

**COURSE
GUIDE**

**EMT 411
WATER ANALYSIS**

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Introduction

Water is one of the most important and abundant compounds of the ecosystem. All living organisms on the earth need water for their survival and growth. Earth is the only planet having about 70 % of its surface covered by water. But due to increased human population, industrialization, use of fertilizers in the agriculture and man-made activity, the water bodies within the planet earth are highly polluted with different harmful contaminants. Therefore, it is necessary that the quality of drinking water should be checked at regular time interval, as human population had suffered greatly from various water borne diseases due to the use of contaminated drinking water.

Water samples are collected and analyzed to ascertain characteristics of a body or mass of water. The sample is usually only an infinitesimal part of the total volume and is therefore representative of the total mass only to the degree that uniformity of chemical composition exists within the total mass. In their natural state, surface and ground water are subjected to forces that promote mixing and homogeneity. The fact that such tendencies exist, however, is not sufficient cause for assuming that a body of water is so well mixed that no attention to sampling technique is required. Often, because of local conditions, the body of water may not have uniform composition.

The composition of water is subject also to change with the passage of time. The chemical quality of surface or ground water is the resultant of the geologic, hydrologic, biologic, and cultural environment of the water and varies from time to time as well as from place to place. Generally, changes in the quality of surface water are more pronounced and rapid than in ground water. However, marked changes in ground-water quality can, and often do, accompany such shifts in hydrologic equilibrium as variations in recharge or discharge rate, salt-water encroachment, or induced infiltration of surface water.

Sampling

Sampling of water for Hydro-geochemical analysis can either be from surface water or groundwater. The type of investigation, purpose of the study, and the anticipated variation in chemical quality determine to a large degree, the location of the surface- or ground-water sampling site and the frequency of sample collection.

Samples of surface and ground water should be collected at intervals such that no important change in quality could pass unnoticed between sampling times. This requisite immediately gives rise to two additional questions: What magnitude of change is important, and what are the physical and economic factors that must be considered in obtaining the record? By necessity the sampling schedule adopted is usually a

compromise between the accuracy and detail desired in the water-quality record and the funds and personnel available for the work.

Surface water sampling

Sampling of surface water is usually carried out to determine the discharge of dissolved constituents past a point, to describe the changes in water quality with respect to time, to collect data that will aid in predicting water quality in the future or in estimating the nature and magnitude of past events, to study the effect of geologic, hydrologic and cultural changes on water quality, or a combination of these purposes.

Groundwater sampling and analysis

Groundwater taken from any given place contains a wide variety of dissolved constituents. We have a variety of means for analyzing water, both in the field and in the laboratory, which characterize the concentrations of dissolved solutes in the water. Ground water is analogous to a surface-water reservoir in that most usable ground water is in motion, although the rate of movement may be very slow and the areal extent very wide. A well can be considered as a sampling point in a large body of slowly moving water, which differs in chemical composition vertically as well as aurally. Most of the forces which cause mixing in bodies of surface water are absent or much weaker in groundwater reservoirs. Turbulence is virtually nonexistent. The major forces that tend to mix ground water are probably the differences in velocities as the water moves through material of heterogeneous permeability, pressure differentials and, to a lesser extent, ionic diffusion. The degree of movement induced by pumpage and natural discharge affects the quality. The diversified nature and solubility of the rocks with which the water comes in contact and variations in rate and chemical composition of recharge from precipitation and from the surrounding area tend to make the water heterogeneous.

Sampling programs are planned to determine the mineral content of ground water through the aquifer, although a completely comprehensive answer is not always practical. Efficient collection of water-quality data and intelligent selection of the ground-water sampling site generally require more judicious consideration than the selection of a surface-water sampling site because the elements influencing water quality are not as easily observed.

Because of the diversified purposes of ground-water investigations, it is impractical to attempt specific direction for the selection of sampling sites. Nevertheless, some general suggestions can be given. If changes in ground-water quality are not considered in the investigation, there are perhaps two equally satisfactory approaches to the problem of adequate

and economical coverage of ground-water quality of an area; both employ comprehensive and partial analyses.

One approach utilizes the determination of key constituents (one or several) in a large number of samples collected over the entire area. By this means an aerial water-quality pattern is developed that is then of value in selecting the sites for collection of samples for comprehensive analysis. In some investigations, the identity of the key constituents may be unknown at the beginning of the investigation. Then, the reverse approach may be required, and comprehensive analyses may be made early in the study, and these data augmented by partial and additional comprehensive analyses of samples collected at other sites to complete the water-quality picture. Either method requires the greatest of care in the selection of sampling points from available sites.

When analyzing groundwater, it is common practice to measure temperature, pH, **alkalinity**, **total dissolved solids** (TDS), and **specific conductance**.

- pH is defined as the inverse log of hydrogen ion activity in the water (activity is basically like concentration). For example, a pH of 7 means that the activity (or concentration) of hydrogen in the water is equal to 1×10^{-7} mol/L. A pH of 5.6 means that hydrogen activity is equal to $1 \times 10^{-5.6}$ mol/L.

- **Alkalinity** refers to the ability of the water to neutralize an acid. This is directly related to specific dissolved species in the water; in most groundwater systems, the predominant acid-neutralizing species is the bicarbonate ion. Therefore, alkalinity is usually used as a direct measurement of the concentration of bicarbonate in groundwater. Alkalinity is usually measured in the field, when the samples are taken, because exposure to air can cause some of the bicarbonate in solution to turn into carbon dioxide and leave the water.

- **The total dissolved solids** represent the total concentration of dissolved constituents in the water; usually measured by evaporating a liter of the sample and measuring the weight of the remaining solids. TDS is measured in mg/L. Shallow groundwater (within 200 meters of the surface) generally ranges from 100 mg/L to 10,000 mg/L TDS (seawater is 35,000 mg/L). The standard limit for drinking water is generally considered to be less than 1000 mg/L, with less than 500 preferable (although people can tolerate up to 2000 mg/L).

- **Specific conductance** is a measure of the ability of the sample to conduct electricity. This acts as an approximation of the TDS, since the

electrical conductivity of water is a function of the amount of dissolved material in the water.

In addition to these basic chemical parameters, we also analyze for the concentration of individual constituents in the water. Most of the dissolved constituents in groundwater are inorganic cations and anions derived from the dissolution of minerals. In any natural groundwater sample about 95-99% of the dissolved constituents (by weight) will consist of the following:

- Bicarbonate
- Calcium
- Chloride
- Magnesium
- Silicon
- Sodium
- Sulfate
- Carbonic acid

These are usually referred to as the **major constituents** or **primary constituents**, and generally have concentrations greater than 5 mg/L. These constituents come directly from the dissolution of mineral phases in the subsurface, and a set of laboratory analyses will generally test for them. **Minor constituents**, which generally occur in concentrations ranging from 0.1 –10 mg/L, include:

- Boron
- Carbonate
- Fluoride
- Iron
- Nitrate
- Potassium
- Strontium

In addition to these, there are a host of **trace constituents** that occur in concentrations less than 0.1 mg/L. Some of these are heavy metals that are toxic in small quantities. These constituents are generally not analyzed for. If we analyze a water sample for the major and minor constituents, we will identify just about all of the mass dissolved in the sample. There are ways that we can check our analytical results, to make sure that we are measuring correctly.

- If we add up the concentrations of the individual species, as determined by various lab procedures, we can compare that sum to the total dissolved solids concentration as determined by evaporation. If the two are different, then most likely there is a problem with the lab analyses

- Water is electrically neutral; for every positive ion in solution, there is an equal number of negative charges to offset the charge. We can do a **charge balance** to see if the positive charges equal the negative. This is done by converting the concentrations to meq/L, then adding up the meq of the cations and subtracting from that the meq of the anions. Ideally, they should be within 5% of each other (owing for analytical uncertainty and the trace elements that were missed in the analysis).

Sample Containers

Factors that are pertinent in selecting containers used to collect and store water samples are;

- i. Resistance to solution and breakage,
- ii. Efficiency of closure,
- iii. Size,
- iv. Shape
- v. Availability
- vi. Cost

Preferences for one type of container over another varies, and selection is guided largely by experience, supposition of the possible effect of the container on the water sample, and use of containers in the individual laboratories. No adequate study of all factors has been made. Hard rubber, polyethylene and perhaps other plastics, and some types of borosilicate glass are believed to be suitable on the basis of experience and the reports of others in water chemistry. A limited investigation, conducted by the American Geological Survey Agency, of the relative merits of four common types of bottles showed that storage in Pyrex and polyethylene did not significantly alter the silica, sodium, total alkalinity, chloride, and boron content, or the specific conductance, pH, or hardness of the water during a storage period of about 5 months, although some investigators have avoided Pyrex because of suspected contamination from the boron in the glass.

Before use, all new bottles must be thoroughly cleansed, filled with water, and allowed to soak several days. The soaking removes much of the water-soluble material from the container surface. Because of their design and construction material, some bottles are more satisfactory for transporting water than others. The bottle must be resistant to impact and to internal pressure, which is increased by expansion of the water or by release of dissolved gases at elevated temperatures. Well-sealed fragile bottles of liquid when shipped by air may not withstand the large differential pressures or freezing temperatures in the rarefied atmosphere. In respect to fragility alone, polyethylene bottles are more satisfactory than glass. However, samples in polyethylene bottles must be protected from compression else the liquids may be squeezed out around the threads of the cap.

Samples subjected to freezing temperatures are very likely to be lost through breakage of glass bottles but are retained by polyethylene. However, this advantage may sometimes be more apparent than real. The chemical analysis of a previously frozen sample is always suspect because the original chemical character may not be completely reconstructed after the sample thaws. Although the analysis of the previously frozen sample is usually of some value,

Determination of Physico- Chemical Parameters of water

It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Water must be tested with different physico-chemical parameters. Selection of parameters for testing of water solely depends upon for what purpose we are going to use that water and what extent we need its quality and purity. Water contain different types of floating, dissolved, suspended and microbiological as well as bacteriological impurities. Some physical test should be performed for testing of its physical appearance such as temperature, color, odour, pH, turbidity, TDS etc, while chemical tests should be performing for its Biochemical oxygen demand, BOD, chemical oxygen demand, COD, dissolved oxygen, alkalinity, hardness and other characters. For obtaining more and more quality and purity of water, it should be tested for its trace metals, heavy metal contents and organic i.e. pesticide residues. It is obvious that drinking water should pass these entire tests and it should contain required amount of mineral level. Only in the developed countries all these criterias are strictly monitored. Due to very low concentration of heavy metal and organic pesticide impurities present in water, there is a need for highly sophisticated analytical instruments as well as trained manpower. The following different physico- chemical parameters are tested regularly for monitoring quality of water.

Temperature

In an established system the water temperature controls the rate of all chemical reactions, and affects fish growth, reproduction and immunity. Drastic temperature changes can be fatal to fish.

pH

pH is most important in determining the corrosive nature of water. The lower the pH value the higher is the corrosive nature of water. pH can be positively correlated with electrical conductance and total alkalinity. The reduced rate of photosynthetic activities affects the rate of assimilation of carbon dioxide and bicarbonates which are ultimately responsible for increase in pH, the low oxygen values coincided with high temperature during the summer months. Various factors bring about changes in the pH of water. Higher pH values suggest that carbon dioxide, carbonate-

bicarbonate equilibrium is affected more due to change in physico-chemical condition.

EC (Electrical Conductivity)

Conductivity shows significant correlation with ten parameters such as temperature, pH value, alkalinity, total hardness, calcium, total solids, total dissolved solids, chemical oxygen demand, chloride and iron concentration of water. It is measured with the help of EC meter which measures the resistance offered by the water between two platinized electrodes. The instrument is standardized with known values of conductance observed with standard KCl solution.

Carbon Dioxide

Carbon dioxide is the end product of organic carbon degradation in almost all aquatic environments and its variation is often a measure of net ecosystem metabolism. Therefore, in aquatic biogeochemical studies, it is desirable to measure parameters that define the carbon dioxide system. CO₂ is also the most important green house gas on Earth. Its fluxes across the air-water or sediment-water interface are among the most important concerns in global change studies and are often a measure of the net ecosystem production/metabolism of the aquatic system. There are various readily measurable parameters of aquatic carbon dioxide system: such as pH (pCO₂), total dissolved inorganic carbon (DIC) and total alkalinity (TA). Surface water pCO₂ can be measured by photometric method.

Alkalinity

It is composed primarily of carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻). Alkalinity acts as a stabilizer for pH. Alkalinity, pH and hardness affect the toxicity of many substances in the water. It is determined by simple dil HCl titration in presence of phenolphthalein and methyl orange indicators.

Dissolved Oxygen (DO)

DO is one of the most important parameters. Its correlation with water body gives direct and indirect information e.g. bacterial activity, photosynthesis, availability of nutrients, stratification etc. The high DO in summer is due to increase in temperature and duration of bright sunlight has influence on the percentage of soluble gases (O₂ & CO₂). DO in sample is measured titrimetrically by Winkler's method after 5 days incubation at 293 K. The difference in initial and final DO gives the amount of oxygen consumed by the bacteria during this period. This procedure needs special BOD bottles which seal the inside environment from atmospheric oxygen.

Carbonate

Whenever the pH touches 8.3, the presence of carbonates is indicated. It is measured by titration with standardized hydrochloric acid using phenolphthalein as indicator. Below pH 8.3, the carbonates are converted into equivalent amount of bicarbonates. The titration can also be done pH metrically or potentiometrically.

Bicarbonate

It is also measured by titration with standardized hydrochloric acid using methyl orange as indicator. Methyl orange turns yellow below pH 4.0. At this pH, the carbonic acid decomposes to give carbon dioxide and water.

Biochemical Oxygen Demand (BOD)

BOD is a measure of organic material contamination in water, specified in mg/L. BOD is the amount of dissolved oxygen required for the biochemical decomposition of organic compounds and the oxidation of certain inorganic materials (e.g., iron, sulfites). Typically, the test for BOD is conducted over a five-day period.

Chemical Oxygen Demand (COD)

COD is another measure of organic material contamination in water specified in mg/L. COD is the amount of dissolved oxygen required to cause chemical oxidation of the organic material in water. Both BOD and COD are key indicators of the environmental health of a surface water supply. They are commonly used in waste water treatment but rarely in general water treatment.

Sulphate

It is measured by nephelometric method in which the concentration of turbidity is measured against the known concentration of synthetically prepared sulphate solution. Barium chloride is used for producing turbidity due to barium sulphate and a mixture of organic substance (Glycerol or Gum acetia) and sodium chloride is used to prevent the settling of turbidity.

Ammonia (Nitrogen)

It is measured spectroscopically at 425 nm radiation by making a colour complex with Nessler's reagent. The conditions of reaction are alkaline and cause severe interference from hardness in water.

Calcium

It is measured by complexometric titration with standard solution of EDTA using Patton's and Reeder's indicator under the pH conditions of more than 12.0. These conditions are achieved by adding a fixed volume of 4N Sodium Hydroxide. The volume of titre (EDTA solution) against

the known volume of sample gives the concentration of calcium in the sample.

Magnesium

It is also measured by complexometric titration with standard solution of EDTA using Eriochrome black T as indicator under the buffer conditions of pH 10.0. The buffer solution is made from Ammonium Chloride and Ammonium Hydroxide. The solution resists the pH variations during titration.

Sodium

It is measured with the help of flame photometer. The instrument is standardized with the known concentration of sodium ion (1 to 100 mg/litre). The samples having higher concentration are suitably diluted with distilled water and the dilution factor is applied to the observed values.

Potassium

It is also measured with the help of flame photometer. The instrument is standardized with known concentration of potassium solution, in the range of 1 mg to 5 mg/litre. The sample having higher concentration is suitably diluted with distilled water and the dilution factor is applied to the observed values.

Chloride

It is measured by titrating a known volume of sample with standardized silver nitrate solution using potassium chromate solution in water or eosin/fluoresce in solution in alcohol as indicator. The latter indicator is an adsorption indicator while the former makes a red colored compound with silver as soon as the chlorides are precipitated from solution.

Silicates & Phosphate

These are also measured spectroscopically. Yellow colour is developed from the action of phosphates and silicates on molybdate ion under strong acidic conditions. The intensity of colour is directly proportional to the concentration of phosphate and silicates in the sample. Phosphate complexes are reduced by weak reducing agents such as ascorbic acid or tartaric acid (potassium antimonyl tartarate) whereas silica complexes require strong reducing conditions of hydrazine or bisulphite. The colour of reduced complex is sky blue.

Microbial analysis of water

The microbial analysis involves measurement of the quantity or nature of micro-organism that is present in water. The bacteria in the water could be any of the following species; *Escherichia coli*, *Enterobacter spp.*, *Citrobacter spp.*, *Proteus spp.*, *Serratia spp.*, *Shigella spp.*, *Providencia*

spp. *Morganella* spp., *Salmonellae* spp. and *Klebsiella* spp. *Escherichia coli*

Enteric bacteria in the family Enterobacteriaceae reside normally in the guts of many animals, including humans (Wawire et al., 2013). Some members of Enterobacteriaceae such as *Escherichia coli*, *Enterobacter* spp., and *Serratia* spp. are natural inhabitants of the gastro-intestinal tract of human beings and are used as indicators of faecal contamination of the environment. The pathogenic members of Enterobacteriaceae that infect the gastro-intestinal tract of humans include *Salmonella* spp., *Shigella* spp., *Proteus* spp., *Campylobacter* spp. and *E. coli*. They get access to the human when ingested through contaminated water, food and oral contact with infected surfaces. World Health Organization (WHO) developed microbiological quality guidelines based on intended water uses. The guidelines stipulate that faecal coliforms (FC) should not exceed 10² per 100 ml of water used in irrigation of crops that are eaten uncooked, sports fields, and public parks in unrestricted regions. Bacteriological analysis involves determination of the levels of total coliforms and *E. coli* using the 3 M *E. coli*/coliforms Petri film count plates.

Table 1. Different analytical water quality parameters with their analytical technique and guideline values as per WHO and USEPA

Sr. No.	Parameter	Technique used	WHO standard	EPA guidelines
01	Temperature	Thermometer	-	-
02	Color	Visual/color kit	-	-
03	Odour	Physiological sense	Acceptable	-
04	Electrical conductivity	Conductivity meter/Water analysis kit	-	2500 us/cm
05	pH	pH meter	6.5 – 9.5	6.5 – 9.5
06	Dissolved oxygen	Redox titration	-	-
07	Total Hardness	Complexo-metric titration	200 ppm	< 200 ppm
08	Alkalinity	Acid – Base titration	-	-
09	Acidity	Acid – Base titration	-	-
10	Ammonia	UV Visible Spectrophotometer	0.3 ppm	0.5 ppm
11	Bi carbonate	Titration	-	-
12	Biochemical Oxygen Demand (B.O.D.)	Incubation followed by titration	6	5
13	Carbonate	Titration	-	-

14	Chemical Oxygen Demand (C.O.D.)	C.O.D. digester	10	40
15	Chloride	Argentometric titration	250 ppm	250 ppm
16	Magnesium	Complexometric titration	150 ppm	30 ppm
17	Nitrate	UV Visible Spectrophotometer	45 ppm	50 mg/l
18	Nitrite	UV Visible Spectrophotometer	3 ppm	0.5 mg/l
19	Potassium	Flame Photometer	-	-
20	Sodium	Flame Photometer	200 ppm	200 ppm
21	Sulphate	Nephelometer /Turbidimeter	250 ppm	250 ppm

Table 2. Different analytical water quality parameters their source of occurrence and their potential health effects using WHO standard

Parameters	Sources of occurrence	health effect of the parameters
turbidity	soil run-off	Higher level of turbidity are associated with disease causing bacteria's
colour	Due to presence of dissolved salts	-----
Odour	Due to biological degradation	Bad or unpleasant odour
Electrical conductivity	Due to different dissolved solids.	Conductivity due to ionizable ions. High conductivity increases corrosive nature of water.
pH	pH is changed due to different dissolved gases and solids.	Affects mucous membrane; bitter taste; corrosion
Dissolved oxygen	Presence due to dissolved oxygen.	Dissolved Oxygen corrodes water lines, boilers and heat exchangers, at low level marine animals cannot survive
Total hardness	Presence of calcium (Ca ²⁺) and magnesium (Mg ²⁺) ions in a water supply. It is expressed. Hardness minerals exist to some degree in every water supply.	Poor lathering with soap; deterioration of the quality of clothes; scale forming
Total Alkalinity	Due to dissolved gases (CO ₂)	Embrittlement of boiler steel. Boiled rice turns yellowish
TDS	Presence all dissolved salts	Undesirable taste; gastro-intestinal irritation; corrosion or incrustation
Calcium	Precipitate soaps, anionic	Interference in dyeing, textile, paper industry etc
Magnesium	surfactants, anionic	-----

Ammonium	Due to dissolved gases and degradation of organics	Corrosion of Cu and Zn alloys by formation of complex ions
Barium	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits	Increase in blood pressure
Biochemical Oxygen Demand (B.O.D.)	Organic material contamination in water	High BOD decreases level of dissolved oxygen
Carbonates	Due to dissolution of CO ₂	Product imbalance Unsatisfactory production Short product life
Chloride	Water additive used to control microbes, disinfect.	Eye/nose irritation; stomach discomfort. Increase corrosive character of water
Nitrate	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits	Effect on Infants below the age of six months Symptoms include shortness of breath and blue-baby syndrome
Phosphate		stimulate microbial growth, Rancidity Mold growth
Sodium	Natural component of water	-----
Sulphates	Due to dissolved Ca/Mg/Fe sulphates	Taste affected; gastro-intestinal irritation. Calcium sulphate scale



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