

ANALYSIS OF WATER POLLUTANTS

The analysis of the most common industrial solvent water is extremely important as it contains a large number of impurities or pollutants which are necessary to be checked before the water is used for any specific purpose. For example, in municipal water, which is used for drinking purpose, it is most essential to determine colour, turbidity, dissolved solids, hardness, alkalinity or acidity, iron, manganese, fluoride, free chlorine etc. In addition, a complete mineral examination as well as bacteriological examination is also necessary.

Water analysis is usually expressed in **milligrams per litre** and in **parts per million (ppm)**, where

$$1 \text{ ppm} = \frac{\text{One part of substance}}{10^6 \text{ parts of water}} ; 1 \text{ ppm} = 1 \mu\text{g g}^{-1} \text{ and } 1 \text{ ppb} = 1 \text{ ng g}^{-1}; 10 \text{ ppb} = 1 \text{ ng}$$

Parts per million (ppm) means the number of parts of substance per million parts of water. This unit is also known as **milligram per litre (mg/litre)** or **grams per cubic metre**.

Analysis of water pollutants involves following examinations :

- (a) Chemical and physical examination of water.
- (b) Bacteriological examination.
- (c) Biological examination, and
- (d) Radiological examinations.

CHEMICAL AND PHYSICAL EXAMINATION OF WATER

For chemical and physical analysis of water, sufficient water samples (2-litres) are collected under different conditions. Sampling involves :

Sample container – Generally **glass container or stoppered Winchester quart bottle** of 2.5 litres capacity is used. When composite samples are to be collected, it is advisable to use wide mouthed bottles of capacity 200-300 mL for the subsamples.

Samplers – Point samplers, depth-integrating sampler and displacement samplers (for the determination of dissolved oxygen) are employed to meet the specific requirements.

Grab sample and composite sample- Liquid samples may be instantaneous, spot, snap grab samples and continuous or composite samples.

TAKING THE SAMPLE

When the liquid is **homogeneous**, it is better to take the **grab sample** in a bucket or sample bottle. In case of a **heterogeneous** liquid like sewage, a **composite sample** is taken.

Sampling potable waters – Sample of potable waters should be taken from a tap directly connected to the main line. If water from a well is to be collected, then the well has to be pumped for a long time so that the sample represents the ground water that feeds the well.

Sampling industrial effluents and waste waters- The sampling and analysis of industrial effluents require great care. It is therefore, advisable to study during sample collection, the character of effluents, the waste load, major sources of wastes within a plant, recovery of useful materials and the effect of discharged wastes on the receiving body of water. Industrial effluents are subjected to rapid changes due to breakdowns, spills, floor washings and numerous other causes. So suitable sampling points, the frequency and type of sample to be collected should be selected first. Generally, sampling points are located where flow conditions encourage a homogeneous mixture.

Sampling sewage- Sampling sewage involves the collection of grab samples in a bottle of capacity 1000 mL and combining them in a single container after 24 hour period.

Sampling near treatment plant- It requires sampling of the raw and treated water. For a water supply of constant composition, samples drawn at 8-hours intervals are collected.

Time interval between collection and analysis - **Generally, the shorter the time between collection and analysis, the more accurate will be the results.** Time interval depends upon the nature of the sample conditions of storage and the constituent to be analysed. Determinations like pH, dissolved gases such as oxygen, carbon dioxide and hydrogen sulphide can be made immediately while other constituents may be fixed and analysed in the laboratory.

PRESERVATION AND PRE-CONCENTRATION METHODS

There are number of **problems** which cause the analysis to be inaccurate.

For example, an anaerobic water sample may absorb oxygen from the atmosphere and thus soluble iron (II) and manganese (II) get oxidised to insoluble iron (III) and manganese (IV) compounds and these oxidation-reduction or redox reactions cause large errors in the actual analysis. Colour, odour and turbidity of the sample may change if the sample is kept for a long time. Na, SiO₂ and boron etc. may dissolve in the water sample from the walls of the containing glass vessel. Moreover, microbial activity may reduce phenol or chemical oxygen demand (COD), disrupts the NO₃⁻ – NO₂⁻ – NH₃ balance, or may even change the relative proportions of SO₄²⁻. The S²⁻, I⁻ and CN⁻ ions present in water may oxidise, while Cr(VI) may be precipitated as Cr(III) after getting reduced.

These problems can be greatly minimized or even reduced by making use of careful **preservation techniques**, which are equally as important as the collection of sample techniques.

Before preservation, it is also important to preconcentrate the collected samples because many of the water pollutants are largely diluted. Various **pre-concentration methods** have been used before the analysis. For example :

(1) **Carbon absorption method-** Absorption on activated charcoal is a common concentration technique, in which a large volume of collected water, say 1000 gallons, is allowed to pass over activated charcoal. The organic matter absorbed on activated carbon is extracted from the dried charcoal with CHCl_3 followed by alcohol. The solvents are evaporated and the weights of the extracts are expressed as $\mu\text{g/L}$ of **carbon-chloroform extract (CCE) and carbon-alcohol extract (CAE)**. Organic pollutants, such as phenols and oils, which impart tastes and odour to water are usually present in CCE. A large number of other organic compounds, such as phenols, fulvic acid, pesticides, polycyclic aromatic hydrocarbons, carboxylic acids, sulphonic acids etc. can be characterised from these extracts by making use of a number of separation techniques.

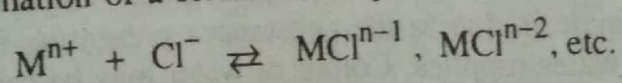
The carbon absorption method, though, widely been used due to its speed, efficiency and simplicity, but it has a number of **disadvantages**. For example,

- (a) *There is a possibility of a chemical reaction on the surface of activated charcoal.*
- (b) *During evaporation of solvents, some organic material may also evaporate.*
- (c) *Some organic compounds are not likely to be completely extracted from the water sample.*

(2) **Freeze concentration method-** In this process, the water sample is allowed to freeze, as a result of which pure crystals of ice are formed and water soluble impurities are left behind in the liquid phase of much reduced volume. The process of freezing also minimizes the loss of volatile constituents in the sample.

(3) **Solvent extraction method-** The liquid extraction, which is used in so many analytical separations, is a technique in which a substance dissolved in one phase (usually an aqueous phase) is more or less completely transferred to the second phase, essentially immiscible with the first, i.e., an organic liquid such as benzene, ether, chloroform etc. Thus in solvent extraction, organic matter soluble in water is separated by using a water insoluble organic solvent. When an organic substance is more soluble in an organic solvent than in water, it is possible to concentrate it in small amount of organic solvent by making use of the process of solvent extraction. Chlorinated pesticides have successfully been isolated in this manner. **Parts per billion (ppb)** amounts of various metals such as Co(II) , Fe(III) , Pb(II) , Zn(II) , Ni(II) , etc. in saline water can be determined by solvent extraction method in which metal complexes of these metals with ammonium pyrrolidine dithiocarbamate are first extracted with methyl isobutyl ketone solvent and then the resulting organic extract is analyzed by feeding into an **atomic absorption spectrophotometer**.

(4) **Ion exchange method-** Ion exchange chromatography has extensively been used for the concentration and separation of metal ions from natural and waste waters. The ions are first concentrated on a suitable ion exchange column and then selectively eluted. Many inorganic ligands, such as HF , HBr , HI , HNO_3 , H_2SO_4 , Na_2CO_3 and H_3PO_4 etc have been used as eluting agents for the separation of metal ions, but the one ligand that has widely been used is **chloride ion**, where HCl is used as a source of chloride ions. The reaction between a metal ion and chloride ion is a stepwise formation of a series of complexes.



In general, the metal ion is converted to an anion (metal chloro complex). The appropriate eluting conditions for placing each metal ion on the resin column can be determined by trial and error process and different HCl concentrations are used as the eluting agent. In this manner, it is possible to establish the HCl concentration required for keeping the metal ion on the resin

and that required to take it off. Quantitative separation of a trace quantity of a metal from a macro amount of another metal is also possible. The more common quantitative techniques that compliment this separation procedure are **spectrophotometry, atomic absorption, emission method, polarography and EDTA titrations**. The latter is particularly useful because of its simplicity, speed and versatility. In this procedure total free ion content of a water sample is determined by passing the sample through H^+ cation exchanger and then titrating the liberated acid with a standard alkali solution. The total hardness of water is determined by titrating an aliquot with **EDTA**. Organic compounds having ionic character (acidic or basic) can also be separated on anion and cation exchange resins. Both weak as well as strong acidic or basic types of resins are used. It should be noted that different states of metal in water may be defined following sample treatment following collection. A water sample which is to be analyzed for dissolved metals, is first filtered through a $0.45\ \mu m$ membrane filter as soon as possible after the collection of the sample. Use the first portion of the filtrate in rinsing the container and a requisite amount sufficient for analysis is then collected in order to ensure storage for some time before analysis. The sample collected for analysis is acidified to pH 2-3, because acidification prevents **hydrolysis** as well as **precipitation**.

In case of suspended solid for metals, the solid is collected by filtering about 100 mL of a mixed sample on a $0.45\ \mu m$ membrane filter, which after filtration, is transferred to a beaker where it is digested with warm conc HNO_3 . The sample is finally diluted with distilled water to a known volume and then analyzed by making use of **atomic absorption spectrophotometer**.