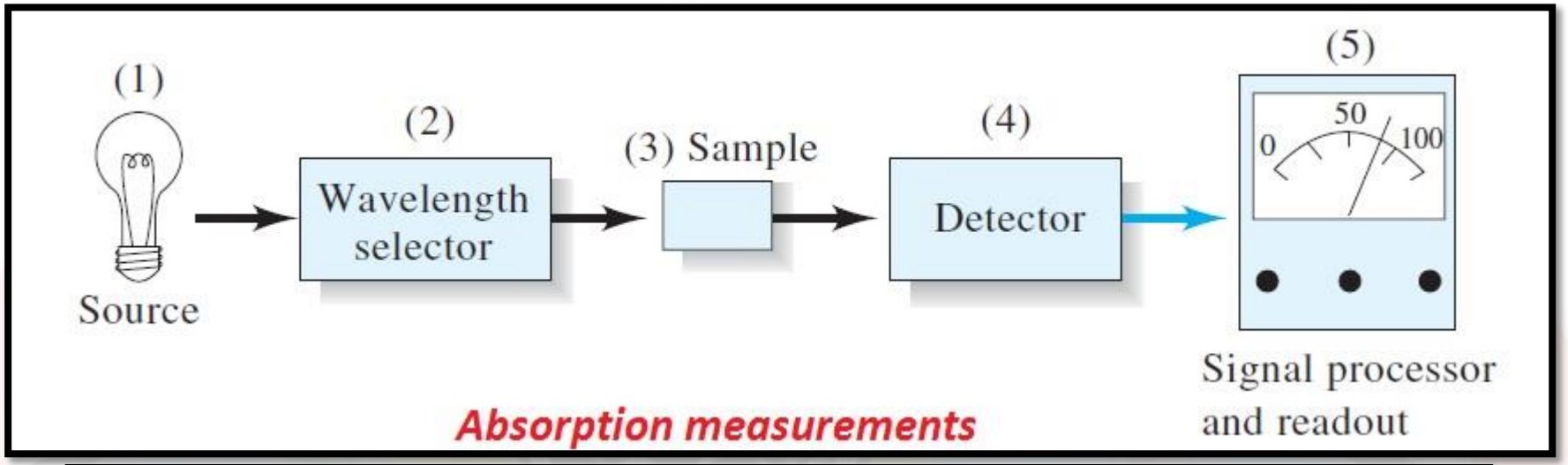
Instrumentation of UV-VIS Spectroscopy

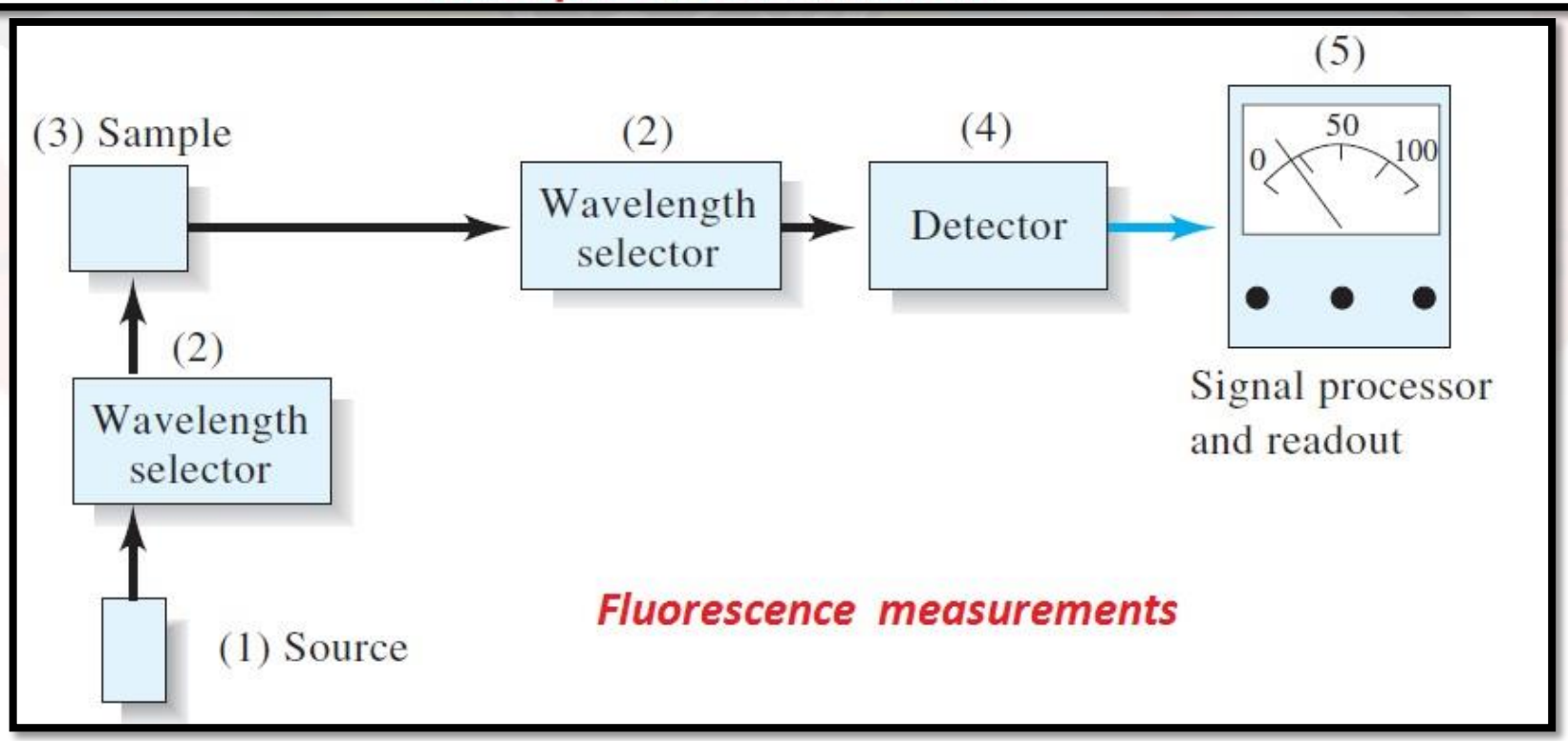
UV/Visible Spectroscopy: Instrumentation

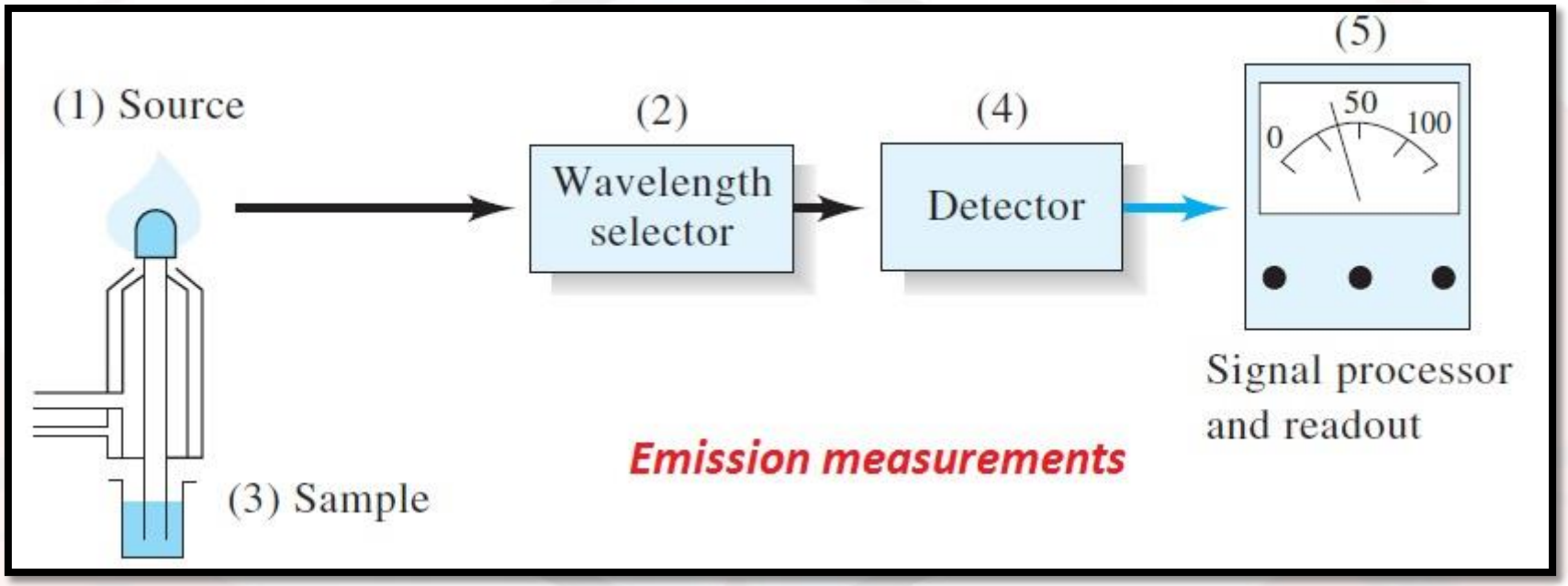
Most spectroscopic instruments in the UV/visible and IR regions are made up of five components:

- ✓ **A stable source of radiant energy**
- ✓ **A wavelength selector to isolate a limited region of the spectrum for measurement**
- ✓ **One or more sample containers**
- ✓ **A radiation detector, to convert radiant energy to a measurable electrical signal**
- ✓ **A signal-processing and readout unit consisting of electronic hardware and in modern instruments a computer.**

Configuration of optical spectroscopic instruments

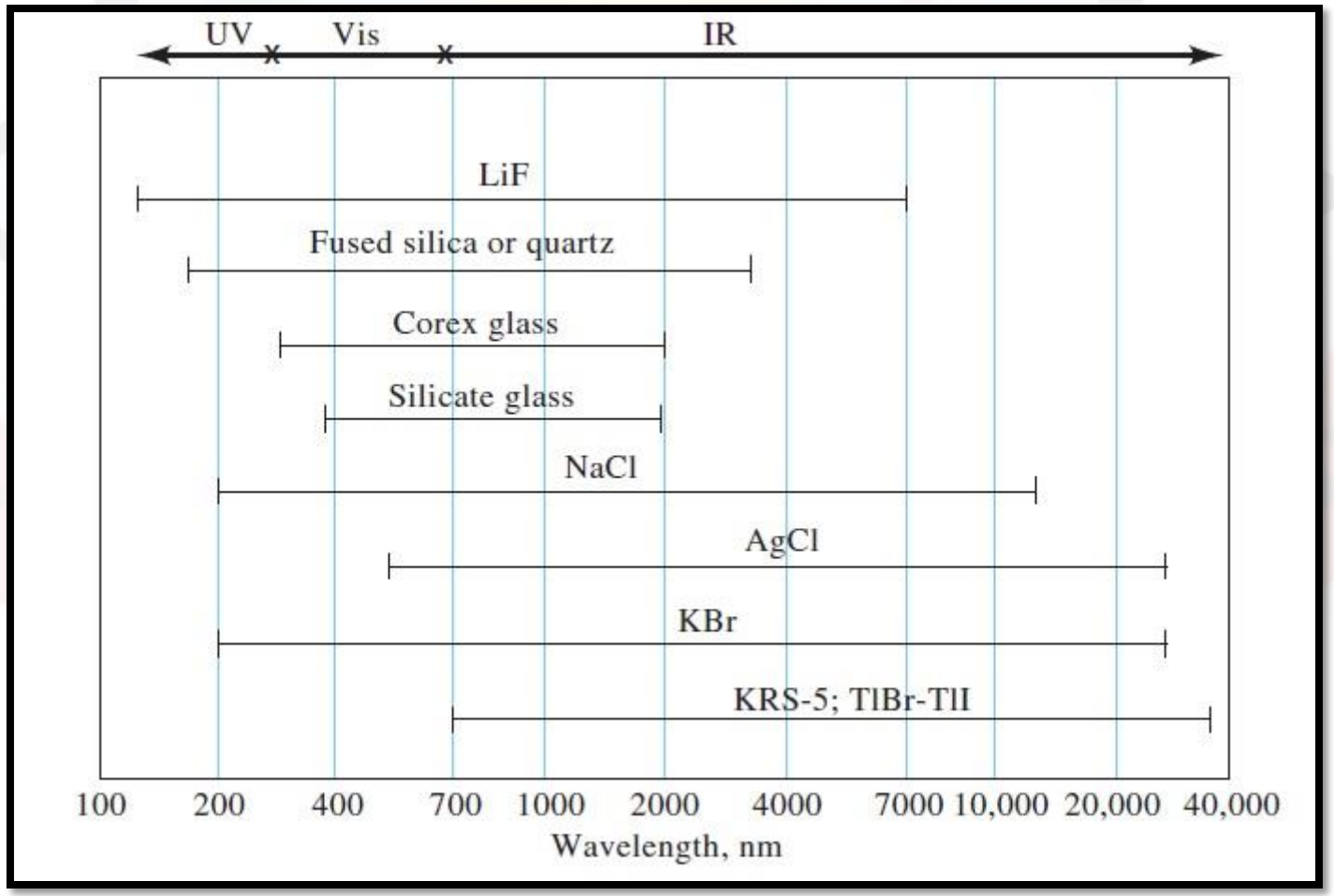





(1) Source
(2)
Wavelength selector
(4)
Detector
(5)
0
50
100
Signal processor and readout
(3) Sample
Emission measurements

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.



Spectroscopic sources

- **Two points should be taken into consideration when select a radiation source:**

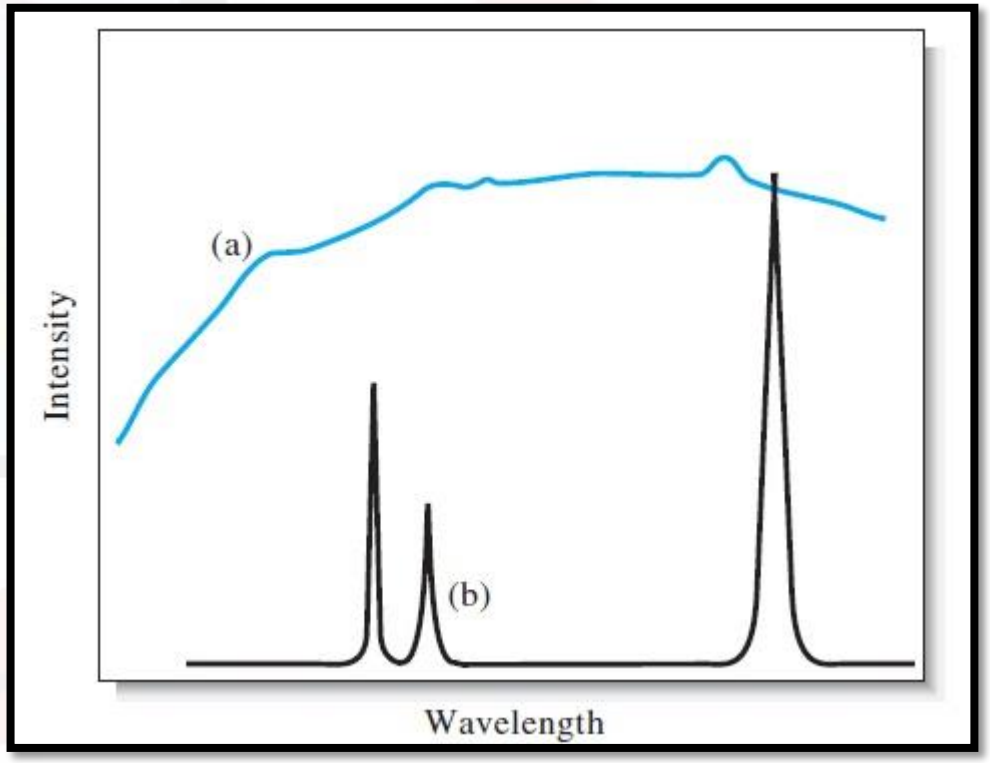
❑**It must generate a beam of radiation that is sufficiently powerful for easy detection and measurement**

❑**It should be stable for reasonable periods of time.**

- **<u>Spectroscopic sources are of two types:</u>**

a. ***<u>Continuum sources</u>*, which emit radiation continuously with time, it changes in intensity only slowly as a function of wavelength, so it is much broader**

b. ***<u>Line or (pulsed) sources</u>*, which emit a limited number of spectral lines (in bursts), each of which spans a very narrow wavelength range.**



Continuum Sources in the Ultraviolet/Visible Region

Source	Wavelength Region, nm	Type of Spectroscopy
Xenon arc lamp	250–600	Molecular fluorescence
H_2 and D_2 lamps	160–380	UV molecular absorption
Tungsten/halogen lamp	240–2500	UV/visible/near-IR molecular absorption
Tungsten lamp	350–2200	Visible/near-IR molecular absorption
Nernst glower	400–20,000	IR molecular absorption
Nichrome wire	750–20,000	IR molecular absorption
Globar	1200–40,000	IR molecular absorption

Line Sources in the Ultraviolet/Visible Region

- ***Low-pressure mercury arc lamps*** are common sources for use in liquid chromatography detectors. The dominant line emitted by these sources is the **253.7 nm** Hg line.
- ***Hollow cathode lamps*** are also common line sources that are specifically used for atomic absorption spectroscopy

Wavelength Selectors

- Devices are used to restrict the radiation being measured to a narrow band that is absorbed or emitted by the analyte. Such devices greatly enhance both the selectivity and the sensitivity of an instrument.

- Many instruments use a ***monochromator*** or a ***filter*** to isolate the desired wavelength band so that only the band of interest is detected and measured.

- ***Filters*** isolate a single band of wavelengths. They provide low resolution wavelength selection suitable for quantitative work. ***Monochromators*** produce high resolution for qualitative and quantitative work. With ***monochromators***, the wavelength can be varied continuously, whereas this is not possible with ***filters***.

- Others use a ***spectrograph*** to spread out, or disperse, the wavelengths so that they can be detected with a multichannel detector.

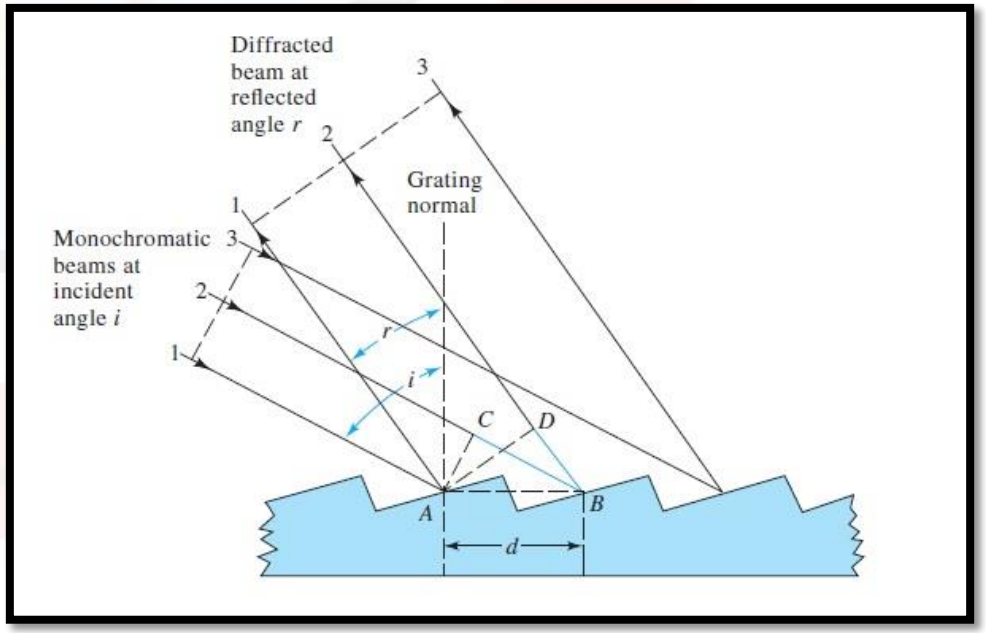
Monochromators and polychromators:

- Both a ***monochromator*** and a ***polychromator*** use a diffraction grating to disperse the spectrum, **BUT** a ***monochromator*** contains only one exit slit and detector while a ***polychromator*** contains multiple exit slits and detectors.

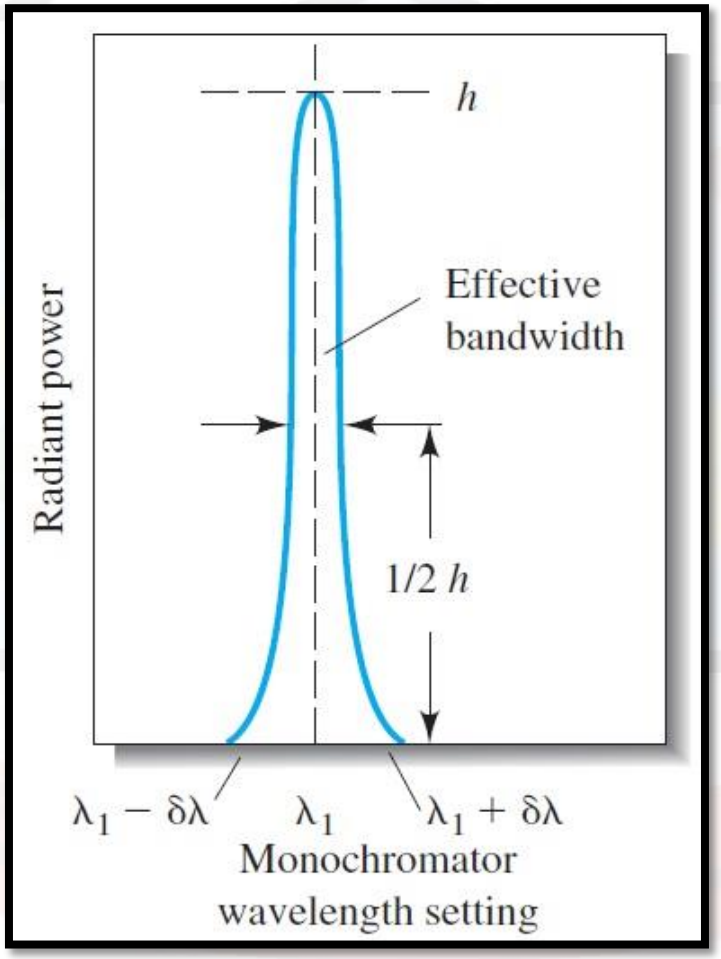
- A ***monochromator*** can be used to monitor one wavelength at a time while a ***polychromator*** can monitor several discrete wavelengths simultaneously.

Gratings:

- **It consists of a hard, optically flat, polished surface on which have been ruled with a suitably shaped diamond tool a large number of parallel and closely spaced grooves.**
- **A grating for the ultraviolet and visible region typically has from 50 to 6000 grooves/mm, with 1200 to 2400 being most common.**
- **It is usually coated with aluminum or sometimes gold or platinum so that it reflects electromagnetic radiation.**



- **The effective bandwidth** is the width of the band of radiation in wavelength units at half-peak height.
- It can be less than **1 nm** for moderately expensive instruments to greater than **20 nm** for inexpensive systems.



Radiation filters

- **They operate by blocking or absorbing all but a restricted band of radiation.**

Interference filters

- Used with UV-Visible radiation
- Depend on optical interference to provide a narrow band of radiation (**5-20 nm**)
- More **expensive** and **less rugged**
- They generally transmit a much **greater** fraction of radiation

Absorption filters

- Visible radiation only
- Absorption effect provides a bandwidth of **30 to 250 nm**
- **Inexpensive** and **more rugged**
- They generally transmit **less** fraction of radiation

Detecting and measuring radiant energy

- A ***detector*** is a device that identifies, records, or indicates a change in one of the variables in its environment such as pressure, temperature, or electromagnetic radiation.

- A ***transducer*** converts nonelectrical quantities, such as light intensity, pH, mass, and temperature, into electrical signals that can be subsequently amplified, manipulated, and finally converted into numbers proportional to the magnitude of the original quantity.

  - ***Phototubes*** consist of a single photo-emissive surface (cathode) and an anode in an evacuated envelope. They exhibit low current, but have no inherent amplification.
  - ***Solid-state photodiodes*** are semiconductor devices that respond to incident light by forming electron-hole pairs. They are more sensitive than phototubes.

❖ ***Sample containers:***

- ***Quartz or fused silica*** is required for the UV region (wavelengths less than **350 nm**) and may be used in the visible region.
- ***Silicate glass*** is usually used for the **375–2000 nm** region because of its low cost compared to quartz. Plastic cells are also used in the visible.
- The most common window material for IR studies is **crystalline sodium chloride**, which is soluble in water and in some other solvents.
- The best cells have windows that are **perpendicular to the direction of the beam** in order to minimize reflection losses.
- The most common cell path length for studies in the UV and visible regions is **1 cm**
- The variations in **path length and reflection losses** at the curved surfaces can cause significant error
- Fingerprints, grease, or other deposits on the walls **may alter** significantly the transmission characteristics of a cell. Thus, it is important to clean cells both before and after use, and the windows must not be touched after cleaning is complete.
- Matched cells should **never be dried by heating in an oven or over a flame** because this may cause physical damage or may change the path length. Matched cells should be calibrated against each other regularly with an absorbing solution.