CHAPTER 1

Analytical Chemistry: An Introduction

Analytical chemistry involves the application of techniques and methodologies to obtain and assess qualitative, quantitative and structural information on the nature of matter. In many respects, analytical chemistry acts as a foundation for other branches of chemistry.

An element, species or compound, which is the subject of analysis is known as an *analyte*. The remainder of the material or sample of which the analyte(s) form(s) a part is known as the *matrix*.

Analysis is classified into two broad categories:

1. *Qualitative analysis*: It involves the identification of elements, species and/or compounds in a sample. This is used to ascertain the type of substance present in a sample. It is generally used to identify the presence or absence of impurities.
2. *Quantitative analysis*: It involves the determination of amounts of different constituents present in a system. It is used for determination of the absolute or relative amounts of elements, species or compounds present in a sample.

Different techniques of analysis along with their principle and the nature of analysis are summarized in Table 1.1.

Table 1.1 *Different techniques, their principles and nature of analysis*

S. no.	Technique	Principle involved	Nature of analysis
1.	Titrimetry	Volume of standard reagent solution reacting with the analyte	Quantitative
2.	Gravimetry	Weight of pure analyte or compound of unknown stoichiometry	Quantitative
3.	Chromatography	Differential rates of migration of analytes through a stationary phase by movement of a liquid or gaseous mobile phase	Qualitative and quantitative

(*Continued*)

Table 1.1 (*Continued*)

S. no.	Technique	Principle involved	Nature of analysis
4.	Infrared spectrometry	Vibrational molecular absorption	Qualitative
5.	Nuclear magnetic resonance spectrometry	Nuclear absorption (change of spin states)	Qualitative
6.	Mass spectrometry	Ionization and fragmentation of molecules	Qualitative
7.	Ultraviolet spectrometry	Electronic molecular absorption	Quantitative
8.	Radiochemical analysis	Characteristic ionizing nuclear radiation emitted by the analyte	Qualitative and quantitative

1.1 Common Apparatus and Basic Techniques

While doing the practical work in laboratory one should pay special attention to cleanliness and tidiness of benches; glassware must be perfectly clean and free from grease.

Cleaning of glassware: It can be achieved by using the following:

1. Detergents.
2. A cleaning mixture. A saturated solution of powdered sodium dichromate or potassium dichromate in concentrated sulphuric acid.
3. Degreasing agent. It can be obtained by dissolving 100 gm of potassium hydroxide in 50 mL of water and making up to 1 L with industrial methylated spirit after cooling.

To avoid impurities during analysis, apparatus made from resistance glass have to be used. A borosilicate glass is preferred for most purposes.

Some of the glasswares that can be used are:

1. **Beaker:** The most satisfactory beakers for general use are beakers with a spout, which have the advantage of pouring, making an outlet for steam or gases, etc. The most useful sizes are 250 and 500 mL.
2. **Conical flask:** Conical flasks of 150, 250 and 500 mL capacity are used frequently.
3. **Pipettes:** There are three kinds of pipettes:
   a. *Transfer pipettes:* These have one mark and deliver a constant volume of liquid. It is made up of long glass tube with large central cylindrical bulb. A calibration mark is present around the upper tube while the lower delivery tube is drawn out to a fine tip. Transfer pipettes are constructed with capacities of 1, 2, 5, 10, 20, 25, 50 and 100 mL.

b. *Graduated pipettes or measuring pipettes:* These are graduated or marked and used to deliver small volume as required. They are made up of straight, fairly narrow tubes with no central bulb. They deliver a measured volume from a top zero to a selected graduation mark or to the jet, i.e. the zero is at the set. Three different types are available:

Type 1 delivers a measured volume from a top zero to a selected graduation mark.

Type 2 delivers a measured volume from a selected graduation mark to the jet, i.e. the zero is at the jet.

Type 3 is calibrated to contain a given capacity from the jet to a selected graduation mark and thus to remove a selected volume of solution.

c. *Syringe pipettes:* These have a fixed or variable volume and are usually employed for dispensing large numbers of identical volumes very quickly. They have a push button design in which the syringe is operated by pressing a button on the top of the pipette; the plunger travels between two fixed stops and a reliable constant volume of liquid is delivered.

4. **Burettes:** Burettes are long cylindrical tubes with uniform bore throughout the graduated length, a narrow lower end with a glass stopcock and a jet. Before using, it is thoroughly cleaned with a cleansing agent, rinsed well with distilled water and the solution is filled with the help of a funnel up to zero mark. Burettes are constructed with capacities of 25 and 50 mL.

1.2 Analytical Balance

To measure the mass of a substance a *balance* or *laboratory balance* is used. It consists of a pivoted horizontal lever of equal length arms, called the *beam*, with a weighing pan, also called *scale* or *scale pan* or *bason* suspended from each arm. The unknown mass is placed in one pan, and standard masses are added to the other pan until the beam is as close to equilibrium as possible.

An *analytical balance* is an instrument used to determine mass to a very high degree of precision. It consists of a transparent enclosure with doors so dust does not collect and also any air currents in the room do not affect the delicate balance. The main components are the beam supported on a pillar of metal and the pans. The beam is a rigid piece of metal which rests through a knife edge of agate on a plate of agate attached to the pillar top. On each end of the beam, at equal distance from the central knife edge, are two terminal knife edges of agate facing upwards. Each terminal agate supports a suspension from which a pan is hung. To the centre of the beam a long pointer is attached which moves over a scale at the foot of the pillar. The top of the beam is divided accurately for the

use of a rider. The two adjusting screws at each end of the beam are used for adjusting the equilibrium position, a state when the pointer rests at the centre of the scale and the beam is horizontal when unloaded. The pillar is fixed on a rectangular stable base. The balance is fixed with levelling screws at the bottom and the plumb line suspension. On both sides of the top of the pillar a horizontal metallic piece extends, which is monitored by a key placed centrally in front of the base. This is called as *beam arrest*. When the key is moved to the left the beam oscillates. It has a maximum load capacity of 100–200 g and a sensitivity of 0.1 mg.

Weight Box

The weights are used to determine the mass of an object. The unit of mass that is employed in the laboratory work is gram. The weights are made of heavy metal alloy and are cylindrical in shape, each with a knob at the top. An ordinary set has 100, 50, 20, 10, 5, 2 and 1 g weights. The set contains a pair each of 20 and 2 g weights. Weights less than 1 g are called as *milligram* (mg) weights or fractional weights. They are leaf shaped foils of aluminium or other suitable metal with one of the sides turned up for picking up with forceps. The fractional weight set has 500, 200, 100, 50, 20, 10, 5, 2 and 1 mg weights. In a weight box, 200, 20 and 2 mg weights are present in a pair. Weights smaller than 10 mg are generally not used, instead the use of rider is recommended for this purpose. All the weights are kept in a wooden box lined with velvet. The weights should be calibrated.

Rider

A rider is a piece of suitable wire appropriately shaped to ride on the beam of the balance. The commonly used rider weighs 10 mg, when the beam is graduated. The beam scale is divided into 10 equal parts on each side from the centre, each part being subdivided into five parts. The right hand section of the beam is normally used and the left hand section is seldom used. The rider is placed at division 0 before adjusting the balance. If the rider is placed at marking 10 on the right hand section of the scale the effect is equal to that of 0.01 g weight placed on the right hand pan of the balance; if it is hung at marking 4 the effective weight is equal to 0.004 g. The distance between two small divisions represents a weight of 0.002 g. Thus, if the rider is placed on the second small division between the markings 6 and 7, the weight is 0.0064 g. The placing of the rider on the beam scale is manipulated by means of a sliding hook.

Some of the balances have the beam scale subdivided into 10 parts instead of 5 parts and with such balances 5 mg rider is used. Here, the distance between two small divisions represents a weight of 0.001 g.

Care and Use of the Balance

While using a balance care should be taken about the following:

1. The balance should be placed on a firm platform. The balance and pan should be clean.
2. The balance should be tested and adjusted so that the pointer swings freely and to equal distance on either side of the zero point of the pointer scale.
3. The object to be weighed is placed on the left hand pan and the weights on the right hand pan.
4. The chemicals to be weighed must not be placed directly on the balance pan. This should be placed and weighed in a weighing bottle or over a watch glass.
5. The object should be cooled to room temperature, if it is hot before weighing.
6. When the final weighing is made the doors of the balance must be closed.
7. During weighing when the objects are being placed or removed from the pans, the beam and pan must be arrested.
8. All the weights should be handled with forceps and not with fingers.
9. The balance must not be overloaded.
10. When the weighing has been completed, the object and weights should be removed from the pans. Any spilled material should be immediately removed with the help of a camel hair brush.
11. If the balance is in disorder, do not try to rectify the defect yourself. Bring it to the notice of an instructor.

1.3 Methods of Weighing

The weighing of the samples may be done by adopting either of the following methods:

1. *Weighing by difference*: This is the standard procedure of weighing in analytical work.
   a. Take a thoroughly clean and dry stoppered weighing bottle.
   b. Place the sample to be weighed in it, and weigh accurately (x g).
   c. Take out the bottle from the balance.
   d. Pour out the required amount of the sample into the flask or other vessel by rotating and gently tapping the weighing bottle.
   e. Weigh the bottle and its contents again (y g).
   f. The difference between the weights represents the weight of the sample transferred.

   Record the observation in the following manner:

Weight of the weighing bottle and the substance	=	x g
Weight of the weighing bottle and the substance after transference	=	y g
Weight of the substance taken out	=	$(x - y)$ g

2. *Weighing by addition*: This method is generally adopted for preparing standard solutions. The weighing container can be a clock glass, watch glass, weighing bottle or a small beaker.
   a. The clean and dry container is weighed.
   b. Introduce the sample into the container in small portions until the correct weight has been added.
   c. Weigh the container and the contents.
   d. Take out the container and hold it over the receiving vessel (beaker or funnel on the mouth of a flask) and pour the contents carefully into the receiving vessel.
   e. Wash the container thoroughly with a jet of water, washings being collected into the receiving vessel.

1.4 Volumetric Analysis

Titration is a common laboratory method of quantitative chemical analysis that can be used to determine the unknown concentration of a known reactant. Volumetric analysis (titrimetric analysis) is the determination of the volume of a solution of known concentration which is required to react quantitatively with a solution of the substance being analysed. A solution of accurately known strength is called *standard solution* (titrant). It contains known weight of the solute in a definite volume of the solution. The strength of a solution is commonly expressed as normality, molarity or molality.

Normality is defined as the number of gram equivalents of a solute present in 1 L of a solution. Thus, a solution which contains one gram equivalent of the solute per litre of the solution is called a *normal solution*. It is represented as 1 N. Gram equivalent is the weight of a substance in grams numerically equivalent to its equivalent weight. Thus, one gram equivalent of H_2SO_4 is 49.

The equivalent weight of an acid is that weight of it which contains 1.008 g of replaceable hydrogen. The equivalent weight of a base is that weight of it which contains one replaceable hydroxyl group. Thus, the equivalent weights of hydrochloric acid and sodium hydroxide are equal to their molecular weights. Sulphuric acid and oxalic acid each have two replaceable hydrogens, hence their equivalent weights are equal to half the respective molecular weights.

Normalities of Some Acids

Concentrated sulphuric acid	36–38 N
Concentrated hydrochloric acid	10–12 N
Concentrated nitric acid	16 N
Glacial acetic acid	17.5 N

Molarity is defined as the number of gram molecules of a solute present in 1 L of a solution. A solution which contains 1 g molecule of the solute per litre of the solution is known as a *molar solution*. It is expressed as 1 M. Gram molecule is the weight of a substance in grams numerically equivalent to its molecular weight. Thus, one gram molecular weight of H_2SO_4 is 98.

Molality is defined as the number of gram molecules of a solute contained in 1 kg of a solution. A solution which contains 1 g molecule of the solute per kilogram of the solution is known as a *molal solution*.

Standardization deals with the determination of the strength in terms of normality, molarity or molality of a solution. It can be achieved by use of another standard solution of a substance with which the solution reacts quantitatively (called a *secondary standard*), or by use of a carefully weighed substance of a high purity (called as *primary standard*). Thus a solution of sodium hydroxide may be standardized using a standard solution of sulphuric acid (secondary standard) or by using a sample of potassium hydrogen phthalate of high purity (primary standard). A substance which is to be used as a primary standard should satisfy the following conditions:

- Should have been obtained in a pure state
- Should have stability, i.e. no change on atmospheric exposure during weighing, should not be hygroscopic and should not get oxidized by air or affected by carbon dioxide
- Should have relatively high molecular weight
- Should be available in high solubility, i.e. should readily soluble in water and react instantaneously with the standard solution

The point at which a substance to be analyzed react with the standard solution of the another substance in chemically equivalent amounts is called as *stoichiometric point* commonly called as the *end point*. This change in some property of the reaction mixture made detectable to the eyes with the help of some complex organic substances called *indicators*. The end point can also be detected with the help of the following:

- A potentiometer, an instrument that measures the electrode potential of the solution. These are used for titrations based on a redox reaction; the potential of the working electrode will suddenly change as the endpoint is reached.
- A pH meter, a type of potentiometer that uses an electrode whose potential depends on the amount of H^+ ion present in the solution. This allows the pH of the solution to be measured throughout the titration. At the endpoint, there will be a sudden change in the measured pH. It can be more accurate than the indicator method, and is very easily automated.

- Thermometric titrimetry, an extraordinarily versatile technique. This is differentiated from calorimetric titrimetry by the fact that the heat of the reaction (as indicated by temperature rise or fall) is not used to determine the amount of analyte in the sample solution. Instead, the endpoint is determined by the rate of temperature change.
- Spectroscopy which measures the absorption of light by the solution during the titration, if the spectrum of the reactant, titrant or product is known. The relative amounts of the product and reactant can be used to determine the end point.

The titration is actually stopped at this point.

Types of Titration

Titrations can be classified into five types depending on the type of reaction involved:

1. *Acid–base titrations*: Acid–base titrations are based on the neutralization reaction between the analyte and an acidic or basic titrant. This is also known as *neutralization reactions*. This method most commonly uses a pH indicator, a pH meter, or a conductance meter to determine the endpoint.
2. *Redox titrations*: Redox titrations are based on an oxidation–reduction reaction between the analyte and titrant. These titrations most commonly use a potentiometer or a redox indicator to determine the endpoint.
3. *Complexometric titrations*: Complexometric titrations are based on the formation of a complex between the analyte and the titrant. These titrations generally require specialized indicators that form weaker complexes with the analyte.
4. *Precipitation titration*: Precipitation titration is a type of analysis which involves the formation of insoluble substance or precipitate. The end point in these analyses is detected by complete formation of precipitate or by the use of indicator or by some instrumental methods.
5. *Diazotization titration*: Diazotization is a reaction that converts an aromatic primary amine into diazonium compound. The end point in these analyses is detected by complete formation of blue colour due to liberation of iodine on treatment with starch iodide paper.