Water sampling and preservation techniques

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Standard Operating Procedure (SOP)

- Analytical method
- Safety
- Waste management
- Apparatus and equipments
- Reagents and standards
- **Sample collection**
- **Preservation**
- Shipment
- Storage conditions
- Acceptance criteria
- Calibration and standardization
- Data validity

Sample collection

Objective:

- Objective of sampling is to collect a portion of material small enough in volume to be transported comfortably and yet large enough for analytical purposes while still representing the material being sampled.
- It is to demonstrate whether continuing compliance with specific regulatory requirements has been achieved

Selection of sample containers

- Selection of sample container is utmost importance in sampling. Containers are generally made of glass or plastic. Some sample analytes may get absorbed into the walls of plastic containers and/or some contaminants may leach into samples.

- Trace level of some metals and pesticides may get adsorbed and/or absorbed onto the walls of the glass container. In the same way, silica, sodium, and boron may be leached from soft glass.

- Always use hard glass containers for all organics analyses such as pesticides, volatile organics, PCBs, and oil & grease.

- Some of the analytes like pesticides, PAH etc. are light sensitive. Hence collect them in amber-coloured glass containers to minimize photo degradation

Selection of type of sampling

- **Grab**
- **Composite**
- **Integrated**

Grab sampling

- Grab samples are also called as spot or catch samples. Grab samples are single samples collected at a specific spot at a site in specified time. Grab samples are to be collected only when the source is known to be constant in composition for an extended period of time. Examples are, ground water samples, well mixed surface waters, large lakes, rivers, estuaries, shorelines, wastewater streams that are expected to be constant in composition over an extended period of time, like spent wash line in a distillery.

- When the source composition varies from location to location, like upstream and downstream of a river, then grab samples can be collected from appropriate locations. This helps in finding out the extent of variation and duration of variation.

Composite sampling

- Composite sampling is carried out when the liquid matrix is expected to be heterogeneous and varies from time to time or depth or at many sampling locations. This type of sampling provides a representative sampling for this type of matrix and is carried out by combining portions of multiple grab samples collected at regular intervals. If the flow is expected to be constant, then volume based sampling can be carried out. If the flow varies, like sewerage line, then sampling can be done by flow based composite, i.e., collecting sample that is proportional to the discharge. Time composite sampling represents a 24-hour period, with interval being 1-3 hours

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- Use composite samples only for parameters that will remain unchanged under the sampling conditions, preservation and storage. For parameters like pH, temperature, residual chlorine, carbon dioxide, alkalinity, sulfide, dissolved oxygen, Oil&Grease etc. avoid composite sampling and analyse individual samples as soon as possible, preferably in the field itself, except for sulfide and Oil &Grease

Integrated sampling

- Integrated sampling is carried out by collecting mixture of grab samples collected from different points simultaneously. The points may be horizontal or vertical variation. Examples include river, stream or reservoir or lake that varies in composition across the width and depth. Also in industries that have different streams and combined treatment is proposed, than integrated sampling of different streams can be made to understand the significant effect on treatment.

Selection of sampling points

- Selection of sampling points plays an important role in sampling. The site selection should be based on the objective of the study. If the monitoring is carried out for judging suitability of water for drinking purpose, then the sampling point shall be near the intake point. Always samples must be taken from locations that are representative of the source, treatment plant, storage facilities, point of discharge, and point of use. Eventhough there is no methodology for site selection on a cook book basis some general basic rules can be followed to have a sound sampling programme

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Always have a reference station upstream of any discharge point like industrial outfall, city sewage drain etc. The reference point allows us to ascertain the background water quality. Additional downstream stations can be fixed to assess the extent of influence of discharge and to find the recovery point

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The points chosen should generally yield samples that are representative of the system as a whole. For this it is important to select a well-mixed zone. When samples are collected from a river or stream, the observed results may vary with depth, flow and distance from the shore. Hence, if equipments are available collect an integrated sample from top to bottom in the middle of the lake or river or from side to side at mid-depth. Otherwise, preferably collect samples at various points of equal distance across the water body. If only one sample can be collected, collect it in the middle of the water body at mid depth

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Avoid areas of turbulence and at weirs. Generally collect samples beneath the surface with the mouth directed towards the current. For oil and grease, collect sample at the surface.

In case of groundwater sampling, select wells that are in continuous use.

Selection of type of filling the container

Depending on the type of analysis to be performed, fill the container full or leave space for aeration. For most organic compound determination like pesticides, PAH, VOC etc. and for sulphide fill the container with out any air space. For microbiological and inorganic analyses leave space for aeration and mixing. The space to be left for aeration and mixing should be atleast 1% of the container volume. If the bottle is with preservative take care that the preservative added is not lost or diluted by overflow

In – situ measurements

Parameters like pH, conductivity are temperature dependent. Hence, if the temperature varies significantly, the results of these parameters also vary. Delay in analysis may also lead to loss of dissolved gases like carbon dioxide, oxygen. Hence some of the parameters like temperature, ORP, dissolved gases, shall be analysed in situ and parameters like pH, conductivity, alkalinity, residual chlorine immediately after sample collection

Sample labeling

- Labeling is an important part in sampling programme. The following information should be included in the label. Use water proof ink to record all the information.

- Date and time of sampling
- Sample field code
- Sampling point
- Nature of sample: Effluent / Surface water / Ground water / Others
- Type of sample (Grab/Composite/Integrated)
- Pre-treatment or preservation carried out on the sample
- Any special notes for the analyst
- Name and sign of sample collector.

Collection and preservation of samples for organics and trace metals

Special care is required for samples containing trace metals and organic compounds like PAH, pesticides etc. The concentration of these constituents may be very low and may be lost or easily contaminated when proper sampling and preservation procedures are not followed

Pesticides

Phthalate esters, widely used as plasticizers, can be leached by water and can cause positive ECD response and are source of interferences. Hence avoid plastic containers to avoid interference from containers.

Wash the container with soap water followed by tap water, distilled water, acetone and finally with high grade hexane. If the container is heavily contaminated, wash the container as given above, and heat in a muffle furnace at 400'C for 15-30 min. After drying store inverted or cover mouth with aluminium foil.

Ensure that all the sampling equipments are clean before use. Collect minimum 1000mL, either by grab or composite sampling and fill the bottle with out any air gap. Transport under iced condition and submit the sample to laboratory as early as possible so that the laboratory can extract with in the specified period.

Trace metals

The best sample container to be used for trace metals is either container made of polypropylene or polyethylene with a polyethylene cap. Also, hard borosilicate glass can be used. Thoroughly clean container with metal –free non-ionic detergent solution, rinse with tap water, soak in acid, and then finally with metal free water. Use 1+1 HCl or 1+1 HNO_3 for soaking.

Ensure that all the equipments to be used for sampling are clean before use. Collect minimum 1000mL, either by grab or composite sampling. Leave an air space of approximately 1% of container volume. Immediately preserve samples by acidifying with highly pure concentrated nitric acid (HNO_3) to pH <2 to minimize precipitation and adsorption on container and transport in ice cold condition.

If mercury is to be analysed, collect separate sample for mercury and preserve by using HNO3 to pH <2 and transport in ice cold condition (Temp. <6'C).

Polynuclear Aromatic Hydrocarbons (PAH)

Select amber coloured hard glass bottles fitted with a screw cap lined with TFE. Wash the container with detergent, rinse with tap water followed by distilled water. Rinse container with acetone or methylene chloride and dry at 105'C for 1 hr. When bottles are cool, seal the mouth using TFE seals or with aluminium foil.

Collect 1000 mL of sample either by grab or composite sampling technique. Fill the bottle with out any air gap. If composite sampling technique is followed, collect samples in refrigerated glass containers and protect from light during composting. If residual chlorine is present, add 80mg sodium thiosulfate per litre of sample and mix well. Transport in ice cold condition and submit the sample to laboratory as early as possible so that the laboratory can extract with in the specified period

Flow measurement

Flow measurement is a fundamental step for design of treatment plants, wastewater collection and for disposal facilities. Flow measurement also plays an important role in conservation of water. By knowing the amount of water withdrawn, from any water source, water utilized for some purpose and water discharged, one can calculate the amount of water lost or unaccounted. The data can be used to calculate the total discharge of any industrial effluent into a water body and also to calculate the load of some important parameters like BOD, COD, etc.

Now a days, flow metering devices are available for accurate measurement of flow. It consists of two elements: (1) a sensor and (2) a converter device. The sensor is exposed to the flow and the converter is a device used to translate the signal from the sensor into a flow reading

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Flow measurement by Bucket method:

This method is suitable for small drains/ streams where free fall of water is available. Take a bucket of known volume. Insert the bucket in to the flow and note the time taken for the bucket to get filled up. Calculate the flow in litre / min

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Flow measurement by using V-Notch:

V-Notch is a triangular weir used to measure small discharges. The upper edge of the section is always above the water level and hence the channel is always triangular simplifying calculation of the cross-sectional area.

It is generally angled at 90 degrees and provided at the inlet and outlet of water treatment plants for measurement of flow. For 90 degree angled V-Notch, the formula for measurement of flow is as follows.

$Q = 1.4 \times h^{2.5}$

Where,

Q= Flow, m3/sec

H=Height of water level, mts.

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Flow measurement in rivers and sewerage lines:

Select a place where there is free flow of water. Measure the breadth and depth. Fix the length and mark the starting and end point. Place a ball or wooden float at the starting point and start the stop watch immediately. Note the time taken to reach the end point. Calculate the flow using the below given formula.

$Q, m^3/s = (L \times B \times D) / T$

Where,

L=Length in mts.

B=Breadth in mts

D=Depth in mts

T=Time in seconds.

Measurement of temperature

Thermometers are generally calibrated for total immersion. This means that the meniscus of the mercury column is level with the surface of the liquid being measured. If part of the mercury column is visible above the liquid surface, a correction may be necessary. The equation for correction is as follows:

$$\text{Corrected temperature, } T = t + \frac{(t - t') \times (t - t'')}{6000}$$

Where,

t = Actual temperature reading, ° C

t’ = Ambient temperature, ° C

t’’ = Temperature at immersion point, ° C

Measure the ambient temperature (t’). Take sample in a beaker and insert the thermometer. Note t and t’’. Calculate the actual temperature and report to the nearest 0.1 or 1.0° C.

Table-I SAMPLING AND HANDLING REQUIREMENTS

Parameter	Container	PRESERVATION	MAX.STORAGE
Acidity	P,G	Refrigerate	24 h
Alkalinity	P,G	Refrigerate	24h
BOD	P,G	Refrigerate	6h
Boron	P,G	HNO3 to pH <2	28d
Carbon, Total	G(B)	Analyse immediately or add HCl to pH<2	7 days
Carbon dioxide	P,G	Analyse immediately	15 min
COD	P,G	Analyse immediately or add H2SO4 to pH<2, refrigerate	7 days
Chloride	P,G	Refrigerate	--
Chlorine, residual	P,G	Analyse immediately	15 min
Chlorophyll	P,G	Unfiltered, dark, 4'C	48 hours
Colour	P,G	Refrigerate	48 h
Conductivity	P,G	Refrigerate	48h
Cyanide, Total	P,G	Add NaOH to pH>12, refrigerate in dark	24 h
Fluoride	P	--	28 days
Hardness	P,G	Add HNO3 to pH<2	6 months
Metals, General	P(A),G(A)	Add HNO3 to pH<2	
Metals, Dissolved, General	P(A),G(A)	Filter immediately, add HNO3 to pH<2	
Chromium VI	P(A),G(A)		
Nitrogen, Ammonia	P,G	Analyse immediately or add H2SO4 to pH<2, refrigerate.	7 days
Nitrogen, Organic	P,G	Refrigerate, add H2SO4 to pH <2.	7 days
Nitrate	P,G	Analysis as soon as possible, refrigerate	48h
Nitrite	P,G	Analysis as soon as possible, refrigerate.	--
Nitrate+Nitrite	P,G	Add H2SO4 to pH<2, refrigerate	2 days
Oil & Grease	G(S),Wide mouth	Add H2SO4 to pH<2	28 days
Oxygen, dissolved	G	Analyse immediately	15 minutes
Pesticides	G(S)	Refrigerate, add ascorbic acid if residual chlorine is present	7 days

SUMMARY

Parameter	Preservative	Remarks
COD, NH_3-N, TKN, Phenol, NO_3+NO_2-N, Total phosphorous	H_2SO_4 to pH <2	Cool < 6° C
Hardness	HNO_3 or H_2SO_4 to pH <2	
Oil & Grease	HCl or H_2SO_4 to pH <2	Cool < 6° C
Cyanide	NaOH to pH >12	Add Thio, if TRC is present. Cool < 6° C
Sulphide	4 drops of 2N Zinc acetate/100mL; Add NaOH to pH >9	
Boron, Metals	HNO_3 to pH <2	
Hexavalent chromium	Adjust pH to 9 using buffer solution and 0.6mL of 5N NaOH.	Cool < 6° C
Mercury	HNO_3 to pH<2	Cool < 6° C
Dissolved oxygen	--	Titration may be delayed after acidification.
Acidity, alkalinity, BOD, Colour, EC, Solids, Sulphate	--	Cool < 6° C
Nitrate, Colour, Nitrite, Odour, Turbidity	--	Analyze as soon as possible.
TRC, pH, Temperature	--	Analyze immediately
Chloride, Fluoride	None required	--

Dissolved oxygen measurement in biological flocs

This modification is used to determine DO for biological flocs such as activated sludge process, which have high oxygen utilization rate.

Requirements: 1 lit. reagent bottle, siphon tube, BOD bottle, reagent

Add 10mL Copper sulphate-sulfamic acid inhibitor to a 1 litre glass stoppered bottle. Collect sample, stopper and mix by inverting. Allow the suspended solids to settle and siphon the supernatant into a 300mL BOD bottle. Add 1 mL manganous sulphate solution, followed by 1mL alkali-iodide-azide reagent by holding pipette just above liquid surface. Stopper carefully and mix by inverting bottle few times.

Sludge Volume Index (SVI)

It is the volume in milliliters occupied by 1g of a suspension after 30 min settling. SVI value is typically used to monitor settling characteristics of activated sludge and other biological suspensions. Smaller the value, easier is the settling of sludge

SVI = (Settled sludge volume, mL/L x 1000) / Suspended solids, mg/L

Inference:

< 100 - Very Good settling

100 – 150 - Good settling

150 – 200 - Poor settling

Food to Microbe ratio (F/M):

This parameter is also related to settling characteristics of activated sludge or any biological flocs.

$$F/M = \frac{\text{Inlet BOD x Flow}}{\text{MLSS x Aer. Tank volume}}$$

Where

BOD = mg/L

Flow = m3 / day

MLSS = mg/L

Aeration tank volume = m3

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Optimum value: 0.3 to 0.6

Low F/M ratio (< 0.3): Poor settling - Amount of food present is insufficient to maintain the growth of microbes. Hence cells become weak and become light and resist sedimentation. Sludge obtained under these conditions is referred to as “Dispersed floc”.

High F/M ratio (>0.6): Bulking sludge - Amount of food is high and this lead to growth of some microbes which are filamentous in nature. This type of growth does not settle well, remain in suspension almost indefinitely. Sludge obtained under these conditions is referred to as “ Bulking sludge”.

THANK YOU