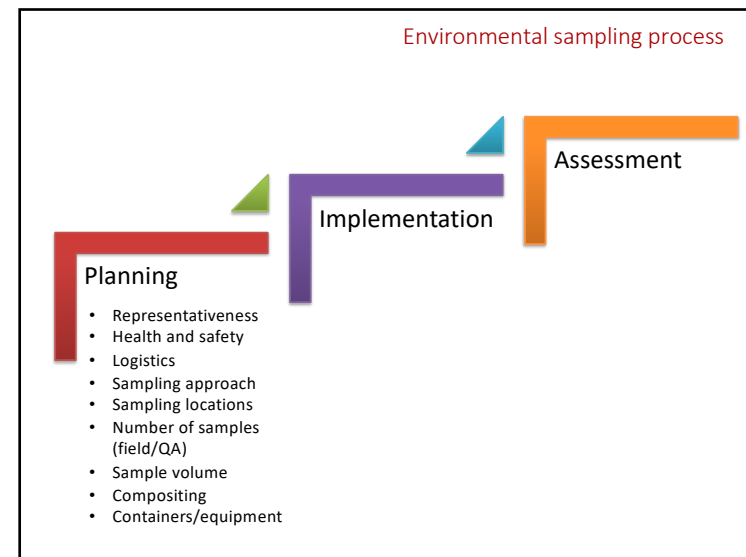
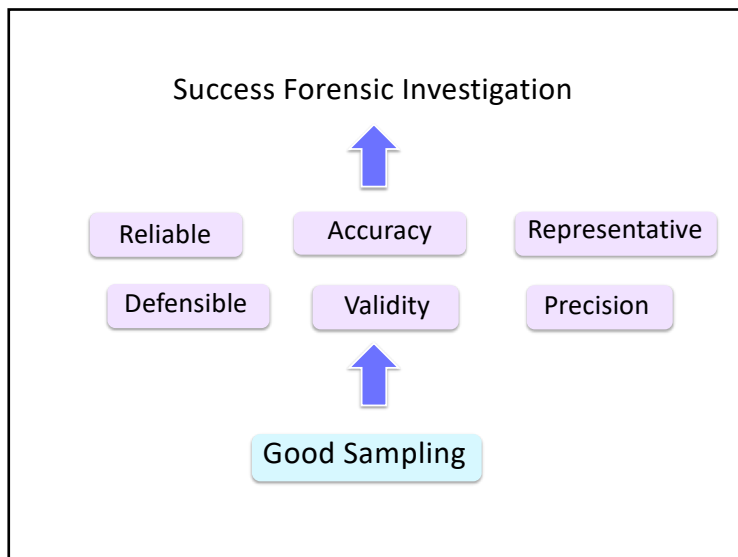
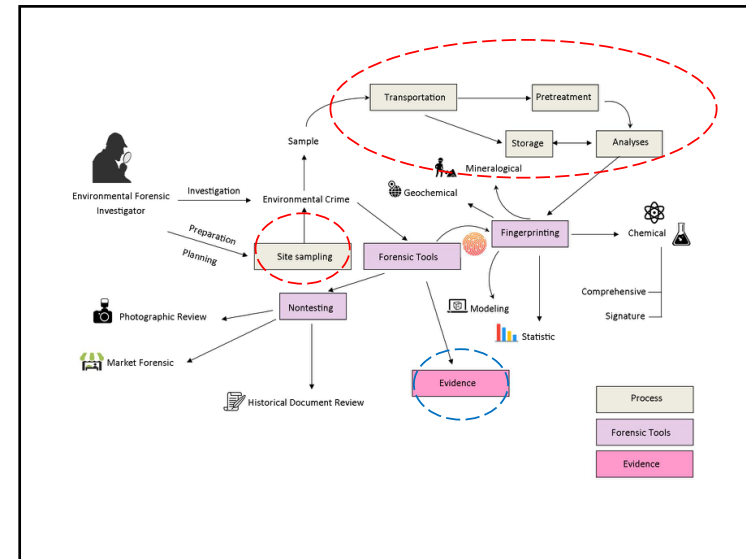


COURSE ON INTRODUCTION AND APPLICATION OF ENVIRONMENTAL FORENSICS

Environmental Forensics

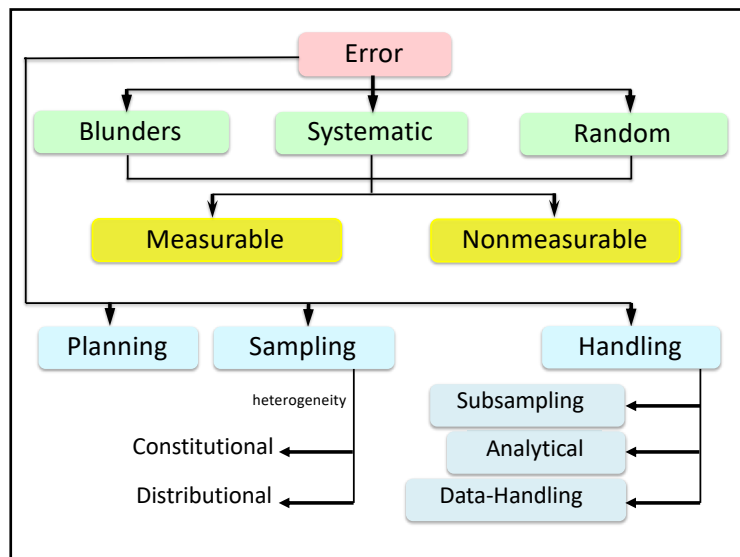
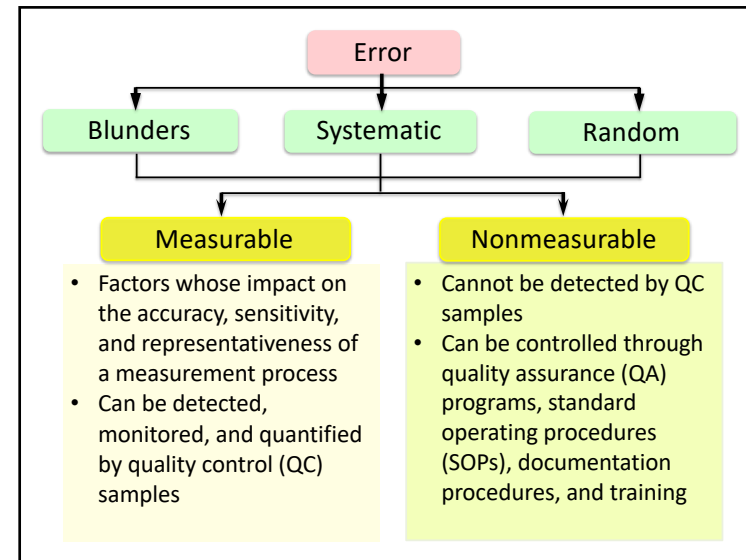
Lecture 2: Environmental Forensics Sampling

Prof. Dr. Ahmad Zaharin Aris, CEnv, MRSC, FGS
 Faculty of Environmental Studies
 Universiti Putra Malaysia

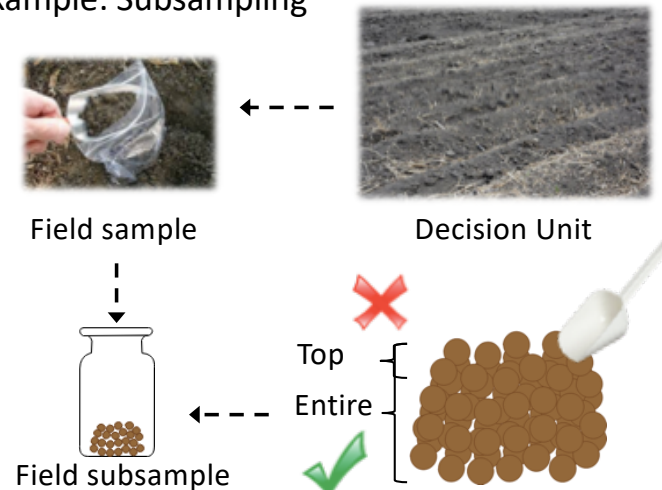


Sampling Error – Categories

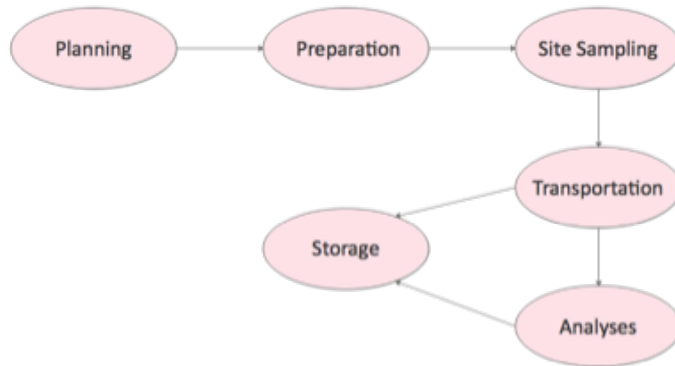
- ① **Blunders**
 - ✓ Mistakes that typically occur only occasionally
 - ✓ Eg: misweighing or mislabeling
- ② **Systematic errors (bias)**
 - ✓ Measurement that are consistently different from their true value
 - ✓ Underreporting a contaminant concentration
- ③ **Random errors (imprecision)**
 - ✓ Difficulty of repeating sampling and analytical processes
 - ✓ Heterogeneity of population



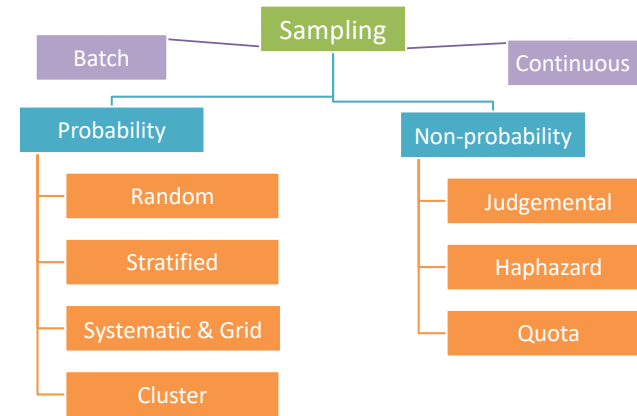
Example: Subsampling



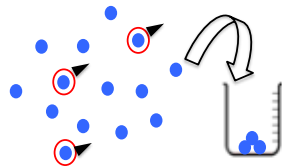
Sampling Flow Chart



Sampling Strategies

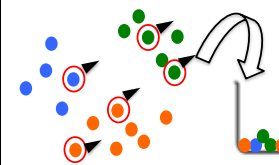


Simple random sampling

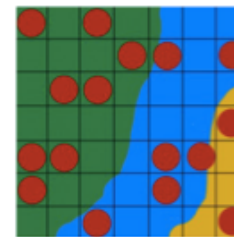


- Homogenous population (eg: no major “hotspot” are expected)
- Statistically unbiased estimates of the mean, proportions, and variability
- Easy to understand and implement

Stratified random sampling

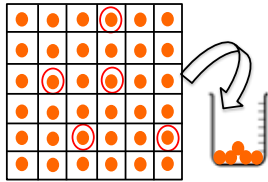


- Target population is separated into nonoverlapping strata/logical zones
- Sub-populations vary, but are similar within groups
- Sampling occur within groups
- Greatest precision in estimate mean and variance

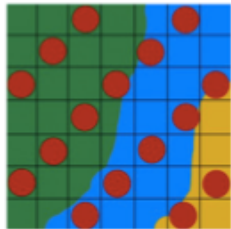


Stratified random sample of an area (green – forest; blue – arable land; yellow – mountain)

Systematic & Grid sampling

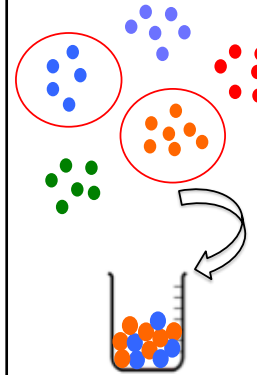


- Samples are taken at regularly spaced intervals over space/time
- Initial location/time – random, the remaining sampling stations are defined at regular intervals over an area (grid)/time (systematic)



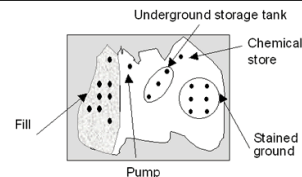
Systematic & grid random sample of an area (green – forest; blue – arable land; yellow – mountain)

Cluster sampling



- Sampling technique in which the population is divided into groups (clusters)
- Heterogeneity within subgroups
- Homogeneity between subgroups
- Whole groups sampled
- Useful for estimating rare characteristics

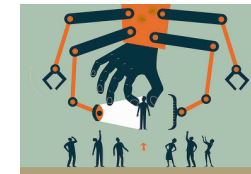
Judgmental sampling



- Based on the researcher's judgment and knowledge about the population.
- Samples are based on prior knowledge of the site
- Used when a limited number of individual possess the trait of interest
 - ✓ Expert witnesses used in court

Haphazard sampling

- Most common – fast, inexpensive, easy & subject readily available
- Samples/subjects are selected because of their convenient accessibility & proximity to the researcher
- Researcher selects anyone he or she happens to come across
- Also known as **accidental / convenience** sampling
- Example:
 - “Man on the street”
 - volunteer samples



Quota sampling

- Nonrandom sample
 1. Identifies general categories into which cases/people will be placed
 2. Select cases to reach a predetermined number in each category



Batch sampling

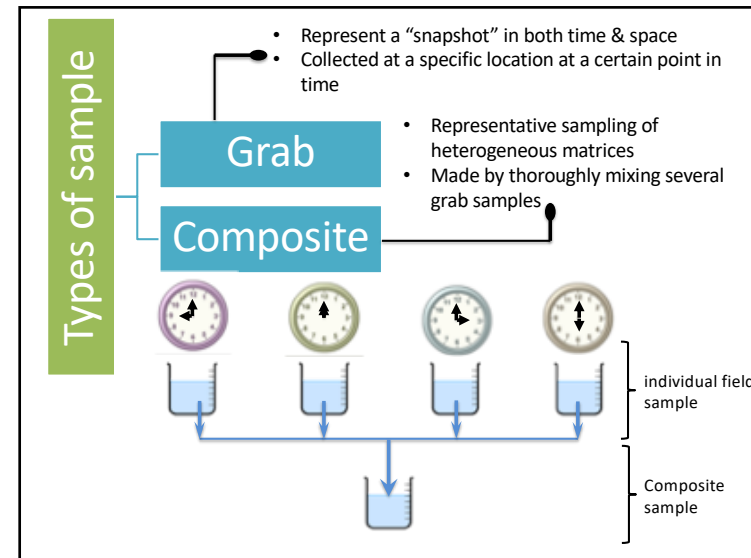
- Involves taking a sample from the environment and performing an analysis either on site or later on in the laboratory
 - For example, batch sampling of a wastewater effluent for pH analysis would imply that a volume (e.g. 100 mL) of the effluent is collected and then analysed for pH.
 - These samples are collected at a specific time and place and are also called **grab samples**
- Batch sampling is the easiest and most common method of obtaining a sample and it is widely used in environmental surveys.

Continuous sampling

- Involves continuously monitoring the environmental parameter of interest – real-time measurement
 - Same as before
 - Continuous analysis of the effluent pH would involve placing a pH electrode directly into the effluent stream and recording the pH on a chart recorder or a data logger
 - In this way of continuous record of the effluent pH is obtained
 - This kind of sampling could detect important changes in the effluent that would be missed by batch sampling

- Continuous sampling is generally combined with an instrumental method of analysis, and the term given to this combination is **continuous monitoring**.
- This method of analysis is being adopted more extensively in many applications (e.g effluent monitoring, air monitoring)
- Usually, the method is combined with some kind of alarm system to alert the operator when standards are being exceeded.

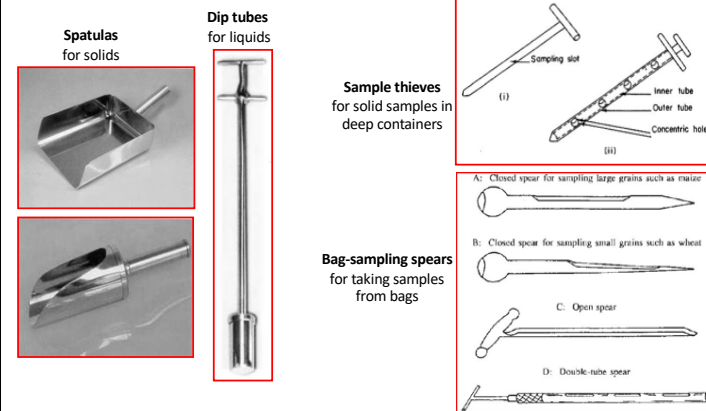
- For example, if the level of pollutant in an effluent stream is found to exceed the emission standard, an alarm may be activated and the plant personnel could switch off the process and attempt to resolve the problem.
- Application
 - Air quality
 - Water level (flood)
 - Pollution status (i.e effluent)



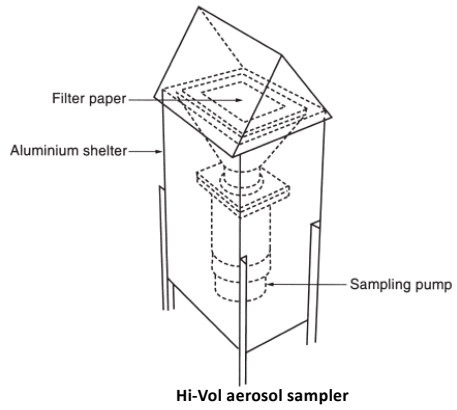
Composite sample

- Prepared by mixing several batch samples, usually collected at the same place but at different times
- These are used to evaluate the average concentration in a medium in which the concentration may vary with time.
- For example, batch samples of waste water are collected every 3 h over a 24-h period and pooled into one container.
- The concentration in the mixture is supposed to reflect a 24-h average

Examples of types of sampling



Examples of types of sampling tools



Hi-Vol aerosol sampler

Examples of types of sampling tools



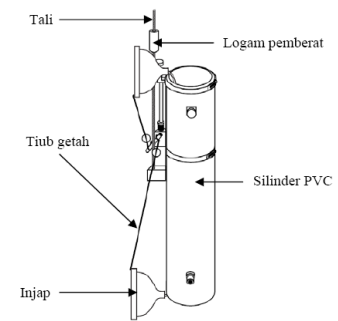
Water sampler

Examples of types of sampling tools



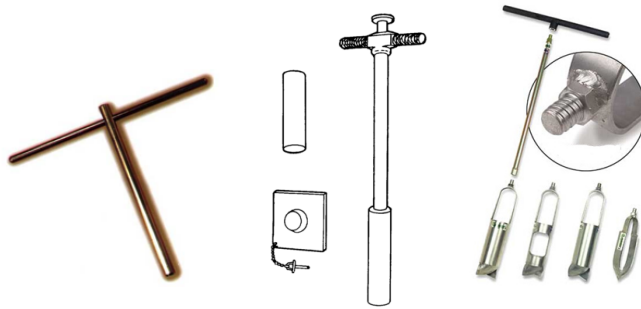
Water sampler

Examples of types of sampling tools



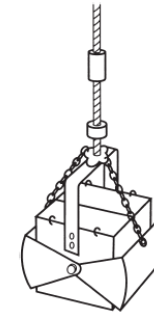
Van Dorn sampler for taking water samples at different dept

Examples of types of sampling tools



Soil sampler

Examples of types of sampling tools



Eckman sediment sampler

Examples of types of sampling tools



Bomb Sampler

Problems

- Unique problems of obtaining representative samples from water, air, effluent gases, dust, and soil
- Some questions that need to be addresses are:
 - When and where should the sample be taken ?
 - How many samples should be taken ?
 - How much sample is required ?

How to ?

- Usually decide on the best location, time, and number of samples to be taken (the so-called random sampling)
- Considerations of site accessibility, time, and expense are often more influential factors than purely scientific considerations.
- Anyway, several samples are collected at each site in order to obtain some indication of variability in analyte concentration at the site, and in case some of the samples are lost, spoilt, or incorrectly analysed
- Obtaining as representative a sample as possible is paramount since the analyst cannot obtain the same sample again.

Remember

The environment is a dynamic system, which is constantly changing, and returning to the same site later date may give completely different results

Sampling operation

- **Written sampling procedure:** operations to be performed on a defined material for a specific purpose, including health/safety aspects
- **Sampling plan:** description of the location, number of units and/or quantity of material that should be collected, and associated acceptance criteria.
- Make sure that representative samples are taken in sufficient quantity. **Representative sample:** sample obtained according to a sampling procedure designed to ensure that the different parts of a batch or the different properties of a non-uniform material are proportionately represented.
- Samples should never be returned to the bulk.

Sampling operation

- Sampling operations should be supervised and documented => **sample collection form** => always kept together with the collected sample.
- **Sample collection form:** written record of the sampling operations, containing: batch number, sampling date/place, reference to sampling protocol used, description of containers and materials sampled, possible abnormalities, any relevant observations, name/signature of the sampler...
- Store the sample in a properly **labelled container:** sample type, name of material, identification code, batch number, code, quantity, date of sampling, storage conditions, handling precautions

[SAMPLING LOG SHEET] [REDACTED]

Sampling Point : _____
 Weather Condition : _____
 Time : _____ am/pm Date : _____
 Groundwater Level : _____ (m) a.m.s.l
 Altitude : _____ m / _____
 Distance from shorelines : _____ m

Still in operation Abandoned / Pumping : Yes No. If yes, sampling after : _____ minutes
 Coordinate : _____ N _____ E (Locality : _____)

IN SITU PARAMETERS

	pH	mV (pH)	Temp. (°C)	Cond. (µS)	DO (mg/l)	Sal (ppt)	ORP	TDS (ppm)
1								
2								
3								
MEAN								

Ahmad Zaharin Aris | zaharin@env.upm.edu.my [REDACTED]

Test kits and portable laboratories

- In many instances, it is necessary to analyse pollution on the spot in the field rather than taking the sample back to the laboratory
- This may be necessary for the following reasons:
 - To avoid any changes in the sample composition due to chemical or biological reactions during transport to the laboratory
 - To obtain results immediately as, for example, during an emergency following a spillage or hazardous chemicals, when a delay in analysis could have grave consequences

Test kits and portable laboratories

- Many test kits and portable systems are commercially available for the on site analysis of pollutants
- These can vary in sophistication from simple colorimetric methods involving visual comparisons to portable laboratories and instruments

Sample handling

Analyte	Container	Preservation	Maximum holding time
Inorganics and microbial tests			
Acidity	PS	Cool, 4°C	14 d
Alkalinity	PS	Cool, 4°C	14 d
Bacteria, Coliform (total and fecal)	PS	Cool, 4°C, add 0.009% Na ₂ S ₂ O ₃ if residual chlorine is present	6 h
Biochemical oxygen demand	PS	Cool, 4°C	48 h
Bromide	PS	None required	28 d
Chloride	PS	None required	28 d
Chlorine, residual	PS	None required	Analyze immediately
Chemical oxygen demand	PS	Cool, 4°C, H ₂ SO ₄ to pH=2	28 d
Cobalt	PS	Cool, 4°C	48 h
Cyanide	PS	Cool, 4°C, pH=12, 0.6 g ascorbic acid	14 d
Fluoride	P	None required	28 d
Hardness	PS	pH=2 with HNO ₃ or H ₂ SO ₄	6 mon
Iodine	PS	None required	Analyze immediately
Kjeldahl nitrogen	PS	Cool, 4°C, pH=2 with H ₂ SO ₄	28 d
Metals (except chromium-VI, boron and mercury)	PS	HNO ₃ to pH=2	6 mon
Chromium-VI	PS	Cool, 4°C	24 h
Mercury	PS	HNO ₃ to pH=2	28 d
Boron	P	HNO ₃ to pH=2	28 d
Nitrate	PS	Cool, 4°C, H ₂ SO ₄ to pH=2	28 d
Nitrite	PS	Cool, 4°C	48 h
Oil	G	None required	Analyze immediately
Oil and grease	G	Cool, 4°C, H ₂ SO ₄ or HCl to pH=2	28 d

Sample handling

Analyte	Container	Preservation	Maximum holding time
Inorganics and microbial tests			
Oxygen, dissolved	G (BOD bottle)	None required	Analyze immediately
pH	P/G	None required	Analyze immediately
Phenolics	G	Cool 4°C, H ₂ SO ₄ to pH<2	28 d
Phosphorus elemental	G	Cool, 4°C	48 h
orthophosphate	P/G	Cool, 4°C	48 h
total	P/G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 d
Residue			
Total	P/G	Cool, 4°C	7 d
Filterable	P/G	Cool, 4°C	7 d
Nonfilterable (TSS)	P/G	Cool, 4°C	7 d
Settleable	P/G	Cool, 4°C	48 h
Volatile	P/G	Cool, 4°C	7 d
Silica	P	Cool, 4°C	28 d
Specific conductance	P/G	Cool, 4°C	28 d
Sulfate	P/G	Cool, 4°C	28 d
Sulfide	P/G	Cool, 4°C, zinc acetate plus NaOH to pH >9	7 d
Sulfite	P/G	None required	Analyze immediately
Surfactants	P/G	Cool, 4°C	48 h
Taste	G	Cool, 4°C	24 h
Temperature	P/G	None required	Analyze
Total organic carbon	G	Cool, 4°C, HCl or H ₂ SO ₄ to pH<2	28 d
Total organic halogen	G (amber bottles)	Cool, 4°C, store in dark, HNO ₃ to pH<2, add Na ₂ SO ₄ if residual chlorine present	14 d
Turbidity	P/G	Cool, 4°C	48 h

Sample handling

Organics tests			
Purgeable halocarbons	G (Teflon-lined septum)	Cool, 4°C, no headspace (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine is present)	14 d
Purgeable aromatics	G (Teflon-lined septum)	Cool, 4°C, no headspace (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine is present), HCl to pH<2	14 d
Pesticides, chlorinated	G (Teflon-lined cap)	Cool, 4°C, pH 5-9	7 days until extraction; 40 days after extraction
PCBs	G (Teflon-lined cap)	Cool, 4°C	7 days until extraction; 40 days after extraction
Phthalate esters	G (Teflon-lined cap)	Cool, 4°C	7 days until extraction; 40 days after extraction

Sample handling

Organics tests			
Purgeable halocarbons	G (Teflon-lined septum)	Cool, 4°C, no headspace (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine is present)	14 d
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PCBs	G (Teflon-lined cap)	Cool, 4°C	7 days until extraction; 40 days after extraction
Phthalate esters	G (Teflon-lined cap)	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitroaromatics	G (Teflon-lined cap)	Cool, 4°C (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine present), store in dark	7 days until extraction; 40 days after extraction
Nitroaromatics	G (Teflon-lined cap)	Cool, 4°C (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine present), store in dark	7 days until extraction; 40 days after extraction
Polynuclear aromatic hydrocarbons	G (Teflon-lined cap)	Cool, 4°C (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine present), store in dark	7 days until extraction; 40 days after extraction
Halocethers	G (Teflon-lined cap)	Cool, 4°C (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine present)	7 days until extraction; 40 days after extraction
Phenols	G (Teflon-lined cap)	Cool, 4°C (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine present)	7 days until extraction; 40 days after extraction
Dioxins and dibenzofurans	G (Teflon-lined cap)	Cool, 4°C (add 0.008% Na ₂ S ₂ O ₃ if residual chlorine present)	7 days until extraction; 40 days after extraction

Note: P: polyethylene, G: glass. If there is no residual chlorine in the sample, the addition of Na₂S₂O₃ may be omitted.

Storage

- Once the sample has been collected, it is transported to the laboratory for analysis
- Sometimes it is possible to carry out the analysis at the site using portable test kits, or inside on-site laboratories, but most often the sample has to be transported some distance
- It is desirable to perform the analysis as soon as possible after sample collection
- On many occasions this is not possible and the sample has to be stored until the analysis can be performed
- During transportation and storage, it is important to preserve the integrity of the sample

Storage

Once the sample has been collected inside the sampling vessel, the following processes may threaten the integrity of the sample



Chemical reactions



Biological reactions



Interaction with
sampling bottle material

Storage

- The analyte under investigation may be destroyed or created by chemical or biological reactions, it may be adsorbed onto the walls of the sampling bottle or interfering substances may be leached from the walls of the bottle.
- Contamination of the sample during sampling, transport, and storage is a real possibility and all measures must be taken to avoid this
- Many of the analytes are present at trace and ultra-trace levels in environmental samples and it is quite easy to contaminate the sample

Storage

Containers

- Containers used to store a sample should comply with the storage directions
 - should not interact with the sampled material.
 - should not allow contamination.
 - should protect the sample from light, air and moisture.
 - should be sealed and adequately labelled.
 - avoid mix-up when containers are opened (screw caps, separate lids).
 - manipulations/unauthorised opening should be easy detectable.
 - transported in such way as to avoid breakage.



Storage

Rooms for sample storage

- Security and adequate storage conditions (light, ventilation, safety requirements, and any special requirements) should be ensured for the rooms in which samples are stored.
- Samples should be stored according to the storage conditions as specified for the respective method
- Packaging materials similar to those in which the bulk is supplied should be used for long-term storage.



Preservation

Several preservation procedures have been recommended for nutrient samples when they cannot be analysed promptly:

- **Refrigeration.** This slows down, but doesn't eliminate, bacterial and chemical reactions; reaction rates at 4 °C are about a quarter of the rates at 25 °C.
- **Freezing.** This reduces bacterial and chemical reactions even further.
- **Addition of acid.** Lowering the pH greatly reduces bacterial activity.
- **Addition of a bactericide.** Many bacterial agents have been used to completely eliminate the activity of microorganisms; chloroform and mercuric chloride are the most common.

Sample treatment

- Various other treatments can also be applied
 - Drying
 - Sieving
 - Ignition
 - Boiling
 - Precipitation
 - Complexation
 - Reduction
 - oxidation

Sample treatment

- Although some samples may be analysed directly most often the sample has to be prepared for analysis.
- A variety of sample treatment methods are used depending on the type of sample, the analyte to be determined, and the kind of analytical method to be used.
- The purposes of sample treatment are three-fold:
 - to convert the sample and analyte into a form suitable for analysis by the chosen method,
 - to eliminate interfering substances, and
 - to concentrate the sample.

Filtration

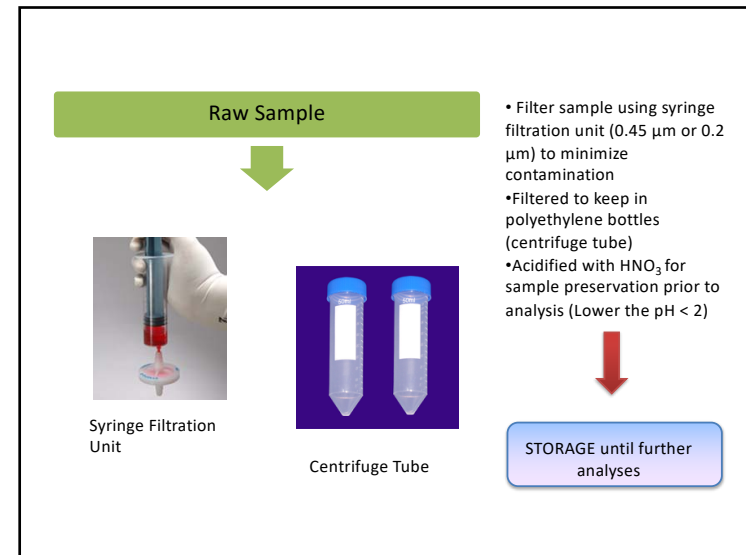
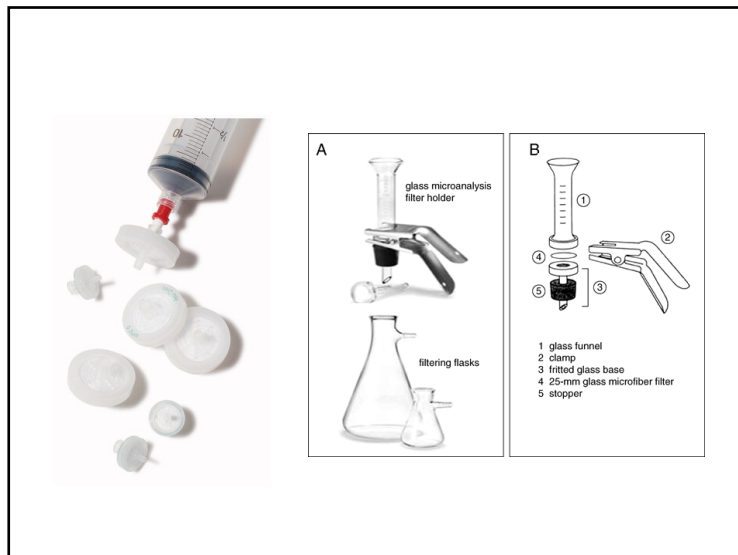
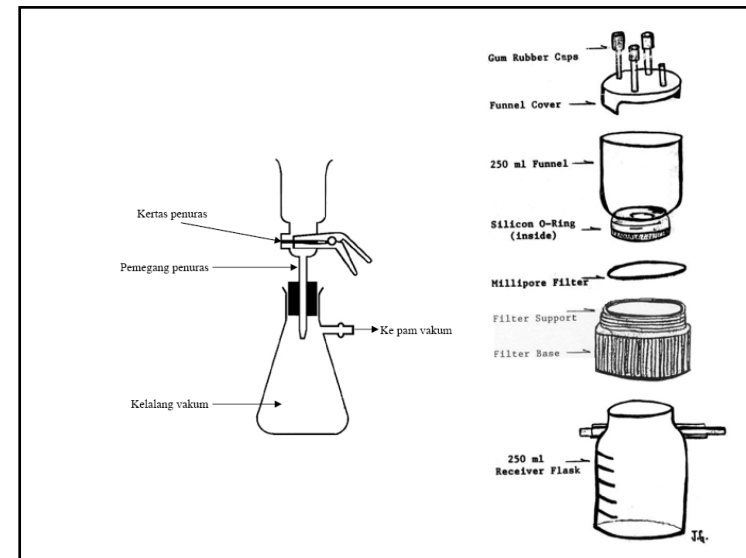
Aqueous samples are usually filtered. For example, when determining soluble components it is customary to filter out the suspended particles from solution as these may interfere in the analysis.



Filtration

Filtration is often employed in water analysis to separate dissolved components from those present in suspended matter. However, filtration can present several problems:

- **Penetration of insoluble material through the filter.** The standard procedure is to filter the sample through a filter with a nominal pore size of $0.45\ \mu\text{m}$, and components passing through the filter are deemed to be “dissolved” or “soluble”.
- **Contamination.** Substances present in the filter material may dissolve into the sample during filtration. This is especially a problem when analysing trace metals in relatively clean samples. Filters for trace metal analysis should be washed with acid before use, so as to remove any metal contaminants from the filter material.
- **Adsorption.** Some analytes may adsorb onto the filter material or filtration unit. For example, certain metals may be adsorbed onto the walls of glass filtration units.





THANK YOU

“We have made clear to you the signs;
perhaps you will understand.”

(57:17)

H₂O

Water Research
<http://research.upm.edu.my/hydro>