# ANALYTICAL CHEMISTRY

## Sampling and Sample Preparation

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# Chapter Description

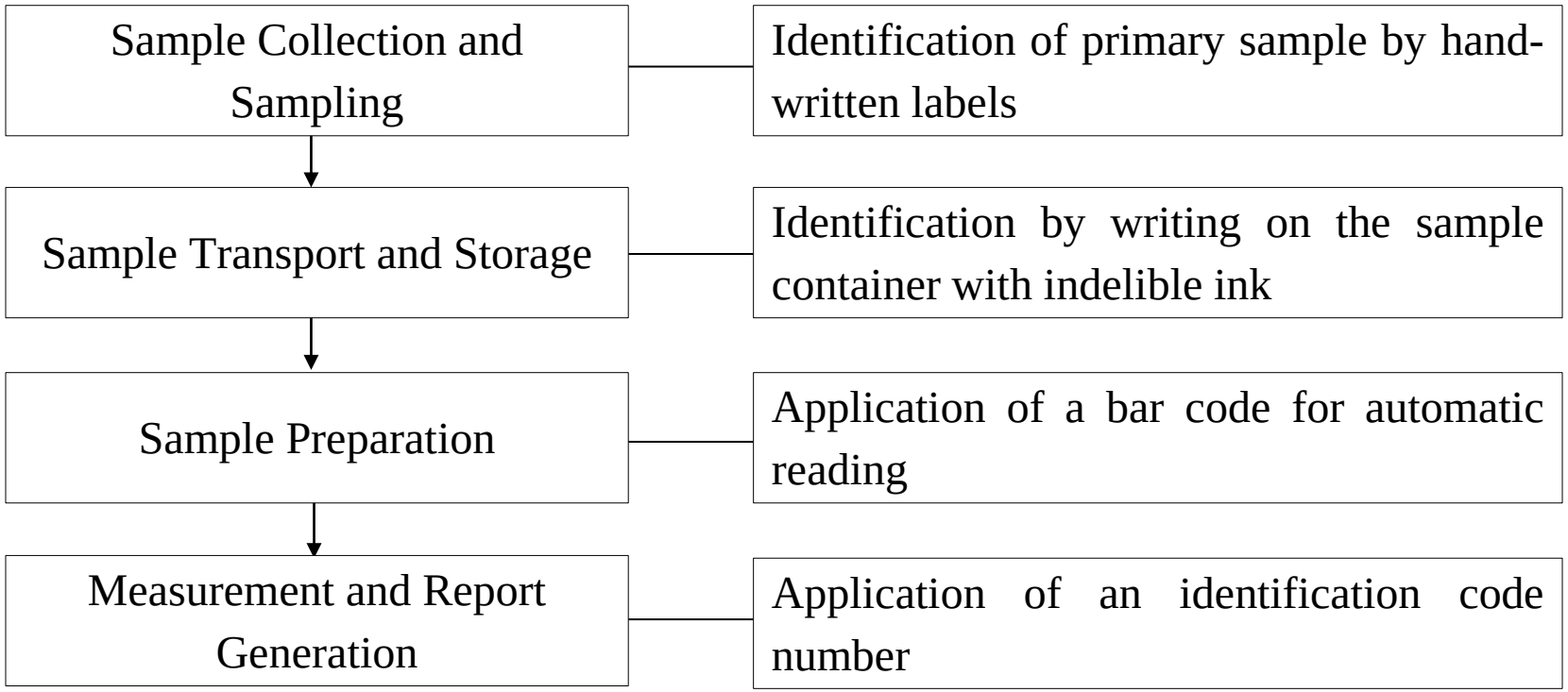
- Expected Outcomes
  - Describe the proper collection of sample during the sampling process.
  - Understand and apply the basic technique of transporting the sample from the point of collection to the analytical laboratory.
  - State the proper selection of the laboratory sample.
  - Describe the sample method used to convert sample into a suitable form for the measurement step.

# Contents

- Sampling
  - Homogenization of Samples
  - Sample Integrity
  - Physical Separation on Sampling
  - Types of Sample
  - Types of Sample Matrices
- Sample Preparation
  - Percentage Recovery
  - Optimization of Chemical Form
  - Separation and Preconcentration Techniques
  - Dissolution

# SAMPLING

**Sampling** is the process of collecting a representative sample for analysis.



# STATISTIC OF SAMPLING

**Choosing a sample size**

If *n* particles are drawn at random from a mixture of particles A and B, the expected number of particles of type A is *Np* and the standard deviation on many drawings is given by: $\sigma_N = \sqrt{Npq}$

| | | |
|---|---|---|
| Where | σN | is the standard deviation in sampling operation |
| | *N* | is the number of particles drawn at random |
| | *p* | is the fraction of particle A |
| | *q* | is the fraction of particle B |

The relative standard deviation is $\sigma_N/N$ given by the equation

$$\frac{\sigma_N}{N} = \frac{\sqrt{Npq}}{N} = \sqrt{\frac{pq}{N}}$$

# STATISTIC OF SAMPLING

Relative variance ≡ $R^2 = \left(\frac{\sigma_N}{N}\right) = \frac{pq}{N}$

$$NR^2 = pq$$

The mass of sample drawn is proportional to the number of particles described by the following expression

$$mR^2 = K_s$$

where $m$ is the mass of sample drawn
$R$ is the relative standard deviation (expressed as a percentage)
$K_s$ is the sampling constant

# STATISTIC OF SAMPLING

**Choosing the number of replicates**

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

We can then estimate the *N* value so that the confidence limit is some fraction of *x.* Let *R* be the maximum allowable relative error (relative standard deviation). Thus,

$$R\bar{x} = t\frac{s}{\sqrt{N}}$$

# SAMPLING TECHNIQUES

The choice of sampling method depends on a number of factors:

- The **chemistry** of the material to be assayed.
- The **size** of the bulk sample
- The **physical state** of the fraction to be analysed (e.g. crystalline solid, glassy solid, liquid, gas, etc.)

# SAMPLING TECHNIQUES

**"Cone and quarter"** method.

Suppose you have a pile of material to analyze. The following are the logical steps in the sampling:

- Divide the pile of material into quarters (it can at least be done through imagination, since it is difficult to divide a few tons sample pile).
- Take samples from each quarter of the pile. Crush these samples and form into a smaller conical pile.
- Flatten the conical pile and cut into equal quarters and the two opposite quarters are chosen at random.
- Crush the quarter further, mix it thoroughly and repile.

# HOMOGENIZATION

One of the treatments for a **solid** sample is homogenization.
This can be carried out by

- Crushing
- Pulverizing
- Grinding
- Rendering it into a thoroughly mixed powder

Samples should contain large number of particles because:

- Variation in content between individual samples in minimized
- Each sample should be more representative of the material

# SAMPLE INTEGRITY

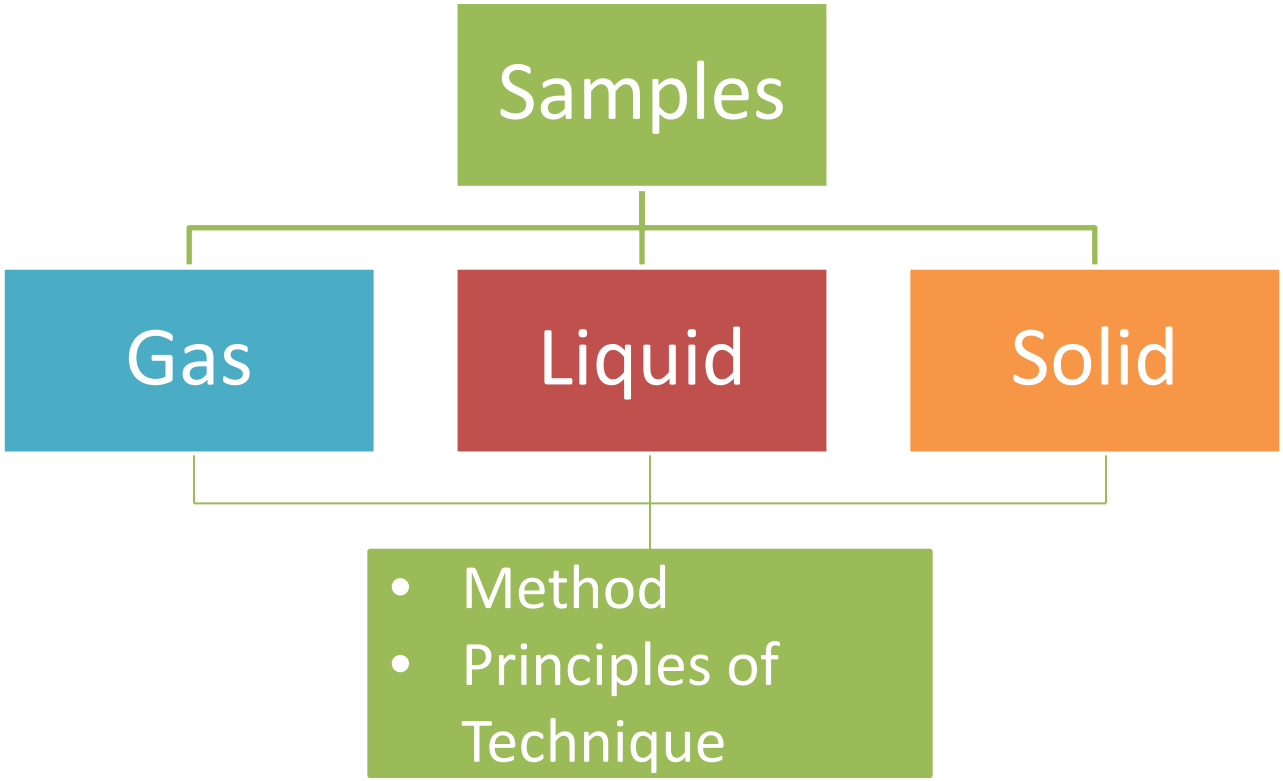
Effect of some important factors such as:

- Time
- Temperature
- Humidity level
- Sample acidity
- Oxygen content
- Exposure to light
- Selection of container (must not contribute interferents and adsorb or absorb analytes significantly

# PHYSICAL SEPARATION ON SAMPLING

| Original matrix | Material separated | | |
|---|---|---|---|
| | **Solid** | **Liquid** | **Gas** |
| **Solid** | By density-flotation<br>By solubility differences | By heat and trap | By melting solid and gas purging gas |
| **Liquid** | By filtration<br>By centrifugation | By distillation<br>By decantation of immiscible liquids | By purge and trap<br>By gas-permeable membranes |
| **Gas** | By filtration (suspended particles removed) | By filtration (liquid aerosols removed) | By differential diffusion<br>By selective freezing |

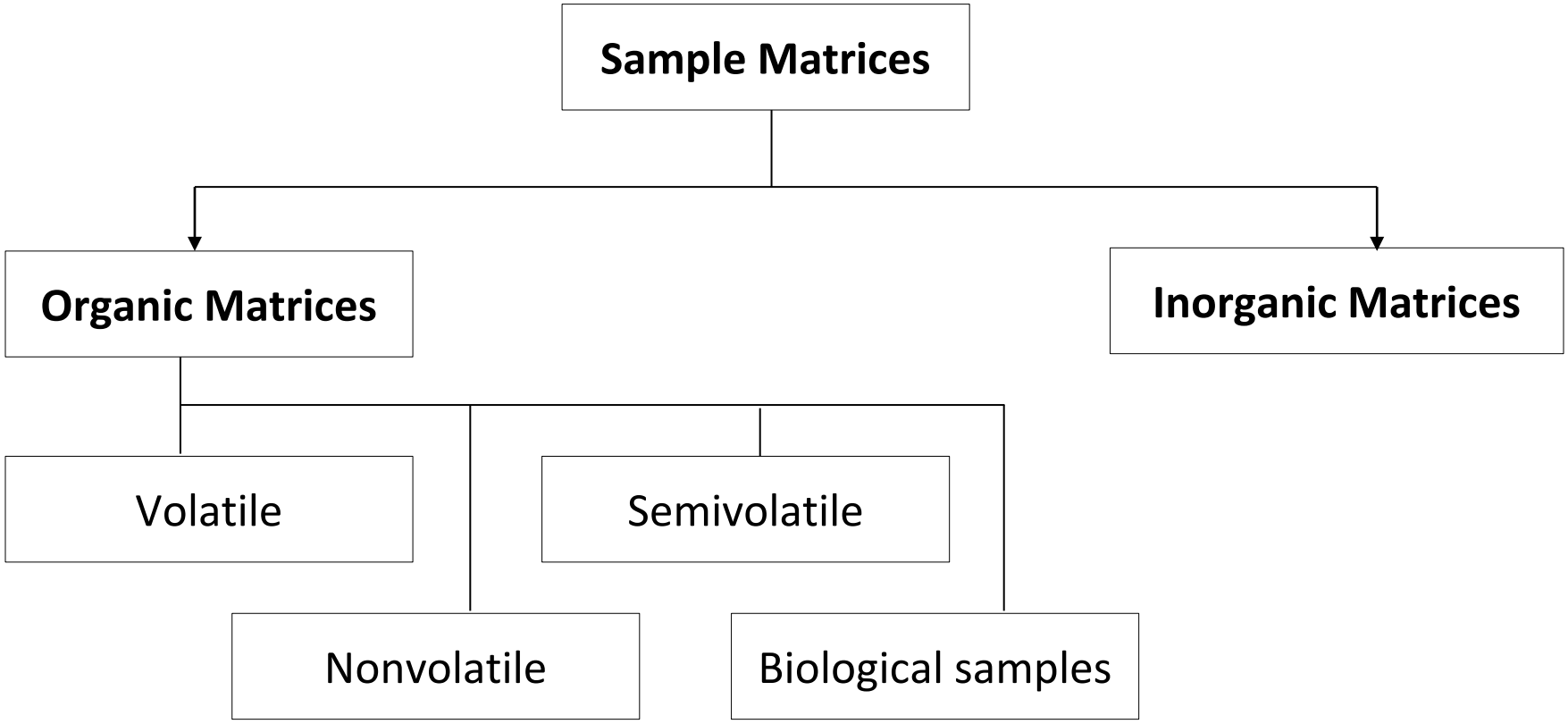
# TYPES OF SAMPLE



# TYPES OF SAMPLES

| Method | Principles of Technique |
|---|---|
| **Sampling bag** | Fill a plastic bag with ambient air, seal the bag, and transport it to the laboratory. Gas can be used directly. |
| **Centrifugation** | **Sample placed in tapered centrifugation tube and spun at high force and forced to the bottom of tube, liquid is decanted. It is slow; depends on settling rate.** |
| **Classical methods** | |
| **Dissolution** | Solid sample is dissolved in solvent without chemical change. Inorganic solids may require acid or base to enhance solvation. Heat may be required for some sample. |
| **Modern methods** | |
| **Accelerated solvent extraction (ASE)** | Pressurized liquid extraction. Solid sample is placed in sealed container and heated to above its boiling point. Extracted analyte is removed and transferred to vial for further treatment. |

# TYPES OF SAMPLE MATRICES



# SAMPLE PREPARATION

The general principles of sample preparations are:

- Sample preparation **should not lose** any analyte
- Bring the analyte into the **best chemical form** for assay method used
- **Remove interferences**
- Should not add the inappropriate sample - **cross contamination**
- If necessary, **dilute** the sample or **concentrate** the sample

# PERCENTAGE RECOVERY

$$\% \text{ recovery} = \frac{Analyte\ concentration\ in\ assay}{Analyte\ concentration\ in\ sample} \times 100$$

or

$$\% \text{ recovery} = \frac{Weight\ of\ analyte\ from\ assay}{AWeight\ of\ analyte\ from\ sample} \times 100$$

# OPTIMIZATION OF CHEMICAL FORM

| Sample | Drying conditions |
|---|---|
| Inorganic sample | Heat at 110°C |
| Common organic samples | Heating depends on nature of sample. Heating can remove organic vapours adsorbed by solid organic samples |
| Biological sample | Heat at <100°C |
| Hygroscopic sample | Drying in a vacuum desiccator |
| Oxidizable sample | Vacuum desiccator or under nitrogen |
| Heat-sensitive sample (eg. Biological sample) | Freeze-drying (sample in frozen, then moisture is removed from the frozen sample by vacuum) |

# SEPARATION & PRECONCENTRATION TECHNIQUES

When the analyte is present in a matrix containing interfering species, there are three different ways to measure the analyte:

- Use a **selective analytical technique**, such as ion-selective electrode
- Perform **selective derivatization** of the analyte that quantitatively convert the analyte into another chemical species that can be measured more easily.
- Remove the analyte from the sample matrix by a **separation or extraction process**.

# DISSOLUTION PROCEDURES

| Category | Description |
|---|---|
| Dry ashing | • Requires high temperature and oxygen to convert the sample into more soluble oxides.<br>• Similar to combustion techniques except that it is usually carried out i n a combustion tube or bomb placed in a furnace, or plasma source. |
| Oxidative fusion | • A powerful technique for dissolving difficult samples such as refractories.<br>• Large quantities of flux material (e.g. salts) must be mixed with the sample before the fusion reaction (10-20 g of flux: 1 g sample) |
| Wet oxidation (sample digestion) | • Requires mineral acids (usually hydrochloric acid , nitric acid, perchloric acid, sulfuric acid and hydrofluoric acid) and heat.<br>• Carried out in open or closed containers with as much heat as can be tolerated by container. |

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