Collection and Preservation of Samples and Field Analysis

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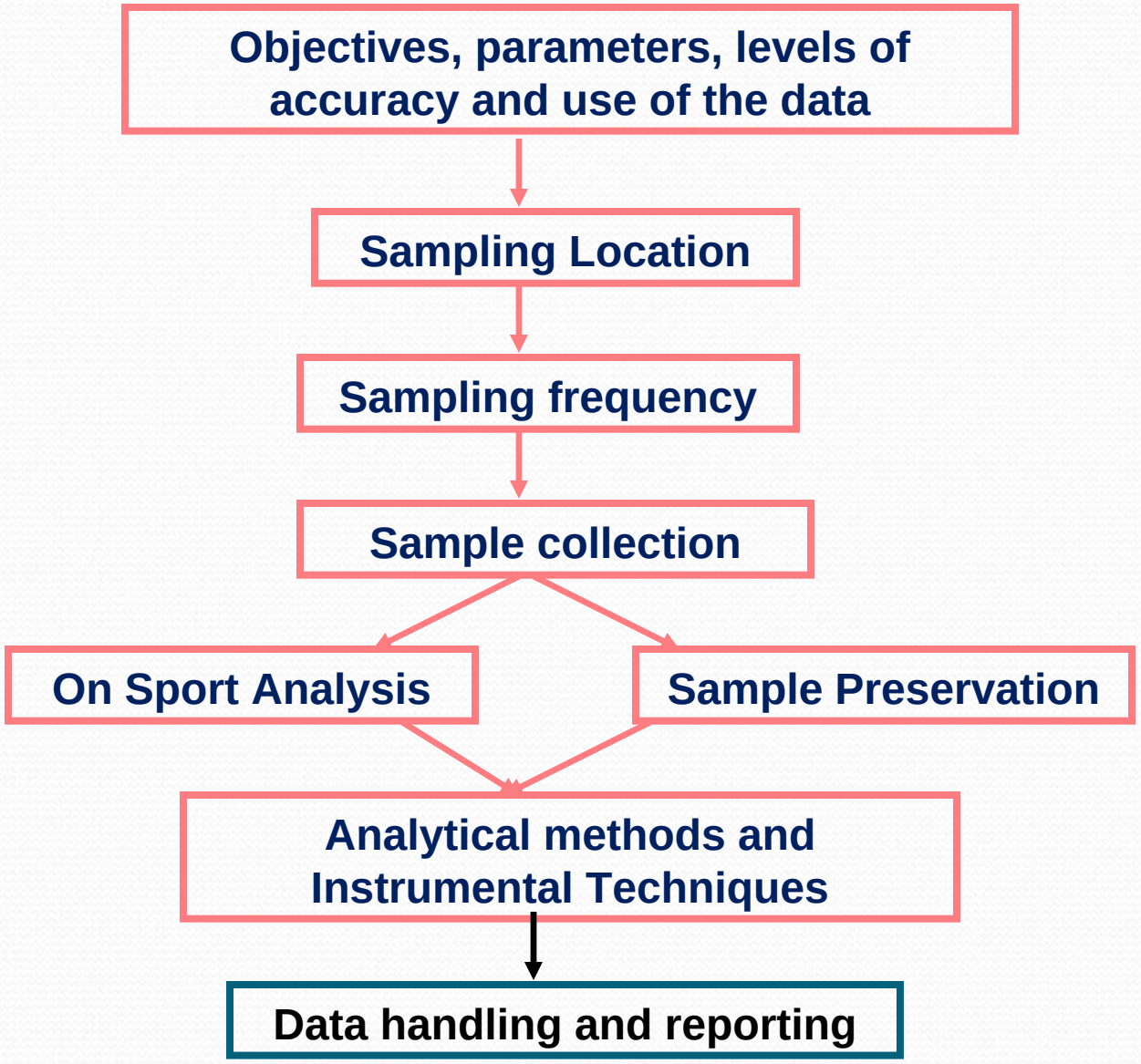
Step-5: Sampling

Sample: A part of the whole, that can be examined to see what the rest is like

Objectives of Water Sampling

- Baseline Water quality
- Impact assessment
- Assessment of Technology
- Performance assessment of treatment plant
- Assessment of products and processes

Design of Water Sampling Programme



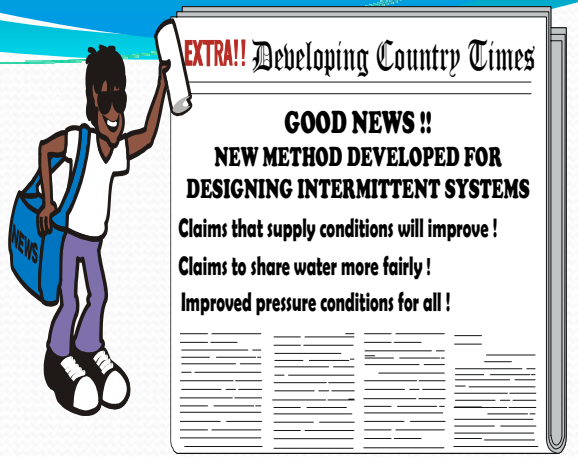
Planning for Sampling

When planning a sampling programme the number of sampling stations or wells that can be sampled in one day is required.

For this is necessary to know the required time needed for sampling, and other actions required, at the site.

Since purging is a time consuming activity an estimate of the required purging time is a must to arrive at a fair estimate of the sampling time.

Check list for the field visit



- ✓At least one day before sampling, make sure that all the arrangements are made as per the check list.
- ✓Make sure, how to reach sampling site(s).
- ✓Take help of location map
- ✓Field operator may make his/her own personal checklist.
- ✓Decide on the number of each item that would be required depending on the number of samples to be collected.
- ✓It is always safer to carry a few numbers in excess.
- ✓If the laboratory conducting analyses is different from the laboratory doing sampling...informed the concerned laboratory to receive samples on time, particularly those which would need immediate attention.
- ✓In case there is any deviation in the collection point, record it.

Checklist for Field Visit

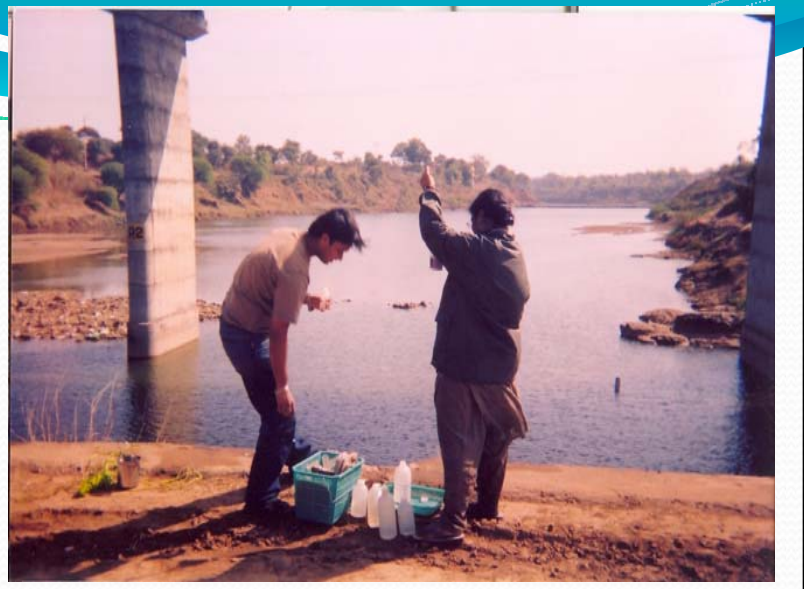
• Itinerary for the trip (route, stations to be covered, time schedule)	• Personnel and sample transport arrangement
• Area map	• Sampling site location map
• Icebox filled with ice or icepacks	• Weighted bottle sampler
• BOD bottles	• Rope
• Special sample containers: bacteriological, heavy metals, etc.	• Sample containers
• Sample preservatives (e.g. acid solutions)	• Thermometer
• Tissue paper	• Other field measurement kit, as required
• Sample identification forms	• Labels for sample containers
• Field notebook	• Pen / pencil / marker
• Soap and towel	• Match box
• Spirit lamp	• Torch
• Drinking water	• Knife
• First-aid box	• Gloves and eye protection
• Dump sampler to check well conditions	• Submersible pump and accessories

General Guidelines for Sampling

- Rinse the sample container 3 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.
- Label the sample container properly.
- The sample code and the sampling date should be clearly marked

- Complete the sample identification form for each sample.
- The sample identification form should be filled for each sampling occasion at a monitoring station.
- If more than one bottle is filled at a site, this is to be registered on the same form.
- Sample identification forms should be kept in a master file at the laboratory where the sample is analysed.

Surface Water 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.

- Samples from reservoir sites will be collected from the outgoing canal 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.

- DO is determined in a sample collected in a DO bottle using a DO sampler. The DO in the sample must be fixed immediately after collection, using chemical reagents.

- DO concentration can then be determined either in the field or later, in a level I or level II laboratory.

Groundwater Sampling

Samples for groundwater quality monitoring would be collected from one of the following 3 types of wells:

- *Open dug wells in use for domestic / irrigation*
- *Tube wells fitted with a hand pump or a power-driven pump: domestic /* irrigation
- *Piezometers (built for recording of water level & WQM).*

- Open dug wells, which are not in use (or abandoned), will not be considered as WQM station. However, such wells could be considered for water level monitoring.
- Use a weighted sample bottle to collect sample from an open well about 30 cm below the surface of the water.
- Samples from the production tube wells will be collected after running the well for about 5 minutes.
- Non-production piezometers should be purged using a submersible pump. The purged water volume should equal 4 to 5 times the standing water volume, before sample is collected.
- For bacteriological samples, when collected from tubewells/hand pump, the outlet of the pump should be sterilised under flame by spirit lamp before collection of sample.

Sample Labeling

Label the sample container properly, preferably by attaching an appropriately inscribed tag or label.

Alternatively, the bottle can be labelled directly with a water-proof marker.

Information on the sample container or the tag should include:

- Sample code number (identifying location)
- Date and time of sampling
- Source and type of sample
- Pre-treatment or preservation carried out on the sample
- Any special notes for the analyst
- Sampler's name

Sample Preservation and Transport

Samples for BOD and bacteriological analyses should be stored at a temp. < 4^{o}C (ice/cold packs) and in the dark as soon as possible after sampling. Once in the laboratory, samples should be transferred as soon as possible to a refrigerator.

COD analysis is to be done on the day of collection or they should be preserved below pH 2 by addition of conc. H_2SO_4. This procedure should also be followed for samples for ammoniacal nitrogen, total oxidised nitrogen and phenol analysis.

For metals: Samples should be acidified to below pH 2 with conc. HNO_3. Such samples can then be kept up to 6 months before they need to be analysed; mercury determinations should be carried out within 5 weeks.

Samples should be transported to concerned laboratory as soon as possible, preferably within 48 hours. Analysis of bacteriological samples should be started and analysed within 24 hours of collection.

Importance of the sampling procedures

Often the quality control aspects are only related to the analytical part, whereas the control procedures for the sampling are neglected.

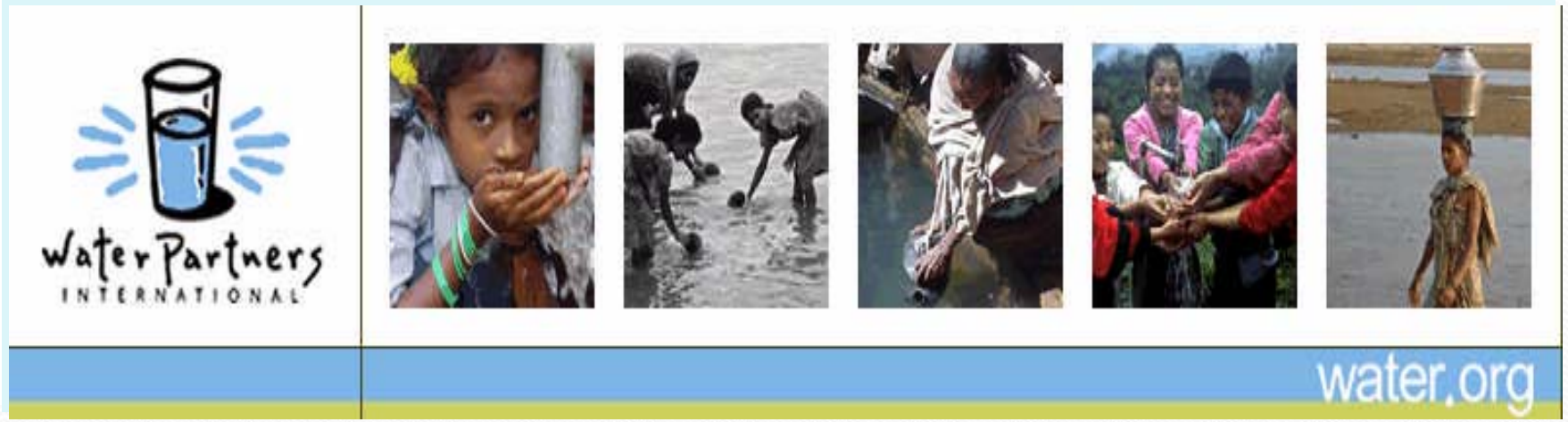
There appears to be a need for a detailed description of the sampling and preservation procedures.

The objective of sampling is to collect a portion of material from an environmental compartment (either water, sediment or biota) small enough in volume to be conveniently transported & handled in the laboratory, while still accurately retaining its representativity.

This implies that the relative proportions or concentrations of the components of interest should be the same in the samples and original environment. This requires that the sample will be handled and treated in such a way that no significant changes in composition occur that may hamper proper analysis.

In other words, no addition (e.g. contamination), loss (e.g. adsorption to the wall of the sample bottle) or deterioration (e.g. physico-chemical or biological degradation or transformation) can be allowed.

TYPES OF SAMPLES



1) Grab (spot or catch) sample

A source is known to be fairly constant

- In composition
- Over a considerable period
- For substantial volume
- Over spatial dimensions

Condition of source

- Fairly steady = Represent the composition
- Varies with time = Suitable intervals
- Varies in space = Appropriate locations

2) Composite samples

- In most cases, the samples refer to a mixture of spot samples collected at the same sampling site at different times.
- Useful technique in case of temporal variation in water quality.
- The series of spot samples are not mixed but analyzed individually, also information on the daily variability can be obtained, and afterwards the average can be computed.
- Sometimes the indication 'time-composite‘ (24-hour period) is used to distinguish from 'location composite‘ sampling.
- To evaluate the nature of special discharges (e.g. variable in volume or irregular in time), sampling at time intervals representing the period during which such discharges occur.
- This type of sampling is also required to measure the flux of pollution load discharged through a point source.

3) Integrated samples

- Sometimes samples are collected at the same location but, due to horizontal or vertical variation in the composition of the river (or in water flow) or lake, they come from different points in the cross-section that are regarded with a different relative importance.

- To evaluate the average composition, total load or mass balance, integrated samples are collected, often in proportion to the river flow of the areas of sample collection.

- Collection of integrated samples may require equipment to collect sample from various depths

4) In-situ measurements

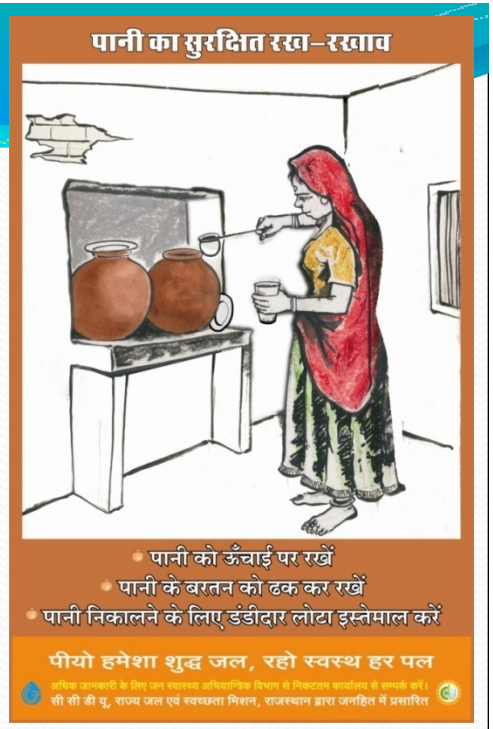
- Some determinations are more likely to be affected by sampling and sample storage.
- In several cases the expected changes are so large, that it is impossible to store the sampled material for a correct analysis at a later moment.

- If possible, these parameters should be analyzed on the sampling site or, even better, in-situ.
- Important parameters: pH, DO, temperature, conductivity and sometimes turbidity.
- Require special measuring devices.
- Numbers and diversity of organisms is also to be considered as in situ analysis.

Contamination control

Contamination may occur from: sampling equipment, sample bottle, preservatives, ambient atmosphere, personnel taking the sample etc. Utmost care should be maintained during sampling - in order to prevent contamination.

Often sampling bottles need to be cleaned in a special way, depending on the parameter. To avoid cross-contamination, the same bottles should be used only for identical selected parameters.



- Separate sets of bottles should be used for natural waters and for effluents.
- To prevent contamination by the hands, plastic (PE) gloves are needed.
- Atmospheric dust and (exhaust) fumes are readily available to contaminate the sample: minimum contact of the sample with the atmosphere is essential, here.
- The person taking a sample (and the analyst) should take care not to touch the inside of bottle and cap.
- The sampling bottles should be kept clean from dust and dirt.
- Pipettes or pipette tips should (in the field and in the laboratory) only be used once.

Cleaning procedures

The cleaning of samplers, sampling bottles and other labware, different cleaning procedures can be applied depending on the parameter

For heavy metals rinsing with 1:1 diluted HNO_3(supra pure quality) for 1 week is needed, followed by 3 times washing with double distilled water.

Bottles for trace organic (chlorinated) compounds, like pesticides, should be cleaned with the solvent used for extraction (also of high purity quality).

Samples for the general physical-chemical characterization allow less vigorous methods. Thorough cleaning with water to remove particulates and two times rinsing with distilled water will usually be sufficient.

Organisms that are to be preserved (alcohol, formalin) should be stored in glass bottles.

All bottles should arrive at the sampling site in a fully cleaned state, protected from accidental contamination.

The last cleaning step is (in most cases) rinsing 2-3 times with the water to be sampled.

Sample Containers

The sample containers needed for a sampling campaign are prepared by the laboratory and given to the person collecting samples.

Table 4: Container Types and Volumes Needed for Sampling

	Analysis	Container	Volume	Preservation
0	On-site analysis	PE bowl	±200	--
1	General (SS TDS major ions)	Glass, PE	1000	--
2	COD, NH_3, NO_2-+NO_3-	Glass, PE	500	H_2SO_4, pH
3	o-PO_4	Glass	100	--
4	BOD	Glass, PE	1000	4^{o}C, Dark
5	Coliforms	Glass, PE	300	4^{o}C, Dark
6	Heavy metals (Cd, Zn)	Glass, PE	500	HNO_3, pH
7	Mercury	Glass	1000	HNO_3, pH
8	Pesticides	Glass, PE	1000	4^{o}C, Dark

Reagent Solutions Instruments (required at field)

- Solutions & reagents for estimation of DO
- Buffer solutions (pH = 4, 7, & 9) to standardise the pH meter
- Standard KCl solution (0.01*M) to standardise the EC meter.*
- For preservation of certain samples, conc. HNO_3, conc. H_2SO_4, etc.
- Distilled water for rinsing equipment.

Instruments

- A (mercury) Thermometer
- pH meter
- EC meter.

Field Analysis

Measurements of colour, odour, temperature, EC, pH and DO 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.

If samples are brought to the 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.

Colour

Determining the colour in the field is relatively easy. Pour an aliquot of approx.10ml of sample into a glass test tube and judge the colour observed. Consider one of the following options:

(1) Light brown

(2) Brown

(3) Dark brown

(4) Light green

(5) Green

(6) Dark green

(7) Clear

(8) Other specify

Odour

Determining the odour should always be done in the field, as soon as possible after collecting a sample. After collection, fill a cleaned odourless bottle half-full of sample, insert stopper, shake vigorously for 2-3 seconds and then quickly smell the odour.

Alternatively, pour an aliquot of approx. 5ml of sample into a glass test tube and judge the odour. Consider one of the following options:

(1) Odour free
(2) Rotten eggs
(3) Burnt sugar
(4) Soapy
(5) Fishy
(6) Septic
(7) Aromatic
(8) Chlorinous
(9) Alcoholic

Temperature

Water temperature should be measured in degrees Celsius, using a mercury thermometer or a thermistor. Normally, if temp. is measured electronically using a thermistor this device is built into an instrument which is capable of making other water quality measurements (e.g. pH and EC).

Whenever possible, the temperature should be measured by directly dipping the thermometer in the natural body of water being studied.

In case it is not possible, collect about 500 ml sample in a plastic or glass container and measure temperature by immersing the thermometer in the sample. Read the temperature after equilibration.

Report the Temperature on the sample identification form in degrees Celsius with 1 digit after the decimal point e.g. 13.2^{o}C.

pH

Before measuring pH, it is necessary to calibrate the meter. This should be done at least once per day, before the first pH measurement is attempted.

The procedure of this is as follows:

- ❑ After removing their protective caps, the electrodes are rinsed in distilled water and carefully blotted dry with soft absorbent paper. *NOTE: needs careful handling*
- ❑ The electrodes are then placed in a fresh buffer solution and after stabilisation, pH reading of the meter is adjusted to the pH of buffer solution (normally pH=7).
- ❑ The electrodes are then rinsed again with distilled water and blotted dry.
- ❑ If a pH measurement is not to be taken immediately, the electrodes should be replaced in their protective caps. Normally, the glass electrode cap is filled with distilled water before replacement to prevent the electrode drying out.
- ❑ Report the pH on the sample identification form in pH units showing one digit after the decimal point, e.g. 7.6.

Once calibrated, the pH meter can be used to measure the pH directly by placing the electrodes in water sample immediately after it is obtained. Care should be taken to ensure that the electrodes are rinsed with distilled water before and after each determination and that distilled water is placed in to the glass electrode cap.

Electrical Conductivity (EC)

Before measuring conductivity it is necessary to calibrate the meter at least once per day (before 1st measurement).

Calibration is achieved by determining the conductivity of a known, fresh solution of KCl and adjusting the meter accordingly. In order to ensure the conductivity reading is accurate, it is necessary to adjust the conductivity reading to compensate for temperature changes.

Once calibrated, the conductivity of the water can be measured by immersing electrode in a sample of water as soon as it is taken. It is important to remember that conductivity meters often take some minutes to stabilise. The reading must, be taken after stabilisation.

Report the EC at 25°C preferably in µmhos/cm with no figure after the decimal point, e.g. 1135 µmhos/cm.

Field Data Protocol

a. Sampling team members

b. Date & time (24 hr method) of collection (time span in case of composite sampling)

c. Nature of the sample: spot/composite/integrated

d. Results of performed in-situ analyses (water/air temp., DO, pH, EC, turbidity, macrofauna composition, macrofauna diversity, and 24 hr oxygen P/R ratio)

e. Exact sampling location and depth of collection

f. Definition of sampling intervals and volumes in case of composite sampling

g. Maximum depth of the river, lake and current velocity in case of river

h. Weather conditions w.r.t. clouds, precipitation, wind (direction & force)

i. Consistency of sediment (sandy, silty etc.)

j. Comments on smell, colour, discharges etc.

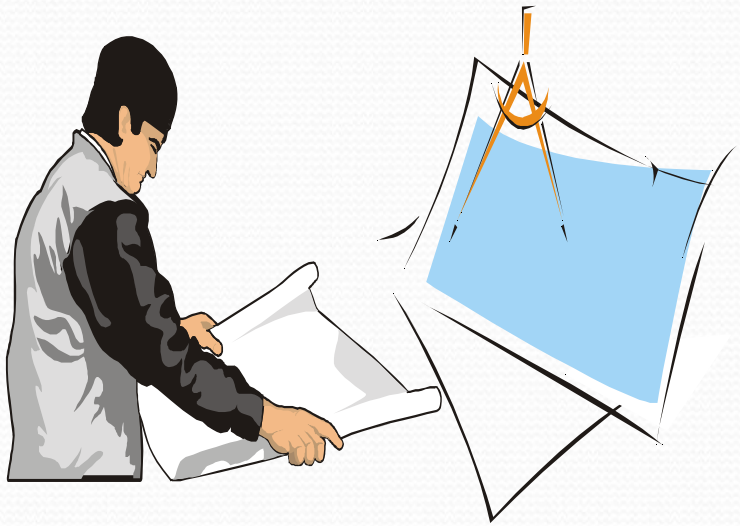
k. Parameter(s) that will be analyzed

l. Sample bottle (number, type, material, volume, preservative)

m. The method of preservation/storage

Analytical result sheets

When offering the samples to the analytical laboratory, each and every series of replicate sample containers has to be accompanied by a prefilled "result sheet".



This sheet is marked with sample specifications identical to the specs marked on the bottle. The individual parameters to be measured in the sample are tabulated, together with the units they should be reported in. The sheet leaves space for the analytical lab to fill in the results of replicate analysis.

Special Care in Water Sampling

In specific situations

- ❑ Inform concern agencies in advance and keep record, if some dispute is anticipated
- ❑ Do not inform the operating agency, if sampling is for monitoring and/or quality control
- ❑ Get relevant details of technology and/or installation, if sampling is for performance assessment
- ❑ Get information on sensitive issues before preceding for filed sampling
- ❑ Ensure infrastructural facilities and safety in sampling programme

WATER IS LIFE!

Thank You