

INSTRUMENTATION OF INFRARED SPECTROSCOPY

■ SPECTROSCOPY

Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample move from one energy state to another energy state. This change may be from ground state to excited state or excited state to ground state. At ground state, the energy of a molecule is the sum total of rotational, vibrational and electronic energy.

In other words, spectroscopy measures the changes in rotational and/or electronic energies.

■ **SPECTROPHOTOMETER**

They are the instruments measure either Absorbance or Transmittance or both. They can be used for a wide wavelength region. The accuracy of instrument is very high since they employ sophisticated monochromators and detectors. They are supported by amplifiers, recorders or plotters for hardcopy.

The recent ones are either microprocessor or computer based for easy data manipulation.

Introduction

Infrared absorption spectroscopy

- The infrared region of electromagnetic spectrum extends from the red end of visible spectrum out to microwave region.
- The region includes radiation at wavelength between 0.75 and 300 microns or in wave numbers between 13,000 and 33 cm^{-1} .
- From application and instrumentation point of view, the infrared region has been subdivided into three regions.

1. Near IR region ($14290 - 4000 \text{ cm}^{-1}$)
 2. Middle IR region ($4000-666 \text{ cm}^{-1}$)
 3. Far IR region ($666-33 \text{ cm}^{-1}$)
- The spectral region of greatest use in analytical applications for studying organic compounds is the mid-infrared region.
 - ❖ The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region.

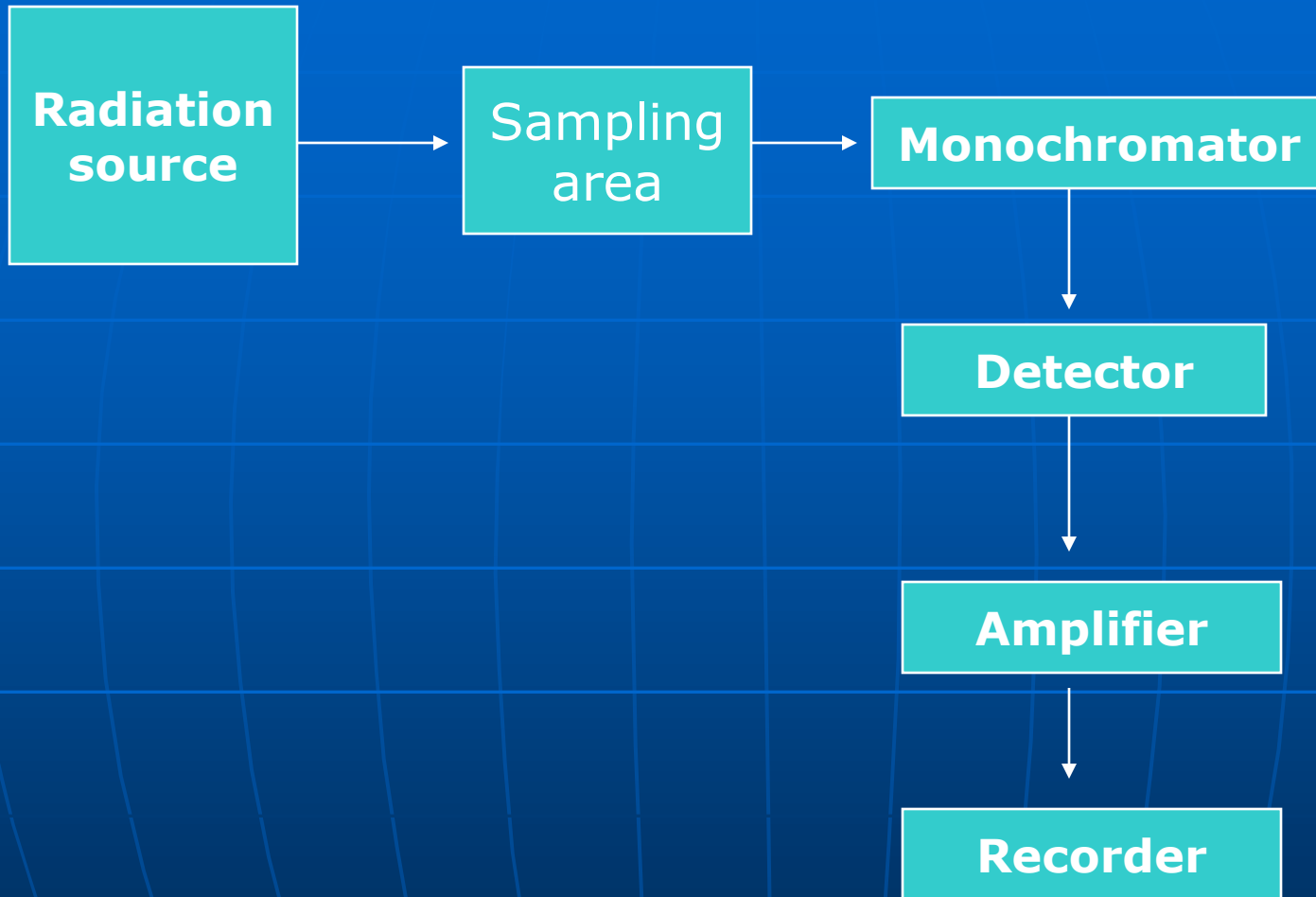
- ❖ After absorption of IR radiations, the molecules of a chemical substance vibrate at many rates of vibration, giving rise to close packed absorption bands, called an IR absorption spectrum. Which extend over a wide wavelength range.
- ❖ Various bands will be present in IR spectrum which will correspond to the characteristic functional groups and bonds present in a chemical substance . Thus, an IR spectrum of a chemical substance is a fingerprint for its identification .

- ❖ Infrared spectra are usually plotted as percent transmittance rather than as absorbance as the ordinate. This makes absorption bands appear as dips in the curve rather than as maxima, as in case of ultra violet and visible spectra.
- ❖ Each dip in the spectrum is called a band or peak and represents absorption of infrared radiation at that frequency by sample.
- ❖ The transmittance is 0%, if all the radiation is absorbed and transmittance is 100% for no absorption.

APPARATUS

Infrared spectrophotometers consists of following components:

1. Light source
2. Monochromators and optical material
3. Sample holder
4. A radiation Detector- which converts radiant energy to a usable signal
5. Instrument for the measurement of response of detector or recorder.



- ❖ The desirable characteristic of these components are:
 - Instruments for measuring infrared absorption all require a source of continuous infrared radiation and a sensitive infrared transducer.
 - A source generate a beam of radiation with sufficient power for easy detection and measurement . In addition, its output power should be stable for reasonable periods.

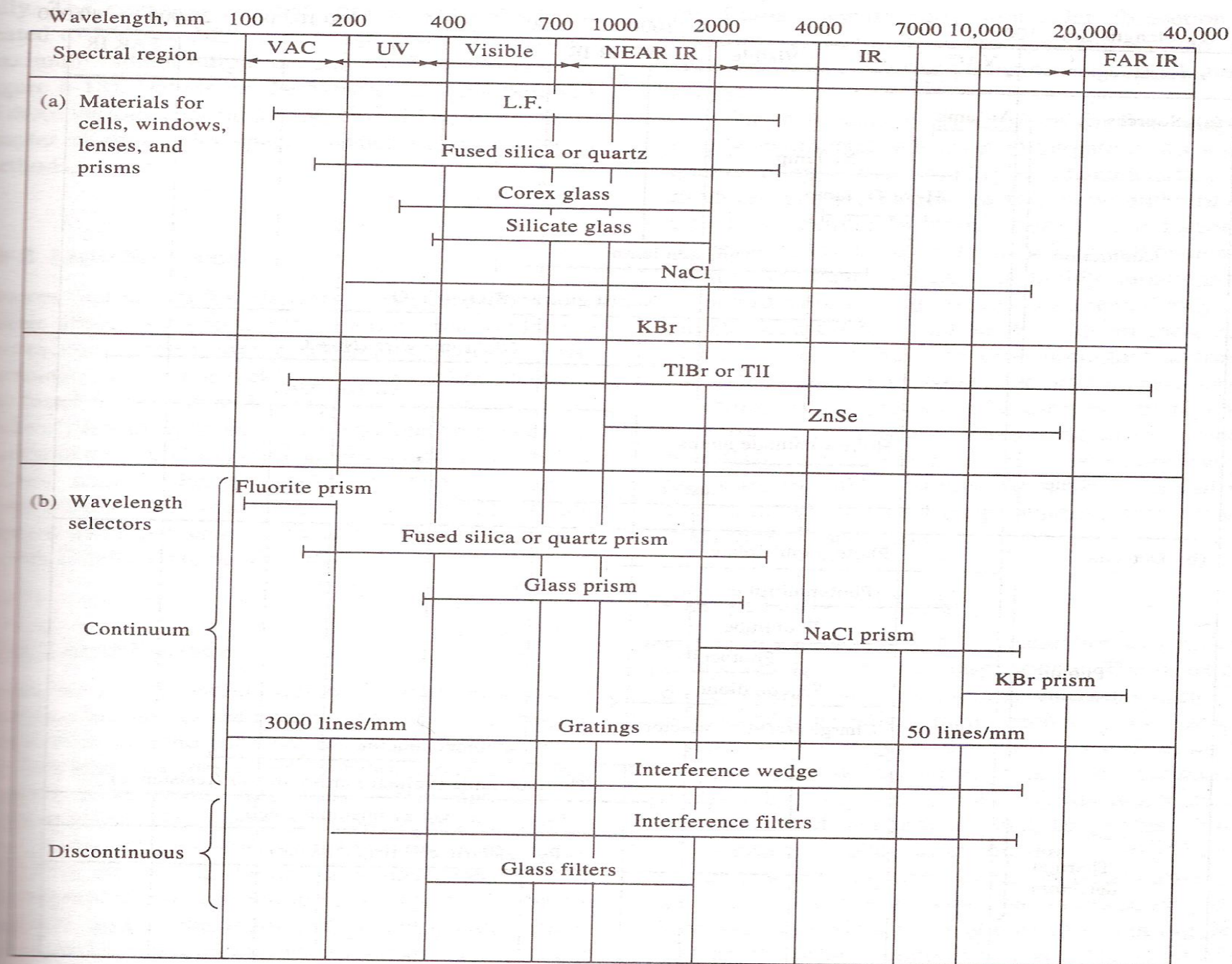


Figure 7-2 (a) Construction materials and (b) wavelength selectors for spectroscopic instruments

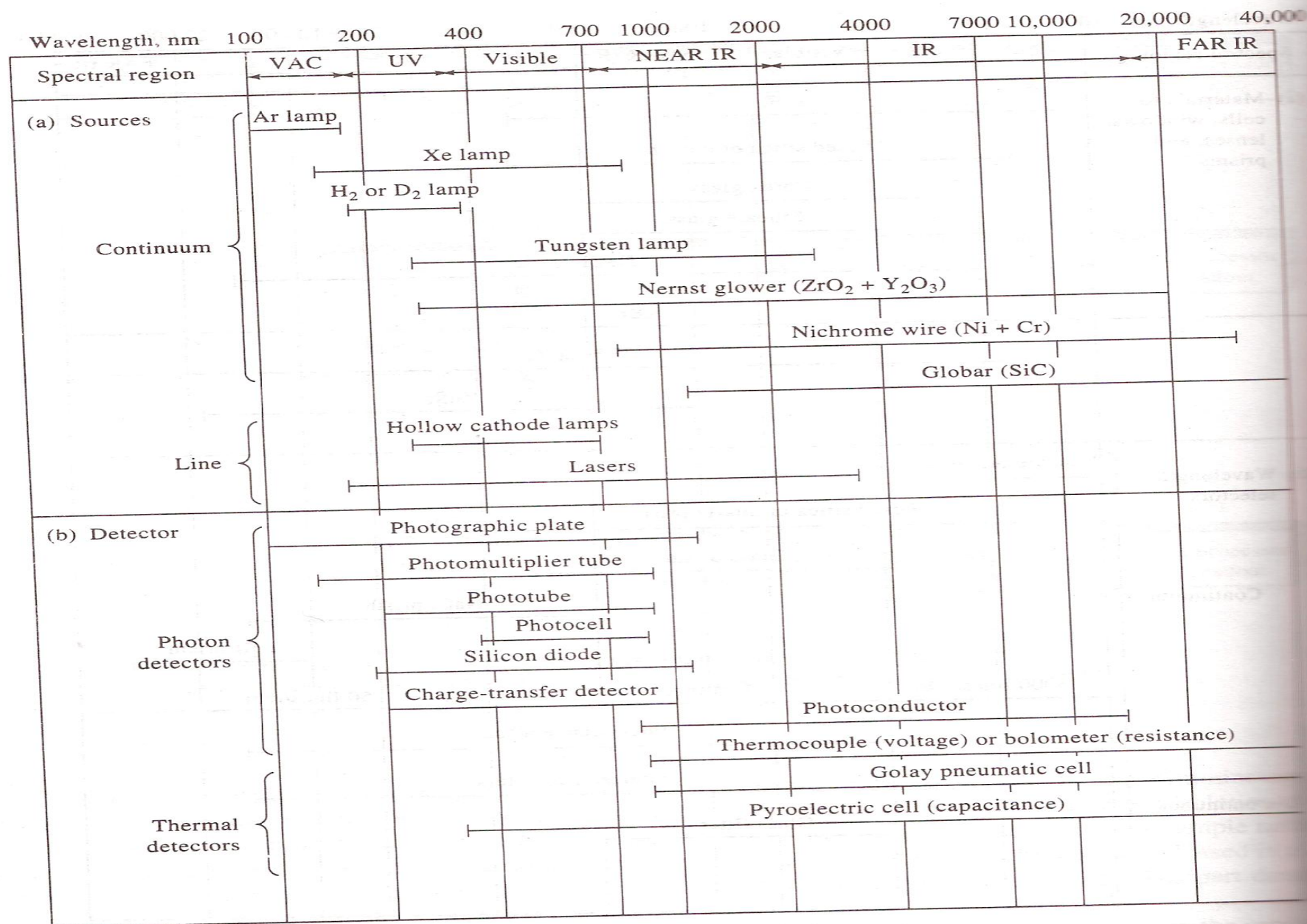


Figure 7-3 (a) Sources and (b) detectors for spectroscopic instruments.

❖ **1:Light source**

Sources for different IR regions are:

a. Near IR region:

Tungsten filament, Nichrome wire,
Rhodium wire.

b. Mid IR region:

Nernst glower and
Globar source

These two are most commonly used IR
sources.

c. Far IR region:

Mercury arc lamp and
carbon dioxide laser.

- ❖ IR sources are hot bodies, which emit continuously through out the IR region and which approximates a black body radiator in its absorption properties.
- ❖ The radiation source must emit IR radiation, which must be
 1. Intense enough for detection
 2. Steady and
 3. Must extend over the desired wavelength.
- Although these radiations are continuous, only selected frequencies will be absorbed by samples.
- An incandescent solid is used as source of IR radiation. The inert solid is heated electrically to 1200-1500° c.

❖ a.Nernst Glower

- Nernst Glower consists of a rod or hollow tube about 2 cm long and 1 mm in diameter , made by sintering a mixture of oxides of Cerium, Zirconium , Thorium and Ytterium.
- Nernst glower is a non conducting at room temperature and must heated external means to bring conducting state .
- It is maintained at higher temperature by making use of electrical heating and can be operated in air, since it is not subject to oxidation.

■ Disadvantage of Nernst Glower:

1. Mechanical failure
2. Its energy is concentrated in visible and near infrared region of spectrum.
3. The Nernst Glower has a large negative temperature coefficient of electrical resistance, and it must be heated externally (1000-1800°C) to a dull red heat before the current is large enough to maintain the desired temperature.

❖ b. Global Source

- Global is a silicon carbide rod usually about 5cm in length and 0.5cm in diameter.
- It has an advantage of positive co-efficient of resistance. When heated to temperature between 1300-1700°C, it strongly emits radiation in IR region.
- Unlike Nernst Glower, the global source is self starting and can be controlled conveniently with a variable transformer .
- The disadvantage is its less intense source than nernst glower. It is more satisfactory because it is worth at wave length longer than 650cm^{-1} .

- Both nernst and globar source provide excellent and easily controlled source for the wavelength band frequency used in analysis.
- However in far infrared region, both these sources loses their effectiveness.
- ❖ c. Mercury arc lamp

Beckman devised the quartz mercury lamp for the far IR region .special high-pressure mercury arc lamps are used.

- At the shorter wavelength, the heated quartz envelope emits the radiation whereas at longer wavelength the mercury plasma provides radiation through the quartz.

d. Tungsten filament lamp

The ordinary tungsten filament lamp is a convenient source for the near-IR region of 4000 to 12800 cm^{-1} .

e. Rhodium wire

Rhodium wire heater sealed in a cylinder has been used.

f. Nichrome wire

It is used when the required wavelength range and intensity are not too great.

2. **MONOCHROMATOR**

The radiation source emits radiations of variable frequencies. But the sample in the IR spectroscopy absorbs only at certain frequencies . It is, therefore., necessary to select desired frequencies from the radiation source and reject the others.

- The selection has been achieved by means of monochromators .
- The prism or grating type monochromators are employed in infrared work. However prism instruments are favored because of greater range and simplicity.

- It has the following components

1. Entrance slit (to get narrow source)
2. Collimator(to render the light parallel)
3. Grating or Prism (to disperse radiation)
4. Collimator(to reform the image of entrance slit)
5. Exit slit (to fall on sample cell)

- Note : neither quartz nor glass is sufficient transparent to infrared, radiations above 3.5 microns.
- These Can not be used as they absorb satisfactory in IR region. Hence crystals of certain halogen salts, which transmit infrared freely have been utilized for optical parts.
- Quartz is employed as material for prism construction and is used for near IR region. It strongly absorbs beyond 4 microns.

Continued..

- The great bulk of analytical work in IR is done with crystalline NaCl as the Prism material. Beyond 20 microns NaCl absorbs strongly. So can't be used.
- Crystalline KBr and Cerium bromide are satisfactory for the far IR region (15-40 microns).
- Lithium fluoride provides Prism material in near IR region (1-5 micron).

Prism

- The prism disperse the light radiation into its individual wavelength .The resolution depends on the size and refractive index of the prism. The material that are transparent to IR is used for the construction for the prism.

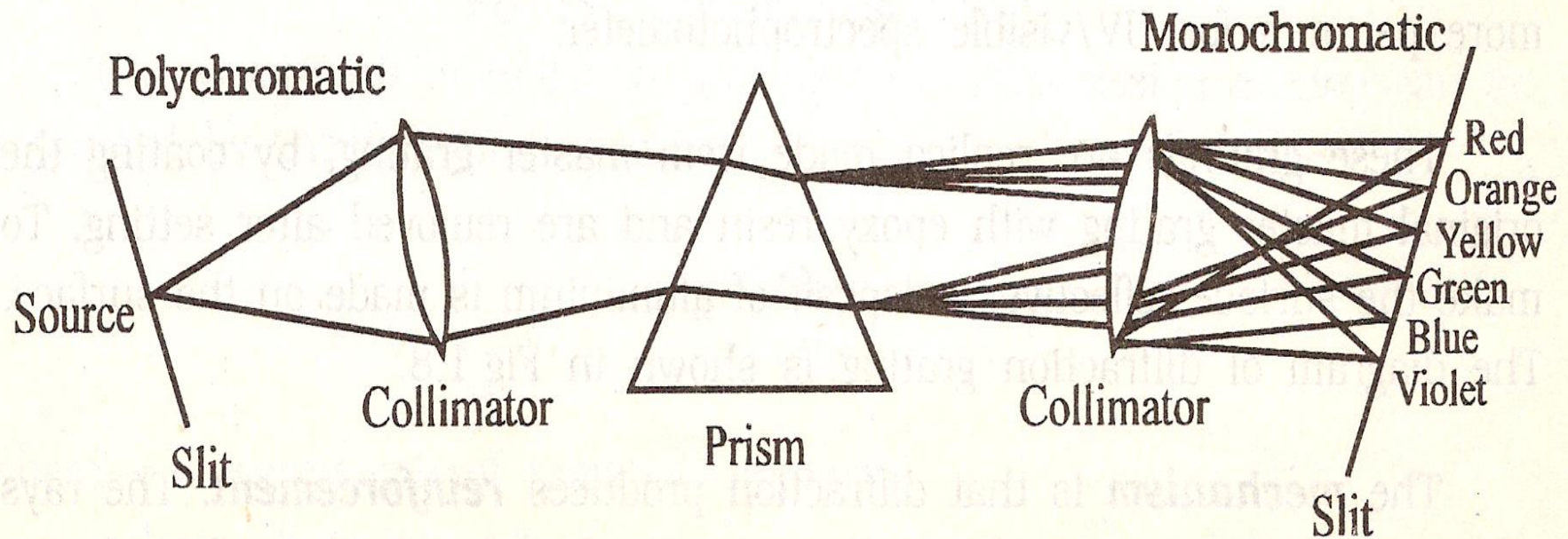
There are two types.

1. Refractive type.
2. Reflective type (littrow type).

1st. Refractive type

- In the refractive type prism, the light from the source through the entrance slit falls on a collimator. The parallel radiation from the collimator are dispersed according to the wavelength. And by using another collimator the image of the entrance slit are reformed. The required radiation in exit slit can be selected by rotating the prism or by keeping the prism stationary and moving the exit slit.

**Fig 1.6. PRISM MONOCHROMATOR
(Dispersive type)**



Reflective type

- The principle of working is similar to the refractive type except that, a reflective surface is present on one side of the prism. Hence the dispersed radiation gets reflected and can be collected on the same side of the source of the light.

Gratings

- Are most effective one in converting a polychromatic light to monochromatic light. As a resolution of ± 0.1 nm could be achieved by using gratings, they are commonly used in spectrophotometers.
- Gratings are of two types.
 1. Diffraction grating.
 2. Transmission gratings.

Diffraction Grating

- Gratings are nothing but rulings made on some material depending upon the instrument like glass, quartz, plastic and for IR alkyl halides.
- The number of rulings per mm is 20 grooves or lines per mm in IR spectrophotometer. these gratings are replica made from master gratings by, coating the original master grating with a epoxy resin and are removed after setting.

Continued..

- To make the surface reflective, a deposit of aluminum is made on the surface .In order to minimize to greater amounts of scattered radiation and appearance of unwanted radiation of other spectral orders, the gratings are blazed to concentrate the radiation into a single order.

types: (i). Diffraction grating (ii). Transmission grating

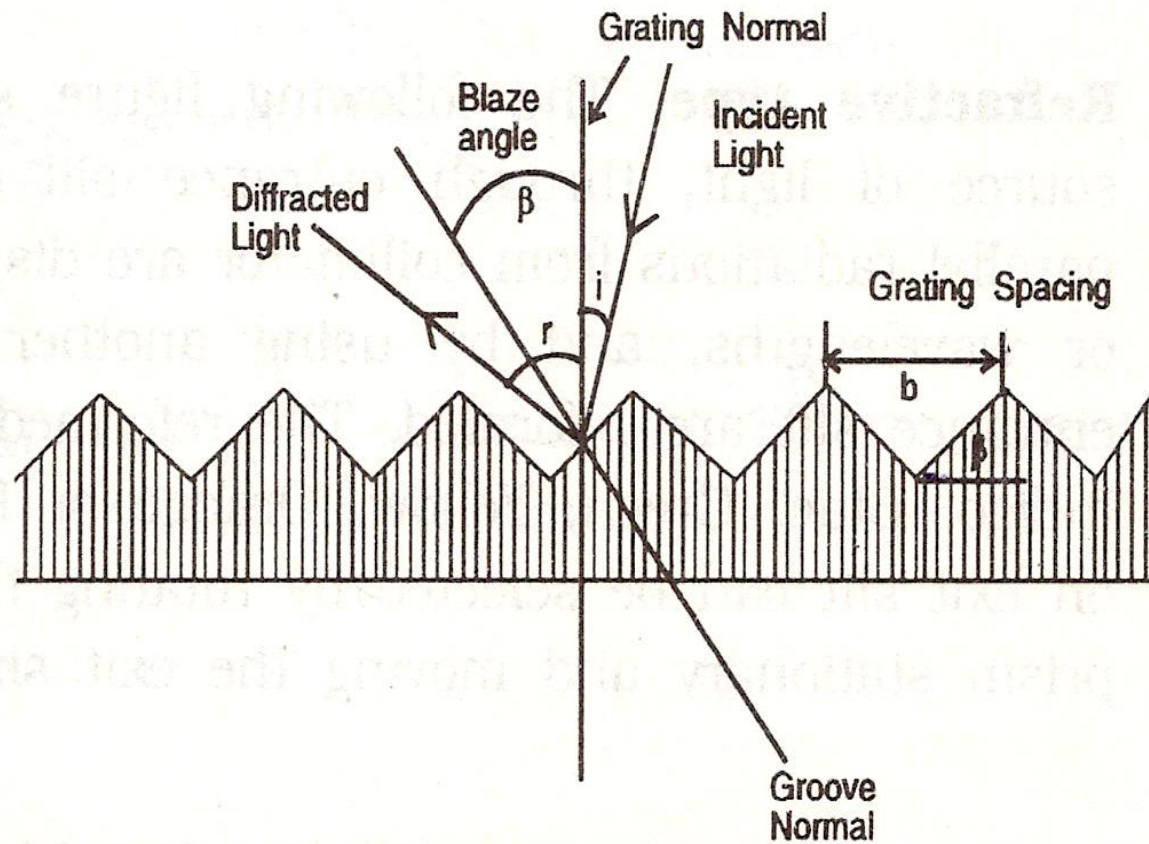


Fig 1.8. Diffraction grating

mm for IR spectrophotometer to 3600 grooves or

- The mechanism is that diffraction produces reinforcement. the rays which are incident upon the gratings, get reinforced with the reflected rays and hence the resulting radiation has wavelength which is governed by the equation

$$m\lambda = b(\sin i \pm \sin r)$$

Where, λ = wavelength of light produced

b = grating spacing

i = angle of incidence

r = angle of reflection

m = order (1,2,3) of light.

The band pass of the grating is ± 0.1 nm, which means they are efficient and hence grating is preferred

Transmission grating

- It is similar to diffraction grating but refraction takes place instead of reflection. Refraction produces reinforcement. this occurs when radiation transmitted through grating reinforces with the partially refracted radiation.

...ly reflected radiation. The diagram is shown in Fig.1-9.

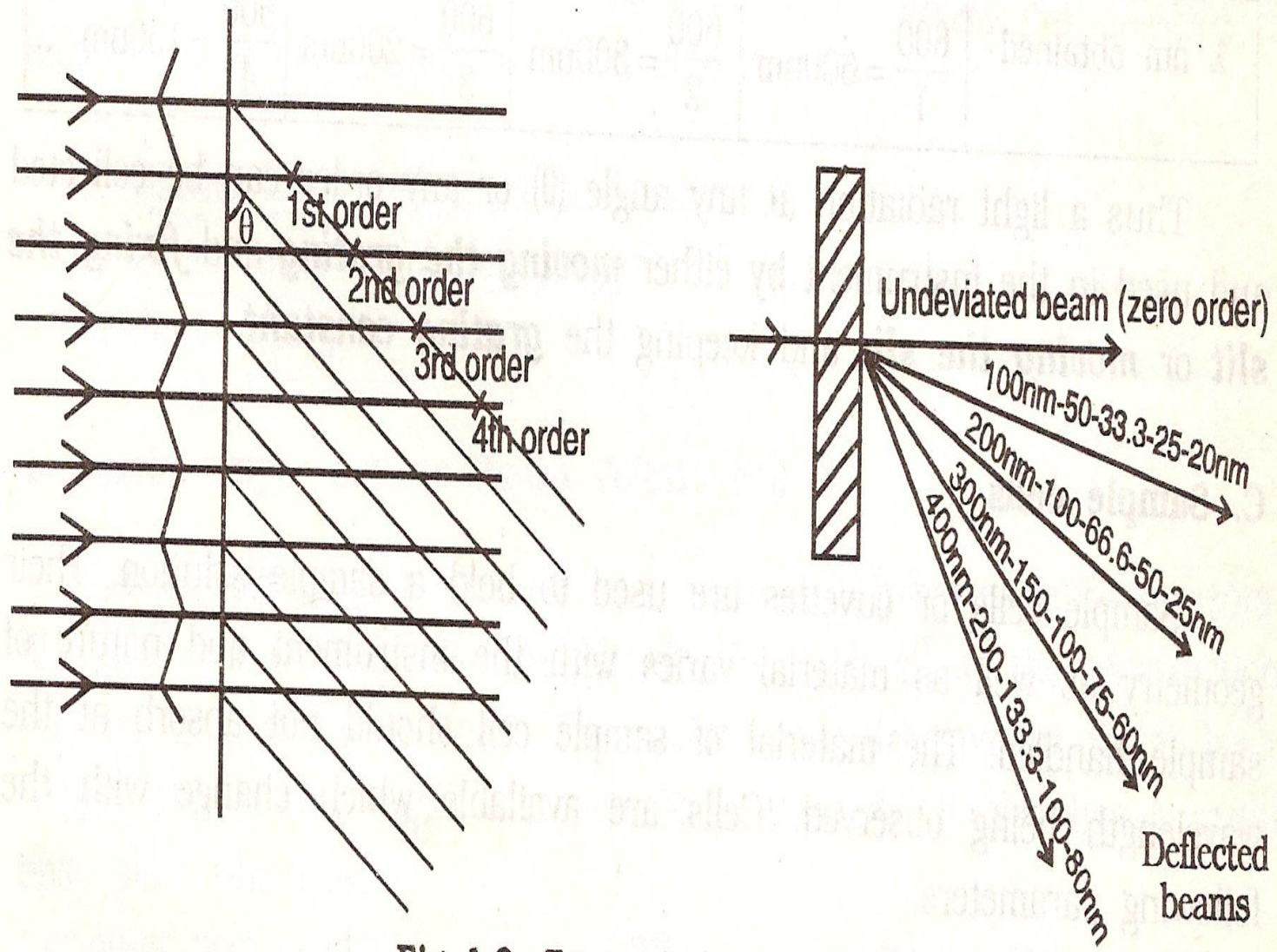


Fig 1.9. Transmission grating

- The wavelength of radiation produced by transmission grating can be expressed by equation:

$$\lambda = \frac{d \sin \theta}{m}$$

where

λ = wavelength of radiation produced

d = lines per cm

θ = angle of diffraction / deflection.

- A radiation at any angle (θ) or any order can be collected and used in the instrument by either moving the grating and fixing the slit or moving the slit and keeping the grating constant.

Note :

- All the common IR transmitting material except quartz are, however, water soluble and are easily stretched.
- protection from condensation of moisture with desiccants or with heat is thus necessary.
- The protection of hygroscopic materials against moisture is accomplished by enclosing the entire Monochromator in a sealed house which is either evacuated or desiccated.

Sample handling

- As IR spectroscopy has to be used for characterization of solid, liquid or gas samples, it is evident that samples of different phases have to be handled and to be treated differently. The common part sampling is that the material containing sample must be transparent to IR radiation. This condition restricts our selection to only certain salts like NaCl, KBr, BaF₂, CaF₂.
- In IR spectrophotometer the source is followed by a sample cell and then monochromators.

- a. Sampling of solids.
 - 1. Pressed pellet technique.

In this technique some amount of finely ground solid a sample is mixed with about hundred times its weight of powdered KBr. KBr will eliminate the problem of additional bands because it wont absorb IR light in the Region 2.5-15Microns.the mixture is pressed under a high pressure (10000-15000pounds/sq inch) in a die to form a small pallet.

Mull technique

- In this technique the finely ground solid sample is mixed with nujol (mineral oil) to make a thick paste which is then made to spread between IR transmitting windows. This is then mounted in a path IR beam and the spectrum is run. This method is good for qualitative but not for quantitative analysis.
 - Disadvantage
- It shows absorption of maximum at 2915 cm^{-1} , 1462 cm^{-1} , 1376 cm^{-1} , 719 cm^{-1} .
- Polymorphic changes, degradation and other changes may occur during grinding.

Solid films

- If a solid is amorphous in nature the sample is deposited on the surface of KBr or NaCl cell by evaporation of a solution of a solid. This method is useful for rapid qualitative analysis and become useless for carrying out quantitative analysis

■ **Solid Run in solution:**

- Solid may be dissolved in a non aqueous solvent provided there is no chemical interaction with the solvent and also the solvent does not absorb in the studied range. the various solvent used are acetone, acetonitrile, benzene , CCl_4 , CS_2 , cyclohexane, tetrachloro ethylene, methylene chloride. Among these only CCl_4 , CS_2 are ideal as they show very few absorption bands themselves.

■ **Sampling of gases:**

- Gas samples are examined in the IR spectrometer after removal of water vapour. the simplest gas cell consists of metal bar glass cylinder of 10 cm. long and closed with a appropriate window. The gaseous sample is passed through a stop cock via a suitable gas handling apparatus and partial pressure of 5-15 mm Hg gives a reasonable level of absorption In most cases. The end wall of gas cell is made of NaCl and for low concentrated gases long path lens are required. Multi reflection can be used to make effective oath length as long as 40 cm so that constituent of gas can be determined.

- **Sampling of liquid:**

- Sample that are liquid at room temperature are usually put frequently with no preparation into a rectangular cell made up of NaCl, KBr or ThBr and their IR spectra is obtained directly. the same thickness is so selected that the transmittance lies between 15 and 20 %. For most samples this will be represent a thin layer of 0.001-0.05 mm of thickness. Some times the liquid samples can be dissolved in suitable solvents and scanned in the IR region using suitable cell.

Detectors

- Near-infrared : lead sulfide photoconductive
- Mid-infrared: Thermopile, Thermistor or Pyroelectric
- Far -infrared: Golay, pyroelectric.

At the shorter- wavelength end , below about 1.2 microns, the preferred detection methods are the same as those used for visible and U V radiation. The detectors used at longer wavelengths can be classified into 2 groups

- The detectors used at longer wavelengths can be classified into 2 groups
- 1, Thermal detectors; in which the infrared radiation produces a heating effect that alters some physical property of detector, and
- 2. Photon detectors, which use the quantum effects of the IR radiations to change the electric properties of a semiconductor

- Photon detectors consists of thin layer of lead telluride or lead sulphide supported on a glass and enclosed in a evacuated glass envelope. Lead sulphide photoconductive cells are sensitive to infrared radiation upto 3 microns. When IR radiation is focused on lead sulphide A sufficiently energetic photon that strikes an electron in the detector can raise that electron from a non conducting state into a conducting state, its conductance increases and causes more current to flow, which is amplified and measured.



Advantage of photon detectors

1. Response time is 0.5milli sec.
2. Sensitive,
3. Fast.

Disadvantage

- When operated at room temperature, it has a restricted range (near IR)

Thermal detectors

- Generally thermal detectors are used in IR spectroscopy. Radiations above 1 micron are detected by its heating-effects, either by a sensible thermocouple or by resistance thermistors. When either of these instrument is connected to a galvanometer, a deflection is noted which is in proportion to the transmitting radiant power.

- So thermal detectors give response for all frequencies, the radiant power is low for IR region, i.e. The detector signal will also be low. In order to locate these low signals, a preamplifier is fixed to the detector and the radiant beam is modulated with a low frequency light interrupt 10- 26 cps. Thus to detect such signals, thermal detector must possess a short response time and the absorbed heat must be lost rapidly

- The active element in any thermal detector is as small as possible to maximize its temperature change for any level of infrared radiant energy. For the same reason, the element is blackened and thermally insulated from its substrate.
- Material properties affected in thermal detectors include
 - 1, An expansion of a solid or fluid (Golay cell)
 2. Electrical resistance (Thermistor)
 3. Voltage induced at the junction of 2 dissimilar materials (Thermocouple and thermopile) and
 4. Electric polarization (Pyroelectric)

■ Advantage

1. Thermal detectors are usable over a wide range of wavelength, which includes both visible and infrared radiation, and
2. They operate at room temperature.

■ Disadvantage

1. Slow response time (milliseconds)
2. Lower sensitivity relative to other types of detectors.

Bolometer.

- A bolometer is based upon the fact that the electrical resistance of a metal changes with increase of temperature. It consists of a resistor made up of sintered oxides of manganese, cobalt and nickel, which have high temperature coefficient of resistance.

BOLOMETER continued..

- The constructed metal or semiconductor that exhibits a large change in electrical resistance as a function of temperature. When radiation falls on the bolometer, its temperature changes and hence the resistance of conductor also changes. The degree of changes in resistance is a measure of amount of radiation falls on the bolometer.

- Advantage

1. response time is 4 milliseconds
2. high sensitivity

- Disadvantage :

Highly fragile

b.Thermistors:

- Is a resistor made by fusing together several metallic oxides of manganese , cobalt and nickel which have a high temperature coefficient of resistance .

- **c. Golay cell**

- It uses the expansion of a gas as the measuring device. The unit consists of a small metal cylinder closed by a rigid blackened metal plate at one end and by a flexible silvered diaphragm at other end. The chamber is filled with xenon. The radiation passes through a small IR transmitting window and is absorbed by the blackened plate. Heat conducted to the gas causes it to expand and deform the flexible diaphragm (mirror).

- To amplify distortions of the mirror surface, light from a lamp inside the detector housing is focused on the mirror, which reflects the light beam on to the phototube. With the flexible mirror in its rest position, an image off the moiré grid falls on the other half so that no light passes through. Flexing of the mirror moves the image off the grid laterally so that varying amount of light can reach the phototube.

- An alternative arrangement, the rigid diaphragm is used as one plate of a dynamic condenser. A perforated diaphragm a slight distance away serves as second plate. The distortion of solid diaphragm relative to a fixed plate alters the separation and hence the capacity (response time is approximately 20 msec).
- The Golay cell has sensitivity similar to that of thermocouple. It is significantly superior as a detector for the far IR region. Since the angular aperture is 60 degree, the detector must be used with a system of condensed mirrors to concentrate the incident radiation.

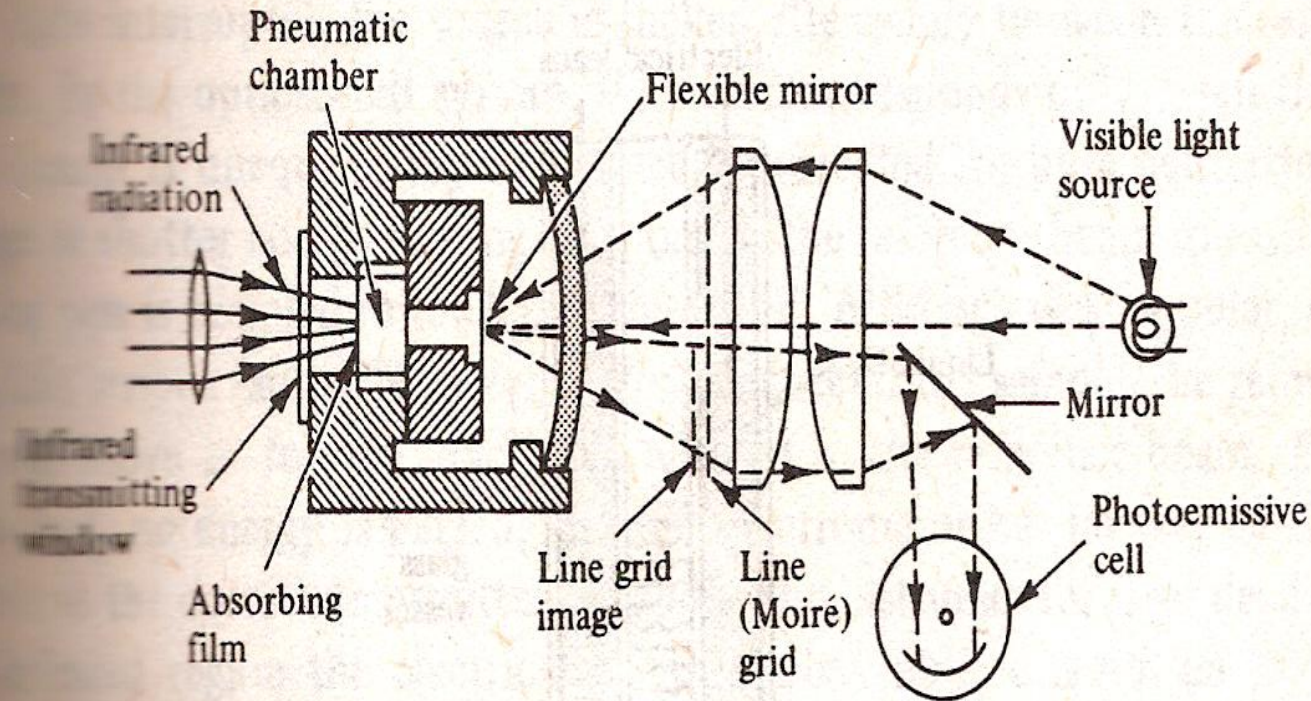


FIGURE 7-14 Golay pneumatic infrared detector.

The Golay pneumatic detector, shown in Fig. 7-14, utilizes the expansion of a gas as

d.Thermocouple:

- This is most widely used in error detection. It is based on fact that an electric current will flow in two dissimilar metals (like bismuth And antimony). Wires are connected together at both ends, a small voltage is produced proportionally to the temperature differential exists between the two ends. Several thermocouples like this connected in series forms a thermopile so that their voltage adds.

- The end exposed to IR radiation is called the hot junction (blackened gold foil in order to increase the energy gathering efficiency). It is usually a black body. The other connection, the cold junction and is thermally insulated and carefully screened from stray light.
- The electricity which flows is directly proportional to the energy differential between two junctions. A thermocouple is closed in a evacuated steel casing with a IR transmitting window, KBr to avoid losses of energy by convection. The thermopiles offer the simplest and most direct means for converting radiant energy into electric signal.

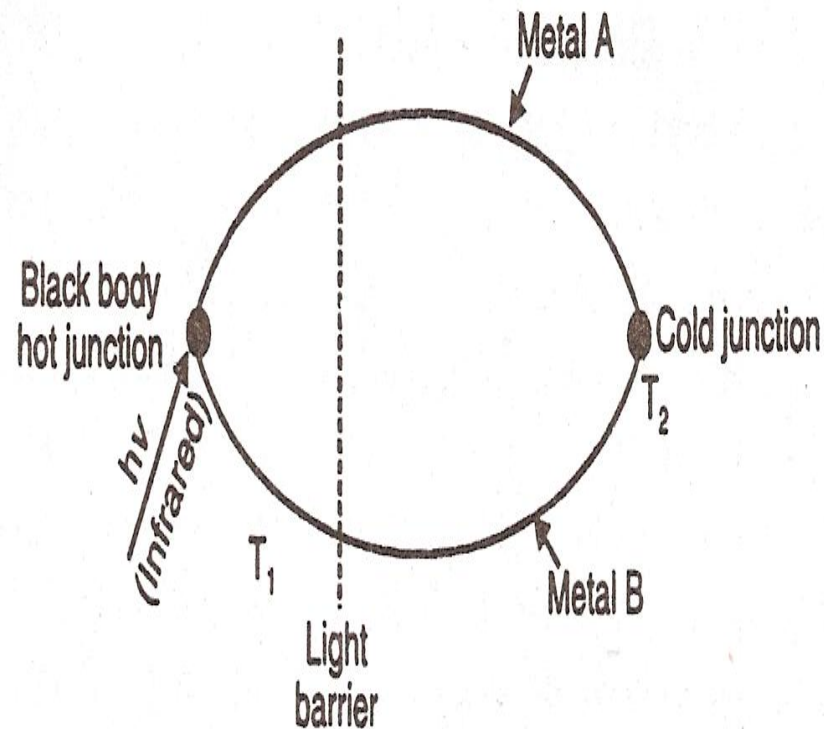


Fig. 3.16 : Schematic diagram of a thermocouple. The "hot junction" is exposed to the infrared radiation. The "cold junction" is insulated from it. Current is proportional to $T_1 - T_2$.

■ Advantage:

- Can be used over a wide range of wavelength.
- Response time is about 60 msec.

Disadvantage:

Low sensitivity.

e. Pyroelectric detector.

when a dielectric is placed in an electric field it become polarized depending on their dielectric constant. If the field is removed, the polarization usually disappears except with ferroelectric compounds, which retains a strong residual polarization . Some time this residual polarization is temperature sensitive, such materials are Pyroelectric.

continued..

a Pyroelectric detector consists of a thin dielectric flake on the face of which an electrostatic charge appears when the temperature of the flake changes. This happens upon exposure to the IR radiation . The electrode attached to the flake collects the charges and a voltage is created .

The most common pyro electric is glycine sulphate (TGS).& also duterated Triglycine sulphate .

Advantage of Pyroelectric detector :

- short response time.

Disadvantage

1. Expensive
2. Crystals are hygroscopic.

- **Single beam spectrophotometer:**

- In a single beam system the radiation is emitted by the source through the sample and then through a fixed prism and a rotating littrow mirror. Both prism and littrow select the desired wavelength and then allow it to pass on to a detector. The detector measures the intensity of a radiation after it passes through the sample.
- Knowing the original intensity of radiation, one can measure how much radiation has been absorbed. By measuring the degree of absorption at wavelengths, the absorption spectrum of the sample can be obtained

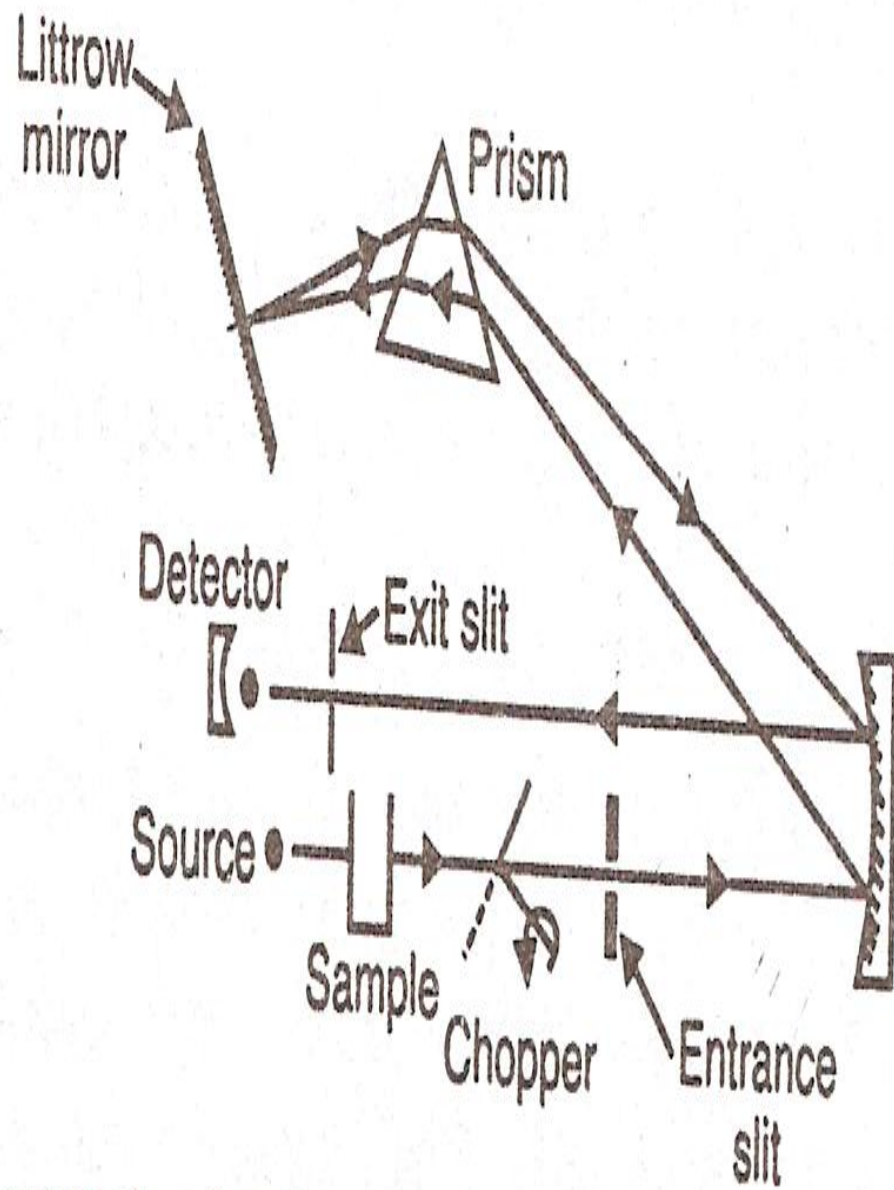
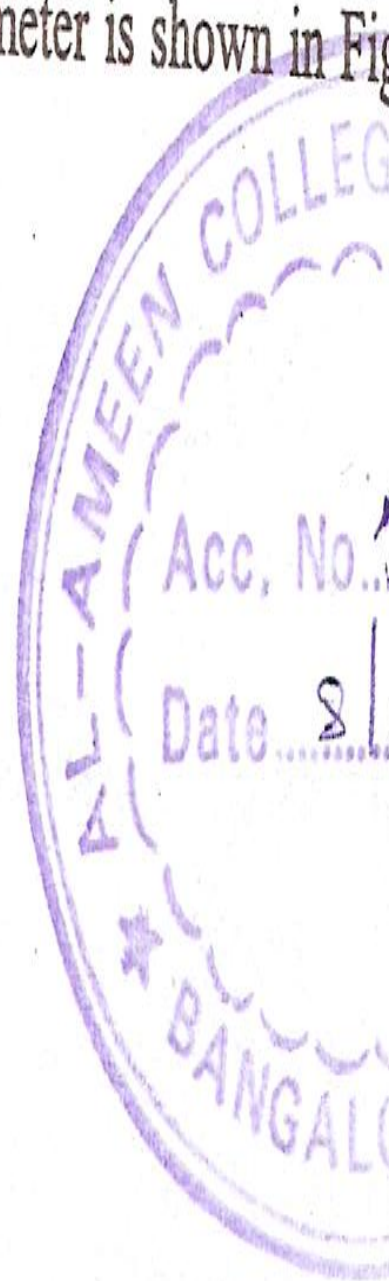


Fig. 3.19 : Schematic diagram showing the optical path in a single beam infrared spectrophotometer



■ Disadvantages:

1. This type of instrument has the basic disadvantage that the intensity of the emission of the radiation source varies from point to point in IR absorptions spectrum, therefore the resulting spectrum is considerably deformed. The necessary correction by the continuous variation of slit is cumbersome.
2. When the sample is analyzed in solution, the bands of solvent appear on the spectrum. In this case a spectrum of the sample is obtained by subtracting the spectrum of the solvent from the resultant spectrum, the former must be recorded under identical conditions (thickness of layer etc..).

- In order to overcome the above mentioned difficulties a double beam spectrophotometer is used.

- **Double beam IR spectrophotometer :**
- The energy emitted by the radiation source is split by the instrument into two beams, which are energetically and optically identical. One of the beam passes through the sample and the other through the reference sample.
- The sample is placed in the sampled beam and a reference material, such as the solvent used in the sample, is placed in the reference beam. the two half beams are combined and passed along the optical path to the detector.

- When there is no sample in a reference beam it arrives at the detector unabsorbed. When there is no sample in the sample cell the half beam traveling along the sample beam is not absorbed and is equal to the reference beam. When these two equal half beams recombine, a steady signal reaches the detector.
- When the sample cell contain the sample the half beam traveling through it undergoes a decrease in intensity and the two half beam are recombined, they produce an oscillating signal which is measured by the detector. The signal from the detector is passed on to the recording unit through a servomotor.

In order to overcome the above mentioned difficulties, a double-beam spectrophotometer is used. This is shown in Fig. 3.20.

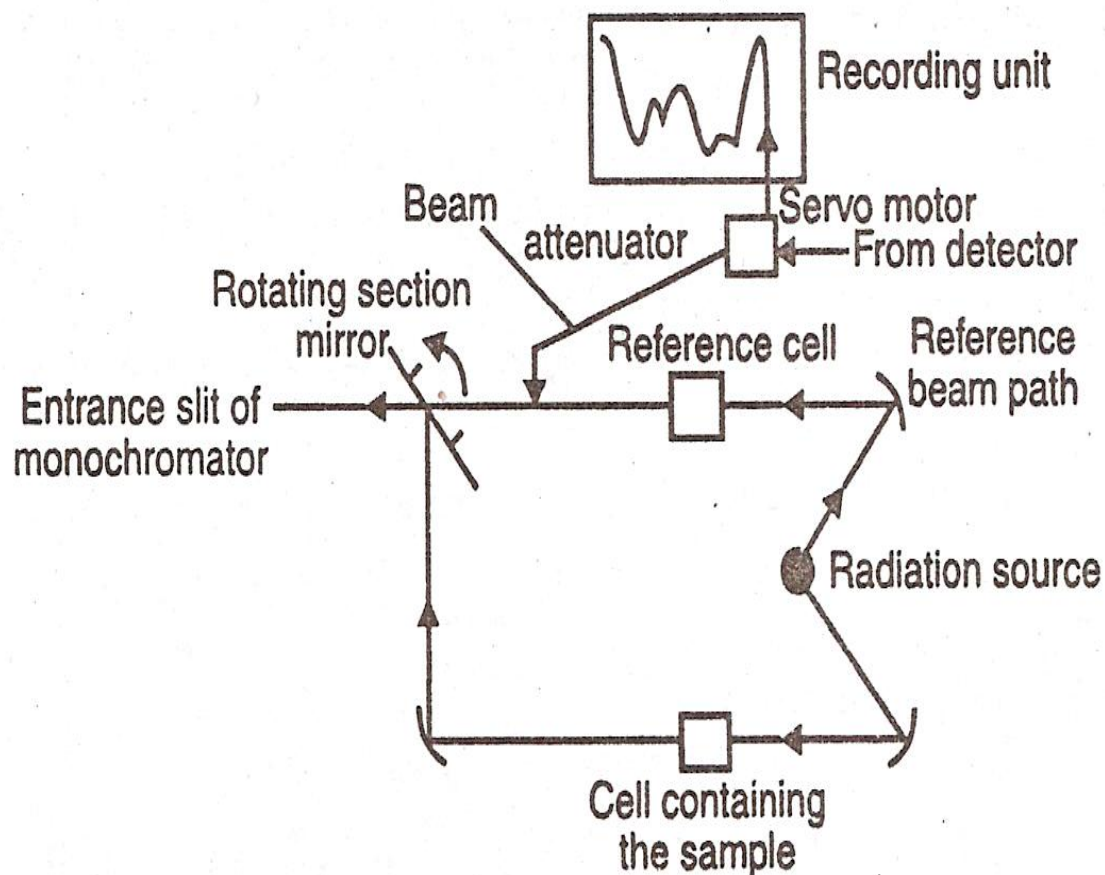


Fig. 3.20 : Schematic Diagram of a Double-Beam Infrared Spectrophotometer.

References

1. Instrumental methods of analysis
- Willard / Merritt page. 189-199.
2. Instrumental method of chemical analysis – B.k.Sharma (261-267)
3. Instrumental analysis
by Skoog, Holler (145 and 146)

Thank you