D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARM

DEPARTMENT OF PG CHEMISTRY

INSTRUMETNAL METHODS OF ANALYSIS –II

IV SEMESTER

Presented By

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UNIT-I

Flame Photometry

Flame Photometry is also called as flame emission spectroscopy. Flame Photometry is branch of atomic spectroscopy. It is used to detected certain metal ions like sodium,potassium,magenisum etc.

PRINCIPLE :-

Sample is sprayed into a flame and it converted to droplets. Due to the thermal energy of the flame the solvent in the droplets evaporate, leaving behind fine residue, which are converted to neutral atoms. This neutral atoms are get energy form thermal energy and go exited state but they are unstable at exited state so they are return to ground state with emission of specific wave length radiation. The wavelength of the radiation emitted is characteristic of the elements and is used to identify the elements (Qualitative Analysis). The intensity of the radiation emitted depends upon the concentration of the element analyzed (Quantitative Analysis).

Liquid sample

↓

Formation of droplets

↓

Fine residue

↓

Formation of neutral atoms

↓

Excitation of atoms by thermal energy

↓

Emission of radiation of specific wavelength

↓

λ& Intensity of emitted radiation measured

The wavelength of the radiation emitted is given by the following equation :-

$\lambda = hc/ E_2 - E_1$

Where,

h = Planks constant

c= Velocity of light

$E_{2,E1}$= energy levels of exited and ground state respectively

BOLTZMAN LAW

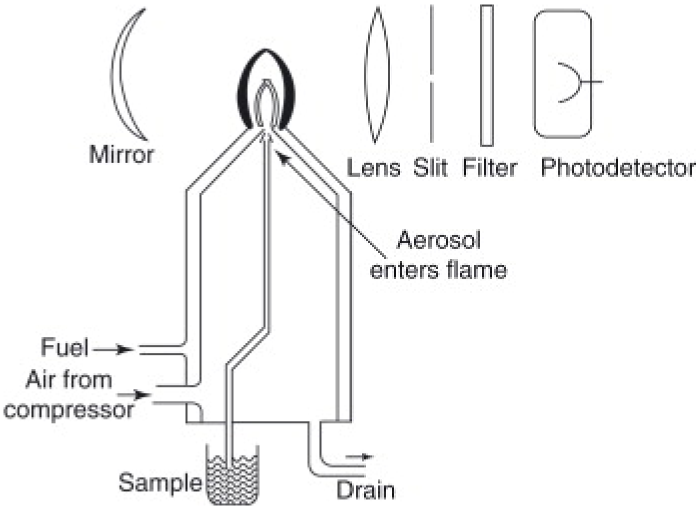
The fraction of free atom that are thermally exited is governed by a Boltzman Distribution

$\mathbf{N^* / N = Ae^{-\Delta E/kT}}$

- N* =is the number of exited atom
- N = is the number of atom remaining

- in the ground state
- AE = is the difference in energies levels
- k = The Boltzman constant
- T = the tempeature

INSTRUMENTATION OF A FLAME PHOTOMETER :-



COMPONENTS OF A FLAME PHOTOMETER

1. Burner (With fuel and oxidant)
2. Filter/Monochromator
3. Detector
4. Read out device

1.Burner :-

There are different burners available which are used to spray the sample solution into fine droplet mix with fuel and oxidant so that a homogenous flame of stable intensity is obtained. The most common ones are mecker burner, total consumption burner and laminar flow burner.

TOTAL CONSUMPTION BURNER

- Due to the high pressure of fuel and oxidant the sample solution **is** aspirate through capillary and burnt at the tip of burner
- Hydrogen and oxygen are generally employed as fuel and oxidant.
- The advantage over other is the entire consumption of sample,
- It's disadvantage is the production of non uniform flame and turbulent.

PREMIX BURNER

- In this burner the sample , fuel oxidant are thoroughly mixed before aspiration and reaching to flame
- The main advantage of is the uniformity of flame produced.
- The main disadvantage is the heavy loss of mix up to 95%.

FUEL AND OXIDANTS :-

FUEL	AIR	OXYGEN
Propane	2100°C	2800°C
Hydrogen	1900°C	2800°C
Acetylene	2200°C	3000°C

2. FILTER / MONOCHROMATOR :-

In flame photometry the wavelength as well as intensity of the radiation emitted by the elements has to be monitored. Hence a filter or monochromator is to be used. A simple flame photometer contains a filter wheel and when a particular elements has to be analyzed the specific filter is selected.

3.DETECTOR :-

The radiation emitted by the elements is mostly in the visible region. Hence conventional detectors like photo voltaic cell or photo tubes can be used. In a flame spectrophotometer, photomultiplier tube is used as detector.

4. READ OUT DEVICE :-

The signal from the detector is shown as a response in the digital read out device. The readings are displayed in an arbitrary scale (% Flame Intensity).

APPLICATION :-

•To estimate sodium, potassium, calcium, lithium etc. level in sample of serum, urine, CSF and other body fluids.

•Flame photometry is useful for the determination of alkali and alkaline earth metals.

•Used in determination of lead in petrol.

•Used in the study of equilibrium constants involving in ion exchange resins.

•Used in determination of calcium and magnesium in cement.

Atomic Absorption Spectroscopy Principle: In AAS, measurement of unexcited (Ground state) atoms is done by flame method. When solution containing metal salt /metallic compound is aspirated in to the flame, it undergoes vaporization and gaseous atoms are formed. Some atoms gain energy and get excited while large number of atoms remain in ground state.(unexcited) Ground state atoms are capable of absorbing radiant energy at their resonance wavelength. When radiation passed through the flame having gaseous state atoms, then part of radiation is absorbed by these atoms. Extent of absorption is proportional to the number of ground state atom present in the flame. Total amount of radiation absorbed is given by

$$\upsilon = \pi\square\ 2\ \square.\square\ .Nf$$

m = mass of electron

υ =Frequency absorbed by the atoms

C= velocity of light

e= charge on electron

N= Total number of atoms

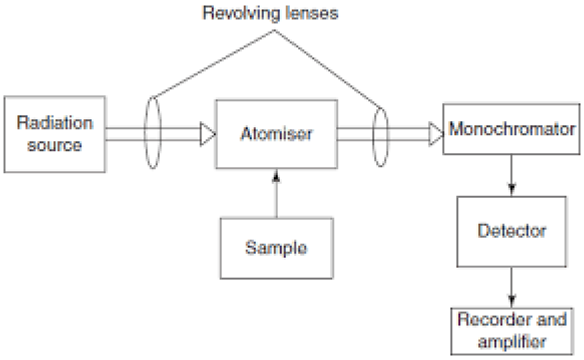
f= oscillator strength

AAS Process

Metallic sample → MX Solution → Mist or droplets MX evoparation → Solid MX → vaporisation

Gas MX dissociation → M(gas) + X(gas) Absorption of radiation → M*

Atomic Absorption Spectroscopy Instrumentation:



1) Radiation source

2) Chopper

3) Atomizers

4) Nebuliser

5) Monochromator

6) Detector

7) Amplifier

8) Read out device

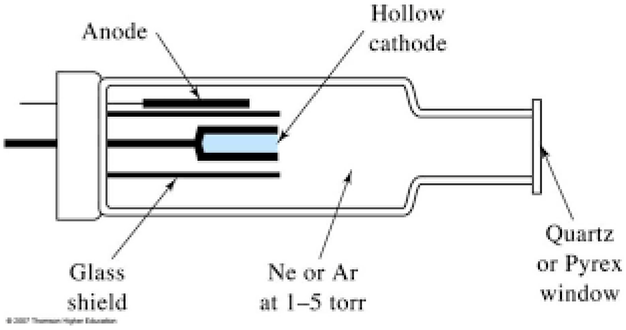
1) Hallow cathode lamp: It is used as a source of intense narrow electromagnetic radiation

Working

- High potential (200 to 600 V) is applied across the electrodes.

• Due to this ionization of inert gas take place and ions are produced. positive ions are attracted towards negative electrode (Cathode) and strike on the surface of cathode. As a result of this atoms from the surface of the cathode are ejected, this process is called as sputtering.

• These gaseous atoms absorb energy by colliding with cations of inert gas and goes to excited state and return to ground state by emitting energy. This radiation is used for further analysis



2) Chopper: A rotating wheel placed in between Hallow cathode lamp and the flame is known as chopper. Function of chopper is to break the steady light from HCL in to intermittent light. This gives alternating current in photocell.

3) Automizer: Automizer convert sample solution in to atomic vapour. Important functions of flame

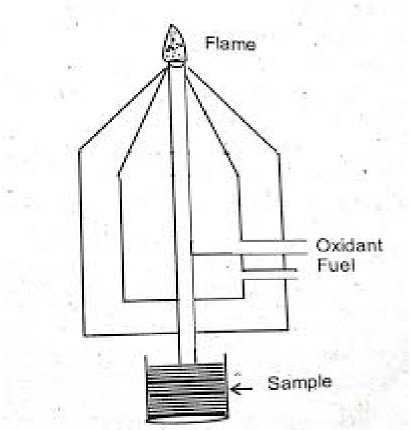
1) To evaporate solvent

2) To dissociate sample in to molecule

3) To provide ground state atoms for analysis

Temperature of flame is kept low, because at high temperature ionization of atoms take place which do not show absorption

1) Total consumption burner:



Sample solution, fuel gas and oxidising gas are passed through separate inlet and mixed at the top of the flame. Sample solution is converted to tiny droplets, which on evaporation form residue and residue finally produce ground state atoms.

Advantages: 1) High sensitivity 2) No risk of explosion

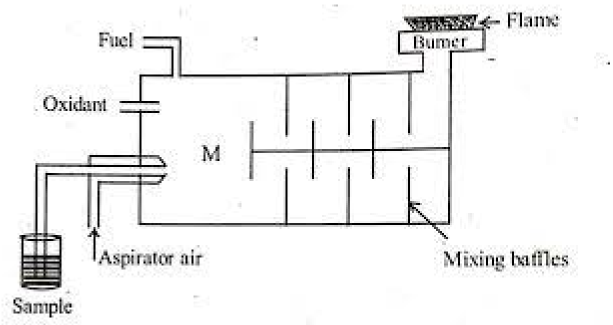
Disadvantages: 1) Clogging is possible

2) Poor reproducibility

3) Noisy operation

4) Rate of sample introduction depends on viscosity of solution

2) Laminar flow /Premix burner:



Sample solution, fuel gas and oxidising gas are mixed in mixing chamber This mixture is then passed through a series of baffles where thorough mixing and formation of uniform droplets of the sample take place.

Advantages: 1) Atomization efficiency is high as droplets are finer

2) Sensitivity is very high due to mixing baffles.

3) Good reproducibility

4) Little tendency to clog

5) No noisy operation

Disadvantages: 1) Rate of sample introduction is slow

2) Possibility of explosion in mixing chamber.

3) Selective evaporation of mixed solvent can lead to analytical errors.

4) Nebulizer: In nebulization sample is converted in to a fine mist or droplets using a jet of compressed gas. The flow carries the sample into the atomization region.

- Pneumatic Nebulizers : The liquid sample to be analyzed is sucked by a capillary with high pressure by a gas moving at high velocity. This is process is also called as aspiration. Because of high velocity sample breaks into a fine droplets (mist) and carries it to the atomization region.

5) Monochromator: Commonly used monochromators in AAS are prisms and gratings. Monochromator select monochromatic light from polychromatic light emitted by a hallow cathode lamp

i) Prism: It is triangular shape piece of glass or quartz. It work on refraction phenomenon.

ii) Diffraction Grating: It is dispersing element that can isolate a selected band of wavelength. It is prepared by ruling a large number of parallel equidistance groves upon highly polished metallic surface. Approximately 15,000 to 30,000 groves per square inch are present on diffraction grating, these groves acts as scattering centers.

6) Detector:

Photomultiplier tube Construction: It contain photosensitive half cylinder of metal which act as cathode. Inner surface of cathode is coated with light sensitive material like Cs2O, Ag2O and K2O. It consist of 9 dynodes which having coating of cesium metal which emits several electrons (2 to 5). These electrons are collected by collecting electrode (anode)

Working: When light strike on cathode surface, it eject electrons due to photoelectric effect. These electrons strike on the surface of first dynode and ejection of 2 to 5 electrons take place. These electrons strike on surface of second dynode and ejection of more electron take place. This process is continued up to 9 th dynode. Emitted electrons are collected by collecting electrode and current begin to flow. This current is amplified and measured by read out device.

7) Amplifier: It amplifies the current from photomultiplier tube.

8) Read out device: Chart recorder is the most common read out device. Micro ammeter is the other read out device used in AAS.

Interferences in AAS:

Interference :

Any process which causes error in determination is called interference. Interferent is the substance present in the sample, blank or standard solution which affects the signal of the analyte.

1) Chemical Interference: Because of formation of stable compound which cannot undergo decomposed at flame temperature.

Example Aluminum and magnesium form a thermally stable mixed oxide, thus low results are obtained for magnesium in presence of aluminum.

Chemical interference affects the number of free atoms reaching to the optical path to be absorbed. Precipitation, viscosity, surface tension and pH are some factors which causes chemical interference.

2) Spectral Interference: When spectral lines overlap with each other then this kind of interference is observed. Absorption or emission of an interfering species either overlaps or lies so close to the analyte band that resolution by the monochromator become difficult. In AAS spectral interference is rare.

Element	Wavelength	Element	Wavelength
Al	308.33	V	308.21
Cu	324.44	Eu	324.76
Fe	271.90	Pt	271.90
Ga	403.30	Mn	403.31
Hg	253.65	Co	253.65

3) Ionization Interference: Due to high flame temperature (air -acetylene or nitrous acid-acetylene) ionization of atoms take place.

Atoms with low ionization potential undergo ionization and reduce the population of ground state atom and excited state atoms.

To overcome this effect easily ionizable elements such as K, Na, Cs are added to the sample (1000 microgram/ liter)

Due to easily ionizable atoms large number of electrons are produced which suppressed the ionization of analyte atoms

4) Background Absorption : It is caused by absorption of the species other than the atoms at resonance wavelength.

This is observed due to scattering of light due to small, un-volatilized particles present in the flame.

It is wavelength dependent phenomenon and gives a positive error in the analysis.

It can be minimized by using Deuterium arc background correction (continuum source)

Qualitative Analysis:

Different hallow cathode lamp is required for different element. (It is able to detect only element whose hallow cathode lamp is used) hence scope of AAS in qualitative analysis is limited. Quantitative Analysis: A.A.S is the powerful technique for the quantitative analysis of trace metals.

1) Concentration of unknown sample:

- 100 % transmittance or zero absorbance is adjusted by keeping Hallow cathode lamp on,

- Standard solutions of element to be analyzed are prepared.

- Absorbance of each standard solution is measured.

- Calibration curve (absorbance vs concentration) is plotted

2) Simultaneous multicomponent analysis: By using multicomponent hallow cathode lamp, elements like Zn, Cd, Ni, Ca, Fe, Mn, Cu and Mg can detected in spectral region 232 to 328 nm. 3) Analysis of biological material and food material: Trace metals from biological system, Ni from vegetable oil, Cu from beer, Na and K from blood serum can be analyzed by AAS. It is also used to find out impurities present in food material. 4) Determination of lead in petrol: Tetra ethyl lead ($(C_2H_5)_4Pb$)and tetramethyl lead ($(CH_3)_4Pb$) are two anti knocking agents used in petrol. (antiknock agent is an additive used for reducing engine knocking property and to increases fuel's octane rating.)

a) Direct method: Absorbance of standard solution and sample solution is measured at 283.3 nm. Calibration curve is plotted and concentration of lead in petrol is determined. b) Indirect method: Standard solutions of lead containing 50,25,10,5 μg/mL are prepared by using deionized water . Absorbance is recorded at 283.3 nm. Unknown sample is treated with Br2 and Pb is converted to PbBr2 , It is extracted in dil. HNO3 and absorbance is recorded

Concentration is measured by using below equation

□□ □□μg/mL = □2 − □1 /□0 − □2 □ □ □ 1 /10 □ □□□□□□□□ □□□□□□□ □□ □□□□□□

S0 = absorbance for blank (1%HNO3)

S1 = absorbance for unknown solution (sample)

S2 = absorbance of standard solution

C = Concentration of lead in μg/mL in standard solution

ICP-AES Principle:

ICP-AES is an emission spectrophometic technique exploiting in fact that excited electrons emit energy as a given wavelength as they return to ground stage after excitation by high temperature argon plasma.

The fundamental characteristic of this process is that each element emit energy at specific wavelength peculiar to its atomic character. The energy transfer for electrons when they fall back to ground stat is unique to each element as it depend upon the electronic configuration of the orbital the energy transfer is inversely proportional to the wavelength of electro magnetic radiation.

E=hc/λ and hence the wavelength of light emitted is also unique. Although each element emits energy at multiple wavelengths in the ICP-AES technique it is most common to select single wavelength by a given element.

The intensity of a energy emitted at a chosen wavelength is proportional to the amount of element in the sample being analyzed. Thus by determine which wavelength are emitted by a sample and determining their intensities the analyst can quantitatively and qualitatively find the elements in the given sample related to reference standard

ICP-MS

Working Principles:

Inductively coupled plasma mass spectrometry (ICPMS) is an analytical instrument used for elemental determination. The sampled material is introduced into high-energy argon plasma that consists of electrons and positively charged argon ion. In the plasma, the material is split into individual atoms. These atoms will lose electrons and become (singly) charged positive ions. To allow their identification, the elemental ions produced in the plasma (ICP) must be transferred from 7000 K to room temperature and from atmospheric pressure to high vacuum. To do so, the ions are extracted through a number of apertures. Besides ions also photons are produced in the plasma.

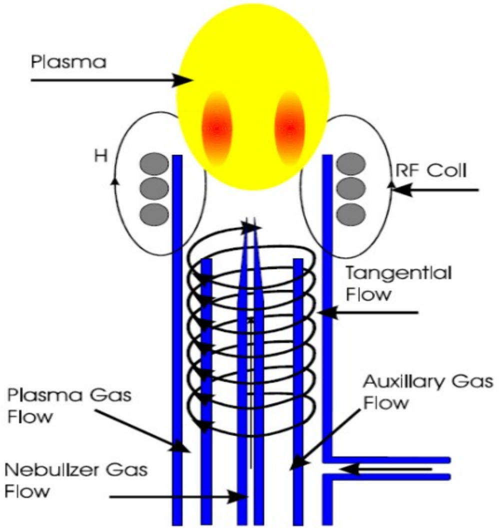
Sample Introduction

The first step in ICP-MS is sample introduction. There are multiple ways in which a sample can be introduced, and the method of introduction depends on the physical characteristics of the sample. The various methods .samples requiring ICP-MS analysis are in a liquid form. However, the samples must be introduced to the torch in either a gaseous form or an aerosol form. Therefore, liquid samples require sample nebulization, The liquid sample is pumped from a vial, via a peristaltic pump, into the nebulizer. Liquid droplets are formed on the tip of a needle, where they become nebulized due to argon gas flowing through a second needle perpendicular to the sample needle. A small amount of aerosol created is swept into the torch, but the majority of sample condenses on the walls of the nebulizer and is wasted to the drain.

If a solid sample requires analysis, the most likely method of introduction would be via electrothermal vaporization. An electrothermal vaporizer uses electric current to rapidly vaporize a solid sample, which can then be swept into the ICP torch via argon gas flow.

Inductively coupled plasma torch:

Definition: An ion source that consists of a torch that is surrounded by a radio frequency generator that ionises argon gas inside the torch to form a high-temperature (up to 10,000 K) plasma that can be used to ionise analytes.



Plasma torch

- The quartz torch surrounded by the copper induction coil.
- The copper coil is made from copper tubing and is kept cool by circulating water.
- RF energy is supplied to the coil which inductively heats the argon gas to approximately 10,000°C.
- At this temperature the gas turns into a plasma of positively charged atoms and electrons.

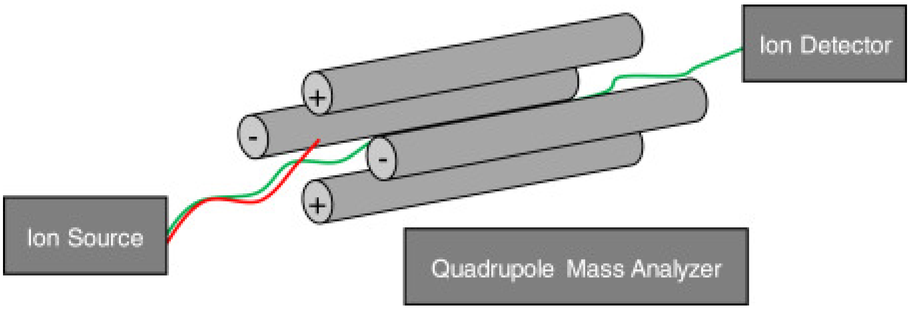
- The plasma is kept off the sides of the quartz torch by a separate flow of argon supplied tangentially to the inside torch.

Torch alignment

- The torch design shall include a quick release, Pre-aligned mounting block which minimizes torch alignment when reinstalling.
- Doesn't require tools for removal.
- The mount shall incorporate the plasma gas connections so that when the torch is inserted gases will be automatically connected.
- As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP Torch, electrons are stripped off of the argon atoms, forming argon ions.

Quadrupole Mass Analyzer

The quadrupole mass analyzer commonly consists of four parallel conducting rods spaced about a central axis (Fig. 2). A positive DC potential is applied to one pair of rods, a negative DC potential is applied to the opposite pair, and a constant frequency RF voltage is applied to all four rods. The DC potential is applied such that adjacent rods are of opposite polarity. On entering the quadrupole, positively charged ions are attracted to the pair of negative rods. However, as the potential on the rods alternates, these rods become positive, and the ions are repelled and attracted to the opposite pair of rods which now have the negative potential. By alternating the applied potential in this manner, ions travel in a spiral pathway through the quadrupole. For a given ratio of RF and DC amplitudes, only ions within a narrow *m/z* range will have a stable trajectory through the quadrupole and reach the detector; all other ions will hit the rods and be neutralized.



To obtain a full mass scan, which plots all *m/z* values across a specified range, the RF and DC amplitudes are increased, while maintaining a constant RF:DC ratio. However, a drawback to full mass scan mode is that ions of each *m/z* value only spend a very short time in the analyzer and, hence, only a small fraction actually reaches the detector per scan cycle. To improve sensitivity, selected ion monitoring (SIM) can be used, in which only the RF and DC potentials corresponding to specific *m/z* values of interest are applied. In SIM mode, fewer *m/z* values are scanned during a given scan cycle such that a greater proportion of ions of the targeted *m/z* values reach the detector, leading to increased sensitivity.
The quadrupole mass analyzer is currently the most common analyzer used in bench top GC–MS instruments. These analyzers exhibit constant resolution of around 0.3 *m/z* across the mass range, with practical ranges spanning 10–2000 *m/z*.

Applications of ICP-AES

1. Environmental analysis .

Water analysis including, natural, effluent, waste water, and ocean.

Water analysis requirements & outcome

- The Liberty 200 Inductively Coupled Plasma Atomic Emission Spectrometer
- All standard solutions were prepared from high purity ICP 10 000 ppm stock standards
- Standard 1: Mn, Be, Cd, Pb, Zn.
- Standard 2: Cu, Fe, V, Co.
- Standard 3: Al, Cr, Ni.
- Multi-element standards were prepared in 10% v/v HCl and contained 5 mg/L of each element. The blank solution was 10% V/V HCl solution.

ELEMENT	WAVELENGTH (nm)	DETECTION LIMIT (mg/ml)
Al	167.081	1.5
Be	234.802	0.2
Cd	228.803	1.5
Co	238.893	5
pb	220.353	14

Soil analysis, sediment analysis, contaminated land, landfill sites, sludge analysis- solid and digested wastes

Air - chimney exhaust filters, air filters of contaminated sites, dusts

2. Petro chemical analysis...

- Specifically oils & greases,
- Petrochemicals applications at weak metal analysis for industrial fleets, heavy industry by-products.
- Pains, additives, pigments, ink.

3. Metallurgical analysis....

- Steels and alloys.
- Precious metals.
- Bulk materials- bronze, brasses.
- Traces- contaminants.

4. Geological analysis...

- Rock samples, cements, ceramics, glasses...etc.,

5. Food stuff analysis...

- Animal feed, crop analysis, toxins in food
- Trace analysis in micronutrients, metallic compounds in wine, arsenic in food, and trace element in bound protein.

6. Coals and paper products...

UNIT-II

THERMAL METHODS OF ANALYSIS

TGA (Thermo Gravimetric Analysis)is an important characterization technique which measures change in mass of a material with variations in temperature. It operates in two modes: 1) change in mass is measured with increasing temperature (called scanning mode having constant heating rate); and 2) change in mass is measured with time (called the isothermal mode with constant temperature or constant mass loss). This change of mass is due to both physical and chemical phenomenon like absorption, sublimation, vaporization, oxidation, reduction and decomposition likewise.

Types of TGA

1. Dynamic TGA:. In case of dynamic TGA, specimen is heated with a constant heating rate (i.e. normally linear increase with time).

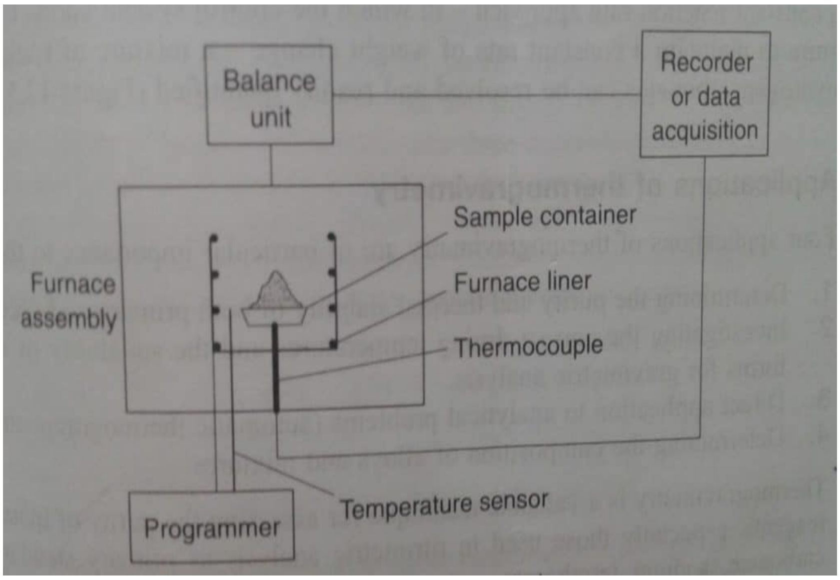
2. Isothermal or static TGA: In case of isothermal TGA, specimen is kept at a constant temperature for predefined time and the variations in weight (or mass) of the specimen are monitored.

3. Quasi static TGA: In this method, the specimen is heated to a constant weight at each step of the series of increasing temperature.

Principle

Microbalance records the change in weight of a specimen against the temperature or time, in specific controlled conditions including rate of heating, gaseous medium, flow rate, and crucible type, etc. Graph of change in weight with temperature is called thermo gravimetric curve or thermo gram.

Instrumentation



Instrumentation of TGA:

- Recording balance
- Sample holder
- Furnace
- Temperature programmer /controller (thermocouple)
- Recorder

Recording balance :

A microbalance is used to record a change in mass of sample/ substance. An ideal microbalance must possess following features:

- It should accurately and reproducibly record the change in mass of sample in ideal ranges of atmospheric conditions and temperatures.

- It should provide electronic signals to record the change in mass using a recorder. • The electronic signals should provide rapid response to change in mass.

Null point balances:

It consists of a sensor which detects the deviation from the null point and restores the balance to its null points by means of restoring force.

Sample holder:

- The sample to be studied is placed in sample holder or crucible. It is attached to the weighing arm of microbalance.

- There are different varieties of crucibles used. Some differ in shape and size while some differ in materials used. 15 shape and size while some differ in materials used.

- They are made up from platinum, aluminum, quartz or alumina and some other materials like graphite, stainless steel, glass etc

There are different types of crucibles. They are:

1. Shallow pans(used for volatile substances)
2. Deep crucibles (Industrial scale calcination)
3. Loosely covered crucibles (self generated atm. Studies)
4. Retort cups (Boiling point studies)

Furnace:

- The furnace should be designed in such way that it produces a linear heating range.

- It should have a hot zone which can hold sample and crucible and its temperature corresponds to the temperature of furnace.

- There are different combinations of microbalance and furnace available. The furnace heating coil should be wound in such a way that there is no magnetic interaction between coil and sample or there can cause apparent mass change

Temperature programmer/controller:

- Temperature measurement is done in no. of ways thermocouple is the most common technique.

- The position of the temperature measuring device relative to the sample is very important.

- The major types are:

a). The thermocouple is placed near the sample container and it has no contact with the sample container. This isn’t a good arrangement where low-pressure are employed.

b). The sample is kept inside the sample holder but not in contact with it. This arrangement is better than that of (a) because it responds to small temperature changes.

c) . The thermocouple is placed either in contact with sample or 20 c . The thermocouple is placed either in contact with sample or with the sample container. This is the best arrangement of sample temperature detection.

Recorder:

The recording systems are mainly of 2types

1. Time-base potentiometric strip chart recorder.

2. X-Y recorder.

- In some instruments, light beam galvanometer, photographic paper recorders or one recorder with two or more pens are also 22 used.
- In the X-Y recorder, we get curves having plot of weights directly against temperatures.
- However, the percentage mass change against temperature or time would be more useful.

Factors affecting TGA:

Factors affecting the TG curve The factors which may affect the TG curves are classified into two main groups.

(1) Instrumental factors:

(a) Furnace heating rate

(b) Furnace atmosphere

(2) Sample characteristics :

(a) Weight of the sample

(b) Sample particle size

1. Instrumental factors :

a. Furnace heating rate:

The temperature at which the compound (or sample) decomposes depends upon the heating rate. When the heating rate is high, the decomposition temperature is also high. A heating rate of 3.5°C per minute is usually recommended for reliable and reproducible TGA. usually recommended for reliable and reproducible TGA.

b. Furnace atmosphere: The atmosphere inside the furnace surrounding the sample has a profound effect on the decomposition temperature of the sample. A pure N 2 gas from a cylinder passed through the furnace which provides an inert atmosphere.

2. Sample characteristics:

(a)Weight of the sample: A small weight of the sample is recommended using a small weight eliminates the existence of temperature gradient throughout the sample.

(b)Particle size of the sample: The particle size of the sample should be small and uniform. The use of large particle or crystal may result in apparent, very rapid weight loss during heating.

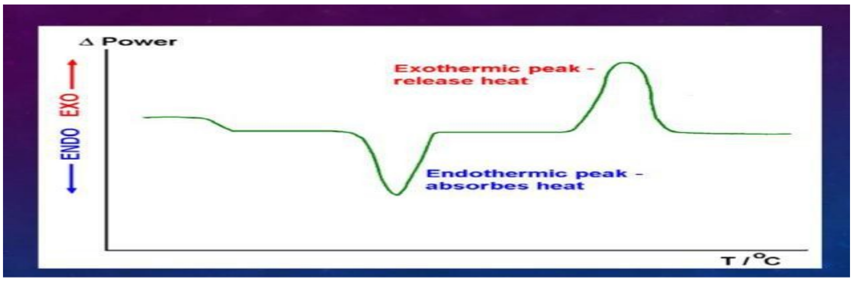
Differential Thermal Analysis (DTA)

- **Principle**:

The basic principle involved in DTA is the temperature difference (ΔT) between the test sample and an inert reference sample under controlled and identical conditions of heating or cooling is recorded continuously as a function of temperature or time, thus the heat absorbed or emitted by a chemical system is determined.

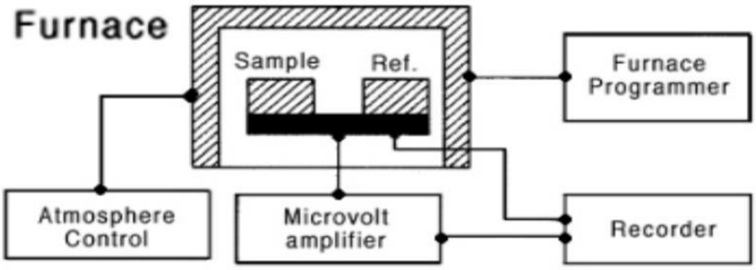
- If any reaction takes place in the sample, then the temperature difference will occur between the sample and the reference material.
- In an endothermic change (such as melting or dehydration of the sample) the temperature of the sample is lower than that of the reference material (i.e) ΔT = -ve (for endothermic process)
- In an exothermic change or process the sample temperature is higher than that of the reference material.
- (i.e) ΔT = + ve (exothermic process)

The shape and the size of the peak give information about the nature of the test sample. Sharp endothermic peaks indicate phase changes (such as melting, fusion etc.) Transition from one crystalline form to another crystalline form. Broad endothermic peaks are obtained from dehydration reactions



Chemical reactions like oxidative reactions are exothermic reactions

Instrumentation for DTA :



Block Diagram of the DTA apparatus consists of the following components

1. Furnace sample and reference holder with thermocouple assembly.

2. Sample holder furnace: To heat the sample

3. Furnace temperature controller: To increase the furnace temperature steadily

4. Furnace atmospheric control system: To maintain a suitable atmosphere in the furnace and sample holder)

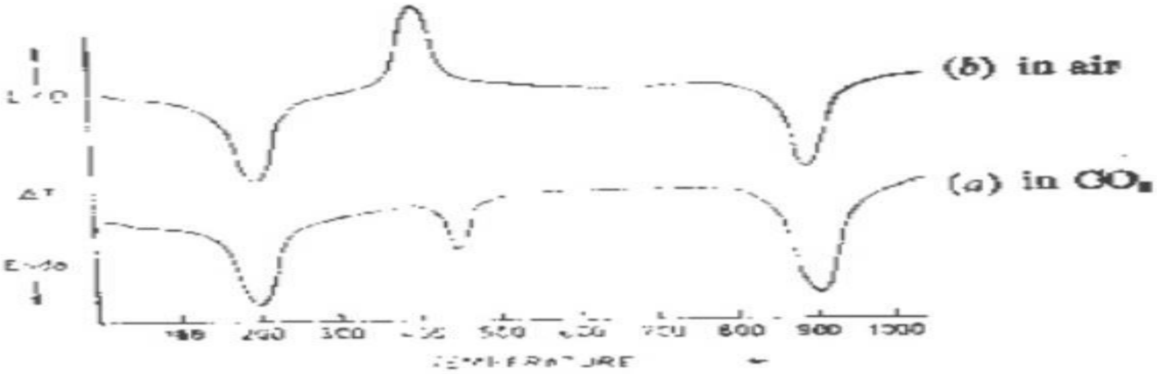
5. Low level DC amplifier

6. Recording device(Recorder)

7. Differential temperature sensor: To measure the temperature difference between the sample and reference material) the sample and reference holder are kept inside the furnace and the temperature of the furnace and sample holder is controlled by using furnace controller.

DTA of calcium oxalate monohydrate The DTA curve for the decomposition of calcium oxalate monohydrate

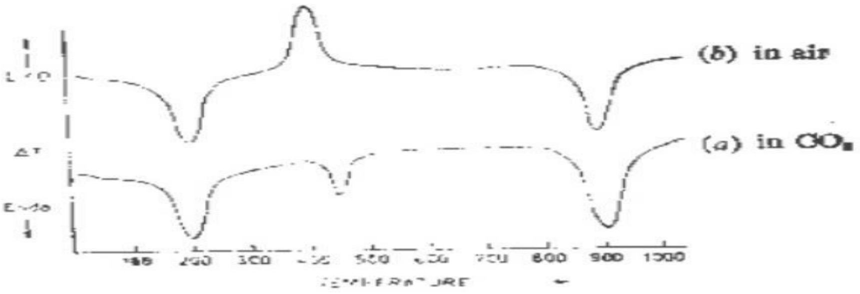
($CaC_2O_4 .H_2O$) is shown in the diagram.



DTA of calcium oxalate monohydrate

• The thermo gram of calcium oxalate monohydrate has three peaks corresponding to the successive elimination of H_2O, CO and CO_2 .These three points of weight loss corresponds to the three endothermic process.

- Curve (b) represents the DTA diagram for the same compound in air. The second peak in this curve is sharply exothermic, but corresponds to the same weight loss as in carbon dioxide atmosphere. This peak represents the exothermic burning of carbon monoxide in air at the temperature of the furnace.



Applications of DTA

1. DTA curves for two substances are not identical. Hence they serve as finger prints for various substances.

2. Used to study the characteristic of polymeric material.

3. This technique is used for testing the purity of the drug sample and also to test the quality control of number of substances like cement, soil, glass,etc.

4. Used for the determination of heat of reaction, specific heat and energy change occurring during melting etc.

5. Trend in ligand stability (thermal stability of the ligands) gives the information about the ligands in the coordination sphere

DSC (Differential Scanning Calorimetry)

Differential scanning calorimetry (DSC) is one of the thermal analysis techniques. In case of DSC, differences in heat flow between a specimen and reference are measured against the temperature or time while the specimen is continuously heated under controlled conditions. Function of calorimeter is to measure the heat content which comes in and out of the sample. Throughout the experiment both reference and sample are maintained at nearly constant temperature. Usually for DSC analysis temperature program for sample holder is designed in such a way that its temperature increases linearly with time. For DSC analysis only few mg material is required. It is the most used thermal technique due to its speed, availability and simplicity. DSC technique is used for quantitative analysis.These measurements give both quantitative as well as qualitative information regarding the physical and chemical changes which involves endothermic and exothermic processes or variations in heat capacity of the sample.

Principle:

To maintain the sample and reference at equal temperature during the physical transformations of the sample (like phase transitions), either more or lesser amount of heat is required to be applied on itthen that required for the reference sample or an empty sample pan. This heat required depends on the nature of the transformation process, that is, whether it is exothermic or endothermic. For instance, ata constant heating rate, when a solid sample changes to liquid, more heat is required to be applied to the sample for increasing its temperature. This happens because heat is absorbed by the sample whileit changes state from solid to liquid. However, if there is exothermic process in the sample (for instance, crystallization), less amount of heat is needed to increase the temperature of the sample. Thus, by calculating the heat flow differences between the reference and sample, DSC technique can determine the amount of heat released or absorbed during a transition process

Heat Compensated DSC:

Here, both the reference and sample are heated under the same furnace. The difference between the temperatures of the reference and sample is recorded and converted into a power difference and plotted against time or temperature. The main cell assembly of DSC is enclosed within a heated silver block cylinder, from which heat is transmitted onto the specimen by a constantan disc connected to the cylinder. The reference and sample pan are kept on two raised platforms in the system. The underside of both the platforms is connected to the constantan disc via connecting wires and chromel (alloy of nickel and chromium) disks, thereby forming a thermocouple which is used to measure the temperature difference between the two platforms. In addition to this, the individual temperatures of the two platforms can be measured by the junction of alumel wires linking the platforms to the chromel disks. Another separate thermocouple is integrated with the silver block which acts as a temperature controller for programmed heating cycles. Inert gas can be introduced within the cell at constant flow rate of ~40nm/min. Unlike the power compensated DSC, the calibration constant (which converts peak area into joule) in heta flux DSC is a thermal factor.

Total heat flow dH/dt in heat flux DSC is:

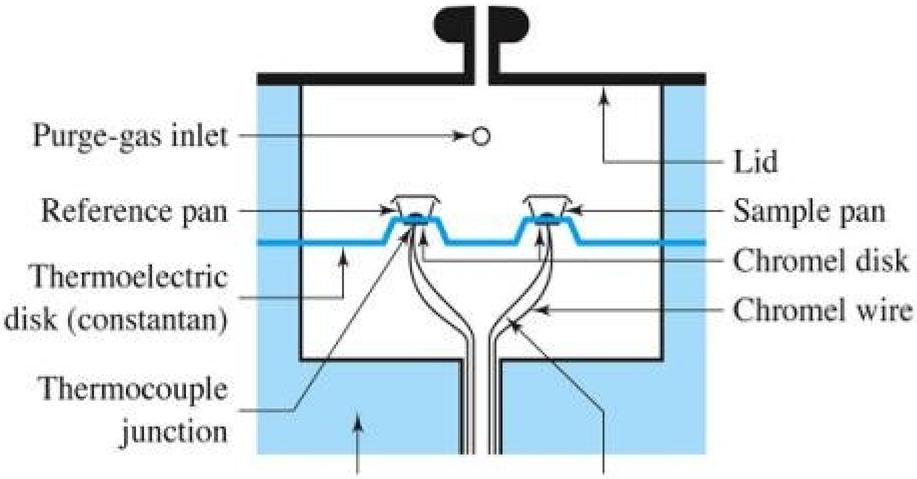
$$dH/dt = C_p\, dT/dt + f(T,t)$$

Where, H is enthalpy in J/mol

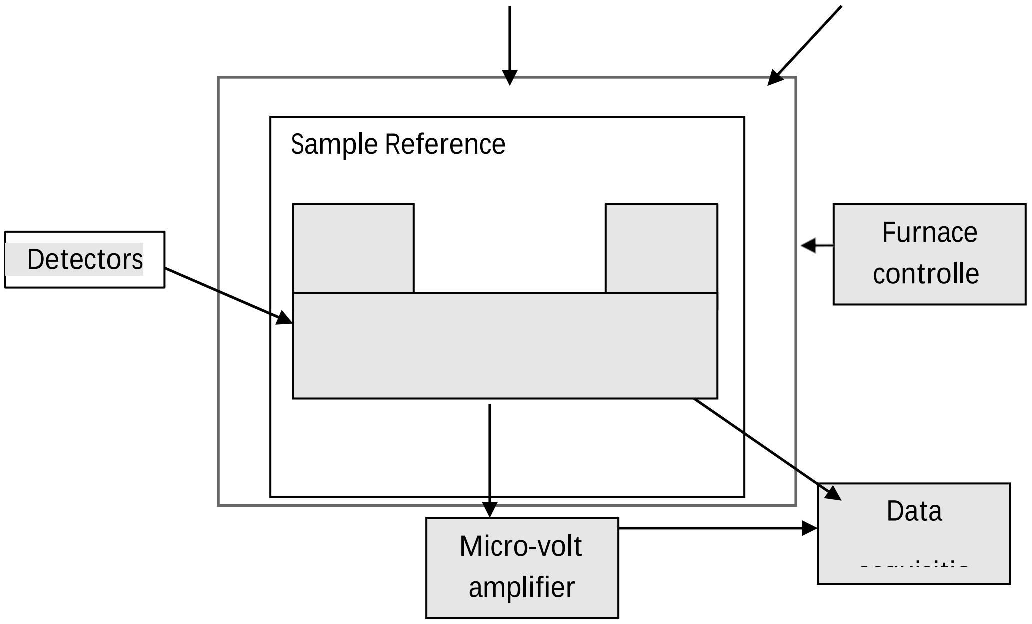
f (T,t) is kinetic response of the specimen in J/mol

C_p=specific heat capacity in $JK^{-1}mol^{-1}$.

Therefore, total heat flow is equal to the sum of the two terms; where one term is related to the kinetic response and the other is related to the heat capacity.



INSTRUMENTATION



Detector: In case of detector thermocouple is used to measure the temperature change while the sample heated under controlled environment. For the case of low temperature copper- constantan or cromel alumel thermocouple is used and for the case of corrosive atmosphere or high temperature pt/13%rh thermocouple is used.

Sample Container: Sample container is designed in such a a way that it can be used under high pressure and thermal environment. For high temperature case platinum or ceramic is used for sample holder and for low temperature case aluminium is used.

Reference material: Generally reference material is made up of calcined alumina Al_2O_3 or carborundum, silicon carbide.

Temperature controller: Temperature controller is used to maintain the temperature of the referenceand sample at the desired value.

Furnace: One block of furnace is required in case of heat compensated DSC and two block offurnace is required in case of power compensated DSC.

Factors affecting DSC curve

Instrumental factors: These include parameters such as – Furnace heating rate, furnace atmosphere, recording speed, geometry of sample holders, location of sensors, sensitivity of the recording system and material of the sample container.

Sample characteristics: Parameters including type and weight of sample, particle size, solubility of evolved gases in the sample, heat of reaction and thermal conductivity.

Applications of DSC

DSC can be used in studying heat of melting, crystallization, percentage of crytallinity, heat capacities, thermal stabilities, purities, oxidative stabilities, food science, drug analysis, and liquid crystals.

UNIT-III
VOLTAMMETRY

Voltammetry is an electrochemical method in which information about an analyte is obtained by current.

Voltage ramp applied to electrode.

Current measure

Reduces ions in the electrode

Commonly uses three electrodes

1. Working Electrode (WE)

2. Auxiliary Electrode (AE)

3. Reference Electrode (RE)

1.The working electrode is the electrode is in the electrode in an electrochemical system on which the reaction of interest is occurring.

The WE is often used in conjunction with an auxiliary electrode.

Types of WE

Glassy carbon

Gold

Platinum

Mercury

2.The auxiliary electrode, often also called counter electrode, used in a voltammetric analysis in which an electric current is expected to flow.

Completes the circuit between the potentiostat and the WE

• Two different types available.

Platinum

Glassy Carbon

3.A reference electrode is an electrode which has a stable and well known electrode potential.

• Provides a reference potential to the WE/AE circuit

• Two types of RE

- Ag/AgCl in KCI

Hg/HgCl in saturated KCI

1. Residual current (ir): The current that flows in the absence of the depolarizer (i.e. due to the supporting electrolyte) is called residual current. This has to be taken into consideration while interpreting the polarograms. It is the sum of the relatively larger condenser current (ic) and a very small faradic current (if). ir = if + ic ic (condenser current) – is due to the formation of Helmholtz double layer at the mercury surface. if (faradic current) – is due to the traces of impurities.

2. Migration current (im): It is due to migration of cations from the bulk of the solution towards cathode due to diffusive force, irrespective of concentration gradient.

3. Diffusion current (id): The difference between Residual current and Limiting current is called Diffusion Current (id). Diffusion current is due to the actual diffusion of electro reducible ion from the bulk of the sample to the surface of the mercury droplet due to concentration gradient.

The Ilkovic equation is a polarography formula that connects the diffusion current (id) with the concentration of the non-polarisable electrode, i.e., the chemical reduced or oxidised at the falling mercury electrode (polarisable electrode).

$(i_d)_{avg} = 607\ ncm^{2/3}\ t^{1/6}\ D^{1/2}$

Where,

i_d = Diffusion current in microamperes

607 = Constant of various numerical factors including: Faraday constant (Π), density of Hg, etc

n = Number of electrons duly involved in the electrode reaction, D = Diffusion coefficient in $cm^2 .sec^{-1}$,

m = Weight of Hg flowing via the capillary in $mg.sec^{-1}$,

t = Drop time in seconds,

C = Concentration in mmol/L.

4. Half wave potential Half wave potential is the potential at which the concentration of oxidised and reduced forms at electrode surface is equal. i.e., 50% of oxidised and 50% of reduced forms are present.

5. Limiting current (il): Beyond a certain potential, the current reaches a steady state value called as the limiting current. At this point, the rate of the diffusion of ions is equal to the rate of reduction of ions, and the state of electrode is said to be concentration polarized

Dropping Mercury Electrode (DME): Dropping mercury electrode (DME) is a working electrode arrangement for polarography in which mercury continuously drops from a reservoir through a capillary tube (internal diameter 0.03 - 0.05 mm) into the solution. The optimum interval between drops for most analyses is between 1 and 5 s. The unique advantage to the use of the DME is that the constant renewal of the electrode surface, exposed to the test solution, eliminates the effects of electrode poisoning.

Construction: The assembly consists of a

- mercury reservoir. It consists of fine capillary having
- bore size ranged from 20-50 μ and 10-15 cm long. The capillary is connected to
- mercury reservoir by rubber tubing. A small glass electrolysis cell in
- which the unknown solution is placed. The height of the mercury

• reservoir is adjusted such that drop time is 1-5 seconds.

Working:

- Dropping mercury electrode (DME) is a polarisable electrode and can act as both anode¬ and cathode. The pool of mercury acts as counter electrode,
  i.e.,anode if DME is cathode or
  cathode if DME is anode.
- The counter electrode is a non-polarisable electrode.
- To the analyte solution, electrolyte like KCl is added i.e., 50-100 times of sample concentration.
- Pure nitrogen or hydrogen gas is bubbled through the solution, to expel (remove) out oxygen.
- Eg: If the analyte solution contains cadmium ions, then cadmium ions are discharged at cathode.
- Cd2+ + 2e- → Cd
- Then, gradually increasing voltage is applied to the polarographic cell and current is recorded.
- Graph is plotted between voltage applied and current. This graph is called Polarograph¬ and the apparatus is known as Polarogram.
- The diffusion current produced is directly proportional to concentration of analyte and this is used in quantitative analysis.
- The half wave potential is characteristic of every compound and this is used in¬ qualitative analysis

Advantages:

1. Surface area is reproducible.

2. Electrode can be renewed and thus eliminates poisoning effect.

3. Mercury forms amalgam (solid solutions) with many metals.

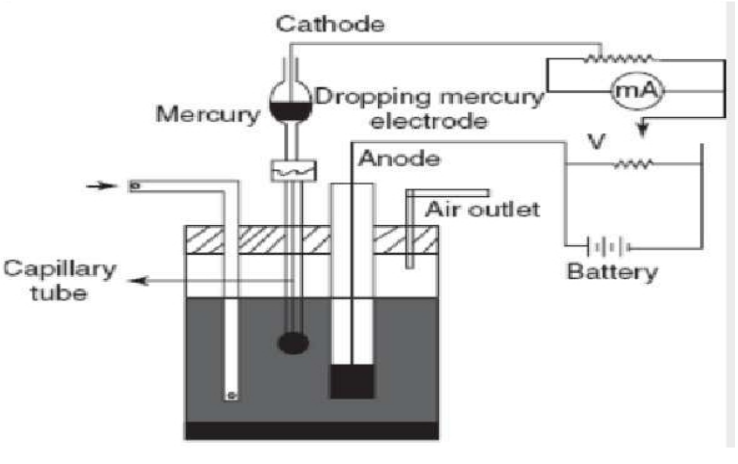
4. The surface area can be calculated from the weight of the drop.

Disadvantages: 1. Capillary is very small and thus can be easily blocked.

2. Mercury is very toxic.

3. Surface area of each drop of mercury is never constant.

4. It cannot be used at higher positive potential due to oxidation of mercury



AC Polarography

A normal current voltage curve is obtained when the concentration of active electrolyte is minimum upto 10-4 M because at lower concentration curve is not defined well. Due to the changing size of mercury drop at DME current fluctuate which causes wrong estimation. Condenser current causes an error in the determination of Id as it is non faradic in nature. Very dilute solution is not correctly estimated as resistance by solvent crops up. For the determination of mixture of ions one needs the E1/2 potential difference 200 mV at least required otherwise there will be no clear separation of wave height.

Principle:

In order to have a clear separation of wave height for the different ions in solution and to know corrected Id and E1/2 etc. a modified method or modification in DC polarography is achieved by incorporating in alternative (AC) in the (DC) polarography. As AC polarography a constant sinusoidal current is fed to the cell containing active electrolyte with ac potential and dc potential superimposed on it. The purpose of dc is to give correct reduction/oxidation current in which there is no attraction/repulsion. Circuit diagram for AC polarogram is shown below:

Pulse Polarography

In pulse polarography, one can measure the changes in diffusion current produce by rectangular pulses of quiet ling duration. The pulse synchronized with the maximum growth of mercury drop. If a dropping mercury electrode is employed then the current is measured from 40 to 60 millisec after the application of pulse to allow the time for the charging current to decay to a very low value. The capacitive current actually decays exponentially at a rate governed by magnitude of capacitance and series of resistance of the system. During this time interval, the faradic current also decays somewhat but doesn’t reach the diffusion control level because the concentration gradient at the instant of current measurement is considerably large. Each succeeding drop is polarized with somewhat large pulse.

The method gives a current-voltage curve similar to that of DC polarography and sensitivity of method is 6-8 V times than that of classical DC polarography. The measured signal is the faradic current that flow at the plus potential and minus any faradic current flowing to the fixed DC potential. Types of pulse polarography are:

Normal pulse polarography:

In this case pulses of gradually amplitude superimposed on a constant preset DC potential. So in the normal pulse polarography mode, the current potential relationship is relatively simple. If the initial potential is detected well before the rise or onset of the wave, the faradic current can be assumed to be equal to zero. The current potential curve for a reversible system is given by approximate equation:

$I = nFCA\surd D/\pi tm \times I/I+P$

Where tm is time interval between the pulse amplification and measured current. As the pulse potential becomes more negative than E1/2 then P approached zero. So the limiting current given by:

$Il = nFCA\ D/\pi tm$

For example determination of ascorbic acid in conserved citrus juice. So ascorbic acid gives a well defined oscillation wave. So the determination can be carried out directly in freshly prepared citrus juice as well as conserved citrus juice.

Filtered the lemon or grape fruit through a porous funnel of size 1 mm. now prepare 25 mL for the graduate flask and add 0.5 mL acetate buffer, 2 mL of juice along with the standard addition of standard ascorbic acid and dilute it to the mark with distilled water.

Differential Pulse Polarography

In this case the superimposition of pulse of constant amplitude on a steadily constant D.C. potential. So the sensitivity is much better in which the current is sampled twice during a drop lifetime just before the drop. So the polarogram represents a current differences ΔI as a function of base plot then the curve is peak shape and height of peak is proportion to concentration of depolarizer. So the normal D.C. voltage ramp is applied to the system near the end of drop life and small amplitude pulse approximately 50 millivolts is superimposed on this range and the measured signal is the drift in the current measured before and after the amplification of current. So a change in current produces by the perturbation gives a peak shaped curve with a peak maxima occurring near E1/2 wave potential if the perturbation is sufficiently small. For example in Pb 2+ in 1 M KCl at the supporting electrolyte with both the ordinary and alternate drop, the decrease in charging current is accompanied by small diminished faradic current value with a pulse width of 0.4 msec drop time 1 sec ∆E = -50 mV and the lead concentration as 40 to160 nanogram per mL.

Applications of Polarography: 1. Qualitative analysis: It helps in characterization of organic matter and various metal interactions from half wave potential of the current v/s voltage graph.

2. Qualitative analysis: Polarography is used in the determination of concentration of drugs, metal ions etc. in the given sample.

3. Determination of inorganic compounds: Polarography is used in determination of cations and anions in the presence of interfering ions.

4. Determination of organic compounds: Polarography is used in determination of structure, quantitative analysis of mixture of organic compounds.

5. Estimation of dissolved oxygen: Amount of oxygen dissolved in aqueous solution or organic solvent can be calculated with the help of Polarography.

6. Pharmaceutical applications: Tetracycline antibiotics, sulphonamides can be analysed by Polarography

Stripping voltammetry:

Consider a conventional DC polographic system set up with an oxygen per solution of supporting electrolyte containing one or more ions reducible at mercury cathode. But quite with a hanging mercury drop electrode. If potiostart of polarograph is said to a fixed value. Which is chooses to be 0.2-0.4v more negative than the highest reduction potential encounter among the reducible ion. The deposition of the metals will take place an HMDE cathode and usual amalgam formation will take place. The rate of amalgam formation will be governed by the magnitude of the current flowing by the concentrations of the reproducible ions and by the rate at which the ions travel of the electrode and in practice electrolysis is carried out for carefully controlled time interval. So that a fraction of the reducible ions are discharge.

This operation is often refer to as a concentration stip. The metals become concentrated into the relatively small volume o of the mercury drop.

The electrolysis current is not stopped. The stirrer switched off then the cell allowed to stand about 30 seconds and alow the solution to become quiescent.

The potential is then caused to break a voltage sweep in reverse, starting from the potential used in the electrolysis this means that a gradually increasing +ve potential is applied to +ve HMDE which is formed the anode of the cell. The current is measured and plotted against the voltage. As the potential approaches the oxidation potential of one of the metal dissolved in mercury. Then ions of that metal pass into solution from amalgam. And the current increases rapidly and attains maximum value. When the potential as a value appropriate to the approximate oxidation potential. The metal is said to be stripped from the amalgam. And is potential is corresponding to the maximum current.

From the nature of the process descried it has been refereed as stripping polarography, but the term anodic in stripping voltammetry is preferred. It is also possible to reverse the polarity of the 2 electrodes of the cell. Thus leading to the technique of cathodic stripping voltammetry.

The continuous rise in the anodic potential fresh peaks will be produced in the curve as the oxidation potentials of the different metals contain in the amalgam are reached. Then the resulting curve is turned as stripping voltagram the above curve or voltagram shows a single metal concentrated in the mercury.

Here the magnitude of the peak current is proportional to be concentration in the amalgam of the metal be stripped and is proportional to its concentration in the original solution.

Coulometric Methods of Analysis

- Coulometric methods of analysis are based on the measurement of quantity of electrical charge that passes through a solution during an electrochemical reaction.

- There is exhaustive elctrolysis of the analyte: that is quantitative reduction or oxidation of the analyte at the working electrode or the analyte reacts quantitatively with a reagent generated at the working electrode.

- The principle is governed by Faraday's laws of electrolysis.

$$n_A=Q/nF$$

Controlled Potential Coulometry (Potentiostatic Coulometry)

Principle

- The working electrode will be kept at constant potential that allows for the analyte's reduction or oxidation without simultaneously reducing or oxidizing other species in the solution.

- The current flowing through the cell is proportional to the analyte's concentration.

- With time the analyte's concentration as well as the current will decrease.

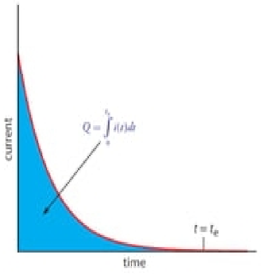
- The quantity of electricity is measured with an electronic integrator.

► Current efficiency is the percentage of current that actually leads to the analyte's oxidation or reduction; to ensure 100% current efficiency is to hold the working electrode at a constant potential, chosen so that the analyte reacts completely without simultaneously oxidizing or reducing an interfering species

As electrolysis progresses the analyte's concentration decreases, as does the current. The resulting current-versus-time profile for controlled-potential coulometry is shown in the

Figure below

► Integrating the area under the curve (equation 3) from (t = 0 to t = te) gives the total charge



We can use the Nernst equation to estimate the minimum potential for quantitatively electrolysis

► If we define a quantitative electrolysis as one in which we reduce or oxidized 99.99% of substance

► Example; Cu2+ (aq) + 2e Cu(s) ....(4) the required potential can be calculated by;

E = E2+ Cu2+/Cu 0.05916 2 -log- 1 [Cu2+]

then the concentration of Cu2+ at te is

[Cu2+] = 0.0001×[Cu2+]。 (6)

where [Cu2+]0 is the initial concentration of Cu2+ in the sample. Substituting equation (6) into equation (5) allows us to calculate the desired potential.

0.05916, E = E -log- Cu2+/Cu 2 1 0.0001x [Cu2+] ...(7)

MINIMIZING ELECTROLYSIS TIME

► In controlled-potential coulometry, as shown in the above figure, the current decreases over time. As a result, the rate of electrolysis becomes slower and complete electrolysis of the analyte may require a long time.

Factors affecting the analysis time:

► We can approximate the change in current as a function of time as i=ie-k

where i0 is the current at t = 0 and k is a rate constant

► For complete electrolysis in which we oxidize or reduce 99.99% of the analyte, the current at the end of the analysis, te, is i <= 0.0001i_{0} ..(9)

► Substituting equation (9) into equation (8) and solving for te gives the minimum time for complete electrolysis as t_{e} = - 1/k * ln(0.0001) = 9.21/k

As k is directly proportional to the area of the working electrode and the rate of stirring, and that is inversely proportional to the volume of solution so factors affecting analysis time are;

3. Stirring rate

► A quantitative electrolysis typically requires approximately 30-60 min, although shorter or longer times are possible.

Constant-Current Coulometry

► Q = ite ;(te = electrolysis time) • For controlled potential coulometry: the current varies with time: Q = What do we measure in coulometry? Current and time. Q & N are then calculated according to one of the above equations • Coulometry requires 100% current efficiency. What does this mean? • All the current must result in the analyte’s oxidation or reduction

UNIT-IV

ION SELECTIVE ELECTRODES

Introduction

- Ion selective electrode (ISE) is an analytical technique used to determine the activity of ions in aqueous solution by measuring the electrical potential.
- Specific Specific ion dissolved dissolved in a solution solution create an electrical potential, which can be measured by a voltmeter or pH meter.
- The strength of this charge is directly proportional to the concentration of the selected ion

Principle

- ISE consists of a thin membrane
- Only specific ion can be diffuse.
- By measuring measuring the electric electric potential potential generated across a membrane by “selected” ions, and comparing it with reference electrode.
- And net charge is determined.

Types of ISE

- Glass membrane
- Solid state electrode
- Liquid based electrode
- Compound electrode

Glass Membrane Electrode

- This method uses the electrical potential of pH-sensitive electrodes as a measurement signal.
- The glass electrode electrode is the most commonly used sensor.
- Not having the disadvantages of the optical methods, it can be used almost universally

Solid State Electrode

- Electrode body of Inorganic crystalline polymer.

- E.g. Special Special Epoxide Epoxide Resin with excellent mechanical properties.
- High temperature stability.

Liquid based electrode

- Formed by a very thin layer of an organic liquid.
- Membrane is like jelly
- Impermeable to water
- only to allow to pass certain certain ion.
- Organic material - Carbon tetrachloride - Benzene – Mesitylene

Types of membrane

A membrane is considered to be any material that separates two solutions

It is across this membrane that the charge develops.

Several types of sensing electrodes are commercially available

They are classified by the nature of the membrane material used to construct the electrode

It is this difference in membrane construction that makes an electrode selective for a particular ion.

Glass membrane

Glass membranes are made from an ion-exchange type of glass (silicate or chalcogenide)

This type of ISE has good selectivity, but only for several single-charged cations; mainly H^+, Na^+, and Ag^+

Chalcogenide glass also has selectivity for double-charged metal ions, such as Pb^{2+}, and Cd^{2+}

The glass membrane has excellent chemical durability and can work in very aggressive media

A very common example of this type of electrode is the pH glass electrode

pH electrode

Glass membrane manufactured from SiO_2 with negatively charged oxygen atom

Inside the glass bulb, a dilute HCl solution and silver wire coated with a layer of silver chloride is kept

The electrode is immersed in the solution and pH is measured

Crystal-Membrane Electrodes

Made from mono- or polycrystallites of a single substance

They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response

Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance

An example is the fluoride selective electrode based on Lanthanum fluoride crystals

The membrane consists of a single lanthanum fluoride crystal which has been doped with europium fluoride to reduce the bulk resistivity of the crystal

It is 100% selective for Fions and is only interfered with by OH which reacts with the lanthanum to form lanthanum hydroxide, with the consequent release of extra F ions

This interference can be eliminated by adding a pH buffer to the samples to keep the pH in the range 4 to 8 and hence ensure a low OH concentration in the solutions.

Gas-sensing electrodes

Are available for the measurement of dissolved gas such as ammonia, carbon dioxide, nitrogen oxide, and sulfur dioxide

These electrodes have a gas permeable membrane and an internal buffer solution

Gas molecules diffuse across the membrane and react with a buffer solution, changing the pH of the buffer

The change is detected by a combination pH sensor within the housing

Due to their construction, gas sensing electrodes do not require an external reference electrode.

Enzyme electrodes

Enzyme electrodes definitely are not true ion-selective electrodes but usually are considered within the ion-specific electrode topic

Such an electrode has a "double reaction" mechanism - an enzyme reacts with a specific substance, and the product of this reaction (usually H+ or OH-) is detected by a true ion-selective electrode, such as a pH-selective electrodes

All these reactions occur inside a special membrane which covers the true ion-selective electrode, which is why enzyme electrodes sometimes are considered as ion-selective

An example is glucose selective electrodes

Advantages of (ISE) Technique

Relatively inexpensive (as compaired to Atomic Adsorption Spectrophotometry or lon Chromatography), simple, have an extremely wide range of applications and wide concentration range.

It is a real-time measurement, which means it can monitor the change of activity of ion with time.

As it measure the activity, instead of concentration, it is particularly useful in biological/medical application.

It can determine both positively and negatively charged ions.

Not interfered by color or turbidity in the sample

• Ideal for monitoring environmental pollution or water quality etc. - where the operator simply wants to be sure that a certain ion is below a particular threshold value, or where only the order of magnitude may be required

ISEs can be used in aqueous solutions over a wide temperature range. Crystal membranes can operate in the range 0 C to 80 C and plastic membranes from 0 C to 50 C.

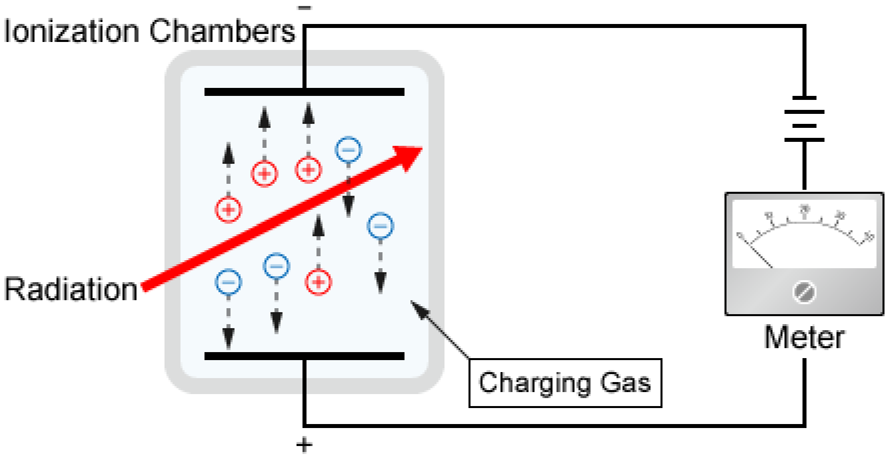
Other applications of ISE

- Pollution Monitoring: Cyanide, Flourine, Sulphur, Chlorine, Nitrate
- Agriculture: NO3, CI, NH4, K, Ca, I, CN in soils, plant material, fertilisers and feedstuffs.
- Food Processing: NO3, NO2 in meat preservatives.
- Salt content of meat, fish, dairy products, fruit juices, brewing solutions.
- F in drinking water and other drinks.
- Ca in dairy products and beer.
- K in fruit juices and wine making.
- Corrosive effect of NO3 in canned foods.
- Detergent Manufacture: Ca, Ba, F for studying effects on water quality.
- Paper Manufacture: S and Cl in pulping and recovery-cycle liquors.
- Explosives: F, CI, NO3 in explosive materials and combustion products.
- Electroplating: F and Cl in etching baths; S in anodising baths.
- Biomedical Laboratories: Ca, K, Cl in body fluids (blood, plasma, serum, sweat).
- F in skeletal and dental studies.
- Education and Research

Radio chemical methods of analysis:

Detection and measurement of radio activity

Ionization chamber:



An electroscope consists of an earth connected box divided into two chambers while an isolated metallic plate. The lower chamber is made of sheet of lead. This is known as ionization chamber. It consists of a lead block in which the radioactive sample is placed. The upper chamber contains a gold leaf electroscope attached to the metallic plate. The gold leaf electroscope and metallic plate are charged positively and divergence of the gold leaf is noted on the scale.

The radio active substance is put in the rays from the substance ionizes the gas in the ionization chamber. This results in the leakage of charge and the metal plate and gold leaf falls slowly rate of fall is noted. The experiment is repeated with another sample of known activity under similar conditions. To note their relative activity.

The ionization is mainly due to α rays because, β,γ rays are weak ionizes of gases. If we cover the lead cavity with 0.1mm thick aluminum foil α rays are cutoff and ionization will be due to β,γ rays.

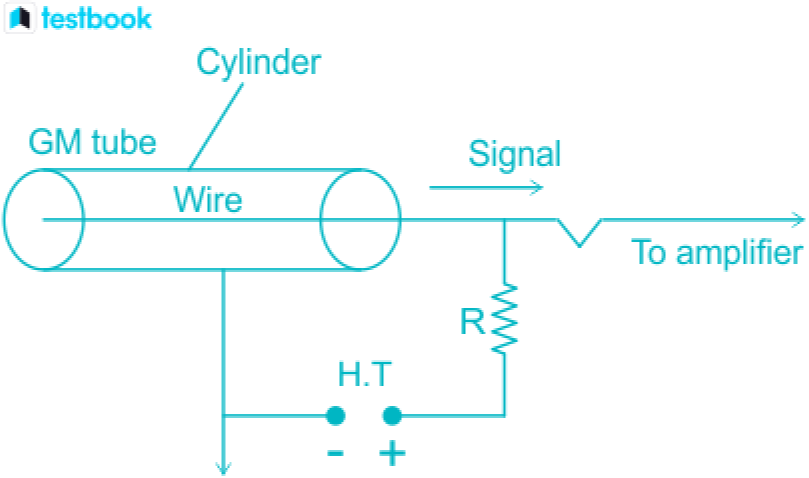
If the lead cavity is covered with 5mm thick aluminum foil α,β rays are cut foff and ionization will be only due to γ rays.

So we get the rates of emission of three types of rays separately.

The activaties of different radio active substance differ widely

Eg: Radium atoms have 3 million times the activity of iridium atoms.

GIGER MULLER COUNTER:



This device used to detect and measure the rate of emission of α,β particles it consists of a cylindrical metal tube (cathode) and central wire which is anode the anode is filled with Argon gas can reduce pressure (0.1atmp) an potential difference of nearly1000v is apply across the electrodes when α or β particles enters the tube through the mica window it ionizes the Argon atoms.

$$Ar \rightarrow Ar^{+} + e^{-}$$

The argon ions are attached towards the cathode and electrons towards the anode. So a function of the pulse of electrical current flows b/w the electrodes and completes the circuit around each electrical pulse makes the entry of one α or β particles into the tube. This is recorded in an automatic counter. The no. of pulses determined by radio active substance per minute to gives the intensity of its radio activity.

Radio active tracer:

An importance use of radio activity which finds applications in science is known as radio active indicators or radio active tracers or isotropic tracers The radioactive tracers classified into two types. They are used due to certain properties of radiation emitted by them irrespective of the chemical nature of the radiating atoms.

The chemical properties of radio isotopes are important and the radiation emitted acts as means of identifying the radiating atoms this is known as trace application . it is widely used in chemical research and analytical chemistry

Tracer technique is useful in tracing the element in this technique first take tracer material. This material is tagged with radio isotope of molecule. The tagged compound is now introduced in to system and experiment is carried out. The resulting products are analyzed radio chemically.

Stable isotopes may also be used as tracer .radio isotopes are useful than stable isotopes. All artificial isotopes used as tracer technique are β emitter. The measuring instruments are electroscope, electrometer, GM- counter for radio isotopes, while stable isotopes,masss spectrometer are used.

Applications :

D1. Determination of solubility of sparingly soluble salt.

Havesy and Paneth used this method depends on radio element added to the same element will persists in a definite ratio

Eg: solubility of lead chromate is determined :

An known amount radio lead is added to soluble salt of lead. The resulting solution is measured. By electroscope. The soluble mixture of lead ions is precipitated as lead chromate and kept at constant temperature till equilibrium is attained.

The ppt is filtered dried and weighed portion is mixed with water and saturated solution is prepared. A known volume of solution is taken and evaporated to dryness the activity of residue is determined as activity of residue is determined as activity is proportional to amount of salt present. We can calculate wt of lead dissolved in a known amount of solution. Thus the amount of salt present is calculated.

2.Mechanisam of chemical reaction:

Deuterium and isotopes of C,N.O are used in mechanism of reactions

Eg. Structure of $S_2O_3^{-2}$ ions

When sulphur is heated in presence of labled sulphde ions the of S2O3- is firned

$S+SO_3^{-}*\rightarrow S_2O_3^{-2}$

When S2O3 -2 ion is broken down is acid solution the reverse reaction occurred. So decomposition of labeled sulphur remains linked to be oxygen atom in the is not effected at all

Structure of $S_2O_3^{-2}$

3. Exchange reaction:

When a compound contains OH- or COOH is placed in heavy water then D2 exchange itself for hydrogen atoms. This shown hydrogen atoms are not static but ionize to be replaced by D2 atom

Activations analysis :

Most of the elements becomes radio active when irradiated with nuclear particle such as protons. Neutrons and α particles. The resulting activity provided by quantitative analysis.

The method of activation analysis depends on the formation of radio nuclides from elements in the sample when they are subjected to bombardment by energetic particles

Principle:

The process in which the sample is subjected to nuclear bombardment and then analyzed for its radio-active contents is known as Activation Analysis in optical emission spectroscopy activation of spectrometry occur simultaneously. In neutron activation analysis they are separate steps

A complete analysis by neutron activation may include below steps

1. Activation of the sample
2. Isolation of the Nuclide
3. Quantitative assay for the nuclide

Activation analysis classified into two types

1. Absolute method
2. Comparator method

1. Absolute method:

The elements to be determined are made radioactive slow neutron irradiation and this radio activity after suitable chemical separation is necessary. And measure of mass of the element originally present.

When an element is made radioactive and it is in homogeneous flux of energetic charged particle of neutrons, the activity ‘A’ produced in the element given by

.Advantages:

- The method is very simple compare to other methods.
- It is highly sensitive and used for determination of element presence in tracer.
- It is non destructive technique and does not require the removal of sample to be analyzed.

Applications:

It has been used for estimating the trace amounts of the undesirable impurities in various samples.

In Germanium, silica, oxygen used in steel neutron capturing element in construction materials and moderators used in nuclear reactors

It is used in dating of geological specimen method.

It is used for estimating the trace elements like Zn, Mn, Co, Cu etc in animals and plants.

Trace amounts of elements in rocks soils sand estimated and trace elements in meteorites ad determination of ages of these object that galls from space to earth.

Composition of human hair in respective of several trace elements determined.

Composition of the surface of the moon can also be analyzed

This method used for identifying the geographic origin of specimens.