SAMPLING

I. SAMPLING OF SOLIDS, LIQUIDS AND GASES

1. **Sampling*:*** Sample size, sampling unit, gross sample, laboratory sample, homogeneous and heterogeneous samples, statistical standards for good sampling, and sampling basis and purpose are all covered.

2. **Sampling of Solids:** The BCone and quartering method, the long pile and alternate shovel method, the safeguards for maintaining solid samples, and the sampling of metals and other solids—particularly gold, silver, iron, and other metals—as well as rods, wires, sheets, and plates.

3. **Sampling of different types of liquids:** various methods of sampling, industrial effluent and drinking water sampling, sampling safety measures, and preservation of liquid samples gathered.

4. **Sampling of gases:** adsorption or absorption method pre-concentration, sampling and instantaneous monitoring, sampling in samplers and subsequent monitoring, various kinds of gas samplers, sample preservation measures, systematic sampling, and random sampling.

II. BASIS OF SAMPLING

The goal of analysis is to ascertain the composition or quality of a material; therefore, appropriate sampling techniques must be used if the analytical results are to be legitimate or meaningful. The practice of selecting a tiny portion that accurately reflects the makeup of the entire substance from a vast quantity of material is known as sampling.

Sampling methods fall into three main groups:

1. Those in which al1 the material is examined;
2. Casual sampling on an ad hoc basis;
3. Techniques wherein sections of the content are chosen according to statistical possibilities.

Typically, Procedure (1) is not feasible because most of the methods used are destructive, and, moreover, the quantity of material for examination is often excessive. Even with a reasonably sized sample, the analysis would be exceptionally time-consuming, necessitate substantial amounts of reagents, and tie up instruments for extended periods.

Adhering to (2) for sampling lacks scientific rigor and may result in decisions being made with insufficient data. When sampling is entirely haphazard, it becomes impossible to implement any genuine form of analytical control or oversight.

Therefore, the sole dependable foundation for sampling must be statistical in nature, guided by mathematical principles and probabilities. In this approach, not every item or part of the sample is subjected to analysis; instead, the limitations of the selection are meticulously computed and predetermined. By calculating the acceptable level of risk or margin of variation, a sampling plan is chosen to maximize the collection of information and control while maintaining swift turnover of samples. Consequently, when sampling from batches, individual samples are selected following specific random tables, ensuring that personal biases do not impact the selection process.

Since chemical analyses utilize only a small portion of the total sample, the sampling procedure plays a crucial role. It's imperative that the fractions of the sandy and loam soil samples depicted in the photo, which are collected for analysis, accurately represent the larger bulk materials. Understanding the appropriate quantity to collect and how to subdivide the sample for laboratory analysis is a vital aspect of the analytical process. This chapter focuses on sampling, standardization, and calibration, with statistical methods being an essential component in all three of these processes.

In the majority of cases, a chemical analysis is conducted on only a small portion of the material of interest. For instance, this could involve examining a few milliliters of water from a polluted lake. To yield meaningful results, it is imperative that the composition of this selected fraction closely mirrors the average composition of the bulk material. The process of obtaining such a representative fraction is known as sampling. Sampling is often the most challenging step in the entire analytical process and can significantly affect the accuracy of the procedure. This challenge is particularly pronounced when the material to be analyzed is a large and non-uniform liquid, like a lake, or a non-uniform solid, such as an ore, soil, or a piece of animal tissue.

The study of a small laboratory sample will lead to conclusions about a much greater amount of material, hence statistics are a necessary tool when sampling for a chemical analysis.

III. DESIGNING A SAMPLING PLAN

A sampling plan should align with the objectives of an analysis. In characterization studies, the purity of a sample often stands as the paramount parameter. For instance, a materials scientist investigating the surface chemistry of a metal is more inclined to opt for a freshly exposed surface, which can be achieved by fracturing the sample under vacuum, rather than a surface that has been exposed to the atmosphere for an extended period. In qualitative analysis, the sample's composition need not be an exact match to that of the substance under examination, provided that a sufficient quantity of the sample is taken to ensure the detection of all components. In fact, when the aim of an analysis is to identify trace-level components, it may be advantageous to selectively exclude major components during the sampling process.

Nevertheless, in a quantitative analysis, the composition of the sample must faithfully mirror that of the target population. Therefore, the primary emphasis in this section is placed on crafting a sampling plan for quantitative analyses.

Five questions should be considered when designing a sampling plan:

1. From where within the target population should sample be collected?
2. What type of samples should be collected?

3. What is the minimum amount of sample needed for each analysis?
4. How many samples should be analysed?
5. How can the overall variance be minimized?
6. Each of these questions is considered below in more detail.

IV. PURPOSE OF SAMPLING

The Importance of Accurate Sampling: In chemical analysis, only a small portion of a material is selected, weighed, dissolved, and subjected to analysis to determine its composition. However, for this analysis to be meaningful, the small portion examined must be drawn from a larger, uniformly distributed quantity. In such cases, the analyzed portion represents a true sample, and the analysis reflects the composition of the entire material. Therefore, in metallurgy, every meaningful determination necessitates two equally crucial and separate operations: sampling and chemical analysis.

The purpose of sampling is to extract a small quantity from the entire material whose composition is of interest, ensuring that this sample accurately reflects the overall composition. It is evident that without a representative sample, even the most precise chemical analysis cannot provide the desired information, which is the true composition of the material in question. While ore or in situ mineral sampling is typically not the chemist's responsibility, for all other objectives necessitating metallurgical analyses, the chemist either personally conducts or supervises the sampling process, requiring meticulous attention.

1. **Classification of Materials:** The type of material to be sampled will determine the sampling technique. To facilitate the analysis of sample, metallurgical materials can be categorized into the subsequent classes:

   - Fluids (a) Liquids water, oil, molten metals, slags, etc.
     (b) Gases flue gas, producer gas, etc.
   - Tough or sectile materials metals, alloys, etc.
   - Brittle or frangible materials ores, fluxes, coal, brittle metals, alloys, etc.

2. **Homogenous and Heterogeneous Solutions:** Solutions that have the same content and characteristics throughout are called homogeneous solutions. A cup of coffee, perfume, cough medicine, a sugar or salt solution in water, etc. are a few examples.

   Heterogeneous solutions are solutions with non-uniform composition and properties throughout the solution.

3. **Statistical criteria for good sampling:** Solution of oil and water, water and chalk powder and solution of water and sand, etc.

V. STATISTICAL CRITERIA OF VALID SAMPLING

A sampling scheme is set up with several objectives, which can be stated in statistical terms as follows:

- An impartial approximation of the population mean (Section 26-5) should be provided by the sample mean. Only when every member of the population has an equal probability of being selected for the sample will this goal be accomplished.

- The primary aim is to ensure that the sample offers an unbiased estimation of the population variance, enabling the application of significance tests. This is achieved when each potential unit of a preselected size has an equal probability of being selected. For example, consider a population comprising chemical packages moving on a conveyor belt. If packages are randomly chosen, such as with the aid of a table of random numbers, each package has an equal chance of being included in the sample. Even if samples are drawn at regular intervals, selecting the first unit randomly satisfies the requirement for equal chances. For instance, if every 10th package is systematically taken, and the initial choice is determined by the first appearance of a specific digit in a column of random numbers, each package has a 0.1 probability of being in the sample. However, this method produces only 10 distinct samples of a specific size out of numerous possible samples, which fails to fulfill the second objective. Conversely, if the entire sample is chosen based on the column of random numbers, every feasible 1-in-10 sample has an equal probability of being selected.

- A third objective can be defined in terms of efficiency. Within a given budget or time frame, the sampling process should yield estimates of central value and dispersion with the highest possible accuracy. Conversely, it should aim to minimize the cost or effort for a given level of accuracy. To achieve this objective, there are instances where it becomes necessary to employ a non-random sampling procedure, at least partially. If the population can be divided into subdivisions or sections through a random process, and if the variation among these sections significantly exceeds the variation within each section, it is more likely that a more accurate result can be obtained by accurately sampling each section instead of employing a completely random process to select the same number of units. This type of stratified approach carries a potential bias risk that cannot be assessed using conventional significance tests. These tests rely on probability theory, which is based on the assumption of random selection. An orderly procedure disrupts this randomness to some extent. However, the risk can be mitigated by striving to make the procedure as genuinely representative as possible.

The errors arising in sampling, particularly in the case of heterogeneous solids, may be the most important source of uncertainty in the subsequent analysis of the material. If we represent the standard deviation of the sampling operation (the sampling error) by $\mathbf{S_S}$and the standard deviation of the analytical procedures (the analytical error) by $\mathbf{S_A}$then the overall standard deviation $\mathbf{S_T}$(the total error) is given by

$$s_T = \sqrt{s_S^2 + s_A^2}$$

or

$$s_T = \sqrt{V_S + V_A}$$

Where V stands for the proper variance. The analysis of variance approach can be used to evaluate the sampling variance (Vs) and the analytical variance (VA) separately. The within-sample variance, which represents the analytical error, and the between-sample variance, which represents the sampling error, can be compared.

1. Sample Size

- **On the basis of sample size, the analytical methods are again classified in to following**

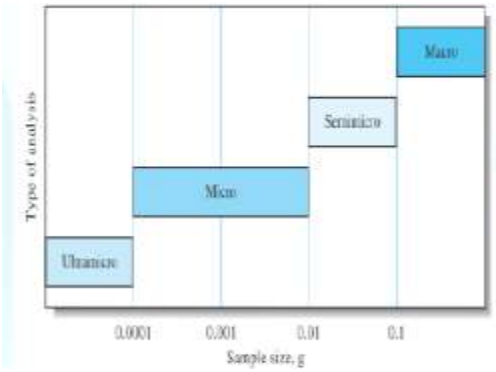
    - **Macro Analysis-** Macro analysis is concerned with the quantities of 0.1 g or more.
    - **Meso Analysis or semimicro-** This analysis measures quantities ranging from 10^{-2} g to 10^{-1} g.
    - **Micro Analysis-** This type of analysis deals with the quantities ranging from 10^{-3} g to 10^{-2} g.
    - **Sub micro Analysis-** In sub micro analysis the sample quantities ranging from 10^{-4} g to 10^{-3} g.
    - **Ultra micro Analysis-** It deals with quantities below 10^{-4} g.

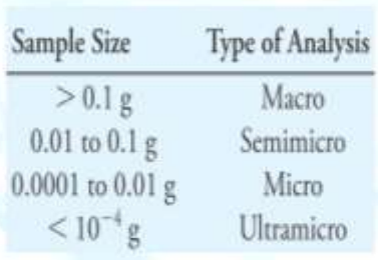
- **On the basis of concentration of constituents in the sample, analysis is again classified in to following**

    - **Major Constituent Analysis-** It is one, which accounts for 1-100 percent of sample under investigations.
    - **Minor Constituent Analysis-** In this type of analysis, the minor constituent is present in the range of 0.01-1 percent.
    - **Trace Constituent Analysis-** Here trace constituent is analysed which is present at a concentration of less than 0.01 percent.

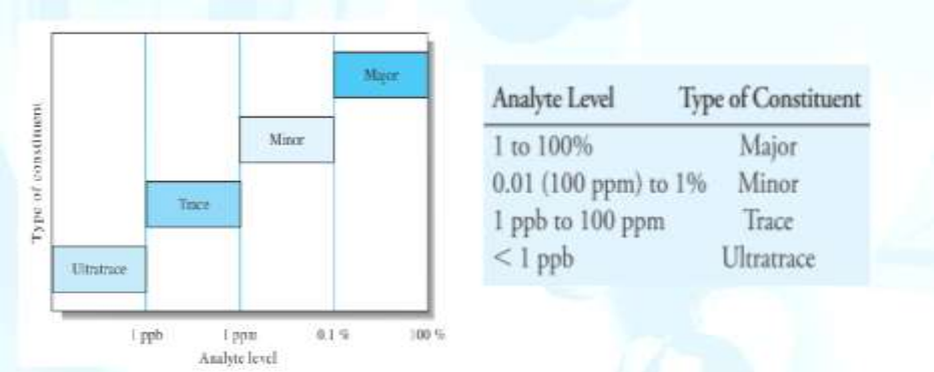
2. Further Division

- **Trace Analysis-** Corresponds to 10^{2}-10^{4} µg per gram, or 10^{2}-10^{4}ppm.
- **Micro traces Analysis-** Corresponds to 10^{2}-10^{-1}pgper gram, or 10^{-4}-10^{-7}ppm.
- **Nano trace Analysis-** Corresponds to 10^{2}-10^{-1}fmper gram, or 10^{-7}-10^{-10}ppm.
- **Sub traces Analysis-** when the sample weight is less than 0.01percent.
- **Ultra trace Analysis-** when the sample is less than 0.001 percent.





Sample Size	Type of Analysis
> 0.1 g	Macro
0.01 to 0.1 g	Semimicro
0.0001 to 0.01 g	Micro
< 10^{-4} g	Ultramicro

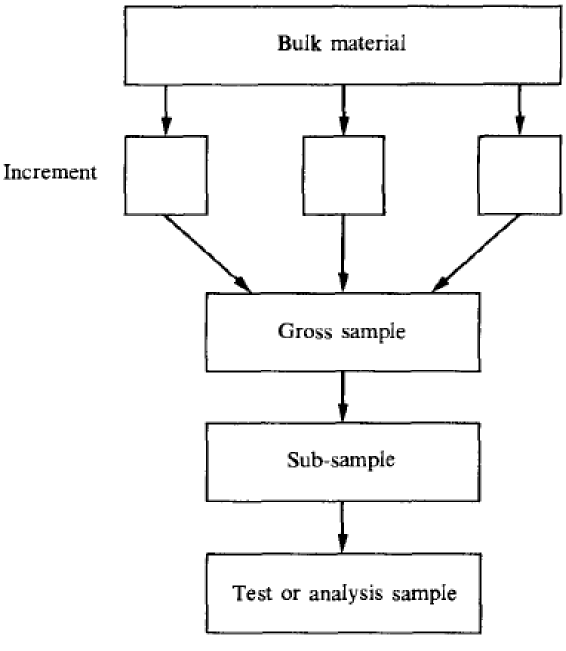


Analyte Level	Type of Constituent
1 to 100%	Major
0.01 (100 ppm) to 1%	Minor
1 ppb to 100 ppm	Trace
< 1 ppb	Ultratrace

VI. SAMPLING PROCEDURE

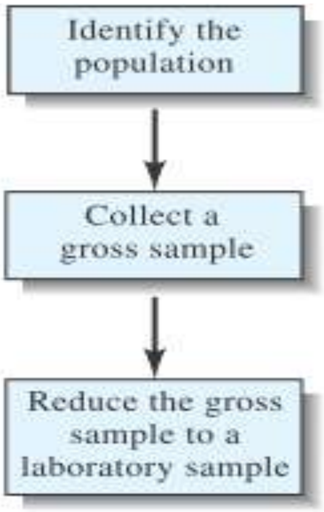
The sampling process typically comprises multiple stages before the material is analyzed, as illustrated in Figure 1. Most bulk materials, such as minerals, sediments, and foodstuffs, are inherently non-homogeneous. They may contain particles with varying compositions that are not uniformly distributed throughout the material. In such instances, several increments are randomly collected from different locations within the bulk material, ensuring that each part has an equal opportunity of being chosen. These increments are then combined to create the gross sample. Often, the gross sample is too extensive for immediate analysis and necessitates further division to generate a sub-sample.

Before obtaining the analytical sample, the sub-sample may need specific treatment, such as particle size reduction or thorough mixing. It's crucial that the analytical sample maintains the same composition as the gross sample. However, it's worth emphasizing that in some cases, the entire object may serve as the analytical sample, as is the case with a moon-rock specimen. In such instances, non-destructive analysis methods are preferred. Occasionally, the bulk material may exhibit homogeneity, as seen in certain water samples, where only one increment is necessary to determine the bulk properties. This increment should be of an appropriate size to facilitate replicate analyses.



1. Obtaining a Representative Sample

- Those selected for analysis are frequently referred to as sampling units or sampling increments.
- The accumulation of these sampling units or increments is referred to as the gross sample.
- In preparation for laboratory analysis, the gross sample is typically resized and blended to form the laboratory sample.
- It is imperative that both the gross sample and the laboratory sample closely mirror the average composition of the overall material mass slated for analysis.



2. **The Gross Sample:** A small-scale copy of the total quantity of material to be examined is what the gross sample should ideally look like. It is the assemblage of distinct sampling units. It ought to be reflective of the entire in terms of particle size distribution and composition.

   Size of the Gross Sample is determined by

- The uncertainty that can be tolerated between the composition of the gross sample and that of the whole,
- The degree of heterogeneity of the whole, and
- The level of particle size at which heterogeneity begins.
  - ➢ The quantity of particles, denoted as N, necessary in a gross sample can vary from a few particles to as many as 10^12 particles.
  - ➢ This numerical value is contingent upon the level of acceptable uncertainty and the degree of heterogeneity present in the material.
  - ➢ Homogeneous gases and liquids do not require a substantial number of particles.
  - ➢ The composition of a gross sample randomly extracted from a bulk of material adheres to the principles of probability.

3. **Preparing a Laboratory Sample**

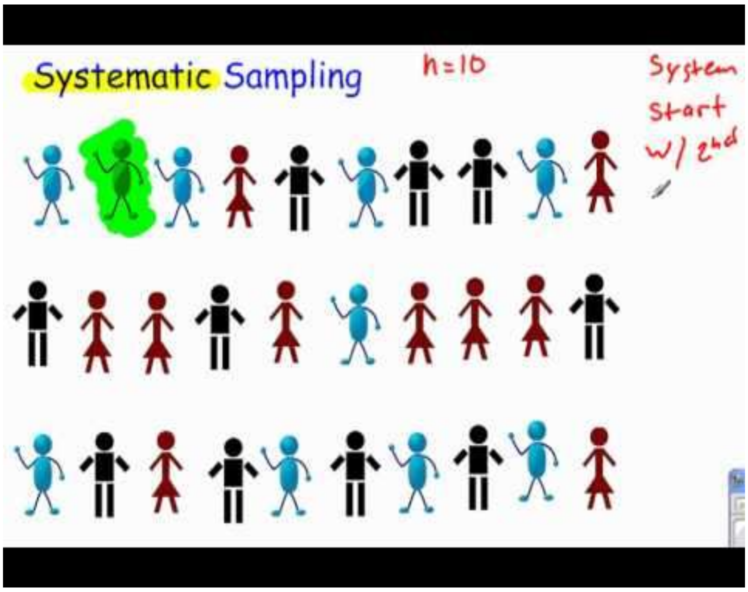
   - When dealing with heterogeneous solids, the mass of the gross sample can span from several hundred grams to kilos or more.
   - It is imperative to convert the gross sample into a finely ground and uniform laboratory sample, typically no more than a few hundred grams.
   - This procedure entails a sequence of operations, including crushing, grinding, sieving, mixing, and subdividing the sample, often dividing it into two portions, to diminish its mass.

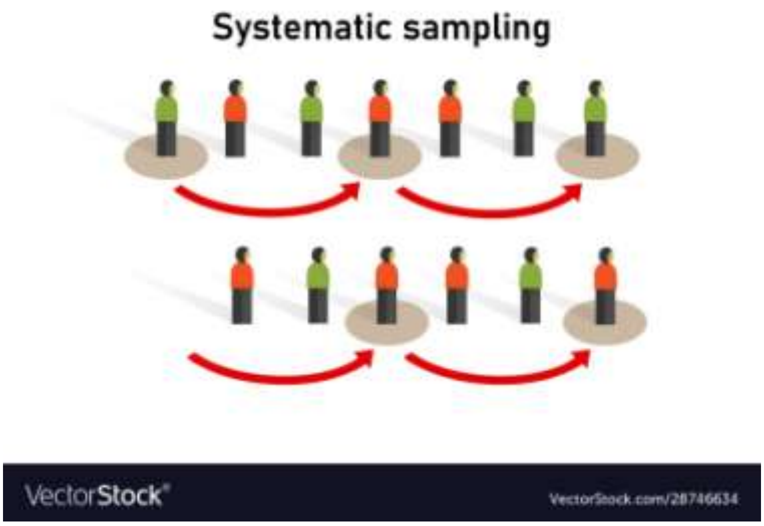
4. **Grab:** Any single sample that is taken without being composited or combined with additional samples is called a grab sample. A grab sample, which is comparable to a snap photo, is typically suitable for sampling from smaller facilities. Furthermore, it is a suitable technique for gathering data on non-conservative parameters like temperature, dissolved oxygen, and ammonia nitrogen. Throughout storage, these sample attributes could change. Grab samples obtained at different times of the day are the most effective way to assess parameters that are known to fluctuate during the day, like dissolved oxygen.

5. **Composite:** A composite sample is made up of several distinct samples that were gathered over a predetermined amount of time. A composite sample can be thought of as a continuous film and is statistically more dependable than a grab sample. Concentrations of water pollutants frequently change over time, especially during the day. As a result, a composite sample shows the substance's average concentration. A automated sampler placed at the outfall or an in-stream sampling point, with the sample taken at the conclusion of the sampling period, is frequently used for composite sampling. Composite sampling is utilized for BOD and total suspended solids, and is suitable for conservative metrics like metals.

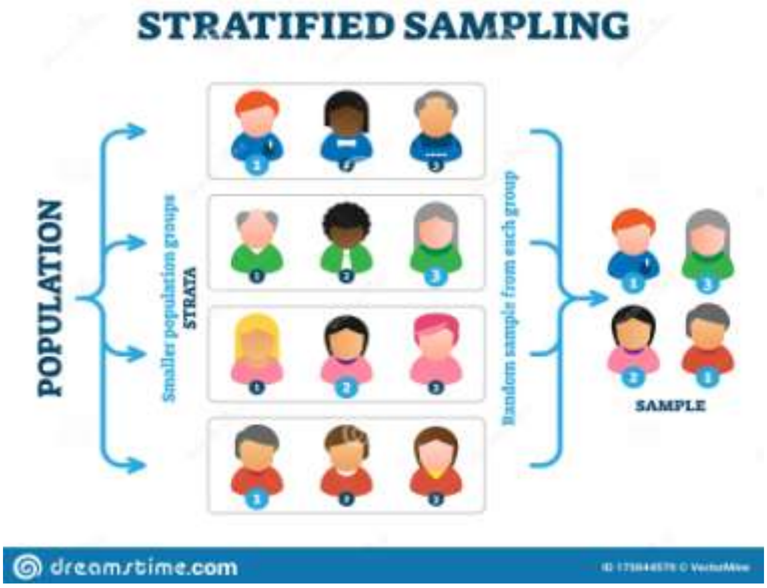
6. **Random Sampling:** Every sample has an equal chance of being selected when using random sampling as a sampling technique. The purpose of a randomly selected sample is to provide an objective depiction of the entire population. A sampling error occurs when a sample fails to accurately reflect the population for any reason.

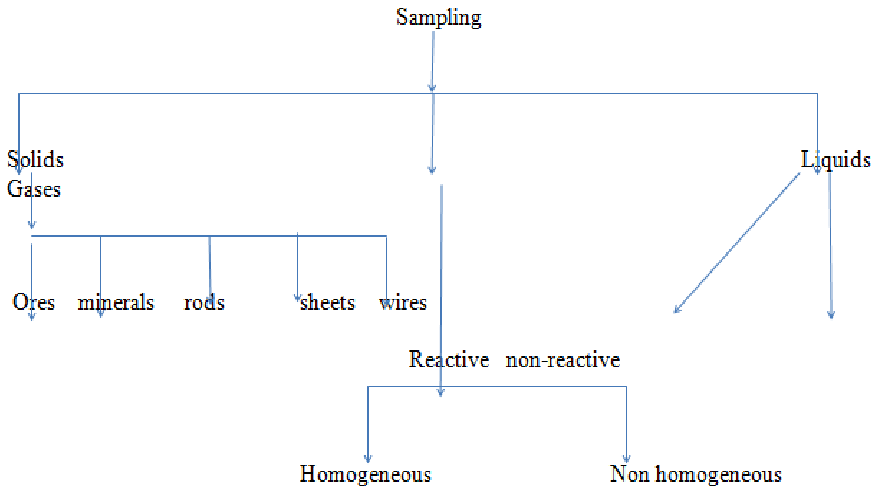
7. **Systematic Sampling:** Systematic sampling is a form of probability sampling in which individuals from a larger population are chosen based on a random initial point and a consistent, regular interval. This interval, known as the sampling interval, is computed by dividing the population size by the intended sample size. Even though the sample population is predetermined, systematic sampling is considered a random method as long as the periodic interval is established in advance and the initial point is chosen randomly.





8. **Stratified Sampling:** Stratified sampling is a type of sampling method in which the total population is divided into smaller groups or strata to complete the sampling process. The strata are formed based on some common characteristics in the population data. After dividing the population into strata, the researcher randomly selects the sample proportionally.





VII. SAMPLING OF SOLIDS

The process of preparing solid samples for analysis is often more intricate compared to gases or liquids. This is primarily due to the initial step of solubilizing the sample. Occasionally, the sample dissolves easily, making it ready for injection or additional pre-treatment. However, in other instances, the sample matrix remains insoluble in typical solvents, necessitating the extraction of the analytes.

When it comes to sampling solids, challenges arise from the material's lack of homogeneity, disparities in particle size, and variations within individual particles, making it a more complex process than with other substances. The simplest yet typically less dependable approach to sampling a material is the grab sample, which involves taking a single sample at random and assuming it represents the entire material. A grab sample proves adequate only when the source material is homogeneous.

Unless the sample is reasonably uniform, it is advisable to take 1/50 to 1/100 of the total bulk for the gross sample in order to get the most trustworthy findings. The gross sample size increases with particle size.

Solids typically vary in composition and have localized concentrations of contaminants. The kind of solid will determine the process used to get a representative sample.

In order to convert the gross sample to representative sample we can use two methods

Gross sample Reduction of sample → representative sample

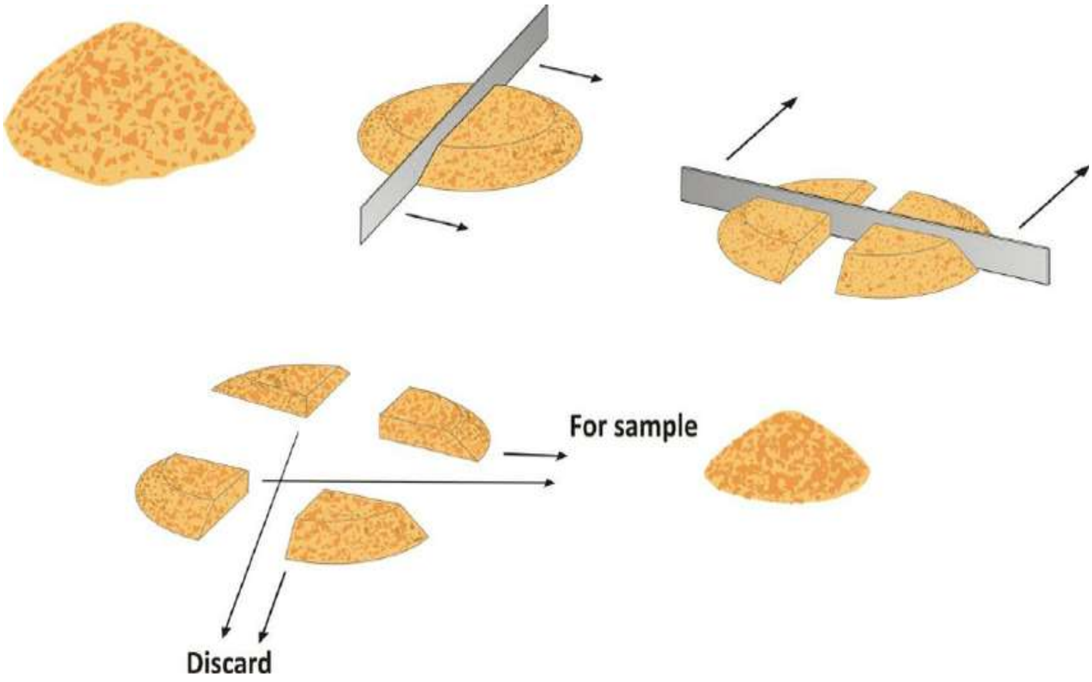
1. Cone and Quartering method

For homogenization Reduction of sample

2. Long pile and alternative shovel method

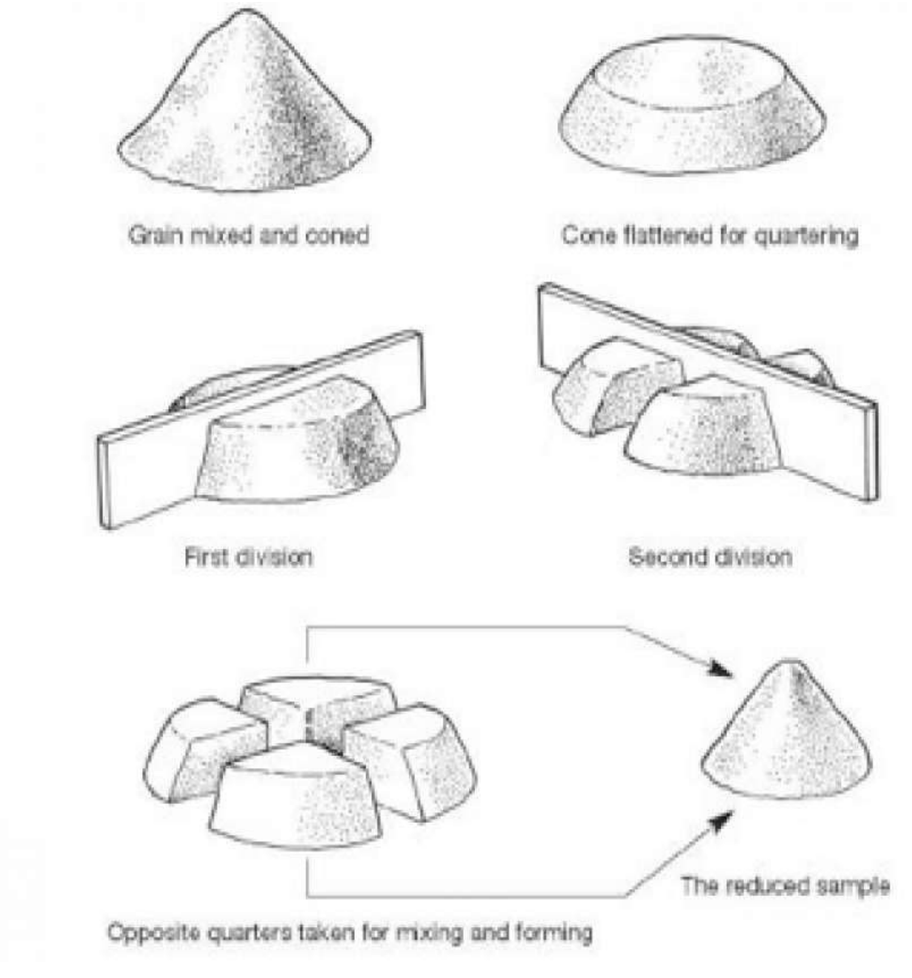
For homogenization Reduction of sample size

VIII. CONE AND QUARTERING METHOD



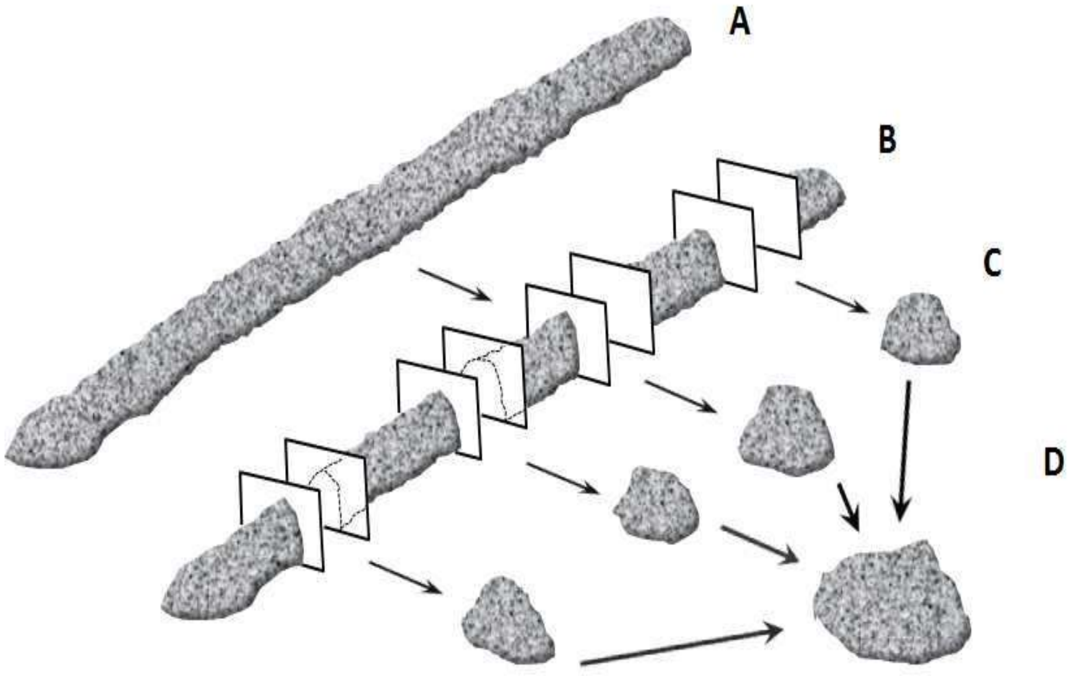
Coning and quartering is a technique employed by analytical chemists to diminish the size of a powder sample while avoiding the introduction of systematic bias. This method entails pouring the sample in a manner that results in a conical shape, followed by flattening it into a cake. The cake is subsequently divided into quarters, with two opposing quarters being discarded, while the remaining two are merged to form the reduced sample. This process is repeated until the desired sample size is achieved, and analyses are conducted using the retained sample.

This method is particularly suitable for handling large quantities of material and can be conveniently executed using shovels or even front-end loaders for exceptionally large samples. Initially, the material is mixed and shoveled to create a uniformly conical pile. It's essential to construct the pile in a manner that ensures the natural segregation within the cone is radially symmetrical. The cone is then expanded from the center to produce a flattened disc of material. This disc is subsequently sectioned into quarters using perpendicular boards. One set of opposing quarters is eliminated, while the other set serves as the sample. If the sample is still too extensive, it can be subjected to the coning and the desired sample size is achieved. However, it's important to note that this procedure is susceptible to human error.



IX. LONG PILE AND ALTERNATIVE SHOVEL METHOD

Using this technique, the sample is poured out of the bag and laid out in a long pile on a level surface (Figure 8A). The pile's height should not be greater than its width, and its length should be at least 20 times that of its width. After a few cross sections are removed from the pile, the original sample is mass reduced when all the cross sections are added together. The ideal approach is to take a enough number of somewhat sized parts. The distance between each of the several cross sections is not uniform, despite the fact that this should ideally be random. It is advisable to take at least ten cross sections if heterogeneity is unknown. This method is recommended when a low sampling ratio (less than a factor 10) is required, similar to the spoon method. In essence, the method attempts to replicate, on a static sample, what occurs when a sample is in motion and cross sections are obtained at a certain location. In this case, the cross sections are scattered across the pile and the sample is stationary.



1. **Sampling of Ores**

   - A chemical analysis is most often performed on only a small fraction of the sample.
   - The composition of this fraction must reflect as closely as possible the average composition of the bulk of the material if the results are to be meaningful.
   - The process by which a representative fraction is acquired from bulk of the material is called **sampling.**
   - Only 0.5 – 1 gm sample required for analysis and has to be taken from 50 – 250 tons of material.

2. **Sampling of Metals and Alloys:** Metal and alloy samples can be obtained through drilling, milling, or sawing. By sawing the piece at random intervals and gathering the "sawdust" as the sample, one can create a representative sample.

   Large particles, like those found in ores, smaller particles, like those found in soils and sediments, tablets, pellets, and capsules used in the dispensing of pharmaceuticals and animal feeds, sheet materials, like polymers and rolled metals, and tissue samples from biological specimens are typical examples of solid samples.

3. **Sample Collection:** Solid materials are typically non-uniform, necessitating careful collection of samples. Sediments located at the bottom of bodies of water, such as

streams, rivers, lakes, estuaries, and oceans, are typically gathered using either a bottom grab sampler or a corer. Grab samplers are designed with a pair of "jaws" that close upon contacting the sediment, effectively scooping it up. These samplers offer advantages in terms of ease of use and the capacity to collect substantial samples. However, they have certain drawbacks, including the tendency to lose finer sediment particles as water drains from the sampler, as well as the compromise of spatial information, both horizontally and in terms of depth, due to the blending of the sample.

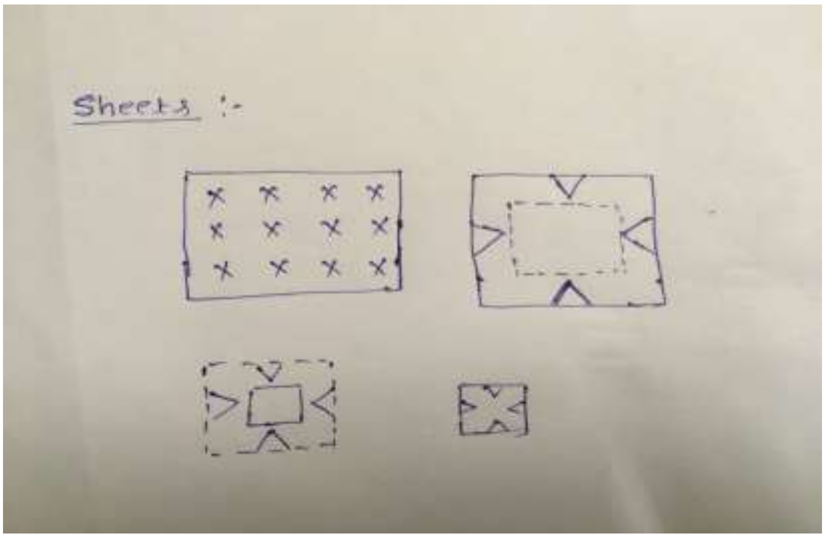
Soil samples gathered from depths of up to 30 cm are readily collected using scoops or shovels, although this method tends to exhibit higher sampling variance. A more effective approach for acquiring near-surface soil samples is to employ a soil punch. This thin-walled steel tube retains a core sample when inserted into the soil and withdrawn. Soil samples from depths exceeding 30 cm are procured by digging a trench and collecting lateral samples with a soil punch. Alternatively, an auger can be employed to drill to the desired depth, and the sample can then be collected using a soil punch. Sampling particulate materials is often contingent upon particle size. Larger particulate solids, such as coal and ores, can be sampled by either randomly collecting samples with a shovel or using a riffle. A riffle is a trough divided into compartments, with adjacent compartments emptying on opposite sides. When particulate material is introduced into a riffle, it is separated into two portions. By repetitively passing half of the separated material back through the riffle, a sample of the desired size can be obtained. Smaller particulate materials, like powders, are best collected using a sample thief, which enables simultaneous collection from multiple locations.

When sampling a metal, it is typically essential to acquire material from both its surface and interior. In the case of a metal sheet, random samples can be procured using a metal punch. For metal wires, samples can be obtained by randomly cutting pieces of suitable length. Larger metal items, like bars or bricks, are most effectively sampled by sawing the metal at randomly chosen locations and collecting the resulting "sawdust." Alternatively, drilling through the metal and gathering the shavings is another viable method. Surface coatings can be sampled directly in their place or by dissolving the coating using an appropriate solvent.

To sample biological tissue, the organ is removed and homogenized before smaller sections are extracted for analysis. As an alternative, a composite sample can be created by combining multiple tiny pieces of tissue. After homogenizing, the composite sample is examined.

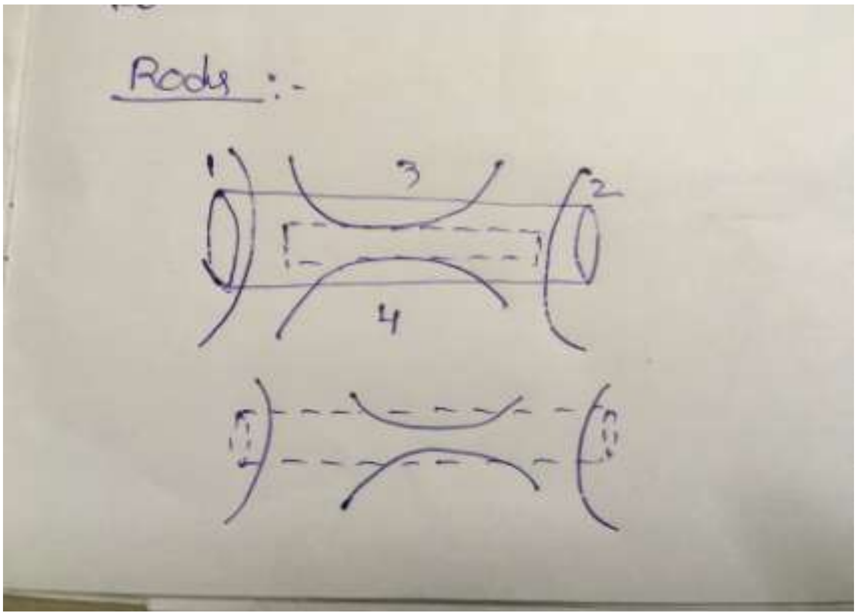
4. **Sample Preservation:** In the absence of preservation, the chemical composition of numerous solid samples might alter as a result of biodegradation, volatile material loss, and chemical reactivity, especially redox processes. While there is less chance of biodegradation and volatile material loss in samples kept at lower temperatures, phase separations and fracture could still cause issues. To reduce the amount of volatile material lost, make sure the sample fills the container all the way to the top without creating a headspace where gases can gather. Samples taken from materials that have not come into contact with oxygen are more prone to oxidation processes. For instance, it's important to keep anaerobic sediments and air apart.

5. **Sheets:** In case of sheets the sampling is difficult, the sampling doing as follows



In sheets we select the some species as random manner and cut it and all these are added and converted to homogeneously and again form as sheet and again some species are taken from different position here the different positions are different from the before positions and all species are added and make sheet doing this process for some times here systematic sampling also doing.

6. **Rods**



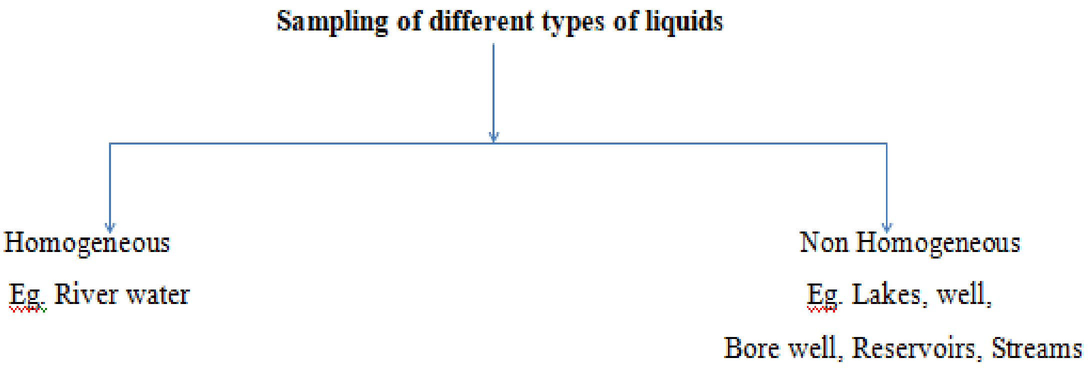
In case of rods we take the rods and cut these at two ends or sometimes at different points and all these species are again make it as a rod and continue this process for some times then small rod piece is for quality.

If Rods, sheets and wires are more we selected randomly and doing the above process.

Gold is present in minor amounts within clays, pyrite, and nearly all ores containing silver, copper, bismuth, lead, zinc, tellurium, and antimony. Given the highly diverse composition of geological samples and the low levels of gold and silver they contain, regardless of the analytical technique employed, the process of determining their concentrations involves two distinct stages. The initial stage involves isolating gold and silver from the non-precious components of the ore, while the subsequent stage involves quantifying the concentrations of the separated silver and gold.

Ore refers to naturally occurring rock or sediment harboring one or more valuable minerals, often containing extractable metals that can be economically mined, processed, and marketed. Ore is sourced from the Earth through mining and undergoes treatment or refining, frequently involving smelting, to isolate the valuable metals or minerals. The ore's grade denotes the concentration of the sought-after substance it contains. Evaluating whether a rock is considered ore hinges on weighing the worth of the metals or minerals it contains against the extraction costs to ascertain if its grade is high enough to warrant mining, thereby granting it the classification of ore.

Only gold, silver, copper and the platinum group occur native in large amounts. Over geological time scales, very few metals can resist natural weathering processes like oxidation, so mainly the less reactive metals such as gold and platinum are found as native metals.



7. **Solutions:** Liquid samples typically come from commercial solvent containers; drinks (like milk or fruit juice); natural waters (like lakes, streams, seawater, and rain); body fluids (like blood and urine); and suspensions (like those in many oral medications).

X. SAMPLE COLLECTION

It is simple to sample homogeneous liquids using a pipet, syringe, decanter, or siphoning. Sadly, there aren't many completely uniform options. In cases when the material to be sampled is small enough, homogeneity can frequently be achieved with manual shaking. After that, samples can be gathered using a vial, syringe, or pipet. That being said, most solutions cannot be sampled in this way. The technique used to gather the gross sample needs to be modified to fit the type of material being sampled in order to reduce the impact of heterogeneity. Numerous techniques for sampling solutions are aptly demonstrated by environmental sampling of fluids and wastewaters. Both flow rate and depth have an impact on the chemical makeup of surface waters, which include lakes, rivers, streams, estuaries, and oceans. Shallow lakes that are less than five meters deep and swiftly flowing are often well-mixed and exhibit minimal stratification as they get deeper. It is convenient to get grab samples by dipping a capped container below the surface and unscrewing the cap. When gathering the sample, one avoids the air–water contact because it could be contaminated with oil or enriched with heavy metals.

The sample bottle is filled, then the cap is put back on and the bottle is taken out. Significant stratification may be seen in lakes larger than five meters, estuaries, oceans, and slowly flowing streams and rivers. While samples at deeper depths are obtained using a weighted sample bottle that is dropped to the required depth, grab samples from close to the surface can be obtained as previously mentioned. The sample vial is opened, allowed to fill, and then closed before being retrieved once it has reached the correct depth.

Grab samples can be examined separately to learn more about how the analyte's concentration varies with depth. As an alternative, the grab samples might be combined. Groundwater sample collection wells need to be purged prior to sample collection since the water's chemical makeup in the well-casing and surrounding matrix might differ greatly from the groundwater's composition. These variations could be the consequence of impurities injected during the well-drilling process or variations in the redox potential of the groundwater upon exposure to ambient oxygen. Wells are often purged by pumping out enough water to fill multiple well casing volumes, or until the water's specific conductance, pH, and temperature remain constant. Since the chemical makeup of water left lying in pipes might differ greatly from the treated water supply, samples taken from municipal water supplies also need to be purged. At faucets, samples are taken after two to three minutes of pipe flushing. Samples of industrial discharges and municipal wastewater treatment facility samples are frequently collected as 24-hour composites. An automatic sampler that regularly eliminates individual grab samples is used to acquire samples. In response to variations in flow rate, the volume of each sample increment and the sampling frequency may either remain constant or fluctuate.

Glass or plastic are common materials for sample containers used to gather solutions. One benefit of using borosilicate glass containers from Pyrex or Kimax brands is that they are easy to clean, sterilisable, and inert to all solutions other than very alkaline ones. Glass containers have three drawbacks: price, weight, and breakage risk. Numerous polymers, such as Teflon (polytetrafluoroethylene), polyethylene, polypropylene, polycarbonate, and polyvinyl chloride, are used to make plastic containers. Plastic containers are affordable, strong, and lightweight—that is, unless they are made of Teflon. Glass or plastic bottles can be used in most situations, though polyethylene bottles are usually used due to their lower cost.

Since these species frequently come into contact with plastic surfaces, glass containers are always utilized when gathering samples for the examination of pesticides, oil and grease, and organics. Plastic bottles are ideal when gathering samples for trace metal analysis because glass surfaces readily absorb metal ions. The sample vial often has a large aperture that makes it simple to fill and withdraw the sample. When it is not desirable to expose the sample to the outside environment or the container cap, a narrow-mouth sample vial is employed. Polyethylene is used to make sample bottle caps, unless there is a concern about plastic exposure. The container cap has an inert Teflon or neoprene interior lining when polyethylene must be avoided.

1. **Sample Preservation:** Chemical, biological, or physical processes might alter a liquid sample's chemical composition after it is extracted from its target population. Samples are kept after collection by regulating the pH and temperature of the solution, preventing light or air exposure, or adding a chemical preservative. Samples can be securely preserved for further examination after preservation. The stability of the analyte and the efficiency of sample preservation determine the maximum amount of time that can pass between preservation and analysis.

Parameter	Preservation	Maximum Holding Time
Ammonia	cool to 4 °C; H_2SO_4 to pH <2	28 days
Chloride	None required	28 days
metals—Cr(VI)	cool to 4 °C	24 h
metals—Hg	HNO_3 to pH < 2	28 days
metals—all others	HNO_3 to pH < 2	6 months
Nitrate	none required	48 h
Organo chlorine pesticides	1 mL 10 mg/mL $HgCl_2$;	7 days without extraction
pH	none required	analyze immediately

2. **Drinking Water Samples:** The gathering of samples of drinking water and the management of sample preservatives. To help gather a suitable sample and preserve the sample's integrity after collection, adhere to the guidelines outlined below.

- Develop a Sampling and Analysis Plan (SAP) outlining the sampling locations, sample quantities, types, and quality control requisites for the project.
- Prior to sample collection, consult with the laboratory to confirm the acceptability of sampling equipment, preservatives, and collection procedures. Ideally, acquire sampling materials directly from the analyzing laboratory, and assemble all necessary equipment and supplies for the project.
- Exercise caution when handling the acids and bases used to preserve various sample types as detailed in this document, as they can be hazardous. Always wear protective gloves and eye gear when working with preservatives. When opening a preservative

container, especially a glass ampoule, break it away from yourself and others. Keep acid/base neutralization materials, such as baking soda, readily available in case of spills. If acid comes into contact with your skin or clothing, remove contaminated clothing and rinse the affected area with water; do not apply baking soda, as the exothermic reaction could lead to burns.

- Collect samples in an environment devoid of excessive dust, precipitation, snow, or other potential sources of contamination.
- Choose a cold water faucet for sampling that lacks contaminating features like screens, aeration devices, hoses, purification equipment, or swivel mechanisms. Ensure the faucet is clean, and if it is in disrepair, opt for an alternative sampling location.
- Gather samples from faucets positioned high enough to accommodate a bottle beneath them, typically a bathtub or kitchen sink, while preventing contact between the container's mouth and the faucet.
- Turn on the faucet and thoroughly flush the water lines. Generally, flushing for 2 to 3 minutes is adequate, but longer durations may be necessary, especially when dealing with lead distribution lines. The water temperature will usually stabilize, indicating the completion of flushing. After flushing, adjust the flow to prevent splashing against the walls of the bathtub, sink, or other adjacent surfaces.

3. Some Tips on Collecting Samples

- Remove any attachments on the faucet
- Allow water to flow for 5 or 6 minutes before sampling
- Do not rinse or overfill container
- Always collect cold water; never sample hot water
- Do not touch the inside of the sample bottle or its cap

4. Special Precautions for Wastewater Sampling

- Every time a new place is sampled, a fresh pair of disposable gloves that aren't powdered will be worn; the gloves need to be put on right away before sampling. When the gloves' cleanliness is compromised during sample collection, they should be changed. The gloves should not come into touch with the medium being sampled.
- Sample containers must be kept apart from other samples in case they are thought to have significant levels of pollutants.
- From the least suspected polluted area to the most suspected contaminated area, sample collecting operations must be carried out gradually. It is not acceptable to put background/control or environmental (i.e., low contamination level) samples in the same ice chest as trash or severely contaminated media samples.
- While the other members of the field sampling team gather the samples, one person should, if at all possible, take all the notes, take pictures, complete tags, etc.
- When collecting samples for analyses of organic compounds or trace metals, field investigators must use brand-new, confirmed certified-clean disposable or non-disposable equipment that has been cleaned in accordance with the guidelines outlined in the SESD Operating Procedure for Field Equipment Cleaning and Decontamination

5. **Sample Handling and Preservation Requirements:** Wastewater samples are typically collected through direct filling of the sample container or via an automated sampler or a similar apparatus.

When transferring samples from a collection device during the sampling process, it's imperative to prevent any contact between the collection device and the sample containers.

- Place the samples into appropriately labeled containers. For samples intended for VOC analysis, it's critical to eliminate any headspace (as detailed in Section 7.4, Volatile Organic Compounds). Other sample containers should be filled with a margin to account for potential expansion.
- Samples requiring preservation must be preserved as promptly as practically feasible, preferably right at the moment of sample collection. If preserved VOC vials are utilized, they will be preserved with concentrated hydrochloric acid by personnel from the Analytical Support Branch (ASB) prior to heading out for the field investigation.
- Any samples preserved using pH adjustment (excluding VOCs) should undergo verification using pH strips to ensure adequate preservation. This can be accomplished by placing a small volume of the sample over the pH strip without immersing the strip in the sample. Samples that necessitate cold storage should be immediately placed on ice.

XI. SAMPLING PROCEDURES

1. **General:** Extreme care should be taken to avoid contamination:

- Prior to collecting samples, mark bottles. By doing this, confusion-causing situations are avoided, as well as the challenge of writing on damp bottles.
- Only remove the tops off sample bottles while you are really sampling.
- AVOID placing test bottle tops on the floor.
- AVOID touching the bottles' or caps' inside with your hands or sample tools.
- Avoid washing sample bottles.
- As soon as the sample is collected, the bottles need to be sealed.

2. **Gases:** Compressed gases, industrial smokestack emissions, vehicle exhaust, and atmospheric gases are typical examples of gaseous samples. Solid aerosol particles are also present in gaseous samples.

3. **Sample Collection:** The most straightforward method for gathering a gas sample is to transfer a portion of the gas into a container, like a Tedlar/Teflon bag or a stainless steel canister. The gas is pumped into the container, and it is sealed when the container has been flushed for a set amount of time. Compared to other collection procedures, this method offers the advantage of gathering a more representative sample of the gas. The presence of reactive gases, such as ozone and nitrogen oxides, which may alter the chemical composition of the sample over time or react with the container, the tendency for some gases to adsorb to the walls of the container, and the presence of analytes at concentrations too low to detect precisely are among the drawbacks. Many of these drawbacks can be avoided when utilizing a stainless steel canister by applying cryogenic

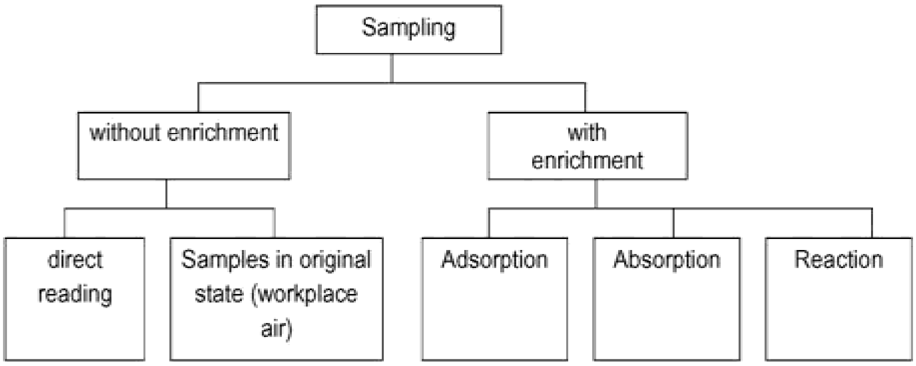
cooling, which turns the sample from a gaseous to a liquid condition. The majority of gas samples are obtained by filtering or by employing a trap with a solid sorbent because it is difficult to store gases. Filtration is used to collect nonvolatile gases, and solid sorbents are used to collect volatile gases (vapor pressures more than or equal to 10–6 atm) and semivolatile gases (vapor pressures between or equal to 10–6 atm and 10–12 atm).

To sample solid sorbent, run the gas through a canister filled with sorbent particles. When gathering volatile substances, 2–100 L of gas are typically collected, and when gathering semi-volatile gases, 2–500 m3. Numerous organic and inorganic polymers as well as carbon sorbents have been employed. Molecular sieves, silica gel, alumina, magnesium aluminum silicate, and other inorganic sorbents are effective polar compound collectors. Their sorption ability for many organic molecules is, however, limited by their effectiveness in gathering water.

The sorbent's low ability to hold onto gaseous analytes is one of the biggest issues with sorbent sampling. A portion of the analyte will pass through the canister without being kept if a sorbent's capacity is surpassed before sampling is finished, making an accurate assessment of the analyte's concentration impossible. Because of this, it's usual practice to position the second sorbent canister downstream of the first. It is safe to presume that the first canister's capacity has not been surpassed if the analyte is not found in the second canister. The breakthrough volume is the amount of gas that can be sampled before it is more than the sorbent's capacity.

4. **Sample Preservation and Preparation:** Generally speaking, sample preparation or preservation is not necessary after the gross sample is collected. When a gas sample is obtained by cryogenic chilling, filtering, or employing a solid sorbent, its chemical composition is often stable. Gaseous chemicals can be extracted using an appropriate solvent or eliminated by heat desorption when employing a solid sorbent before analysis. As an alternative, the concentration of the analyte in the sample can be ascertained by measuring the rise in the mass of the sorbent when it is selective for a single analyte.

5. **Sampling of Gases**



The materials to be identified are either absorbed in a solution or adsorbed onto a solid collection phase for enrichment sampling. Samples must then be prepared in order for them to be examined later.

XII. PRINCIPLES OF ABSORPTION

1. **Introduction:** The absorption of pollutants into different media holds significant importance in the field of air pollution monitoring, especially within wet-chemical analysis methods. In the era predating the widespread use of continuous monitoring instruments, absorption-based techniques were both cost-effective and state-of-the-art.

   Absorption, in this context, refers to the process "in which one or more gaseous components are transferred into a liquid or solid medium where they dissolve." The absorption of gaseous pollutants into a solution is a common practice in atmospheric sampling due to the various analytical methods available for studying the resulting solution. These methods encompass photometric, conductimetric, and titrimetric techniques, and detailed procedures for sampling and analyzing specific gaseous pollutants through absorption are available elsewhere. Here, we will focus on elucidating the gas-liquid absorption process and delving into the factors that impact collection efficiency. We will also explore devices frequently employed in gas-liquid absorption and touch upon various contemporary applications.

2. **Types of Absorption:** Within gas-liquid absorption, the liquid used for collection, referred to as the absorbent, may undergo changes either in its chemical composition, physical properties, or even both, during the absorption process. Gas-liquid absorption sampling encompasses two main forms: (a) physical absorption and (b) chemical absorption.

   To illustrate a typical chemical absorption process, it entails passing a specific volume of air through a solution that interacts with the gaseous contaminant, resulting in the formation of a non-gaseous compound. For example, this may involve drawing an acid mist through a sodium hydroxide solution. The acid and base react to create a stable salt. The remaining unreacted base can then be quantified by titration using a standard acid, providing insights into the quantity of pollutant that has undergone a reaction.

3. **Physical Absorption:** Physical absorption entails the actual dissolution of the pollutant in a liquid medium. Typically, this process is reversible, as the pollutant possesses a relatively noticeable vapor pressure. The solubility of the pollutant within a particular absorbent hinges on several factors, including the pollutant's partial pressure in the surrounding atmosphere, the temperature, and the purity of the absorbent.

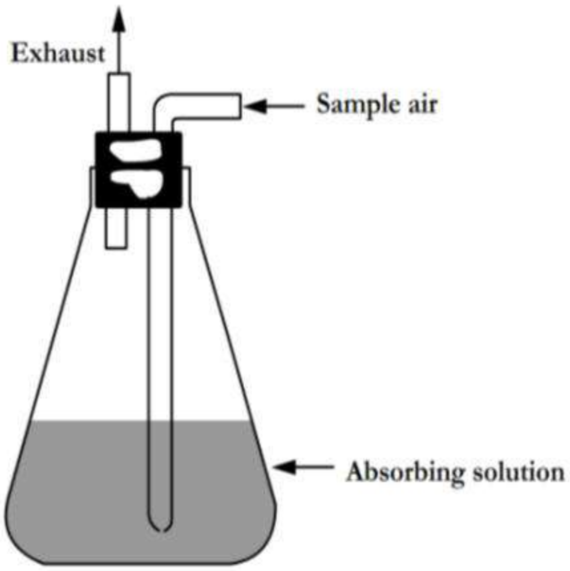
   An ideal solvent should ideally meet certain criteria, such as being relatively non-volatile, cost-effective, non-corrosive, chemically stable, of low viscosity, non-flammable, and non-toxic. In numerous instances, distilled water satisfies many of these requirements, which is why it is utilized as the solvent for capturing certain gases.

   The physical absorption mechanism encompasses the capture of the pollutant through its dissolution in the absorbent medium. Subsequently, the solution is subject to an analysis to determine the pollutant's concentration using an appropriate analytical method. Typically, physical absorption yields lower efficiency unless the pollutant is highly soluble, and the ratio of dissolved gas to liquid volume remains minimal. Consequently, physical absorption is seldom the sole absorption method used when collecting gaseous pollutants.

4. **Chemical Absorption:** In contrast to physical absorption, chemical absorption is a process where a liquid absorbent undergoes a chemical reaction with the pollutant, resulting in the formation of a nonvolatile product. The chosen solvent should engage in an irreversible reaction with the pollutant, such as the reactions of ammonia and carbon dioxide gases with acidic and basic solvents. These reactions lead to the creation of carbonic acid (H2CO3) and ammonium hydroxide (NH4OH). These acids and bases exhibit significantly higher solubilities compared to gaseous CO2 or NH3. The primary factors influencing the choice of absorbent in chemical absorption encompass the pollutant's solubility, the reactivity of the pollutant and absorbent, and the subsequent analytical method to be applied. Particular attention must be given to avoid the selection of an absorbent that might interfere with subsequent chemical analysis.

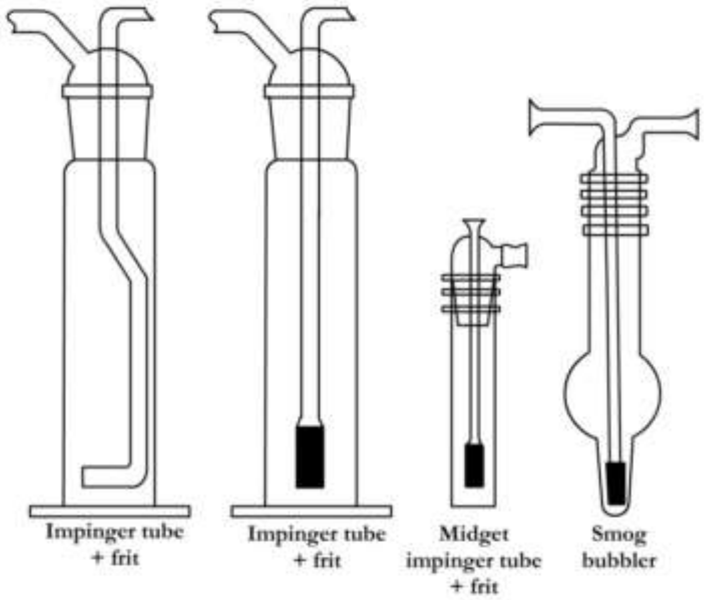
   An example of a chemical absorption process involves the reaction of sulfur dioxide (SO2) with aqueous hydrogen peroxide (H2O2), resulting in the production of sulfuric acid (H2SO4). The concentration of SO2 can be determined by titrating the H2SO4 produced with barium perchlorate (Ba (ClO4)2). This method currently serves as the standard for quantifying SO2 emissions from stationary sources. Nevertheless, in contemporary practice, an automated continuous equivalent method (e.g., UV Fluorescence) is typically employed to offer real-time data.

6. **Absorption Devices:** Many tools have been employed to collect atmospheric pollution samples. A typical gas-washing bottle with the absorbent and a gas-dispersion tube to introduce the pollutant into the solution is one of the most basic and often used instruments.



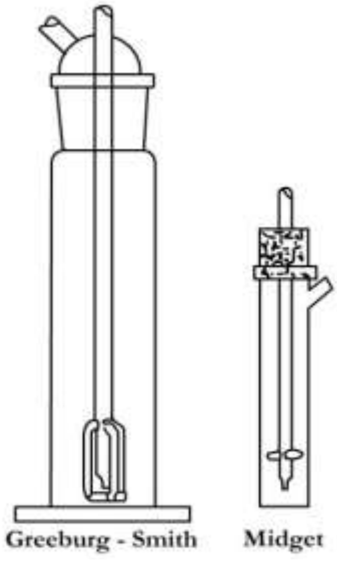
7. **Absorption device adapted from an Erlenmeyer flash:** Gas enters the absorbent solution through the uncontrolled aperture. These absorbers come in a range of varieties. They are often made of glass and might have a cylindrical or conical shape. The several devices have typical flow rates ranging from 1 to 5 liters per minute. Two types of absorbers are commonly utilized in atmospheric sampling: (a) fritted-glass absorbers, also known as bubblers, and (b) impingers.

8. **Fritted-Glass Absorbers:** A great variety of shapes and sizes of these absorbers are being used.



9. **Typical fritted-glass absorbers:** These units often offer the highest efficiency in collecting gaseous pollutants. In addition to the commercially accessible units, DIY devices can be fashioned using standard gas-dispersion tubes. The fritted component of the dispersion tube can be easily obtained in the shape of a disc or cylinder, with a range of pore sizes available. The coarse and extra-coarse frits enable effective pollutant dispersion while minimizing head loss.

10. **Impingers:** Impingers are often used in sampling for gaseous and vaporous pollutants from the atmosphere.



11. **Two types of impingers:** Initial research suggests that the impinger is marginally less effective than the fritted absorber when it comes to gathering gaseous pollutants. Under ideal operating conditions, the fritted-glass absorber was observed to outperform midget

impingers in terms of efficiency. Furthermore, it was noted that the minimum concentration required for collection with the midget impinger was slightly higher than that for several types of fritted-glass absorbers. It's worth noting that, unlike fritted-glass absorbers, impingers can also be employed for particulate matter sampling.

XIII. PRINCIPLES OF ADSORPTION

1. **Basic Principles:** Adsorption refers to the process wherein gases, liquids, and solutes within liquids are drawn, accumulated, and held at the interface of various materials. This interface can exist between a range of substances, such as gas-liquid, liquid-liquid, gas-solid, liquid-solid, or solid-solid. Among these interactions, the adsorption processes between liquids and solids and gases and solids have been extensively studied. The former is primarily associated with purifying substances by removing them from a solution using a solid adsorbent. On the other hand, the latter is focused on eliminating gaseous pollutants using high-surface-area solid adsorbents.

   In the field of air pollution control, adsorption methods are frequently employed to capture a particular gas or a mixture of gases. The procedure typically involves directing a gas stream through a vessel containing an adsorbent material like activated charcoal, alumina, or silica gel. Molecular forces cause the gas to become attached to the adsorbent, and unless condensation takes place, the gas retains its physical and chemical properties. Once collected, the gas can be extracted from the adsorbent for analysis or eventual disposal by employing techniques like heating, passing inert carrier gases through the system, or chemical treatment.

2. **Physical Adsorption:** Physical adsorption is a frequently observed phenomenon, and a typical example of this type of adsorption is the adsorption of various gases onto charcoal. At sufficiently low temperatures, nearly all gases experience a degree of physical adsorption. The amount of gases adsorbed under similar conditions is primarily influenced by the condensation properties of these gases. Gases with higher boiling points or critical temperatures tend to exhibit greater adsorption. We will delve into this concept in greater detail in subsequent discussions.

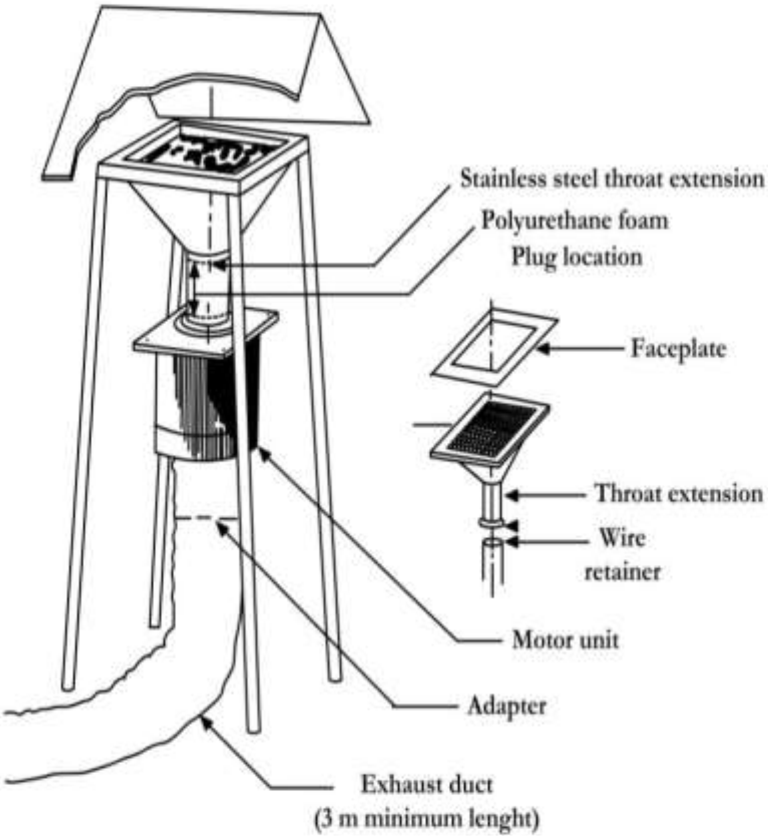
3. **Chemical Adsorption:** This results in a significantly stronger attachment of gas molecules to the surface. Heats of adsorption are comparable in magnitude to those seen in chemical reactions, indicating that the process entails the formation of a surface compound through the combination of gas molecules with the adsorbent. This form of adsorption resembles chemical bonding and goes by various names, such as chemical adsorption, activated adsorption, or chemisorption. As an illustration, when oxygen is adsorbed on tungsten, it has been observed that tungsten trioxide sublimes from the tungsten surface at around 1200 K. Nonetheless, even at temperatures exceeding 1200 K, oxygen remains on the surface, presumably in the form of tungsten oxide. Other instances of chemical adsorption include carbon dioxide on tungsten, oxygen on silver, gold on platinum, and carbon and hydrogen on nickel.

4. **Adsorption Losses in Air Sampling:** Each adsorption medium used in atmospheric sampling has different limitations and problems. The problems most frequently encountered are:

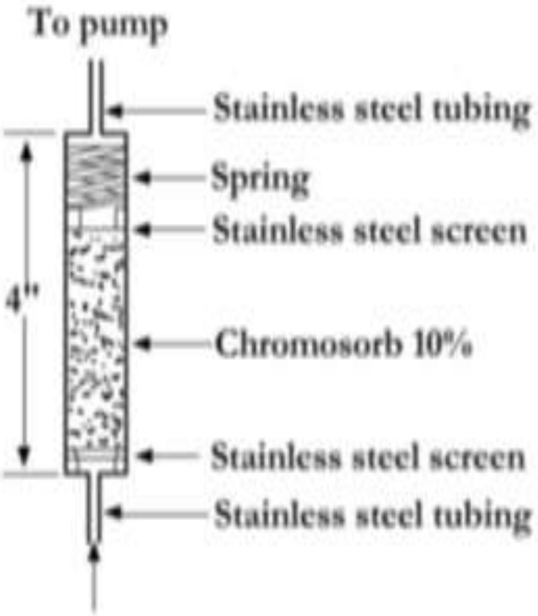
- Irreversible adsorption,
- Variable desorption efficiency, and
- Interference by water vapor.

Activated carbon is widely employed due to its strong attraction to organic substances. However, carbon sampling devices often encounter two significant challenges: irreversible adsorption and varying desorption efficiencies. Carbon can also act as a potent catalyst, potentially leading to in situ reactions during sampling. In recent times, alternative adsorption media, such as thermally stable polystyrene divinyl benzene co-polymers, have gained popularity in air sampling. These media are used at room temperature to capture volatile organic compounds. Subsequently, the volatile organic compounds are extracted through thermal desorption, followed by gas chromatographic analysis. These polymers are non-polar and have minimal affinity for water, which addresses a common issue in the analysis process. Adsorption sampling devices find primary application in the collection of volatile organic compounds.

5. **Current Applications of Adsorption in Atmospheric Sampling:** Carbon and porous polymers, including Porapack Q, Porapack P, Tenax GC, XAD resins, and polyurethane foam, have found widespread use in the collection of pesticides, polychlorinated biphenyls, and various organic compounds present in the surrounding air. These media can be integrated into sampling devices, which can be adaptations of high-volume samplers. Specifically, polyurethane foam is employed for the collection of organic compounds, such as PCBs.

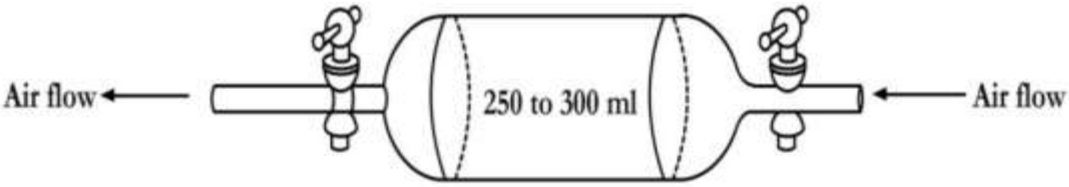


6. **Assembled sampler and shelter with exploded view of the filter holder**



XIV. HIGH-SPEED ORGANIC VAPOR COLLECTOR

1. **Air Displacement or Purging:** Collectors are made of cylindrical tubes with stopcocks on both ends. The tube is fully purged after the stopcocks are opened. The tube needs to be kept in place after sampling until the aspirating device has been taken out and the stop cocks have been closed.

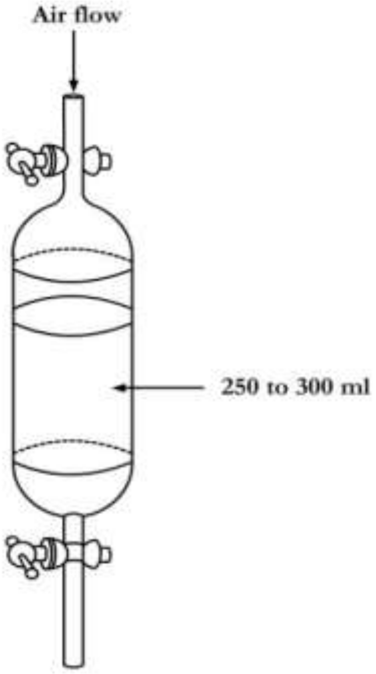


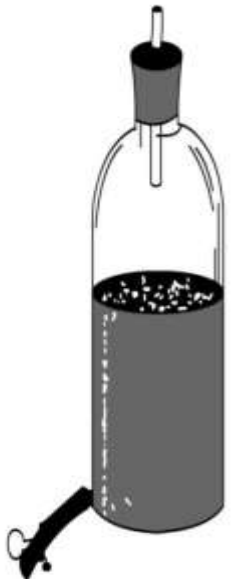
2. **Gas-displacement collector:** Although metal containers with similar general designs have been used, numerous samples have been discovered to react with them. The fact that they are nearly indestructible is their true advantage. Using a range of pumps, the sample air is pulled through the container. To fully remove any potential old, unrepresentative air, enough air must be sucked through.

   While the exact amount of air needed will vary depending on the situation, it will always be at least several times larger than the container's volume. It is theoretically impossible to pump out all of the old air. It's not exactly an instantaneous sample because this pumping procedure could take a while.

3. **Liquid Displacement:** Liquid displacement is another technique used in gas sampling. Using this technique, a liquid is let to drain from the bottom of a container, and gas is able to enter and fill the void the liquid left behind. You can use any appropriate liquid as long as it won't dissolve the sample or react with it. The material to be tested will determine

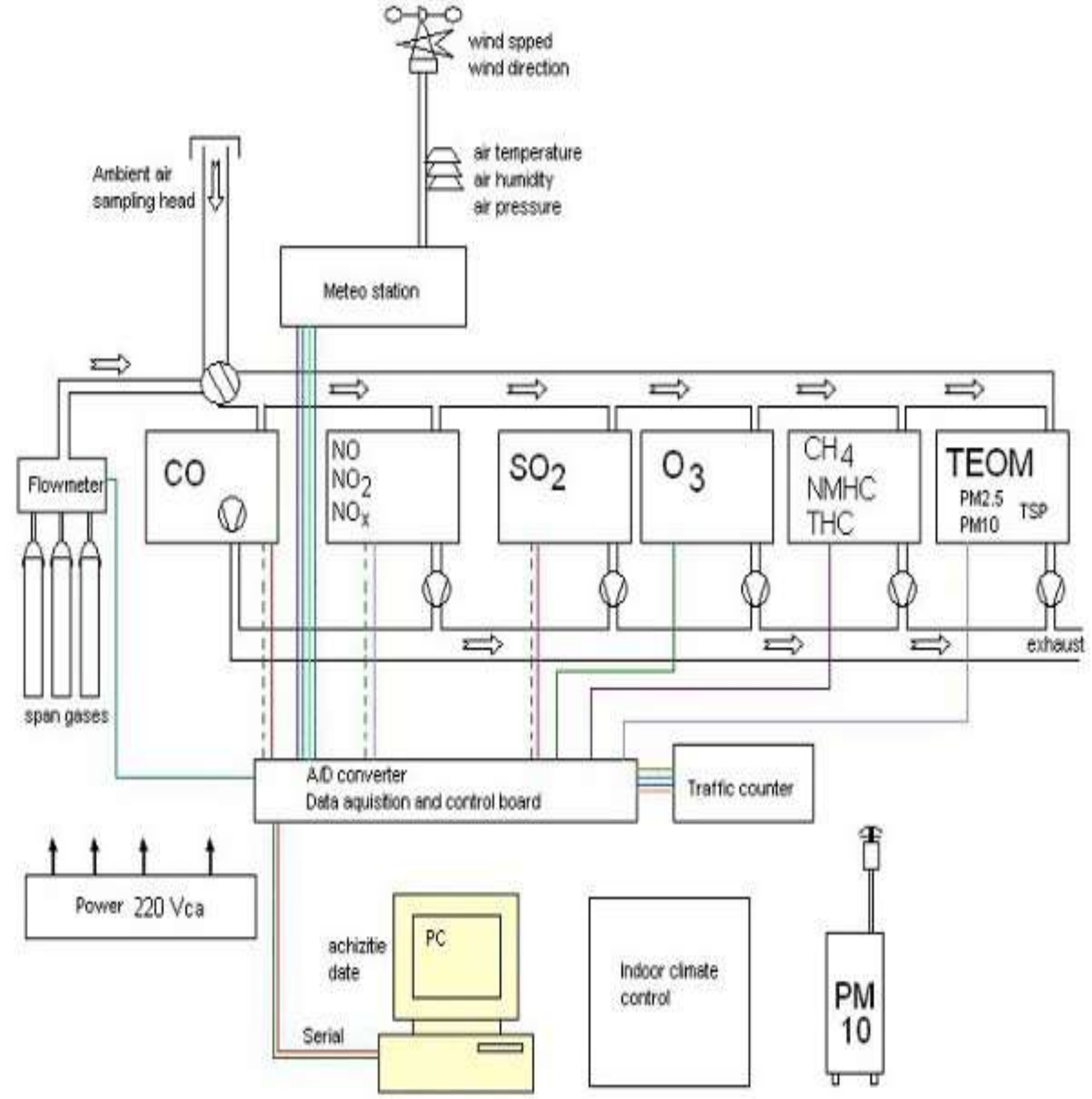
which liquid is best; popular liquids include water, brine, mercury, or water that has been saturated with the gas to be sampled. There are two main types of containers that are used: an aspirator bottle and a glass tube with two stopcocks for air displacement. Liquid-displacement collector. Aspirator bottle.





XV. INSTANTANEOUS MONITORING OF AIR POLLUTION

Numerous vital considerations pertain to environmental management through the real-time monitoring of air quality. Air pollution has far-reaching consequences, impacting soil, water, crops, vegetation, man-made structures, wildlife, climate, transportation, economic values, personal comfort, and overall well-being. In our current era, marked by a knowledge-based society, both the populace and policymakers are increasingly committed to preserving biodiversity, a cornerstone of human welfare and economic progress. Biodiversity plays a pivotal role in meeting human needs by upholding the ecological processes vital for our survival. These wide-ranging ecological systems offer essential benefits such as clean air and freshwater, crucial to individuals in both urban and rural environments. In line with national standards and established international methodologies, the primary pollutants that require measurement encompass NOx (NO, NO2), CO, SO2, PM10, O3, TOC (Total organic carbon), and VOC (Volatile organic compounds).



Apart from the specialized instruments designed for the precise measurement of pollutants, a range of other instruments is available for the monitoring of meteorological parameters. These include measurements such as wind direction, wind speed, temperatures, global radiation, rain duration, dew formation, and rainfall volume. Additionally, an electronically controlled computer system is employed for recording, calculating, and storing these values. The computer system also regulates valve timing and accurately archives the measured data in accordance with the specified valve positions. Half-hourly mean values, or other designated averages, are computed and retained in memory or printed out for reference. Further data analysis is subsequently conducted on an extensive computing infrastructure. To enhance safety measures, the recorded values are redundantly documented using multi-channel continuous-line recorders or multipoint recorders, independently of the computer-controlled data recording system.

1. **Transport of samples:** The collected sample must be sealed appropriately and transported immediately to the laboratory as described in the following:

- Ensure that sampling tubes are hermetically sealed with appropriate caps or stoppers and then transfer them into a protective container to prevent damage during transit.
- Filters should be transported using suitable transport cassettes to guarantee the preservation of the collected substances and prevent any losses.
- Seal washing bottles and impingers with suitable caps and package them securely to avoid breakage during transportation.
- When samples are sent to the analytical laboratory via postal or parcel services, it's essential to use proper transport containers.
- The chosen transport container should offer resistance against various environmental and external factors, such as elevated temperatures and mechanical forces, to the greatest extent possible.
- Upon arrival at the laboratory, carefully inspect the samples to ensure there has been no damage, including checking whether the sealing caps on the sampling tubes remain secure and if any visible precipitates have formed in the filter cassette.

2. **Storage of samples:** As previously noted, it is crucial to conduct laboratory sample analysis promptly after sampling. Nevertheless, certain laboratory conditions may necessitate the storage of samples for several days or even weeks. When this occurs, it is imperative to store the samples in a manner that minimizes any changes in their state. To address this concern, it is advisable to conduct storage experiments to determine the maximum duration for which samples can be stored without significant alterations.

    - Samples can be kept for a few weeks or even longer if the analytes are stable. Since the sample is shielded from external factors like light and temperature fluctuations as much as possible, the laboratory refrigerator is frequently a good choice for storage.
    - Analyte losses typically have a greater impact on analytical results at lower concentrations than at higher ones, hence storage tests should be conducted at varying sample concentrations.