WATER QUALITY ANALYSIS: SAMPLING, PRESERVATION AND ANALYSIS

M K Sharma
National Institute of Hydrology, Roorkee – 247 667, Uttarakhand

E. mail: mks@nih.ernet.in

The environment and the human health are closely interrelated. The wellbeing of the people is the reflection of the healthy environment, but both can damage by pollution. Pollutants released into air, water and soil can find their way in to human body by breathing, eating and drinking. Growing urbanization, rapid industrialization without proper plan, excess use of chemical fertilizers, insecticides, pesticides in agriculture field has deteriorated the quality of water, causing water pollution. In broad perspective "Pollution" means such contamination of water or such alteration of the physical, chemical or biological properties of water or such discharge of any sewage or trade effluent or of any other liquid, gaseous or solid substance into water (whether directly or indirectly) as may, or is likely to, create a nuisance or render such water harmful or injurious to public health or safety, or to domestic, commercial, industrial, agricultural or other legitimate uses, or to the life and health of animals or plants or of aquatic organisms (Govt. of India, 1974). Pollution in water bodies can enter through one or more of the following ways:

I. Point Sources: Transfer of pollutants from municipal, industrial liquid waste disposal sites and from municipal and household hazardous waste and refuse disposal sites. The pollution from these sources can be measured directly or otherwise quantified and one can evaluated their impact directly.

II. Non-point Sources or Diffuse Sources: Wash off and soil erosion from agricultural lands carrying material applied during agricultural use, mainly fertilizers, herbicides and pesticides. Runoff from urban streets, commercial activities, industrial sites and storage areas and there is no single outlet of such source but consists of a number of outlets.

III. Change in the hydraulic regime of water system due to excessive water abstraction, construction of developmental works.

Broadly, the major sources of water pollution can be divided as urban and domestic waste, industrial waste, agricultural sources, mining wastes, induced

contaminated source, radioactive substances etc. In municipal areas the solid waste is produced at a rate of 0.33 kg/capita/day and thus the production of solid waste by the urban population of the country is around 23 million tons per year. Therefore, urban and domestic wastes play a significant role in polluting the water. Industrial wastes discharge plays an important role in the deterioration of water quality specially in urban and industrial areas. Besides several environmental guidelines for industries in India, there is lack of facilities to treat the solid and liquid waste and the same is generally dumped in low lying/open area by these industrial units, which moves downwards to lower reaches causing pollution in ground water regime. To increase the yield, indiscriminate use of fertilizers has also resulted into higher concentration of some constituents like Nitrates and Phosphate. Pollution is therefore considered as a major threat at the system level involving environmental implications and needs to make efforts for its control and remediation.

Various pollutants present in water are measured through water quality parameters and can be broadly classified into following categories:

Physical parameters: appearance, temperature, turbidity, colour, taste, odour

Chemical parameters: all inorganic and organic substances (e.g. pH, acidity, alkalinity, hardness, conductivity, chlorides, sulphates, nitrates, nitrites, ammonia, fluoride, boron, heavy metals, pesticides, detergents, phenols, cyanide, radioactivity, oil and greese, organics, BOD, COD, DO etc.

Biological parameters: Total Coliform, MPN, Total plate count (TPC)

Chemicals and Reagents

All chemicals used for analysis should of analytical reagent grade. De-ionized water should be used throughout the analysis work. All glassware and other containers used for trace element analysis should be thoroughly cleaned by soaking in detergent followed by soaking in 10% nitric acid for 48 h and finally rinsed with de-ionized water several times prior to use. All glassware and reagents used for bacteriological analysis should be thoroughly cleaned and sterilized before use. All glassware for pesticides and poly aromatic hydrocarbons analysis should be rinsed with chromatography grade solvents prior to use.

Physico-chemical and Bacteriological Analysis

The physico-chemical and bacteriological analysis should be performed as per standard methods (APHA, 1992). The details of analytical methods and equipment are described in Table 1.

Table 1. Analytical methods and equipment used for Water Quality Analysis

S. No.	Parameter	Method	Equipment
A.	**Physico-chemical**		
1.	pH	Electrometric	pH Meter
2.	Conductivity	Electrometric	Conductivity Meter
3.	TDS	Electrometric	Conductivity/TDS Meter
4.	Alkalinity	Titration by H_2SO_4	-
5.	Hardness	Titration by EDTA	-
6.	Chloride	Titration by $AgNO_3$	-
7.	Sulphate	Turbidimetric	Turbidity Meter
8.	Nitrate	Ultraviolet screening	UV-VIS Spectrophotometer
9.	Phosphate	Molybdophosphoric acid	UV-VIS Spectrophotometer
10.	Fluoride	SPADNS	UV-VIS Spectrophotometer
11.	Sodium	Flame emission	Flame Photometer
12.	Potassium	Flame emission	Flame Photometer
13.	Calcium	Titration by EDTA	-
14.	Magnesium	Titration by EDTA	-
15.	Boron	Carmine	UV-VIS Spectrophotometer
16.	BOD	5 days incubation at 20°C followed by titration	BOD Incubator
17.	COD	Digestion followed by titration	COD Digestor
B	**Bacteriological**		
18.	Total coliform	Maximum Probable Number (MPN) method	Bacteriological Incubator
19.	Faecal coliform		
C.	**Heavy Metals**		
20.	Iron	Digestion followed by Atomic Spectrophotometry	Atomic Absorption Spectrometer
21.	Manganese		
22.	Copper		
23.	Nickel		
24.	Chromium		
25.	Lead		
26.	Cadmium		
27.	Zinc		
28.	Arsenic	Ion chromatography	Ion chromatograph
29.	Mercury	Cold Vapour Generation followed by Atomic Spectrophotometry	Mercury Analyser
D.	**Pesticides and Polynuclear Aromatic Hydrocarbons**		
30.	Organochloro-pesticides	Gas chromatography	Gas Chromatograph with ECD, NPD and FID
31.	Organophospho-pesticides		
32.	PAH		

The water is being used as multipurpose resource in India. The main uses of water are public water supply, outdoor bathing & recreation, fisheries & wildlife propagation, irrigation & other agricultural uses, cooling in power plants, navigation and disposal of wastes. Most of these uses are often conflicting. In order for any water body to function adequately in satisfying any one of the above mentioned use, it must have corresponding degree of purity. In terms of quality, drinking water needs highest level of purity, whereas disposal of wastes can be done in any quality of water. Therefore there is great need to maintain the quality of water as it is as important as the quantity.

The Central Pollution Control Board has classified all water bodies including coastal waters in the country according to their "designated best uses" as given in the Table 2.

Table 2. Designated Best Use Classification of Surface Water

Designated Best Use	Quality Class	Primary Water Quality Criteria
Drinking water source without conventional treatment but with chlorination	A	Total coliform organisms (MPN*/100 ml) shall be 50 or less pH between 6.5 and 8.5 Dissolved Oxygen 6 mg/L or more, and Biochemical Oxygen Demand 2 mg/L or less
Outdoor bathing (organized)	B	Total coliform organisms (MPN/100 ml) shall be 500 or less pH between 6.5 and 8.5 Dissolved Oxygen 5 mg/L or more, and Biochemical Oxygen Demand 3 mg/L or less
Drinking water source with conventional treatment	C	Total coliform organisms (MPN/100 ml) shall be 5000 or less pH between 6 and 9 Dissolved Oxygen 4 mg/L or more, and Biochemical Oxygen Demand 3 mg/L or less
Propagation of wildlife and fisheries	D	pH between 6.5 and 8.5 Dissolved Oxygen 4 mg/L or more, and Free ammonia (as N) 1.2 mg/L or less
Irrigation, industrial cooling and controlled disposal	E	pH between 6.0 and 8.5 Electrical conductivity less than 2250 micro mhos/cm, Sodium Absorption Ratio less than 26, and Boron less than 2 mg/L

Drinking Water Specifications

The Bureau of Indian Standards (BIS) earlier known as Indian Standards Institution (ISI) has laid down the standard specifications for drinking water (BIS, 1991). In order to enable the users, exercise their discretion towards water quality criteria, the maximum permissible limit has been prescribed especially where no alternate sources are available. The national water quality standards describe essential and desirable characteristics required to be evaluated to ascertain suitability of water for drinking purpose. The important water quality characteristics as laid down in BIS Standard are given in Table 3.

In water quality control technology, the principal indicator of suitability of water for domestic, industrial or other uses is the coliform group of bacteria. The density of coliform group is the criteria for the extent of contamination and has been the basis for bacteriological water quality standard. In ideal situation all the samples taken from the distribution system should be free from coliform organisms but in practice, it is not attainable always and therefore, following standard for water has been recommended (BIS, 1991):

- 95% of water samples should not contain any coliform organisms in 100 ml throughout any year.
- No water sample should contain E.Coli in 100 ml water.
- No water sample should contain more than 10 coliform organisms per 100 ml.
- Coliform organisms should not be detected in 100 ml of any two consecutive water samples.

However, from bacteriological point of view, the objectives should be to reduce the coliform count to less than 10 per 100 ml and more importantly the absence of faecal coliform should be ensured.

Further, the presence of faecal colifirms in ground water is the indicator of a potential public health problem, because faecal matter is a source of pathogenic bacteria and viruses. The faecal coliform bacteria contaminate ground water through percolation from contamination sources (domestic sewage and septic tank) into the aquifers and also because of poor sanitatory system.

Table 3. Drinking water specifications (IS:10500:1991)

S.No.	Characteristics	Desirable limit	Permissible limit
Essential Characteristics			
1.	Colour, Hazen units, Max	5	25
2.	Odour	Unobjectionable	-
3.	Taste	Agreeable	-
4.	Turbidity, NTU, Max	5	10
5.	pH value	6.5 to 8.5	-
6.	Total hardness ($CaCO_3$), mg/L, Max	300	600
7.	Iron, mg/L, Max	0.3	1.0
8.	Chlorides, mg/L, Max	250	1000
9.	Residual free chlorine, mg/L, Max	0.2	-
Desirable Characteristics			
10.	Dissolved solids, mg/L, Max	500	2000
11.	Calcium, mg/L, Max	75	200
12.	Magnesium, mg/L, Max	30	75
13.	Copper, mg/L, Max	0.05	1.5
14.	Manganese, mg/L, Max	0.1	0.3
15.	Sulphate, mg/L, Max	200	400
16.	Nitrate, mg/L, Max	45	100
17.	Fluoride, mg/L, Max	1.0	1.5
18.	Phenolic compounds, mg/L, Max	0.001	0.002
19.	Mercury, mg/L, Max	0.001	-
20.	Cadmium, mg/L, Max	0.01	-
21.	Selenium, mg/L, Max	0.01	-
22.	Arsenic, mg/L, Max	0.05	-
23.	Cyanide, mg/L, Max	0.05	-
24.	Lead, mg/L, Max	0.05	-
25.	Anionic detergents	0.2	1.0
26.	Chromium as Cr^{6+}, mg/L, Max	0.05	-
27.	PAH, mg/L, Max	-	-
28.	Mineral oil, mg/L, Max	0.01	0.03
29.	Pesticides, mg/L, Max	Absent	0.001
30.	Alkalinity, mg/L, Max	200	600
31.	Aluminium, mg/L, Max	0.03	0.2
32.	Boron, mg/L, Max	1	5

Biochemical Oxygen Demand (BOD)

When biodegradable organic matter is released into a body of water, microorganisms especially bacteria feed on the wastes, breaking it down into simpler organic and inorganic substances. When this decomposition takes place in an aerobic environment, i.e. in the presence of oxygen, the process produces nonobjectionable, stable end products such as carbon dioxide, sulfate, orthophosphate and nitrate. A simplified representation of aerobic decomposition is given by

In aerobic environment

$$\text{Organic matter} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{New cells} + \text{Stable products}$$

When insufficient oxygen is available, the resulting anaerobic decomposition is performed by completely different microorganisms. They produce end products that can be highly objectionable, including hydrogen sulfide, ammonia and methane and this process can be represented by

In anaerobic environment

$$\text{Organic matter} \xrightarrow{\text{microorganisms}} CO_2 + CH_4 + \text{New cells} + \text{Unstable products}$$

The methane produced is physically stable, biologically degradable and a potent green house gas. When emitted from bodies of water it is often called swamp gas.

The amount of oxygen required by microorganisms to oxidize organic wastes aerobically is called the Biochemical Oxygen Demand (BOD). BOD is most often expressed in mg of oxygen required per liter of wastes.

The time required for completely degrade a sample of waste is several weeks making it impractical. Therefore it has become standard practice simply to measure and report the oxygen demand over a shorter, restricted period of 5 days realizing that the ultimate demand is considerably higher. The 5-day BOD or BOD_5 is the total amount of oxygen consumed by microorganism during the first 5 days of biodegradation. To standardize the procedure, the test is run at a fixed temperature 20^0C. Saturated value of DO for water at 20^0C is 9.1 mg/L, it is usually necessary to dilute the sample to keep final DO above zero. If during the 5 days the DO drops to zero, then the test is invalid (Masters, 1991).

$$BOD5 = \frac{DO_i - DO_f}{P}$$

DO_i = initial DO of the diluted wastewater
DO_f = final DO of the diluted wastewater

$$P = \text{dilution fraction} = \frac{\text{Vol. of wastewater}}{\text{Vol. of wastewater + dilution water}}$$

Taking into account of BOD of seeded dilution water (Blank)

$$BOD_5 = \frac{(DO_i - DO_f) - (B_i - B_f)(1 - P)}{P}$$

DO_i = initial DO of the diluted wastewater
DO_f = final DO of the diluted wastewater
B_i = initial DO of the Blank
B_f = final DO of the Blank

The methodology of BOD test is to compute a difference between initial and final DO of the samples after incubation. Minimum 1.5 L of sample is required for the test. DO is estimated by iodometric titration. This test is applied for fresh water sources (rivers, lakes), wastewater (domestic, industrial), polluted receiving water bodies, marine water (estuaries, coastal water), and also for finding out the level of pollution, assimilative capacity of water body and also performance of waste treatment plants. General guidelines for dilution range are as follows:

0.1% to 1%	:	Strong trade waste
1% to 5%	:	Raw or settled sewage
5% to 25%	:	Treated effluent
25% to 100%	:	River Water

Guideline BOD values for classification of raw untreated water is given below

Guideline BOD values for classification of raw untreated water

Quality class	Designated best use	BOD value	Note
A	Drinking water source without conventional treatment but with chlorination	2 or less	Could cause problems in treatment, larger Cl_2 demand and residual taste/odour problem.
C	Drinking water source with conventional treatment	3 or less	

Source: CPCB (2001)

This test measures the oxygen utilised for the biochemical degradation of organic material (carbonaceous demand) and oxidation of inorganic material such as sulphides and ferrous ions during a specified incubation period. It also measures the oxygen used to oxidise reduced forms of nitrogen (nitrogenous demand) (NBOD) unless their oxidation is prevented by an inhibitor. NBOD is an additional demand caused by the oxidation of nitrogen compounds.

Nitrification

In aerobic environments

$$2NH_3 + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 2H^+ + 2H_2O$$

$$2NO_2 + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^-$$

Under anaerobic conditions, certain denitrifying bacteria are capable of reducing NO_3 back into NO_2 and N_2, completing the nitrogen cycle. It is a matter of days before the rate of oxidation of ammonia is sufficient to create a significant oxygen demand. NBOD does not normally begin to exert itself for at least 5-8 days, so most 5-day BOD tests are not affected by nitrification.

Sample collection, preservation and storage

Grab or composite samples are collected. Keep composite samples at or below 4°C during compositing. Samples for BOD may degrade significantly during storage. Minimise reduction of BOD by analysing samples promptly or by cooling it to near freezing temperature during storage. The maximum holding time recommended between collection and analysis is 48 hours. Warm chilled samples to 20-27°C ± 3°C before analysis.

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) test determines the oxygen requirement equivalent of organic matter that is susceptible to oxidation with the help of a strong chemical oxidant. It is an important, rapidly measured parameter as a means of measuring organic strength for streams and polluted water bodies. The test can be related empirically to BOD, organic carbon or organic matter in samples from a specific source taking into account its limitations. The test is useful in studying performance evaluation of wastewater treatment plants and monitoring relatively polluted water bodies. COD determination has advantage over BOD determination. COD results can be obtained in 3-4 hrs as compared to 3-5 days required for BOD test. Further, the test is relatively easy, precise, and is unaffected by interferences as in the BOD test. The intrinsic limitation of the test lies in its inability to differentiate between the biologically oxidisable and biologically inert material and to find out the system rate constant of aerobic biological stabilisation.

Sample collection, preservation and storage

Preferably collect samples in glass bottles. Homogenise samples containing settleable solids. If there is delay in collection and analysis, preserve sample by acidification to pH≤2 using concentrated H_2SO_4. Samples can be preserved for maximum 7 days.

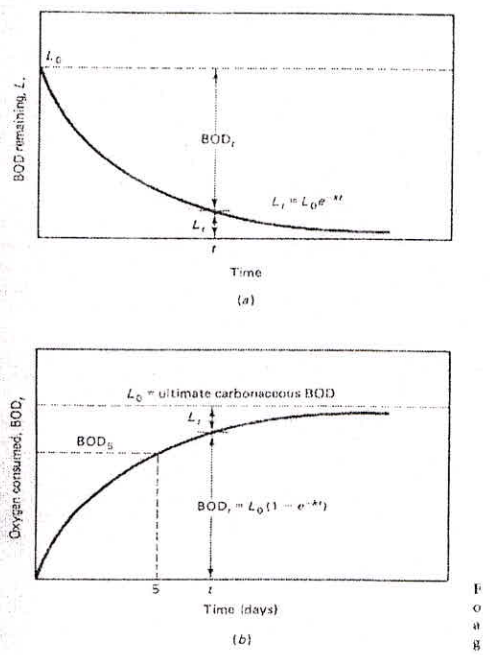


Fig. 1. Idealized carbonaceous oxygen demand

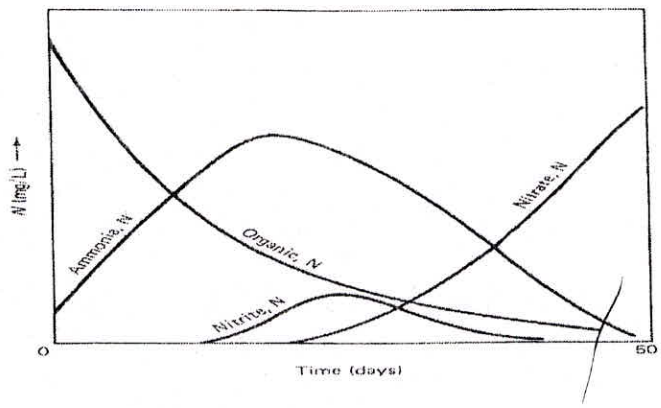


Fig. 2. Changes in nitrogen forms in polluted water under aerobic conditions

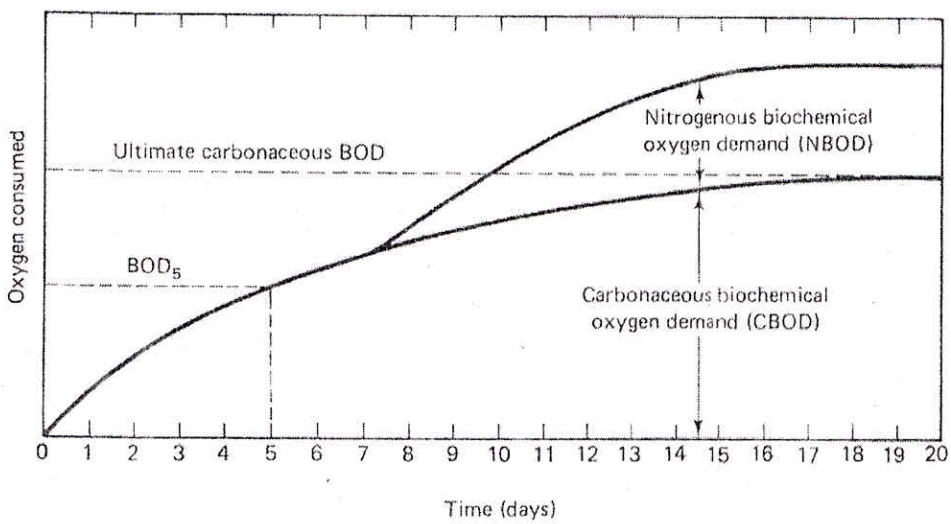


Fig. 3 Carbonaceous and nitrogenous biochemical oxygen demand
Source: Masters (1991)

TOXIC POLLUTANTS

Some of the pollutants are of serious concern and can not be neglected, are Heavy metals (zinc, copper, cadmium, lead, mercury, nickel, iron, manganese, arsenic, chromium) and Pesticides and Polynuclear Aromatics Hydrocarbons (PAH). Heavy metal pollution in its inorganic and organic forms is mainly caused by uncontrolled discharge of wastewaters of different types of industries. Leachates from landfill sites and mining waste dumps are other contributors of metal pollution. Organic pollutants (mostly organochloro and some persistent toxic substances in water bodies) got importance

because of their carcinogenic character. They enter water bodies through point sources, non-point sources as well as through long range atmospheric transportation. The process of bio-accumulation and bio-magnification of these organic pollutants fresh water eco-system is of great importance.

HEAVY METALS

Metals are characterized by high thermal and electrical conductivity, high reflectivity and metallic luster, strength and ductility. From a biological perspective, however, it is more common to use broader definition that says a metal is an element that will give up one or more electrons to form a cation in an aqueous solution. With this definition, there are about 80 elements that can be called metals. The term heavy metal is less precisely defined. In chemical terms it can refer to metals with specific gravity greater than about 4 or 5, but more often, the term is simply used to denote metals that are toxic. The list of toxic metals includes aluminium, arsenic, beriyllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, strontium, thallium, tin, titanium and zinc. Some of these metals, such as chromium and iron, are essential nutrients in our diets, but in higher doses are extremely toxic.

In recent years, fluxes of the many metals from terrestrial and atmospheric sources to the aquatic environment have increased considerably. The metals can enter the aquatic environments through atmosphere and releases from point and non-point source. Point sources of metals include municipal sewage sludge and effluent outfalls to surface waters, direct releases to water courses from industrial units, and in some areas, acid mine drainage. Non-point sources of metals include natural weathering of geologic materials and anthropogenic sources such as runoff from manure and chemical fertilizers from farm fields and irrigation return flow. The sources for different metals in the environment include agriculture (As, Cu, Hg, Pb, Se and Zn), electrical power (As, Cd, Cu, Hg, Pb, Ni, Se and Zn), metallurgy (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn), and wood and pulp processing (As, Cd, Cr, Cu, Hg and Pb). The elevated levels of Cu, Pb, Zn, and to a lesser degree Cd, can be due to corrosion within the urban water supply network (Preuss and Kollmann, 1974). The use of detergents also creates a possible pollution hazard, since common household detergent products can affect the water quality. Angino et al. (1970) also reported presence of various elements, viz., Fe, Mn, Cr, Co, Zn, Sr and B in most detergents.

The elevated levels of trace metals in natural water systems pose a severe threat to the aquatic environment. Heavy metals are not biodegradable and enter the food chain through a number of pathways causing progressive toxicity due to the accumulation in human and animal organs during their life span on long term exposure to contaminated environments. Despite the presence of trace concentrations of Cr, Mn, Co, Cu and Zn in the aquatic environment, which is essential to a number of life processes, high

concentrations of these metals become toxic. Therefore it is necessary to analyse the concentration of these metals in aqueous solution like water for water quality management. To estimate such metals in very very small quantities, advance technique and equipments are required. Atomic absoption spectroscopy has been proved itself to be most effective instrumental technique for quantitative determination of metals in liquid.

Sampling, Preservation and Processing

Non-breakable high density polyethylene plastic should be used for collection of samples for metal analysis. The containers should soaked in 10% nitric acid for 48 h and rinsed with deionized water several times prior to use. For dissolved metal analysis, water samples should be filtered through Whatmann 0.45µm pore diameter membrane filters. The filtered samples should then be preserved by acidifying with concentrated ultra pure nitric acid to pH<2 (5 mL concentrated HNO_3 per litre of sample) and stored at 4^0C in polyethylene bottles. For total metal analysis, 100 mL of unfiltered water samples should be acidified with 2 mL ultra pure nitric acid and digested on a hot plate till the volume reduced to around 30 mL. The digested samples should then be filtered and final volume should be made upto 100 mL with deionised water and stored at 4°C for total metal analysis. The difference between the total and dissolved metal concentrations gives the concentration of particulate metal.

For volatile metal mercury, take 50 ml sample, add 5 ml conc. HNO_3, then add 10 ml 50% H_2SO_4 followed by 5 ml 6% $KMnO_4$. Keep this mixture at room temperature overnight. Reduce excess $KMnO_4$ by dropwise addition of 20% hydroxylammonium hydrochloride. Make up the content to 100 ml. Use the resultant for mercury estimation on AAS-VGA. For arsenic, take 100 ml sample, add 5 ml conc. HNO_3, then digest the sample on a water bath to reduce the volume 5 ml. Finally make up the volume 10 ml with 7 N HCl.

Techniques available for Metal Detection

- Atomic absorption spectroscopy
- Flame Emission
- Vapour Generation Accessory (VGA)
- Graphite Tube Atomizer (GTA)
- ICP Emission
- Ion Chromatography

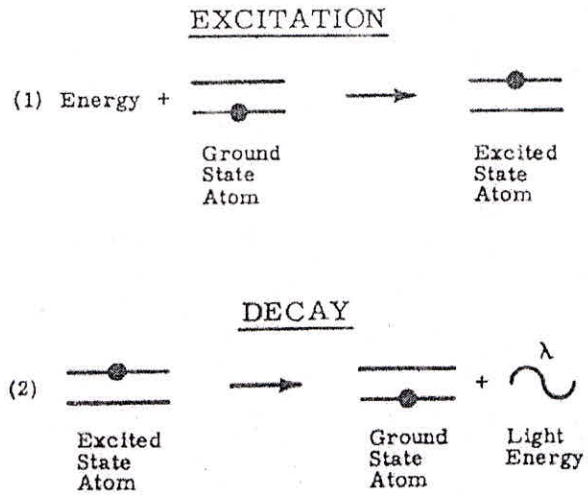
Atomic absorption spectroscopy

Atomic absorption spectroscopy is an absorption method where radiation is absorbed by non excited atoms in the vapour state. This technique involves the study of the absorption of radiation by neutral atoms in the gaseous state. In this technique, the sample is first converted into an atomic vapour and then the absorption of atomic vapour is measured at selected wavelength which is characteristic of each individual element.

Atomic Emission and Absorption

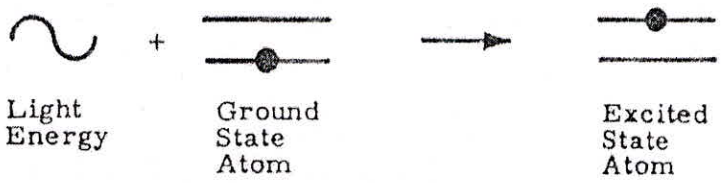
Every element has a specific number of electrons associated with its nucleus. The normal and most stable orbital configuration of an atom is known as the "ground state." If energy is applied to an atom, the energy will be absorbed and an outer electron will be promoted to a less stable configuration known as the "excited state." Since this state is unstable, the atom will immediately return to the "ground state," releasing light energy.

In atomic emission, the processes of excitation and decay are both involved. The sample is subjected to a high energy thermal environment in order to produce excited-state atoms. This environment can be provided by a flame or, more recently, a plasma. However, since the excited state is unstable, the atoms spontaneously return to the "ground state" and emit light. The emission spectrum of an element consists of a collection of emission wavelengths called emission lines because of the discrete nature of the emitted wavelengths. The intensity at an emission line will increase as the number of excited atoms of the element increases.



In the process of atomic absorption, the "ground state" atom absorbs light energy of a specific wavelength as it enters the "excited state." As the number of atoms in the light path increases, the amount of light absorbed also increases. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made. The use of special light sources and careful selection of wavelengths allow the

specific determination of individual elements.



As we can see, there are some basic differences between atomic emission and atomic absorption. Using atomic emission, the flame serves a dual purpose. It converts the sample aerosol into an atomic vapor and then thermally elevates the atoms to an excited state. When these atoms return to the ground state, they emit light which is detected by the instrument. The intensity of light emitted is related to the concentration of the element of interest in solution. In atomic absorption, the only function of the flame is to convert the sample aerosol into atomic vapor which can then absorb light from the primary light source (hollow cathode lamp or electrodeless discharge lamp).

A schematic diagram of atomic absorption instrument is shown below:

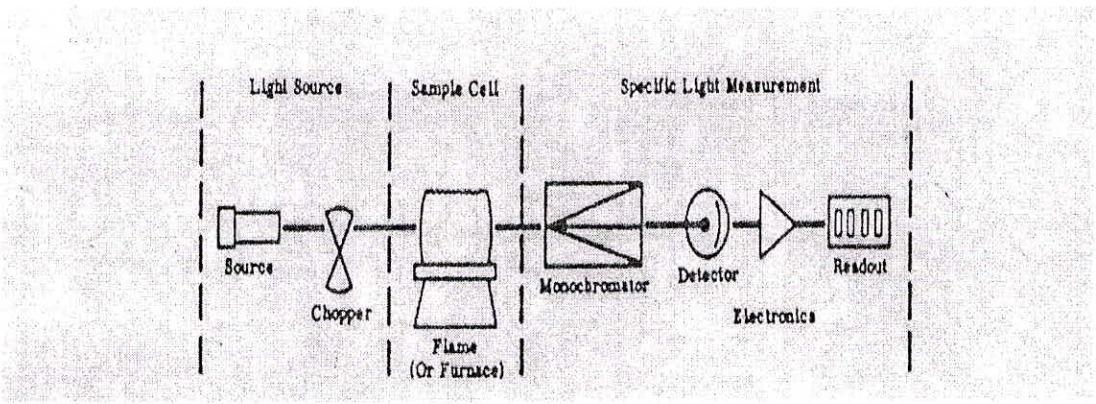


Fig. 4. Atomic Absorption Spectrometer
(Source: Operation Manual, Atomic Absorption Spectrometer, Perkin Elmer 3110)

Flame Emission Technique

This technique is generally used for such case where energy source (lamp) for that particular metal is not available. It provides better detection limits than that atomic absorption for Al, Ba, Li, K, Na and V. In this technique, optimum instrumental conditions will be the same as for absorption. The result will be better in emission if

nitrous oxide-acetylene flame is used. The interferences will be the same as for the absorption technique.

Vapour Generation Accessory (VGA)

Some atoms As, Se, Sb, Sn vaporize when they come in contact of air-acetylene flame causing less atoms for absorption. Therefore, in order to have maximum concentration, they are converted into their respective hydride and atomized at lower temperature (upto 1000°C) using diffused flame.

Graphite Tube Atomizer (GTA)

In this technique, small liquid sample (5-25 µl) or solid (mg) are transferred directly to an electrically heated graphite tube or rod. The temperature programming is done. At low temp (~100°C) solvent is removed, at elevated temp (400-900°C) organic matter is destroyed by ashing and finally at high temp (2500-3000°C) residual material containing analyte is vaporized and atomized. Measure absorption at analyte wavelength.

ICP Emission

This technique is suitable for analysis of refractory elements U, B, P, Ta, Ti & W which are relatively insensitive to atomic absorption. Here, a chemically inert environment is created and to achieve very high temperature. Interferences present in atomic absorption is eliminated but spectral interferences are more common.

Ion Chromatography

Ion chromatography is an analytical technique which encompasses all HPLC methods to determine inorganic and organic ions. The combination of ion exchange columns and conductivity detection continues to represent the most important type of ion chromatography and two different were used in practice. In this technique with chemical suppression, the background conductivity is suppressed both chemically and electronically.

PESTICIDES

Pesticides contamination in natural water is a world wide problem and has become a challenge for the all world scientists. In recent years increasing population pressure, evolving industrial chemical society and advances in science and technology resulted in many questions about the safety of drinking water in countries, like India China and many other countries, where the majority of population live in villages with bare infrastructure facilities, illiteracy and lack of awareness.

The term pesticide is used to cover a range of chemicals that kill organisms that humans consider undesirable and includes the more specific categories of insecticides, herbicides, rodenticides, and fungicides. However, the chemical pesticides are usually not target specific and therefore, may cause harm to non-target species and many of them are quite persistent for long periods in the environment. The indiscriminate application of pesticides provides the pollutional effect to a considerable extent. The pesticides join the water courses through the runoff from agricultural lands, industrial and urban effluents, spray operations for crop and disease vector control etc and may ultimately reach to the ground water through percolation. The pesticides may impart toxicity to the ground water and causes various health hazards. The unused pesticides and their degradation product and metabolites in the various compartments are known as Pesticide Residue.

Presently, synthetic organic pesticides are largely used to control insects and other pests. There are three main groups of synthetic organic insecticides:

a. Organo-Chlorine Pesicides: Also known as chlorinated hydrocarbons includes polychlorinated organic compounds mainly
   - Dichloro diphenyl trichloroethane (DDT) (o,p′-DDT, p,p′-DDT, p,p′-DDD, p,p′-DDE)
   - Diene group e.g. Benzene Hexa Chloride (BHC) isomers (α-BHC, β-BHC, γ-BHC & δ-BHC)
   - Endosulfan
   - Aldrin
   - Methoxychlor

b. Organo-Phosphorous Pesticides: Phosphorous containing organic compounds e.g.
   - Ethion
   - Dimethoate,
   - Malathion
   - Methyl Parathion

c. Carbamates: Nitrogen containing organic compounds used as insecticides (derivatives of carbamic acid) e.g. propoxur, carbaryl, and aldicarb

In addition, a number of herbicides, including the chlorophenoxy compounds 2,4,5-T (which contains the impurity dioxin, which is one of the most potent toxins known) and 2,4-D are common water pollutants.

One of the most well-known organochlorine pesticides was DDT (dichlorodiphenyltrichloroethane) which had been widely used to control insects that carry such diseases such as malaria, typhus, and plague. It was its impact on food chains, rather than human toxicity that led to its ban even in India also. The main properties of

organochlorine pesticides, that cause them to be particularly disruptive to food chains, are i) they are very persistent, which means they last a long time in the environment before being broken down into other substances, and ii) they are quite soluble in lipids, which means they easily accumulate in fatty tissue.

Organochlorine pesticides (OCPs), also existing as typical persistent toxic substances (PTS), have been of increasing concerns the world due to their salient features of persistence, bioaccumulation, and toxicity. In the twelfth Stockholm Convention, nine organochlorine pesticides, including aldrin, toxaphene, DDTs, chlordane, dieldrin, endrin, heptachlor, mirex, and hexachlorobenzene, were proposed to be controlled as persistent organic pollutants (POPs), a variety of organic chemicals which have lasting harms to environment and eco-system. Due to their intensive utilization in agricultural and industrial activities, residues of the OCPs have been widely identified and reported across the world, even in Antarctica and the Arctic Zone. Moreover, a majority of these pesticides belongs to endocrine-disrupting chemicals, which have been well proved as a series of most harmful substances to the endocrine system of human being and wild animals.

The organophosphates, such as parathion, malathion, diazinon, TEPP (tetraethyl prophosphate), and dimethoate, are effective against a wide range of insects and they are not persistent. However, the toxicity is much more than the organochlorines that they have replaced. They are rapidly absorbed through the skin, lungs, and gastrointestinal tract and, hence, unless proper precautions are taken, they are very hazardous to those who use them. Some of organo-chlorines are quite stable and persistent in aquatic medium while some of organo-phosphorous are significantly unstable in water and may degrade, hydrolyse or transform to other forms. The DDT metabolites are very stable.

Humans exposed to excessive amounts have shown a range of symptoms including tremor, confusion, slurred speech, muscle twitching, and convulsions. Acute human exposure to carbamates has led to a range of symptoms, such as nausea, vomiting, blurred vision, and in extreme cases, convulsions.

Sampling and Preservation

For collection of sample for pesticide analysis, high quality dark glass container should preferably be used with teflon stopper. Polyethylene plastic container should not be used for collection of sample for pesticide analysis. Wash the container with acid, detergent, tap water, distilled water, acetone and finally with the working organic solvent. Store the samples at 4^0C.

Techniques available for Pesticide Detection

The detection of pesticide is done using the Chromatographic technique. The term "Chromatography" is the general name for a wide range of physico-chemical separartion processes in which the components to be separated are distributed between a stationary and a mobile phase. This technique is based on the difference in the rate at which the components of a mixture move through a medium (stationary phase) under the influence of some solvent or gas (moving phase).

The following chromatographic methods are available depending upon mobile and stationary phase:

- Partition chromatography
- Adsorption chromatography
- Paper chromatography
- Thin layer chromatography
- Gas liquid chromatography
- Gas solid chromatography
- Gel chromatography
- Ion exchange chromatography

The analysis of pesticides residue in water is carried out on Gas Chromatograph using concept of Gas Chromatographic Separation. The separation of compounds is much better obtained by gas chromatography (GLC) and High Performance Liquid Chromatography (HPLC) technique. The quantification is ng to pg level (ITRC, 1999).

The water samples collected from the sampling sites can not be analysed directly on the instrument due to various reasons and need some processing before end-analysis. The aqueous phase is not acceptable to the instruments (GLC, HPLC), the compounds to be measured are extracted in some moisture free organic solvent. The concentration levels of pesticides in natural and drinking waters may be very low, therefore the dried organic solvent (extract) requires manifold concentration followed by proper clean up for removal of interfering co-extractives. Although the preprocessing methodology depends on the sample matrix, concentration and components to be analysed, however general steps of the processing are as follows (ITRC, 1999):

- Extraction
- Drying
- Concentration
- Clean up
- End analysis

Computation: If the detector response is linear in the working concentration range that is the peak height (area) versus concentration plot is linear, the concentration of a particular pesticide in unknown water sample can be computed by comparing peak height (areas) observed on the chromatograms for the standard and unknown sample.

The concentration of a particular pesticide in water sample can be computed using the following formula:

$$C_{comp}\,(\mu g/L)\,(ppb) = \frac{H_{sam}}{H_{std}} \times W_{std} \times \frac{V_{ext}}{V_{sam} \times V_{inj}} \times \frac{\text{Purity}}{\text{Recovery Factor}}$$

where C_{comp} is the concentration (computed) of particular pesticide in µg/L (ppb) in water.

H_{sam} = area of peak for unknown water sample
H_{std} = area of peak for standard
W_{std} = total amount of standard pesticide injected to GLC in nanograms (ng)
V_{ext} = final volume of concentrated extract (ml)
V_{sam} = volume of water sample extracted (in litres)
V_{inj} = volume (in µl) of concentrated extract injected to GLC

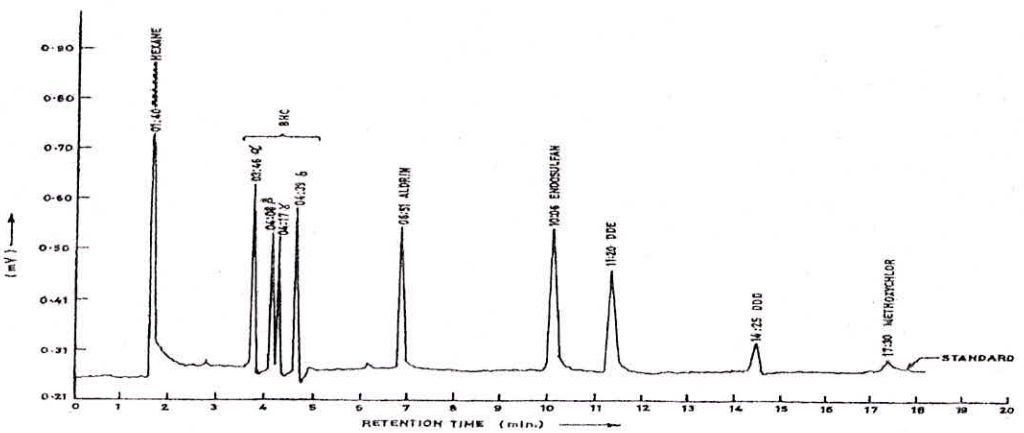


Fig. 5. Chromatogram for a mixed standard of Organochloropesticides

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