-aerated with mechanical devices for about 2–6 days. During this time healthy flocculants sludge is formed there by brings about oxidation of dissolved organic matter. The technique is effective in the removal of BOD up to 90%.

Advantages:

1. The operation and maintenance are relatively simple.

Disadvantage:

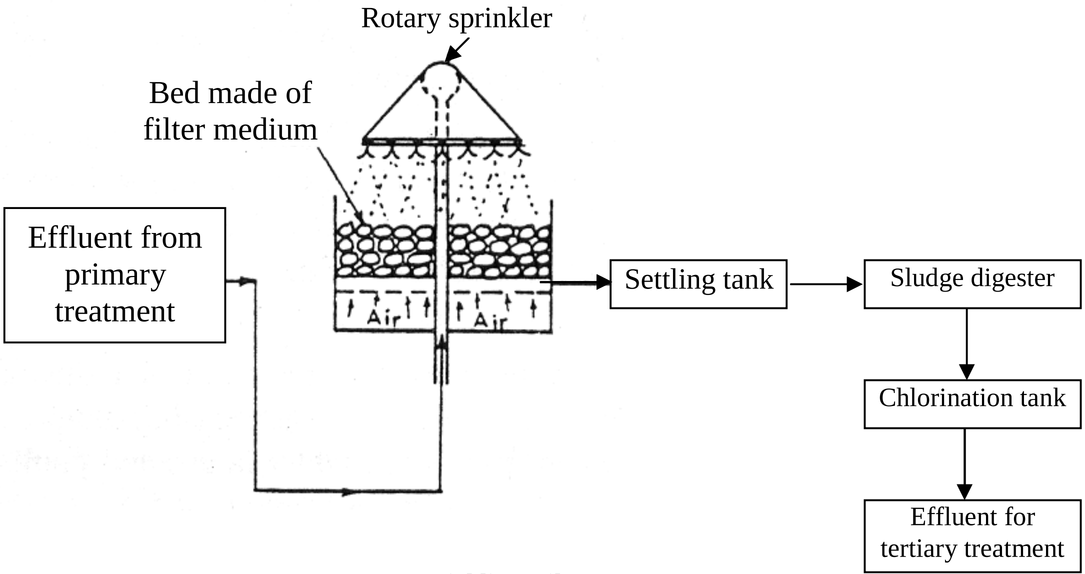
1. Large space is required
2. There is scope for bacterial contamination of lagoon effluent and hence frequent purification is needed.

2. Trickling Filters:

The trickling filters usually consists of circular or rectangular beds, 1m to 3m deep, made of well-graded media (such as broken stones, PVC, coal, coke, synthetic resins, gravel or clinkers) of size 40mm to 150mm, over which wastewater is sprinkled uniformly on the entire bed with the help of a slowly rotating distributor (such as rotatory sprinkler) equipped with orifices or nozzles. Thus, the wastewater trickles through the media. The filter is arranged in such a fashion that air can enter at the bottom, counter current to the effluent flow and natural drift is produced.

A gelatinous film, comprising of bacteria and aerobic micro organisms known as '*zooglea*' is formed on the surface of the filter medium, which thrive on the nutrients supplied by the sewage or the wastewater. The organic impurities in the wastewater are adsorbed on the gelatinous film during its passage and then are oxidised by the bacteria and the other micro- organisms present there in. When the thickness of the film on the medium increases, a part of it gets detached and carried away along with the effluent. Hence, the effluent from the trickling filters is allowed to settle in a settling tank to retain the sludge particles and is then discharged. The sludge is then pumped to the sludge digestion unit.

A schematic diagram of a typical trickling filtration process is given below.



Trickling Filter

Although trickling filtration is classified as an aerobic process, it is indeed a facultative system. Aerobic bacterial species (ex., spore forming bacteria) are mostly present in the upper layer of the filter, where as anaerobic species, such as Desupho vibrio are present in the interfaces of the stones.

The microbial film formed is very sensitive to temperature. The metabolic activity is proportional to the temperature of the wastewater passing through the filter. Thus, the efficiency of the filter decreases in the winter season.

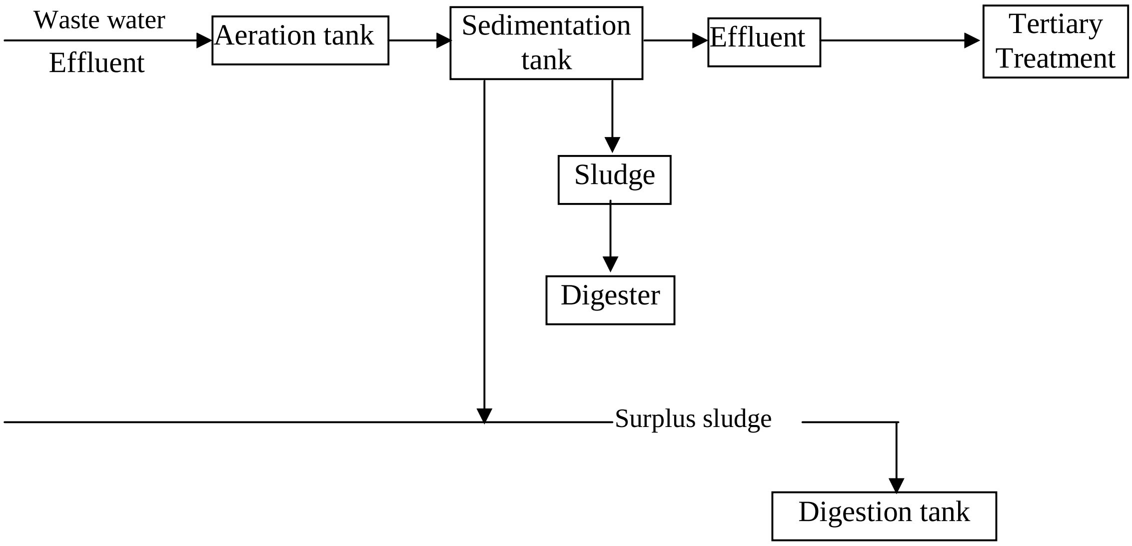
The efficiency of BOD removal level is 65-85%, depending upon rate of filtration.

Disadvantage:

The disadvantage of the process include the cost of construction and the need for ventilation ducts for the under drain system. The efficiency decreases with increased loading of the wastewater. The problem can be overcome by diluting the effluent from the previous treatment. Trickling filters are effectively used for the treatment of industrial wastes from dairy, distillery, brewery, cannery, food processing, pulp and paper mills.

3. Activated Sludge Process:

This is the most versatile biological oxidation method employed for the treatment of wastewater containing dissolved solids, colloids and coarse solid organic matter. In this process, the sewage or the industrial wastewater is aerated in a reaction tank in which some microbial floc is suspended. The aerobic bacterial flora brings about biological degradation of the waste into CO_2 and H_2O, while consuming some organic matter from synthesising bacteria. The bacterial flora grows and remains suspended in the form of a floc, which is called activated sludge.



Activated Sludge

The effluent from the reaction tank is separated from the sludge by settling and is discharged. A part of the sludge is recycled to the same tank to provide an effective microbial population for a fresh treatment cycle. The surplus sludge is digested in a sludge digester along with sludge obtained from primary sedimentation. An efficient aeration for 3 to 6 hours is adequate for sewage, where as for industrial wastes 6 to 24 hours of aeration is required for this process. BOD removal to the extent of 90-95% can be achieved.

The microbial flocs formed in this process compromise of Zoogleal masses of living organisms, embedded with their food and slime material and act as active centre for biological oxidation and that is why it is called 'Activation Sludge'.

Activated sludge process was used satisfactorily for the treatment of effluents from food processing, sugar, textile processing, antibiotic manufacturing industries etc.

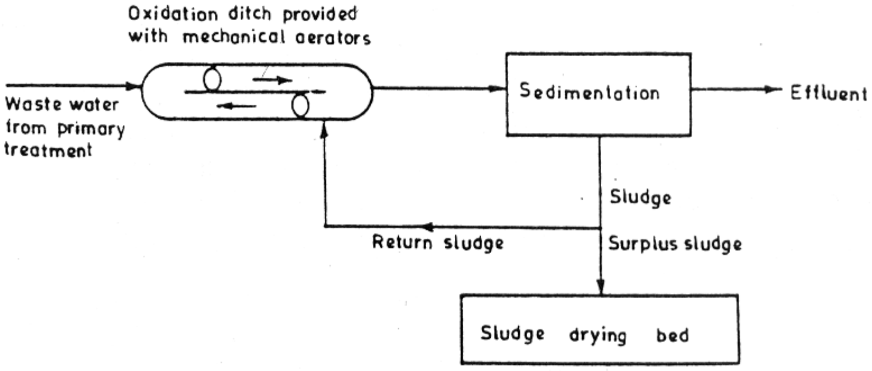
4. Oxidation Ditch:

The oxidation ditch can be considered as the modification of the conventional activated sludge process. Oxidation ditch usually consists of an oval shaped continuous channel, about 1 to 2mm deep and lined with plastic or butyl rubber. Wastewater after screening in the primary treatment is allowed into the oxidation ditch. The mixed liquor containing the sludge solids (MLSS) is aerated in the channel with the help of mechanical rotors. Longer retention times are needed. Most of the sludge formed is recycled for the subsequent treatment cycle.

Advantage:

The major advantages of the oxidation ditch include simplicity in operation, easy maintenance, low cost of construction, operation and maintenance, over all efficiency and flexibility. This process is generally used for waste having low BOD.

Oxidation ditch process is used effectively for the treatment of wastewater from beet- sugar manufacture, vegetable and fruit canning industry, slaughterhouse and meat packing industry.



Schematic representation of oxidation Ditch Process

5. Oxidation Pond:

Oxidation pond is large shallow pond (0.5 – 1.5M depth) with arrangements to measure the inflow and out flow. Stabilisation of organic matter in the waste is brought about mostly by bacteria, such as Pseudomonas, Flavobacterium, Alcaligens, to some extent by flagellated protozoa.

Algae present in the pond provide the oxygen requirement for the metabolism. The algae in turn utilise CO_2 released by the bacteria for their photosynthesis. The oxidation ponds are also called as waste stabilisation ponds.

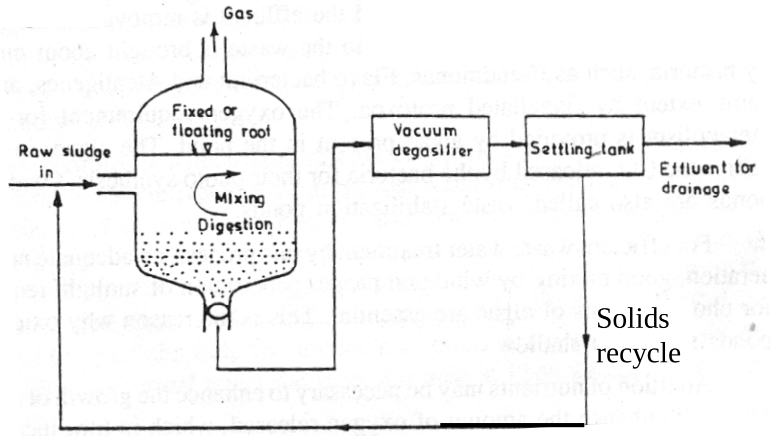
Addition of nutrients may be necessary to enhance the growth of algae. This will enhance the amount of oxygen released, which in turn increases the rate of purification of wastewater. Any deficiency of oxygen may lead to anaerobic conditions and consequent release of bad odours due to putrefaction of wastes. This is the reason why mechanical aeration is also provided at some places in addition to natural aeration.

Although wastewater treatment in oxidation ponds is generally considered as an aerobic process, the purification is performed by a combination of aerobic, facultative, and anaerobic processes. The wastewater present in upper part of the pond (which constitutes the major portion of the waste) undergoes aerobic oxidation to carbondioxide and water. Solids present in the waste, which settle as a layer at the bottom, act as anaerobic phase. Here the organic mater is oxidised by anaerobic bacteria to methane, carbondioxide and ammonia. The facultative zone exists near the anaerobic phase.

Treatment by this technique is cheap, its operation and maintenance is simple. The process can be used for all types of wastes and any degree of purification can be obtained. The heavy metal ions present in waste water are precipitated as hydroxides (due to the high pH of the waste in the oxidation pond) which settle as sludge. However, oxidation ponds require large space. The effluent from the oxidation ponds may require disinfections or further treatment in a separate maturation pond before final discharge.

ANAEROBIC DIGESTION:

This treatment is mainly used for sludge digestion. Sludge is the watery residue from the primary sedimentation tank and humus tank (from secondary treatment). The constituents of the sludge under go slow fermentation or digestion by anaerobic bacteria in a sludge digester, where in the sludge is maintained at a temperature of 35^0C at pH 7–8 for about 30 days. Methane, carbondioxide and some ammonia are liberated as the end products. The schematic representation of the anaerobic sludge digestion process is shown below



Species of pseudomonas, Flavo bacterium, Aerobactor, Alcalagenes etc., converts complex organic compounds to low molecular weight organic acids and alcohols. Methanobacterium, Methanosarcina and Methasnococcus types of bacteria are responsible for the generation of methane in this process. Desulpho vibrio bacteria reduce sulphates to sulphides and thus, hydrogen sulphide is released. The anaerobic digestion process can be accelerated at higher temperatures.

Advantages of anaerobic digestion process:

1. Reduction in volume of the waste by about 65%.
2. The digested sludge is safer to be used as manure than the undigested sludge.
3. The digester gas obtained has the following percentage composition by volume:

CH_4 – 65 to 80%
CO_2 – 5 to 30%
N_2, H_2, H_2S and CO together about 5%

About 0.6 to 1.25m^3 of the gas is produced per Kg of the organic matter destroyed. The gas can therefore be used as a fuel to provide the heat required to warm the digestion tanks.

4. The gas can be used for power generation.

Liquid wastes containing soluble organics from dairy, slaughter house and paper mill industries have been economically and effectively treated by this process.

III. TERTIARY TREATMENT:

Tertiary treatment is the final treatment, meant for “polishing” the effluents from the secondary treatment process, to improve its quality further. The major objectives of the tertiary treatment are

1. Removal of fine suspended solid.
2. Removal of bacteria
3. Removal of dissolved inorganic solids
4. Removal of final traces of organics

Removal of finely divided suspended solids can be achieved with the help of micro-strainers and sand filters. Removal of bacteria, particularly of faecal origin, can be achieved by retaining the effluents from secondary biological treatment plants in maturation ponds or lagoons for specified periods of time. The final effluent is chlorinated if necessary. Removal of dissolved inorganic solids is a major problem with wastewaters from industries such as fertilizers, textile processing, tannery and electroplating.

Depending upon the required quality of the final effluent and the cost of treatment that can be afforded in a given situation, any of the following treatment methods can be employed.

1. Evaporation
2. Ion Exchange
3. Adsorption

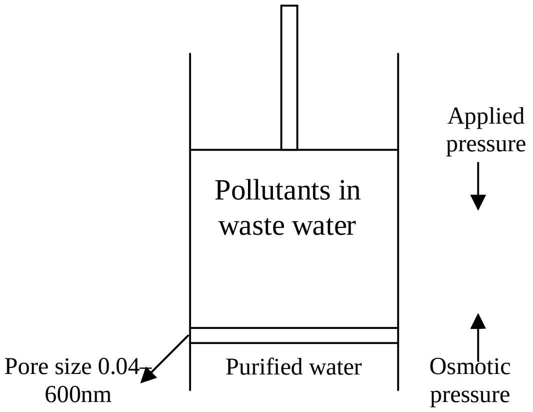
1. Evaporation

This is an energy intensive and hence an expensive process. It is used only when the recovered solids or the concentrated solutions are reused, ex., some electro plating wastes. This method is also used when the volume of the wastewater to be treated is less. This method is also employed when concentrating radioactive liquid wastes. It permits the recovery of a wide variety of process chemicals. It is applicable to remove or concentrate chemicals, which cannot be accomplished by any other means.

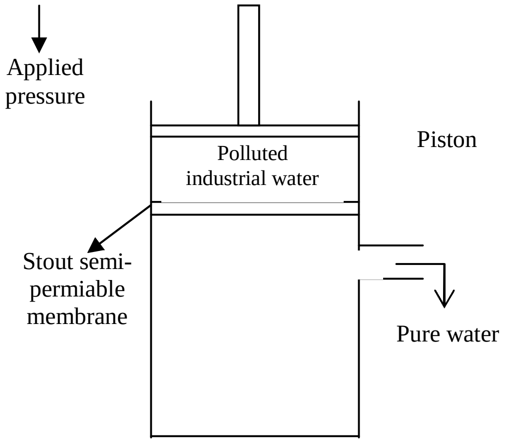
2. Ion Exchange:

Ion exchange membrane finds an important application in the removal of toxic wastes by ultra filtration and reverse osmosis.

Ultra filtration: In Ultra filtration, the solution is passed under pressure through a membrane which contain pores of size 2 to 10,000nm (20 x 10^5 A^0), where by big molecules are retained and effluent that passes is free of large molecules.



Ultra filtration



Reverse Osmosis

Reverse osmosis: In reverse osmosis the membrane pores are smaller to 0.04 to 600nm in size. Both these techniques have found extensive application in purification of industrial wastewater in textile, paper mills.

3. Adsorption:

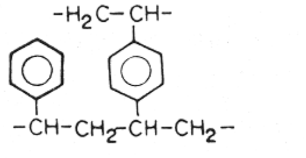
Activated Charcoal Method:

Adsorption by activated carbon is advantageous to remove small quantities of organic contaminants from wastewater. Special adsorbents are commercially available for the removal and retrieval of toxic heavy metal ions from industrial wastewaters. Activated carbon treatment is particularly useful for the removal of pesticides (e.g., DDT) and carbamate insecticides.

The equipment consists of a

1. Long tube with an inlet and out let mechanism
2. The middle portion with an activated charcoal on other hand we can use a synthetic resin.

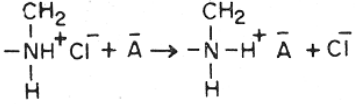
The most commonly used resins are



Styrene–divinylbenzene matrix

$-CO\bar{O}H^{+} + M^{+} \rightleftharpoons CO\bar{O}M^{+} + H^{+}$

Cation exchange resin



$-\underset{\underset{H}{|}}{\overset{\overset{CH_2}{|}}{N}}H^{+}\bar{Cl} + \bar{A} \rightarrow -\underset{\underset{H}{|}}{\overset{\overset{CH_2}{|}}{N}}-H^{+}\bar{A} + \bar{Cl}$

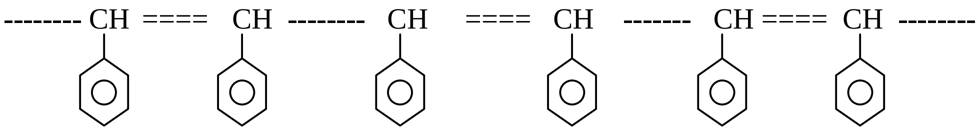
Secondary Amine group Anion exchanger

Filtering industrial wastes by synthetic resin:

Synthetic organic ion exchange resins are essential for removal of industrial waste chemicals. Styrene and divinyl benzene followed by chloromethylation gives anionic exchange resins.

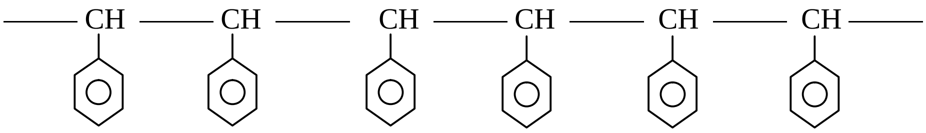
The most commonly used resins are

Styrene



When polymerisation occurs, the double bonds disappears

Polystyrene



The polystyrene when cross-linked with another organic molecule such as divinyl benzene (DVB). A widely used cation exchanger resin is obtained by co-polymerisation of styrene and a small portion of DVB followed by sulphonation. A widely used anion exchanger resin is prepared by co-polymerisation of styrene and a little of DVB followed by interaction by chloromethylation and interaction with base such as trimethyl amine $(CH_3)_3N$.

The activated charcoal with a large surface area is a quite effective filter bed for adsorption of various organic compounds. In this process about 99% reduction with the concentration of several chlorinated hydrocarbons in an effluent system is achieved.

UNIT 4

PURIFICATION OF RAW WATER - A

Lesson 3

Objectives of the lesson: This lesson deals with study of types of water treatment processes.

PURIFICATION OF RAW WATER:

COAGULANTS:

For effective removal of impurities from water it becomes essential that these have first flocculated, that is, have been in a form that could be removed readily by filtration methods. The aim was to obtain particles in excess of 120 microns in diameter; these tend to settle readily in typical aqueous medium. Particles between about 3 and 100 microns tend to settle too slowly for practical purposes.

Flocculation seeks to achieve agglomeration of small particles into larger units and there by speed up the settling process. The most widely used flocculating agent has been alum, a complex salt of aluminium. When this has been added to an alkaline solution a voluminous aluminium hydroxide flocculate has been produced, which readily sinks to the bottom because it has been heavier than water. In its passage downwards it traps tiny particles suspended in the water and thus removes them.

A recent development has been the use of a number of synthetic and natural polymers. These form bridges between adjacent solid particles and cause them to sediment. In many instances polymer sedimentation has been not as effective as alum, because small particles, particularly those with a diameter below 2 microns, tend to possess (usually negative) electric charge. Alum is able to dissipate this charge through the presence of positively charged aluminium ions in solution. However, metal salts have been not without their disadvantages. They are expensive, sometimes give inadequate flocculation and may also leave a ‘carry-over’ of fine turbidity.

Special synthetic polymers are being manufactured which are having the properties of bridging and discharge of electrical potential. Only water-soluble monomer polymer systems can be used for wastewater clarification. The following polyelectrolytes have been used.

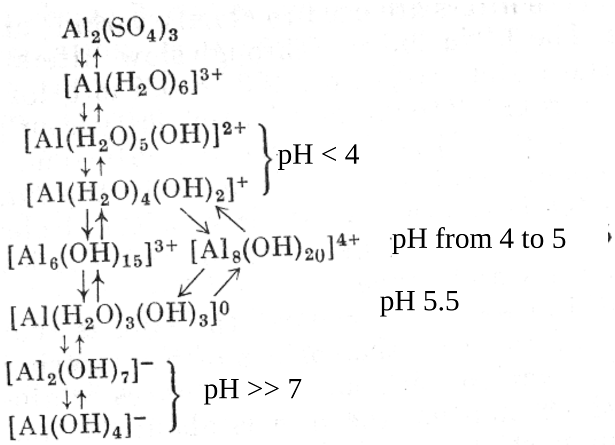
(a) Non-ionic types: Polyols, polyethers, polyamides, polyvinyl heterocyclics;
(b) Anionic groups: Carboxylates, sulphonates, phosphonates;
(c) Cationic groups: Amines, quaternary ammonium compounds, sulphonium and phosphonium compounds.

The most common of all flocculants have been the polyacrylamides, which are having molecular weights in the range 4-10 million.

Example:

Fine disperse particles are removed from water by coagulation. This is mainly used to clarify and decolourise water. Natural waters are polluted with humans, clay, silica etc. Particles of these substances bear a negative charge. They are removed by coagulation with salts of weak bases and strong acids. The coagulants enter into an exchange reaction with the water ions to form complex coordinated compounds. Aluminium sulphate is normally used for this purpose. The hydrolysis of this reagent gives complex ions, whose charge depends on the pH of the medium.

The following diagram illustrates the products of hydrolysis of $Al_2(SO_4)_3$ in order of the increase in pH of the medium.



The optimum dose is the lowest concentration of a coagulant giving the maximum clarifying effect.

Contact coagulation:

It is a process based on the ability of small particles to adsorb on large particles of sand or suspending precipitate through which water is filtered.

Intensifying the coagulation process:

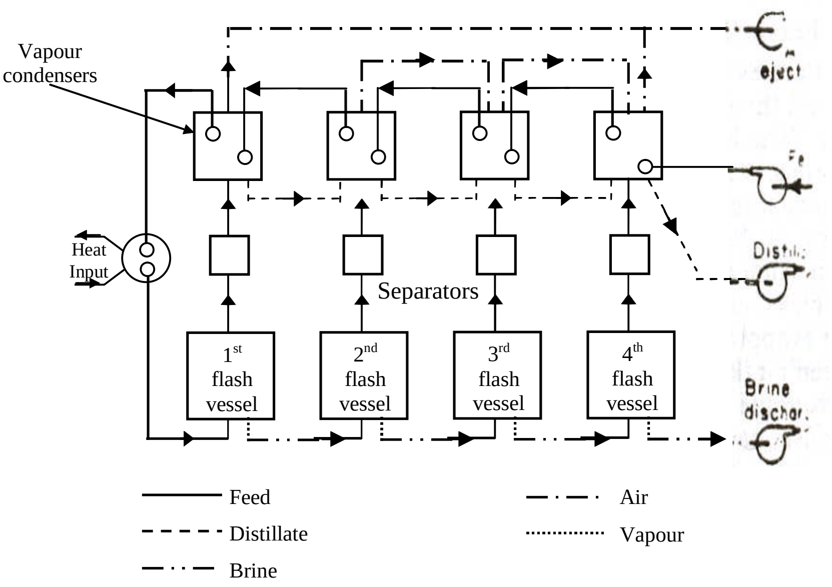
The coagulation process can be intensified by adding special agents known as flocculants. These are substances forming colloidal disperse system with water.

FLASH DISTILLATION:

Pure evaporation of seawater and other brackish water has been still the most widely used of all methods to recover the pure water. The heat needed to boil a kilogram (litre) of pure water at 100^0C has been nearly 2.27 MJ; but the heat needed to boil concentrated solutions of salts is greater as the presence of the salts elevates the boiling point. The main economy of the process has been dependent upon obtaining adequate heat economy.

This could be mainly achieved in two ways. First, solutions can be evaporated at lower pressure when the latent heat needed has been markedly reduced; and second, attempts can be made to use low grade waste heat for the process, especially using waste fuels like refuse, petroleum tail gases etc., for operating sea water distillation plants. There has been a considerable future in the operation of seawater desalination plants, which use distillation on the total energy principle. The most commonly used process employing distillation as a basis has been flash distillation.

Flash distillation is a technique involving of allowing the seawater to boil successively in a large number of chambers, each of which has been maintained at a lower pressure than the one before, to match the lower temperature of the water. The method of flash distillation of seawater has been especially promising when related to the use of waste heat produced in nuclear power stations. It has been feasible to design a nuclear power station, operating on the total energy principle, to produce 400MW of electricity and 283,000 m^3 of fresh water per day.



Layout of a multi-effect flash illustration using waste heat

Operating cycles of a flash evaporator:

The flash evaporator is having twenty to fifty chambers in sequence, which are operating at successive lower pressures. When heated brine flows from one chamber to the next, some of it ‘flashes’ off into water vapour, which then condenses on colder condenser tubes and drops as distillate into trays to be led away into storage.

The brine, when passing from chamber to chamber, gets progressively cooler and it has been this same brine which is eventually pumped back through the condenser tubes to act as the coolant in the condenser section of each chamber. It becomes progressively hotter as it does this; consequently, when it reaches the heat input section before re-entering the first flash chamber, its temperature need only be raised a few degrees. The heat would be normally supplied by low-pressure steam which, in its turn, has been readily obtained by utilization of waste heat from primary power generating sources.

As can be seen from figure the heated brine has been passing from the heat input section to the first flash chamber (1) and from there successively through all the chambers down to the coolest one (6), flashing off a certain amount of water vapour at each stage. It could be then extracted by the brine circulator pump and returned to the tubes of the heat recovery section at (4). In the last few stages the heat rejection section (5) and (6) cold crude seawater has been pumped through the tubes.

This allows condensation to occur in these stages and also extracts an amount of heat equal to that put into the evaporator at the heat input section, thereby allowing permitting a continuous cycle of operation. Some of the seawater, after chemical treatment to disallow scale formation, is added to the circulating brine to make up for the distillate extracted and for brine which must be discarded in order to keep the solute concentration in the evaporator within specific limits.

When seawater has been heated gases such as oxygen and carbondioxide are given off. These could be extracted by a vacuum pump or ejector system. The heat needed in a flash evaporator to produce unit weight of distillate has been given by the following equation;

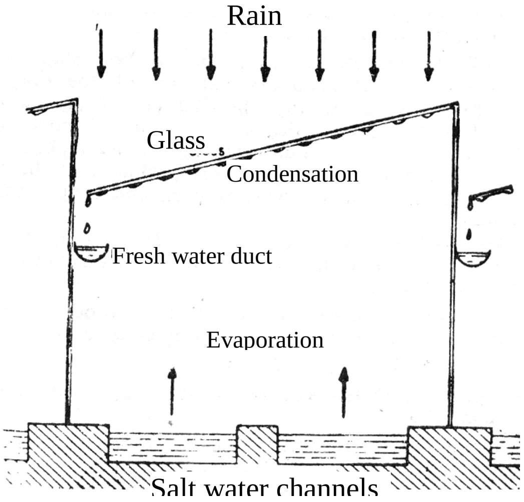
$$(t_e - t_1) / (t_e - t_f) = L$$

Where t_e represents the temperature of the water entering the flash stage in ^{0}C
t_l represent the temperature of the water leaving the tube system in ^{0}C
t_f represents the temperature of the water leaving the first flash stage in ^{0}C

L represents the latent heat of flashed vapour in KJ/Kg. Capital costs for typical evaporator plants have been found to depend upon the operating efficiency. Low-efficiency plants are having a $(t_e - t_1) / (t_e - t_f)$ ratio of 0.25, while the ratio for high efficiency plants has been of the order of 0.1or less. Thus low-efficiency plants are having fuel consumption, which has been 2 ½ times as high as that of high-efficiency plants.

SOLAR STILLS:

These methods have been likely to gain importance in areas of the world where fuel is scarce but there is adequate heat from the sun. A system developed in India uses a large area of glass positioned between 30 and 60cm above the surface painted black, along which seawater is allowed to flow. Solar heat makes water to evaporate, leaving the salt behind, and condensation takes place on the glass cover. The water drips off to an aluminium channel and runs to a storage vessel. The unit has been also equipped to collect rainwater. Distilled water from each m^2 of still surface erected, is about 18p for m^2.



Use of solar energy for desalination of salt water.
The large 'greenhouses' are also used for the collection of rain water.

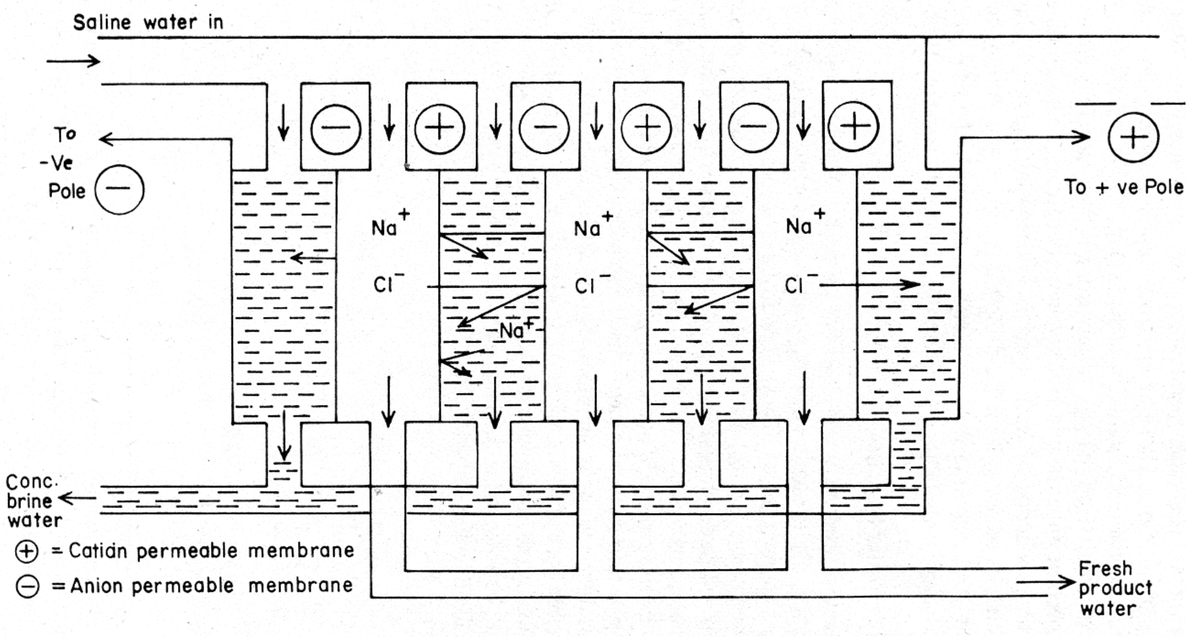
A large solar distillation plant was built near Daytona Beach, Florida. The feed water is having 3.2 percent dissolved salts and the area of land covered is $220m^2$. Each unit is consisting of grooved concrete curbs laid 1m apart to form a bay 20m in length.

There have been plastic basin liners and clear plastic cover domes. Underneath the brine has been a thick layer of insulation, so that the heat generated inside the still has been not conducted away to the soil. Water evaporates from the feed water and condenses against the plastic dome cover, running down towards galvanized steel distillate troughs at the sides of the stills. Solar stills, based on similar designs to the above, are also erected in Greece and Spain.

ELECTRODIALYSIS:

This is a process in which colloidal or dissolved species are exchanged between two liquids through selective ion exchange membrane. An emf brings about the separation of the species according to the charge.

In contrast to the reverse osmosis process electrodialysis employs the removal of solute from the solution rather than the removal of solvent. In this process use is made of selective permeable membrane and an electrical potential difference to extract ions from solution. The figure shows a simple electrodialysis cell in which wastewater may be deionised.



Schematic drawing of electrodialysis cell for producing fresh water from sea water

The cell contains membranes with fixed charges, where by the membranes become impermeable to the opposite ions. The technique is useful for the production of fresh arid and coastal region and is a principle source of salt production in some countries (Japan) from seawater.

Two types of membranes (anionic and cationic) are arranged alternatively to form many compartments between the two electrodes. Voltage is applied across the cell containing the raw water / mineral water. The electrical power required is proportional to the ions removed from water. The process does not require any chemical additives and require low energy and as such it is economical.

Disadvantages:

1. In electro dialysis organic molecules are not removed and will be collected and clotted on the membranes.
2. It still leaves concentrated waste material (brine) to be disposed off by appropriate scheme.

Applications of Electodialysis:

1. Concentration of rinse water to the desired bath strength.
2. Removal of Cu, Zn, Ni, chromic acid, fluoride, cyanide from process water.
3. Recovery of chromium from automobile plating rinse baths.
4. Recovery of valuable metals and radioactive elements.
5. Control of water pollution.
6. Desalination of water.
7. Demineralisation of sugars.
8. Glass etching and battery manufacturing units.
9. In pharmaceutical, medicinal and photographic industries.

UNIT 4

PURIFICATION OF RAW WATER - B

Lesson 4

Objectives of the lesson: This lesson deals with techniques for purification of water like ion exchange, reverse osmosis besides disinfection of water.

ION EXCHANGE

Introduction

According to the observations of Thomson and Way ammonia was adsorbed by soils and calcium oxide is liberated, thus soil is the medium and equal amounts of calcium oxide is being liberated (i.e., is equal to the ammonia absorbed, because of this reason lime deposits are seen in earth). The exchange involves equal quantities of ions and differs from true physical adsorption. A number of common clays, soils, minerals particularly zeolite and synthetic zeolites are known to exhibit ion exchange characteristics.

Definition:

The term ion exchange generally means the exchange of ions of like sign between a solution and a solid highly insoluble body in contact with it. Many substances both natural and artificial have ion exchanging properties.

All ion exchangers have several properties in common

1. They are almost insoluble in water and inorganic solvents.
2. The ion exchange is complex polymeric in nature.
3. The nature of an ionic solid, that the constituent particles of crystalline lattice are ions but not molecules.
4. The crystalline lattice has a core either anionic or cationic in nature with a loosely bound cation or anion (counter ion or active ion).

$$\text{Core Cationic)}^{+}\ \text{Cl}^{-} \qquad \textbf{OR} \qquad \text{Anionic Core)}^{-}\ \text{Na}^{+}$$

5. These active or counter ions are the ions that will exchange reversibly with other ions in a surrounding solution with out any appreciable physical change occurring in the material.

6. The polymer carries an electric charge that is exactly neutralised by the charges on the counter ions. These active ions are cations in cation exchangers anions in anion exchanger. Thus a cation exchanger consists of a polymeric anion and active cation while an anion exchanger consists of a polymeric cation and active anion.

A cation – exchanger resin is defined as a high molecular weight cross linked polymer containing sulphonic, carboxylic, phenolic etc., as groups as an integral part of the resin and an equivalent amount of cations (active ions).

Anionic exchange resin is a polymer containing amine groups as an integral part of the polymer lattice and an equivalent amount of anions such as chloride, hydroxyl or sulphate ions as active ions.

Examples:

1. Sulphonic acid is a strong acid cation exchange resin

$$\text{Resin) } SO_3H^+ + Na^+ \longrightarrow \text{Resin) } SO_3Na^+ + H^+$$

2. Strong base anion exchange resin:
   A cross linked polystyrene containing quaternary ammonium groups are largely ionised in both the hydroxide and salt forms.

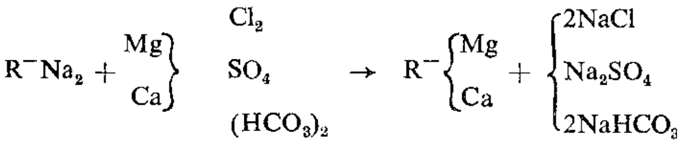
$$2\,(\text{Res.N } \overset{+}{Me_3})Cl^- + SO_4^- \longrightarrow 2(\text{Res.N } \overset{+}{Me_3})\, SO_4^- + 2Cl^-$$

$$2\,(\text{Res.N } \overset{+}{Me_3})OH^- + H^+Cl^- \longrightarrow 2(\text{Res.N } \overset{+}{Me_3})Cl^- + H_2O$$

Use of ion exchange in water treatment:

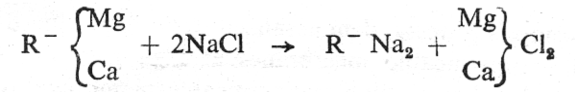
Ion exchange has been used extensively to remove hardness and iron and manganese salts from drinking water supplies. It has also been used to selectively remove specific impurities, and to recover valuable trace metals like chromium, copper, lead, cadmium and nickel from industrial waste discharges. The process takes advantage of the ability of certain natural and synthetic materials to exchange one of their ions with another contained in the water passing through them.

In the water softening process, the hardness producing elements such as calcium and magnesium are replaced by sodium ions. A cation resin operating on the sodium cycle is normally used. The typical exchange reaction is



$$R^-Na_2 + \left.\begin{matrix}Mg\\Ca\end{matrix}\right\} \begin{matrix}Cl_2\\SO_4\\(HCO_3)_2\end{matrix} \rightarrow R^-\left\{\begin{matrix}Mg\\Ca\end{matrix}\right. + \left\{\begin{matrix}2NaCl\\Na_2SO_4\\2NaHCO_3\end{matrix}\right.$$

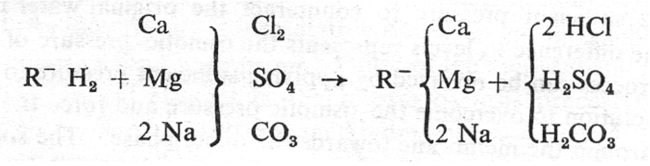
where R represents the solid phase of the exchange resin. The product water thus has high sodium content, which is not likely to be troublesome unless the original water is very hard. When the exchanger is saturated, it has to be regenerated to allow reuse of the expensive resin. Regeneration can be achieved using sodium chloride solution, which removes the calcium and magnesium ions in the form of their soluble chlorides and restores the resin to its original condition.



$$R^-\left\{\begin{matrix}Mg\\Ca\end{matrix}\right. + 2NaCl \rightarrow R^-Na_2 + \left.\begin{matrix}Mg\\Ca\end{matrix}\right\} Cl_2$$

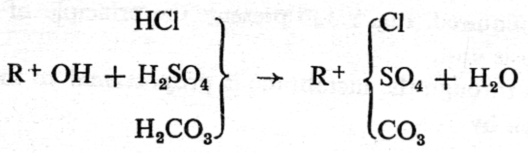
Demineralisation of wastewater is achieved in two steps (the cation and anion exchange steps). The positive ions such as Ca, Na, or Mg are removed in the cation exchanger using a hydrogen cycle.

A typical exchange reaction is



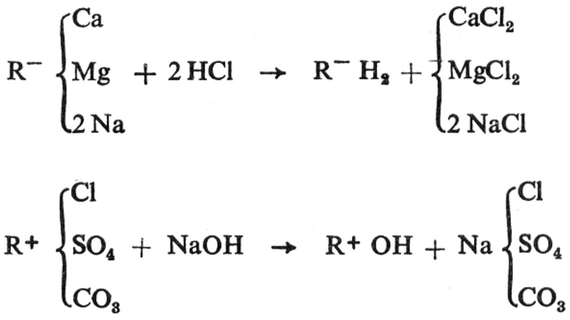
$$R^- H_2 + \left.\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\\ 2\,\mathrm{Na}\end{matrix}\right\} \begin{matrix}\mathrm{Cl_2}\\ \mathrm{SO_4}\\ \mathrm{CO_3}\end{matrix} \rightarrow R^- \left\{\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\\ 2\,\mathrm{Na}\end{matrix}\right. + \left\{\begin{matrix}2\,\mathrm{HCl}\\ \mathrm{H_2SO_4}\\ \mathrm{H_2CO_3}\end{matrix}\right.$$

In anion exchange step the negative ion such as Cl^-, SO_4^- or CO_3^{2-} are removed and demineralised water is produced.



$$R^+ OH + \left.\begin{matrix}\mathrm{HCl}\\ \mathrm{H_2SO_4}\\ \mathrm{H_2CO_3}\end{matrix}\right\} \rightarrow R^+ \left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{SO_4}\\ \mathrm{CO_3}\end{matrix}\right. + H_2O$$

The regeneration is done by treating the cation exchanger with a strong acid and the anion exchangers with caustic soda. The steps are



$$R^- \left\{\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\\ 2\,\mathrm{Na}\end{matrix}\right. + 2\,HCl \rightarrow R^- H_2 + \left\{\begin{matrix}\mathrm{CaCl_2}\\ \mathrm{MgCl_2}\\ 2\,\mathrm{NaCl}\end{matrix}\right.$$

$$R^+ \left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{SO_4}\\ \mathrm{CO_3}\end{matrix}\right. + NaOH \rightarrow R^+ OH + Na \left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{SO_4}\\ \mathrm{CO_3}\end{matrix}\right.$$

Suspended solids in wastewaters can clog the exchangers and cause operational problems. Hence, the feed water to the exchange should be free of suspended matter. Another serious problem is the resin binding caused by residual organic matter in the feed water. Although the ion exchange process is very effective and produces high quality effluents, the cost of this treatment is fairly high at present.

It has been successfully applied for the recovery of chromate from the wastewater in the pigment manufacturing. Resins are also available for particular applications and one natural zeolite, clinoptilolite seems to adsorb both phosphate and ammonium ions and may prove to be of great value in wastewater treatment.

REVERSE OSMOSIS

In the reverse osmosis process demineralised water is produced by forcing water through semi permeable membrane at high pressure. In ordinary osmosis, if a vessel is divided by a semipermeable membrane (one that is permeable to water and not to dissolved materials), and one compartment is filled with water and the other with concentrated salt solution. Water diffuses through the membrane towards the compartment containing salt solution until the difference in water levels on the two sides of the membrane creates sufficient pressure to counteract the original water flow (figure-a).

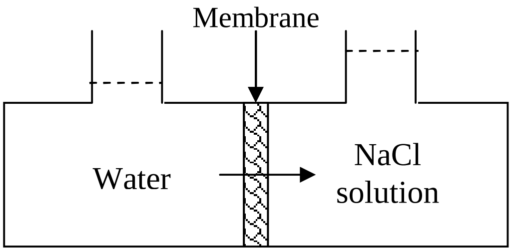


Fig-a: Osmosis

The difference in levels represents the osmotic pressure of the solution. The process can be reversed by applying sufficient pressure to the concentrated solution to overcome the osmotic pressure and force the net flow of water through the membrane towards the dilute phase. The solute concentration builds up on the one side of the membrane while relatively pure water passes through the membrane. In order to obtain an adequate solvent (water) flux through the membrane, pressure of the order of 4000 to 7000 KN/m^2 are required. Figure -b presents the principle of operation of reverse osmosis.

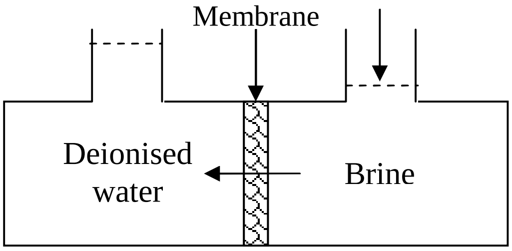


Fig-b: Reverse osmosis

The solvent flux through the membrane is proportional to the pressure gradient and is given by

$$F_m = W(\Delta P - \Delta P_O) \qquad \text{-----------} \quad (1)$$

F_m = Solvent flux through the membrane
W = Membrane coefficient
ΔP = Imposed pressure differential across the membrane
ΔP_O = Osmotic pressure differential across the membrane

In most cases, some amount of the solute passes through the membrane by molecular diffusion and its flux is given by

$$F_i = K_i \, \Delta C_i \qquad \text{-----------} \quad (2)$$

where F_i = Solute(impurity) flux through the membrane
K_i = Overall mass transfer coefficient that includes effects of membrane thickness
ΔC_i = Concentration difference between solutions across the membrane.

Equation 1 and 2 that the water flux is dependent upon the applied pressure, where as the soluble flux is not directly pressure dependent. As the pressure is increased, both the water flux and the degree of salt rejection tend to improve because of the constant solute flux.

The critical element in the reverse osmosis process is the permeable membrane. Some of the best membranes are cast from the mix of cellulose, acetate, acetone, formamide and magnesium perchlorate. In addition for its use to desalting, reverse osmosis has been satisfactorily applied to the separation of toxic ions from plating wastes, concentration of radioactive wastes and removal of organic from vegetables and animal wastes. Some fouling of membranes can be brought about by suspended and colloidal particles and hence pretreatment is necessary to remove these particles.

DISINFECTION OF WATER:

Coagulating and filtering water through sand purify it from suspended solids and partly decrease its bacteriological contamination. Complete disinfection is attained by chemical reagents which kill pathogenic microorganisms. Chlorine gas and chlorine compounds, such as chlorinated lime, chloramines, chlorine dioxide, hypochlorites, as well as ozone, and salts of heavy metals are effective against microorganisms. Ultra-violet radiation, ultrasound and other physical factors also kill pathogenic organisms. But the most common disinfecting agent used to treat water is chlorine and chlorine compounds.

Disinfection with Chlorine and Chlorine Compounds:

The disinfecting action of chlorine and its compounds depends on the oxidation-reduction processes occurring in microbial cells subjected to the influence of these chemicals. It is noticed that hypochlorous acid reacts with bacterial enzymes to interfere with the metabolism inside the cell. Free and bound active chlorine have different oxidation potentials; the reaction rate and the required contact time are also different. Hypochlorous acid is the most effective chlorine compound. The effectiveness of chlorine against microbes depends on the initial dose of chlorine, the residence time in the water, and the pH of the water. Chlorine is consumed to oxidize organic and mineral impurities in water. Chlorine is adsorbed on suspended matter, while microbes inside the doccules or large suspended particles remain intact.

Organic impurities in water are destroyed with chlorine. For example, humins are mineralized to CO_2, ferrous iron is oxidized to ferric iron, divalent manganese is oxidized to tetravalent manganese, and stable suspensions are converted into unstable ones due to the decomposition of the protective colloids. Sometimes, plant and animal organisms destroyed by chlorine in the water are converted into decay products with a strong odour. Chlorination of water containing phenols and other aromatic substances gives an especially unpleasant and stable odour. Smack and odour develop in water containing even very small quantities of phenols. They strengthen with time and do not disappear on heating. Large doses of chlorine are sometimes used to destroy aromatic compounds.

Chlorination is very important for the purification of fine disperse particles from water. It discolours water and provides good conditions for clarification and filtration. When dissolved in water, chlorine forms two acids, viz., hydrochloric and hypochlorous:

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

Hypochlorous acid is very week and its dissociation depends on the pH of the medium.

But chlorination does not ensure complete sterilization of water and single viable organisms remain in it.

Disinfection of Water by Iodine:

Water in swimming pools is iodinated. A saturated iodine solution in water is used. The concentration of the solution increases with temperature. For example, at 1^0 C the solubility of iodine in water is 100 mg per litre, at 20^0 C 300 mg/litre, and at 50^0 C 750 mg/litre.

At pH less than 7, the iodine dose for the disinfection of water from natural sources varies from 0.3 to 1 mg/litre. The odour of iodine cannot be smelled because it can be sensed only at concentrations over 1.5 mg/litre. If the water contains chloramines, iodic acid remains inactive till the moment when a strong oxidant is exhausted. This prolongs the time of the bactericidal action of iodic acid. Water can also be disinfected by organic iodine compounds, iodophores.

Ozonization of Water:

The bactericidal action of ozone has been known since late in the last century but it was only early in this century that ozone actually began to be used for treating water. In 1911, at that time the largest filtration station in the world was put into operation in St. Petersburg. Its capacity was 50,000 cubic metres of drinking water per day. World War One interfered with the normal work of this ozonizing unit; it was closed and drinking water was chlorinated instead. The high technological indicators given by ozonization offer good prospects for its practical use in the treatment of water.

Ozone is an allotropic modification of oxygen. Under normal conditions it is a bluish gas. When in the liquid state, ozone is dark blue and in the solid state, almost black. Its boiling point is minus 111° and melting point minus 250°C. It can be detonated in any state of aggregation. Its solubility in water is higher than that of oxygen. Small concentrations of ozone in the air are beneficial to man, especially in respiratory pathology. But ozone becomes harmful when concentrations reach relatively high levels. Prolonged exposure to ozone (in the air in a proportion of 1 : 1,000,000) causes irritability, headache and fatigue. At higher concentrations nausea, nasal bleeding, and inflammation of the eye mucosa develop. Chronic ozone poisoning results in serious illness.

The bactericidal action of ozone is associated with its high oxidation potential and the ease with which it passes through the cell membranes of microbes. Ozone oxidizes the organic substances in the microbe cell in order to kill it. Owing to its high oxidation potential (2.076 V), ozone has a stronger bactericidal action than chlorine (1.36 V). It works on bacteria more quickly and the amount of gas is less. Sporeforming bacteria are more resistant to ozone than nonsporeforming but they are resistant to chlorine as well. Ozone is detrimental to the hydrobios.

The dose of ozone required for water disinfection depends on the degree of pollution, but usually varies from 0.5 to 4.0 mg/litre. The consumption of ozone increases with water turbidity and higher doses are required for turbid waters. The disinfecting action of ozone almost does not depend on the temperature of the water. Ozonization not only decontaminates water but also gives it a pleasant taste, lowers its colour, and kills off odour produced by oxidation and mineralization of organic impurities. For example, humins are completely broken down by ozone to give carbon dioxide and water.

The ozonization of water has some advantages over chlorination:

(1) it improves the organoleptic properties of water and does not add to its chemical pollution;
(2) ozonization does not require additional processes to remove excess bactericidal agents from purified water (as is the case with dechlorination); hence higher doses of ozone can be used;
(3) ozone can be prepared in situ. Only electricity is required, and a single chemical reagent, silica gel, on which moisture is adsorbed from the air. In industry ozone is prepared by passing dry and clean air through an ozonizer under constant pressure, where it is subjected to an electric discharge. The ozonised air is then mixed with water in special chambers. Modern equipment is provided with bubblers and jet-ejectors.

Ozonization of water is not widely used because of the complexity of ozone manufacture and the large amounts of high frequency and high voltage electricity is required. Ozonization of water is also complicated by the fact that ozone is a corrosive agent. The gas and its aqueous solutions destroy steel, -cast iron, copper, rubber, and ebonite. All apparatus for the manufacture of ozone, and the pipes through which its solutions pass should be of stainless steel or aluminium. Stainless steel can withstand the corrosion for 15-20 years and aluminium for only 5-7 years.

Ozonization of water will be profitable only if a suitable material is found, electric energy is cheap, and the method of bringing water in contact with ozone is improved. Then ozonization will enjoy a wider use, especially in cases where, in addition to disinfection of water, its colour, taste and odour also need to be improved.

Disinfection of Water by Silver Ion (Oligodynamics):

The bactericidal action of silver has been known since time immemorial. Water and wine used to be kept in silver vessels in order to retain their quality over long periods of time.

There are a few hypotheses explaining the bactericidal action of silver. According to one of them, the silver ion interferes with the metabolism of bacteria and thus kills them. According to another hypothesis, the silver ion penetrates inside the microbial cell and destroys its protoplasm. There also exists an opinion that the silver ion is adsorbed on a microbial cell and acts like a catalyst to accelerate the oxidation of plasma by the oxygen of the air.

It is quite possible that all these factors are involved. What is indisputable is that chemical processes are mainly responsible for the disinfecting effect of silver on water. This opinion is confirmed by the fact that the efficiency of the disinfecting effect of the silver ion increases with the concentration of the ion and with the temperature of the water. The rate of a chemical reaction is known to accelerate with increasing concentration of the reactants and with increasing temperature. The higher temperature intensifies the dissociation of the silver salts and decreases the activation energy of the system. Take as an example a sample of water infected with E. coli bacteria. When the water is heated from 0 to to°C and treated with the silver ion for thirty minutes, the disinfecting effect increases four times, while with a rise in temperature to 42°C the same dose of the silver ion ensures the complete purification of the water from micro-organisms in an even shorter time.

Water can be disinfected with silver metal. The silver ion concentration grows if the contact surface increases. The electrochemical dissolution of silver (anodic dissolution) is used in water treatment. This method can be used to accurately control the silver dose and the disinfecting process.

The bactericidal action of silver is affected by the presence of various impurities in natural waters. They can bind the silver ion into complexes, adsorb it on suspended particles, and thus deteriorate the conditions for contact. For example, an increased chloride ion content of water can decrease the solubility of relatively insoluble salt AgCl. The disinfection of water by silver ions can thus be hindered by the presence of large quantities of chloride ions. When water from a new source is treated with silver, its dose should be established experimentally, since it depends on the salt composition of each particular water. Impurities contained in water often change the electrode potentials, due to the physico-chemical changes occurring at their surfaces (galvanic polarization) of the silver ion into the solution. Salts with oxygen-containing ions, such as SO_4^{2-} , also interfere with the electrolytic dissolution of silver. Other oxygen-containing anions, such as $P0_3^-$, CO_3^-, CrO_4^-, NO_2^- give sparingly soluble silver salts, which have the same effect on the electrodes as the chloride ion.

"Silver water" is prepared separately and then added to the treated water. This method is used to disinfect water in sanatoria, hospitals, on board ships, etc. This water can be used to can foods, to treat artesian and common wells, pipes, and also for medicinal purposes. The silver treatment of water is only effective in cases where the water does not contain much salt or suspended matter. Turbid waters are disinfected very slowly and the efficiency is low. Copper also possesses oligodynamic properties. If a body of water is overgrown with aquatic plants, copper ions in the form of a soluble salt $CuS0_4$ are used. Industrial water can be treated by electrolytic dissolution of copper.

Disinfection of Waste with Ultra-Violet Radiation:

The bactericidal action of ultra-violet radiation is explained by its effect on the protoplasm and the enzymes of microbial cells. Wavelengths from 200nm to 295nm have the strongest effect (this region of the spectrum is known as the bactericidal). The ultraviolet rays kill the vegetative forms of bacteria, spores, protozoa, and viruses.

The efficacy of the irradiation depends on the bactericidal energy, on the amount of suspended matter, on the quantity of microorganisms and their morphological and physiological properties, and on the optical density of the water (or its absorbing power). Bacteria are characterized by different resistivities to bactericidal energy. The criterion of bacterial resistance is the amount of energy required to stop the vital processes in the living microorganism in order to attain a given degree of water disinfection.

This is determined by the ratio of the final amount of bacteria P to the initial quantity P_o in a unit volume: P/Po. .

Three ultra-violet radiation levels are distinguished from the physiological standpoint:
(1) a dose which does not kill bacteria;
(2) a minimum bactericidal dose killing a large proportion of a given bacteria;
(3) a full bactericidal dose killing all the bacteria of a given species.

The minimum bactericidal dose (sub-bactericidal dose) of ultraviolet radiation stimulates the growth and propagation of species which would otherwise remain inactive. A longer irradiation kills the bacteria. For example, the study of typhus group cultures has shown that ultra-violet irradiation for 0.017 to 0.17 seconds increases the number of colonies ($P/P_o > 1$) up to 1.6 times. If the irradiation continues from 0.25 to 0.83 seconds, the relative number of colonies decreases ($P/P_o < 1$), in some cases to 0.2-0.3 of the initial level.

A five-second irradiation of objects kills all bacteria of some species. E. coli have the strongest resistance to UV rays of all typhus bacteria. Some of them are not killed even by a 5-second irradiation. E. coli can therefore be an indicator of the efficacy of the disinfection of water infected with pathogenic non-spore forming bacteria. If water contains stable spore forming bacteria (such as anthrax bacilli), the criterion for the irradiation dose should be resistance of spore forming bacteria least sensitive to ultra-violet radiation. Thus treated water does not change its physical or chemical properties. The taste of water also remains unchanged. The disadvantage of this method is the high cost and the possibility of subsequent in

Water Disinfection with Ultrasound:

Oscillations at frequencies over 20,000 Hz, not usually perceived by man, are called ultrasound. Ultrasound oscillations are obtained in industry by piezoelectrical and magnetostrictive methods. The former method is based on the piezoelectrical effect by which the crystals of some substances are mechanically deformed when placed in an electrical field and thus produce ultrasound. Quartz plates, cut from the crystal, are used as sources of ultrasonic frequencies. Plates of equal thickness and lapped to one another (as mosaics) and attached with adhesives between two thick steel plates to which an electric current is applied. Such a system is a powerful source of ultrasound.

The other method is based on the phenomenon of magnetostriction. Then ferromagnetic bodies are magnetized, they change their linear dimensions and volume. The magnitude and sign of the effect depend on the strength of the magnetic field and on the angle between the direction of the field and the crystal axis (for single crystals). The first method has proved to be of greater efficiency.

Ultrasound kills animal and plant cells, protozoa, and microorganisms. The destructive effect depends on the intensity of the ultrasonic waves and on the morphology of the object in question. The bactericidal action of ultrasound is connected with its ability to form minute cavities in water around objects, thus isolating them from the environment to produce around them a local pressure measured in tens of thousands of atmospheres, the phenomenon being known as ultrasonic cavitation. The sharp changes in the physical state of the liquid, occurring at the ultrasound frequency, destroy substances inside the ultrasound field. Bacteria are believed to be killed by the mechanical destruction of their cells by the ultrasound oscillations. The vital functions of the cells are disrupted mainly by the decomposition of the proteinous substances of the protoplasm. It has been established that ultrasound destroys larger organisms which are especially detrimental to the drinking and industrial water supply. These are organisms visible to the naked eye, such as the larvae of some insects (caddis flies, chironomids, may flies), oligochetes, some nematodes, sponges, Bryozoa, Dreissensia, leeches, etc. Some of them live in water treatment plants. Conditions permitting, they propagate .and inhibit large areas. All these organisms are killed by ultrasound. The fauna and flora of marine plankton are also killed by ultrasonic oscillations.
Laboratory experiments show that about 95 per cent of E. coli is killed by ultrasound in 1-2 minutes in thin layers of liquid. There are indications that ultrasound has a bactericidal effect 011 dysentery bacilli, typhus virus, etc. Milk can be sterilized by ultrasound.

Thermal disinfection of water:

The most common method of disinfecting water has been known from time immemorial. It is boiling. Small quantities of water are disinfected by boiling nowadays. Drinking water is boiled in public catering establishments, at hospitals, various institutions, etc. But the method is expensive, it requires large vessels for boiling, and is not therefore used even in minor water supply systems. Furthermore, the thermal method fails to kill spores, and water taken from dubious sources will not necessarily be disinfected by boiling.