

Analysis of major constituents in water

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Outline :

- * **Water Sampling and Storage**
- * **Water Quality Measurement**
- * **Oxygen demand**
- * **pH, Acidity and Alkalinity**

Water Sampling and Storage

- * The types of analysis could vary from:
 - * simple field testing for a **single** analyte
 - * laboratory based **multi component** instrumental analysis.
- * Due to varying period of time, storage conditions:
 - * to avoid undesirable losses
 - * contamination
 - * other changes that could affect the results of the analysis.

Water Sampling

- * The container materials **glass** or **polythene**.
- * Trace **metals** may be depleted by adsorption if stored in **glass** containers, while
- * **sodium, potassium, boron** and **silicates** can be leached from the **glass** into the sample solution.
- * Conversely sample solutions containing **organic** solvents and other organic liquids should be stored in **glass** containers because **organic** compounds may be leached from the walls of the **plastic** containers.
- * If **volatile** materials or dissolved **gases** are to be analysed, the container material must always be **full**.

Water Storage

- * For example samples to be analysed for **nitrate** should be stored at 4°C to minimise the biological degradation
- * samples to be analysed for **pesticides** should be stored in dark to avoid photochemical decomposition
- * samples to be analysed for **metal** ions should be acidified to prevent adsorption of metal ions on the sides of the container
- * samples to be analysed for **phenols** should be made alkaline with sodium hydroxide to lower the volatility.

Water Quality Measurement

- * **suspended solids**
- * **oxygen demand**
- * **total organic carbon**
- * **electrical conductivity**
- * **water hardness**

Determination of suspended solids

The main physical problem :

cut down **light** transmission through the water and so lower the rate of photosynthesis in plants.

It is one of the major parameters used to evaluate the strength of **domestic** waste waters and to determine the **efficiency** of treatment units.

Determination of suspended solids

- * Usually the sample size is limited to **50 ml** or less because of the difficulties encountered in **filtration** of larger samples.
- * The **weight** of solids removed exceed **20 mg** and is often **10 mg**.

Environmental significance of dissolved oxygen

- * **Dissolved oxygen** is the factor that determines whether the biological changes are brought about by **aerobic** or **anaerobic** organisms.
- * The **aerobic** use free **oxygen** for oxidation of organic and inorganic matter and produce innocuous end products,
- * whereas the **anaerobic** bring about such oxidations through reduction of certain inorganic salts such as sulphates, and the end products are often very obnoxious.

Environmental significance of dissolved oxygen

- * it is highly important that conditions favorable to the **aerobic** organisms (aerobic conditions) be maintained.
- * Thus **dissolved-oxygen** measurements are vital for maintaining **aerobic** conditions in natural waters that receive polytonal matter
and
in **aerobic** treatment process intended to purify domestic and industrial waste waters.

Environmental significance of dissolved oxygen

- * Water saturated with **oxygen** at 25°C contains 8.24 mg L⁻¹.
- * The material used **O₂** could be organic, as already discussed but could also be inorganic. For example iron in the form of Fe²⁺ can deplete oxygen by oxidation to Fe³⁺.

Measurement of dissolved oxygen

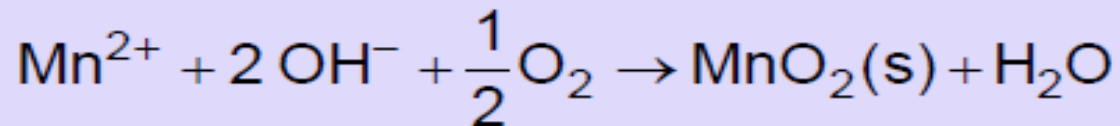
- * There are **two** distinctly different analyses which are useful to monitor environmental waters for **oxygen**:
- * **1-** the **oxygen** concentration in the sample (river sample) is measured **directly**. This result would give an indication of the health of the river **at a particular location and at the time of sampling**.
- * **2-** In the second analysis, the amount of material known as **oxygen** demand which, given time, could deplete the **oxygen** in the river is measured.

Measurement of dissolved oxygen

- * The **dissolved oxygen** can be determined either by the **Winkler (iodometric)** method or by the use of **dissolved oxygen electrodes**.
- * The concentration of **oxygen** in saturated water is dependent on:
 - * *Temperature*
 - * *pressure*
 - * *salinity of the water*

Winkler (iodometric) method

In the **Winkler's** method the dissolved **oxygen** is reacted with **Mn²⁺** immediately after sampling which is added in the form of **manganese sulphate**, together with an **alkaline iodide/ azide** mixture:

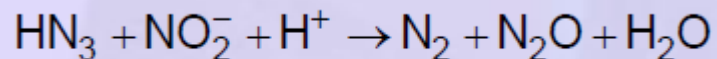
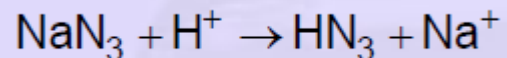
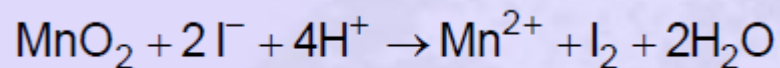


Winkler (iodometric) method

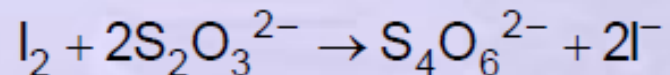
- * The **iodide** is necessary for the analytical procedure in the laboratory and the **azide** is present to prevent interference from any **nitrite** ions.
- * **Nitrite** ions oxidise I^- to free I_2 under acidic conditions that can lead to erroneous results.
- * **Nitrite** interference can be overcome by the use of **sodium azide** (NaN_3)

Winkler (iodometric) method

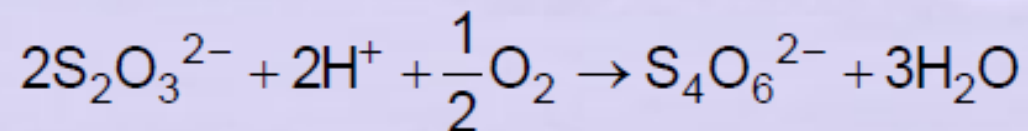
After transport to the laboratory, the sample is acidified which results in the reaction.



The released iodine can then be titrated with sodium using **starch** as indicator.



The overall reaction is

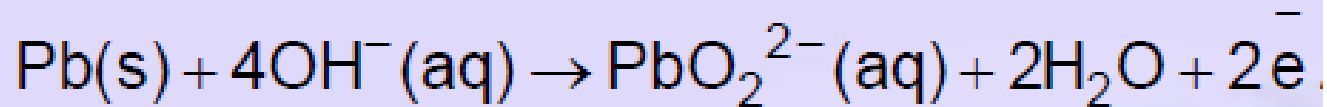


4 mole of **thiosulphate** in the final titration is equivalent to **1** mole of oxygen in the sample.

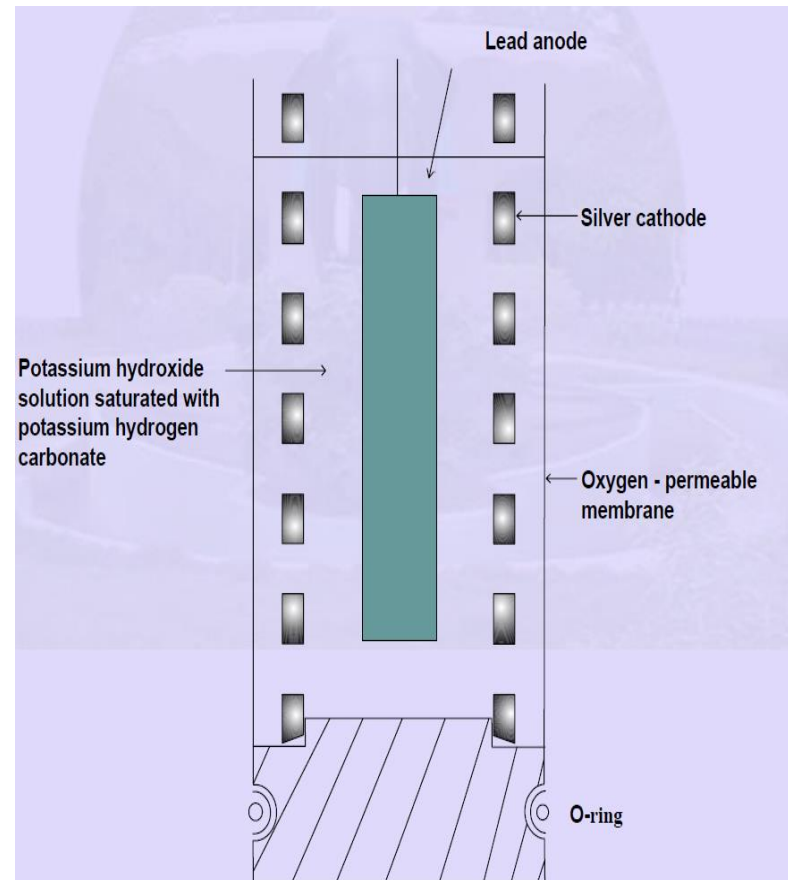
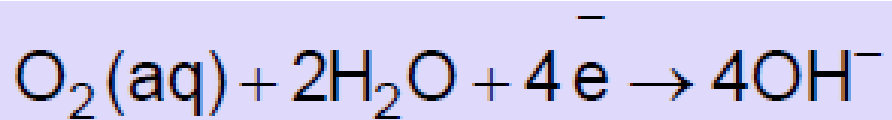
Oxygen Electrode method for dissolved oxygen measurement

The cell has a **lead** anode and a **silver** cathode set close together in an **alkaline solution**, often with **1M KOH**.

At the anode, the reaction is



A semipermeable membrane through which only oxygen can diffuse surrounds the electrodes, and then the reduction takes place.



Oxygen demand (OD)

- * Apart from rise in temperature, dissolved oxygen levels can be depleted by the biochemical breakdown of organic materials present in water.
- * The most widely used and accepted measure of biodegradable organic content of waste water is the 5-day, 20°C **BOD** value.

Measurement of biochemical oxygen demand (BOD)

- * Two **300ml** bottles are filled with water sample and dissolved oxygen of the first bottle is determined **immediately** by either of the methods already described.
- * The second bottle is **incubated** under 20°C (adjusted to pH between **6.5** and **8.5** in the **dark** under standard conditions) for **5 days** which are designed to be ideal to promote **microbial** activity and the dissolved oxygen is **once more** measured.
- * The difference between the **two** DO values is the amount of oxygen that is consumed by **microorganisms** during the **5 days** and is reported as **BOD⁵** (5-day BOD) value of the sample.

BOD values of effluents from some industries

Effluents from	BOD in mgl^{-1}
1. Domestic wastes	800-2000
2. Dairy Wastes	800-4000
3. Farm yard wastes	1500-3000
4. Paper pulp	3000-27,000
5. Pharmaceutical	800-10,000
6. Wool scouring	800-10,000

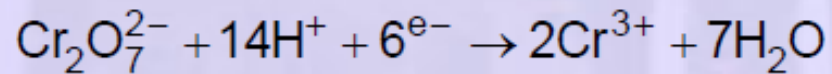
The advantage of **BOD** measurement is that it parallels the natural processes closely, although it is a lengthy measurement to complete.

Measurement of Chemical oxygen demand (COD)

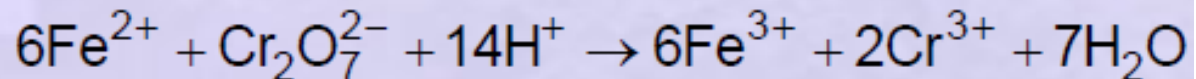
- * A sample of **waste water** containing organic material is mixed with an excess of **potassium dichromate** and **sulphuric acid** and the mixture is heated under total reflux conditions for a period of **two** hours.

Measurement of Chemical oxygen demand (COD)

During digestion, the chemically oxidisable organic material reduces a stoichiometrically equivalent amount of dichromate;



the remaining dichromate is titrated with standard ferrous ammonium sulphate solution



The amount of potassium dichromate reduced gives a measure of the amount of oxidisable organic material.

Measurement of Chemical oxygen demand (COD)

- * The **COD** test is much more **useful** than the **BOD** test for estimating the oxygen requirements of certain industrial wastewaters. It is valuable for wastes where **BOD** test is not applicable due to:
 - * the presence of **toxic** substances
 - * **low rate** of oxidation
- * **BOD** tests can be applied for long term monitoring of natural water and **COD** tests can be applied for rapid analysis of heavily polluted samples.

Measurement of total organic carbon (TOC)

- * This is done by quantitatively oxidising **all** the organic matter in the sample to **carbon dioxide**
- * The carbondioxide produced is measured either by **conductivity** after absorption in solution or by catalytic conversion to **methane** which is then passed to a flame ionisation detector (FID) as used in **gas chromatography**.
- * The **TOC** test can be performed in a relatively short period of time (few minutes) compared to **BOD** and **COD** measurements

pH, Acidity and Alkalinity

pH ranges for environmental waters

Type of water	pH range
Soft water	5.3-7.4
Hard water	7.6-8.8
Sea water	8.2-9.2
Water affected by acidic pollutants	2.2-4.8
pH of water in equilibrium with atmosphere	5.6

It should be noted that the unpolluted rain water is slightly acidic due to the presence of dissolved carbon dioxide (pH=5.6).

pH, Acidity and Alkalinity

- * The change of **pH** of fresh water to acidic condition has a profound biological effect on the aquatic organisms.
- * For example the population of salmon start to decrease below **pH 6.5**, perch below **6.0** and eels below **pH 5.5** with little life possible below **pH 5.0**.
- * Thus the eradication of life can result from a change of little more than **1 pH** unit.

Acidity

- * Traditionally standard **acidity** is measured by titration with standard **NaOH** to end point of **pH 3.7** or **8.3**.
- * The former is known as **methyl orange** acidity and the latter **phenolphthalein** acidity or total acidity.

Alkalinity

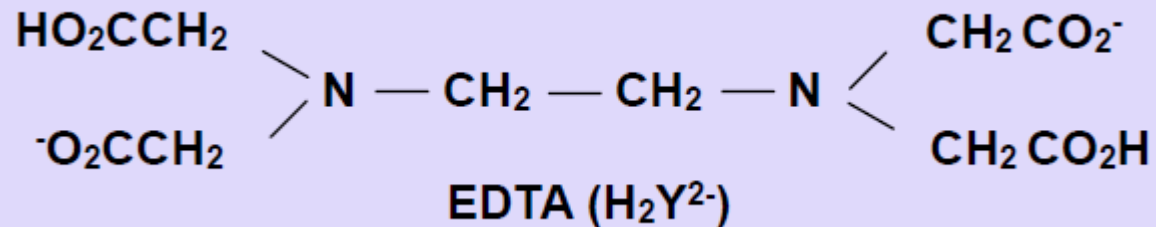
- * presence of **hydroxide, carbonate, and bicarbonate**
- * Weak bases such as **phosphates, silicates and borates**
- * **Alkalinity** is measured by titrating a measured volume of a sample of water against a standard acid solution to a designated end point usually **pH 8.3** (**phenolphthalein** alkalinity).

Determination of water hardness

- * The **hardness** in water is derived largely from contact with the **soil** and **rock** formations.
- * **Hard waters** originate in areas where top soil is thick and limestone formations are present.
- * **Soft waters** originate in areas where the top soil is thin and limestone formations are sparse or absent.

Determination of water hardness

Analysis is normally performed by **complexometric** titration using the disodium salt of ethylene diamine tetra acetic acid (**EDTA**).



The **total hardness** is conventionally expressed in **mg L⁻¹** units as **calcium carbonate**, even if it is due to calcium sulphate, magnesium carbonate or any other polyvalent metal salt.

Determination of water hardness

Assessment of water

mg l⁻¹(CaCO₃)	Assessment
0-50	soft
50-100	moderately soft
100-150	slightly hard
150-200	moderately hard
200-300	hard
>300	very hard

Total dissolved solids (TDS) by conductivity measurement

- * The units of conductivity applicable to environmental samples are $\mu\text{s cm}^{-1}$, a typical value of **200 $\mu\text{s cm}^{-1}$** being found for water with a substantial ionic salt content.
- * The general assumption that all ions having the same charge have approximately the same conductivity will not hold good in the case of environmental water samples. Since most environmental water samples contain ions with different charges in varying concentrations. However the following approximate equation gives the total concentration of salts with a reasonable accuracy.
- * Total salt concentration = $A \times \text{Conductivity (mg L}^{-1}\text{)}$ where A is a constant in the range 0.55 – 0.80.



END