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BALVEER SHARMA

Author

BASICS OF ANALYTICAL CHEMISTRY

INTRODUCTION

Analytical Chemistry studies and uses instruments and methods to separate, identify and quantify materials. Analytical Chemistry is a branch of chemistry with interdisciplinary character. We know the importance of chemicals in our life. The foods, clothes and medicines and so on are made up of chemicals. We all know the importance of chemical analyses in all these products.

The development of chemical analytical methods lies in the discipline of analytical chemistry. Therefore, in this chapter we will learn about the analytical chemistry and its important and about different chemical methods of analysis like gravimetry and volumetry analyses,classification of electrical methods of analysis including potentiometry, amperometry, voltammetry, coulometry, etc. In the latter part of the chapter we have introduced optical method of analysis like emission, absorption, UV, IR, and Raman spectroscopic, nuclear and thermal methods of analysis briefly. Separation of the chemicals compounds is a very important part of analytical chemistry.

When a students of Chemistry see a material, two questions are raised in his mind: What is it? And how much? The answer of these questions is given by chemical analysis. In chemical analysis he is able to analysis compounds to see what and how much of a given chemical constituent they contain. However, before an analysis can be made, a method must be available.

In developing methods of analysis, the analytical chemists tried to use the principles of science like chemistry, physics, biology, biochemistry, geology, engineering and computers, etc. The constituents to be analysed may be elements, ions, radicals or functional groups molecules. Analytical Chemistry is thus concerned with the theory and practice of methods used to determine the composition of substances. Now days there is no material is taken into production or released without analytical data which characterize its quality and suitability for various uses and purposes. The

qualities of food materials and medicines, etc. need analytical results before to be used. These results not only form the basis of all processing calculations but they also determine the costs of materials, which form the basis of financial estimates. This makes an analytical laboratory as an important part of chemical industry.

The late 20th century (After 1970) witnessed an exciting phase in the development of new and improved analytical techniques which permit separation, detection, structure elucidation and quantification of much lower levels of chemical species, multi-component analysis and a much short duration required for analysis.

The analytical methods can be divided into- chemical method, physical method and physico-chemical methods. The chemical methods are the classical (Old) methods whereas the physical and physicochemical methods are known as instrumental methods or modern method of analysis.

The analytical technique should be based on the measurement of a property which is related to either the nature or the amount of the substance under evaluation. The analytical chemist must understand the relation between the properties to be measured and the nature and the quantity of the desired chemical species to be studied. The property which depends on the nature of the substance is helpful in qualitative analysis, whereas the property which depends on the amount of the substance is useful in quantitative analysis. Mostly a quantitative analysis is preceded by the qualitative analysis, while a qualitative analysis may give a rough idea of the relative amount of the constituents present in the sample. (The part of the material which is examined). In analytical chemistry we take

small samples to perform the chemical analysis and these results are taken as a measure of the results of whole material.

Before starting chemical analysis of a Sample, the analytical chemist select the most advantageous method available in the laboratory. For choosing a suitable technique, the analyst must know what type of samples is to be analysed, what information is needed and for what purpose. The way performing an analysis will depend on experience of Chemist, the equipment available and the preparation of the sample for analysis, the time and the cost involved. A chemist also choose an analytical method on the basis of accuracy, sensitivity and selectivity. While choosing an instrumental technique chemist should be aware that most instrumental methods are relative methods. Therefore, they must be calibrated with standards. Usually an analytical calibration curve of instrument response versus concentration or amount of the substance is prepared prior to analysis of unknown sample.

CLASSIFICATION OF DIFFERENT ANALYTICAL METHODS/TECHNIQUES

Analytical chemistry a branch of chemistry involves the development of methods for chemical analysis. These analytical methods depend on the measurement of some physical property. Physical properties which are characteristics of a particular substance or its constituent. These characteristics or constituents made the basis of an analytical technique. The analytical techniques can be classified on the basis of type of properties. These are –

A. Classical or Chemical methods of analysis

B. Electrical methods of analysis

C. Optical methods of analysis

D. Nuclear radiation methods of analysis

E. Thermal methods of analysis

F. Separation methods

These methods can further be classified into different techniques depending on the measurement of a characteristic property .This property is based on either the nature or the amount of the desired constituent of the sample.

A. CHEMICAL METHODS OF ANALYSIS OR CLASSICAL OR CHEMICAL METHODS OF ANALYSIS

The Chemical methods of analysis are based on the primary role of a chemical reaction. In these methods the direct measurement of mass is carried out either by weighing gravimetry or by measuring volume volumetry.

(i) Gravimetry or Gravimetric analysis: -

It means analysis by weight and pertains to all determinations wherein the final results are obtained by means of the analytical balance. Gravimetry is an accurate macro-analysis procedure which mainly depends upon precipitation of an ionic or molecular substance on the basis of a chemical reaction. The precipitate is then separated, dried and weighed. And amount of the desired constituent (analyte) is determined by simple calculation.

(ii) Volumetry or Volumetric analysis or Titrimetry:-

The amount of the analyte (Desired Constituent) can be found in another way by measurement of the volume. The Volumetry or Volumetric analysis is based on accurate measurement of volume of a reagent solution of known concentration, taken for a reaction.

The measurement of volume makes considerable saving of time. The greater speed of volumetric analysis is an important advantage of this method over gravimetry

The volumetric analysis is involves titration, hence the method is also known as titrimetry. In this analytical method, a known volume of the reactant substance is taken in a beaker and the titrant is added from a burette to it till the reactant completely reacts with the titrant (equivalence point) which is indicated by an indicator. The volume of the titrant required to reach the equivalence point is noted on the burette and the calculations are made to get the amount of the constituent of the reactant. The reaction for volumetry should be rapid, so that, practically speaking, zero time will be needed after each volume addition of titrant for the reaction to reach equilibrium.

B. ELECTRICAL METHODS OR ELECTROANALYTICAL METHODS OF ANALYSIS: -

An electrical method or electroanalytical method can be defined as one, in which an electrochemical property of a solution is measured. A classification of electroanalytical methods based on different electrical quantities, such as, potential, current, quantity of current, resistance and dielectric constant. These methods have different names on the basis of the measurement of these quantities such as.

(i) Potentiometry (Potential measurement): -

Analytical methods based on the measurement of potential difference across an electrochemical cell to interpret the results of an analysis are designated by the term potentiometry. The term potentiometry is derived from the word "potential" which is half-cell potential (electrode potential) obtained by measuring voltage across an electrochemical cell with the help of a standard electrode. The result of the analysis can be computed directly from the voltage of the cell, or the equivalence point of a titration known as potentiometric titration. In potentiometric titrations we discuss redox titration curves based on half-cell potentials and describe the necessary procedures to obtain the sample analyte in the correct oxidation state for titrations

A special group of potentiometry where the potential of an indicator electrode is measured as a function of hydrogen ion concentration is designated as pH-metry. By suitably modifying the common voltmeter to high impedance mV meter and usually making use of a glass electrode as a hydrogen ion indicator electrode suitable pH- meters can be designed to measure phi instantaneously.

(ii) Amperometry (Current Measurement): -

Amperometry involve current measurements. The unit of current is Ampere. Amperometric methods are generally applied to the determination of equivalence point of titration and method is known as amperometric titration which involves one microelectrode as an indicator electrode (which is also polarized electrode the other electrode is the reference electrode and is non-polarized). Here the current at a fixed potential is measured as a function of titrant volume. On plotting the data two straight lines with different slopes are obtained on both the sides of equivalence point.

The modified amperometric titration involves the use of two polarized microelectrodes and is known as biamperometry or the dead stop end point titration. Here the two identical microelectrodes are immersed in a well stirred solution of the sample. A small potential is applied between these electrodes and the current is measured as a function of the volume of the titrant added.

(iii) Voltammetry: -

In voltammetry current is measured at varied potentials. In voltammetry an electroactive matter is consumed oxidized or reduced only at the surface layer of the indicator electrode in an electrolytic cell. The resulting current. (Due to electron transfer process) is measured as a function of applied potential. The current versus potential curves (current voltage curves or current-potential curves or I-E curves). The shape of this curves depends on the polarization of the indicator electrode, are plotted whereas the other electrode (reference electrode) remains non-polarized. In voltammetry we study the relationship between the current and electrode potential and its application to chemical analysis.

When a special type of micro electrode, (dropping mercury electrode) is used as the indicator electrode the technique is known as polarography. A continuous changing potential is applied across the dropping mercury electrode and the reference electrode and the resulting current is monitored by a current measuring device. The current- potential curves are known as polarograms or polarographic waves. The half wave potential (E) of a polarographic wave can be a useful for qualitative identification whereas the height of the wave is used for quantitative estimation of the particular species. A recent development in polarography has been made by the use of three electrodes. This modification makes it

possible to obtain polarographic waves from non-aqueous solvents that have low electrical conductivities.

(iv) Coulometry: -

In coulometry the current is used to oxidize or reduce only the analyte. Analytical methods based on the measurement of the quantity of electricity are known as Coulometry. "Coulomb", which is one of the units used for quantity of current. A fundamental requirement of all coulometric methods is that the substances determined interacts with 100% current efficiency.

Coulometry is performed by following two techniques: -

(a) coulometry at constant potential, known as potentiostatic coulometry.

In this coulometry the potential at the working electrode (the electrode at which the analytical reaction occurs) is maintained at a controlled level. Here current is initially high and decreases exponentially with time.

(b) Coulometry at constant current known as amperostatic coulometry. In the coulometry at constant current, a constant current is operated for a time until a signal indicates the completion of the analytical reaction. These methods are called as coulometric titrations.

(v) Conductometry and High Frequency Methods: -

1.Conductometry methods: -

The measurement of conductance (the reciprocal of the resistance) can sometimes be useful in chemical analysis. conductometry based on electrical conductance measurements. Conductometry is performed in two different ways: in one an analysis can be computed directly from conductance measurements and in other conductometry is applied to the

determination of the equivalence point of titrations (conductometric titrations). Conductometric titrations where the change in conductance is related to concentration changes of the ionic species involved in the titration reaction are more frequently applied. In conductometry conductances are generally measured by using alternating current of 3-6 volts with frequency of 50-1000 Hz. The technique has the advantage of and good sensitivity

2.High frequency method: -

In conventional conductometric method conductance measurement are made by using alternating current at relatively low frequencies (50-1000 Hz) The technique can be modified by using much higher frequencies (several mega Hz) and the methods are called as high frequency methods. These methods can be applied to the measurement of dielectric constant and also for several titrations where the electrodes do not come in the intimate contact of the solution.

(C) OPTICAL METHODS OR SPECTROSCOPIC METHODS OF ANALYSIS: -

In these methods, the first instruments were developed for use of visible region and therefore called optical methods. All spectroscopic methods are based on the interaction of electromagnetic radiation with the quantized energy states of the matter. Here we study the measurement of a quantity based on emission, absorption, scattering or change in some property of electromagnetic radiation (emr) depending on the nature or applications lies in the amount of the constituent of the sample. The classification may be based on either to qualitative and the type of effect (emission, absorption or scattering) or the type of the emr (x-ray, UV-vis, IR etc.) used. The important spectroscopic methods are mentioned below.

(i) Emission Spectroscopy: -

It is the method in which the characteristic spectrum produced by excitation of elements is applied to qualitative and quantitative analysis. The spectroscopy depends on the electromagnetic radiation produce when the analyte is excited by thermal, electrical or radiant energy. Each element has a characteristic emission spectrum, this is applied to qualitative analysis. Quantitative determinations are also solid particles are possible, as during the burning of the sample under controlled conditions the energy emitted for a given spectral line of an element is proportional to the number of atoms that are excited and consequently to the concentration of element in the sample.

(ii) Absorption Spectrometry: -

It is based on the measurement of the absorption of electromagnetic radiation (a process by which a chemical species in a transparent medium selectively absorbs the photons of certain precise methods are electromagnetic radiation) by matter the absorption varies with the wavelength of incident radiation. Measurement of absorption can be made at single wavelength range of wavelengths. When the selection of a narrow wavelength range is made with Raman spectroscopy the help of filters the analytical technique is known as filter photometry and When the measurements are made for approximately monochromatic radiation obtained with the help of a monochromator (such as: prism or grating) the technique is known as spectrophotometry or absorption spectrometry.

(iii) Ultraviolet and Visible Absorption Spectroscopy: -

These methods of chemical analysis involve the measurement of absorption of ultraviolet and visible radiation (wavelength ranges from 180

to 780 nm) by an atomic, lonic, or molecular species are known as ultra violet and visible spectroscopic methods. Ultraviolet and Visible spectroscopy involves transitions between electronic levels of absorbing chemical species and used for qualitative as well as quantitative analysis. For qualitative analysis uv-visible spectra provide a valuable tool in the identification of unsaturated organic compounds and elucidation of their structure. However, these methods particularly in the visible range are mainly used for quantitative analysis of substances of different categories.

(iv) Infrared Absorption Spectroscopy: -

This spectroscopy involves the absorption of infrared radiation (wavelength range from 0.78 to 1000 um) depending on increasing the energy of vibration or rotation associated with a covalent bond, provided that such an increase results in a change in the dipole moment of the molecule. Infrared spectroscopy (IR spectroscopy) can further be subdivided into near IR, middle IR and far IR spectroscopy. Majority of applications lies in the middle IR region. IR spectroscopy widely used for qualitative and quantitative analyses.

(v) Fluorophotometry: -

It is the measurement of the intensity of fluorescence.The energy of the photons of incident radiation absorbed and changes the absorbing species to excited state. Certain chemical substances (known as photoluminescent) after excitation can re-emit radiation. Re-emission of radiation can be immediately ($<10^{-8}$ sec) after the absorption and is known as fluorescence. The fluorescence intensity is practically proportional to the concentration of fluorescent substance.

When re-emission of radiation takes longer time (ranges minutes to days) the phenomenon is known as phosphorescence and the related technique as phosphorimetry.

(vi) Turbidimetry and Nephelometry: -

In turbidimetry method determinations are made by measuring opacity of suspension of small particles with the help of measuring intensity of transmitted light.

In Nephelometry method is based on the measurement of intensity of light scattered by a suspension of small particles.

These methods are applied to determine the concentrations of suspensions where small solid particles are homogeneously dispersed in the liquid medium.Turbidimetric and nephelometric methods frequently give erratic results, therefore these methods are applied only when the results need not to be very accurate and other precise methods are not available.

(vii) Raman Spectroscopy: -

This method of chemical analysis involves the scattering of electromagnetic radiation by a liquid (solution) following Raman effect (scattering with change of wavelength). The shift in wavelength in Raman effect is caused due to extraction of energy from the quanta of incident radiation and utilize to raise molecules to higher vibrational state. The scattered radiation thus has less energy and higher wavelength. Raman and infrared are complimentary to each other. An important advantage of Raman spectra over IR spectra lies in the fact that water does not interfere in Raman spectroscopy and aqueous solutions can be handled very well.

Other optical methods, such as flame photometry, refractometry, polarimetry are not considered due to their less importance.

(D) NUCLEAR METHODS: -

This analytical method provide analytical information based on nuclear properties. Nuclear method is of following types: -

Nuclear Methods of Analysis

Sr.No.	Name of the method	Property measured	Mechanism involved
1.	Radiochemical methods	Radioactivity	Radioactive disintegration of radioisotopes can be measured with high sensitivity and specificity.
2.	Mossbauer spectroscopy	Rasonance absorption of Y-rays	Resonance fluorescence of y-rays and involves intranuclear energy levels.
3.	Nuclear magnetic rasonance spectroscopy	Position of signals (chemical shift) and their intensity in NMR spectrum	Interaction of quantized nuclear spin with an applied magnetic field
4.	Mass spectrometry	Position and intensity of signals of mass spectrum	Mass to charge ratio of ionized atoms or molecules

(i) Radiochemical Methods: -

This is method measured radioactivity and mechanism involved is radioactive disintegration of radio isotopes can be measured with high sensitivity and specificity. Very small amounts of radioactive substances (natural or artificial radioactive isotopes) having measurable activity, makes the development of sensitive analytical methods known as radiochemical methods. Radiochemical methods are classified into three categories, namely radiometric analysis, isotopic dilution methods and

activation analysis. All these methods have high sensitivity, specificity and good accuracy.

(ii) Radiometric Methods: -

In this methods a radioactive reagent is employed to separate the analyte completely from the bulk of the sample.

The activity of the isolated material is then measured. In an alternate way when a radioactive reagent is used to titrate the analyte and the end point is established process by the measurements is known as radiometric titration.

(b) Isotopic Dilution Methods: -

In an isotopic dilution method a known amount of the same substance containing an active isotope is added to the unknown sample and thoroughly mixed with it. A sample of the pure substance is then isolated from the mixture and its activity is measured. The quantity of the substance in original material is then determined by simple calculation. The technique is suitable for compound isolating in pure state. This method has the advantage of not requiring quantitative separation of the analyte.

(c) Activation Analysis: -

This methods of analysis are based upon the measurement of radioactivity induced in the samples by irradiation with suitable particles such as neutrons, protons, deutrons or helium-3 ions. The thermal neutrons from a nuclear reactor are the most commonly used particles and this technique is known as neutron activation analysis.

(ii) Mossbauer Spectroscopy:

This analytical methods based on the study of the phenomenon of the resonance fluorescence of gamma rays. It measure resonance absorption of Y (gamma)-rays. It involves intranuclear energy levels. An important characteristic of this radiation is the extreme sharpness of lines.

(iii) Nuclear Magnetic Resonance (NMR) Spectroscopy: -

NMR method of chemical analysis is based upon the measurement of absorption of electromagnetic radiation in radiofrequency region by nuclei of atoms of certain elements (isotopes) in the influence of strong magnetic fields. Since a nucleus bears a charge its spin gives rise to a magnetic field, the resulting magnetic dipole is oriented along the axis of spin and has value based on the nature of the nucleus. In this process certain atomic nuclei on exposure to a magnetic field would lead to splitting of their energy levels. The position of the signals of NMR spectra is characterized in terms of chemical shift which is very useful in structure elucidation. Electron spin resonance (ESR) an analogous method to the NMR spectroscopy is based upon the absorption of microwave radiation by an unpaired electron when it is exposed to a magnetic field.

(iv) Mass Spectrometry: -

Mass spectrometry is a method based on the study converting molecules into charged particles (molecular ions). The separation of charged particles is takes place on the basis of mass to charge ratio and measurement of the relative intensity of lines of mass spectrum. The instrument used is a mass spectrometer which separates the charged gas molecules (ions) according to their masses.

Mass spectrometry provides qualitative and quantitative information about either the atomic or the molecular composition of the sample.

It is an important tool for explaining the structure of organic compounds.

(E) THERMAL METHODS OF ANALYSIS: -

In thermal methods of Chemical Analysis some property of the system is measured as a function of temperature. In some of these methods the temperature is used as an independent variable while in some others as a dependent variable. The recorded curves are helpful in interpreting the thermal behaviour of the sample. Thermal methods are grouped into many varieties. Out of these some important and commonly used methods are:

(i) Thermogravimetric Analysis (TGA): -

It involves the measurement of mass of sample as its temperature is increased at a linear rate. In this method a suitable solid sample undergoes reaction as **Reactant(r)→ Product(p) + Gas↑** causing a loss of mass due to gas being evolved. Plot of mass versus temperature known as thermogram determine the thermal stabilities and sample compositions at different temperature.

(ii) Derivative Thermogravimetry (DTG): -

This chemical analysis is carried out by the plot of first derivative of thermogram. In DTG a plot is prepared in dw/dT versus T. In DTG curves the changes are observed in the form of maxima or minima which make the weight changes very clear even those which are not so clear in thermograms,

(iii) Differential Thermal Analysis (DTA): -

In this chemical analysis the difference in temperature between sample and reference is measured as a function of temperature. From the plot of AT versus T. the transition temperature and the nature of the change (exothermic or endothermic) can be determined.

(iv) Differential Scanning Calorimetry (DSC): -

In this type of chemical analysis, the sample and the reference material are subjected to precisely programmed temperature change. When a

thermal transition occurs in the sample, the temperature changed in balanced by adding thermal energy to either the sample or the reference. DSC can measure directly both the temperature and enthalpy of a transition.

(iv) Thermometric Enthalpy Titrations (TET): -

In the thermochemical methods of chemical analysis where a titration process is followed by the measurement of enthalpy change during the course of a reaction carried out under controlled conditions usually in a small Dewar flask.

Property measured and instrument used for Thermal methods are given in Following tabular form

Sr.No.	Name of sub method of Thermal the method	Property measured	As a function of	Instrument
1.	Thermogravimetric Analysis (TGA)	Change in weight	Temp	Thermobalance

2.	Derivative thermo-gravimetry (DTG)	Rate of change in weight	Temp	Thermobalance
3.	Differential Thermal Analysis (DTA)	Heat absorbed or evolved	Temp	DTA apparatus
4.	Differential Scanning Calorimetry (DSC)	Thermal Transition	Temp change	DSC cell
5.	Thermometric Enthalpy Titrations (TET)	Temp change	Volume of titrant	Titration calorimeter

(F) SEPARATION METHODS

A substance which is free from interfering substances. However, in natural samples interfering substances are present. Due to this reason a few methods may be specific or even selective and accuracy in determinations by most methods are affected by the interfering substances. It is, therefore, frequently necessary to perform quantitative separations with the objective either for isolation of the analyte or to remove the interfering substances. Therefore, separation is a prerequisite procedure for such determinations. Though separation is not a purely analytical technique but it is commonly required prior to many analyses.

The separation method of chemical analysis falls under two categories which are -

(1) Classical methods or Old method includes

(a) Precipitation, (b) Distillation, (c) Sublimation and (d) Formation of complexes

We are well aware about the classical methods and only the modern methods will be discussed here briefly.

(2) Modern methods include following Separation methods: -

(a) Chromatography: -

This method of separation process in which the sample is applied on a stationary phase over which a mobile phase is percolated. Various solutes present in the sample are separated on the basis of differential migration Chromatography can be classified into various kinds depending on the nature of stationary and mobile phases and the mechanism of distribution involved. These are (i) Liquid Chromatography, (ii) Partition Chromatography, (iii) Thin-Layer Chromatography, (iv) Paper Chromatography, (v) High Performance Liquid Chromatography or High-Pressure Liquid Chromatography (HPLC), (vi) Gas Chromatography (GC), (vii) Gel Chromatography, (viii) Electro Chromatography, (ix) Ion Exchange Chromatography, (x) Adsorption Chromatography etc.

Chromatography has been used in the separations of inorganic, organic and biochemical substances. The separations of vitamins, hormones, natural pigments, fission products of uranium and steroids etc. are some examples of its scope and success.

(b) Solvent Extraction: -

In this method a desired solute can be isolated/extracted by distributing it between two immiscible liquids. It exploits the differential solubility of a given solute in two immiscible solvents to separate it from the given mixture. Solvent extraction can be applied as a single stage procedure or a multistage procedure called counter current extraction.

(c) Ion Exchange: -

This method involves using relationship between reactants and / or products in a chemical reaction to determine desired quantitative data. Ion exchange is a stoichiometric process in which a solid (insoluble) material (ion exchanger) when comes in contact with an electrolyte solution takes either positive or negative counter ions and releases the ions of like charge (to maintain the stoichiometry) to the solution. The solid materials having cations as exchangeable ions are known as cation exchangers and having anions as exchangeable ions are known as anion exchangers. Ion exchange is a reversible process. The exchanged ions can be replaced by other ions of like charge. Ion exchangers find great utility in separating the ionic species of similar nature. Some separations of common interest are of rare earth elements and of amino acids.

(d) Electrophoresis: -

In this method, the movement of charged particles in the influence of an electric field takes place. If the components of a mixture have different velocities under the influence of the electric field, it is possible to separate them. This method has been used for the separation and characterization of polysaccharides, nucleic acids, hemoglobin and other high molecular weight compounds. Small organic and inorganic ions discipline with in can also be separated with the help of this technique ionophoresis.

BASIC PROCESS OF ANALYTICAL TECHNIQUES

Analytical chemistry is deals with the development of methods for chemical analysis which are utilized in detection, determination and separation of chemical constituents and structural explanation of chemical compounds. For example, the chemical formula of an unknown substance

is determined from the percentage contents of its constituents found by analysis. Now a days, with the help of newer techniques, like mass spectrometry, NMR spectroscopy, high performance liquid chromatography, etc., the structure determination has become more perfect.

Utility of analytical techniques is to be found in various fields of a variety of scientific problems and of industrial problems. Analytical Chemistry provides valuable information in many branches of science and technology. Mechanisms in so many chemical reactions has been thought through kinetic studies employing quantitative measurements of the rate at which reactants are consumed or products are formed.

The results of a quantitative analysis are based on for said two series of measurements. One of which is related to the amount of sample taken for the chemical analysis. And the second to the relative amount of the desired constituent present in the taken sample. On the basis of the amount of the sample taken, the methods are known as macro- meso- micro- and ultramicro methods. On the basis of the relative amount of the desired constituent, the results take the form of numerical data in suitable units such as percent, parts per million (ppm), parts per billion (ppb) or in some other form.

In order to understand the criteria for assessment the utility of the analytical techniques it is useful to identify the several steps in performing quantitative analysis. A complete analysis consists of the following main steps:

1. Sampling:-

The central point of the quantitative analysis is to obtain a sample with great care through a number of manipulations without accidental losses and without introducing foreign material, since the sample is representative of all components and their amounts as contained in the bulk a knowledge of statistics is of considerable importance to establishing sampling programmes. So that data obtained may be subjected to statistical treatment when necessary.

Sampling techniques are based on different in different cases. Each type of material has its own special sampling instructions which take into account the specific characteristics of the material such as the quantity taken, purpose, etc.

2. Dissolution of the Sample: -

Most analysis are performed on solutions of the sample. So that suitable solvent required to dissolve the sample rapidly and under conditions in which there is no loss of the analyte. The dissolution process depends on the nature of the sample material.

There are two methods employed in dissolving inorganic sample are (1) treatment with hydrochloric acid, nitric acid, mixture of hydrochloric (HCl) acid and nitric acids (HNO_3) , sulphuric acid (H_2SO_4) or perchloric acid, and (2) fusion with an acidic or basic flux followed by treatment with water or an acid.

Organic solvents are preferentially taken to dissolve the samples of organic nature. There are special methods for dissolving a silicate material, polymer or a sample of animal tissue.

3. Separation of Interfering Substances: -

The interfering substances are the chemicals compounds or elements which prevent the direct measurement of the sample being determined. So that, before an analytical measurement it is usually necessary to solve the problem of interference by their separation from the analyte.

There are two methods to achieve separation-

(i) by isolating the desired constituent in a measurable form

(ii) by removing the interfering substances from the desired constituent.

In the separation techniques the sample is transferred from one phase to another with few exceptions. Therefore, the separation procedures can be classified on basis of the type of phases involved in these procedures. There may be four such combinations are recognized (i) Solid-Liquid, (ii) Liquid-Liquid, (iii) Solid-Gas and (iv) Liquid-Gas.

4. Measurement: -

The way of measurement depends upon the type of analytical technique which will be used. A gravimetric method involves the measurement of weight of a suitable form of the analyte. In a volumetric method, the measurement of the volume of a solution of known concentration which is required to react with the analyte. A characteristic feature of most instrumental methods is the necessity for finding empirically the value of the intensity factor corresponding to the mass or concentration of a given sample. The majority of these methods therefore, require calibration by the use of a standard containing a known amount of constituent, serving as a basis for comparison in the measurement.

The established procedure must be followed carefully in individual quantitative desired determination. The success or failure of an analysis is often critically dependent upon the proper selection of method.

The analytical chemistry can save much time and improve the accuracy of results by a critical comparison of the various methods on the basis of certain criteria. Following are must be considered during measurement of sample.

(a) The complexity of the materials to be analyzed; (b) The probable concentration of the species of interest; (c) Accuracy; (d) Sensitivity and detection limit; (e) Selectivity; (f) Duration of an analysis; and (g) Cost of equipment

5. Interpretation of the Measurement: -

After proper calculation result of an analytical measurement is usually reported in relative terms, that is, in some way that expresses the quantity of the analyte present per unit weight or volume of the sample. Thus the results take the form of numerical data in suitable units such as percent, parts per million or so on.

The methods of statistics are commonly used and are especially useful in expressing the analytical results.

EMERGING NEEDS AND RECENT TRENDS

Analytical chemistry is based on the development of methods for identification, determination and separation of chemical substances. Identification of a new compound and its structure elucidation, need the result of chemical analysis for its conformation. It is impossible to understand a chemical reaction without knowing the quantities involved.

The study of the mechanisms of all chemical reactions at one stage or the other requires the use of analytical chemistry. Now a days there is a great need of chemical analysis in industry, because it provides the means of testing raw materials and for assuring the quality of products. Most industrial products such as pharmaceuticals, fuels, food materials, paints, etc, cannot be supplied to the consumer without the chemical analytical information written on the label of the product. It is the analytical chemistry which decides, whether or not, an ore can be used for profitable extraction of an element, whether a product manufactured in an industry is under quality control or not only in chemistry but in such diverse branches of science as biology, geology, mineralogy, medical sciences physics etc.

Analytical chemistry fulfil both the fundamental and the applied aspects of basic science and technology. The explosion of industrial and technological developments facing analytical problems which demand increasingly sophisticated knowledge and instrumentation for their solution. The principles & process of Analytical chemistry used for- determination of impurities at parts per billion (ppb) levels in semiconductor materials, determination of pesticide residues at the trace level in food products, detecting traces of pollutants in the environment, analysing a blood sample, or analysing a giant protein molecule.

At early stage the study of the fundamental laws of chemistry are based on quantitative analysis. The earliest analytical determinations systematically developed were based on the determination of the mass of a constituent. **Antoine Lavaisier** has been considered as the "**Father of Analytical Chemistry"** because of the careful quantitative analysis he performed on conservation of mass (using the analytical balance).

Historically, the first quantitative analysis were gravimetric made possible by the invention of precise balance. Gravimetric analysis means analysis by weight, was properly developed in the 17th century.

Soon after the development of gravimetric analysis, it was found that carefully calibrated glassware made possible considerable saving of time through the volumetric measurement of standardized solutions. This technique is known as volumetric analysis or titrimetry.

Both gravimetry and volumetry methods are performed with high accuracy and simple as well as involve no prior calibration. These methods are now known as classical methods or old methods of chemical analysis.

The methods developed mainly in the 20th century are known as modern methods of chemical analysis. In general, a technique at early stage is first developed. The modern methods are classified into two groups;

(i) Non-instrumental method: -

These methods are mainly the methods of separation that are required prior to analysis and the important ones are: chromatography, ion exchange, electrohoresis and solvent extraction.

(ii) Instrumental methods: -

The instrumental methods are more sophisticated as the instruments are composed of rather complicated electronic, optical and mechanical parts. In this techniques the principles of physics and physical chemistry are applied to study a particular property as a function of nature or amount of the substance of interest. The function of an instrument is to translate the chemical composition into information directly observable by the operator.

The interest in instrumental analysis has been increased, mainly, because of two reasons such as -

(a) they greatly reduce the duration of many analyses which are quite tedious and much time consuming by classical methods,

(b) they can be applied to the determination of substances under conditions in which classical methods fail (e.g. trace analysis).

Instrumental methods are developed only recently mainly because of two reasons:

(i) The physical properties on which these methods are based were not known earlier.

(ii) The design of the instrument required a lot of investment. Furthermore, for every physical property to be measured, a separate instrument is to be designed, e.g., a spectrophotometer to measure absorbance, a pH-meter to measure pH and a conductometer to measure conductance. The invention of spectroscope brought with it an extremely fruitful analytical approach and gradually a few colorimetric methods were investigated. After that it was found that electrical measurements could detect end points in titrations and several electroanalytical methods were developed. Somewhere in the middle of the 20^{th} century the rapid development of sophisticated instrumental components, vacuum-tube amplifier, photoelectric tube, photomultiplier tube, transistors, semiconductor devices etc. has resulted in the establishment of many analytical instruments based upon them.

Although there is no clear demarcation between non-instrumental and instrumental methods, the difference is just of degree.

The recent trends in analytical techniques have followed closely the development of new measuring instruments to find faster and convenient ways for sensitive and selective determination of desired constituent. Today we have a number of instrumental methods which can analyze in minutes what was done in days before. Not only the time has been shortened but with the help of new techniques it is now possible to detect and determine trace constituents at micro and nano or lower levels, and to analyze mixtures which could not be analyzed by the earlier methods.

Thus, there have been three major contributions in the present vitality of analytical chemistry-

(i) The flow of theory from physical chemistry and physics into analytical chemistry,

(ii) Application of electronics by analytical chemists for assembling new, faster and more sensitive instruments,

(iii) Application of computers for both data processing and automated control of instruments.

Such contributions have resulted in development in regard to the kinds of samples to be analysed and the sensitivity of the identification and determination of the analyte. This also resulted in a great decrease in time and human labour required for each determination.

One of the recent developments in analytical chemistry during the last few decades has been achieved by the appearance of commercial automatic analytical systems. Here the readymade analytical data is provided in a much smaller time with minimum efforts of the operator. Initially these systems were applied for routine analyses of clinical laboratories. Now,

they find their utility in diverse fields of routine chemical analysis and control of industrial processes.

Often the analysts have to handle a large number of samples and/or require to process vast amounts of data. Instruments can be designed that will automatically perform many or all the steps of an analysis. Computer techniques can be applied to the analytical instruments and the results can be automatically interpreted as desired. Such automation is very helpful to get continuous online analytical information of the quality control of an industrial plant process.

Now it is possible to perform all steps of an analysis starting from sampling through measurement to data display using automatic analytical instruments of new sophisticated design. These devices make the analysis very rapid either as continuous process or discrete analysis.

QUESTIONS

1. Who is the father of Analytical Chemistry?

2. When gravimetric analysis was developed?

3.Define

(a) turbidimetry, (b) nephelometry.

4. What are the contributions in the present time of analytical chemistry.

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