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Ministry of Jal Shakti

Department of Water Resources,
River Development and Ganga Rejuvenation

CENTRAL WATER COMMISSION

FIELD WATER ANALYSIS MANUAL

JANUARY, 2020

सत्यमेव जयते

Government of India
Ministry of Jal Shakti,
Department of Water Resources, RD& GR
Central Water Commission

Field Water Analysis Manual

River Data Compilation -2 Directorate
Planning and Development Organisation
New Delhi 110066

2020

Member (River Management) &
Ex-Officio Additional Secretary
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PREFACE

Central Water Commission has been playing a major role in the water quality monitoring of river water since year 1963 and at present, is observing water quality at 552 key locations (519 on HO network and 33 WQSS) covering major river basins of India. Water quality monitoring stations on various rivers of India is monitoring 6 in-situ parameters (pH, Electrical Conductivity, Colour, Odour and Temperature). This Water Analysis Manual is to provide the common techniques, methods and standards for sample collection, handling and analysis at site for above 6 parameters.

It provides information on how to collect water samples to analyse for different water quality parameters that can be measured in the field and transportation of sample to level II/II+ and III laboratories of CWC for further analysis. This manual should be used as a guideline document for CWC level - I WQ sites for collection of samples, transportation and analysis thereof by persons and organisations involved in the monitoring of in-situ parameters at field stations. This manual will help users to find appropriate protocols that can be used for river water quality sampling in India. This will also ensure that water quality data and samples collected at sites are consistent and scientifically accurate.

I would like to place on record my appreciation of Shri Ravi Shankar, Chief Engineer (P&D), CWC; Shri Pankaj Kumar Sharma (Director) RDC-2, CWC and his team for excellently bringing out first edition of this publication. I also appreciate the efforts made by Dr Jakir Hussain, Research Officer, RDC-2, & In-charge, NRWQL, CWC for the preparation of the Field Water Analysis Manual.

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1. WATER QUALITY

Water is the source of life on earth, and human civilizations blossomed where there was reliable and clean freshwater. Use of water by humans – for drinking, washing, and recreation – requires water free from biological, chemical, and physical sources of contamination. Plants, animals, and the habitats that support biological diversity also need clean water. Water of a certain quality is needed to grow food, to power cities, and to run industries. Water quality is as important as water quantity for satisfying basic human and environmental needs, yet it has received far less investment, scientific support, and public attention in recent decades than water quantity, even though the two issues are closely linked.

Water Quality Activities in CWC

Central Water Commission is a premier Technical Organization of India in the field of Water Resources and is presently functioning as an attached office of the Department of Water Resources, River Development and Ganga Rejuvenation, Ministry of Jal Shakti, Government of India. The Commission is entrusted with the general responsibilities of initiating, coordinating and furthering in consultation of the State Governments concerned, schemes for control, conservation and utilization of water resources throughout the country, for purpose of Flood Control, Irrigation, Navigation, Drinking Water Supply and Waterpower Development. It also undertakes the investigations, construction and execution of any such schemes as required.

Mandates and objectives of water quality monitoring

Being the apex national body for development of water resources in the country, its mandate is assessment of water resources in general. This would include the following objectives in regard to water quality monitoring:

- Establishment of baseline water quality
- Assessment of suitability of water for various uses
- Detection of trends in water quality changes.
- Dissemination of water quality information upon request

Central Water Commission has a well-established 'Water Quality Monitoring Network' consisting of monitoring stations at 552 key locations (519 on HO network and 33 WQSS) covering all the major river basins of India. The water quality monitoring network consists of field laboratories called the level-I laboratories located at field water quality monitoring stations on various rivers of India for monitoring of 6 in-situ parameters, eighteen (18) level-II laboratories for the analysis of 25 physico-chemical plus bacteriological parameters, and five (05) level-III/II+ laboratories for the analysis of 41 parameters including heavy metals / toxic parameters and pesticides.

Water Quality Monitoring Network in CWC at present

At present, Central Water Commission follows a three-tier laboratory system for providing analytical facilities for the analysis of river water samples collected from 531 water quality monitoring stations belonging to the Water Quality Monitoring Network and covering all the major river basins of India.

The three tier laboratory system consists of:

1. **Level-I Laboratories:** These are the field laboratories which are located at field water quality monitoring stations on various rivers of India where in-situ values of six, five physical parameters and one chemical parameter (Dissolved Oxygen) of river water are monitored. There are a total number of 295 level-I laboratories located at field water quality monitoring stations on various rivers of India.

2. **Level-II Laboratories:** There are 18 level-II laboratories located at division offices to analyse 25 physico-chemical and bacteriological parameters of river water. The list of level-II laboratories in CWC is given at **(Table-1).**

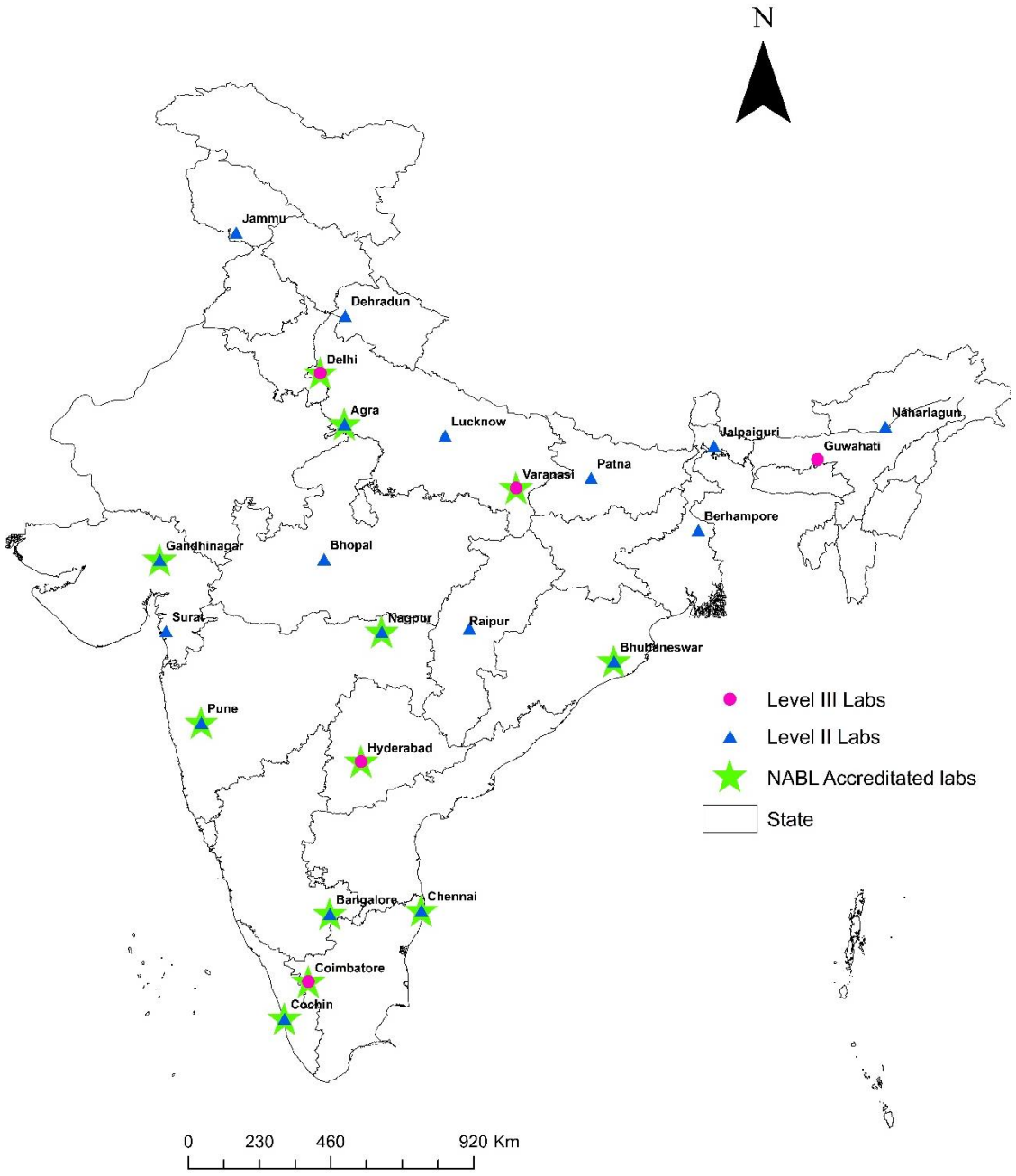
3. **Level-III/II$^+$ Laboratories:** There are five (05) regional level-III / II$^+$ laboratories for analysis of 41 parameters including heavy metals / toxic parameters and pesticides. The list of level-II$^+$/III laboratories in CWC is given at **(Table-1).**

4. **National River Water Quality Laboratory (NRWQL), New Delhi**
   The level-III laboratory at New Delhi under Yamuna Basin Organisation is the National Laboratory named as "National River Water Quality Laboratory (NRWQL), New Delhi".

Table : 1 - List of Water Quality Laboratories in CWC			
S. No.	**Location of laboratory**	**Level of Laboratory**	**Organisational Jurisdiction**
1	National River Water Quality Laboratory (NRWQL), New Delhi	III	YBO, New Delhi
2	Lower Cauvery Water Quality Laboratory (LCWQL), Coimbatore	II+	C&SRO, Coimbatore
3	Upper and Middle Ganga Water Quality Laboratory, Varanasi	III	UGBO, Lucknow
4	Krishna and Godavari River Water Quality, Hyderabad	II+	K&GBO, Hyderabad
5	Upper Cauvery Water Quality Laboratory, Bangalore	II	C&SRO, Coimbatore
6	South Western Flowing Rivers Water Quality Laboratory (SWFRWQL), Kochi	II	C&SRO, Coimbatore
7	Upper Krishna Division Water Quality Laboratory (UKDWQL), Pune	II	K&GBO, Hyderabad
8	Mahi Division Water Quality Laboratory (MDWQL), Gandhinagar	II	NTBO, Gangdinagar
9	Lower Yamuna Water Quality Laboratory, (LYWQL), Agra	II	YBO, New Delhi
10	Eastern Rivers Water Quality Laboratory (ERWQL), Bhubaneswar	II	M&ERO, Bhubaneswar
11	Hydrology Division, Chennai	II	C&SRO, Coimbatore
12	WainGanga Division, Nagpur	II	Nagpur
13	Middle Brahmaputra Division, Guwahati	III	B&BBO, Shillong
14	Lower Brahmaputra Division, Jalpaiguri	II	B&BBO, Shillong
15	U.B. Division, Dibrugarh	II	B&BBO, Shillong
16	Chenab Division, Jammu	II	IBO, Chandigarh
17	Lower Ganga Division, Berhampore	II	LGBO, Patna
18	Middle Ganga Division -V , Patna	II	LGBO, Patna
19	Mahanadi Division, Raipur	II	M&ERO, Bhubaneswar
20	Narmada Division, Bhopal	II	NBO, Bhopal
21	Tapi Division, Surat	II	NTBO, Gangdinagar
22	Himalayan Ganga Division, Dehradun	II	UGBO, Lucknow
23	Middle Ganga Division -I , Lucknow	II	UGBO, Lucknow

Note: Laboratories from Sl No 1 to 12 above are NABL accredited (as on 31.12.2019)

Figure 1: NABL accredited Water Quality Laboratories in CWC



- **National River Water Quality Laboratory, New Delhi**
- **Krishna & Godavari River Water Quality Laboratory, Hyderabad**
- **Upper & Middle Ganga Water Quality Laboratory, Varanasi**
- **Lower Cauvery Water Quality Laboratory, Coimbatore**
- Upper Cauvery Water Quality Laboratory, Bangalore
- Lower Yamuna Water Quality Laboratory, Agra
- West Flowing Rivers Water Quality Laboratory, Kochi
- Upper Krishna Division Water Quality Laboratory, Pune
- Mahi Division Water Quality Laboratory, Gandhinagar
- Eastern River Water Quality Laboratory, Bhubaneswar
- East Flowing Rivers Water Quality Laboratory, Chennai
- WainGanga Division, Nagpur

2. MONITORING CATEGORY

The 'Monitoring' Category comprises the following types:

• Baseline

• Trend

• Flux

Baseline stations

Baseline stations mean the monitoring location where there is *no influence of human activities* on water quality.

Frequency of sample collection in CWC is once every two months.

Trend stations

“Trend station” means the monitoring location designed to show how a particular point on a watercourse varies over time due, normally, to the influence of man’s activities.

Frequency of sample collection in CWC is once every month.

Flux stations or Impact stations

“Flux stations or Impact stations” means the location for measuring the mass of particular pollutant on Main River stem for measuring the extent of pollution due to human interference or geological feature at any point of time and is necessary for measuring impact of pollution control measures adopted.

Frequency of sample collection in CWC is thrice every month.

3. TYPES OF SAMPLE

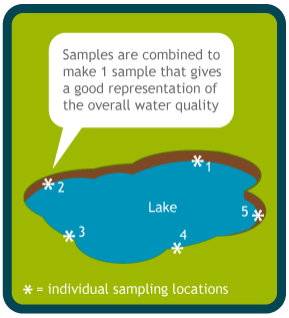
There are three types of sample

1. Grab or catch samples
2. Composite samples.
3. Integrated samples

Grab Sample

The simplest, a “grab” sample, is taken at a selected location, depth and time. Normally, the quantity of water taken is sufficient for all the physical and chemical analyses that will be done on the sample. Sometimes, if the s is small and many analyses are to be done, two grab samples will be taken at the station and will be mixed in the same transport container. Grab samples are also known as “spot” or “snap” samples.

Composite sample



The term composite refers to a mixture of grab samples collected at the same sampling point at different times. A composite sample of 24 h period is considered standard for most of the determination. It provides more meaningful data than the grab samples.

- Sometimes a composite sample representing one shift or a shorter time period or a complete cycle of a period operation may be preferable.
- Take at least 120-150mL of sample in each h, in some cases even at intervals of 30 min (if composition varies within an hour) and mix at the end of sampling period or combine in a single bottle as collected.
- A final volume of 4-5 L is sufficient.
- Sent the water sample to the Level II and III WQ laboratory as per the table no. 1

Integrated samples

For certain purpose, the information needed is provided best by analyzing mixture of grab samples collected from different points simultaneously.

- Such samples are useful for rivers or streams that vary in composition across the width and depth. For collection of integrated samples, special sampling device is needed.
- Sample is collected at a known depth without disturbing the surface water.
- Sent the water sample to the Level II and III WQ laboratory as per the table no. 1

4. WATER QUALITY PARAMETERS & ITS IMPORTANCE

Water in its chemically pure form occurs rarely in nature. In fact, water is commonly found to carry a variety of constituents. When water in its precipitate form reaches the surface of the earth, it has already collected a number of substances and properties that characterise natural water. Gases have been absorbed or dissolved, dust particles have been picked up, and it has obtained a certain temperature. In case of a high radioactive washout or high acidity pickup, atmospheric water may not even be clean in the general sense and may not be suitable for some uses.

Atmospheric water is subject to further changes of quality both upon reaching the earth's surface and during its travel underground. The ability to dissolve salts is gained in the topsoil where carbon dioxide is released by bacterial action on organic matter. The soil water becomes charged with carbon dioxide resulting in formation of carbonic acid. Under the acidic conditions that develop many soil and rock constituents are dissolved.

Man's influence on the quality of water is quite apparent and is now a major concern. Mixing with municipal and industrial waste waters may result in drastic changes in the water quality of natural waters. Agriculturally oriented activities such as irrigation, use of fertiliser, pesticides, herbicides, etc., may lead to diffuse pollution of both surface waters and ground water. Irrigation return waters also tend to increase total salts in the receiving water. Construction schemes, such as those connected with river training, flood control, low flow augmentation, etc., considerably influence the quality regime. Mining activities often cause substantial water quality changes.

There is a great range of water quality parameters that can be used to characterise waters. Largely the water quality measurement objectives and the previous history of the water body will determine selection of parameters. It is true, however, that some parameters are of special importance and deserve frequent attention.

4.1 Temperature

The temperature of a surface water body depends on its location, season and time of the day. The temperature of tropical and sub-tropical rivers may vary from 10 to 30^{o}C. Temperature of rivers receiving water from snow melt in their upper reaches may be even lower than 10^{o}C. Warm temperatures result in:

- decrease of solubility of gases in water, such as, O_2, CO_2 and N_2
- increase in the metabolic and growth rates of the aquatic organisms
- increase in volatilisation and chemical reaction rates of substances

- increase the die-away rate of micro-organisms, which are not normal inhabitant of the aquatic environment

Considering the above factors, it is seen that the warm water environment, along with organic pollution, would lead to a greater stress on the oxygen resources of the stream. In the case of addition of nutrients, it would also lead to eutrophication of the water body.

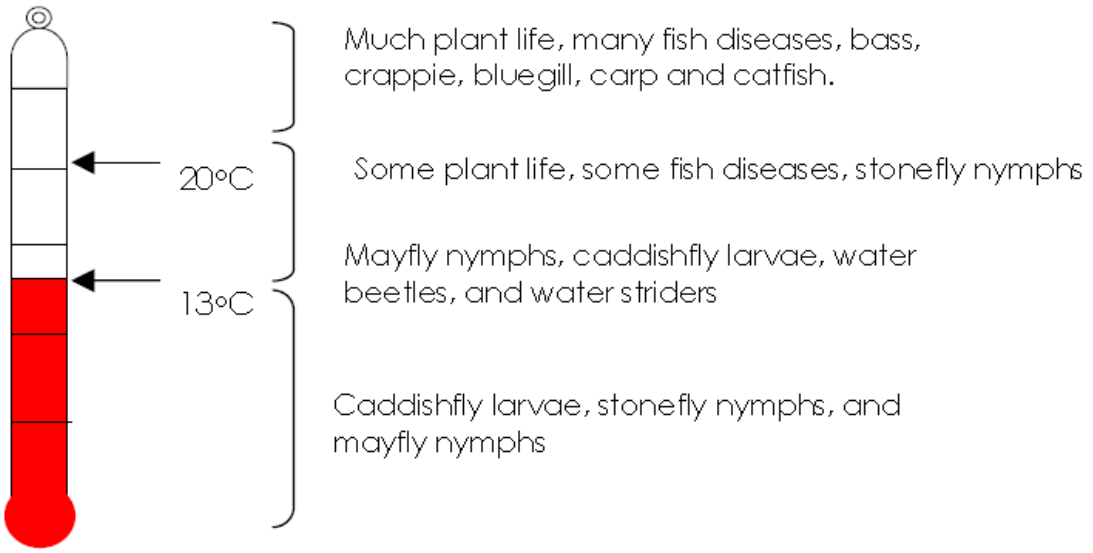


Figure 2: Temperature Tolerance Level of Selected Aquatic Organisms

River systems both consume and produce oxygen. It gains oxygen from re-aeration from the atmosphere and from plant photosynthesis. Running water, because of its churning, dissolves more oxygen than still water. Most aquatic organisms need oxygen to survive and grow. Some species, such as trout and stoneflies, require high levels of DO, while other species, such as catfish, worms and dragonflies, do not. If there is not enough oxygen in the water, the following may result: death of adult and juvenile fish; reduction in growth; failure of fish eggs/insect larvae to survive; changes in species present; and/or growth of toxic or smothering bacteria, fungi, or algae.

4.2 Colour

Ordinarily, surface waters do not have any true colour. Naturally present minerals and humic acids in dissolved state may impart their characteristic hues. Presence of suspended matter may give an apparent colour. Green, yellow-brown or red colour may be the result of presence of different microorganisms, particularly, algae. Presence of suspended, inorganic matter may also result in an apparent colour. Water Quality Standards specified by Bureau of Indian Standards (Tolerance Limits) are defined below:

4.3 Odour

Fresh water is odour free. Presence of odour suggests higher than normal biological activity due to the presence of decomposable organic material contributed by human or industrial wastes or excessive growth of algae and other plants. Odour is caused by production of volatile organic compounds and inorganics, such as, NH_3 and H_2S. It is more pronounced when the dissolved oxygen in water is less than about 25% of its saturation value. Industrial wastes can also create odours directly.

4.4 pH

The hydrogen ion concentration in water is expressed in terms of pH. It is defined as the logarithm of inverse of hydrogen ion concentration in moles/L. pH is a term used to indicate the alkalinity or acidity of a substance as ranked on a scale from 1.0 to 14.0. The pH scale measures the logarithmic concentration of hydrogen (H^+) and hydroxide (OH^-) ions, which make up water ($H^+ + OH^- = H_2O$). When both types of ions are in equal concentration, the pH is 7.0 or neutral. Below 7.0, the water is acidic (there are more hydrogen ions than hydroxide ions). When the pH is above 7.0, the water is alkaline, or basic (there are more hydroxide ions than hydrogen ions). Since the scale is logarithmic, a drop in the pH by 1.0 unit is equivalent to a 10-fold increase in acidity. So, a water sample with a pH of 5.0 is 10 times as acidic as one with a pH of 6.0, and a pH of 4.0 is 100 times as acidic as a pH of 6.0. The pH value of natural waters mostly depends on free carbon dioxide, bicarbonates and carbonate ions.

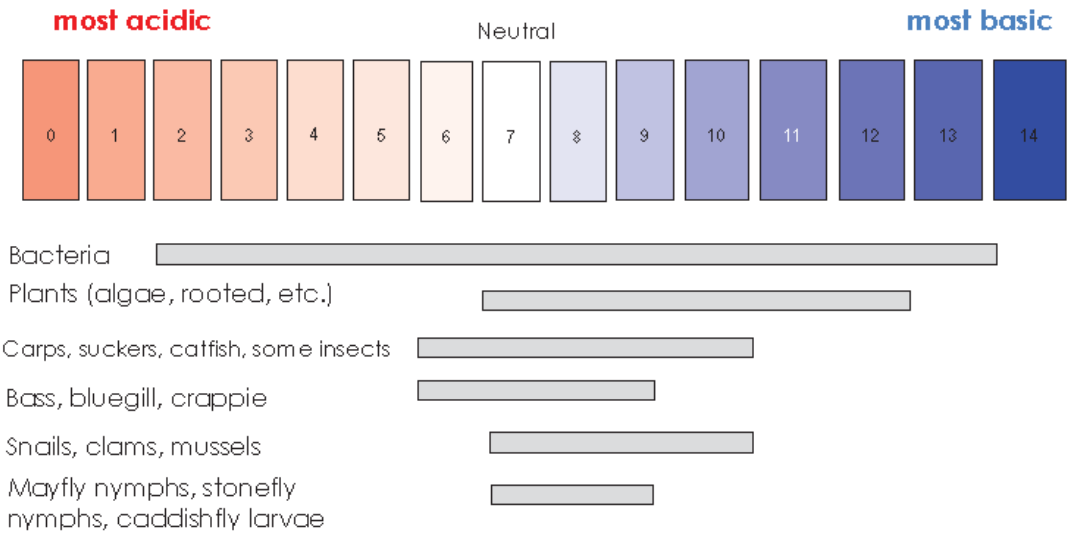


Figure 3: pH Ranges that Support Aquatic Life

The optimal range of pH for most aquatic life is 6.5 to 8.0. Prolonged exposure to pH less than 6 or greater than 9 can cause death for trout, salmon, and frogs. pH less than 5 causes death of most aquatic life, including insects and all fish.

pH affects many chemical and biological processes in the water. For example, different organisms flourish within different ranges of pH. The largest variety of aquatic animals prefers a range of 6.5 - 8.0. pH outside this range reduces the biodiversity in the stream because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements and compounds to become mobile and “available” for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life, particularly to sensitive species like rainbow trout. Changes in acidity can be caused by atmospheric deposition (acid rain), surrounding rock, and certain wastewater discharges. The pH water quality objective set by the SWRCB for the Central Valley states that the pH shall not be depressed below 6.5 nor raised above 8.5.

The equilibrium condition may be changed by the intensity of photosynthetic process (which consumes carbon dioxide) and the biochemical oxidation of organic substances (which produces carbon dioxide), as well as chemical conversions of some mineral substances, such as reduction-oxidation reactions of ammonia, sulphur containing minerals, iron, etc. The pH value is also affected by the presence of naturally present humic substances and various acids and alkalis, which may be discharged into the body of water through wastes.

Alkalinity and *acidity* are related parameters, which reflect the capacity of a water sample to neutralise acid or alkalinity, respectively. Measurement of these parameters along with pH may be required when solubility and ionic equilibria of various chemical species are under investigation.

4.5 Conductivity

Conductivity or electrical conductivity (EC) of natural water is due to the presence of salts, which dissociate into cations and anions. It is the ability of a solution to conduct current. The units of EC are µmhos/cm or µS/cm and is expressed at 25^{o}C. Even in cases where the chemical composition of water is represented almost exclusively by inorganic ions, the correlation between their content and EC may change considerably since different ions conduct electricity to different extents.

The value of EC may serve as an approximate index of the total content of dissolved substances in water samples. TDS, mg/L may be obtained by multiplying EC, µmhos/cm, by a factor ranging between 0.55 and 0.9. A commonly used value is 0.67. In order to increase the accuracy of the evaluation of the mineral content of waters from EC measurements, it is necessary to establish such correlations, for each body of water. The conductivity of most fresh waters ranges from 10 to 1000 µmhos/cm. It is, at times, used as an indication of ingress of sea water in estuarine region of a river.

Most aquatic biota tolerate a range of conductivity, however the ionic composition of the water can be critical. For example, cladocerans (water fleas) are far more sensitive to potassium chloride than sodium chloride at the same concentration. Conductivity will vary with water source such as ground water, water drained from agricultural fields, municipal wastewater and rainfall. Therefore, conductivity can indicate groundwater seepage, a sewage leak or another source of pollution has entered a stream.

4.6 Dissolved Oxygen

The dissolved oxygen (DO) saturation concentration of water varies with temperature, salinity and atmospheric pressure. In fresh waters, at sea level, it ranges from 15 mg/L at 0^{o}C to 7.5 mg/L at 30^{o}C. In water samples, it may be expressed in absolute terms as mg/L or as percent of saturation value.

Deviation in the concentration of DO from the saturation equilibrium value in a surface water body may exist due to aerobic biochemical oxidation of organic matter and photosynthetic activity of plants in water. These reactions, combined with atmospheric reaeration may result in establishing a different equilibrium concentration at a location, which may be below or above the saturation value. Oxygen content of fresh, unpolluted water bodies, having normal biological activity, ranges from 80% to 100% of saturation DO level. Lower levels indicate presence of organic pollution. DO in grossly polluted waters may be less than 25% of the saturation value. At this level, a drastic shift from the biological community of fresh waters may be expected. The water also becomes turbid and foul smelling.

In the main current of a stream the DO is usually the same at all depths because of mixing. However, in still water areas there may be stratification. This is particularly true for lakes. In eutrophic waters, the variation in DO with depth is very pronounced. Further, it is important to record the time of sampling since wide variation in DO at a location may occur over a 24-hour period.

River systems both consume and produce oxygen. It gains oxygen from re-aeration from the atmosphere and from plant photosynthesis. Running water, because of its churning, dissolves more oxygen than still water. Most aquatic organisms need oxygen to survive and grow. Some species, such as trout and stoneflies, require high levels of DO, while other species, such as catfish, worms and dragonflies, do not.

If there is not enough oxygen in the water, the following may result: death of adult and juvenile fish; reduction in growth; failure of fish eggs/insect larvae to survive; changes in species present; and/or growth of toxic or smothering bacteria, fungi, or algae.

5. COLLECTING THE SAMPLE

Samples will be collected from the selected site at the intended date and time of sampling. At that time the collector should collect the required volumes of water in the allocated container(s). Usually, unless specified otherwise, the samples to be collected are grab-samples taken from the well-mixed section of the main current.

In the event that the monitoring is meant to check the water quality for a specific water use function (i.e. surveillance monitoring), then the sample should be collected at the point of use. For example, if water quality monitoring is meant to check bathing water quality, a sample should be collected at the bathing location. For water quality monitoring to check drinking water quality, a sample should be collected at the point of water abstraction.

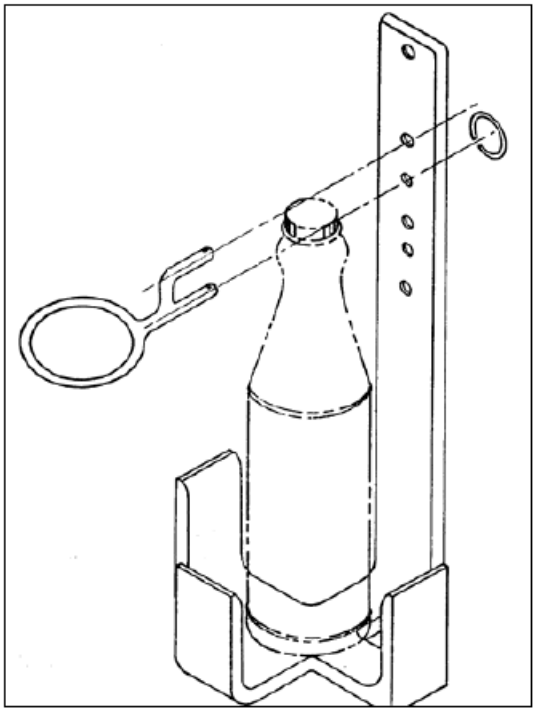


Figure 4: Sample bottle holder for sampling

The simplest form of a water sampling device is a bottle or bucket attached to a string. However, this will not sink easily below the water surface. To lower a plastic or glass bottle in a body of water it is necessary to use a bracket or holder of sufficient weight to overcome the buoyancy of the bottle and allow it to sink rapidly to the required depth, usually 20-30 cm below the water surface. Such a holder designed to contain a one or two-litre bottle is shown in Figure 4.

Where feasible a sample may be collected by holding the sample bottle in hand and submerging it. Collect the sample from the well-mixed section of the river, approximately 20-30 cm below the water surface (see Figure 5) . Care must be taken not to catch any floating material or bed material into the container. If the water is less than 40cm, the sample should be collected at half the actual water depth. If possible, sampling from shallow waters (less than 40cm) should be prevented by moving, within the site, to a deeper part of the river or stream.

Samples from reservoir sites will be collected from the outgoing canal, power channel or water intake structure, in case water is pumped. When there is no discharge in the canal, sample will be collected from the upstream side of the regulator structure, directly from the reservoir.

Rinse the sample container three times with the sample before it is filled. Leave a small air space in the bottle to allow mixing of sample at the time of analysis.

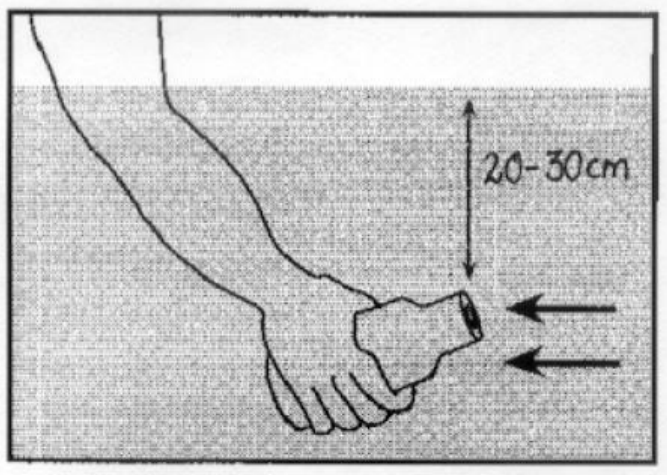


Figure 5: Collecting a sample from surface water

Collecting Water Sample for DO Test :

If the probe cannot be lowered into the stream or river or lake, depending on the situation, water sample can be collected using a sample container. Collect the water samples in accordance with the procedures below –

I. Carefully wade into the stream. Stand facing one of the banks; do not stand upstream of the bottle. Make sure that the water is deeper than the sample bottle, i.e., it can be reached with both arms underwater.

II. Remove the cap of the sample bottle. Lower the bottle into the water slowly, pointing it downstream, until the lower lip of the opening is just submerged.

III. Allow the water to fill the bottle very gradually, avoiding any turbulence (which would add oxygen to the sample). When the water level in the bottle has stabilized (it won't be full because the bottle is tilted), slowly turn the bottle upright and fill it completely. Keep the bottle under water and allow it to overflow for 2 or 3 minutes to ensure that no air bubbles are trapped.

IV. Cap the bottle while it is still submerged. Lift it out of the water. Look around the "collar" of the bottle just below the bottom of the stopper. If air bubble is present, pour out the sample and try again. An air bubble will produce false, high readings.

V. In a clean work area near the bank, uncap the bottle and place the probe below the surface.

VI. Follow steps (iv) to (v) of the direct measurement procedure above for measuring the DO level using the meter and probe.

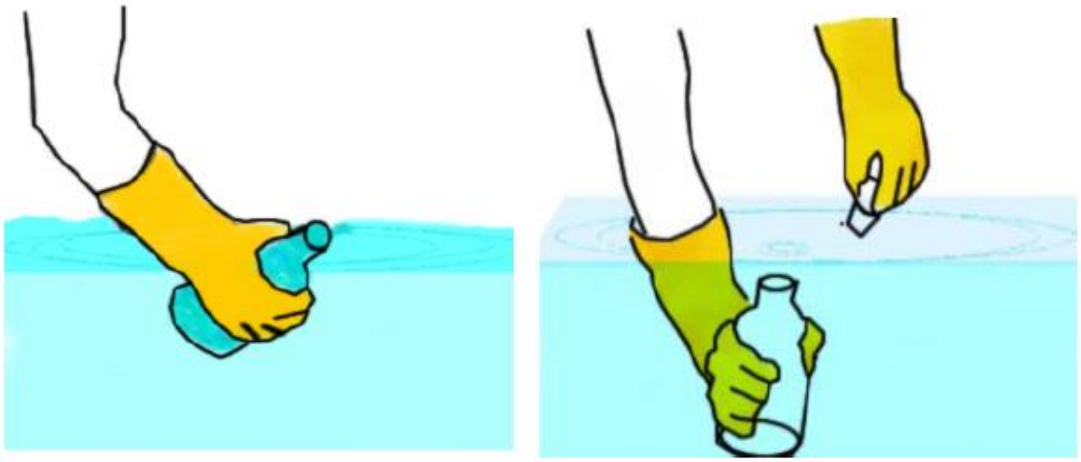


Figure 6: Collecting Water Sample for DO Test

Figure 7 : Technique for taking hand – held grab samples

Remember to wash hands thoroughly after collecting samples suspected of containing fecal contamination. Take care not to touch eyes, ears, nose or mouth until after washing hands.

6. LABORATORY PREPARATION FOR SAMPLING, SAMPLE HANDLING, PRESERVATION AND TRANSPORATION

In addition to sampling, field operatives also need to be able to take measurements and chemically 'fix' certain samples so that their parameter values do not change prior to laboratory analysis. The measurements which need to be taken on site are those of temperature, pH and conductivity. These can most usefully be determined in the field by means of a small portable instrument capable of measuring all these parameters. As meters of this type require at least daily calibration and regular maintenance a supply of distilled water, pH buffers, standard solutions, batteries and basic spare parts should also be carried with the meter.

Samples for metals analysis should be acidified with concentrated nitric acid as soon as they are obtained. The sampler also needs to carry a bottle of concentrated nitric acid in a bottle carrier, therefore. Samples for dissolved oxygen concentration of water can change rapidly due to chemical and biological activity in the sample bottle. To prevent this change, the sample must be chemically 'fixed' as soon as it is obtained. This fixing is carried out by adding 1 millilitre of manganous sulphate solution, 1 millilitre of alkaline iodide-azide solution and 1 millilitre of sulphuric acid to the sample in the bottle as soon as it has been taken. Thus it is necessary to equip every field operative with these solutions.

6.1 Sample Containers

In order to cover the range of parameters which need to be sampled and analysed, a variety of sample containers are used. The different types are reviewed here again and briefly discussed:

- 1000 millilitre glass (or teflon) bottles with teflon lined caps - for pesticides and phenols 500 millilitre polyethylene bottles - for metals (except mercury)
- 100 millilitre glass bottles - for mercury and phosphorus
- 1000 millilitre polyethylene bottles for all other chemical parameters
- BOD bottles, with ground glass stoppers, of a volume consistent with the dissolved oxygen samplers (possibly 300 millilitre)
- strong thick-walled glass bottles of at least 300 millilitre capacity for microbiological analysis. When collecting the bacteria sample, consider wearing gloves to minimize potential contamination. You should also use a sterilized, sealed pre-preserved bottle - do not use if the seal has been broken. These should be fitted with screw caps capable of maintaining a good seal even after multiple sterilisations in an autoclave.
- For volatile organic compounds, use clear or brown bottles or vials with screw caps or stoppers lined with tetrafluoroethene resin films, or similar products, which can be closed to provide a gas-tight seal.

❖ For semi-volatile or non-volatile organic compounds, use clear or brown glass jars with a stoppers or Teflon lined screw caps

Steralized Bottle

Polyethylene bottles

Brown Bottles

BOD Bottle

Figure 8: Sampling bottle

The sample containers needed for a sampling campaign are prepared by the laboratory and given to the person collecting samples. An overview of the types of containers and preservation is given in Table 2.

Table 2: Types of containers and preservation

S. No.	Analysis	Container	Volume (mL)	Preservation
1	On site analysis	PE bowl or container	± 200	-
2	General (SS, TDS, Major ions, Chlorophyll-a)	Glass, PE	1000	-
3	COD, NH_3, NO_2^-, NO_3^-	Glass, PE	500	H_2SO_4, pH <2
4	P	Glass	100	-
5	DO	Special BOD bottle	300	DO fixing
6	BOD	Glass, PE	1000	4^0C, dark
7	Coliform	Glass, PE, Sterilized	300	4^0C, dark
8	Heavy metals (Cd, Zn)	Glass, PE	500	HNO_3, pH<2
9	Mercury	Glass	1000	HNO_3, pH<2
10	Pesticides	Glass, Teflon	1000	4^0C, dark

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6.2 Preparation and Sterilisation of Equipment

In general, bottles which are to be used for collecting samples must be thoroughly washed and rinsed before use. Washing can be done by hand but, if there are many bottles to wash, it is often best undertaken by machine. Bottles which are to be used for collecting microbiological samples must be thoroughly washed and sterilised before use. Sterilising can be carried out by placing the bottles in an autoclave at 121°C for fifteen minutes or, if the caps of the bottles do not contain plastic or rubber materials, in an oven at 170°C for at least two

hours. Thus, any laboratory that needs to prepare bottles for microbiological samples requires either an autoclave capable of comfortably sterilising at least twenty bottles at one time or an equivalent size sterilising oven.

Bottles to be used for the collection of pesticides are to be rinsed with organic solvent (e.g. hexane) prior to use. This should be done in the laboratory. Some samples need to be preserved or fixed in the field. For dissolved oxygen fixing, every field operative should bring three pipetted glass or plastic stoppered 500 millilitre bottles containing the DO fixing solutions. As these solutions can be corrosive the three bottles should be carried in an appropriately sized bottle carrier to ensure they do not tip over and spill their contents.

For other parameters, (e.g. COD, NH_3, NO_2^-, NO_3^-) addition of concentrated sulfuric acid should be done in the field after sampling. For heavy metals, addition of nitric acid needs to be done in the field after sampling. Therefore, the field operative should be equipped with two pipetted glass or plastic stoppered 100 millilitre bottles containing the two acids.

Table : 3 Water Quality parameters, preservation, holding and sampling instrument

Contents	Classical Chemistry Constituents and Nutrients	Classical Chemistry Constituents and Nutrients Requiring Acid Preservation as Listed	Metals	Biological Contaminants
Water Quality Parameters	Unpreserved Classical Chemistry Constituents Including Nutrients, Anions and Other Analytes as Listed Acidity, alkalinity, chloride, color, conductivity, fluoride, nitrate, nitrite, odor, o-phosphate, silica, sulfate, TDS, TSS, turbidity	Ammonia; nitrate + nitrite combined; kjeldahl and organic nitrogen; total phosphorus	Antimony, arsenic, barium, beryllium, cadmium, calcium, chromium (total), magnesium, manganese, mercury, nickel, selenium, sodium, silver, thallium, lead, copper, zinc and other trace metals	Total coliforms; fecal coliforms; *E. coli*; enterococci; heterotrophic bacteria; or coliphage
Bottles to use	Plastic or glass bottles may be used but plastic is preferred.	Plastic or glass bottles may be used but plastic is preferred.	Plastic or glass bottles may be used but plastic is preferred.	Sterile 125 or 150 mL plastic bottles must be used.
Preservative to use	Cool to ≤ 4 °C (≤ 39.2 °F)	Sulfuric acid (H_2SO_4) to pH < 2	Nitric acid (HNO_3) to pH < 2	Sodium thiosulfate if sample is chlorinated and Cool to < 10 °C (< 50 °F) for source water
Holding times	Most of these analytes have short holding times. Deliver samples to the lab the same day if possible or ship via overnight delivery. Check with the lab regarding the holding times for the specific analytes of interest.	28 days	28 days for mercury, 6 months for other metals	Holding times are generally very short – 8 hours for source water compliance samples.

6.3 Sample Preservation

Samples for BOD and bacteriological analyses should be stored at a temperature below 4°C and in the dark as soon as possible after sampling. In the field this usually means placing them in an insulated cool box together with ice or cold packs. Once in the laboratory, samples should be transferred as soon as possible to a refrigerator.

Samples for DO measurement should be chemically fixed immediately after collection:

a) With the stopper in the bottle, drain any liquid in the flared lip of the BOD bottle containing the sample.

b) Remove stopper and add 1 mL of $MnSO_4$ followed by 1 mL alkali-iodide-azide reagent. Hold the pipette tip just below the liquid surface touching the side of the bottle. Wash the pipette before returning to the reagent bottles.

c) Stopper the bottle carefully to exclude air bubbles. Mix by inverting the bottle a few times.

d) Allow the brown manganese hydroxide floc (white floc indicates absence of DO) to settle approximately to half the bottle volume, then add 1.0 mL conc H_2SO_4 and re-stopper. Mix by inverting several times until dissolution is complete. Such samples can then be kept up to six hours before titration.

If samples collected for chemical oxygen demand (COD) analysis cannot be analysed on the day of collection they should be preserved below pH 2 by addition of concentrated sulphuric acid. This procedure should also be followed for samples for ammoniacal nitrogen, total oxidised nitrogen and phenol analysis.

Samples which are to be analysed for the presence of metals, should be acidified to below pH 2 with concentrated nitric acid. Such samples can then be kept up to six months before they need to be analysed; mercury determinations should be carried out within five weeks, however.

After labelling and preservation, the samples should be placed in an insulated cool box for transportation (Figure 9). Samples should be transported to concerned laboratory (level II or II+) as soon as possible, preferably within 48 hours.

Analysis of bacteriological samples should be started and analysed within 24 hours of collection.

If samples are being brought to a Level I laboratory for the 'field determinations', they should be transported in less than 24 hours.

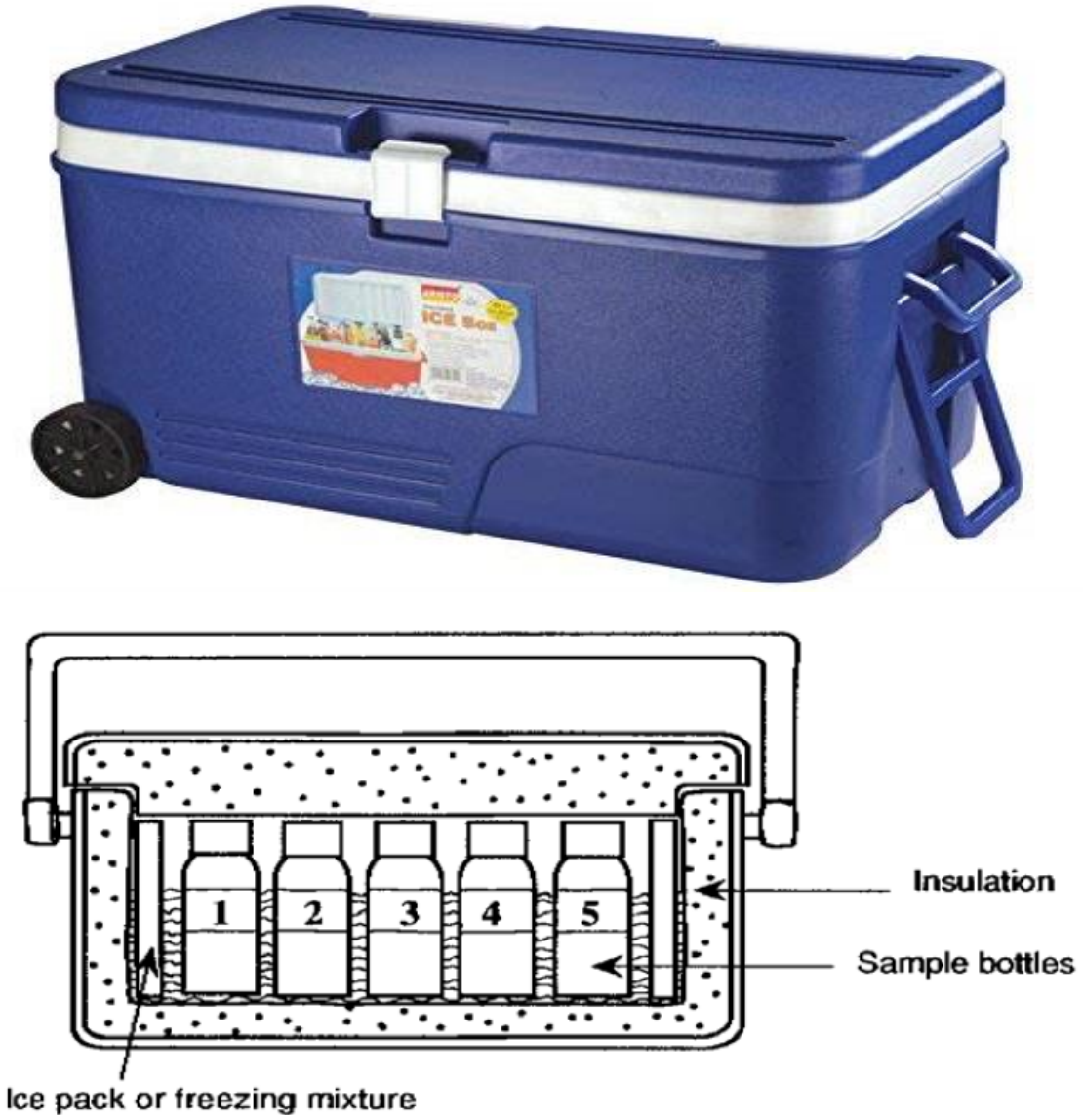


Figure 9: - Insulated bottle carrier for water quality samples

6.4 Handling and Shipping of the Sample

Samples should be packaged and shipped to the laboratory for analysis as soon as possible. Generally, the shorter the time between sample collection/processing and sample analysis, the more reliable the analytical results will be. Before shipping samples to the laboratory:

- Check that sample bottles are labelled correctly.
- Complete an Analytical Request Form (ARF).
- Pack samples carefully in the shipping container to prevent bottle breakage, shipping container leakage, and sample degradation. Check that the bottle caps are securely fastened.

6.5 Labelling Sample Bottles:

Each sample bottle must be correctly labelled with the station identification number, date, time, and sample designation. Sample designation is established by the laboratory. Laboratory codes that are added or deleted from the analytical schedule requested should be recorded on the analytical request forms that accompany the samples—not on the sample bottles.

A bottle with an unreadable label or no label is a wasted sample.

1. Label each bottle with a permanent, waterproof marker, or use pre-printed labels that will remain securely attached to the bottles, even if they become wet.
2. Write legibly and include as a minimum the following information:
   - Station identification number.
   - Date and time of sample collection
   - Sample designation code

6.6 Filling out an Analytical Request Form

Each set of samples must include an Analytical Request Form. To ensure correct processing of samples, the information recorded on the AR form must correspond to each sample in the shipment.

- Never send a sample to the laboratory without an analytical request form.
- Information recorded on AR forms must be legible and completed in permanent ink or by computer.
- Record the field-measurement values of pH, specific electrical conductance (conductivity), Colour, Odour, temperature and Dissolved Oxygen.
- Fill out the AR form as follows, including as much information about the sample(s) as possible:
- Keep a copy of the completed Analytical Request Form in the level I office files.

6.7 Analytical Request Form

The Analytical Request Form provides a record of all important information concerning the sample collected. Complete the sample identification form at each monitoring site, detailing the samples that are collected at that site. Note that if more than one bottle is filled at a site, for different types of analyses, this is to be registered on the same form. Local conditions, such as weather, human activity on the banks, state of water body, etc., at the sampling site should be recorded on the form, at the time of sampling. Such information may be useful in analysis of data.

The form for identifying the sample and recording the field measurements and site conditions is given in Figure 10.

Analytical request forms should be given to the laboratory analyst together with the samples. The forms should all be kept in a master file at the level II or II+ laboratory where the samples are analysed.

Figure 10: Analytical Request Form

Sample code											
Observer					Agency				Project		
Date Time					Station code						
Parameter Code	**Container**				**Preservation**				**Treatment**		
	Glass	**PVC**	**PE**	**Teflon**	**None**	**Cool**	**Acid**	**Other**	**None**	**Decant**	**Filter**
(1) Gen											
(2) Bact											
(3) BOD											
(4) COD, NH_3,NO_3^-											
(5) H. Metals											
(6)Tr. Organics											

Source of sample				
Waterbody	***Point***	***Approach***	***Medium***	***Matrix***
o River o Drain o Canal o Reservoir	o Main current o Right bank o Left bank	O Bridge O Boat O Wading	o Water o Susp matter o Biotap o Sediment	o Fresh o Brackish o Salt o Effluent

Sample type	o Grab o Time-comp o Flow-comp o Depth-integ o Width-integ
Sample device	o Weighted bottle o Pump o Depth sampler

Field determinations			
Temp °C	**PH**	**EC μmho/cm**	**DO mg/L**

Odour Code	(1) Odour free (2) Rotten eggs (3) Burnt sugar (4) Soapy (5) Fishy	(6) Septic (7) Aromatic (8) Chlorinous (9) Alcoholic (10) Unpleasant	**Colour code**	(1) Light brown (2) Brown (3) Dark brown (4) Light green (5) Green	(6) Dark green (7) Clear (8) Other (specify)

Remarks	
Weather	o Sunny o Cloudy o Rainy o Windy
Water vel. m/s	o High (> 0.5) o Medium (0.1-0.5) o Low (< 0.1) o Standing
Water use	o None o Cultivation o Bathing & washing o Cattle washing o Melon/vegetable farming in river bed

6.8 Photo Documentation

If possible, take photographs of the sampling sites and sampling activities. Site photographs are helpful in identifying sites for future monitoring and could also aid in assessing changes in the water body over time. By photographing fixed stations or monitoring sites on a regular basis, the changes occurring at the site are clearly documented. Take enough photos on the first visit to the site to establish a complete photo record of the site and its surroundings and describe the photo points in detail in the field or record notes. The photos can later be transferred to a computer file and can form part of the report. When included in reports, photos would enable readers who have not been to the site to visualize the site conditions.

Take photographs where there are naturally occurring landmarks such as a large tree or boulder or bridge site. It is better to establish specific points where the photographer will position himself every time photographs are taken (photopoint). For instance, he/she can take photographs from one side of a bridge or culvert during each visit to the site. If there are no naturally occurring landmarks at a given site, a photo point may be established, e.g., with a pile of rocks.

Indicate the date and time photos are taken. Captions are meant to provide brief explanation of where the photo was taken and the condition at the time it was taken. As far as possible, take photo of the established monitoring station every time sample is taken. For a surface water station, take two photos; one upstream of the sample point looking downstream at the sample point; and one downstream of the sample point looking upstream at the sample point.

6.9 Packing Samples

When packaging samples for shipment to the laboratory, remember that all bottles must be protected from breaking (especially glass bottles) and (or) leaking.

When packaging samples:

1. Make sure bottle labels are waterproof and that information is legible.
2. Tighten all bottle caps to prevent leakage.
3. Line all shipping containers, including those without ice, with doubled heavy-duty plastic bags.
4. Use adequate packing material to prevent bottle breakage.
    - Ship all glass bottles in foam sleeves or wrap them with bubble wrap.
    - Pack bottles so that they do not touch each other.

After labelling and preservation, the samples have to be packed for transport, preferably in an sulated cool box. After sampling, many water quality parameters undergo chemical or biochemical reactions in the sample bottle causing the concentration to change from that which was present in the watercourse. To prevent this alteration of parameter values, ideally

all samples should be kept at a temperature below 4°C and in the dark until they are analysed. If this is not possible, then at least samples for BOD, coliforms, pesticides and other organics that are likely to volatilise MUST be kept at 4°C, and dark.

Remaining samples can have no preservation. In the field, the best way to ensure that samples are kept cold is to pack them into insulated cool boxes containing either an ice/water mixture or a large number of ice packs. Thus, sufficient cool boxes to contain a full day's sampling campaign should be available to each field operative that is required to take water quality samples.

6.10 Preparation of Samples for Transport

Samples should be transported to concerned laboratory (level II, II+ & III) as soon as possible, preferably as per protocol. If samples are being brought to a Level I laboratory for the 'field determinations', they should be transported in less than 6 hours.

Whenever possible, ship samples to the laboratory on the day of collection. Check laboratory hours of operation—keep in mind that the laboratory might not receive samples on Saturdays/ Sundays, or holidays. The integrity of chilled samples sent late on a Thursday or on a Friday could be compromised if not received by the laboratory in time to be unpacked and refrigerated.

Sample integrity must be maintained. Ship samples with enough ice to Keep chilled at 4°C or below without freezing until the sample is logged in at the laboratory.

7.0 GUIDELINES ON STANDARD ANALYTICAL PROCEDURES

Measurements of colour, odour, temperature, electrical conductivity, pH and dissolved oxygen are considered to be 'Field Determinations' and should be made as soon as possible after collecting a sample. Measurement of these parameters can be made in the field if field meters are available. This is the best option, as the analyses will be made immediately. Another option is to bring samples to the nearest Level I laboratory, where equipment for analyses is set up. If samples are brought to the level one laboratory, the travel time should be very short, so that parameter values do not change between the time the sample is collected at the time of analysis. Note that the DO sample must be 'fixed' immediately after collection and that the temperature must be measured at the site.

The *'Guidelines on Standard Analytical Procedures for Water Analyses'* for detailed procedures including preparation of reagents are given here for the following analyses:

- Odour
- Colour
- Temperature
- pH
- Electrical Conductivity
- Dissolved Oxygen

7.1 Colour

Colour may occur in drinking water for any one or more of several reasons. It may be due to the presence of coloured organic substances originating in the decay or aqueous extraction of natural vegetation, such as in soil runoff; the presence of metals such as iron, manganese and copper, which are abundant in nature, are weathered from rock or corroded from distribution systems by water, and are naturally coloured; or the presence of highly coloured industrial wastes, the most common of which are pulp and paper and textile wastes.
The presence of colour in water is not objectionable from health point of view, but may spoil the colour of the clothes being washed. The standard unit of colour is that which is produced by one milligram of platinum cobalt dissolved in one litre of distilled water.

Determining the colour in the field is relatively easy. Pour an aliquot of approximately 10mL of sample into a glass test tube and judge the colour observed. Assign one of the colour codes from Table 4 to the sample. In case the colour of water does not fall under code 1 to 7, select code 8 and note down the details of the colour observed. Report the colour code on the sample identification form.

Some natural phenomena can change water colour but it does not necessarily mean that the water is of bad quality. The different colour numbers correspond mainly to these types of water bodies:

- **Indigo blue to greenish blue with high light penetration (1-5 FU scale).** These waters have often low nutrient levels and low production of biomass. The colour is dominated by microscopic algae (phytoplankton).
- **Greenish blue to bluish green (6-9 FU scale).** The colour is still dominated by algae, but also increased dissolved matter and some sediment may be present. Typical for areas towards the open sea.
- **Greenish (10-13 FU scale).** Often coastal waters which usually display increased nutrient and phytoplankton levels, but also contain minerals and dissolved organic material.
- **Greenish brown to brownish green (14-17 FU scale).** Usually with high nutrient and phytoplankton concentrations, but also increased sediment and dissolved organic matter. Typical for near-shore areas and tidal flats.

Table 4 : Colour codes for field determination of colour

Colour Code	Light brown
	Brown
	Dark brown
	Light green
	Green
	Dark green
	Clear
	Other specify

- **Brownish green to cola brown (18-21 FU scale).** Waters with an extremely high concentration of humic acids, which are typical for rivers and estuaries.

7.2 Odour

(QUALITATIVE HUMAN RECEPTOR)

Odour in drinking water may be defined as that sensation that is due to the presence of substances that have an appreciable vapour pressure and that stimulate the human sensory organs in the nasal and sinus cavities. In general, offensive odours in drinking water may be of biological or industrial origin. Some of the odours of natural origin may be indirectly due to human activities; for example, the dumping of raw sewage into the aquatic environment enhances biological growth and consequently odours.

Odour in water is usually measured in terms of its threshold odour number (TON), the number of times a sample must be diluted with an equal volume of odourfree water to become just detectable by 50% of a panel of judges under very carefully controlled test conditions (APHA, 2017).

As odour cannot be measured objectively, a maximum acceptable limit for drinking water has not been specified.

Procedure

a) As soon as possible after collection of sample, fill a cleaned odourless bottle half - full of sample, insert stopper, shake vigorously for 2 to 3 seconds and then quickly observe the odour. The sample should be at ambient temperature.

b) Report the odour as: -
odour free, rotten egg, burnt sugar, soapy, fishy, septic, aromatic, chlorinous, alcoholic odour or any other specific odour. In case it is not possible to specify the exact nature of odour, report as agreeable or disagreeable.

7.3 Temperature

Temperature a measure of warmth or coldness of a substance with reference to a standard value. It is an important factor to consider when assessing water quality. water temperature at a field site are essential for water-quality data collection. In addition to its own effects, temperature influences several other parameters and can alter the physical and chemical properties of water (Fondriest). In this regard, water temperature should be accounted for when determining the following-

- pH
- Oxidation reduction potential (ORP)
- Conductivity and salinity
- Dissolved oxygen and other dissolved gas concentrations
- Water Density
- Metabolic rates and photosynthesis production
- Biological activity

A temperature in degrees Celsius can be converted to Fahrenheit or Kelvins by the following equations:

°F = (1.8*°C) + 32

K = °C + 273.15

Apparatus

Digital thermometer having a scale marked for every 0.1^0C.

Procedure

a) Immerse thermometer in the sample up-to the mark specified by the manufacturer and read temperature after equilibration.
b) When a temperature profile at a number of different depths is required a thermistor with a sufficiently long lead may be used.
c) Immerse the thermometer in the water to reading depth and wait until the reading is constant (approx. 1 min.). If it is not technically possible to measure directly, the water sample is taken in a vessel containing at least 1 litre.

Reporting

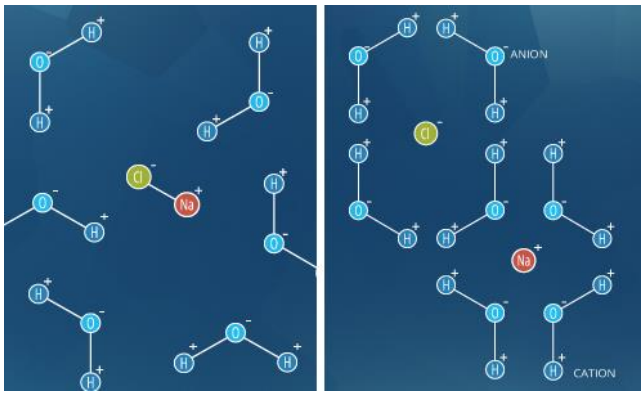
Report the temperature in units of degree Celsius with 1 figure after the decimal point, e.g. 13.2 °C.

Water temperature has been defined as the "abiotic master factor" by JR Brett due to its effect on aquatic organisms

7.4 Electrical Conductivity

(CONDUCTIVITY CELL POTENTIOMETRIC)

Conductivity is a numerical expression of the ability of a water sample to carry an electrical current and varies with the number and types of ions the solution contains. Most dissolved inorganic substances in water are in the ionised form and hence contribute to conductance. Specific conductance, or the conductivity of a solution, is attributed to the ionic species (cations and anions) present in the water sample.



The important ions that impart conductivity in water are:

i. anions: Cl^- , SO_4^{+2}, CO_3^{-2};, HCO_3^- and NO_3^-;

ii. cations: Ca^{2+}, Mg^{2+}, Na^+ and K^+

Conductivity is customarily reported in micromhos per centimeter (µmhos/cm). In the International System of units (SI) the reciprocal of ohm is the Siemens (S) and conductivity is reported as µmhos/cm per meter (mS/m).

1 mS/m = 10 µS/cm = 10 µmhos/cm and 1 µS/cm = 1 µmhos/cm

Freshly distilled water has a conductivity of 0.5 to 2 µmhos/cm, and this increases after a few weeks of storing up to 2 to 4 J µmhos/cm. This increase is caused by absorption of atmospheric CO_2.

Apparatus

a. Conductivity meter capable of measuring conductivity with an error not exceeding 1% or 0.1mS/m whichever is greater.

b. Conductivity cell, Pt electrode type. For new cells not already coated and old cell giving erratic readings platinise according to the following procedure. Clean the cell with chromic – sulphuric acid cleaning mixture. Prepare platinising solution by dissolving 1g chloroplatinic acid, H2Pt Cl6.6H2O and 12 mg lead acetate in 100 mL distilled water. Immerse electrodes in this solution and connect both to the negative terminal of a 1.5 V dry cell battery (in some meters this source is built

in). Connect the positive terminal to a platinum wire and dip wire into the solution. Continue electrolysis until both cell electrodes are coated with platinum black.

Reagent

a. Conductivity water - use distilled water boiled shortly before use to minimise CO2 content. Electrical conductivity must be less than 0.1 µmho/cm.

b. Standard potassium chloride solution, KCl, 0.01*M*, conductivity 1412 µmho/cm at 25^0C. Dissolve 745.6 mg anhydrous KCl (dried 1 hour at 180 °C) in conductivity water and dilute to 1000 mL. This reference solution is suitable when the cell has a constant between 1 and 2 per cm.

Procedure

a. Rinse conductivity cell with at least three portions of 0.01M KCl solution. Measure resistance of a fourth portion and note temperature.

b. In case the instrument indicates conductivity directly, and has internal temperature compensation, after rinsing as above, adjust temperature compensation dial to 0.0191/ °C and with the probe in standard KCl solution, adjust meter to read 1412 µmho/cm. continue at step d.

c. Compute the cell constant, KC according to the formula:
The value of temperature correction [0.0191 x (t-25)+1] can be read from Table 5.1.

d. Rinse cell with one or more portions of sample. The level of sample aliquot must be above the vent holes in the cell and no air bubbles must be allowed inside the cell. Adjust the temperature of sample to about 25°C (outside a temperature range of 20 - 30°C, error increases as the sample temperature increasingly deviates from the reporting temperature of 25°C). Read sample conductivity and note temperature to nearest 0.1°C.

e. Thoroughly rinse the cell in distilled water after measurement, keep it in distilled water when not in use.

Calculation

a. When sample conductivity is measured with instruments having temperature compensation, the readout automatically is corrected to 25^0C If the instrument does not have internal temperature compensation, conductivity at 25^0C is:

Reminder:
Specific conductance should never be measured in sample water that had earlier been used for pH measurements.

The value of temperature correction [0.0191 x (t-25)+1] can be read from Table 5.1.

$$K_C = \frac{1412}{C_{KCl}} \times [0.0191(t-25)+1]$$

where: K_C = the cell constant, 1/cm

C_{KCl} = measured conductance, µmho

t = observed temperature of standard KCl solution, °C

b. Record the meter reading, the unit of measurement and the temperature of the sample at the time of reading. Report the electrical conductivity at 25°C. Report conductivity preferably in µmho/cm.

Table 5: Value of [0.0191 X (T-25)+1) for Temperature Correction of EC measurement

T (°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
15	0.810	0.812	0.814	0.816	0.818	0.820	0.821	0.823	0.825	0.827
16	0.829	0.831	0.833	0.835	0.837	0.839	0.840	0.842	0.844	0.846
17	0.848	0.850	0.852	0.854	0.856	0.858	0.859	0.861	0.863	0.865
18	0.867	0.869	0.871	0.873	0.875	0.877	0.878	0.880	0.882	0.884
19	0.886	0.888	0.890	0.892	0.894	0.896	0.897	0.899	0.901	0.903
20	0.905	0.907	0.909	0.911	0.913	0.915	0.916	0.918	0.920	0.922
21	0.924	0.926	0.928	0.930	0.932	0.934	0.935	0.937	0.939	0.941
22	0.943	0.945	0.947	0.949	0.951	0.953	0.954	0.956	0.958	0.960
23	0.962	0.964	0.966	0.968	0.970	0.972	0.973	0.975	0.977	0.979
24	0.981	0.983	0.985	0.987	0.989	0.991	0.992	0.994	0.996	0.998
25	1.000	1.002	1.004	1.006	1.008	1.010	1.011	1.013	1.015	1.017
26	1.019	1.021	1.023	1.025	1.027	1.029	1.030	1.032	1.034	1.036
27	1.038	1.040	1.042	1.044	1.046	1.048	1.049	1.051	1.053	1.055
28	1.057	1.059	1.061	1.063	1.065	1.067	1.068	1.070	1.072	1.074
29	1.076	1.078	1.080	1.082	1.084	1.086	1.087	1.089	1.091	1.093
30	1.095	1.097	1.099	1.101	1.103	1.105	1.106	1.108	1.110	1.112
31	1.114	1.116	1.118	1.120	1.122	1.124	1.125	1.127	1.129	1.131
32	1.133	1.135	1.137	1.139	1.141	1.143	1.144	1.146	1.148	1.150
33	1.152	1.154	1.156	1.158	1.160	1.162	1.163	1.165	1.167	1.169
34	1.171	1.173	1.175	1.177	1.179	1.181	1.182	1.184	1.186	1.188
35	1.190	1.192	1.194	1.196	1.198	1.200	1.201	1.203	1.205	1.207

Table 6: Conversion for units of electrical conductivity

Multiply	By	To obtain
µS/m	0.01	µmhos/cm
mS/cm	10	µmhos/cm
mS/cm	1000	µmhos/cm
µS/cm	1	µmhos/cm
mmho/cm	1000	µmhos/cm

1S = 1mho

Reporting

Report electrical conductivity in units of µmho/cm, with 0 digits after the decimal point, e.g. 1135 µmho/cm. Use Table 5.2 for conversion of units.

7.5 pH
(POTENTIOMETRIC)

The pH is determined electrometrically by measuring the difference in potential between the measuring electrode (glass electrode) and the reference electrode with known potential (saturated calomel electrode used instead of the normal hydrogen electrode).

It is important in almost every phase of environmental engineering practice, such as of water supplies, water softening, disinfection and corrosion control. Low pH causes corrosion, high pH causes taste, soapy feel; pH < 8.0 is preferable for effective disinfection with chlorine.

Apparatus

a. pH meter with temperature compensating device, accurate and reproducible to 0.1 pH unit with a range of 0 to 14.
b. Reference electrode preferably with quartz liquid junction. Follow manufacturer's instructions on use and care of the reference electrode. Refill non-sealed electrodes with correct electrolyte to proper level and make sure junction is properly wetted.
c. Follow manufacturer's instructions on use and care of electrode.
d. Distilled Water
e. Magnetic Stirred

Reagents

Buffer solutions of pH of 4.0, 7.0 and 9.2. Standard buffer tablets are commercially available. Buffer of different pH can be prepared by dissolving standard pH tablets in distilled water. The above buffer solution can be prepared as follows:

1. **Pthalate buffer (pH 4.0 at 25°C):**
   Dissolve 10.12 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in distilled water to make IL of buffer.
2. **Phosphate buffer (pH 7.0 at 25°C):**
   Dissolve 3.40 g of KH_2P0_4 and 4.45 g of $Na_2HP0_4.2H_2O$ in distilled water to make IL of buffer.
3. **Borax buffer (pH 9.18 at 25°C):**
   Dissolve 3.81 g of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) in distilled water to make IL of buffer.

Store buffer solutions in polyethylene bottles. Replace buffer solutions every 4 weeks.

Procedure

a. Read carefully the operational manual of pH meter to be used.
b. Remove electrodes from storage solution, rinse, blot dry with soft tissue, place in initial buffer solution and standardise pH meter according to manufacturer's instructions.
c. Remove electrodes from the first buffer, rinse thoroughly with distilled water, blot dry and immerse in second buffer preferably of pH within 2 pH units of the pH of the sample. Read pH, which should be within 0.1 unit of the pH of the second buffer.
d. Determine pH of the sample using the same procedure as in (b) after establishing equilibrium between electrodes and sample. For buffered samples this can be done by dipping the electrode into a portion of the sample for 1 min. Blot dry, immerse in a fresh portion of the same sample, and read pH.
e. With dilute poorly buffered solutions, equilibrate electrodes by immersing in three or four successive portions of the sample. Take a fresh sample to measure pH.
f. Stir the sample gently while measuring pH to insure homogeneity.

Reporting

Report results in pH units with 1 digit after the decimal point, e.g. 7.6.

7.6 Dissolved Oxygen

(WINKLER AZIDE MODIFICATION TITRIMETRIC)

Sampling

Samples will be collected from well mixed section of the river (main stream) 30 cm below the water surface using a weighted bottle or DO sampler. Collecting a sample for DO analysis requires special sampling equipment: a purpose-built DO sampler, for collection of undisturbed samples from surface waters. This sampler prevents air bubbles from entering into the sample and changing the DO concentration of the sample. To collect the sample, insert the special ground glass-stoppered bottle (a 'BOD bottle') into the DO sampler. Submerge the sampler, such that water enters the BOD bottle directly by means of a dippipe thus displacing all air from the bottle. Retrieve the sampler after it is full, and then immediately seal the full bottle with a ground glass stopper.

Sample Stabilization

When a sample is being collected for DO analysis by the 'Winkler' method, it is important that, because the DO concentration in the sampling bottle can change rapidly from its original value, the sample is chemically 'fixed'. This ensures that the DO concentration determined is as near as possible to that which prevailed in the water body. Chemical fixing of DO is carried out by adding 1 mL of manganous sulphate solution, 1 ml of alkaline iodide-azide solution and 1 mL of concentrated sulphuric acid to a 300 mL water sample and mixing. The analytical determination may then be carried out up to 8 hours later with no loss of accuracy.

Here are three methods available for measuring DO concentrations. Modern techniques involve an electrochemical or optical sensor, the colorimetric method and the Winkler titration method. Former two methods quick and inexpensive but limited in scope and subject to error due to other redoxing agents that may be present in the water.

The traditional method is the Winkler titration. This method was developed by L.W. Winkler, a Hungarian chemist, in 1888. Also known as the iodometric method, the Winkler method is a titrimetric procedure based on the oxidizing property of DO. This method has long been the standard for accuracy and precision when measuring DO. Herein, analysis for the DO has been done by Azide-Winkler's method .

Wrinkler method (Azide Modification Method)

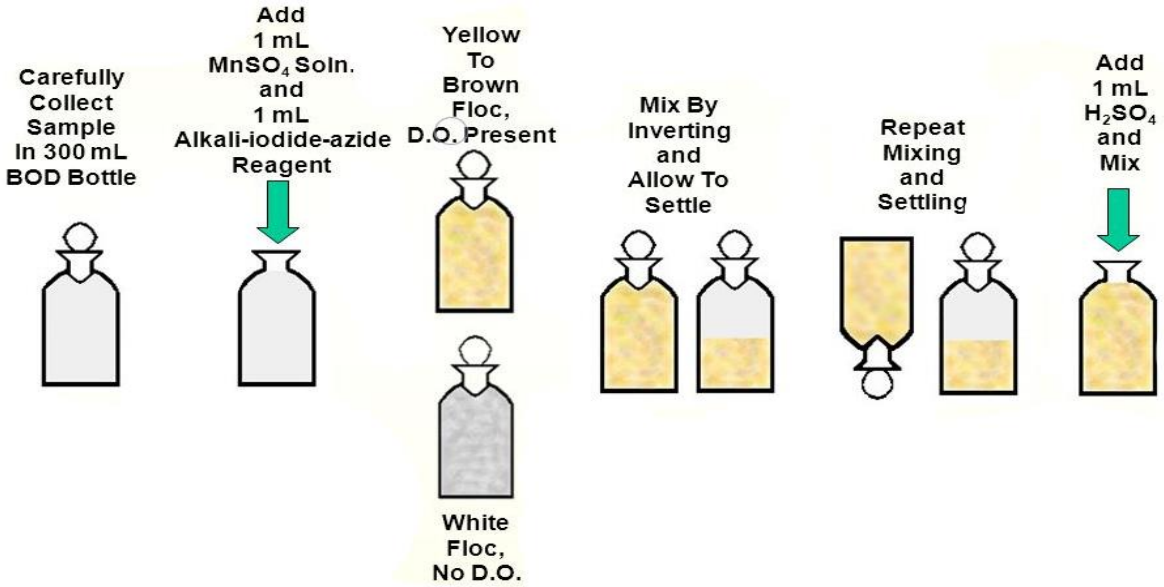
The method is based upon reactions that release iodine equivalent to the amount of oxygen originally present in the sample. The principle involved in this method of determination of DO is to bring about the oxidation of potassium iodide to iodine with the DO present in the water sample after adding $MnSO_4$, NaOH, KI and H_2SO_4. The DO present in the sample oxidizes the Mn^{2+} in alkaline conditions to its higher valiancy $Mn^{+3}[MnO(OH)]$ and $Mn^{+4}[MnO(OH)_2]$ or hydrated MnO_2, which precipitates as a brown hydrated oxide after the addition of NaOH and KI. On acidification, the manganese reverts back to the divalent state and an equivalent amount of iodine is liberated from the KI present. This liberated iodine is titrated against standard sodium thiosulfate (hypo) solution using starch as indicator.

In the *first step* manganous sulphate and alkali iodide reagents are added. If no oxygen is present the manganous ion reacts only with the hydroxide ion to form a white precipitate of manganous hydroxide.

$$Mn^{+2} + 2OH^- \longrightarrow Mn(OH)_2 \text{ (white precipitate)}$$

If oxygen is present the manganous ion is oxidized and brown precipitate of manganese dioxide of formed.

$$Mn^{+2} + 2OH^- + \tfrac{1}{2} O_2 \longrightarrow MnO_2 \text{ (Brown precipitate)} + H_2O$$



In the *second step* upon addition of sulphuric acid (H_2SO_4) iodine (I_2) is formed by oxidation of iodide (KI).

$$MnO_2 + 4H^+ + 2I^- \longrightarrow Mn^{+2} + I_2 + 2H_2O$$

In the *third step* Sodium thiosulphate standard solution is used to titrate iodine (I_2).

$$Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\ NaI$$

The end point of titration is obtained by first titrating iodine to a pale straw colour and then adding starch indicator, which combine with iodine to give a blue colour. The titration is continued till the iodine complexed with starch is also reacted and the blue colour disappears.

Interferences:

Iron, nitrite and microbial mass are the chief sources of interference in this method. Nitrites if present in the sample cause interference by oxidizing iodide.

$$2\ NO_2^- + 2\ I^- + 4\ H^+ \longrightarrow I_2 + NO + 2H_2O$$

NO in turn, is oxidized by oxygen entering the sample during titration:

$$NO + ½\ O_2 + H_2O \longrightarrow 2NO_2^- + 2H^+$$

Thus, it become impossible to reach a definite end point and high results are obtained. The procedure has to be modified depending upon the nature of the interfering substance. Adding sodium azide (NaN_3) can eliminate the interference due to nitrite.

$$2NaN_3 + H^+ \longrightarrow HN_3 \text{ (Hydrazoic acid)} + Na^+$$

$$HN_3 + NO_2^- + H^+ \longrightarrow N_2 + N_2O + H_2O$$

The results obtained discussed in appropriate sections

Apparatus

a. DO sampler, for collection of undisturbed samples from surface waters.
b. BOD bottles, 300 mL, narrow mouth, flared lip, with tapered and pointed ground glass stoppers.
c. A siphon tube, for laboratory use.

Reagents

a. Manganous sulphate solution. Dissolve 480 g $MnSO_4\ .4H_2O$, 400 g $MnSO_4.2H_2O$ or 364 g $MnSO_4.H_2O$ in distilled water, filter and dilute to IL.
b. Alkali-iodide-azide reagent. Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in distilled water and dilute to IL. Add 10 g NaN_3 dissolved in 40 mL distilled water.
c. Sulphuric acid, conc

d. Starch indicator. Dissolve 2 g laboratory grade soluble starch and 0.2 g salicylic acid as a preservative, in 100 mL hot distilled water.

e. Standard sodium thiosulphate titrant, 0.025M (0.025N). Dissolve 6.205 g $Na_2S_2O_3.5H_2O$ in distilled water. Add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL . Standardise with bi-iodate solution.

f. Standard potassium bi-iodate solution, 0.0021M (0.0126N), Dissolve 812.4 mg $KH(I0)_2$ in distilled water and dilute to 1000 mL.

g. Standardisation: Take 100 to 150 mL distilled water in an Erlenmeyer flask. Add approximately 2g KI, dissolve. Add 1 mL 6N H_2S0_4 or a few drops of conc H_2S0_4 and 20 mL bi-iodate solution. Dilute to 200 mL and titrate liberated iodine with thiosulphate titrant to a pale straw colour. Add a few drops of starch indicator. Continue titration to first disappearance of blue colour.

h. Calculate molarity, M of thiosulphate as:

Procedure

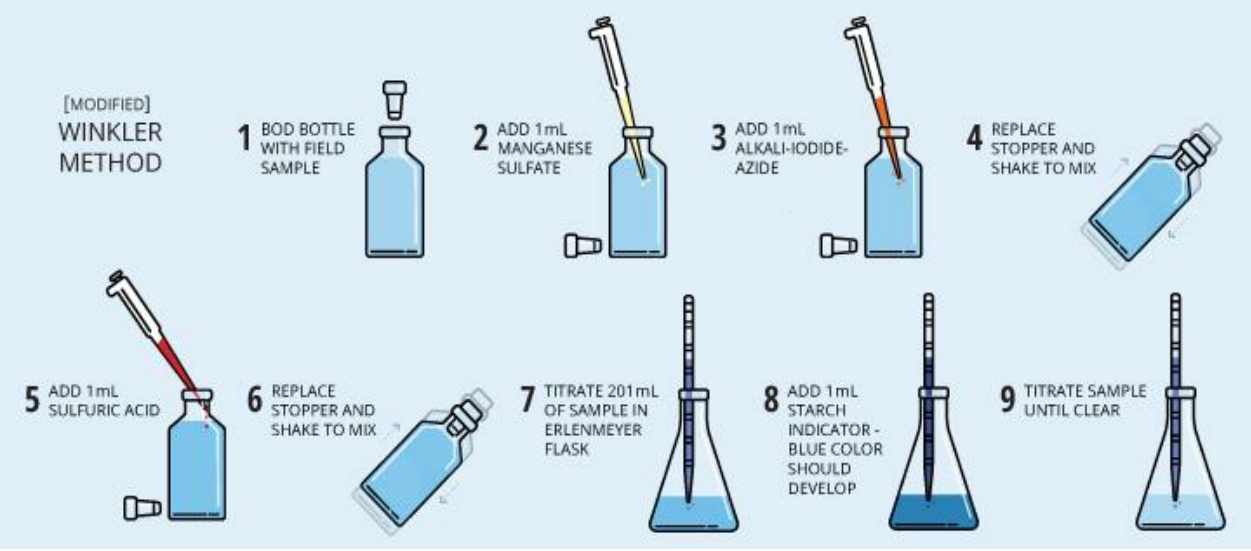
a) Drain any liquid in the flared lip of the BOD bottle containing the sample.

b) Remove stopper and add 1 mL of $MnSO_4$ followed by 1 mL alkali-iodide-azide reagent. Hold the pipette tip just below the liquid surface touching the side of the bottle. Wash the pipette before returning to the reagent bottles.

c) Stopper carefully to exclude air bubbles. Mix by inverting the bottle a few times.

d) Allow the brown manganese hydroxide floc (white floc indicates absence of DO) to settle approximately to half the bottle volume, add 1.0 mL conc H_2SO_4 and re-stopper. Mix by inverting several times until dissolution is complete.

e) Titrate 201 mL sample with standard $Na_2S_2O_3$ as for standardisation procedure described above.



Calculation

Dissolved Oxygen (mg/L) = $\frac{\text{Volume of thiosulphate solution Used X Molarity of } Na_2S_2O_3.5H_2O}{0.025}$

Reporting

Report dissolved oxygen in units of mg/L with 1 digit after the decimal point, e.g. 8.2 mg/L.

8. GOOD LABORATORY PRACTICE

A number of laboratory operations and precautions related to analysis of water quality parameters must be routinely performed in a laboratory to obtain reliable information. These practices are termed *good laboratory practices*. Some analyses, that measure extremely small level of contaminants using use advanced level instrumentation, would require special precautions. Practices that are to be followed routinely and are basic in nature to all determinations are described here.

8.1 Chemical and Reagents

Purity of reagents has an important bearing upon the accuracy that can be attained in an analysis.

Commercially available chemicals are routinely classified as:

- technical grade
- laboratory or analytical reagent grade
- primary-standard grade
- special purpose reagents

Technical grade reagents, in general, are not used in a laboratory. Where bulk quantities may be required or when purity is not of major concern, such as preparation of chromic acid cleaning solution, technical grade reagents may be used.

Routine analyses in a water testing laboratory may be performed mostly using laboratory or analytical reagent grade chemicals. Where primary standards are to be made, primary standard grade reagent should be used.

Special purpose reagents are required for analyses when micro-level contaminants are measured through atomic absorption spectroscopy and gas chromatography.

The following rules should always be followed while handling reagents and chemicals:

- As far as possible, use the smallest packing of chemical that would supply the desired quantity.
- Replace the cap or stopper of the bottle immediately after taking out your requirement.
- Stoppers of reagent bottles should never be placed on the desktop.
- Do not insert spatulas or pipettes in reagent bottles. Take out a slightly excess amount in another container from where uses the required quantity.
- Never return any excess chemical or reagent back to the bottle.

- Some reagents require special storage conditions, such as dark colour bottles for light sensitive chemicals or low temperature solvents and reagents subject to microbial degradation.
- Do not use a reagent after the recommended shelf life.
- Dry solid chemicals for making solutions, in a suitable container, as directed in the standard analytical procedure for the determination.

8.2 Cleaning of Glassware

Volume calibrations are blazed on clean volumetric equipment. Cleanliness of volumetric glassware is, therefore, particularly important if calibration is to have any meaning. Only clean glass surfaces will support a uniform film of liquid; the presence of dirt or oil will tend to cause breaks in this film. The existence of breaks is a certain indication of an unclean surface. A brief soaking in warm detergent is usually sufficient to remove the grease and dirt responsible for causing the water breaks.

Where detergent is not effective, rinse glassware, except that used for chromium and manganese analysis, with a cleaning mixture made by adding 1 L of conc. H_2SO_4 slowly with stirring, to 35 mL saturated sodium dichromate solution. Rinse with other concentrated acids to remove inorganic matter.

Use detergents or conc. HCl for cleaning hard rubber and plastic bottles. After the glassware and bottles have been cleaned, rinse thoroughly with tap water and finally with distilled water. Glassware can be dried by placing inverted on a drying rack. After drying, glassware should be stored in a clean and protected dust-proof cabinet.

DISTILLED OR REAGENT WATER

Distilled water may be classified on the basis of its electrical conductivity (EC) as follows:

Type EC	**µmho/cm**
Type I	< 0.1
Type II	< 1
Type III	< 10

Laboratories are provided with stainless steel water distillation stills. Distilled water obtained from such stills is of adequate purity (Type III) for making reagent solutions for routine analyses carried out in water testing laboratories and cleaning of glassware. However, in case of analyses for micro-level contaminants better quality distilled water (Type I or II) may be needed. Ion exchange columns and double distillation, all-glass water stills, are used to obtain Type I and II distilled water, respectively. Type I distilled water is also called de-ionised water.

8.3 Laboratory Safety

All laboratory employees must make every effort to adhere to certain basic safety rules to protect themselves and their fellow workers. The sources of hazard in a laboratory are corrosive and poisonous chemicals, broken glass, explosion, fire and electrical shock. Some common safety rules are given below. In case a health and safety programme has been developed for your laboratory, you should always follow it.

- Learn the locations of eye fountain, emergency shower, fire blanket and fire extinguisher.
- Eye protection must be worn at all times.
- In handling all chemicals, avoid contact with skin. In the event of such contact, immediately wash the affected area with copious amounts of water.
- Avoid working alone in a laboratory if the procedures to be conducted are hazardous.
- Do not drink, eat or smoke in areas where laboratory chemicals are present. Do not drink from laboratory glassware.
- Do not store food or beverages in storage areas and refrigerators that are used for laboratory operations.
- Always use a suction bulb to draw chemicals in a pipette. Never use the mouth to provide suction.
- Be extremely tentative in touching the objects that have been heated.
- Always fire polish the ends of freshly cut-glass tubing. Never attempt to force glass tubing through a hole in the stopper. Instead, make sure that both the tubing and the hole are thoroughly wet with soapy water and protect hands with towel or heavy gloves.
- Use fume hoods where toxic or noxious gases or fumes are likely to be evolved.
- Use care in testing for odours; use the hand to waft vapours above containers towards nose.
- In some locations it may not be permissible to flush heavy metals or poisonous substances down the drain. In case of such restrictions, alternative arrangements are required.

Annexure - 01

CENTRAL WATER COMMISSION

Parameters : **pH, Electrical Conductivity**
Method Used : Potentiometric , Conductivity Cell (Electrode)
Referred Methodology : APHA / HP / BIS
BIS Standard :
Standards Used : pH 4.0, 7.0, 9.2
for Calibration Conductivity: 0.01 M KCl Solution (1413µmhos/cm)
Analysed by :
Date of analysis :

Results of Chemical Analysis

Lab. ID No.	Location of Sampling	Source (River)	pH	Electrical Conductivity (EC) (µmhos/cm)	Remark

Signature of Analyst

CENTRAL WATER COMMISSION

Parameter : **Dissolved Oxygen**
Analysis Method : **4500 O C. (Azide Modification Method)**
Reference : **APHA**
Detection limit / Range :
Unit of Measurement : **mg/L`**
Equipment Used : **Digital Burette**
Analyzed by :

Uncertainty Measurement :

Standardization of Sodium Thiosulphate

Normality of $K_2Cr_2O_7$ (A) :
ml of $K_2Cr_2O_7$ Solution taken (B) :
Normality of Hypo (C) : A X B / Vol. of Hypo Consumed
Factor : **C X 8 X 1000 / V_2 X (V_1-v) / V_1**

C = Normality of Hypo
V_1 = Volume of BOD Bottle, ml
V_2 = Volume of Contents titrated, ml
V = Volume of $MnSO_4$ and iodide azide added = 1 + 1 = 2 ml

S. No.	Date of Standardization	Volume of Hypo Consumed			Normality of Hypo (C)	Factor	Std. Done By
		Initial	Final	Total			
1							
2							
3							
4							
5							

Signature of Analyst

References

APHA (American Public Health Association). (2017). Standard methods for the examination of water and wastewater (23rd ed.). Washington, DC: American Public Health Association.

DES. 2018. Monitoring and Sampling Manual: Environmental Protection (Water) Policy. Brisbane: Department of Environment and Science Government.

Hydrology Project (Technical Assistants) Water Quality Sampling – Field Manual Volume 6, Government of India & Government of The Netherlands.

(https://www.fondriest.com/environmental-measurements/parameters/water-quality/water-temperature/)

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