“Capacity Building and Strengthening Institutional Arrangement”

Workshop: Analysis and sampling of water

Environmental sampling (Water)

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PURPOSE OF SAMPLING

Sampling consists in collecting a part of a material (target) of specified dimension.

Sample (unit) must be representative of the whole target, so that the final result of the analysis represents the entire system that it is intended to represent.

It means sampling is a critical element of the all analytical process.

Uncertainity associated to sampling on the analytical result can range from 30% to 50%.

There is a need to collect a representative sample

To assure a representative sampling

Definition of objectives ***

Identification of sampling target
(Sampling sites)

Time and frequency of sampling

Sampling techniques

Definition of objectives

Compliance with national legislation

Characterization of water bodies

Identification of pollution sources

Identification of sampling sites

Selection of sampling sites is influenced by the characteristics of the target (sampling in canal, rivers and stream water)

Pay attention to the safety of the personnel involved in the sampling!!!

Rivers and stream

sampling sites in a river may include tidal limit, major tributaries in their confluence and major discharges of sewage or industrial effluent;

monitoring the effects of a discharge, sampling sites should be chosen upstream and downstream the discharge. The downstream sampling should include different sampling sites to assess the effect of the discharge on the river

the selection of sampling sites should include sites where flow data are available.

Canals

to monitor the effects of a discharge in a canal, the considerations for river and streams apply too.

attention to the direction of flow (the pollutants fate!)

flow rate depends on the amount of navigational use and upon weather conditions.

Need of flow measurements

In the sampling programme of a river and estuarine a reliable estimate of the level of pollutant which concentration varies with time is obtained only if the rate of trasport of the substance from the point of discharge is known.

Flow measurements

1. Direction of flow (navigational canals to assess the consequences of aquifer pollution. It can vary with time!)
2. Velocity of flow (to calculate the discharge rate or the time required for a given body of water to move through a given distance)
3. Discharge rate (volume liquid that passes a given point per unit time), information of primary importance for the design and operation of water treatment plants

Time and frequency of sampling

time and frequencies in sampling can be properly decided only after detailed preliminary work, in which a high sampling frequency is necessary to provide the information.

- **Time** representativeness of water quality and its variation
- **Frequency** upon the objectives of the monitoring program

Time and frequency of sampling (2)

Control of levels of parameters within defined control limits

Sampling frequency must be chosen in order to detect an important deviations outside the control limits occurring between successive measurements.

Time and frequency of sampling (3)

Programme for investigation of causes of pollution (pollution control)

This program aims to estimate one or more parameters that characterize the site.

For example the characterization of a lake (regarding Ntot and Ptot) needs a frequency of sampling at least of one for season.

The frequency of sampling in a normal river for the determination of BOD or COD is generally ones a year.

Time and frequency of sampling (4)

Program for investigation of causes of pollution (pollution control)

This program should be designed to determine the cause of polluting discharges of unknown origin, so it is necessary a fairly high frequency in relation to the frequency of appearance of pollution.

Sampling techniques

1. *Types of sample*
2. *Types of sampling*
3. *Sampling equipment*
4. *Preservation of sample*

1. Types of sample

It is recommended that separate sample be used for chemical, microbiological and biological analyses, because the procedures and equipment for collection and handling are different.

The sampling techniques will vary according to the specific situation, the parameter to determine and the utilization of the data will be obtained with the analyses.

1.1. Spot samples

Spot samples are discrete sample collected manually or automatically for the water at the surface, at specific depths and at the bottom.

This type of sample will be representative of the water quality only at the time and place at which it is taken.

Spot sample are recommended to investigate if the values of the parameters of interest are not constant and for the determination of unstable parameters (concentration of dissolved gases, residual chlorine)

1.2. Periodic samples (discontinuos)

The periodic samples can be time, volume or flow dependent

1.3. Continuous samples

The continuous samples can be taken at fixed flow rates or at variable flow, the latter type of sample can reveal variations which may not be observed by the use of the spot sample if a sufficient number of samples is taken and if the samples remain discrete.

1.4. Depth profile samples and Area profile samples

1.5. Composite sample

The composite samples are made of two or more samples or sub samples, mixed together in appropriate known proportion (either discretely or continuously). They provide average compositional data.

1.6. Large volume samples

Namely from 50 litres to several cubic metres i.e. for the analysis of pesticides. An alternative is passing a metered volume through an adsorbent cartridge of filter depending on the parameter to be analysed.

2. Types of sampling

There are many sampling situations, some of which can be satisfied by taking simple spot samples whereas others may require sophisticated instrumental equipment. Every situation must be studied carefully considering the aim of the water sampling program.

3. Sampling equipment

The sampling equipment is chosen considering these factors:

a. type of pollutant;

b. physical and chemical characteristics of the water, the superficial properties of the particulate;

c. Idrological characteristics of the body water to monitor.

The most frequent problems are:

- adsorption onto the walls of the sampler,
- contamination because of improper cleaning of the sampling equipment.

Sampling device

- *Niskin & Van Dorne bottles* are sampler for spot sampling
- Automatic sampling equipment are of two types mainly: *time dependent* and *volume dependent*

Sample container

Criteria of selection of the sample containers:

- resistance to extreme temperatures;
- resistance to breakage;
- size and shape;
- minimization of contamination from the material of which the container is made;
- chemical and biological inertness of the material of which the container is made (no reaction);
- no adsorption of analytes on the walls.

4. Preservation of samples

Waters particularly surface waters and above all waste waters, are susceptibile to being changed as a result of phisical, chemical or biological reactions which may take place between the time of sampling and the analysis.

Cause of variations can be:

- presence of bacteria or algae in the sample;
- oxidation by the the dissolved oxygen present in the sample or by the atmosperic oxygen;
- precipitation phenomena for example $CaCO_3$, $Al(OH)_3$;
- volatilization phenomena.

The extent of this variation is a function of seasonal condition too.

Precautions to be taken

- use of appropriate cointainers;
- filling the container (for physico-chemical determination);
- to make as soon as possible the analyses, for some analyte on site carbon dioxide content);
- preparation of containers (decontamination with acid solution)
- cooling or freezing of the samples
- filtration or centrifuging (removal of suspended matter, bacteria)
- addition of preservatives (acids, basic solutions, biocides etc)

Recommandations for water sample storage

Parameter to be studied	Type of container	Preservation technique	Maximum preservation time
Acidity and alcalinity	Polyethylene or glass	Cooling 2-5 °C	24 h
Ammonia free and ionised	Polyethylene or glass	Acidification to pH<2 with H_2SO_4 Cooling 2-5 °C	24 h
Arsenic	Polyethylene or glass	Acidification to pH<2	3 days
Barium	Polyethylene or Borosilicate glass	Filtration at the place of sampling and acidification of the filtrate to pH 2	1 month
BOD	Polyethylene or glass	Cooling 2-5 °C storage in the dark	24 h
Cadmium		See Barium	
Calcium	Polyethylene or glass	Acidification to pH<2	1month
Carbon dioxide	Polyethylene or glass	Analysis on site	
Chloride	Polyethylene or glass	---	1 month
COD	Polyethylene or glass	Acidification to pH<2 with H_2SO_4 Cooling 2-5 °C and storage in the dark	5 days
Heavy Metals (except Hg)		See Barium	
Oxigen	----	On site	---
Phosphorus total	Glass or Borosilicate glass	Cooling to 2-5 °C	24 h

Raccomandations for sample storage

Parameter to be studied	Type of container	Preservation technique	Maximum preservation time
Pesticide organo-chlorine	Glass (washed with solvent)	Cooling 2-5 °C and storage in the dark	24 h
Pesticide organo-phosphorus	Glass (washed with solvent)	Cooling 2-5 °C and storage in the dark	24 h
pH	Polyethylene or glass	Trasportation at a lower Temperature the initial one	6 h
pH		Analysis on site	---
Phenols	Borosilicate glass	Cooling 2-5 °C Immediate on site filtration necessary	24 h
Phosphorus dissolved	Glass or Borosilicate glass	Acidification to pH<2	1 month
Sulfites	Polyethylene or glass	Fixin on site by addition of 1mL of 2,5%(m/m) solution of EDTA per 100 ml of sample	48 h
Surfactant cationic	glass	Cooling 2-5 °C	48 h
Suspended and sedimentary matter	Polyethylene or glass	--	24h
Total residue(dry extract)	Polyethylene or glass	Cooling 2-5 °C	24 h

To outline..

A refrigerated sample before the analysis must be at ambient temperature.

Before the use a frozen sample must be completely thawed, as the freezing process may have the effect of concentrating some components in the inner part of the sample which freezes last.

The use of preservatives must not interfere with the subsequent laboratory analyses

Final steps of sampling…..

The sample must be identified without ambiguity (give to each sample a specific code).

At the moment of sampling it's necessary to note numerous details (date, hour, nature and amount of preservative, atmospheric conditions etc..)

Pay attention to the transport of the samples, no deterioration, loose of sample, no contamination, storage at cool temperature, protection from light.

Sampling of rivers and streams (examples)

Sampling point selection

The monitoring of the effects of a tributary or an effluent on the stream includes the use of two sampling points; one upstream and the other downstream. The downstream point must be far enough to ensure the mixing is complete. The use of dyes permits to evaluate the right distance. Normally 1 km is enough.

The mixing in the three dimensions (vertically, laterally, longitudinally) must be considered :

- stratification (slow moving waters) several depth samplings
- no lateral mixing two or more samples across the river width (downstream).

Time of travel

The sampling sites may be chosen considering the time of residence of a substance to investigate its rate of change, for example unstable constituents.

Methods to which to refer : ISO 748 (surface floats), ISO 555 (use of tracers)

Choice of sampling point

Normally the sampling site is chosen in areas where the analytes are homogeneously distributed

In the case of sampling in area where the analytes can be heterogeneous several samples are collected to ensure representative results (composite samples).

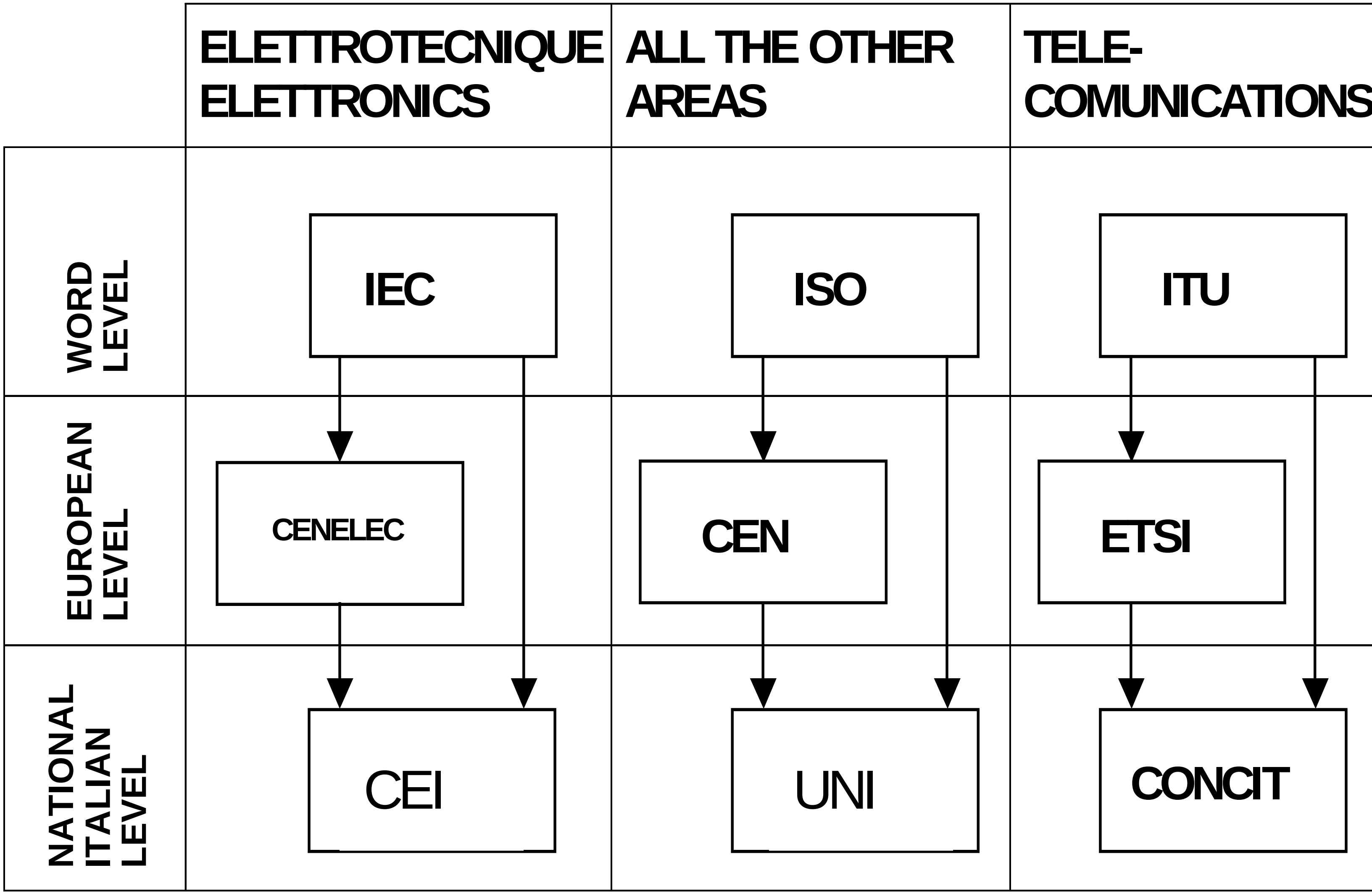
Choice of sampling method

Physical chemical sampling

- when subsurface is acceptable it is often sufficient to immerse a container that will be poured in the storage bottle or directly the storage bottles (sampling of surface film should be avoided),
- sampling at depth is performed with Niskin bottle,
- the dissolved gases sampling should be done with sealed immersion device
- use of silicone or inert plastic for pump tubing to avoid sample contamination
- collection sample for the analysis of suspended matter can't be performed with low-powered peristaltic pumping system (not below 0,5 ml/s nor exceed 3.0 ml/s)
- for representative sampling of undissolved materials, the rate of sampling should be adjusted so that the velocity of water in the inlet of sampling system is the same as that of the water being sampled (isokinetic sampling condition)

Microbiological sampling

- use of clean, sterilized sample bottle (fitted with a large screw cap or other sterizable stopper covered with thin aluminium foil);
- the bottle is filled without rinsing;
- the bottle (holding by the base with the hand or better with a clamp) is plunged to a depth of about 0.3 m below the surface then is titled so that the neck points slightly upwards, the mouth being directed into the direction of flow;
- never the water sampled should come in contact with hands.


ELETTROTECNIQUE ELETTRONICS
ALL THE OTHER AREAS
TELE-COMUNICATIONS
WORD LEVEL
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IEC
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International Standard ISO 5667
Water quality- Sampling

- Part 1: Guidance on the design of sampling programmes
- Part 2: Guidance on sampling techniques
- Part 3: Guidance on the preservation and handling of samples
- Part 4: Guidance on sampling from lakes, natural and man-made
- Part 5: Guidance on sampling of drinking water and water used for food and beverage processing
- Part 6: Guidance on sampling of rivers and streams
- Part 7: Guidance on sampling Guidance on sampling of water and steam in boiler plants
- Part 8: Guidance on sampling of wet deposition
- Part 9: Guidance on sampling from marine waters
- Part 10: Guidance on sampling of waste waters
- Part 11: Guidance on sampling of groundwaters
- Part 12: Guidance on sampling of industrial cooling water
- Part 13: Guidance on sampling of sludges and sediments