SCHEME OF EVALUATION

SUBJECT NAME: ANALYTICAL INSTRUMENTATION

SUBJECT CODE: 14EI703

MONTH, YEAR: JANUARY, 2021

Prepared by: **Signature of HOD**

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14EI703

Hall Ticket Number:

IV/IV B.Tech (Regular/Supplementary) DEGREE EXAMINATION

January, 2021 **Electronics and Instrumentation Engineering**

Seventh Semester **Analytical Instrumentation**

Time: Three Hours **Maximum :** 60 Marks

Answer ALL Questions from PART-A. (1X12 = 12 Marks)

*Answer **ANY FOUR** questions from PART-B.* (4X12=48 Marks)

Part – A

1 Answer all questions (1X12=12 Marks)

a) List the sources for UV radiation.
b) State the Lambert's law.
c) What is grating in spectroscopy?
d) Why sensitive detector is required for Spectrophotometer?
e) Why high intensity magnets are preferred for NMR?
f) Define dead time of a GM counter.
g) What is meant by Ionization?
h) Compare the functions of Prisms and Gratings.
i) How the ESR principle is used in Analytical Instrumentation.
j) Define the term NMR.
k) Give the principle of Fourier Transform IR spectrophotometer
l) Give examples of Scintillating Crystals.

Part – B

2	a)	Discuss the working of double beam ratio recording spectrophotometer.	6 M
	b)	Write about the Prisms and Monochromators in UV-Visible Spectroscopy	6 M
3	a)	Explain different sources of UV and Visible radiations.	6 M
	b)	Outline the principles of visible spectroscopy and detailed comparison of various detecting units.	6 M
4	a)	Explain the working of FT-IR Spectrophotometer with neat diagram.	6 M
	b)	Discuss the various detectors used in IR spectroscopy.	6 M
5	a)	Explain the construction and working of Clinical Flame Photometer	6 M
	b)	Write about the Emission and Recording systems of Flame Photometers.	6 M
6	a)	Describe the constructional details of ESR Spectrometer with a neat sketch.	6 M
	b)	Explain the construction and working principle of FTNMR spectrometer.	6 M
7	a)	Explain in detail about Time of Flight Mass Analyzer.	6 M
	b)	Define Electro Spin? How it is used in Spectroscopy.	6 M
8	a)	Explain in detail about Instrumentation associated with X-Ray Spectroscopy.	6 M
	b)	Explain graphically the comparative operation of ionization chamber, GM counter and scintillation counter. Explain in detail the construction of a GM counter.	6 M
9	a)	Write various applications of X-Ray spectroscopy.	4 M
	b)	Explain the different types of X-Ray Fluorescence spectrophotometers.	8 M

1.a) Hydrogen, Deuterium discharge lamps.

b) The amount of energy absorbed or transmitted by a solution is proportional to the solution's molar absorptivity and the concentration of solute.

c) Grating is an optical component used for wavelength selection in Spectroscopy.

d) Sensitive detector is required for analysis of samples with very low concentrations.

e) High intensity magnetic field is required for Nuclear Magnetic Resonance.

f) Dead time is the time during which the GM counter becomes insensitive to fresh ionizing particles.

g) When nuclear radiation is passed through a gas, by absorbing the radiation the atoms become ionized by losing electrons.

h)Prisms work on the principle of “bending of light of different wavelengths by different angles”.

Gratings work on the principle of “constructive interference of light of a specific wavelength when the path difference is an integral multiple of that wavelength”.

(i) Electron Spin Resonance occurs when atoms absorb rf signal (MW region) under the influence of external magnetic field.

(j) Nuclear Magnetic Resonance: The nuclei of atoms absorb rf radiation when they are under the influence of external magnetic field.

(k) FTIR principle: The Michelson interferometer generates “interferogram” when radiation is passed through it.

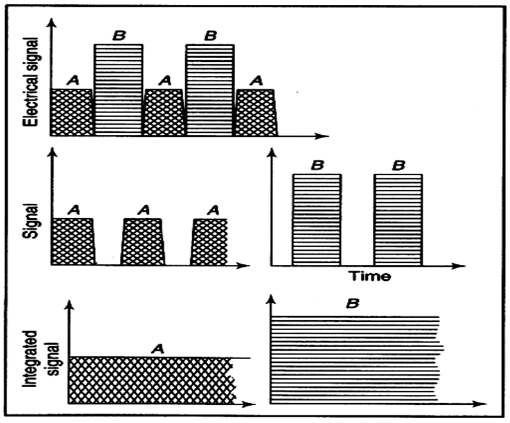
The absorbance at each wavelength can be obtained by applying Inverse Fourier Transform.

(l) NaI crystal.

2.(a)

Diagrams-3M, Description-3M

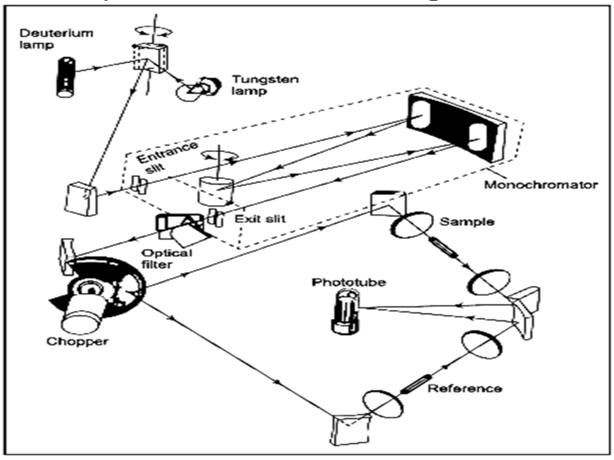
Double-beam Ratio-Recording Spectrometer:



Operation:

In this spectrometer light from source is split into two beams and they are passed through sample and reference solutions alternately by using a chopper. As shown in Figure 1 the output from the detector is an alternating electrical signal. The signal denoted as **‘A’** is the due the sample beam and is of smaller amplitude due to absorption of light by the sample solution and the signal denoted by ‘B’ is due to the reference beam and is larger since the reference solution doesn’t absorb light. The signals ‘**A’** and ‘**B’** are

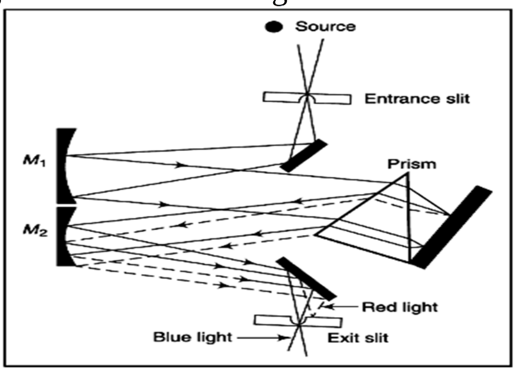
separated and integrated using an electronic integrator. The ratio of these integrated signals is calculated to determine either Transmittance or Absorbance.
Figure shows the optical diagram of the spectrometer. It consists of interchangeable Tungsten and Deuterium Discharge lamp. A sector mirror is used to pass the light through reference and sample beams alternately. Monochromator and optical filter are used for wavelength selection.



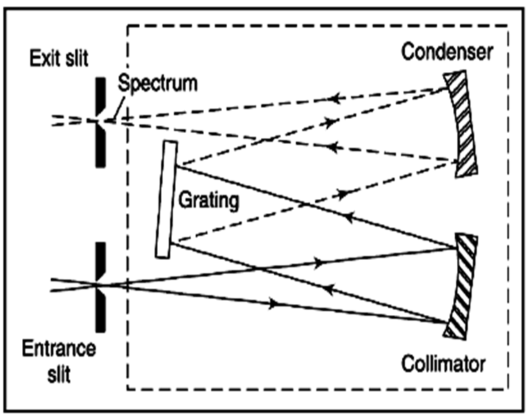
2.(b)

Diagrams-3M, Description-3M

Prisms and monochromators are used for selection of wavelengths from light.
Prisms:
Principle: Light of different wavelengths is bent by different angles when it travels from one medium to another medium (of different refractive indices). So light of different wavelengths are separated and can be selected. When a mirror is placed on the other side of prism light is reflected back and passes through the prism second time. This is called Littrow mounting. This will cause better separation. Prism made up of glass is used visible region and the one with Quartz is used in UV region.



Diffraction grating:
It consists of a highly polished surface upon which number of grooves are present. The light rays reflected from these grooves have either constructive or destructive interference depending on the path difference. Constructive interference occurs when the path difference is an integral multiple of wavelength.
d(sini+sinr)=nλ . Here i is the incidence angle and r is the reflection angle.

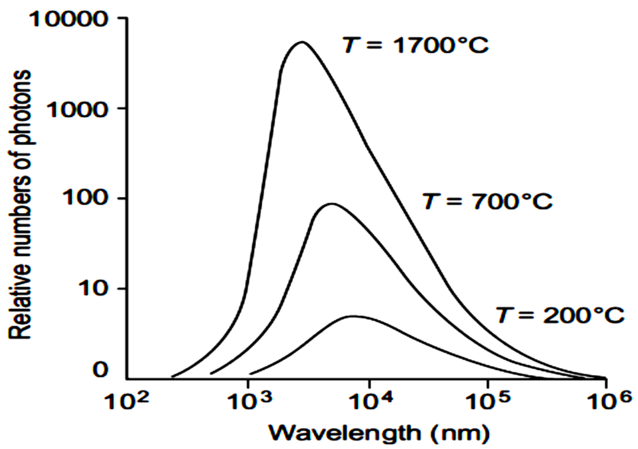


3.(a)
Diagrams-3M, Description-3M

UV-Visible Sources:
(i) Tungsten filament lamp
(ii) Hydrogen/Deuterium Discharge Lamp
(iii) Lasers
(iv) LED

(i) Tungsten Lamp:

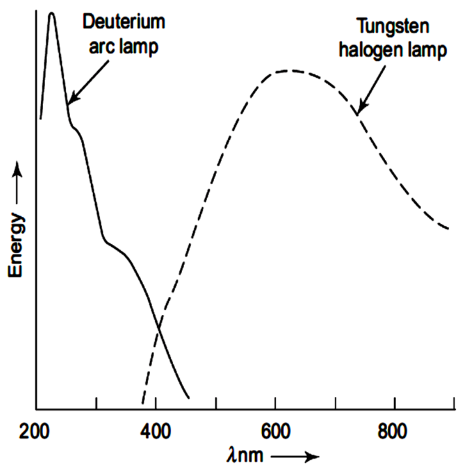
This lamp consists of a tungsten filament enclosed in a glass envelope. It is cheap, intense and reliable. A major portion of the energy emitted by a tungsten lamp is in the visible region and only about 15–20% is in the infrared region. When using a tungsten lamp, it is desirable to use a heat absorbing filter between the lamp and the sample holder to absorb most of the infrared radiation without seriously diminishing energy at the desired wavelength.



(ii) Hydrogen/Deuterium discharge lamp:

Deuterium lamps are the UV source in UV-Vis absorption spectrophotometers. The sharp lines of the mercury and rare gas discharge lamps are useful for wavelength calibration of optical instrumentation. For fluorescent work, an intense beam of UV light is required. This requirement is met by a Xenon arc or a mercury vapour lamp. Cooling arrangement is very necessary when these types of lamps are used.

A deuterium arc lamp provides emission of high intensity and adequate continuity in the 190–380 nm range. A quartz or silica envelope is necessary not only to provide heat shield, but also to transmit the shorter wavelengths of the UV radiation. The limiting factor is normally the lower limit of atmospheric transmission at about 190 nm.



Energy output as a function of wavelength for deuterium arc lamp and tungsten halogen lamp

(iii) Lasers:

The term laser has been coined by taking the first letters of the expression 'Light amplification by simulated emission of radiation'. Although an amplifier, as suggested by the abbreviation, the laser is invariably used as a generator of light. But its light is quite unlike the output of conventional source of light. The laser beam has spatial and temporal coherence, and is monochromatic (pure wavelength). The beam is highly directional and exhibits high density energy which can be finely focused.

(iv) LEDs:

LEDs offer a number of advantages compared to existing light sources in optoelectronic applications. These include increased lifetime, low cost, reduced power consumption, higher brightness, rugged construction, flexible configuration, enhanced spectral purity, small size, and breadth of spectral range. The centre lead (K) is the common cathode for both LEDs, the outer leads (A1 and A2) are the anodes to the LEDs allowing each one to be lit separately, or both together to give the third colour. The use of bi-/tri- colour LEDs can provide a compact rugged multi-wavelength photometer source that can facilitate multi-component analysis.

3.(b)

Diagrams-3M, Description-3M

Principles of visible spectroscopy:

In visible spectroscopy light is passed through sample being analyzed. The sample absorbs light energy. The absorption depends on the distance which the light travels through the sample and the concentration of the sample.

The elements present in the sample absorb light of different wavelengths. By selection of different wavelengths using various optical components the absorbance at different wavelengths is determined and absorption spectrum in drawn. Using absorption spectrum the elements present in the sample and their concentrations can be determined using laws like Beer's law , Lambert's law. (2M)

<u>Detectors:</u>

(i) Photovoltaic of Barrier layer cell:

The photovoltaic cell consists of a semiconductor like Selenium which absorbs light energy and generates electron-hole pairs. The electrons and holes constitute current and is proportional to the light intensity.

The cell consists of selenium deposited on Iron base and a glass window to allow light and the entire set up is enclosed in a plastic case.

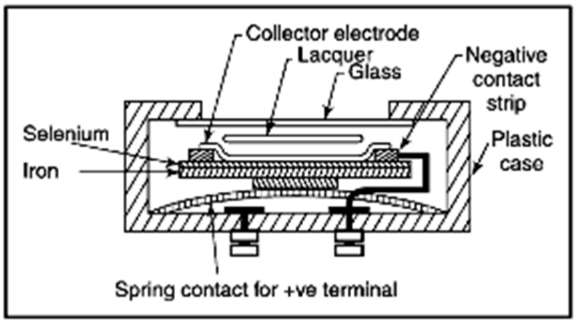
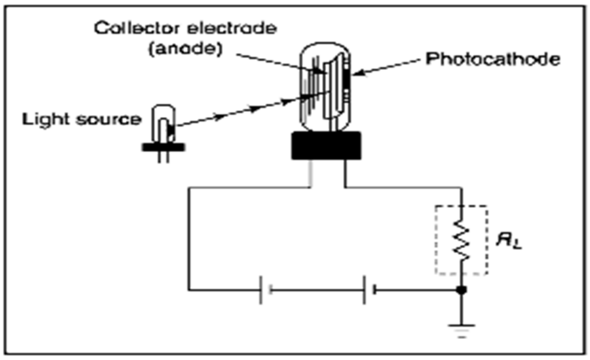


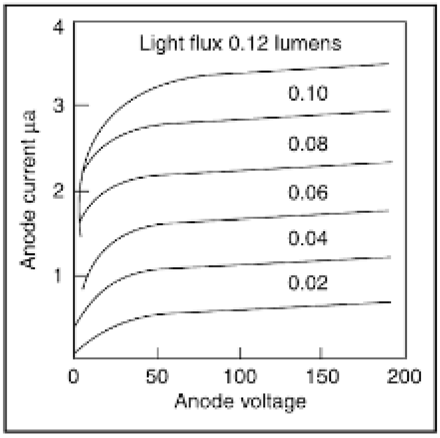
Figure 1

(ii) Photo-emissive cells:

It consists of a semi cylindrical cathode and a wire anode. The cathode is coated with a photo-emissive material. When light falls upon the cathode the photo-emissive material absorbs light energy and emits electrons. These electrons are collected by the anode resulting in a current which is proportional to the light intensity.

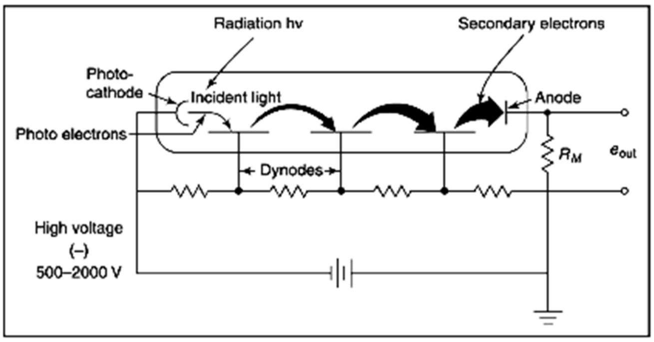


The current increases with applied voltage and light intensity(lumen) as shown below.



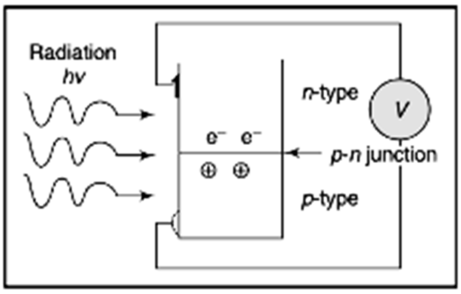
(iii) Photomultiplier tube (PMT):

In a photomultiplier tube along with cathode there are 9 dynodes. The first dynode is +90V more positive than cathode and second dynode is +90V more positive than first one and so on. When light is incident on cathode it generates electrons. These electrons travel towards first dynode and strike it to generate few more electrons. Like this carrier multiplication takes place from dynode to dynode. After 9th dynode huge number electrons are generated and current is large enough to be indicated by a galvanometer and there is no need of amplifier.



(iv) Semiconductor Detector:

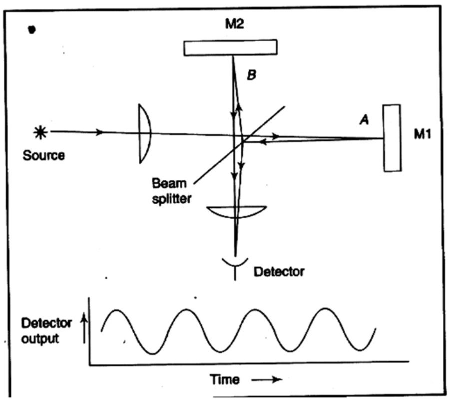
When light is incident near the junction of a p-n junction diode electron hole pairs are generated. These electron-hole pairs constitute some current.



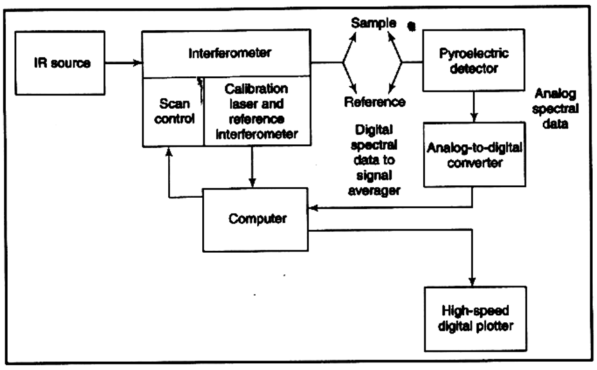
4.(a)

Diagrams-3M, Description-3M

FTIR spectrometer:Heart is two beam interferometer (Michelson interferometer). Radiation is split into two beams and path difference is introduced. When the path difference is an integral multiple of λ constructive interference occurs and intensity is maximum. When mirror M is applied with displacement then path difference changes and intensity changes. The overall detector output as function of time will be the sum of the wave for each frequency component. This represents Fourier Transform and spectral information can be extracted by applying Inverse Fourier Transform.



Block Diagram:



4.(b)

Diagrams-3M, Description-3M

<u>Quantum detectors:</u>

(i) Photoconductive cells:

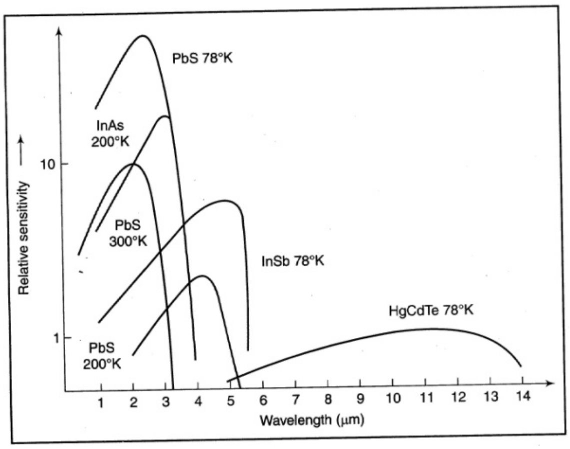
Elecrical resistors whose resistance decreases with intensity of light. Constructed from thin layer of semiconductor like Lead Sulphide (PbS) of Lead Telluride (PbTe) supported on a backing medium like glass and sealed into an evacuated glass envelope.

(ii) Photo detectors:

Semiconductors exhibit photoelectric effect.

Ex: PbS,InSb,CMT etc

Detectors must be cooled to prevent back ground thermal excitation.



(iii) Photodiode:

InGaAs photodiode arrays are used in near IR spectroscopy. Vaccum sealed and antireflective coated windows are present. Cooling arrangement reduces dark current and facilitates longer exposure times.

Thermal detectors:

(i) Thermocouple:

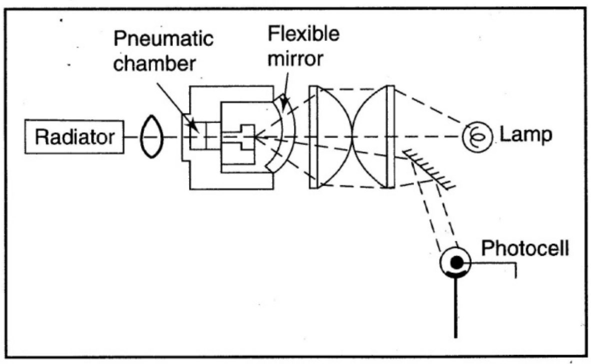
Consists of two junctions formed by two dissimilar metals. These are called as cold and hot junctions. When there is a temperature difference between these junctions emf is generated. This is called as Seebeck effect.

(ii) Bolometer:

Consists of a Pt- strip in an evacuated glass vessel with transparent window in the IR range. Irradiation causes an increase in the resistance of the metal strip, which when placed in a Wheatstone bridge produces output voltage.

(iii) Pneumatic detector:

Contains a chamber of Xenon, a gas of low thermal conductivity. This chamber is sealed at its front by a blackened receiver. The rear wall is a flexible membrane with a mirrored surface on its rear side. A rise in the temp of the chamber produces a corresponding rise in pressure and therefore distortion in mirror diaphragm. Light from a lamp inside detector housing can be focused on the diaphragm, which reflects light onto a photocell.



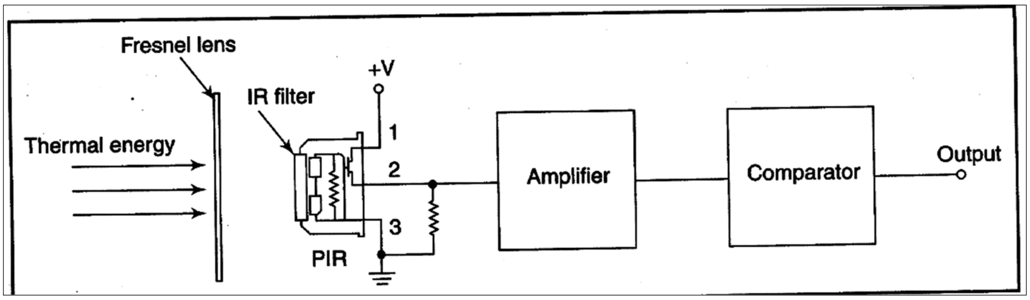
(iV) Pyroelectic detector:

Ferro electric crystals get polarized in a well defined direction known as polar axis. Degree of polarization is temperature dependent. Charge gets accumulated on the faces normal to the polar axis which is proportional to polarization. This is called “pyro-electric effect”.

Signal processing for Pyro-electric detector:

Has two sensing elements and cancels the signals caused by vibration.

An amplifier (FET) , Comparator are present.



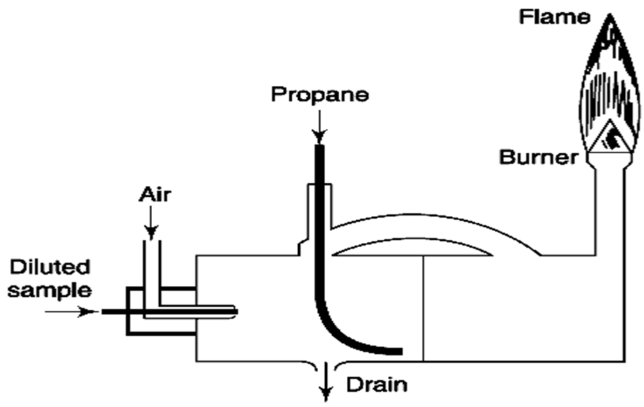
5.(a)

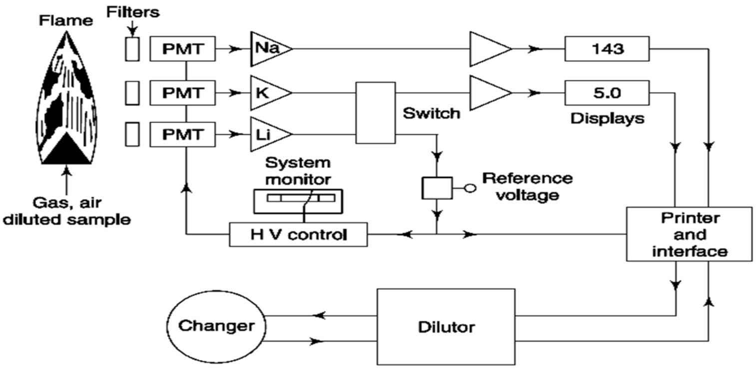
Diagrams-3M, Description-3M

The basis of low temperature flame photometry is the same as that of the simple quantitative analytical flame test. This exploits the fact that compounds of the alkali and alkaline earth metals are thermally dissociated into atoms at the temperature of a Bunsen burner flame and that some of these atoms produced are further excited to a higher energy level. When these 'excited' atoms return to the ground state, they emit radiation, which for the elements of these two groups lies mainly in the visible region of the electromagnetic spectrum. The estimation of the alkali metals by flame photometry is by far its most important application in routine chemical analysis. For this widespread requirement, low temperature flame photometry provides the most reliable and convenient procedure available.

This technique has considerable appeal in the clinical chemistry field as it provides a rapid and reliable means of estimating sodium, potassium and lithium in body fluids. The methodologies of such analyses are well known and indeed well established and shall therefore not be discussed in this page.

However the estimation of the alkali and alkaline earth metals is commonly required in a sample matrix which does not lend itself to simple and direct analysis involving only a dilution step, e.g. sodium in fuel oil.

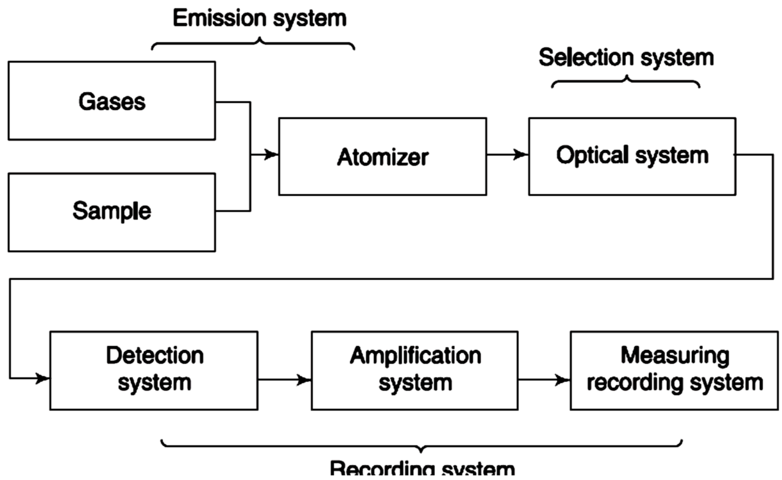




5.(b)

A flame photometer has three essential parts.
Emission System: It consists of the following:
(i) Fuel gases and their regulation: comprising the fuel reservoir, compressors, pressure regulators and pressure gauges.

(ii) Atomiser: consisting, in turn, of the sprayer and the atomisation chamber, where the aerosol is produced and fed into the flame.
(iii) Burner: receives the mixture of the combustion gases.
(iv) Flame: the true source of emission.



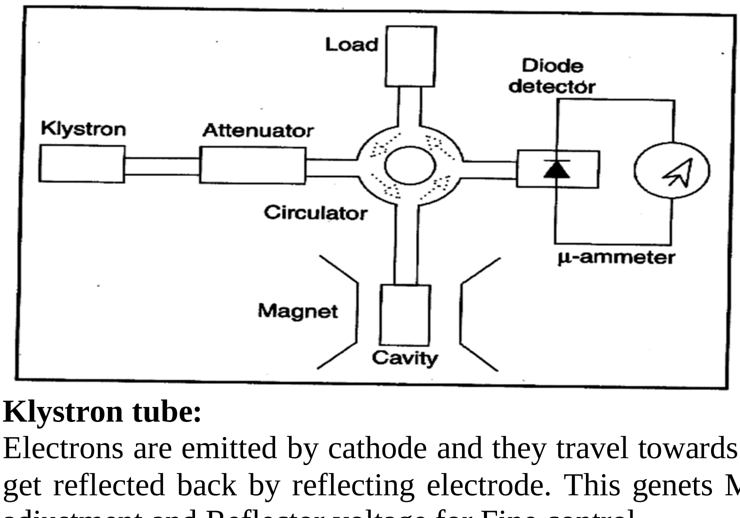
Recording System:

It has the following three systems:

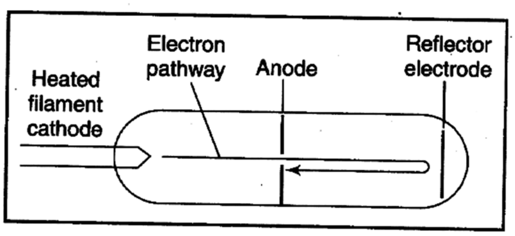
(i) Detection system: Detectors like photovoltaic cells, photo emissive cells and photomultiplier tubes are used.
(ii) Amplification system: Used for amplifying the weak signals from detectors.
(iii) Measuring system: Used to record or display the signal after amplification. Usually galvanometer, cro , strip chart recorder or digital displays are used.

6.(a)

ESR Spectrometer:
Klystron tube: Generator Microwaves
Circulator: Circulates Microwaves from source to cavity then to detector then finally to load.
Diode detector: Produces current proportional to Microwaves.
Cavity: Sample is mounted in the cavity

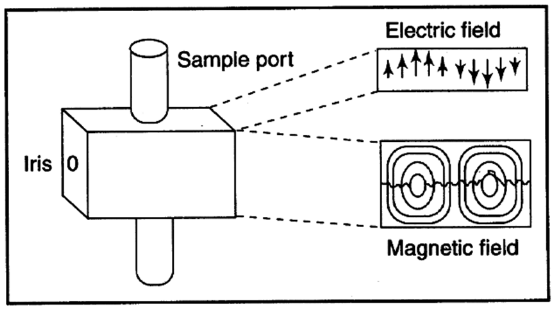


Klystron tube:
Electrons are emitted by cathode and they travel towards anode with velocity and pass trhough the hole and get reflected back by reflecting electrode. This genets Microwaves. Distance is used for coarse frequency adjustment and Reflector voltage for Fine control.

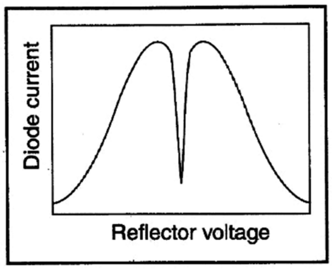


Cavity:

It is a rectangular metal box exactly one wavelength in length. Resonance occurs when the wavelength of MWs equals cavity length.



Diode current vs Reflector voltage:



Dip at cavity resonant frequency.

6.(b)

Pulsed Fourier Transform Spectrometer:

A pulse of Magnetic field or RF signal is applied through a coil. The nuclei are excited and will precess out. When the pulse is over the nuclei will precess in and the nuclear magnetic moment cuts the coil generating a Free Induction Decay (FID) signal. The frequency of the FID signal is equal to the precession frequency of the nucleus. Since the sample consists of different elements the resulting signal is a sum of different frequency FID signals. The frequencies and their amplitudes give the type of element and its concentration. The frequency components can be obtained by applying Fourier Tranformation.

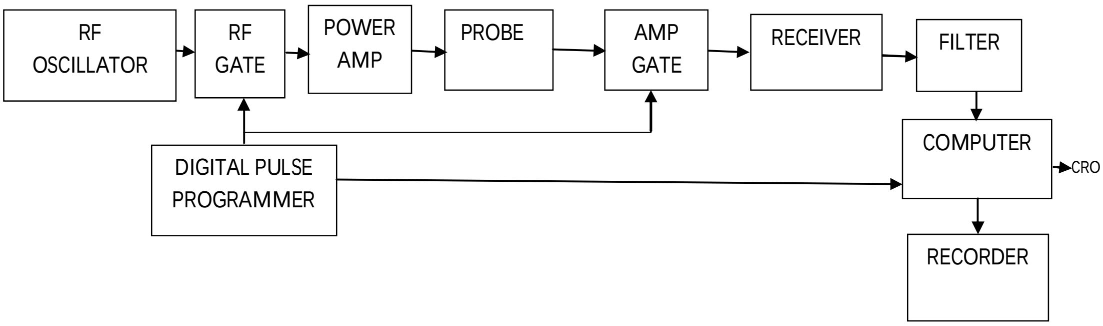
The block diagram of the FTNMR is as shown below.

RF Oscillator: Generates RF signal

RF Gate: Allows RF signal for a specific duration

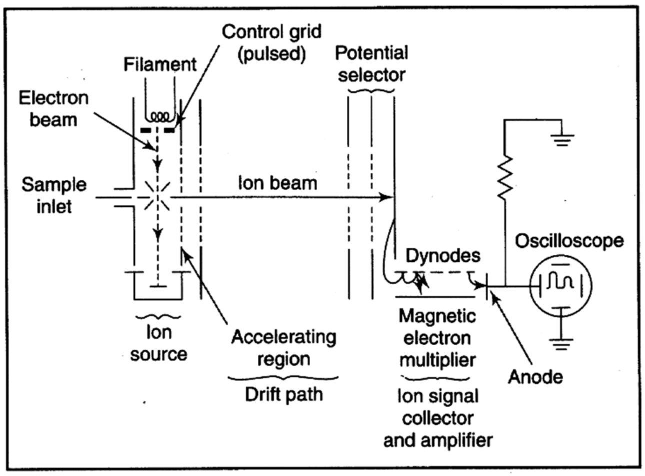
Probe: Houses coils and sample

Digital Pulse Programmer: Synchronizes RF Gate, Amplifier Gate and Computer.



7.(a)

Sample is split into ions by bombarding with high velocity electron beam. These ions are separated by virtue of their differences in their time of flights. Transit time $t = L.(m/2Vz)^{1/2}$. The time resolution will increase with increased drift tube length L.



7.(b)

Electrons possess spin represented by spin quantum number I. The value of I=+/- 1/2 (Clockwise or Anticlockwise rotation). Due to this spin electrons posses magnetic moment. When these electrons are under the influence of external magnetic field they will experience torque and start precessing with some precessional frequency. (Precession is either clockwise or anticlockwise, representing two rotational energy levels). When rf signal is passed through an element, the electrons in the atoms absorb the rf signal (in MW region) under the influence of external magnetic field which is known as Electron Spin Resonance (ESR). By measuring the absorption of MW at different wavelengths, we can perform analysis of samples. This method is known as ESR spectroscopy.

Also known as electron paramagnetic resonance (EPR) spectroscopy, it is a valuable research and analytical tool in Chemistry, Physics, Biology and Medicine. It is used in the study of molecular structures, reaction kinetics, molecular motion, crystal structure, electron transport and relaxation properties.

8.(a)

Components of X-ray Spectrometer:

(i) X-ray source
(ii) Collimator
(iii) Monochromator
(iv) Readout device

(i) X-Ray Source:

X-Ray source consists of cathode and anode. The electrons from cathode hit the anode coated with heavy metals like Molybdenum. Molybdenum emits X-Rays.

(ii) Collimator:

Used for increasing the resolution of X-Rays.

Monochromator:

It is used for selection of wavelengths.

They are of two types: Filter or Analyzing crystal.

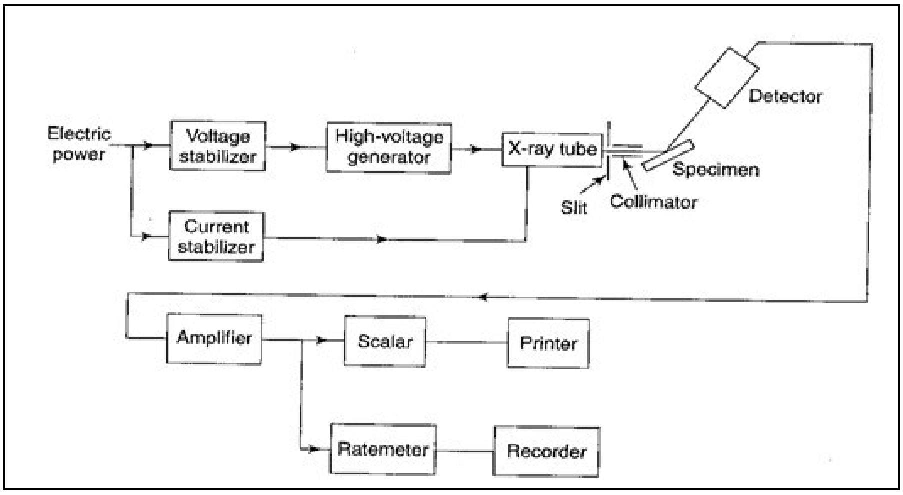
Filter:

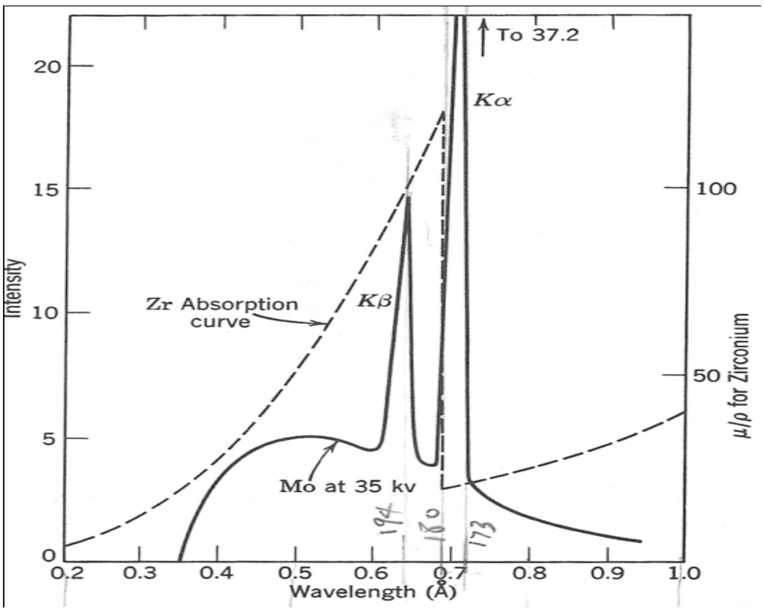
Zirconimum can be used as filter for x-rays from a Molybdenum target if Kβ is to be removed.

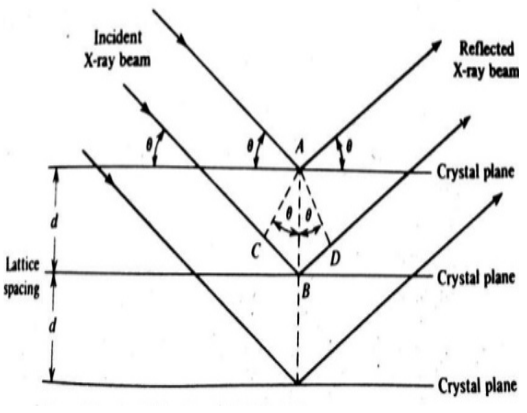
Analyzing Crystal:

Crystal having planes diffract x-rays of different wavelengths depending on the angle of incidence given by Bragg’s Law.

nλ=2dsinΘ

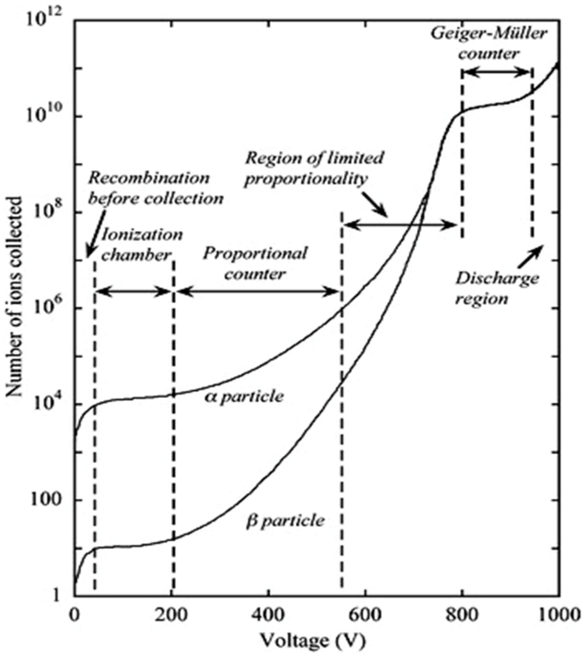






8.(b)

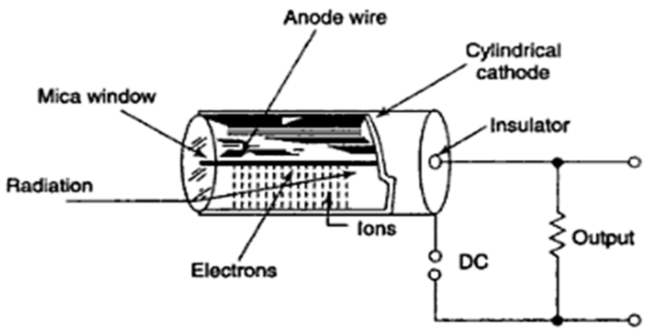
The following characteristic shows different regions of operation of various Nuclear radiation detectors. Ionization chamber is operated at low voltages i.e., upto 200V. Geiger-Muller counter is operated at high voltages i.e., around 900V. Proportional counter is operated between these two counters. In this region output is proportional to the applied voltage.



Geiger-Muller Counter:

It is operated high voltages. At such high voltages the electrons and ions generated due radiation particles move towards anode at high velocities and collide with gaseous atoms and further generates ions and electrons. The electrons thus generated strike the anode material and generate photons. These photons further cause ionization. Due to this the whole chamber is filled within a microsecond.

Dead time: Since mobility of ions is smaller they form a sheath around anode making the counter insensitive to fresh ionizing particles.



9.(a)

Applications:

XFS: (4M)

Analysis of heavy elements

XDS:

Analysis of crystalline samples

XAS:

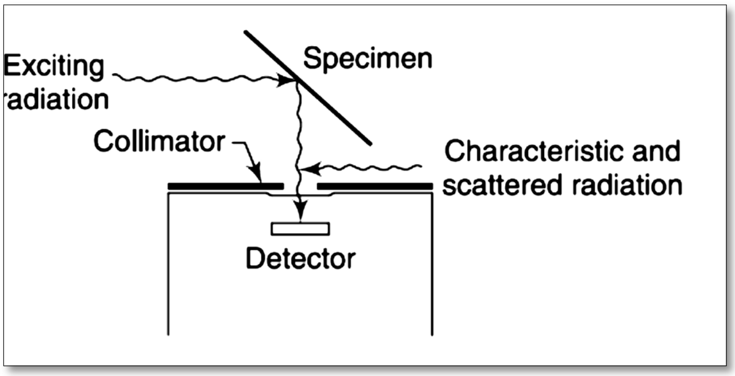
Computed Tomography, Radiography etc.

9.(b) Diagrams-3M, Description-3M

The two main types of spectral analysers used in XRF are:

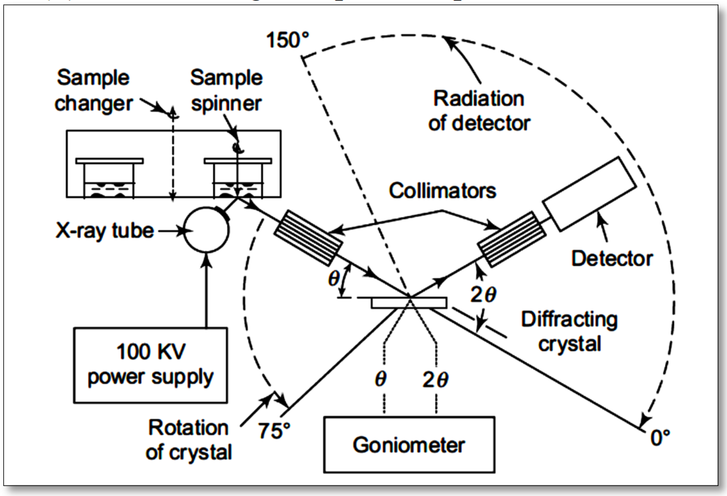
(i) energy-dispersive and (ii) wavelength- dispersive type.

(i) Energy Dispersive Spectrometer:



It consists of an excitation source, a sample and a semiconductor detector. The fluorescent X-radiation resulting from irradiation of the sample reaches a detector, which produces an electrical pulse proportional to the energy of the X-rays. The energy level indicates the element involved, and the number of pulses counted at each energy level over the entire counting time is related to the concentration of the element.

(ii) Wavelength dispersive Spectrometer:



In the wavelength-dispersive systems, X-rays emitted by the sample are diffracted by a crystal to an angle according to the Bragg equation $\sin \theta = n\lambda/2d$. The detector receives the diffracted wavelength of interest and counts the pulses over the period of excitation. The range of wavelengths involved is scanned. Wavelengths at which the intensities peak, indicate the types of atoms involved and areas under the peaks are related to the concentration. The technique derives its name from the fact that the analysis of the X-ray beam by diffraction is similar to spectrum analysis carried out with a diffraction grating. In this case, a crystal is used as a diffracting element. Essentially, the crystal possesses regular three dimensional lattice arrays of atoms and acts as an X-ray grating from which photons can be coherently scattered, so that they are in phase at certain angles. They reinforce each other producing a diffraction pattern.