INSTRUMENTAL ANALYSIS II

Unit 3

Components of Optical Instruments

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Components of Optical Instruments

- In general performance requirements whether the instruments are designed for ultraviolet (UV), visible, or infrared (IR) radiation.
- Because of the similarities, such instruments are frequently referred to as **optical instruments** even though the eye is sensitive only to the **visible** region.
- Optical spectroscopic methods are based upon six phenomena:

1. Absorption
2. Emission
3. Scattering
4. Fluorescence
5. Phosphorescence
6. Chemiluminescence

Components of typical spectroscopic instruments:

- Most spectroscopic instruments for use in the UV /visible and IR regions are made up of five components:

1. A stable source of radiant energy (sources of radiation).
2. A transparent container for holding the sample (sample cell).
3. A device that isolates a restricted region of the spectrum for measurement (wavelength selector, monochromator or grating).
4. A radiation detector, which converts radiant energy to a usable electrical signal (current, voltage, or resistance).
5. A signal processor & readout, which displays the transduced signal, usually consisting of electronic hardware & in modern instruments a computer that can change the electrical signal (current, voltage, or resistance) to a suitable form like absorbance, fluorescence, etc.

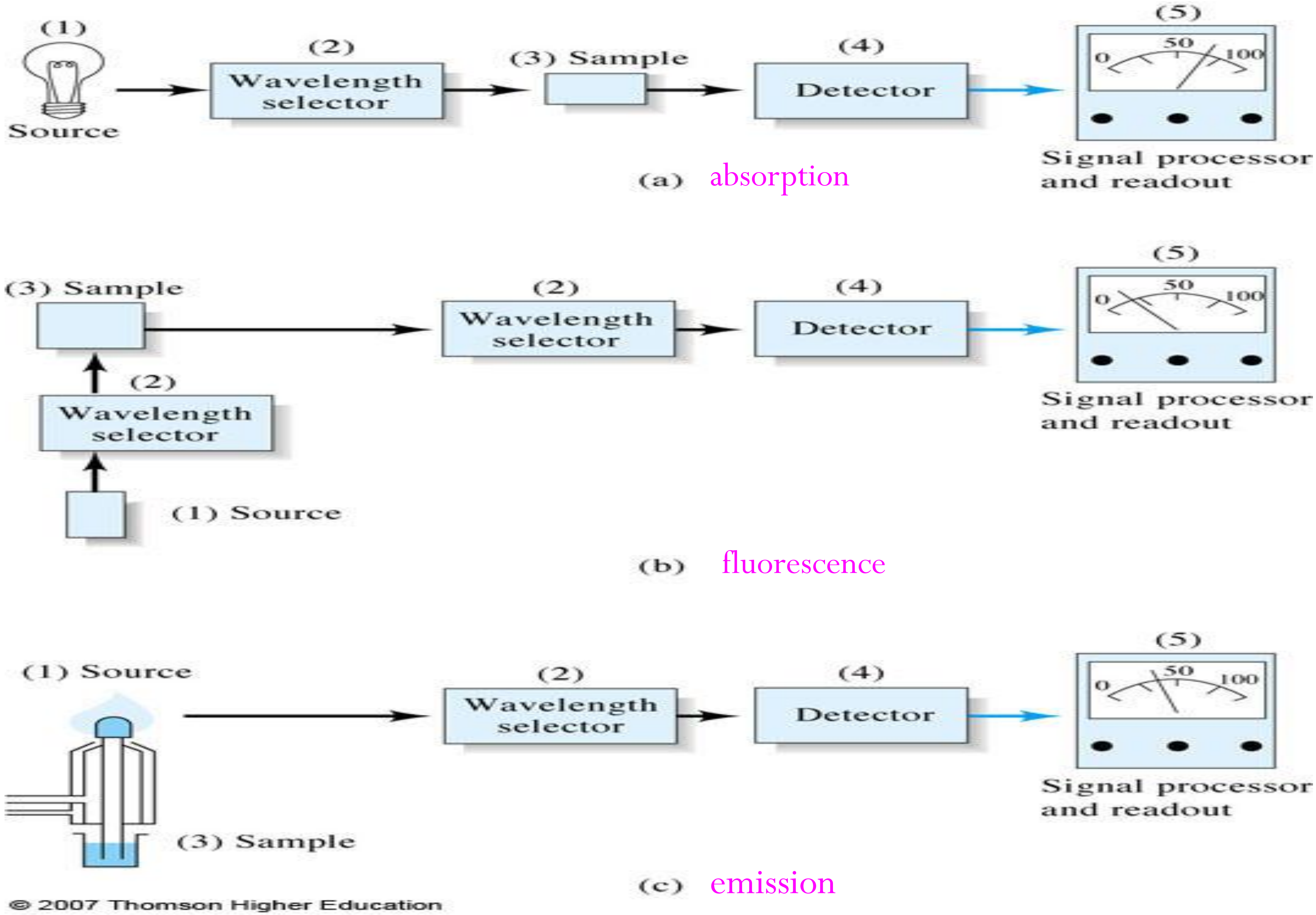

Fig.2.1.Components of various types of instruments for optical spectroscopy

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Components of various types of instruments for optical spectroscopy.

In (a),the arrangement for absorption measurements is shown. Note that source radiation of the selected wavelength is sent through the sample, & the transmitted radiation is measured by the detector-signal processing-readout unit. With some instruments, the position of the sample and wavelength selector is reversed.

In (b), the configuration for fluorescence measurements is shown. Here, two wavelength selectors are needed to select the excitation and emission wavelengths. The selected source radiation is incident on the sample and the radiation emitted is measured, usually at right angles to avoid scattering.

In (c), the configuration for emission spectroscopy is shown. Here, a source of thermal energy, such as a flame or plasma, produces an analyte vapor that emits radiation isolated by the wavelength selector and converted to an electrical signal by the detector.

Optical Materials

- The cells, windows, lenses, mirrors, and wavelength-selecting elements in an optical spectroscopic instrument must transmit radiation in the wavelength region being investigated.
- Ordinary silicate glass is completely adequate for use in the visible region and has the considerable advantage of low cost.
- In the UV region at wavelengths shorter than about 380 nm. glass begins to absorb. and fused silica or quartz must be substituted.
- Also, in the IR region, glass, quartz, and fused silica all absorb at wavelengths longer than about 2.5 μm.
- Hence, optical elements for IR spectrometry are typically made from halide salts(KBr, NaCl, AgCl) are often used in the IR region.
  - ✓ the disadvantages of being expensive and some what water soluble or in some cases polymeric materials.

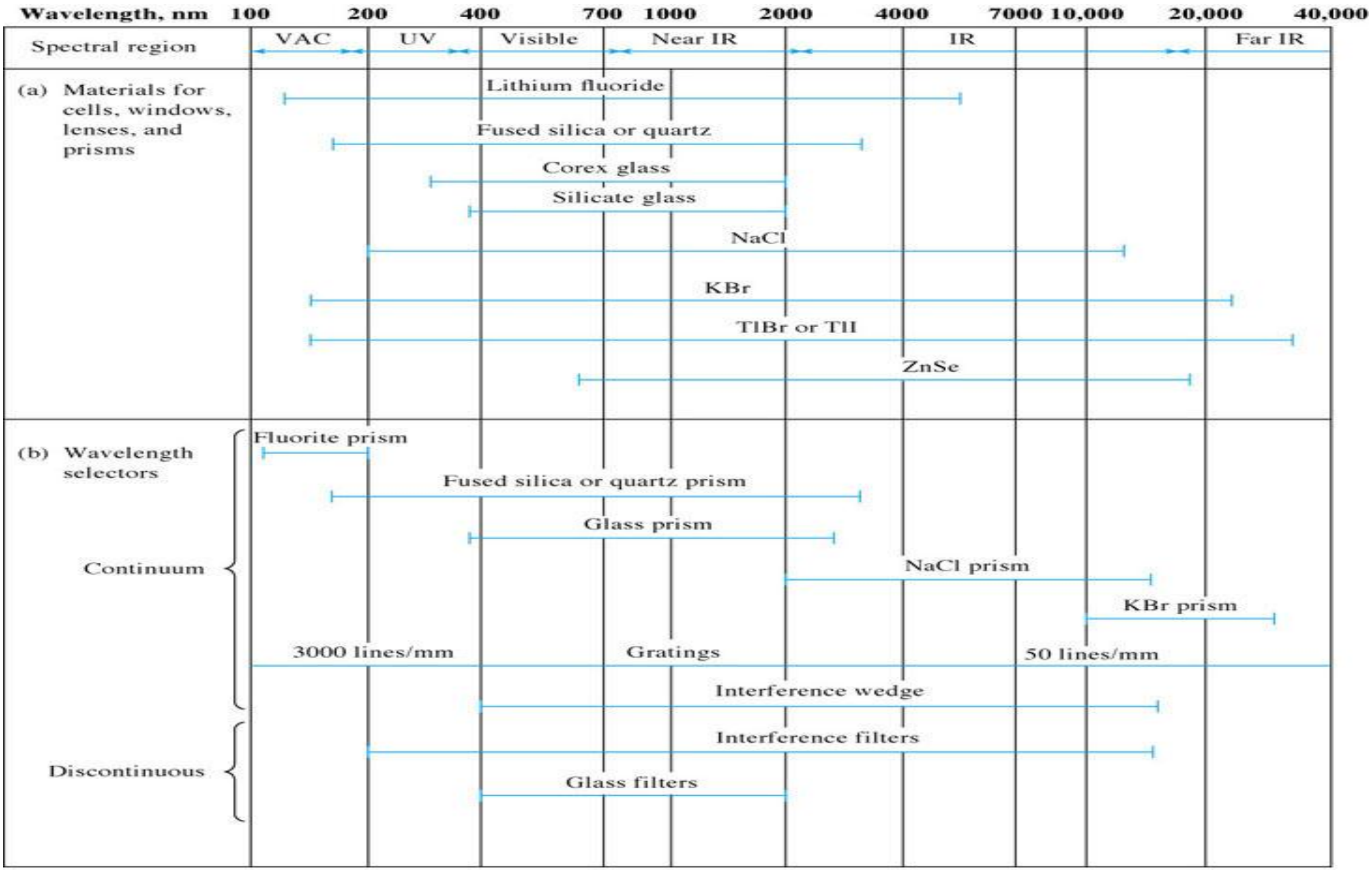

Fig.2.2. (a)construction materials and
(b) wavelength selectors for spectroscopic instruments.

Sources of Radiation

- A source to be used in a selected range of wavelength should have the following properties:

1. It should generate a beam of radiation covering the λ range in which to be used. e.g. a source to be used in the visible region should generate light in the whole visible region (340-780 nm).
2. The output of the source should have enough radiant power
3. The output should be stable with time and fluctuations in the intensity should be minimal.

- Sometimes, a double beam instrument is used to overcome fluctuations in the intensity of the beam with time. In such instruments, the beam from the source is split into 2 halves one goes to the sample while the other travels through a reference.
- Subtraction of the reference beam from that of the sample results in excellent correction for fluctuations in the intensity of the beam. The same intensity of the beam pass through the sample and reference.

Classifications of Sources :

- There can be several classifications of sources.

  i, Based on where their output is in the electromagnetic spectrum.

  ii, Based on whether the source is a thermal or gas filled lamps, etc.

  iii, Based on whether the source is a continuous or a line source.

- **Continuum Sources:** Emit radiation that changes in intensity only slowly as a function of wavelength. (covering the range of wavelength)

  - ✓ For the **UV** region, the most common source is the **deuterium lamp** which has an output in the range from 180-350 nm.

  - ✓ **Tungsten filament lamp** covering the range from 340-2500 nm, thus its output extends through the whole **visible and near IR regions**.

Cont…

- High pressure gas filled arc lamps that contain argon, xenon, or mercury serve when a particular intense source is required.
- The continuum sources for IR radiation are normally heated inert solids .
- A Globar source is a silicon carbide rod; IR radiation is emitted when the Globar is heated to about 1500°C by the passage of electricity.
- A Nernst glower is a cylinder of zirconium and yttrium oxides that emits IR radiation when heated to a high temperature by an electric Current.

Electrically heated spirals of nichrome wire also serve as inexpensive IR sources

Continuous sources, which emit radiation continuously with time, or pulsed sources, which emit radiation in bursts.

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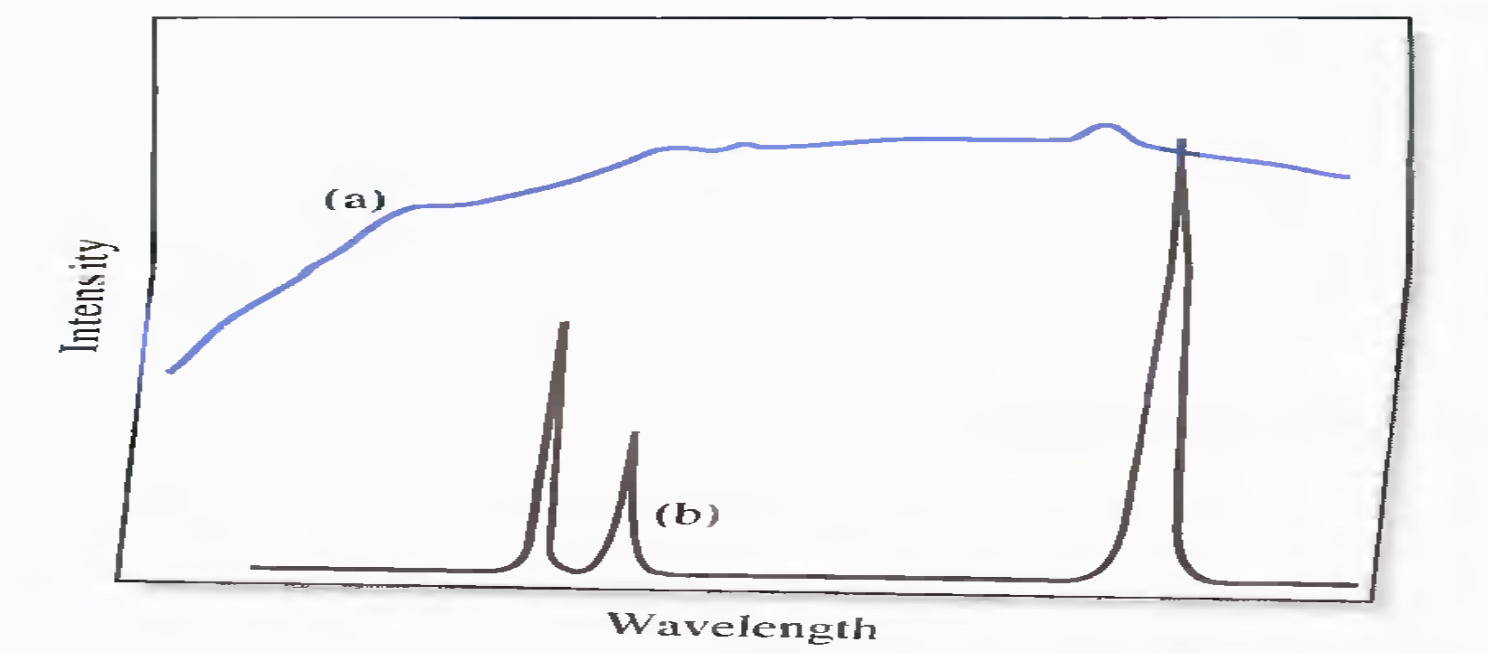

Fig.2.3.Spectral source types. The spectrum of a continuum source (a) is much broader than that of a line source(b).

- **A line source** is a source, which has a line output at definite wavelengths, rather than a range of wavelengths.

- ✓ Hollow cathode and electrodeless discharge lamps are examples of line sources which produce few sharp lines in the UV and Vis.

Lasers:

- The term LASER is an short form for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation.

- All lasers contain an energized substance that can increase the intensity of light that passes through it. This substance is called the **amplifying medium** & it can be a solid, a liquid or a gas.

- The amplifying medium is a rod of yttrium aluminum garnate (YAG , $Y_3Al_5O_{12}$) containing neodymium ions (Nd (III)).
- In a dye laser, it is a solution of a fluorescent dye in a solvent such as methanol.
- In a helium-neon laser, it is a mixture of the gases He and Ne.
- In a laser diode, it is a thin layer of semiconductor material sandwiched between other semiconductor layers.

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~~Light Amplification by Stimulated Emission of Radiation~~

- ~~Emits very intense, monochromatic light at high power (intensity)~~
- ~~All waves in phase (unique)~~
- ~~All waves are polarized in one plane and used to be expensive~~
- ~~Not useful for scanning wavelengths, Monochromatic.~~
- ~~For narrow wavelength ranges, and rugged instruments people now often use LEDs (light emitting diodes) like you see in electronic devices (red, yellow, green, blue, white), stoplights, etc.~~

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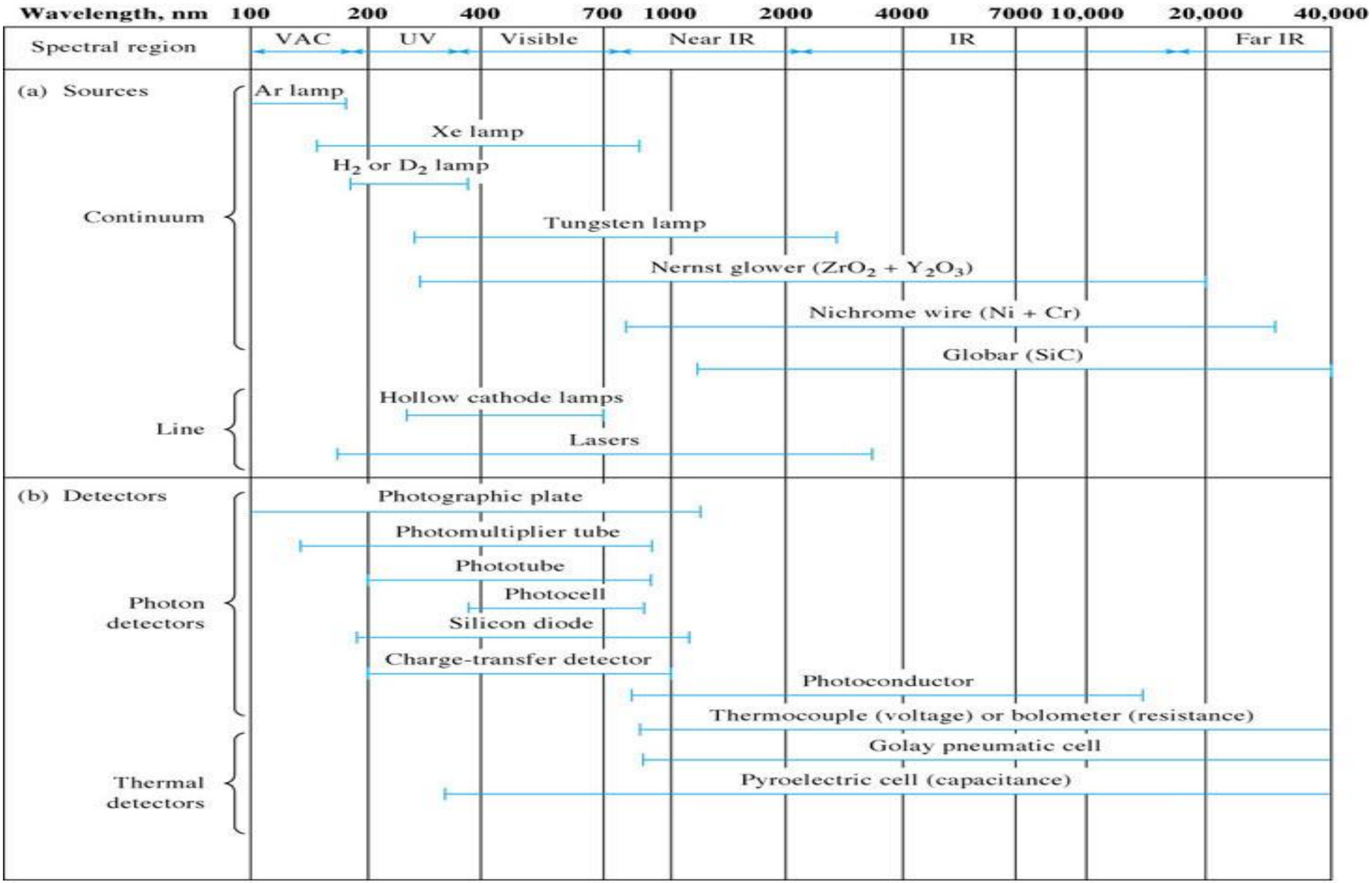

Fig. 2.4 (a) sources and (b) detectors for spectroscopic instruments.

Sample Holders(Cells)

- Sample containers should be transparent to incident radiation.
- Glass is not a good material in the UV region while quartz or fused silica can be used for both UV and visible.
- Also, all windows & optical components through which radiation should be transmitted in a spectroscopic instrument should not absorb incident radiation
- Must: contain the sample without chemical interaction
  - be more or less transparent to the wavelengths of light in use
  - be readily cleaned for reuse
  - be designed for the specific instrument of interest.

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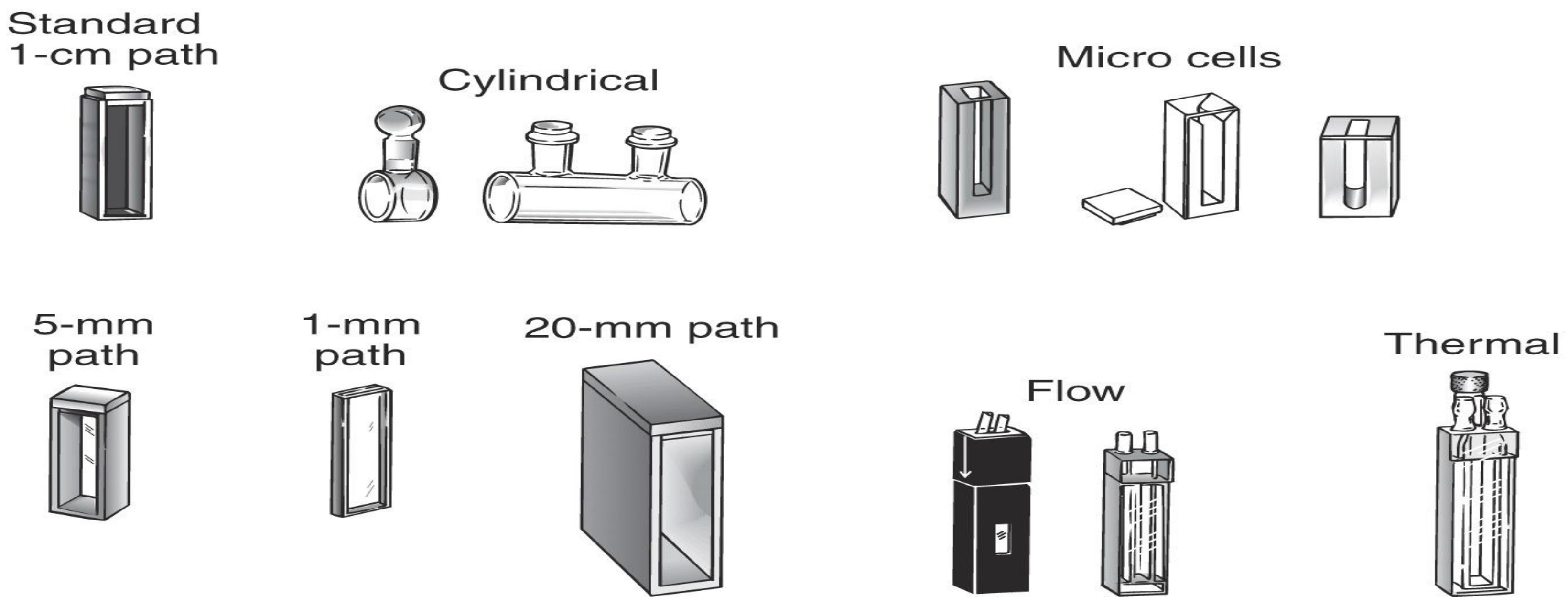
- Cells can be constructed to:
  - transmit light absorbed at 180 degrees to the incident light
  - allow emitted light to exit at 90 degrees from the incident light
  - contain gases (lower concentrations) and have long path lengths (1.0 and 10.0 cm cells are most common)



Wavelength Selectors

- Wavelength selectors are important instrumental components that are used to obtain a certain λ or a narrow band of λs.
- ✓ Used to select the wavelength(wavelength range) of light that either
  - Impinge, contact on the sample (fluorescence and phosphorescence)
  - is transmitted through the sample (absorption and emission)
- ✓ This selected wavelength then strikes the detector
  - the ability to select the wavelength helps you to discriminated between phenomena caused by your analyte and that caused by interfering or non-relevant species.
- ✓ Are often combined with a set of SLITS (discussed later)
- **Various types**

  i. based on filters (CHEAP COLORED GLASS)

  ii. based on prisms (LIMITED APPLICATIONS)

  iii. based on gratings (GREAT STUFF)

I. Filters

- Filters are λ selectors that usually allow the passage of a band of λs

➢ Two types of filters:

1. Interference filters depend on destructive interference of the impinging light to allow a limited range of wavelengths to pass through them (more expensive)
2. Absorption filters absorb specific wavelength ranges of light (cheaper, more common)...

➢ Interference filters have narrower bandwidths than absorption filters, but are more expensive

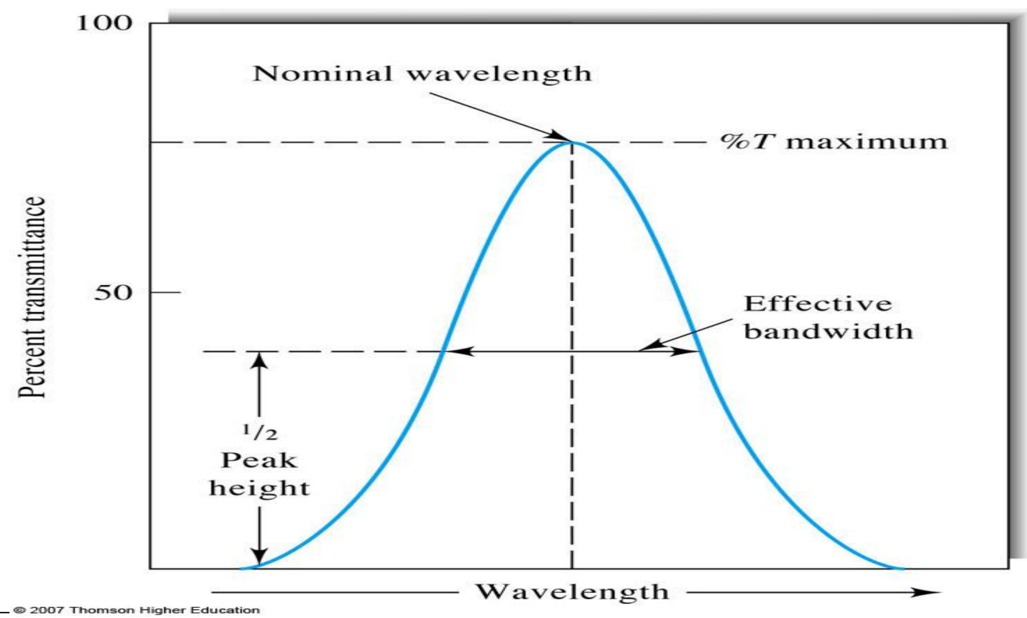


Fig. 2.5: Output of a typical λ selector.

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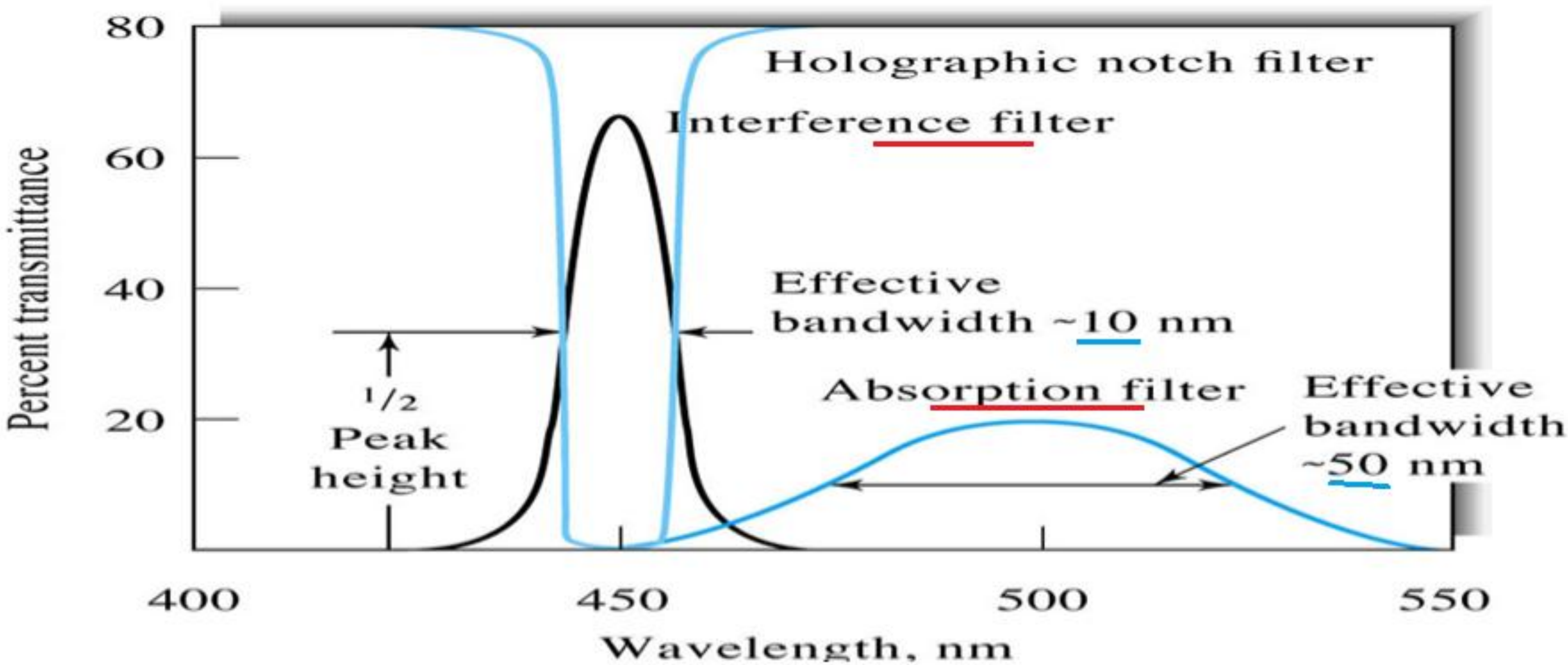

❖ **Two** basic filter functions….

➢ **Cutoff filters** absorb light in a specific range of wavelengths. They "cutoff" this range from the detectors (e.g. cutoff for 550 nm) Absorption filters are cutoffs.

➢ **Band pass filters** absorb light outside of a specific range(e.g. 350-550 nm) Interference filters are band pass or you can make a band pass from a combination of two cutoff filters!

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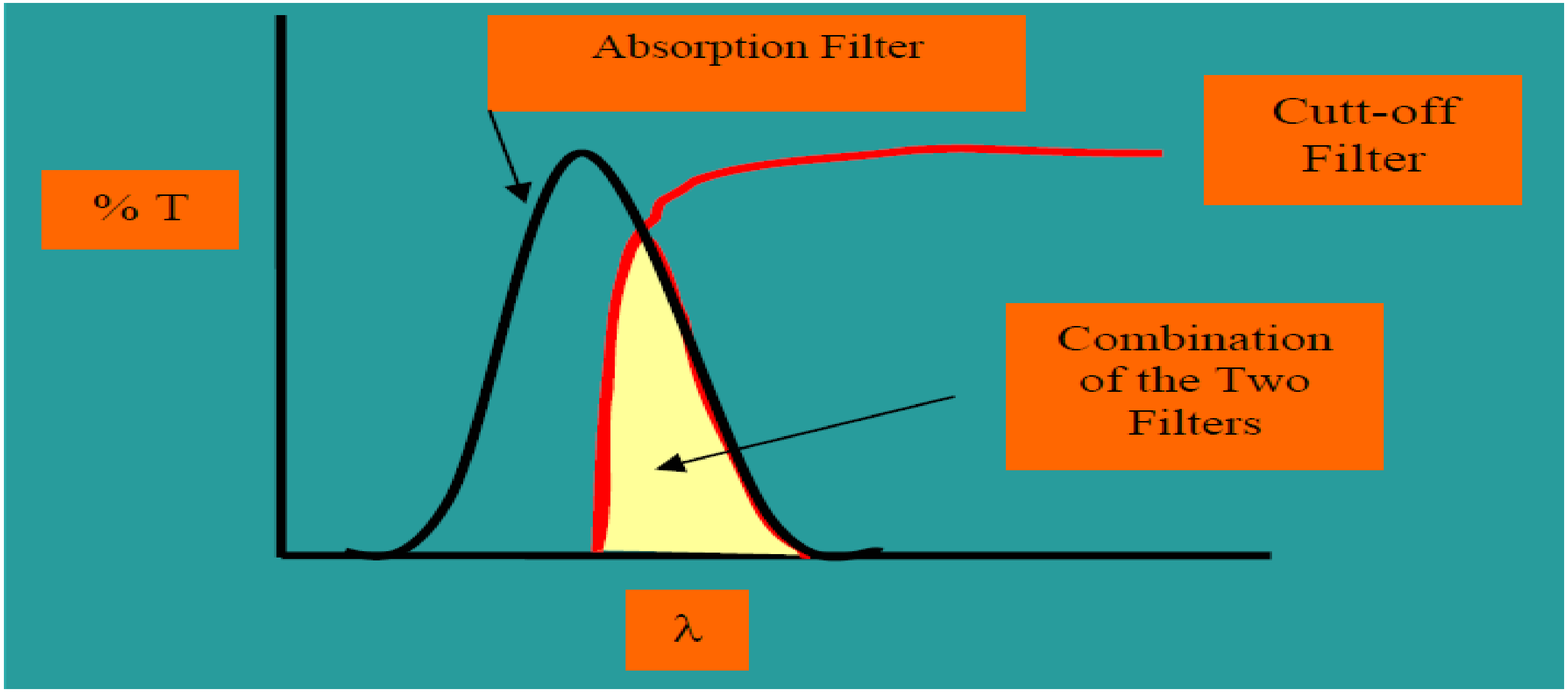
- Usually cut-off filters are not used as wavelength selectors but rather in combination of absorption filters to decrease the bandwidth of the absorption filter or to overcome problems of orders.



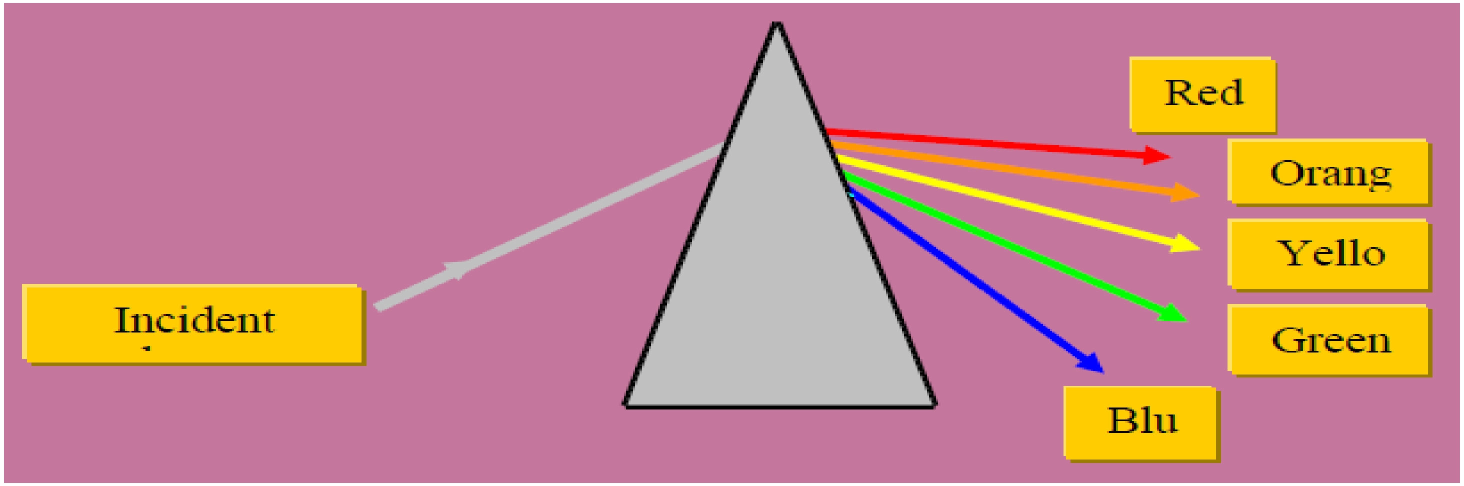
- Only the combination of the two filters (common area or yellow shaded region in the diagram) will be transmitted which has much narrower effective bandwidth than absorption filters alone.

Filters

- Simple, rugged (no moving parts in general),
- Relatively low-cost
- Can select some broad range of wavelengths
- Most often used in field instruments
- simpler instruments and
- Instruments dedicated to monitoring a single wavelength range.

II. Prisms

- **A prism** is a wavelengths selector that depends on the dispersion ability of the incident radiation by the prism material.
- Dispersion is the variation of refractive index with , λ or frequency.
- Since a beam of a polychromatic light is composed of several wavelengths, the dispersion of these wavelengths will be different when they are transmitted through the prism.
- One can see the following dispersion pattern for white light:



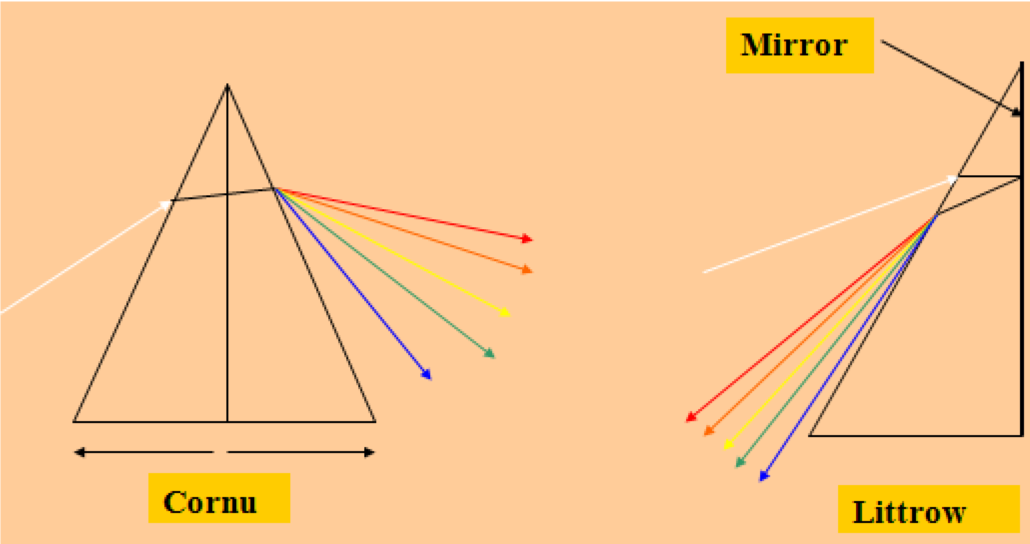
❖ Two common types of prisms can be identified:

i. Cornu Prism: It is a 60° prism which is made either from glass or quartz.

- When quartz is used, two 30° prisms (one should be left handed & the other is right handed) are cemented together in order to get the 60° prism.
- Cementing the left and right handed prisms will correct for light rotation and will transmit the beam in a straight direction

ii. Littrow Prism: A littrow prism is a 30° prism which uses the same face for input and dispersed radiation.

- The beam is reflected at the face perpendicular to base, due to presence of a fixed mirror.



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- Glass is nontransparent to UV radiation.
- Quartz prism should be used when radiation in the ultraviolet is to be dispersed, rather than a glass.
- Quartz serves well in both UV and Vis.
- ✓ It should also be appreciated that the dispersion of a prism is nonlinear since it is dependent on wavelength.
- ✓ Dispersion increases for shorter wavelength.
- ✓ Prisms are very good wavelength selectors in the range from may be 200-300 nm but are bad ones for wavelength selection above 600 nm.

III. Gratings

- A grating is an optically flat polished surface that has dense parallel grooves, dispersion in hard material.
- Two types of gratings are usually encountered.
  - ✓ Transmission and reflection (diffraction) gratings.
- Transmission gratings are rarely used in spectroscopic instruments and almost all gratings, which are used in conventional spectroscopic instruments, are of the reflection type.

❖ Two common types of reflection gratings can be identified:

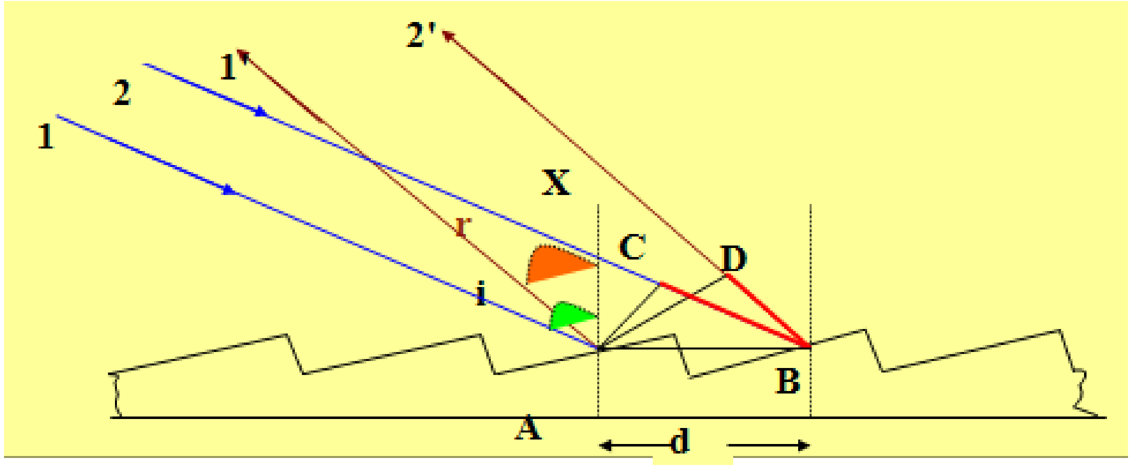
1. **Echellette Gratings:**
   - Echellette gratings contain from 300 to 2000 lines/mm but an average line density of about 1200 to 1400 lines/mm is most common.
   - The echellette grating uses the long face for dispersion of radiation.
   - It is the grating of choice for molecular spectroscopic instruments.
   - In contrast to prisms, gratings usually have linear dispersion of radiation.

2. **Echelle Gratings:**

- These have relatively coarse grooves (~80-300 lines/mm).
- They use the short face for dispersion of radiation and are characterized by very high dispersion ability.

Dispersion by Gratings

- We can visualize what is going on when radiation hits the surface of a grating.



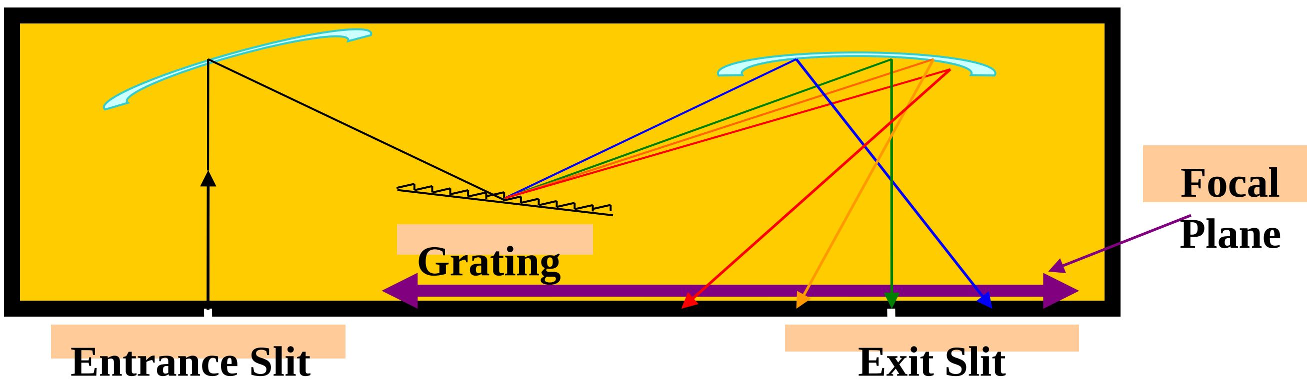
Monochromators

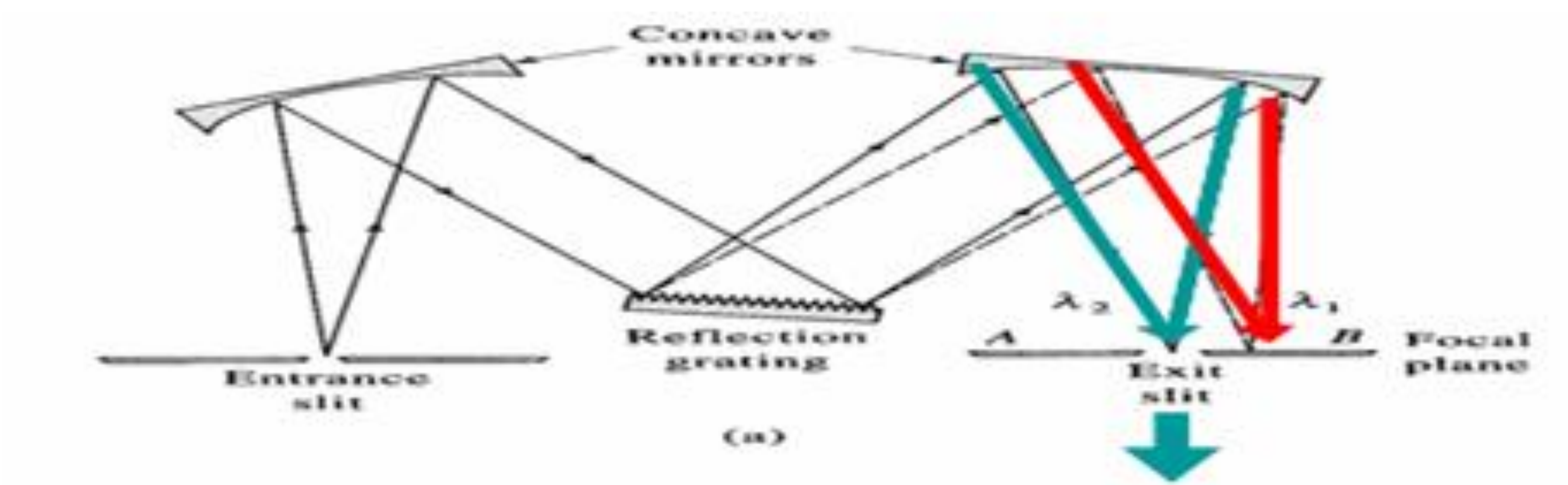
- Is responsible for producing monochromatic radiation.
- It is an essential component of any spectroscopic instrument and is composed of a prism or grating, as the λ selector, in addition to focusing elements; like mirrors or lenses.
- All these components are contained in a box that has an entrance & an exit slit.

❖ Two common types of monochromators can be described:

1. Czerney-Turner Grating Monochromator

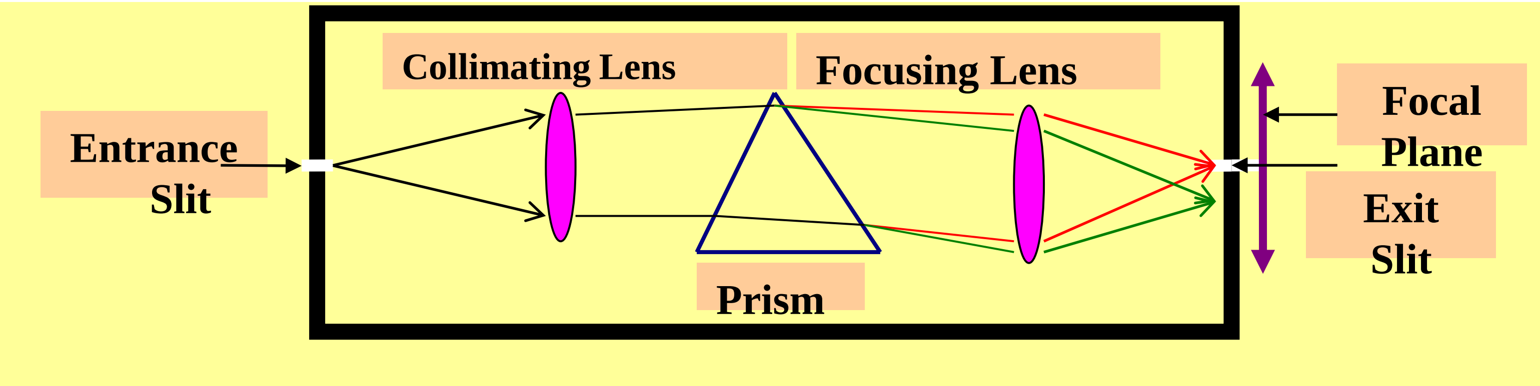
- ➢ This is composed of a grating, two concave mirrors and two slits.
- ➢ The ff setup can be associated with this monochromator system

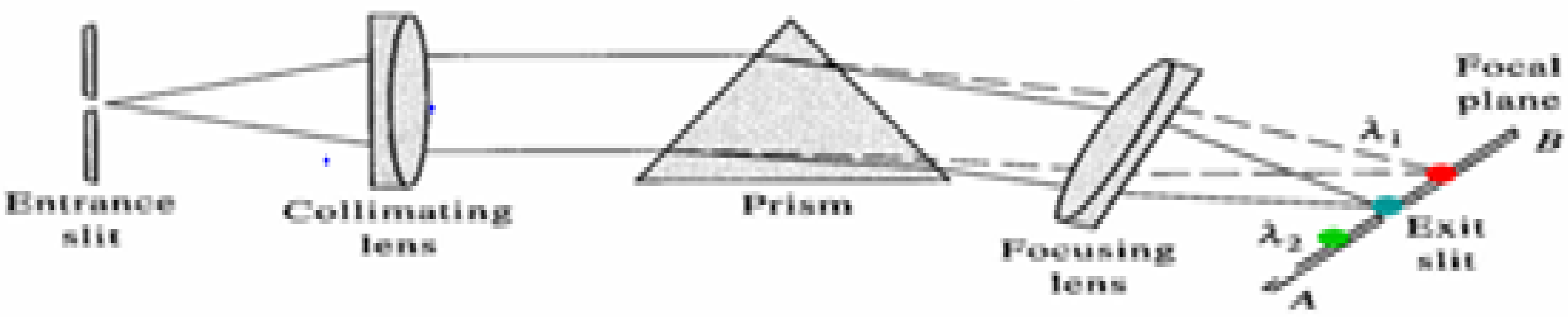




2. Bunsen Prism Monochromators

- This type of monochromators uses a prism as the dispersion element in addition to two focusing lenses and two slits. The setup can be depicted as in the figure below:





Monochromator Slits

- It may be primitive to say that multiple wavelengths hitting the focal plane can emerge from the exit slit if the exit slit is too wide.
- On the other hand, a beam of very low power can emerge from the exit slit when the slit is too narrow.
- The 1st case leads to bad λ selection (bad resolution) as a mixture of λs is obtained, while the other case may make it impossible for the detector to sense the low power beam (bad detectability).
- Therefore, the width of the slits should be carefully adjusted, where some instruments allow such adjustments.
- However, many instruments have fixed slit monochromators optimized for general purpose applications.
- A slit is machined from two pieces of metal to give sharp edges that are exactly aligned (same plane) and parallel.
- The entrance slit of a monochromator can be looked at as a radiation source with an image that will exactly fill the exit slit at a particular grating setting.

Cont…

- Images from other wavelengths will align at the focal plane of the monochromator.

Choice of Slit Width

- Since the effective bandwidth of a monochromator is dependent on its dispersion (Dleff = wD^{-1}) and the slit width, careful choice of the slit width must be done.(D^{-1} linear dispersion, W width, Dl effective bandwidth (Dl_{eff}).)
- In most cases, monochromators are equipped with a mechanism for the adjustment of the slit width.
- It should be appreciated that a narrower slit should be preferred for best wavelengths resolution.
- However, it should be clear that as the slit width gets narrower and narrower, the radiant power reaching the detector will decrease
- As the slit width gets narrower and narrower which is too bad for quantitative analysis.

Cont…

- Therefore, it can be stated that the slit width should be kept as narrow as possible but with enough radiant power reaching the detector, especially in the case of qualitative analysis where we are interested in the features of the spectrum.
- Wider slits can be used for quantitative analysis since, in such applications, we do not look at the fine features of the spectrum.
- Overall, adjustment of the slit width is a compromise between detectability & resolution; an analyst should use his own judgment according to the problem on hand.

Radiation Transducers

- There are several types of radiation detectors or transducers.
- Each detector or class of detectors can be used in a specific region of the electromagnetic spectrum.
- There are no universal detectors that can be used for radiation of all frequencies.
- The purpose of radiation transducers is to convert radiant energy into an electrical signal (current or voltage).

Properties of an Ideal Transducer

1. **High sensitivity**: should be capable of detecting very small signals
2. **Signal to noise ratio (S/N):** A high signal to noise ratio is an important characteristic of a good transducer
3. **Constant response**: When radiation of different wavelengths but of the same intensity are measured, the transducer should give a constant response
4. **Fast response**: A short response time is essential especially for scanning instruments.
5. **Zero dark current**: In absence of light, the detector output read zero.
6. **Zero drift**: If radiation of constant intensity hits the transducer, signal should be constant with time
7. **Signal** (S) should be proportional to intensity of incident radiation

$$\mathbf{S = kI}$$

However, in practice, a fixed value (called dark current, K_d) is usually added to signal

$$\mathbf{S = KI + K_d}$$

Transducers in the UV-Vis range are referred to as photon transducers

Photon Transducers

❖ Several transducers can be introduced under the photon transducers;

1. Photovoltaic or Barrier Cells

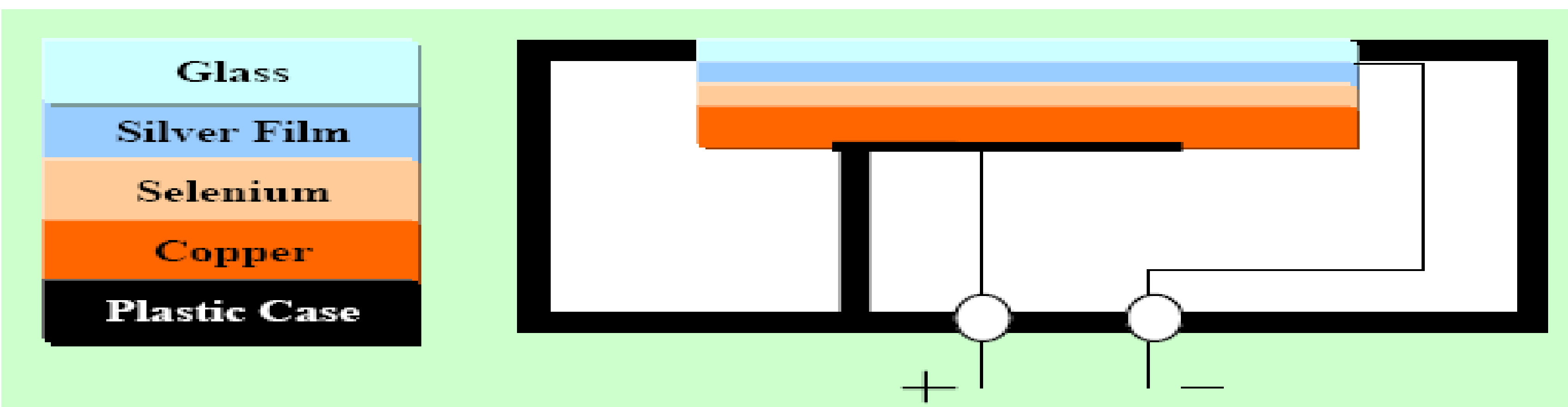
➢ These are simple transducers that operate in the visible region (350-750 nm) with maximum sensitivity at about 550 nm.

✓ The cell is composed of a copper or iron base on which a selenium semiconducting layer is deposited.

✓ The surface of semiconductor is coated with a thin semitransparent film of a metal like silver or gold.

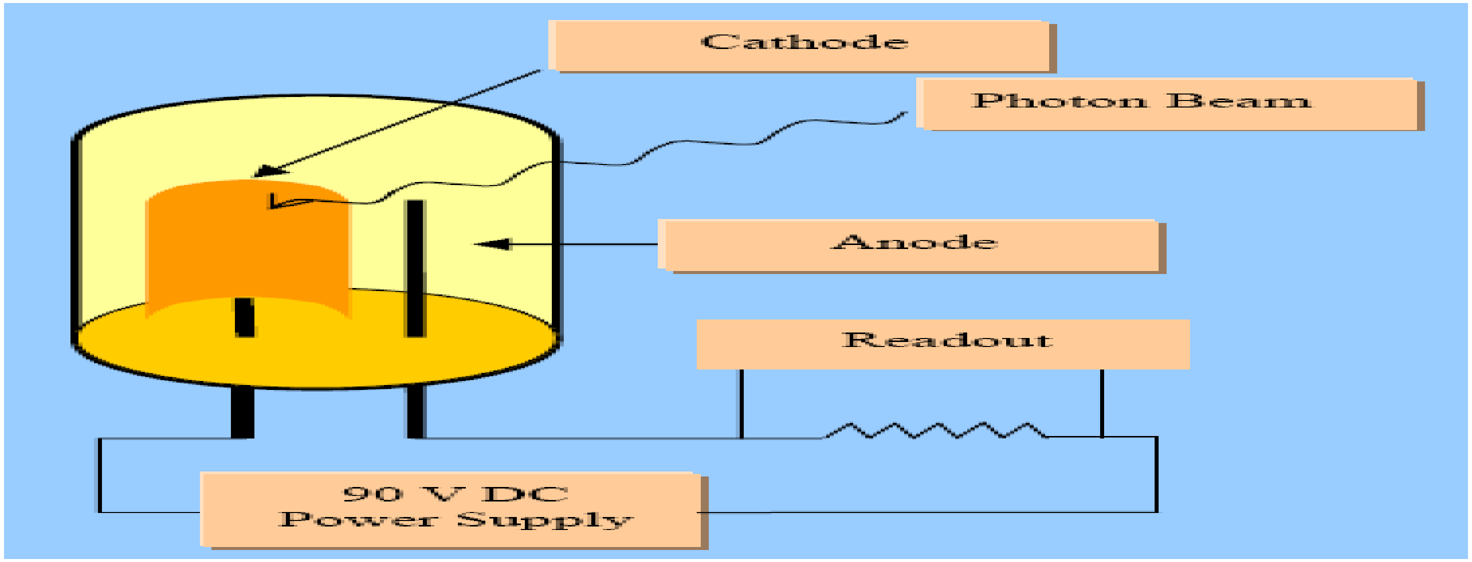
✓ The whole arrangement is covered with a glass plate to protect the array.

✓ The Cu base and Ag thin film are the two electrodes of the cell.



2. Vacuum Phototubes

- A photo tube transducer is one of the most common and wide spreading transducers that are formed from an evacuated glass or quartz envelope that houses a semi cylindrical cathode and a wire anode assembly.
- The cathode surface is coated with a layer of a photo emissive materials like Na/K/Cs/Sb but other formulations exist which have various sensitivities and wider wavelength ranges.
- The voltage difference between the cathode and the anode is usually maintained at about 90 V.
- The incident beam hitting the cathode surface generates electric current that is proportional to radiation intensity.
- This detector has better sensitivities than the barrier cell and does not show fatigue.
- The detector is good for the general detection of radiation intensity in the UV-Vis region and is used in most low cost instruments.

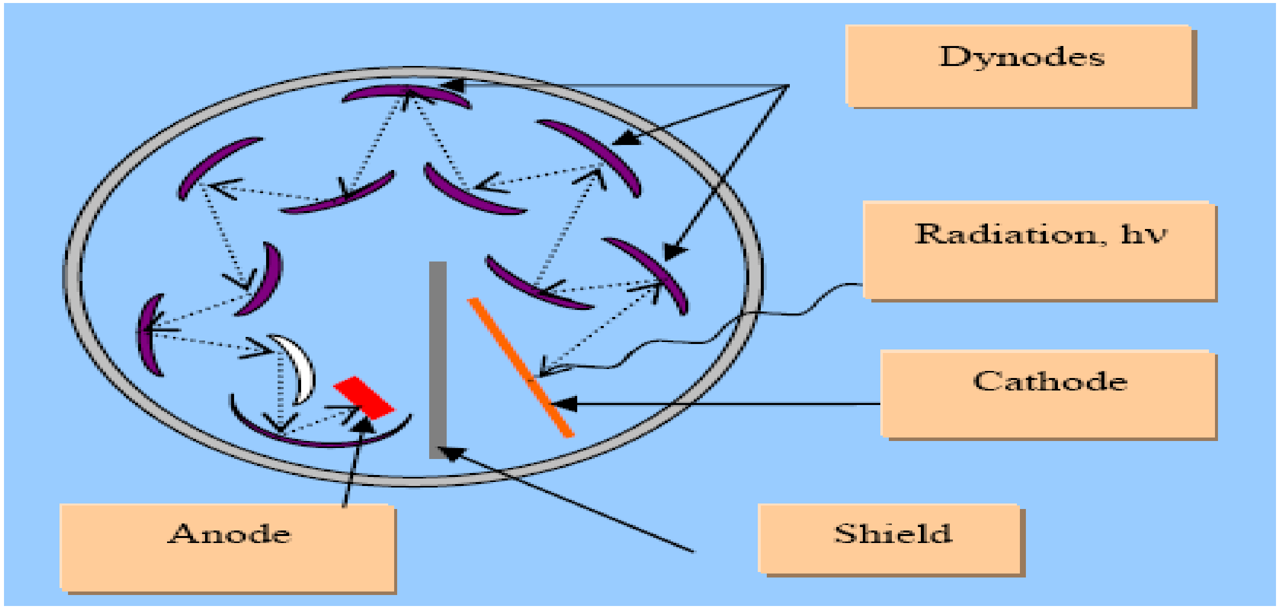


3. Photomultiplier Tubes(PMT)

- A PMT is one of the most sensitive transducers, which can measure radiant powers of very low intensities.
- The operational mechanism of the PMT is similar to the vacuum phototube described above but with extra electrodes (dynodes: same surface composition as cathode) for signal amplification.
- When a photon hits the photo emissive cathode surface, electrons are released and are accelerated to the first dynode at a positive potential to cathode (about 90 V).

Cont…

- Extra electrons are generated since accelerated electrons from cathode strongly hit the more positive dynode surface.
- Electrons are further released from this first dynode to the more positive second dynode (90 V more positive than the first dynode) resulting in release of more electrons.
- This process continues as electrons are accelerated to other more positive dynodes and thus vast amplification of signal results (~106 electrons for each photon).



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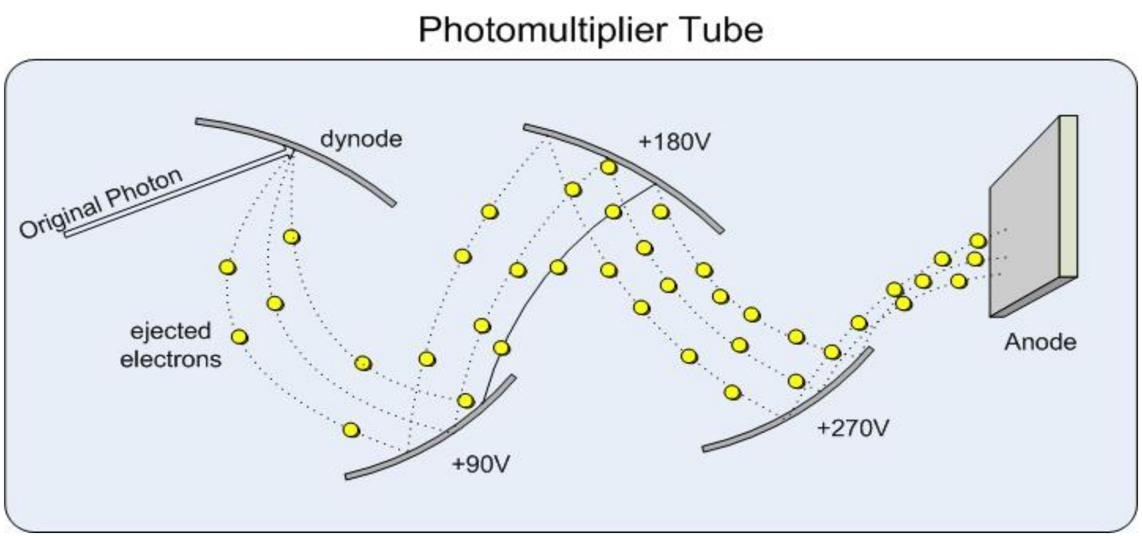
- Photomultiplier tubes are limited to measurement of low radiant power radiation since high radiant powers would damage the photo emissive surfaces, due to very high amplification.
- It is the very high amplification, which imposes a relatively important high dark current value of the PMT.
- Dark current may arise due to electronic components or an increase in the temp.



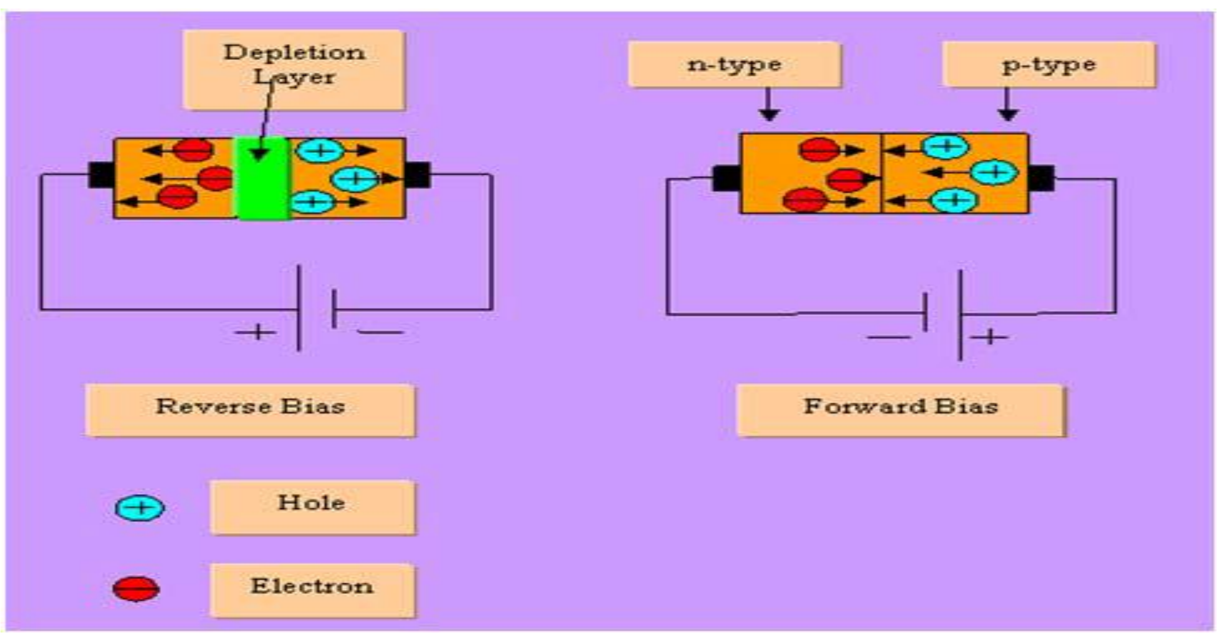
- Cooling of the PMT is suggested to increase sensitivity where cooling to -30°C Can practically eliminate dark current.
- PMTs have excellent sensitivities, fast response time & operational capabilities in both UV & vis regions of the EM spectrum.

4. Silicon Diode Transducers

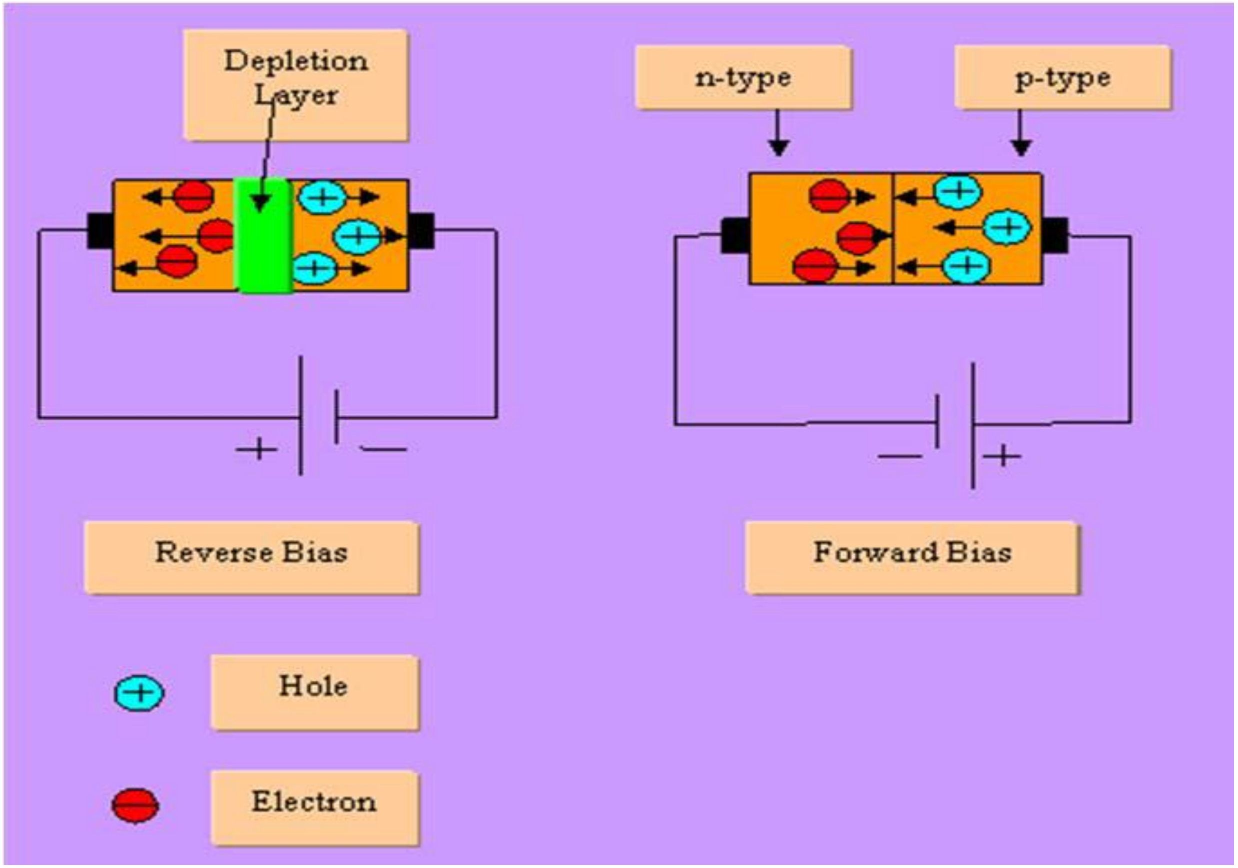
- A semiconductor material like silicon can be doped by an element of group V (like arsenic and antimony) would have more electrons as a group V atom (5e) replaces a silicon atom (4e).
- thus doped semiconductor is called an n-type semiconductor.
- In contrast, when a GIII element (3e) is doped in a silicon matrix, replacement of a silicon atom (4e) with a GIII atom (like indium or gallium, 3e) results in the formation of a less electrons semiconductor or a p-type.
- A diode is a device that has a greater conductance in one direction than the other.
- A diode is manufactured by forming adjacent n-type and p-type regions within the same silicon or germanium single crystal.
- The term pn junction refers to the interface b/n these 2 regions.

❖A diode can be connected to a power supply (a battery) in one of 2 modes:

a. **Reverse bias mode:** the p-type region is connected to the negative terminal of the battery while the n-type region is connected to the positive terminal. In this case, a depletion layer is formed due to migration of positive holes toward the cathode and migration of electrons in the n-type region to the positive anode.



b. Forward bias mode: the p-type region is connected to the positive terminal of the battery while the n-type terminal is connected to the negative terminal of the battery. No depletion layer is observed.



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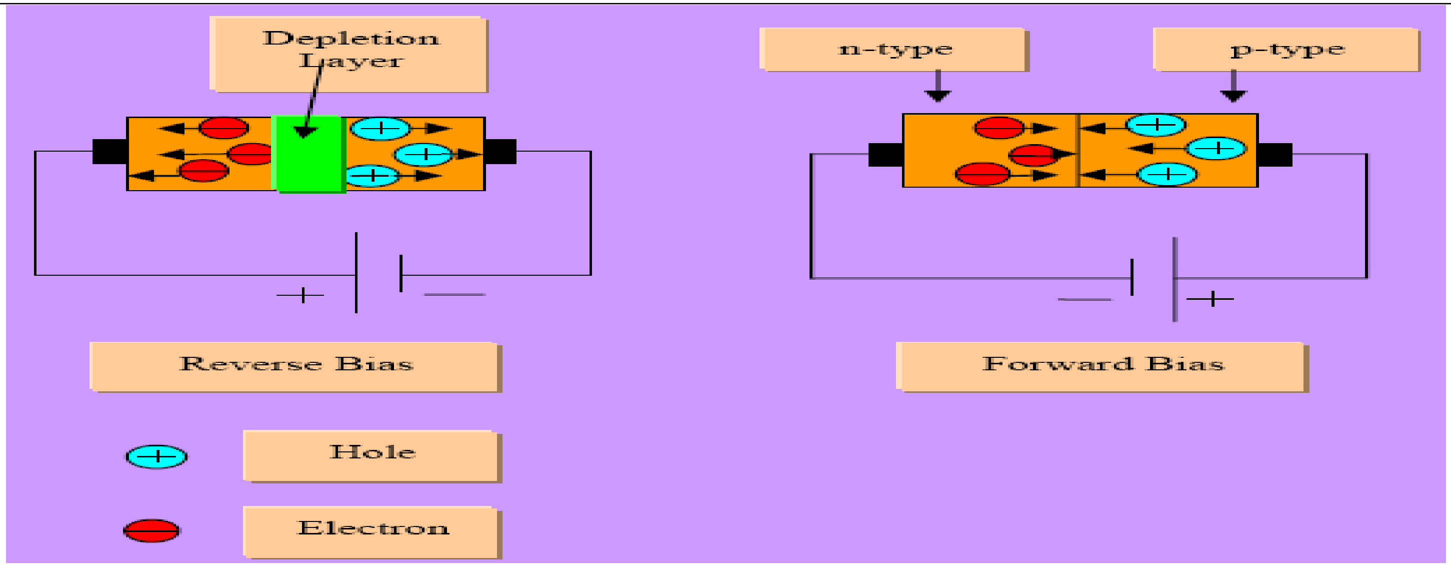


- A silicon diode transducer consists of a reverse-biased pn junction formed on a silicon crystal.
- The application of a reverse bias creates a depletion layer that will ultimately result in zero current.
- When a beam of radiation hits silicon diode, holes and electrons will be formed in the depletion layer thus producing a current proportional to the intensity of incident radiation.
- Silicon diodes are more sensitive than phototubes but far less sensitive than PMTs. They can be used in both UV & vis regions

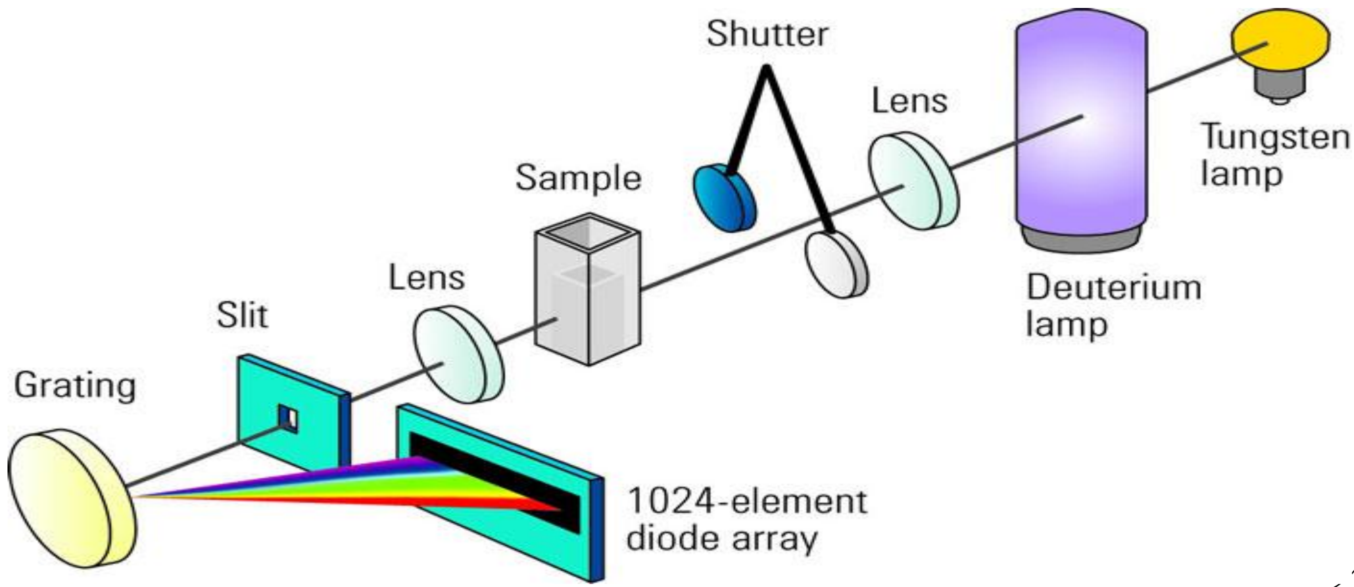
5. Multichannel Photon Transducers

- The simplest multichannel transducer ever made is the photographic film where the full image can be captured in one shot.
- However, the time required for handling & developing the film makes it difficult to practically use it in conventional instruments, although it is still in use in some techniques like x-ray diffraction spectroscopy.

- There are two other major classes of multichannel photon transducers, which find important applications and use in spectroscopic instruments.

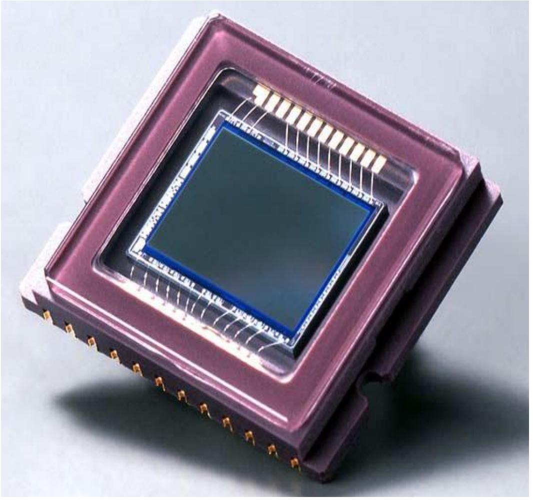
I. Photodiode arrays (PDA)

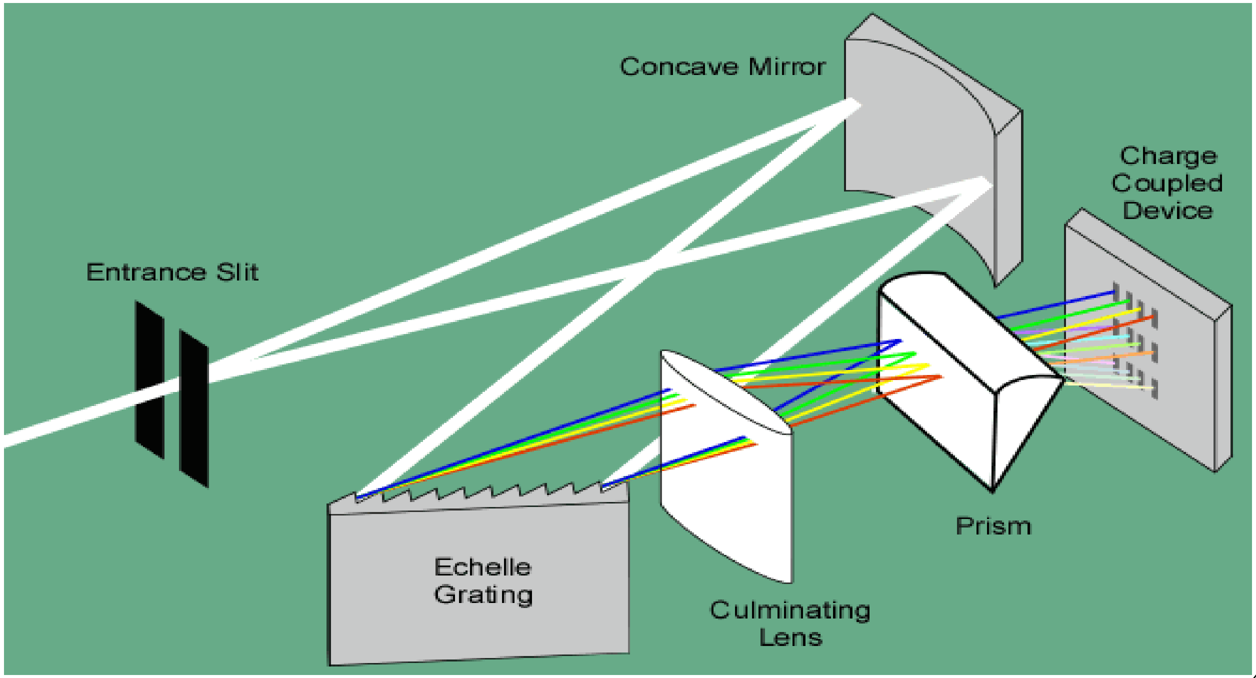
- These are simply linear arrays of silicon diodes described above.
- The number of linear diodes used in each photodiode array usually 64 to 4096 with 1024 silicon diodes as the most common.
- One can imagine the complexity of the electronic circuitry used in such an array as well as the data handling and manipulation requirements.
- The entrance slit is usually fixed at a size enough to fill the surface area of one silicon diode.
- The entire spectrum can thus be instantaneously recorded.
- The arrays are also called diode array detectors (DAD).



II. Charge Transfer & Charge Coupled Transducers

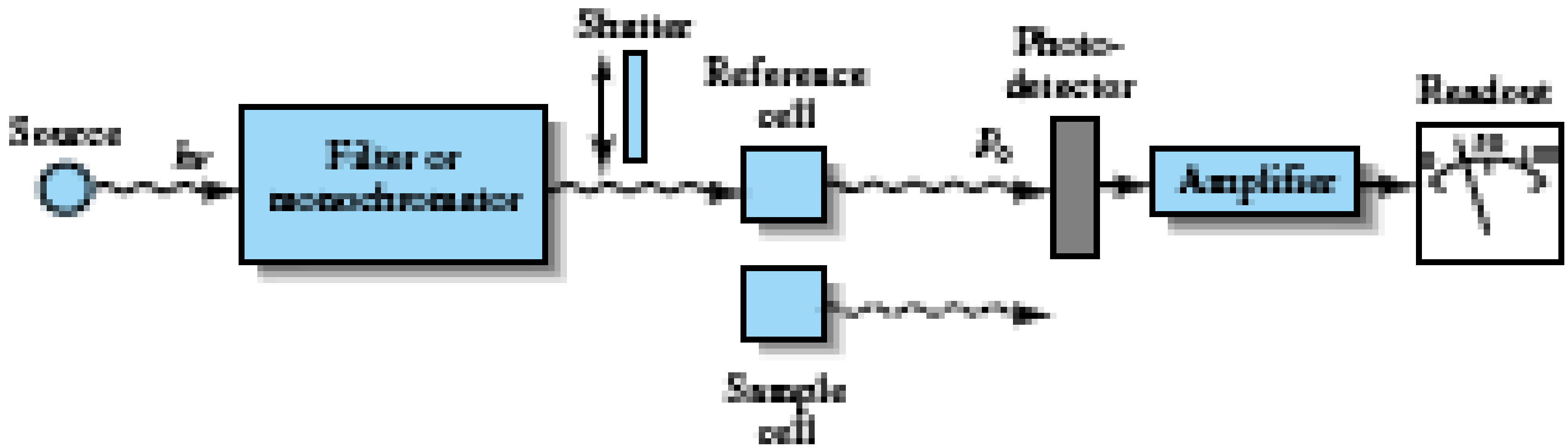
- The photosensitive elements are, in contrary to PDAs, arranged in two dimensions in both charge injection devices (CID) and charge-coupled devices (CCD).
- Therefore, these are very similar to photographic films. For example, a commercially available transducer is formed from 244 rows with each row containing 388 detector elements.
- This will add up to a two-dimensional array holding 16672 detector elements (pixels) on silicon chip that is 6.5 mm by 8.7 mm.





Single and Double Beam General Layouts

Typical Single Beam (e.g. SPEC 20)



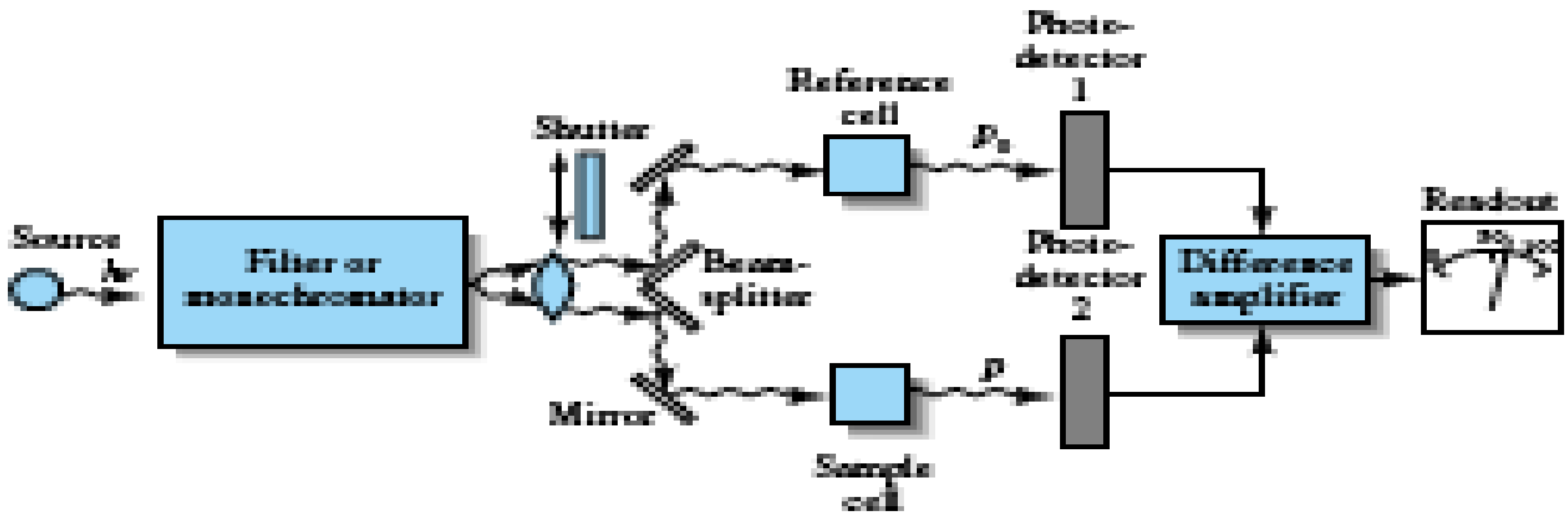
Some Advantages:

- Simple design. Very rugged(strong) and durable. Inexpensive

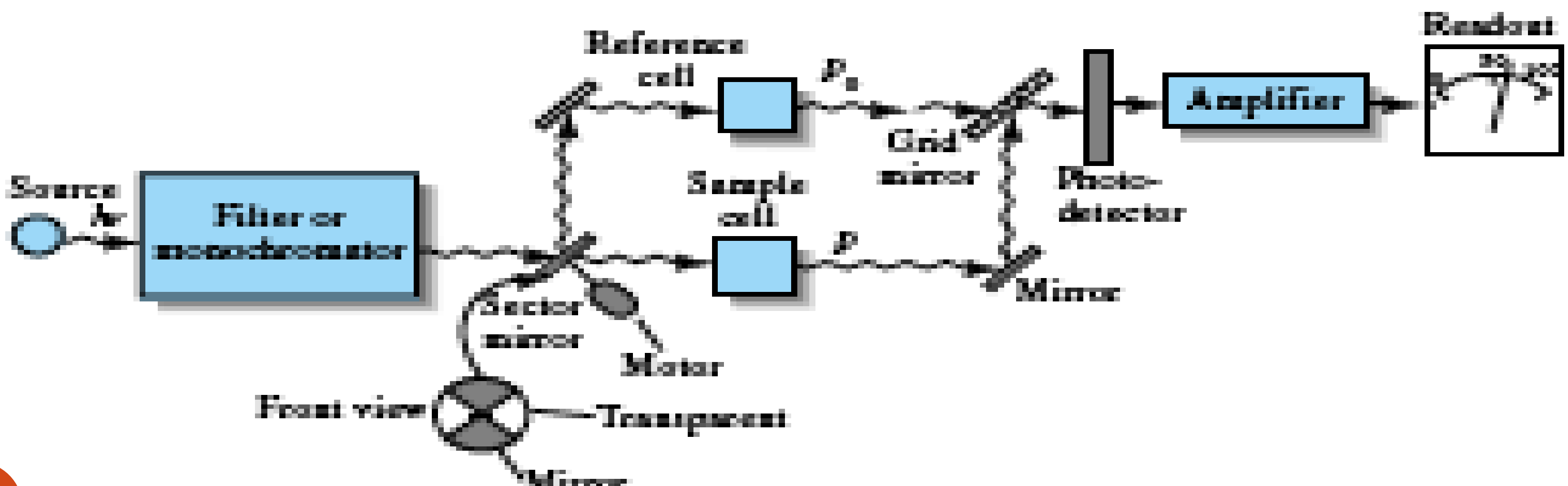
Some Disadvantages:

- Repeated insertion of sample/reference cuvettes can lead to errors.
- Time consuming to measure spectra over many λs.
- Optical components are often simple, leading to limited selectivity (large bandwidth = poor discriminating ability).

Typical Double Beam Designs (diode array's later on)



(b)



Cont…

Some Advantages:

How does a spectrophotometer work- -.MP4

- ✓ "Real Time" Background/Blank subtraction
- ✓ Ease of scanning multiple λs to record a spectrum
- ✓ Elimination of cuvette or cell placement errors
- ✓ Normally higher selectivity than single beam instruments
- ✓ Optical components can be adjusted to control selectivity versus signal strength (the selectivity versus sensitivity compromise)

Some Disadvantages:

- ✓ Higher cost. More delicate and less rugged.
- ✓ More difficult for the beginner user to operate (but not overwhelming)
- ✓ Additional optical/electronic components can lead to a greater number of sources for random error in the measurement.
- ✓ However, this can often be overcome by signal averaging!