Chapter 7

Analytical Chemistry

Time Allocation

Teaching periods = 12
Assessment period = 03
Weightage = 12%

MAJOR CONCEPTS:

7.1 Qualitative and Quantitative Analysis
7.2 Important Parameters
7.3 Classical Methods
7.4 Advanced Instrumental Methods

STUDENTS LEARNING OUT COMES (SLO'S)

- Explain the basic concepts of Analytical Chemistry.(Remembering)
- Define the Qualitative and Quantitative analysis.(Understanding)
- Study the important Parameters, errors, accuracy and precision.(Analyzing)
- Differentiate the classical and instrumental methods.(Analyzing)
- Define the Spectroscopic methods such as Ultra-violet and visible Spectroscopy, infrared spectroscopy.(Understanding)
- Define Chromatographic methods such as high performance liquid chromatography and gas Chromatography.(Understanding)
- Define Electrochemical methods such as Potentiometric and conductometry.(Understanding)
- Understand new methods, scientific investigations.
- Communicate their findings using a variety of conventional and advanced technology in the field of analytical chemistry.

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Introduction

As we know that chemistry is usually known as natural science because it is concerned with the knowledge of natural world and how it works. There is a range of knowledge, theories and applications for human beings in chemistry such as plastic, synthetic fibers, rubber, soaps, medicines, paints, insecticides, pesticides and petrochemical products. Today chemistry has a wide scope in all aspects of life and serving humanity. Chemists are working hard to investigate material and creating chemical material by combining and blending substances. There are many challenges like food problem, environmental protection, biochemical processes, population problems and new resources of energy being faced and solved by chemistry, all of these issues and processes are based on analysis of different substances. These analysis and separation of sample to detect and estimate its components through various techniques and instruments is known as Analytical Chemistry.

7.1A What is Analytical chemistry?

The analytical chemistry provide the methods and tools needed to insight our material World and answer the basic questions about a material

- What?
- Where?
- How much?
- What structure/arrangement/form?

The Analytical Chemistry deals with instruments and methods to separate, identify and quantify the matter. The main objective of analytical chemistry is to develop an understanding of analysis of elements and compound for measurement and problem solving with the help of analytical methods.

The Analytical Chemistry is applied in all fields of chemistry such as Medicine, Clinical laboratories, industries, Agriculture ,food contamination and environmental protection.

Do You Know?

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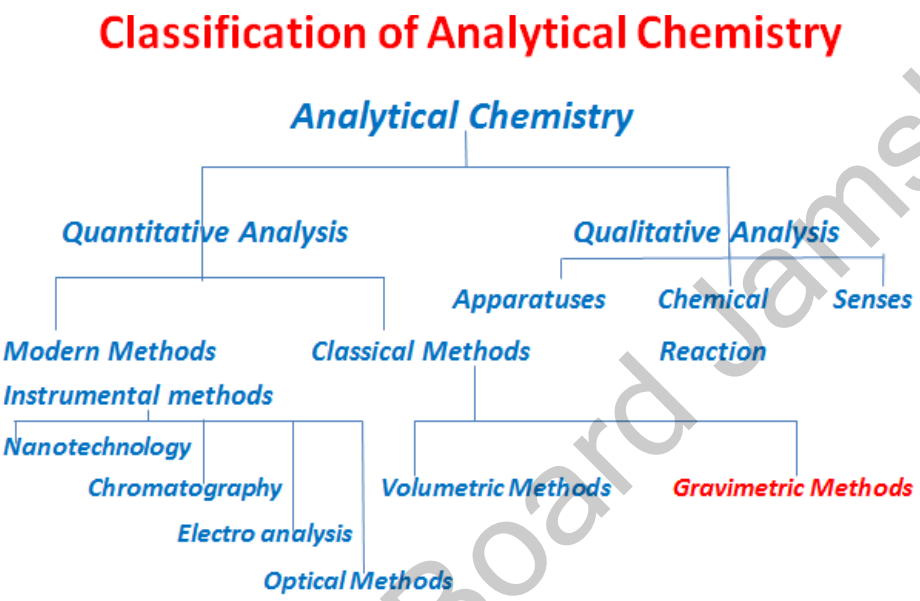
7.1 B Types of Analytical chemistry:



The analytical chemistry consist of two main types of analysis which are as follows

(1) Qualitative Analysis:

The identification of elements, ions or compounds present in sample is called qualitative analysis. The sample may be solid, liquid, gas or a mixture. Qualitative analysis does not measure the quantity of substance but measure the quality of that material. Qualitative analysis is performed by selective chemical reactions or with the use of instrumentation. For example: chemical test and flame test.
Qualitative analysis further divided on the basis of chemical test are as follows

(i) Organic qualitative analysis:

It deals with the identification of presence of different classes of organic compounds or functional groups by producing colors in chemical reactions. For example: formation of white precipitate by adding silver nitrate ($AgNO_3$) in dilute nitric acid (HNO_3) indicate the presence of halide (X^-=F, Cl, Br, I) . as shown in figure (7.1)

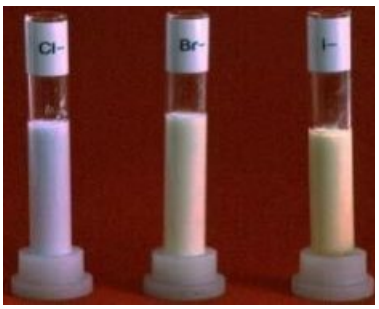


Figure 7.1
Organic qualitative Analysis

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(ii) Inorganic qualitative analysis:

It deals with the identification of elements. For example: flame test of copper halide which shows bluish-green color due to presence of copper. Some other flame test of halide are given below in picture (7.2)

Figure 7.2 Flame test

(2) Quantitative Analysis:

The determination of how much amount or quantity of one or more substance present in compound or sample is called quantitative analysis. It deals with large number of quantifying methods which are classified as physical or chemical.

Physical methods measure physical properties such as density, temperature, absorption of light, magnetic influences, color, and texture. The physical methods used to measure these properties are Fourier transform infrared spectroscopy (FTIR), Atomic emission spectroscopy (AES), trace element analysis and energy dispersive X –ray spectroscopy (EDS).

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Physical methods and instruments are shared in pictures

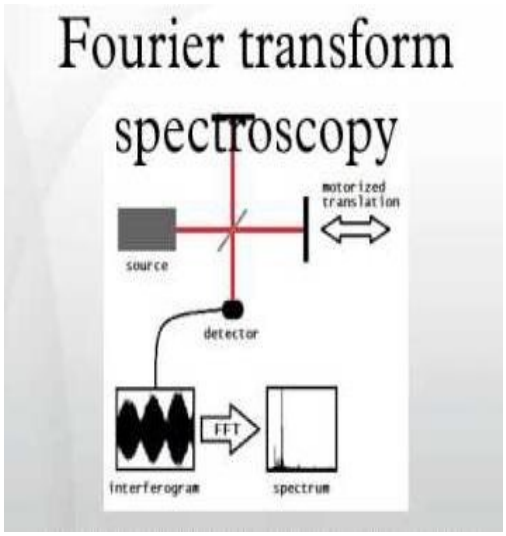

Figure 7.3
Fourier transform spectroscopy

Figure 7.4
Atomic emission spectroscopy

Figure 7.5
Trace element analyzing instrument

Figure 7.6
Energy dispersive X-ray spectroscopy

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Chemical methods measure chemical reactions such as precipitation, oxidation or neutralization and measured by volumetric analysis, gravimetric analysis and combustion analysis.

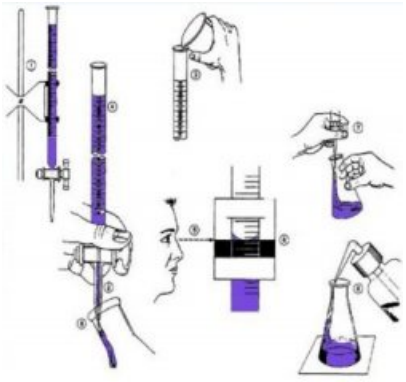

Figure 7.7
Volumetric Analysis

Figure 7.8
Gravimetric Analysis

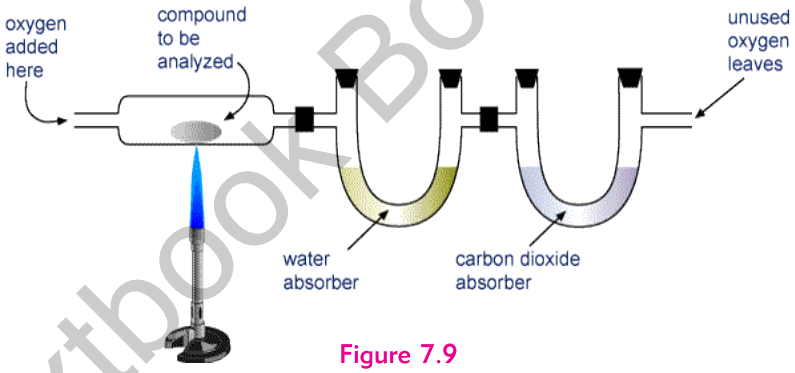

Figure 7.9
Combustion Analysis

Always remember that whenever any chemist start working to quantify any sample first of all qualify that sample to identify the compounds in sample then apply quantitative analysis procedures to determine quantity of compounds in sample.

Test Yourself

- Define analytical chemistry?
- Prove that analytical chemistry is a part of all types of chemistry?
- Justify that qualifying is the first step to quantify any sample?
- Discuss which method deals with physical properties of substances?
- Differentiate between quantitative and qualitative analysis?

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7.2 Important Parameters

The parameter is measureable factor or boundary which define performance and quality of analytical methods. The validation of any analytical method is observed by parameters and various parameters of validation are selectivity, linearity, range,accuracy, precision and error.

In this chapter we will discuss about the three most important parameters

- Error
- Accuracy
- Precision

7.2.1 ERROR

We know that in all type of analytical methods or experiments we observe many errors and deviations. These errors are due to 13% equipment failure, 13% human error, 16% sample preparation and 10% wrong calibration. so we can say that factors which produce the error are defect in instrument, lack in handling the apparatus or improper functioning of the instrument.

Error can be defined as numerical difference between observed value and true value.

Errors in analytical chemistry are classified as systematic and random errors.

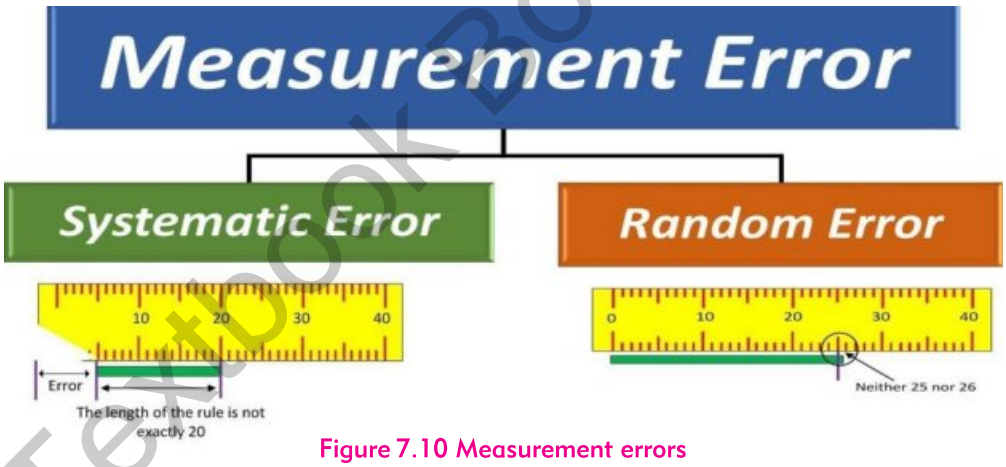

Figure 7.10 Measurement errors

Systematic errors are also known as determinate error and caused by defect in the analytical method or improper functioning of instrument. Systematic error may be instrumental, observational, environmental and theoretical. For example a thermometer, peppet , burette ,analytical balance and volumetric ware shows error in measurement. There is no any specific definition of systematic error because it's different for different experiments.

For example: in acid base titration if pH indicator is not properly prepared then color change will appear before equivalence point or if burette is not properly cleaned or rinsed will cause of systematic error.

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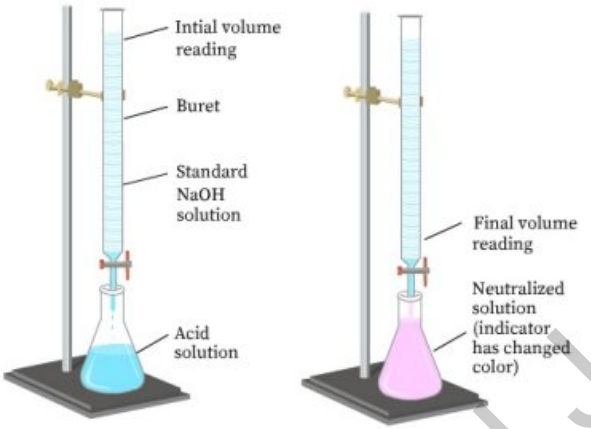

Figure 7.11 Titration

A systematic error can be estimated and eliminated but there is always some uncertainty in every physical measurement and mostly avoided.

Random errors are also known as indeterminate error and caused by variations of procedure, environmental factors and limitations of instrumentation. Random error are unavoidable and may be positive and negative. Measuring a mass of a sample on analytical balance may produce different reading due to effect of air or water on sample or analytical balance.

For example: in acid base titration we are using 50cm^3 burette we can read accurately only to nearest 0.1cm^3. as we discuss random error may be positive and negative and cannot be eliminated from experiment due to this reason we take many reading and average them.

7.2.2 Accuracy

The accuracy of analytical method is the closeness of obtained value to the true value of a sample, for example if you obtain weight 2.5mg of sample or substance but actual or known weight of sample is 10mg then your measurement is not accurate. Accuracy is the most difficult parameter to validate. Accuracy is degree of agreement between the measured value and true value. An absolute true value is very rarely obtained due to this more realistic definition of accuracy is an agreement between a measured value and the accepted true value.

Always remember that accuracy is not dependent on precisions. for example when measuring the density of copper and its true value is 8.99 g/ml and results of measurement are 10.0, 8.0 and 9.3 g/ml and their average is 9.1g/ml which is nearest accepted value and consider as accurate value.

7.2.3 Precision

The Precision is defined as the degree of agreement between replicate measurements of the same quantity. It is repeatability of a result and known as degree of exactness. Precision is measured how much detailed information is given and how much exactly measurement was taken.

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A measurement can be precise but not accurate, accurate but not precise, neither or both. A measurement system is valid if it is both precise and accurate.

For example four students are performing an experiment to measure the density of aluminum (2.7g/ml) and note down the following data which shows different aspects of precision and accuracy, such as measurement of student number 1 is precise because 2.9 is repeating overall but not accurate because it is not closest to true value. Measurement of student number 2 is not precise and not accurate because values are not closest to true value and not repeatable .In the same manner measurement of student number 3 is not precise but accurate due to closeness of measurement with true value ,while measurement of student number 4 is precise and accurate which may consider a valid measurement system.

Student 1	Student 2	Student 3	Student 4
2.924 g/ml	2.316 g/ml	2.649 g/ml	2.701 g/ml
2.923 g/ml	2.527 g/ml	2.731 g/ml	2.699 g/ml
2.925 g/ml	2.941 g/ml	2.695 g/ml	2.702 g/ml
2.926 g/ml	2.136 g/ml	2.742 g/ml	2.698 g/ml
Precise	Not Precise	Not Precise	Precise
Not accurate	Not accurate	Accurate	Accurate

The above example shows that good precision does not assure good accuracy but a valid measurement system needs good precision as well as accuracy.

Test Yourself

- Prove that improper functioning of acid base titration is a systematic error?
- Distinguish between accuracy and precision?

7.3 Classical Method

The classical methods are the fundamental laboratory practicing techniques. It is a traditional method of chemical analysis and also known as wet chemical method. Classical methods are those analytical techniques which does not use any mechanical or electronic instrument rather than weighing balance. This method basically related with the chemical reactions between analyte and reagents.

The classical methods posses' qualititative as well as quantitative analysis. Such as chemical and flame tests are qualitative and titrimatic and gravimetric analysis are quantitative analysis.

7.3.1 Titrimetric Analysis

The titrimetric analysis is used to determine the volume of a solution with known concentration which react with the measured volume of solution of a substance quantitatively .The Titrimetric analysis is also known as volumetric analysis in which general rule of titration is applied in which volumetric measurement of a reagent takes

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place which is known as titrant and this titrant complete its chemical reaction with analyte .The general chemical reaction for titrimetric analysis is as follows

$$aA + tT \longrightarrow \text{Product}$$

Where **a** is number of moles of analyte **A** contain in the sample reacts with **t** moles of the titrant **T** in the titrrant solution and this process is known as Titration. This reaction is carried out in a flask containing dissolved analyte while burette contains titrant solution which volumetrically delivered to the flask for reaction .The Titration is complete when sufficient amount of titrant added with analyte for chemical reaction and an equivalance point reached. An indicator is also added in flask to show the end point of whole reaction. We can also define Titration as

The comparison of volume of a solution of known concentration with the volume of solution of unknown concentration is called Titration.

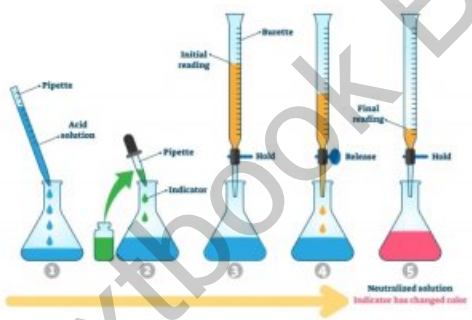

Figure 7.12 Titration

7.3.2 Gravimetric Analysis

Gravimetric analysis is the oldest and important technique for quantitative estimation in chemical analysis .This technique involve determination of constituent by weight, it is one of the most accurate analytical method for quantitative estimation. In this analysis an amount of analyte is determined by converting the analyte to some product and then weighing it. For example you want to determine the amount of chlorine (Cl) present in solution of AgCl then you have to go through following 4 steps for gravimetric analysis.

(1) Preparation of a solution with known weight of sample (AgCl).
(2) Separation of the desired constituent (Cl).
(3) Weighing Separated constituent.
(4) Computation of amount of separated constituent in the sample.

Do You Know?

What is titrant?

A titrant is a solution of known concentration that is added to another solution to determine the concentration of a second chemical species.for example NaOH ,HCl

What is analyte?

A chemical substance that is subject of chemical analysis or constituent going to be measure. For example 24 karat gold, NaCl , water etc

What is indicator?

Indicator is a substance which change the color with acidic and alkaline solution.

Eg:Litmus, Phenolphthalein, Methyl orange

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The gravimetric calculation based on gravimetric factor which convert the grams of the compound in to grams of the single element.
There are four types of gravimetric analysis which are Physical, Thermo, Precompetitive and Electro gravimetric analysis.

Test Yourself

- Explain Titration and which apparatus used in it?
- Explore Why we use indicator in titration?
- List down the steps of gravimetric analysis.

7.4 Advanced Instrumental Methods

Analytical chemistry consists of many advanced methods , which involves use of instrument for analysis and separation of mixtures and compounds. The methods used as quantitative and qualitative analysis .These analytical advanced instrumental methods includes spectroscopy ,chromatography , electrochemical methods ,ultra violet and visible spectroscopy, infrared spectroscopy ,HPLC, gas chromatography, potentiomatric and conductometry. We will discuss these advanced instrumental methods in this chapter in detail.

7.4.1 Spectroscopic Methods

Spectroscopy is the interaction of light with matter. light is composed of electromagnetic waves so interaction of matter with radiative energy as function of wavelength or frequency is called spectroscopy. Spectroscopy used in physical and analytical chemistry for the identification of substances through the emission or absorption spectrum. Interaction of light with matter is shown in figure:

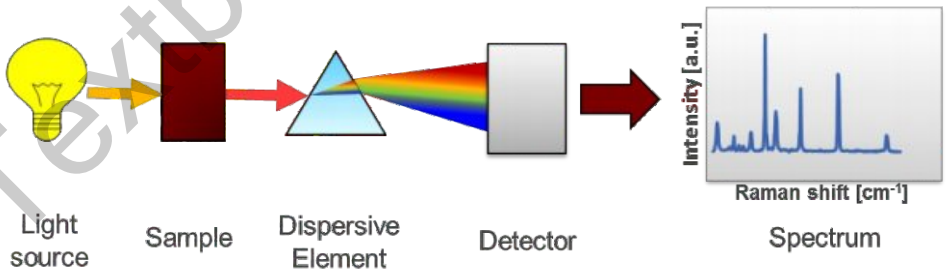

Figure 7.13 Spectroscopic methods

The spectroscopy used to assess concentration or amount of given chemical (atomic, molecular or ionic) and the instruments used for measurement are called spectrometer, spectrophotometer, spectrograph. There are a large number of atomic and molecular spectroscopic methods which depends upon the emission and absorption spectrum , but here we will discuss two main spectroscopic methods of ultraviolet and infrared spectroscopic methods in detail.

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7.4.1.1 Ultraviolet and visible spectroscopy

The ultraviolet and visible spectroscopy is also known as electronic spectroscopy. It is a quantitative technique which measure how much a chemical compound absorb light. This is done by measuring the intensity of light passing through the sample .The basic principal of this spectroscopy is interaction between light and matter but here light wavelength is ultraviolet and process is formation of spectrum due to absorption of ultra violet light to the chemical compound or sample.

The wavelength range of ultraviolet and visible spectroscopy is 192 to 900nm.

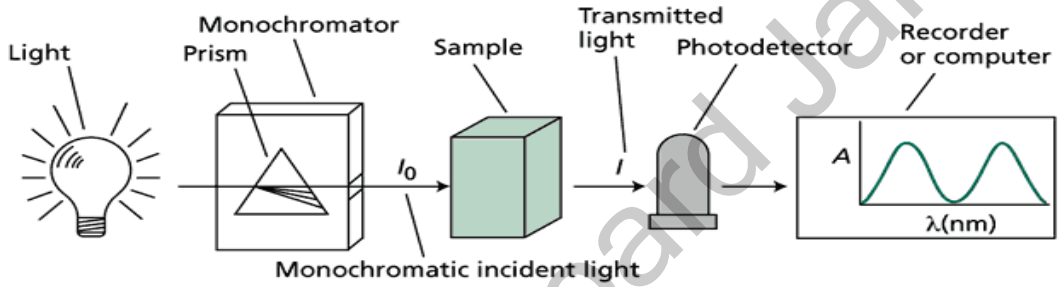

Figure 7.14 Ultraviolet and visible spectroscopy

7.4.1.2 Infrared Spectroscopy

The Infrared spectroscopy is analytical technique introduced in 1950, which qualify and quantify the information about samples in less time and cost effective .it is non hazardous because no any polluting chemical is required for this analysis. It is basically used for specification of functional groups in food products, polymers and industries now a days. It is an effective tool for quality control in different industries.

Electromagnetic radiations lower in energy than visible radiations are called infra- red radiation. The ordinary IR region extends from 2.5 μm(wavelength)to 15 μm(wavelength) or 4000 to 625 cm^{-1} (wave number).

When IR radiations passed through an organic molecule, the energy absorbed by the molecule is sufficient to produce vibrations in the molecules and the energy which is not absorbed is transmitted through the sample .It is also known as Vibrational spectroscopy.

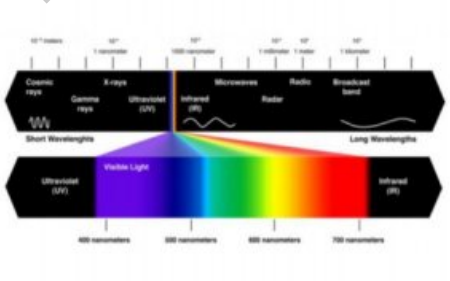

Figure 7.15 Spectrum

Figure 7.16 Spectrophotometer

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7.4.2 Chromatographic Methods

Chromatography is the modern analytical technique which is used for separation of compounds . It also facilitate the purification ,isolation and comparision of components of mixture.It may be employed with all kinds of Voltile and soluble substance,organic and inorganic , polar and non polar etc.

Chromatography process starts with the mobile phase in which solutes are dissolved in substance and carry to next stationary phase. The different components of mixture travel from mobile to stationary phase with different speed and retention time.

The main types of chromatography are gas chromatography and liquid chromatography which are discussed below with detail of advanced instruments of chromatography.

7.4.2.1 High Performance Liquid Chromatography (HPLC)

What is HPLC?

The HPLC stands for high performance liquid chromatography, sometimes it also consider as high pressure liquid chromatography. It is the technique to separate out the substances. HPLC instrument is consisting of reservoir of mobile phase, a pump, an Injector, a separation column, a detector and data acquisition computer .The mobile liquid phase is pumped through the column packed with the absorbent, hence separation becomes more rapid. The pressure mechanical pump ensures the rapid solvent flow. The flow rate of solvent affects the resolution of sample components. As each component passes through the column, the detector notes its elution and gives signal to the recorder.

Do You Know?

What is mobile phase ?

Moving fluid stream of liquid containing sample up to stationary phase is called mobile phase .

What is stationary phase?

Stationary phase is not moveable.

What is retention time ?

The time taken for separation of components in compound from start to the elution or exit is called retention time. this retention time helps to identify the components of compounds.

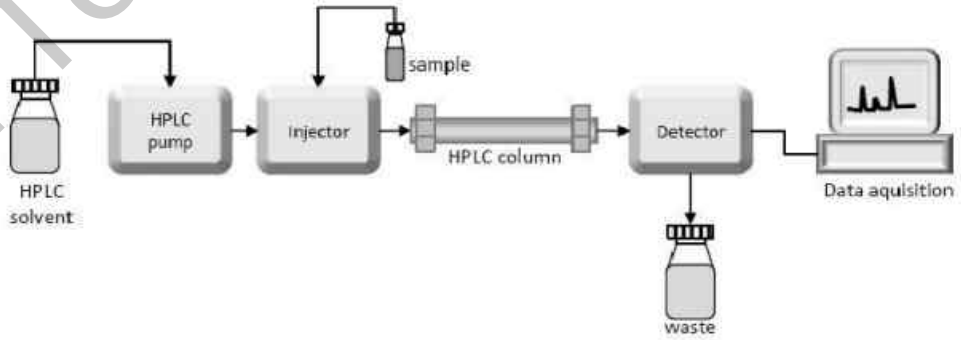

Figure 7.17 HPLC

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These instruments are used in drug discovery, clinical analysis, cosmetic analysis, pharmaceutical, enviormental chemistry and biochemical genetics.

7.4.2.2 Gas Chromatography

What is Gas Chromatography?

A gas chromatography is a technique used in analytical chemistry for the separation of volatile compounds. The word gas chromatography is clear from its word that it is used for the separation of gases and volatile liquids in gaseous state.

The separation takes place by the exchange between a mobile gas phase and a liquid or solid stationary phase. The first gas chromatograph was introduced by noble prize winner John Porter Martin in 1950 and considered as father of modern gas chromatography.

Do You Know?

What are volatile compounds? Volatile compound are those organic compounds which have high vapor pressure and low water solubility and emits gases from certain solids and liquids. such as benzene, formaldehyde, xylene, toluene

The instrument of Gas chromatography is consisting of Gas cylinder, sample injector, Gas chromatograph, detector and data collection device. Where Gas is mobile phase and Gas cylinder controls the gas passage up to sample injector, which proceeds toward two columned gas chromatograph it is a stationary phase with uniform temperature. When compound reach the detector it detect the elution and send signals to data collection device (computer).

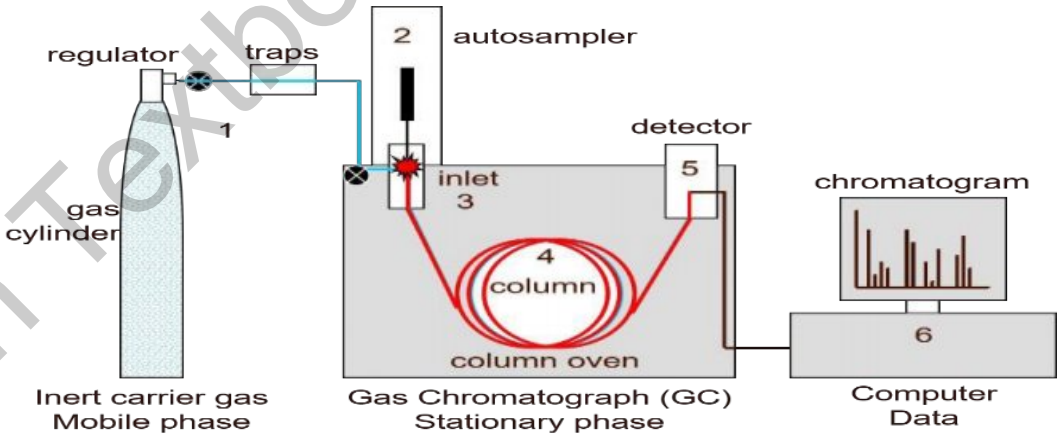

Figure 7.18 Gas chromatography

The gas chromatography used in analysis of inorganic compound, carbohydrates, proteins, lipids, vitamins, pollutants like benzene, plastic materials and dairy product.

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7.4.3 Electrochemical Methods

The electrochemical method is an analytical technique which deal with measurement of potential, charge, electrical quantity or property of a solution .the measurement carried out by the use of certain instrument due to this known as advanced instrumental methods. These methods are useful because of consuming less time and without any suitable indicators.

The electrochemical analytical method is carried out with the help of electrochemical cell which is shown in the following figure, generally it consist of electrodes named as anode and cathode. Anode posses negative sign due to liberation of electrons in oxidation reaction and cathode posses positive sign due to consumption of electrons in reduction reaction.

The electrochemical cells consists of two half cells, both are connected with an electrode (anode and Cathode) and each electrode is dipped in electrolytic solution which is $ZnSO_4$ at Anode and $CuSO_4$ at cathode.

The half cells are connected by means of salt bridge (NaCl) which provides a platform for ionic connectivity without mixing, as we discuss that one of half cell losses electron due to oxidation and other half gains electrons in reduction process. Always remember that when equilibrium phase comes in both half cells the net voltage become zero and production of electricity by cell will stop.

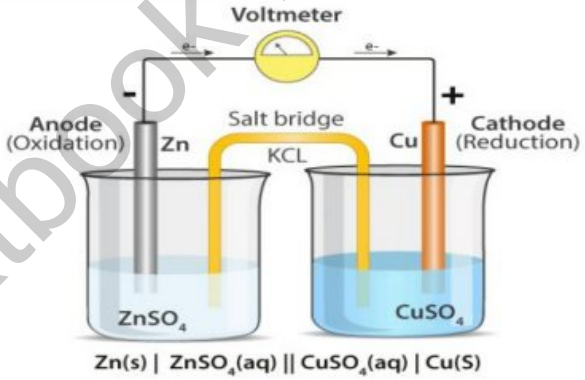

Figure 7.19 Electrochemical cell

7.4.3.1 Potentiometry

Potentiometry is method used in electroanalytical chemistry to find the concentration of solute in solution in potentiometric measurement. The potential between two electrodes is measured by voltmeter. There is no any flow of current.

Potentiometric analysis is used in analysis of pollutant in water, pharmaceutical and drugs, quality control in food industry and clinical chemistry.

Figure 7.20 The voltmeter

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7.4.3.2 Conductometry

Conductometry is one of the important analytical technique which is used in physico – chemical analysis. It can be defined as a technique of analysis which is based on the measurement of electrical conductance.
It is done by the help of conductivity meter.

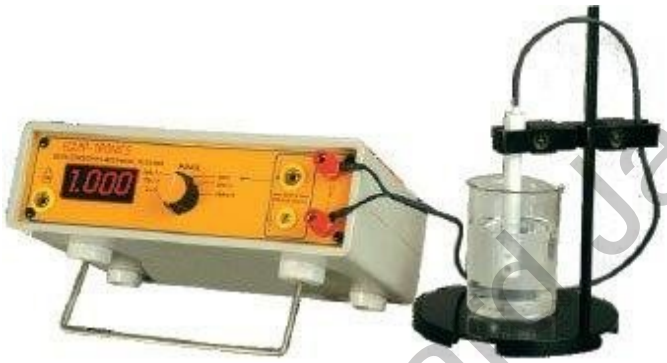

Figure 7.21 Conductometry

Applications of conductometry:

- Degree of dissociation constant can be determined.
- Solubility of a sparingly soluble salt can be determined.
- Rate constant of a reaction can be studied.
- End point of titration can be determined.

Distinguish Between Classical and Instrumental Methods

Classical Method	Instrumental Method
1. Procedure is simple and accurate. 2. Equipment needed is cheap. 3. Methods are based on absolute measurement. 4 Specialized training is not required. 5 Accuracy decreases by decreasing amount. 6 Determination is slow. 7 Large amount of sample is needed.	1 Procedure is sensitive and technical. 2 Equipment needed is expensive 3 Methods are based on reliable measurement. 4 Specialized training is required. 5 Accuracy depends upon instruments. 6 Determination is very fast. 7 Small amount of samples can be used.

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Summary

- The analysis and separation of sample to detect and estimate its components through various techniques and instruments is known as Analytical Chemistry.
- The analytical chemistry answer the basic questions of What, Where, How much about material.
- The Analytical Chemistry is applied in all fields of chemistry such as Medicine, Clinical laborites, industries, Agriculture, food contamination and environmental protection.
- The Analytical Chemistry is consisting of two types Qualitative Analysis and Quantitative Analysis.
- Qualitative analysis is concerned with identification of elements, ions or compounds present in sample and only measure quality, qualitative analysis subdivided in two inorganic qualitative analysis and organic qualitative analysis.
- Quantitative analysis is concerned with the estimation of amount of a chemical substance present either alone or in a simple or complex mixture of other substances. quantitative analysis subdivided in physical quantitative analysis and chemical quantitative analysis.
- Error is a numerical difference between observed value and true value. Errors are classified as systematic and random errors.
- The accuracy of analytical method is the closeness of obtained value to the true value of a sample.
- Precision is defined as the degree of agreement between replicate measurements of the same quantity.
- The classical methods posses' qualititative as well as quantitative analysis. Such as chemical and flame tests are qualitative and titrimatic and gravimetric analysis are quantitative analysis.
- Instrumental methods includes spectroscopy ,chromatography , electrochemical methods ,ultra violet and visible spectroscopy ,infra red spectroscopy ,HPLC, gas chromatography, potentiomatric and conductometry.

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Exercise

SECTION- A: MULTIPLE CHOICE QUESTIONS

1. Encircle the correct answer:

1. The Analytical Chemistry deals with instruments and methods to _____, identify and quantify the matter.
   (a) MIx (b) Separate (c) Differentiate (d) Manipulate
2. The sample may be solid, liquid, gas or a _____ in qualitative analysis.
   (a) Mixture (b) Compound (c) Substance (d) None of these
3. Analysis deals with the identification of presence of functional groups in compounds is.
   (a) Physical qualitative analysis (b) Analytical qualitative analysis
   (c) Organic qualitative analysis (d) Inorganic qualitative analysis
4. Flame test of Copper Halide with bluish-green color identify the presence of.
   (a) Halogen (b) Hydrogen (c) Copper (d) b and c
5. The physical methods used to measure physical properties is called
   (a) Combustion analysis method (b) Atomic emission spectroscopy method
   (c) Volumetric analysis method (d) Gravimetric analysis method
6. The error caused by improper functioning of instrument is:
   (a) Determinant Error (b) In determinant Error
   (c) Systematic Error (d) Both a & c
7. An agreement between a measured value and the accepted true value.
   (a) Error (b) Accuracy (c) Precision (d) All of these
8. Spectroscopy is the interaction of light with :
   (a) Liquid (b) Solid (c) Gas (d) Matter
9. The Gas is mobile phase in:
   (a) Liquid chromatography (b) Solid chromatography
   (c) Gas chromatography (d) None of these
10. It used to assess concentration or amount of given atomic, molecular or ionic chemical.
    (a) Chromatography (b) Spectroscopy
    (c) Conductometry (d) Potentiometry

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SECTION- B: SHORT QUESTIONS:

1. What do you think which method is faster classical or instrumental?
2. How will you compare the analytical techniques to one another?
3. Can you give some examples of error related to your life?
4. What do you mean by quantitative Analysis?
5. Discriminate which of the following collected volumes of a gas in gas preparation is accurate, precise or accurate and precise both or non of these?

32 cm^3 45 cm^3 17 cm^3 23 cm^3		32cm^3 33 cm^3 34 cm^3 35 cm^3	
32 cm^3 45 cm^3 45 cm^3 32 cm^3		32 cm^3 32 cm^3 33 cm^3 32 cm^3	

6. Why we use Potentiomatric Analysis in advance instrumental methods?
7. How scientists are using Infrared spectroscopy in quality control of different industries?
8. List down the applications of Conductometry?

SECTION- C: DETAILED QUESTIONS:

1. Distinguish between following:
   (a) Quantitative Analysis and Qualitative Analysis
   (b)Titrrametic Analysis and Gravimatric Analysis
2. Prove that instrumental analytical methods are more effective then classical analytical methods?
3. Describe Gas Chromatography in detail?
4. Justify that electrochemical methods depend upon Electrochemical Cells?

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