Unit-4 Paper-IV

a) Mass Spectroscopy :-

Principle :-

This technique used when Sample is Isolated on the basis of mass to charge ratio. It is denoted as m/z or m/e.

~~The 1st step in mass Spect~~ when a Sample injected in to the mass spectrometer it passes through a electric and magnetic field and then detected by the mass detector according to theire mass.

The 1st step in mass spectrometer is the production of gas-phase ions of ~~the~~ Sample molecule.

when a beam of electroon will be bombarded to sample molecule, it will leads to removal of one e^- from molecule and form molecular ion.

$$m + e^- \longrightarrow m^{+\cdot} + 2e^-$$

(molecular ion)

this molecular ion is unstable so it under

go fragmentation to form fragment ions get stable.

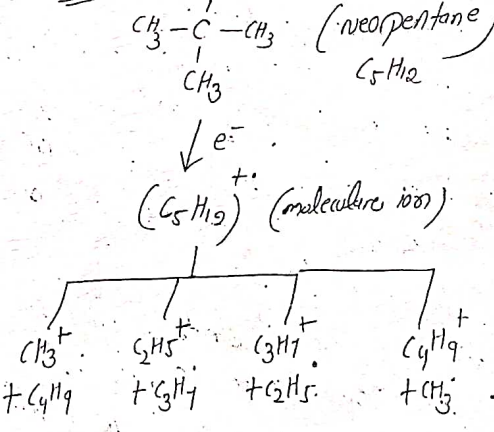
$$m + e^- \longrightarrow m^{+\cdot} + 2e^-$$

$$m_1^+ + m_2 \qquad m_1 + m_2^+$$

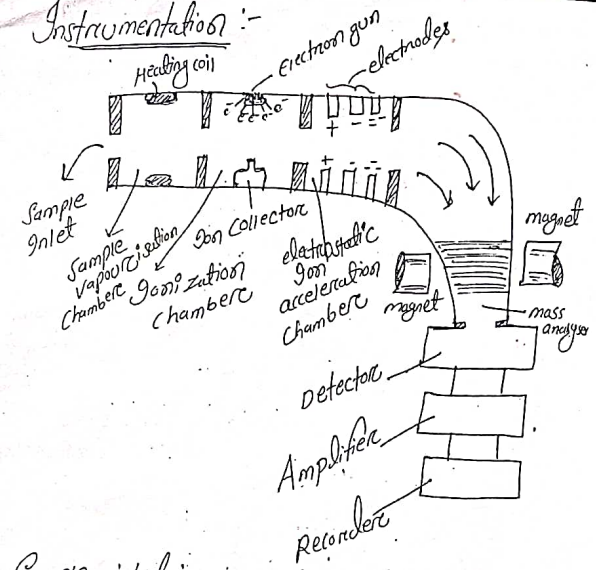
and m_1^+ & m_2^+ are the fragment ions.

Here we get three +ve ions m, m_1, m_2 which are ~~Separ~~ detected / Identify according to their mass.

Ex:-



Instrumentation :-



Sample inlet :-

Here we can take any type of sample such as gaseous / liquid / solid.

If Sample is present in gaseous form then there is no problem but if it is solid / liquid then it has to be converted in to gaseous form.

Due to the heating coil the solid / liquid sample molecule is converted in to gaseous / vapour form.

The purpose of the inlet system is to inlet Sample in to the Ionization chamber.

There are several type of inlet system / those are,

i) batch inlet
ii) direct Probe inlet
iii) Chromatographic and capillary electro-phoretic inlet

1) Batch inlet

It is a Simplest inlet system, in which the Sample is volatilized externally and then allowed to the ionization chamber.

It is applicable to gaseous and liquid Sample having boiling points up to about 500°C.

2) The direct probe inlet

Here solid and nonvolatile liquids can be introduced in to the vapourized chamber by using a Sample holder or Probe and then in to Ionization chamber.

Here in the process of Sample inlet less sample is wasted than compared to batch inlet system.

3) chromatographic & capillary electrophoretic inlet system :-

now a days mass spectrometers are coupled with gas or high-performance liquid chromatographic system or capillary electrophoretic to permit the separation and determination of component of complex mixture.

Ionization chamber :-

In ionization chamber one electron gun is present which produce highly energy electrons.

when the gaseous sample molecule enter in to this chamber it will bombarded with highly energetic electron and leads to removal of $1e^-$ and form molecular ion.

$$m + e^- \rightarrow m^+ + 2e^-$$

Potential required to convert m to m^+ is called "ionization potential" (8-15 eV)

now the molecular ion fragmentized to form fragment ions.

And here ion collector is present which collect the electrons. And only the +vely charged ion move towards the electrostatic ion acceleration chamber.

There are several ionization techniq. used in mass spectrometers.

1) Chemical ionization method :-

Here we take a carriere gas and this gas will be introduced in to the ionization chamber at near atmospheric pressure.

methane is generally used as the carriere gas (also use ammonia, isobutane)

Carriere gas will be ionized due to electron impact from the ionization source

$$CH_4 \xrightarrow{e^-} CH_4^{+\cdot} + 2e^-$$

molecular ion

To get stable it undergo fragmentation to form fragment ions :

$$CH_4^{+\cdot} \longrightarrow CH_3^+ + H^\cdot$$

$CH_4^{+\cdot}$, CH_3^+ are known as primary ion.

These primary ions react with excess of CH_4 will produce secondary ions.

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + CH_3^\cdot$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

CH_5^+, $C_2H_5^+$ are known as Secondary ions. And these Secondary ions will react with Sample molecule and form ion by Proton transfer.

$$M + CH_5^+ \longrightarrow [M-H]^+ + CH_4$$

$$M + C_2H_5^+ \longrightarrow [M-H]^+ + C_2H_4$$

$[M-H]^+$ also known as Quasi molecular ion. and also can be written as, $(M+1)$.

This method causes less fragmentation and so the mass spectra can be interpreted more easily.

2) Electron impact ionization :-

In this method gaseous sample molecule bombarded with the high energy electron which is (70 eV) and lead to removal of $1e^-$ from sample molecule and form molecular ion (M^+). The molecular ion has same mass as the initial molecular M. Thus, it's mass give molecular weight of the compound.

$$M + e^- \longrightarrow M^{+\cdot} + 2e^-$$

Due to high energy and direct bombardment molecular ion converted to fragment ion.

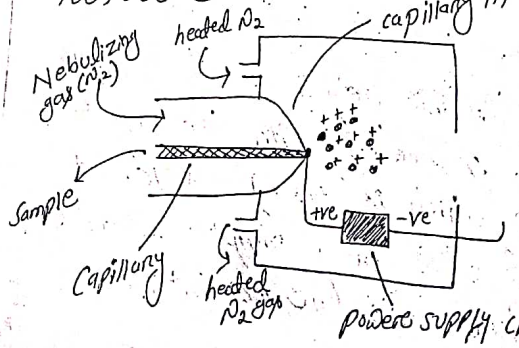
$$M^+ + e^- \longrightarrow M^{+n} + (n+1)e^-$$

And these ion reach towards mass analyser.

3) Electrospray ionization :-

It is a type of evaporating ionization technique.

This technique is used to analyse of Biomolecules such as protein and polypeptides which having high molecular weight 100,000 Dalton or more.

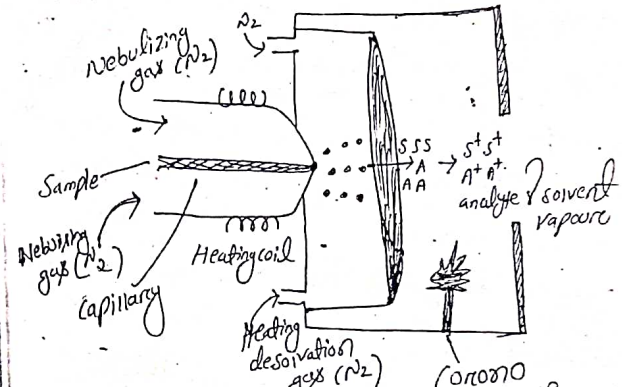


Here one capillary will be present through this sample molecule is injected and at the tip of the capillary high voltage potential is supplied by power supply chamber. due to this are sample will come through capillary and due to presence of Nebulizing gas (N_2) it converted in to sprayed droplet at the tip of the capillary and ~~due to~~ then it will be ionized due to high voltage potential and here also we supply heated N_2 gas. due to this the temp. of the ionization chamber is high and that will remove the solvent from analyte and will converted in the form of molecular ion then it will go towards the ion acceleration chamber.

And the -ve side of power supply chamber is attached to ion acceleration chamber which produce -ve potential and that will help the +ve ion move towards the mass analyser.

4) Atmospheric pressure chemical ionization

This technique carried out in atmospheric pressure. It is the combination of electrospray and chemical ionization.



Sample injected ~~will be~~ through the capillary and then it will be converted in to sprayed droplet due to nebulizing (N_2) and finally converted to analyte and solvent vapour due to heating by N_2. Corona discharge electrode (which emmit β-particle) will ionize the solvent vapour molecule just like production of primary ions in chemical ionization and form MH^+ ion

by mechanism,

$$A + S^+ \longrightarrow M^+ + S^- \text{ (form +ve ion)}$$

Apart this we will also get a -ve charged ion here like,

$$A^+ + S \longrightarrow (M-H)^- + SH^+ \text{ (form -ve ion)}$$

$(M-H)^-$ also written as $(M-1)$.

So in this ionization technique we will get both +ve and -ve ion. And this technique used for analyse the substance whose molecular weight is less than 1500 Dalton.

Electrostatic ion acceleration chamber :-

In ion acceleration chamber charged electrode are present. when the +ve charged ion enter in to the chamber it will repuled by +ve electrode and attracked by -ve electrode and move towards right side. In this way a strong electrostatic field accelerates the ion of mass m_1, m_2 with a specific velocity.

if the ions accelerated in an electric field at voltage V and each particle give energy eV then this is equal to the kinetic energy,

$$\frac{1}{2}mv^2 = eV$$

$$mv^2 = 2eV \quad \text{---(i)}$$

After the charged ions have been accelerated by an applied voltage, they enter a magnetic field (H). This field attracts the particles and move in a curvature path. This attractive force due to magnet is HeV.

whereas the balancing centrifugal force of the particle is $\frac{mv^2}{r}$. Then,

$$HeV = \frac{mv^2}{r}$$

Squaring both side,

$$H^2e^2v^2 = \frac{m^2v^4}{r^2}$$

$$H^2e^2r^2 = m^2v^2$$

$$\frac{H^2e^2r^2}{m} = mv^2 \quad \text{---(ii)}$$

from equn (i) & (ii)

$$\frac{H^2 e^2 r^2}{m} = 2eV$$

$$\frac{e}{m} = \frac{2V}{H^2 r^2}$$

$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$

From this equn we determine how ions are reach to the detector.

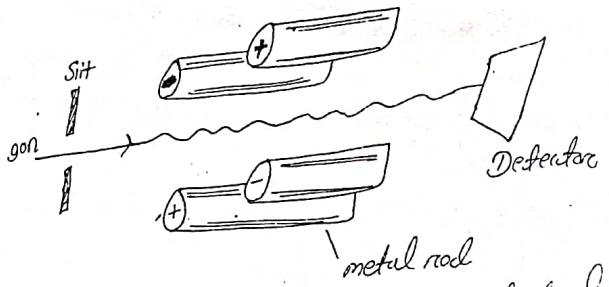
Ion with small size more effected by magnetic field compare to large size ion. So the large size ion hit the detector first and then inter mediate ion and then the small size ion.

Mass Analyser :-

After passing through electric and magnetic field ~~sample~~ tvely charged ions enters to the mass analyser. where they will separated on the basis of theire molecular weight.

In mass spectrometer different type of mass analyser are used those are,

1) Quadrupole mass analyser :-



It consist of four parallel cylindrical metal rod.

The digonal / opposite rod have same charge and a space b/w the parallel rods where radio frequency (Rf) or direct current (DC) voltage is applied.

Due to this a oscillating electrostatic field generate b/w the space of rod.

When the ions enter in to the space b/w rod due to this Rf & DC they acquire oscillation by a way.

If Rf > DC the larger size ion will hit detector first.

if $\Delta f < DC$, then small ion will hit the detectors first and give signal.

In this way only certain m/z ratio containing ions are come out from the analyser and remaining are attached to the side of the rod.

advantage :-

1) cost effective
2) give fast resolution

disadvantage :-

1) Give low resolution peak

2) Time of flight (TOF) :-

→ It is based on velocity of ions.
→ Lighter ion have higher velocity as compared to heavier ion.
→ So the low molecular weight containing ion that mean low m/z ratio ion will reach the detector first as compared to high m/z ratio ion.

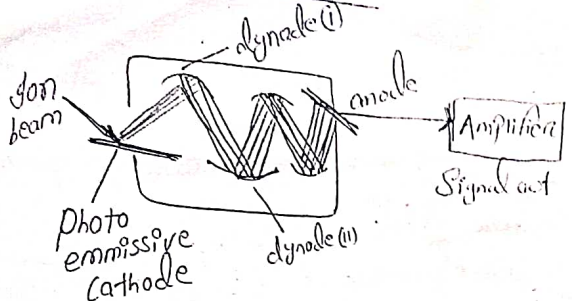
3) Ion trap mass analyser :-

After passing through the ionization chamber ions enter in to the ion trap mass analyser. Here a certain frequency is applied to it, so only respective ions come out from the analyser and remaining ion will be present inside the ion trap.

Detector :-

The specific ions from the mass analyser enter in to the detector where dynodes are present which detect the signal. There are several detector used in mass spectrometer.

Photo multiplier tube :- (PMT)



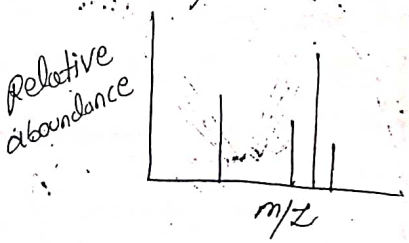
The photo multiplier tube consist of photo emissive cathode, dynodes and anode. When the photo cathode surface is exposed to ions it emits electrons and these e⁻ are attracted towards first dynode and it emit large no. of electrons (secondary electrons) for each striking electrons. and these are move towards 2nd dynode and so on. And these are finally collected at anode and resulting current is measured and send signal to amplifere.

Amplifier :-

After ions are detected by the detectors they go to the amplifiere where amplify signal.

Recorder :-

It Record the Signal and will get a spectrum / peak.



Types of peaks observed on MS :- (types of ion)

There are five type of ions (or) peak observed on mass spectroscopy.

1) Molecular ion / Parent ion :-

Ion formed by the loss of single electroon at lowest ionization potential from a molecule.

$$M + e^- \rightarrow M^{+\cdot}$$
(molecular ion).

2) fragment ion / daughter ion :-

Generated by the fragmentation of Molecular ion in the ionization chamber.

$$\dot{M}^{+\cdot} \left\langle \begin{matrix} m_1^+ \\ m_2^+ \end{matrix} \right\} \text{daughter ion}$$
(parent ion)

these ions generated from Parent ion.

3) Metastable ions :-

Some fragmentation may occure during their flight down the ion tube field free region instead of ionization chamber and known as metastable ions.

→ These ions are low intense and unstable.

→ They reach to the detector at masses lower than the actual mass and if detected by detector then it will give low intense broader peak.

These are less stable than fragment ions.

4) Quasi molecular ion :-

→ It is also called protonated molecular ion.

→ It formed by,

$$M + H^+ \rightarrow MH^+ \ (m+1) \text{ ions}$$

5) Multiple charged ion :-

→ Some double / triple charged ions are observed in some case, called Multiple charged ion. (m^{++}, m^{+++})

→ Different m/z ratio,

∴ If, Molecular wt = 100

charge = 2 (m^{++})

then, $\frac{m}{z} = \frac{100}{2} = 50$

If,

molecular wt = 30

charge = 3 (m^{+++})

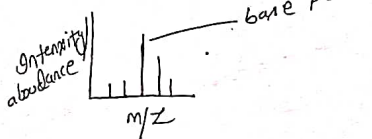
then,

$\frac{m}{z} = \frac{30}{3} = 10$

Base peak

→ The most intense / tallest peak in the mass spectrometer.

→ It is due to greater relative abundance.



→ Not neccessary that, the molecular ion is always the base peak.

Isotope peak

→ Due to presence of heaviere isotope element.

→ Give very less intense peak and it will be undetectable.

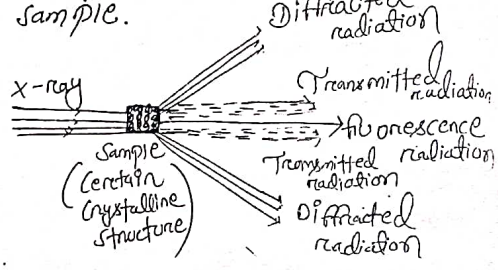
Ex:- ^{12}C - 98.89% } abundance
^{13}C - 1.1 %

unit-4 ⑥ X-ray Spectroscopy

Introduction

Wavelength of x-ray is (0.01 to 10 nm) (or) (0.1 to 100 A°).

It is the Interaction between x-ray and sample.



When x-ray incident on sample we will get a 3 type of radiation.

1) Transmitted radiation
2) Diffracted radiation
3) fluorescence radiation

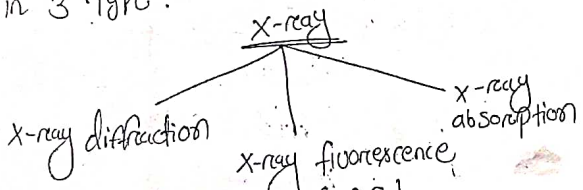
When x-ray incident on sample, that sample will absorb some radiation it called absorb radiation and some

radiation will transmitted called transmitted radiation.

And some radiation will diffracted in different direction due to the atom that present in that sample is called diffracted radiation.

When the X-ray incident on sample, the sample atom will absorb that radiation and their electron excited and come back ground state to emit radiation which is higher wavelength than incident radiation wavelength is called fluorescence radiation.

Based on this X-ray is catogorized in 3 Type.

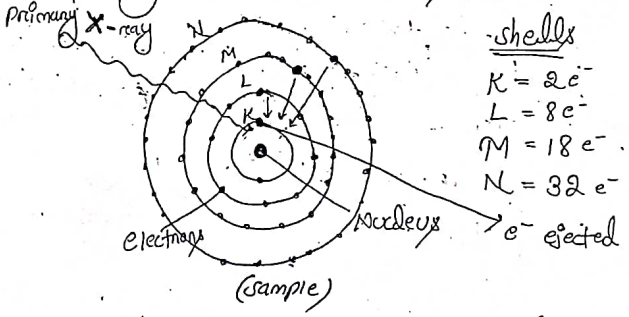


X-ray discovered by - "Wilhelm Konared Roentgen" in 1895

X-ray fluorescence (XRF) (Emission)

Principle

X-ray fluorescence (XRF) provides one of the simplest, most accurate and most economic analytical methods for the determination of elemental composition of many type of materials.



The same atom contain nucleus and various shells which contain electrons.

The energy of outer shell is higher compare to inner shell.

When primary X-ray incident on sample atom, then it remove

ejected one e^- from lower energy shell. So a void/vacancy will produce. So to fill this void may electron come from higher energy shell, by emit/releasing some radiation/energy and that will released in form of X-ray is called (Secondary X-ray) fluorescence radiation.

And this will equal to the difference between the energy of two shell.

$E_{x\text{-ray}} = E_L - E_K$ (if e^- fall from L-shell)

$E_{x\text{-ray}} = E_M - E_K$ (if e^- fall from M-shell)

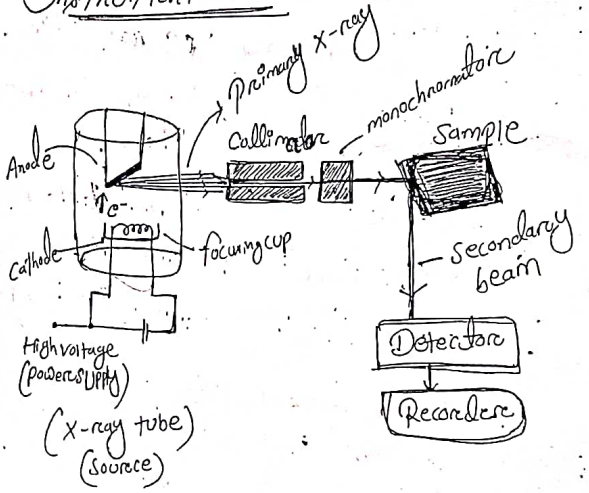
$E_{x\text{-ray}} = E_N - E_K$ (if e^- fall from N-shell)

we can measure the energy and intensity of this secondary X-ray radiation (characteristic x-ray) that comes out of the material (sample) to get information about the elemental composition of the sample.

For measuring the energy and intensity of the emitted characteristic X-ray radiation there are two possible methods,

1) Wavelength dispersive
2) Energy dispersive

Instrumentation



Radiation source :-
(X-ray tube)

It is a large Vacuum tube containing a heated cathode of tungsten filament

Scanned by CamScanner

and a Cu (or) Mo target metal anode.

X-ray tube uses a high voltage to accelerate the electrons released by a hot cathode to a high velocity.

The high velocity electrons collide with the target metal anode, creating the X-rays. (which is randomly directed)

Collimators :-

A collimator is a device that narrows a beam.

Narrow mean to cause the direction of motion to become more aligned in a specific direction.

Collimators contain two closely packed metal plates, separated by a small gap.

Monochromator :-

In X-ray two type of monochromator are used, 1) filtere monochromator
2) crystal monochromator

1) filtere Monochromator (Zirconium filter)

filtere absorb undesirable radiation and passed required radiation.

2) Crystal monochromator

It is made up suitable crystalline materials like NaCl, LiF, quartz.

It attached to collimator.

Monochromator convert polychromatic X-ray in to monochromatic X-ray.

Sample holder :-

The Sample is normally prepared by a flat disc especially of diameter 20-50 mm.

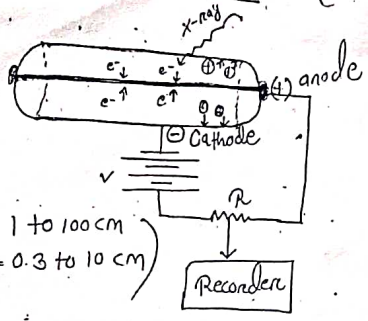
Detectors :-

Here, Detectors convert X-ray in to current signal.

1) Gas Ionization detector (Geiger muller counter)

2) Scintillation detector (PMT)

1) Geigere Muller Counter :- (GM tube)



(length = 1 to 100 cm
diameter = 0.3 to 10 cm)

Geigere muller Counter is nothing but a hollow metalic cylindrical tube, which contain inert gas (He, Ne, Ar).

This cylindere connected with a high voltage battery and center have a metalic electrode which made up tungsten that act as anode and cylindere surface act as cathode.

when x-ray enter in to detector it ionise the gas that present in cylindere and produce free electron and +ve ions which are accelerated towards anode and cathode respectively.

Due to the flow of ions current will generate and flow which detected by detector and signal send to Recorder.

(The amount of current measured ∝ incoming X-ray)

2) PMT (Photo multipiere detector tube)

(Same as on previous chapter I told)

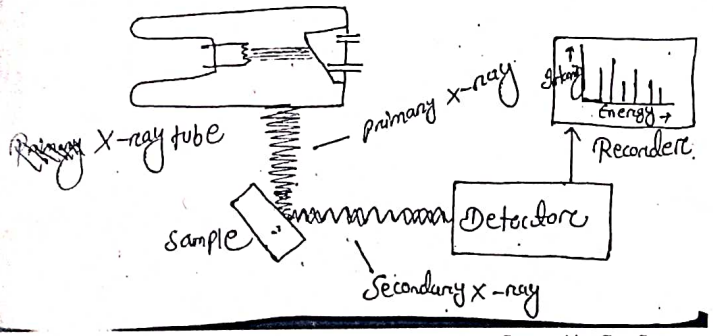
Energy dispersive technique :- (EDXRF)

The primary X-ray beam excites spectral lines from the sample.

In energy dispersive XRF all wavelengths enter the detector at once.

The detector registers an electric current having a height proportional to the photon energy / X-ray fluorescence radiation energy.

The energy dispersive arrangement is much simpler and more compact than the wavelength dispersive case.



(Principle, X-ray tube, Sample, detector, diagram: Same as X-ray instrument)

Energy dispersive technique is used for also chemical characterization and chemical analysis of sample.

The secondary X-ray are directed to a detector.

A detector is used to convert X-ray energy in to voltage signal ; this information is sent to a pulse processor. which measure the energy of a signal.

The current / voltage signal which is measured that proportional to the energy of the incoming X-ray.

Advantage of energy Dispersion technique :-

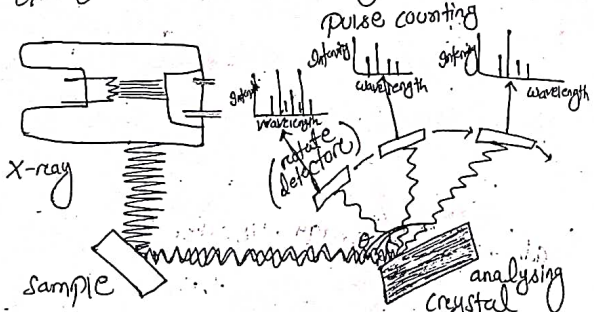
- Simplicity of Instrumentation.
- Simultaneous accumulation of the entire X-ray spectrum.
- qualitative analysis can be performed in 20 sec.

Wavelength dispersive techniques :- (WDXRF)

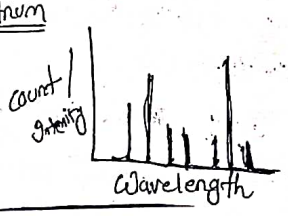
→ In wavelength dispersive spectrometer, x-ray emitted from the sample are dispersed spatially by crystal diffraction (analysing crystal).

The detector receives only one wavelength of light/radiation at a time.

The crystal and detector are made to synchronously rotate through angles of θ and 2θ, respectively.



Spectrum



(X-ray source, principle, sample, Detector write)

Same as x-ray Instrument.

Analysing crystal :-

Wavelength dispersive x-ray spectrometer separate the x-rays of interest using diffraction from a crystal. This follows from the Bragg equn.

$$2d\sin\theta = n\lambda$$

where, λ = wavelength
n = diffraction order
d = interplanar spacing distance
θ = angle of incident

A wavelength dispersive detection system physically separates the x-rays according to their wavelengths.

The x-rays are directed to a crystal, which diffracts (according to Bragg's Law) the x-rays in different directions according to their wavelengths.

Diffracting angles (θ) are measured and

Wavelength (λ) of each element is determined using Bragg's law.

(Analysing crystals such as, TAP, RAP, PET, NaCl, LiF, Quartz)

Advantages of Wavelength Dispersion :-

- Resolution is better
- higher individual intensities can be measured.

Lower detection limits are possible.

Chemical analysis by x-ray spectrometer

For qualitative chemical analysis wavelength dispersive spectrometer is used.

The angle (θ) between the surface of crystal and incident fluorescent beam is gradually change (increased), and the reflected radiation wavelength are measured and recorded as a series of peaks.

If energy dispersive spectrometer is used then the output of pulse height discrimination is recorded.

For qualitative analysis the intensity of the lines of the element to be determined is recorded and peak is observed and counts are collected.

For major element 2000,00 counts are accumulated in one (or) two minutes.

Matrix effect :-

The matrix effect is defined as the Combined effect of all components of the sample others than the analyte.

(or)

Component spectrum originating from sample is over loaded / overlap with the spectrum of interest.

It is important to realise that the x-ray produced in fluorescence process is not only generated from atom at the surface of sample but also below the

Surface.

matrix may cause variation in calculated result either high or LoD.

Ex:- The matrix contain a amount of element that absorb either incident (or) emitted beam then,

$$P_x = P_S W_x$$

where, P_x is relative line intensity

P_S = relative line intensity that would observed under identical counting condition.

W_x = weight fraction of element in sample.

Application of x-ray spectroscopy :-

1) It is used for medical purpose.

2) Ecology and environmental management
measurement of heavy metals in soil, sediments, water and aerosols.

3) Geology and mineralogy :-
qualitative and quantitative analysis of soils, minerals, rocks etc.

4) Metallurgy and Chemical industry
Quality control of raw materials, Production processes and final products.

5) Paint industry
analysis of lead-based paints

6) Jewelry :-
measurement of precious metals Concentrations / identification.

7) Fuel Industry :-
monitoring the amount of contaminants in fuels.

8) Food chemistry :-
determination of toxic metals in foodstuffs.

9) Agriculture :-
Trace metals analysis in soil and agricultural products.

10) Art sciences
study of paintings, sculptures etc.