

Generalized Sampling Considerations

1. Analytes of Interest

Primary analytes - essential, regulated species (i.e., F^- or turbidity in DW)

Secondary analytes - less common or incidental species (i.e., Cl^- or SO_4^{2-})

2. Study Limits (depends on goals of investigation)

- level of precision/accuracy
- detection limits
- turn around time and costs
- # of sites, geographic location, frequency
 - eg. diurnal variations for detailed studies
 - monthly averages for long term monitoring
 - before and after discharge for point source polluters

3. Sampling Points

- specific siting criteria (multiple sites, grid or composite sampling)
- avoid major disturbances, sample at depth to avoid surface contaminants

4. Collection

- process must minimize systematic error
- there are well defined protocols for sampling methods, sample containers and cleaning methods
- run quality assessment by running same analysis with samples collected by different people at same site
- documentation of field observations, sampling numbering system, field log

5. Sampling Handling

- some analytes require filtration in the field (i.e., dissolved metals and inorganic anions)
- some analytes require chemical preserving agents, sealed bottles and/or refrigeration (i.e., dissolved metals require HNO_3)
- analysis must be carried out within specified time limits

- sample splits for replicate analysis
- sample spikes to compensate for losses and/or interferences

Blanks - bottle blanks, sampler blanks, filter blanks, field blanks

6. Some parameters are measured in the field on-site or 'in-situ'.

- temperature, pH, conductivity, turbidity, DO (electrochemical)
- continuous monitoring is becoming more widely available for some measures

DO (Winkler) must be 'fixed' on site with Mn^{2+} and analysis carried out within 3-6 hr

Sample Containers and Storage Protocols

In general, high density polyethylene (HDPE) or teflon sample bottles are acceptable with the following the notable exception of trace organics, such as, hydrocarbons, pesticides, oil and grease.

A number of parameters should be analyzed at the time of sampling and not stored. These include; pH, Temperature, Dissolved Oxygen and Oxidation Reduction Potential

In general, samples for metal ion analysis are not collected in glass containers.

Field samples that are to be transported are typically cooled to 4°C and shipped on ice to be analyzed within a specified time period (maximum holding time).

Dissolved species analysis require sample filtration 0.45 µm in the field. In addition, dissolved metals require 2 mL per L of concentrated HNO₃ as a preservative post filtration.

Total species analysis are not filtered and generally require a digestion step or a strong acid preservative.

Other specific protocols apply and vary with individual employer and jurisdiction.

See further:

Ambient Freshwater and Effluent Sampling, BC. MOE, 1994

Sampling for Water Quality, Environment Canada (TD 370.S28 1984)

Compilation of EPA's Sampling and Analysis Methods (TD 423.C65 1991)

Environmental Sampling and Analysis for Technicians, Maria Csuros, 1995

Sampling from Different Matrices

Types of sample matrix:

- (i) Water; groundwater (wells), surface water (streams, rivers, lakes and reservoirs), effluents
- (ii) Solids; sediments, soils, sludges, minerals
- (iii) Gases; atmospheric particles and gases
- (iv) Biological (tissue, serum, etc)
- (v) Hazardous waste
- (vi) Radioactive waste

Groundwaters

used to monitor geochemical properties and contamination of drinking water (eg. F⁻ in wellwaters, PAH's around underground petroleum tanks)
need to flush system prior to collection

Sludges

semi-solid waste of industrial, municipal treatment plants
often collected in jars with teflon sealed caps, variety of preservatives

Soils

stainless steel specialty equipment and containers

Sediments

scoops for shoreline and shallow waters
cores for deeper waters (many designs depending on nature of substrate)

Air

sample drawn into a container under vacuum
sample pumped through a solid which traps compounds of interest
sample bubbled into solutions that react with and 'traps' the analyte

Specific sample pre-treatments include:

- filtration
- drying
- grinding
- solvent extraction
- acidic digestion
- pre-concentration

Quality Assurance and Quality Control

Sample Labels – contains all information pertinent to the sample, analyte, handling steps (i.e., filtration, preservatives etc) and personnel involved. May be coded to a master list which contains the above information.

Chain of Custody Forms – includes a list of all personnel involved in handling samples from the field to the lab and within the laboratory as a sample is prepared for analysis. May include ‘sign off’ authority and security information.

QA/QC - quality assurance and quality control

QA - quality assurance is a definite plan for laboratory operations that specifies standard procedures that help to produce data with defensible quality and high level of confidence.

QC - quality control is a set of measures within a sample analysis methodology that assures the analytical precision and accuracy is monitored and controlled.

Quality Assessment is a process to determine the quality of the lab measurements through internal and external evaluations. It includes performance evaluation samples, interlaboratory comparisons and internal performance audits.

Control Charts - results of a large number of replicates from an on-going method of analysis are plotted to monitor changes in the precision and/or accuracy (a wide variety of methods). For instance, one or more control samples (SRM's) are analyzed with every batch of analysis. To monitor method accuracy over time, the measured value of the QC sample (either as an absolute concentration or $x_i - \mu$) is tracked by graphing. Precision control charts will track the std deviation or relative std deviation over time. For either type of control chart, operators will have prescribed ‘control limits’ used to trigger ‘warning’ and ‘action’ alarms.

See further:

Quantitative chemical Analysis, 6th edition, D.C. Harris; chapter 29

Quality Assurance in Water Quality Monitoring, Environment Canada, 1993

Quality Assurance for Environmental Measurements, ASTM, 1985

Range Control Charts - monitors variations in precision

Schewart Control Charts - monitors variation in accuracy

