Skoog – Chapter 7

Components of Optical Instruments

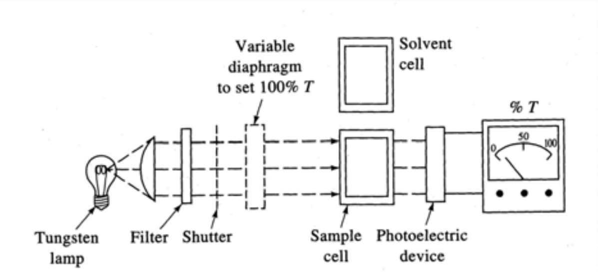
- General Design of Optical Instruments
- Sources of Radiation
- Wavelength Selectors
- Sample Containers
- Radiation Transducers (Detectors)
- Signal Processors and Readouts
- Fiber Optics

Optical spectroscopic based on 6 phenomena:

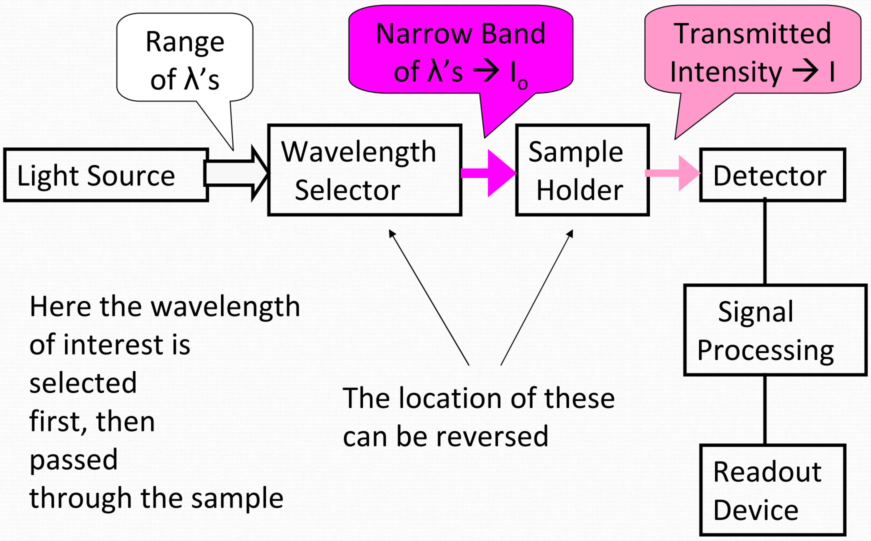
- Adsorption
- Fluorescence
- Phosphorescrence
- Scattering
- Emission
- Chemiluminscrence

Absorption measurements require:

1) source of radiation
2) device for dispersing radiation into component wavelengths
3) a means of putting sample into the optical path, i.e., cell
4) Detector to convert the EM to an electrical signal
5) readout device or circuitry, i.e., meter, computer, recorder, integrator, etc.



Block diagram of instrument for absorption



Range of λ's

Narrow Band of λ's → I_o

Transmitted Intensity → I

Light Source

Wavelength Selector

Sample Holder

Detector

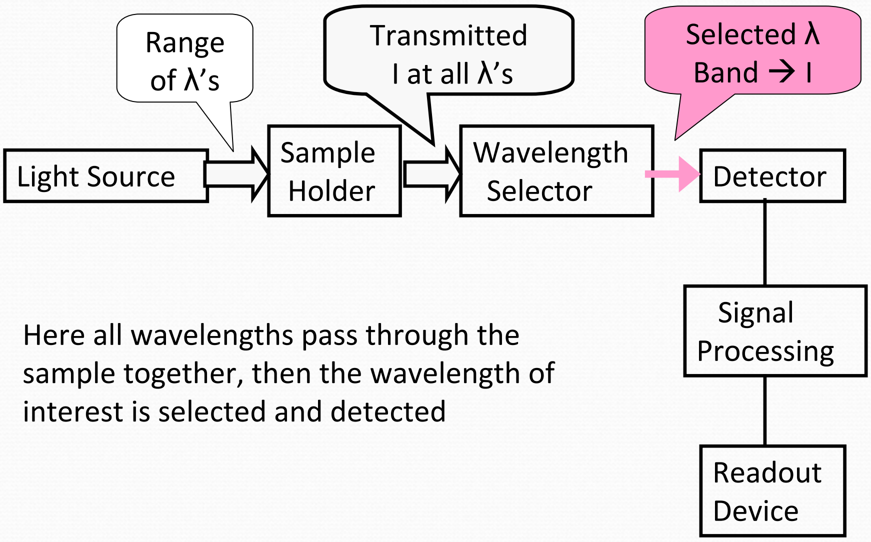
Signal Processing

Readout Device

Here the wavelength of interest is selected first, then passed through the sample

The location of these can be reversed

Block diagram of instrument for absorption


Range of λ's

Transmitted I at all λ's

Selected λ Band → I

Light Source

Sample Holder

Wavelength Selector

Detector

Signal Processing

Readout Device

Here all wavelengths pass through the sample together, then the wavelength of interest is selected and detected

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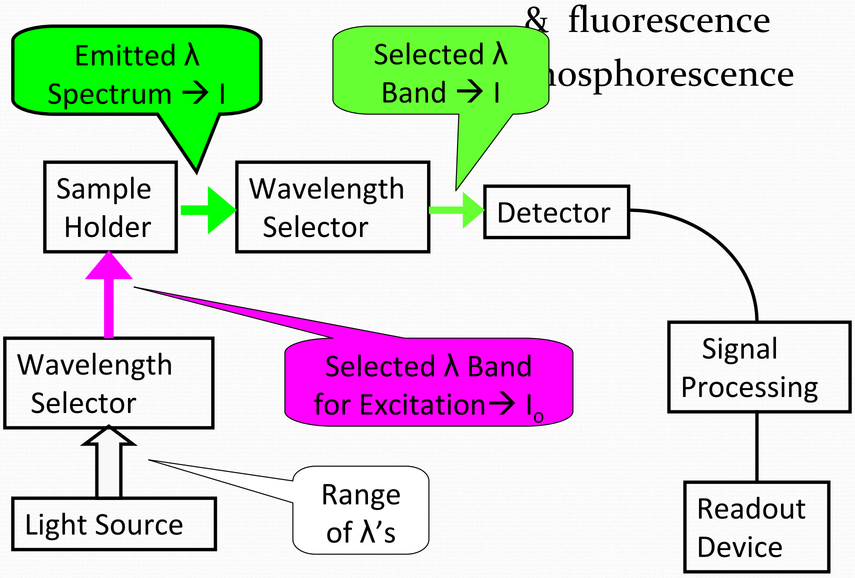
Block diagram of instrument for emission i.e., & fluorescence hosphorescence


Emitted λ Spectrum → I

Selected λ Band → I

Sample Holder

Wavelength Selector

Detector

Wavelength Selector

Selected λ Band for Excitation → I_o

Light Source

Range of λ's

Signal Processing

Readout Device

Emission measurements require:

1) means of exciting emission i.e., way of populating upper energy level which spontaneously emits
2) device for dispersing radiation into component wavelengths
3) a means of putting sample into the optical path, i.e., cell
4) Detector to convert the EM to an electrical signal
5) readout device or circuitry, i.e., meter, computer, recorder, integrator, etc.

The requirements for the various components used in different instruments change with the type of spectroscopy as well as for different kinds of measurements within a type of spectroscopy

We will consider the components separately then combine them to make the overall instrument

And finally look at the measurements with regard to theory and practice

Radiation Source

Sufficient energy for easy detection and measurement

Stable for a reasonable period

Regulated power source (radiant power source varies with voltage power supply)

Double beam design, detection intensity of two beams simultaneously

Sources – important characteristics

1) Spectral distribution i.e., intensity vs. λ (continuum vs. line sources)
2) Intensity
3) Stability – short term fluctuations (noise), long term drift
4) Cost
5) Lifetime
6) Geometry – match to dispersion device

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1) CONTINUUM SOURCES

Absorption and Fluorescence spectroscopy

UV region deuterium

High pressure gas-filled lamp contains argon, xenon or mercury for high intensity source

Visible region

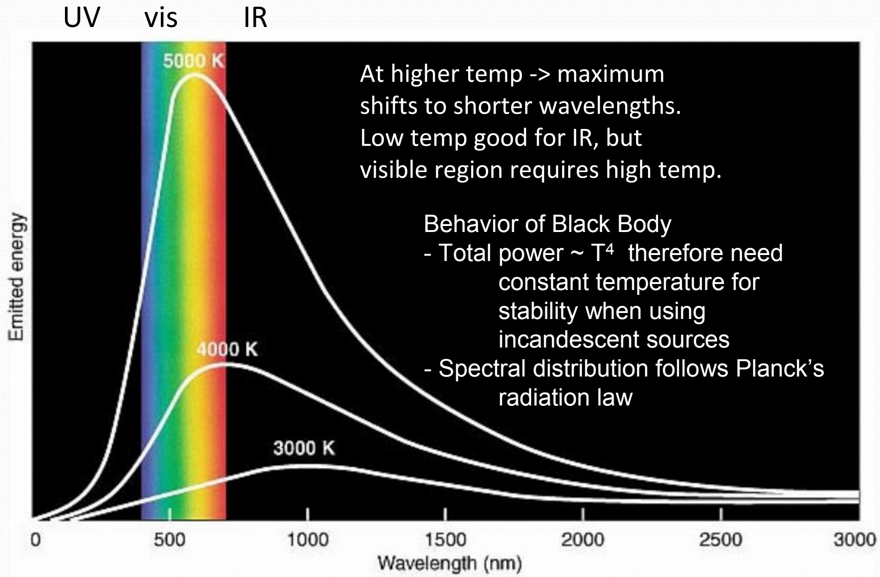
Tungsten filament lamp

IR region

Inert solid heat to 1500-2000k

1) **Thermal radiation** (incandescence) – heated solid emits radiation close to the theoretical “Black Body” radiation i.e., perfect emitter, perfect absorber

Spectral Distribution Curves of a Tungsten (Black Body) Lamp



At higher temp -> maximum shifts to shorter wavelengths. Low temp good for IR, but visible region requires high temp.

Behavior of Black Body

- Total power ~ T^4 therefore need constant temperature for stability when using incandescent sources
- Spectral distribution follows Planck's radiation law

IR Region thermal sources (Black Body) are:

a) Nernst Glower – fused mixture of ZrO_2, Y_2O_3, and ThO_2 normally operated at 1900 °C – better for shorter IR λ's (near IR)

b) Globar – silicon carbide normally operated at 1200 to 1400 °C – better at longer IR λ's (doesn't approach Black Body) 1-40μm

c) Incandescent Wire – e.g., nichrome wire – cheapest way

- All operated at relatively low temperature.
- Good for IR and give some visible emission.
- Operated in air so will burn up if temp goes too high

Advantages

- Nernst Glower – low power consumption, operates in air, long lifetime
- Globar – more stable than Nernst Glower, requires more power & must be cooled. Long lifetime, but resistance changes with use

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Visible Region sources are:

a) Glass enclosed Tungsten (W) filament - normally operated at ~3000 °K with inert atmosphere to prevent oxidation. Useful from 350 nm to 2000 nm, below 350 nm glass envelope absorbs & emission weak

b) Tungsten-Halogen lamps - can be operated as high as 3500 °K. More intense (high flux). Function of halogen is to form volatile tungsten-halide which redeposits W on filament, i.e., keeps filament from burning out. Requires quartz envelope to withstand high temps (which also transmits down to shorter wavelengths). Fingerprints are a problem – also car headlights

2) **Gas Discharge Lamps** – two electrodes with a current between them in a gas filled tube. Excitation results from electrons moving through gas. Electrons collide with gas → excitation → emission

At high pressure → “smearing” of energy levels → spectrum approaches continuum

The higher the pressure, the greater the probability that any given molecule or atom will be perturbed by its neighbor at the moment of emission.

D_2 +E electrical --→ D_2^* --→ D(KE_1) + D(KE_2) +hυ

KE_1 +KE_2 + hυ = E electrical –BDE

bond dissociation energy

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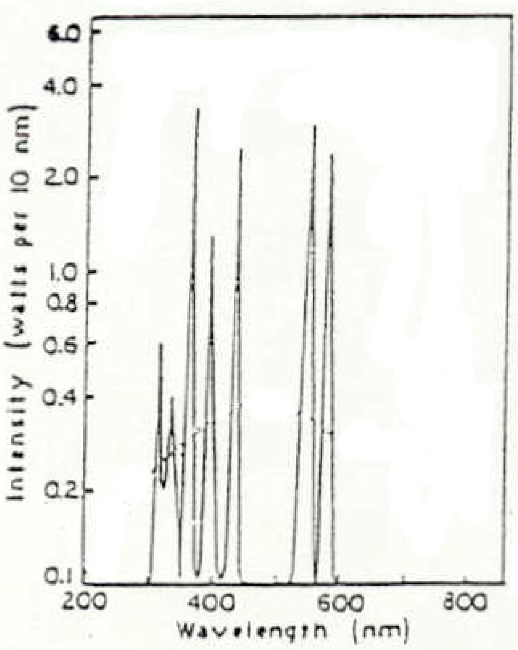
a) Hydrogen Lamp - most common source for UV absorption measurements

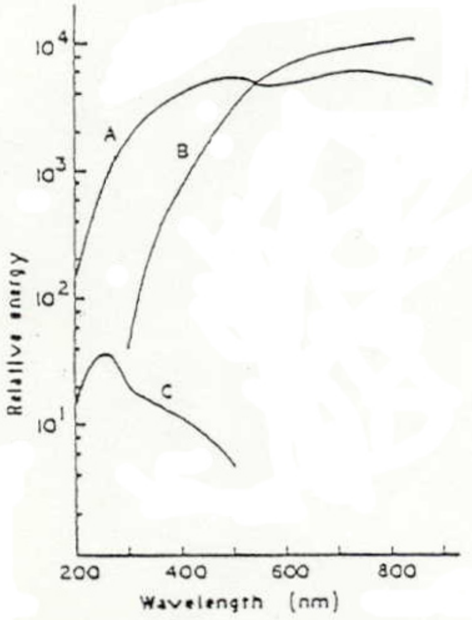
H_2 emission is from 180 nm to 370 nm limited by jacket

Line spectrum from → 100 watt Hydrogen Lamp at low pressure in Pyrex



b) Deuterium Lamp – same λ distribution as H_2 but with higher intensity (3 to 5 times) - D_2 is a heavier molecule & moves slower so there is less loss of energy by collisions

High pressure D_2 → with quartz jacket

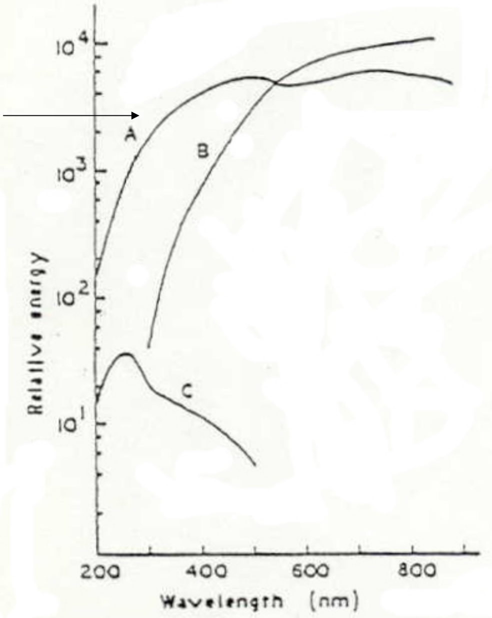


Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

For higher intensity

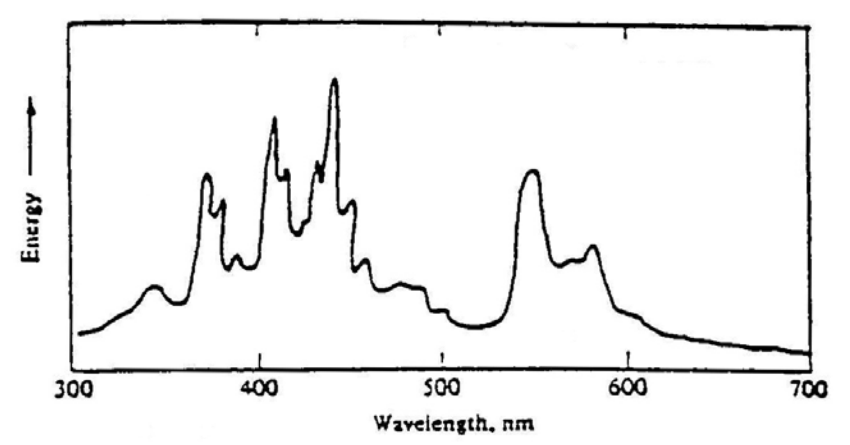
c) Xenon Lamp – Xe at high pressure (10-20 atm)

- high pressure needed to get lots of collisions for broadening leading to continuum
- short life relatively
- arc wander (stabilize)
- need jolt to start
- output = f(time)



Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

d) High Pressure Mercury Lamp – can't completely eliminate bands associated with particular electronic transitions even at very high pressures (e.g., 100 atm)



- For UV-vis absorption spectrophotometry usually use H_2 for UV and tungsten for visible region (switching mid scan)
- Sometimes use D_2 instead of H_2
- For fluorescence spectrophotometry use xenon arc lamp in scanning instruments
- Can use He below 200 nm
- Hg at low pressure is used in fixed wavelength (non scanning) fluorometers
- Can use mixture of Hg and Xe

II) LINE SOURCES

1) **<u>Gas (Vapor) Discharge Lamps</u>** at low pressure (i.e., few torr) – minimize collisional interaction so get line spectrum

- most common are Hg and Na
- often used for λ calibration
- Hg pen lamp
- fluorescent lights are another example
- also used UV detectors for HPLC

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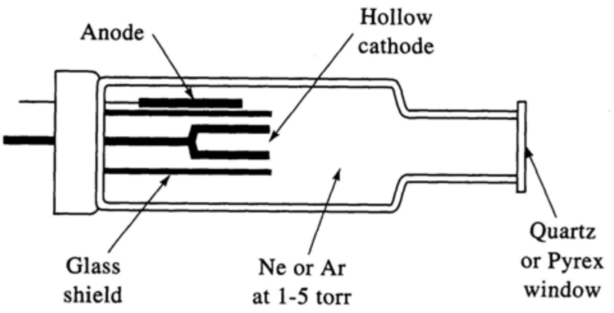
2) **<u>Hollow Cathode Lamps (HCL)</u>** – for AA

Atomic emission hollow cathode lamp

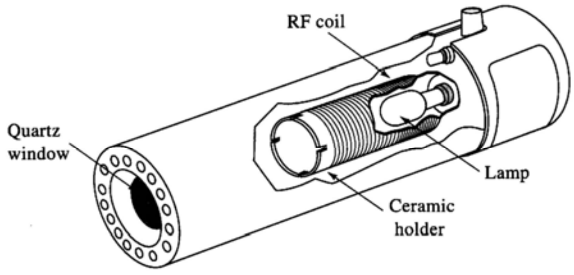
(a) electron bombardment of cathode (b) sputtering of cathode atoms (c) emission from electronically excited cathode atoms



2) **Electrodeless Discharge Lamps (EDL)** - AA

Electrodeless discharge lamps (EDL)

(a) Ar ions created by RF energy (b) ions collide with gaseous metal atoms which then (c) emit excite (Fig. 9-12)



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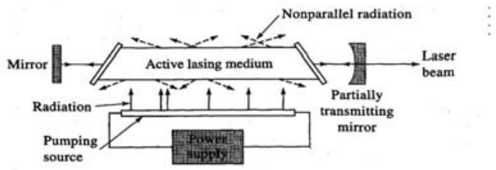
4) **Lasers (Light Amplification by Stimulated Emission of Radiation)** – start with material that will exhibit stimulated emission and populate upper states typically using another light source

Lasing medium can be solid (Nd:YAG, semiconductor diode laser AlGaAs), gas (noble gas Ar^+, He/Ne, CO_2, N_2) or liquid (dye)



(a) pumping; (b) Spontaneous emission; (c) Stimulated emission and (d) Adsorption

Stimulated Emission – photon strikes excited state causing it to emit a burst of photons

Pumping source used to populate upper states can be flashlamp, another laser or electrical

Often use prism to select pumping wavelength

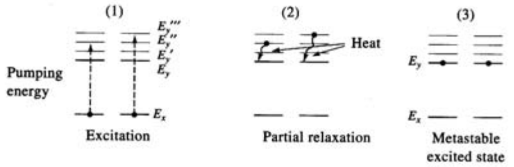
Advantages of lasers

1) Intense
2) Monochromatic – very narrow band or line sources
3) Coherent – all radiation at same phase angle
4) Directional – full intensity emitted as beam

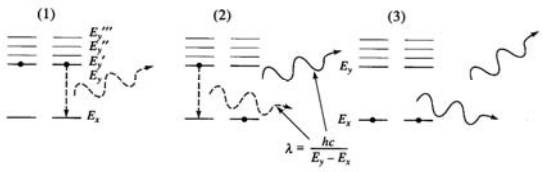
Limitations of lasers

1) High cost in many cases
2) Wavelength range is somewhat limited
3) Many operate in pulsed mode – some are continuous wave (CW)

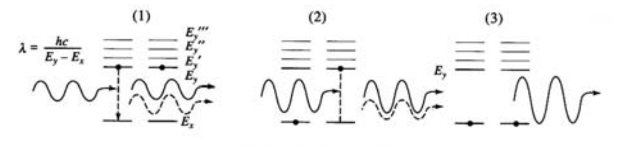
(a) pumping of excited state (b) stimulated emission to produce emission (Fig. 7-5)



(a) Pumping (excitation by electrical, radiant, or chemical energy)

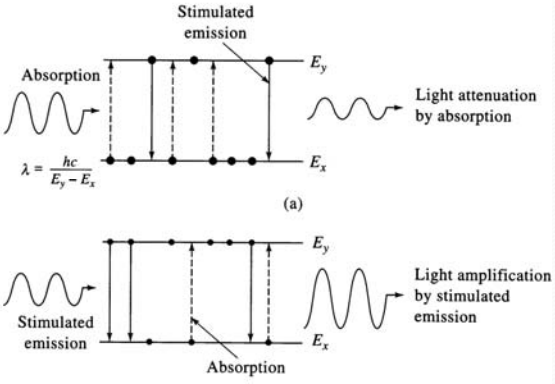


(b) Spontaneous emission



(c) Stimulated emission

Population Inversion and Amplification:

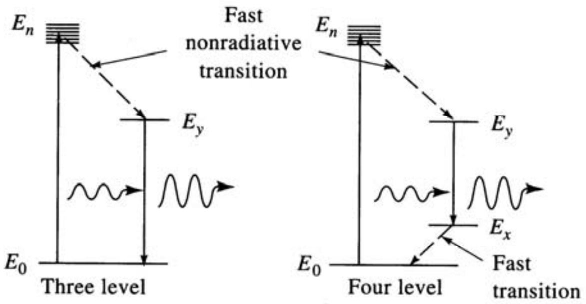


(a)

(b)

Need population inversion for lasing

Cannot produce population inversion in 2-level system (stimulated emission becomes increasingly dominant). Need 3- or 4- levels



(a)

(b)

Fig 7-7

Types of Lasers:

1) **Solid State Lasers** **0.05%**

a) Ruby laser – Al_2O_3 + Cr(III) - 694.3 nm pumped with Xe arc flashlamp – pulsed (can be continuous)

b) Nd/YAG laser – yttrium aluminum garnet + Nd (Neodymium) - 1064 nm Frequency doubled (532nm)

2) **Gas Lasers**

a) Neutral atom – He-Ne – 632.8 nm continuous

b) Ion lasers – Ar^+ or Kr^+ 514.5 nm

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c) Molecular lasers – CO_2 (10,000 nm = 1000 cm^{-1}) or N_2 (337.1 nm) pulsed

d) Excimer lasers – inert gas + fluorine creates excimers ArF^+ (193 nm), KrF^+ (248 nm), XeF^+ (351nm) pulsed

3) **Dye Lasers** – tunable over 20 – 50 nm many dyes available for wide range of λ's

4) **Semiconductor Diode Lasers** – wide range of λ's available, continuous

Wavelength Selection

Three main approaches:

1) Block off unwanted radiation – optical filters

2) Disperse radiation & select desired band – monochromator (prism)

3) Modulate wavelengths at different frequencies - interferometer

FILTERS

1) **<u>Absorption</u>** – colored glass, colored film, colored solutions – cheapest way

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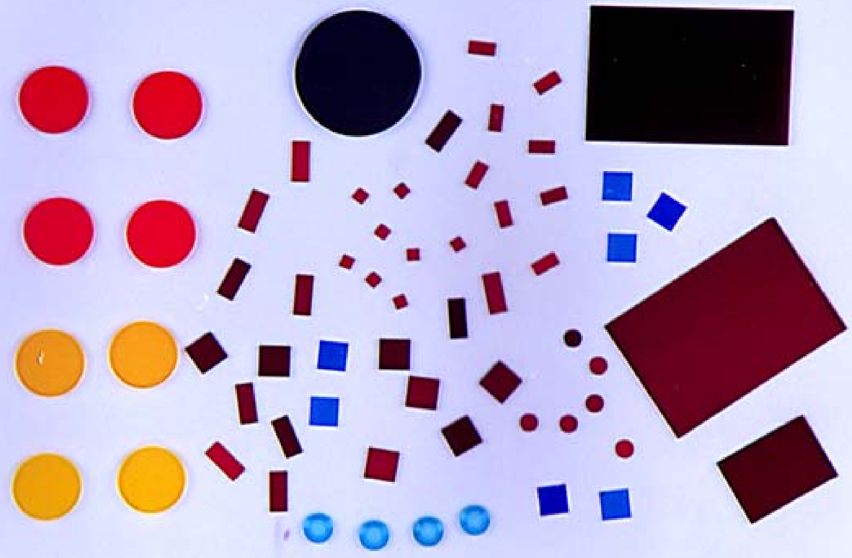
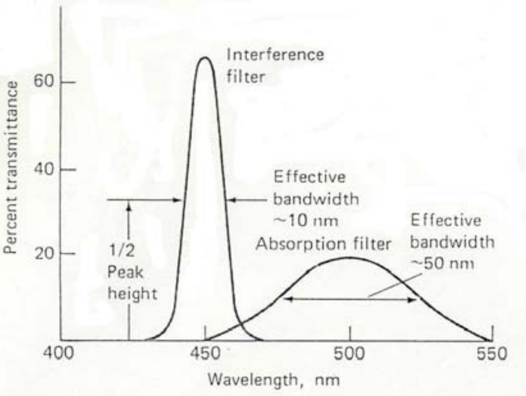
Assortment of Glass & Quartz Optical Filters



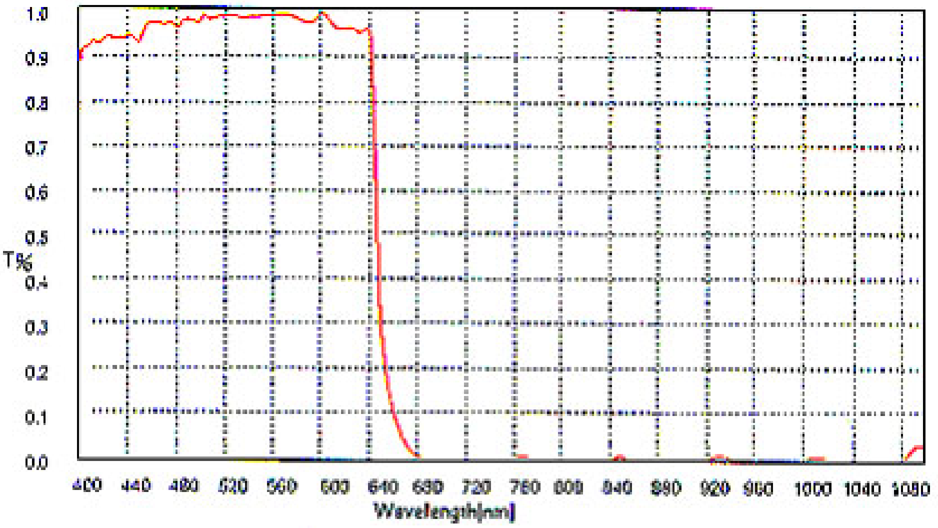
Transmittance Curves for Optical Filters



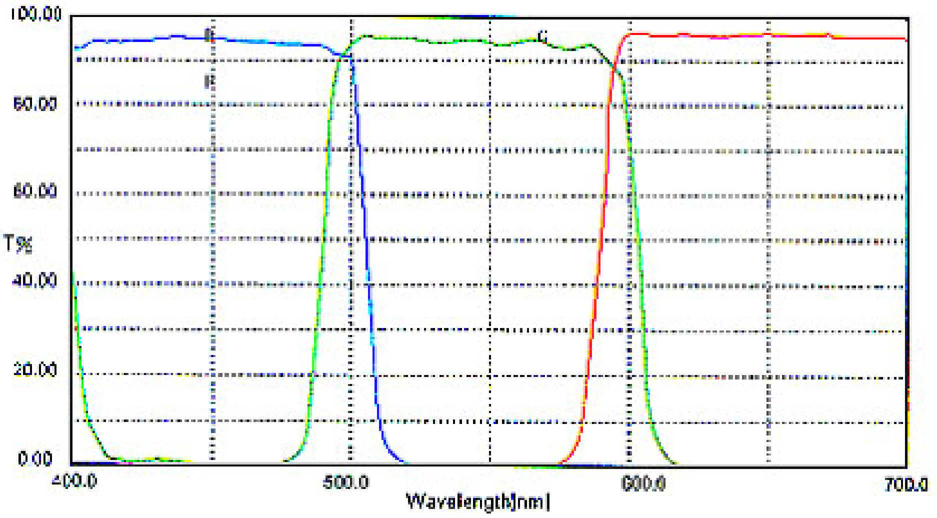
- Absorption filters are also known as bandpass filters
- Usually exhibit low peak transmittance
- Typically have a broad peak profile
- Can use two or more absorption filters together to produce desired transmittance characteristics
- Generic filters are 2 x 2 inch glass or quartz
- Relatively inexpensive

Cut-off filters or sharp-cut filters are also available such as the 650 nm cut-off filter shown here

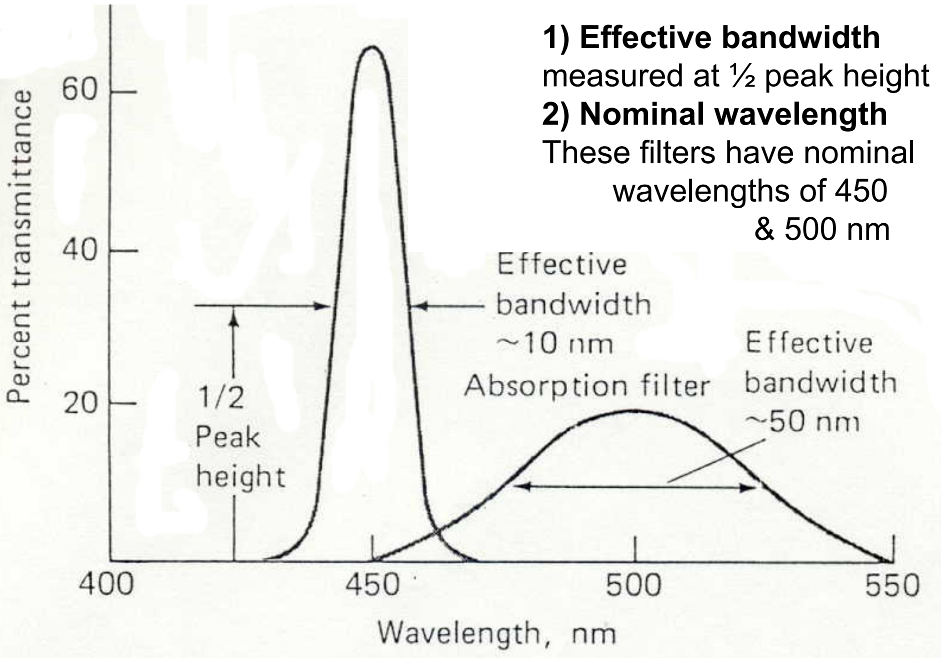
Cut-on filters have reverse profile



Combining two appropriate cut-off filters produces a bandpass filter. The example shown here comes from 3 filters producing bands at 500 & 600 nm.

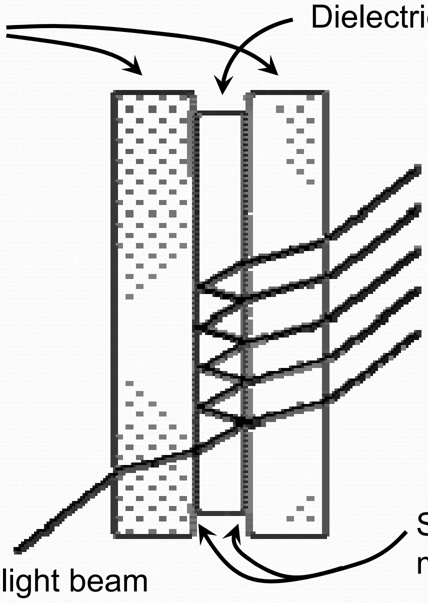


Two terms associated with optical filters are:



1) Effective bandwidth
measured at ½ peak height
2) Nominal wavelength
These filters have nominal wavelengths of 450 & 500 nm

2) **Interference filters** – usually Fabrey-Perot type



Glass layers

Dielectric material (CaF or MgF)

Transmitted radiation

Light bounces back & forth & gets out of phase with itself unless it meets conditions for constructive interference

Semi-reflective metal layers

Incident light beam

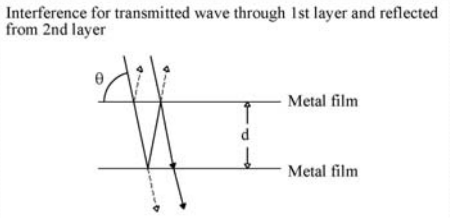
Condition for constructive interference

$$2d = \frac{m\lambda}{\eta}$$

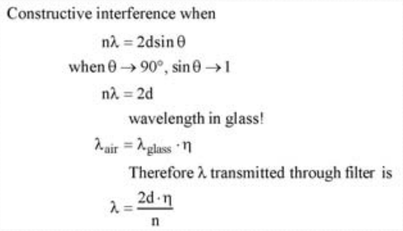
order of interference
A small whole number

refractive index of dielectric

distance between semi-reflective layers



Interference for transmitted wave through 1st layer and reflected from 2nd layer



Constructive interference when

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

$$\text{when } \theta \to 90^\circ,\ \sin\theta \to 1$$

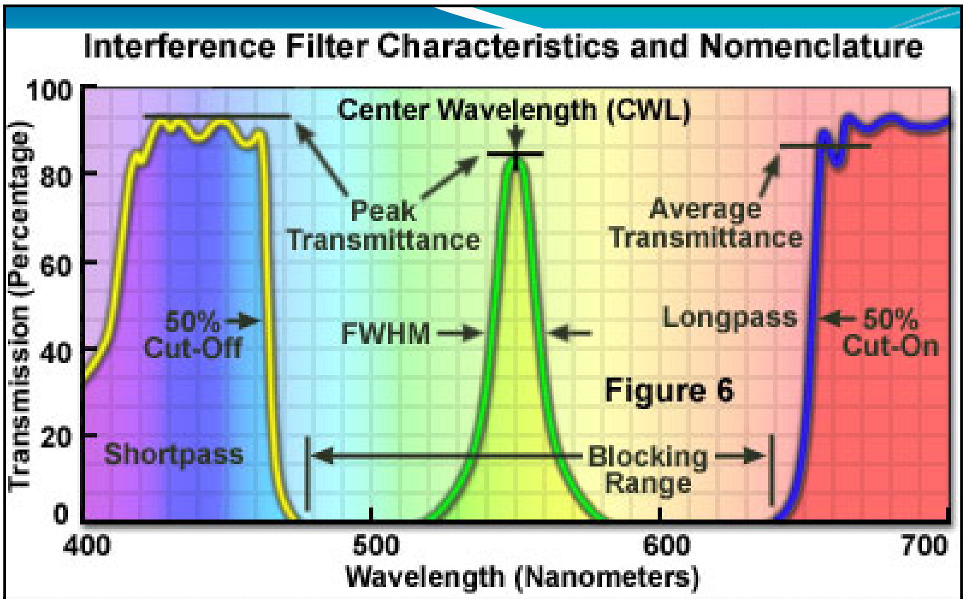
$$n\lambda = 2d$$

wavelength in glass!

$$\lambda_{air} = \lambda_{glass} \cdot \eta$$

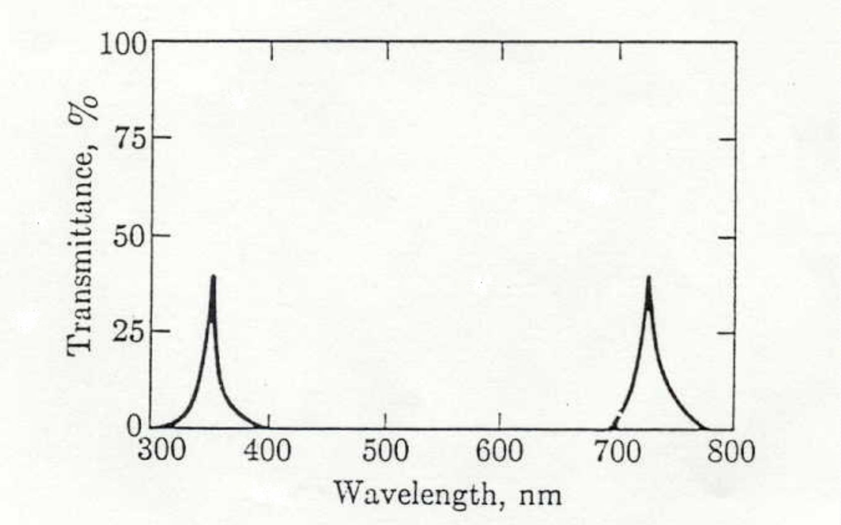
Therefore λ transmitted through filter is

$$\lambda = \frac{2d \cdot \eta}{n}$$

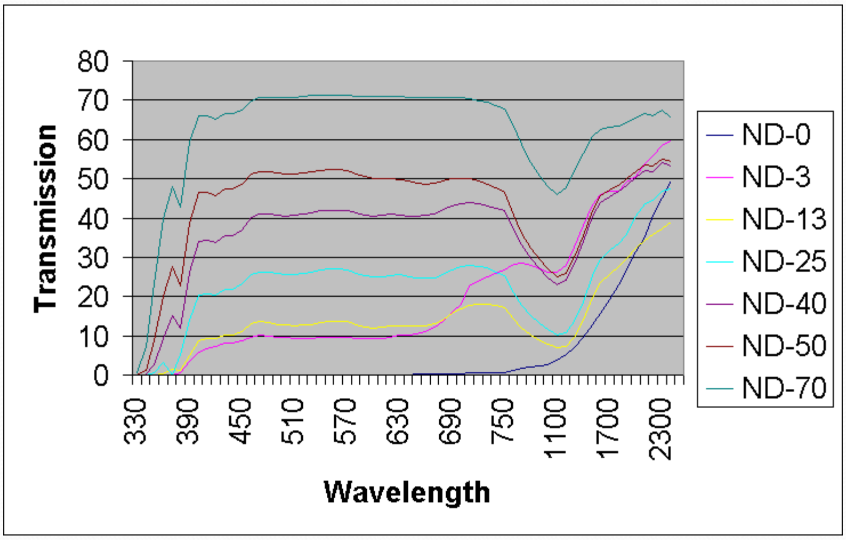


FWHM – full width at half maximum

Transmittance vs. wavelength for typical Fabrey-Perot Interference filter showing first and second order λ's (m = 1 & m = 2)

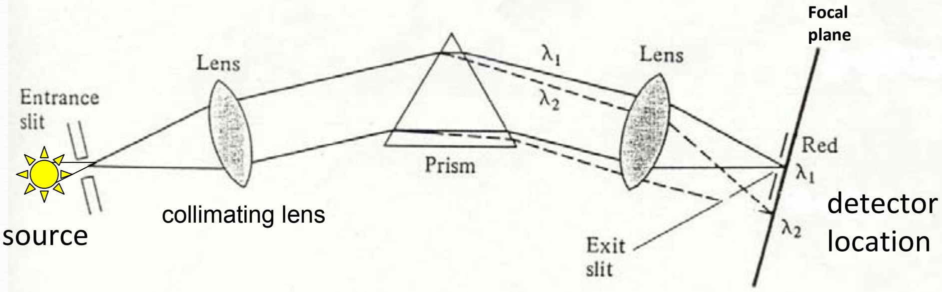


3) **Neutral density filters** – reduces intensity without any λ discrimination



II) MONOCHROMATORS

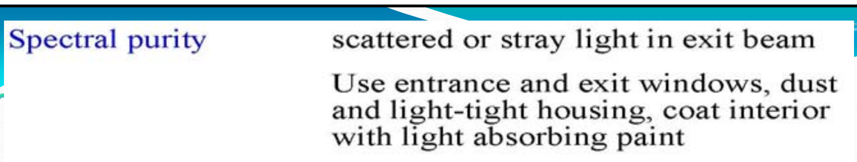
Simple Prism Monochromator



Entrance slit allows source radiation to illuminate the first lens which collimates the light spreading it across the face of the **prism**. Prism disperses radiation into component wavelengths and the second lens focuses the spectrum at the **focal plane**. An **exit slit** selects the band of radiation to reach the detector. Dispersing element can be a **prism** or a **diffraction grating**. Focusing elements can be **lenses** or **mirrors**.

- Optical Materials – need optically transparent materials for lenses, prisms & sample cells
- In visible region – can use glass down to 350 nm
- In the UV region – quartz is material of choice
- In the IR region – NaCl, KBr, etc. The heavier the atoms of the salt, the farther into the IR region (i.e., longer λ) before significant absorption occurs

Problem – sensitivity to moisture



Spectral purity	scattered or stray light in exit beam Use entrance and exit windows, dust and light-tight housing, coat interior with light absorbing paint

Resolution – ability to distinguish as separate, nearly identical frequencies; measured in terms of closest frequencies Δν in a spectrum that are distinguishable

$$R = \frac{\nu}{\Delta\nu} \quad \text{or} \quad \frac{\lambda}{\Delta\lambda} \quad \text{(both dimensionless)}$$

Average wavelength of images

Difference of 2 images

For a benchtop UV it should be 10^3 to 10^4

Dispersion – spread of wavelengths in space

Angular Dispersion – angular range dθ over

which waveband dλ is spread → $\frac{d\theta}{d\lambda}$ in $\frac{\text{rad}}{\text{nm}}$

Linear Dispersion – distance dx over which a waveband dλ is spread in the focal plane of a monochromator → $\frac{dx}{d\lambda}$ in $\frac{mm}{nm}$

Linear Reciprocal Dispersion – range of λ's spread over a unit distance in the plane of a monochromator → $\frac{d\lambda}{dx}$ in $\frac{nm}{mm}$

Related terms **spectral slit width** or **bandwidth** or **bandpass** = range of λ's included in a beam of radiation measured at half max intensity

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Light gathering

light collection efficiency

f/number

$$f = \frac{F_{\text{collimating mirror}}}{\text{dia}_{\text{collimating mirror}}}$$

f/ of a monochromator is important if have a weak source. For lenses in series, the smallest f/ sets the overall f/ for the system.

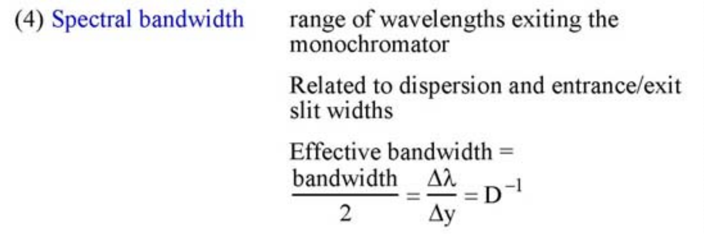
Lens Summary:

1) rugged, easy to use, inexpensive
2) can have chromatic aberrations = focal length depends on η which varies with λ – solution is to fabricate lenses out of a composite glasses so η is constant with λ. This increases cost
3) Each lens results in some light loss due to reflection

Energy throughput must be sufficient for detector to measure signal with adequate precision.

In practice the image of the entrance slit in a monochromator should just fill the exit slit for optimum conditions. Otherwise the larger slit establishes (i.e, limits) the resolution and the smaller slit establishes (or limits) the energy throughput.

There is a theoretical minimum for slit widths imposed by diffraction.



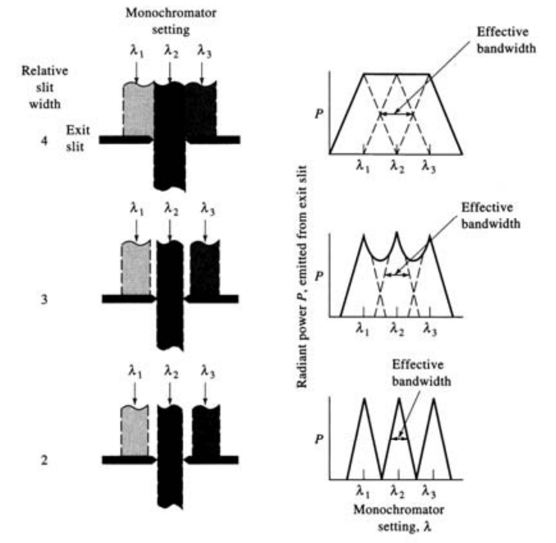
(4) Spectral bandwidth

range of wavelengths exiting the monochromator

Related to dispersion and entrance/exit slit widths

Effective bandwidth =

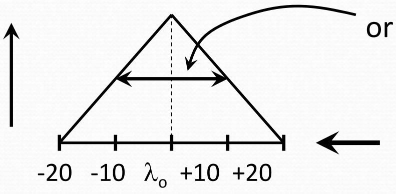
$$\frac{\text{bandwidth}}{2} = \frac{\Delta\lambda}{\Delta y} = D^{-1}$$



Complete *resolution* of two features only possible when slit is adjusted to produce effective bandwidth half (or less) of difference between λ's

Light exiting a monochromator exit slit has a triangular distribution
Optical Efficiency = throughput x resolution
Good criterion for comparing optical systems

Prism Monochromator	<	Grating Monochromator	<	Interferometer



Relative power

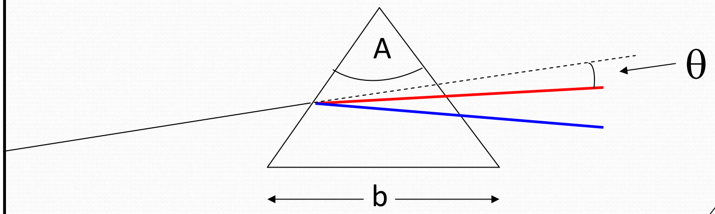
bandpass or bandwidth or spectral slit width

Range of λ's passing when set at λ_o

Dispersion Devices

1) Prisms

A = apical angle
b = base length



function of prism design (i.e. angle A)

Light bends due to η $\eta = \boldsymbol{f}\,(\lambda)$

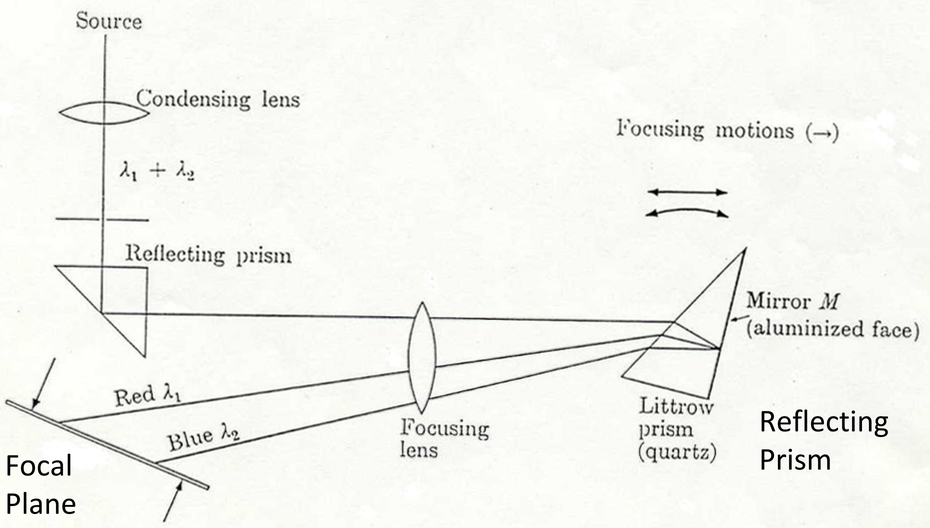
$$\underline{\text{Angular Dispersion}} = \frac{d\theta}{d\lambda} = \frac{d\theta}{d\eta} \times \frac{d\eta}{d\lambda}$$

function of prism material

Angle changes with λ → the larger the better

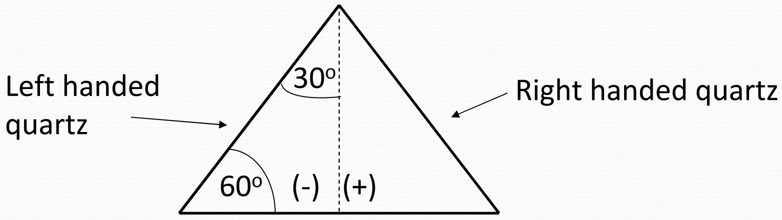
Kinds of Prisms

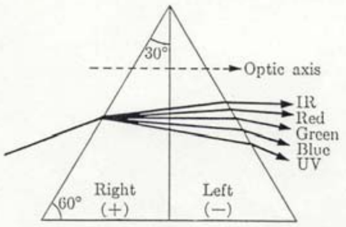
Littrow Prism & Mounting – compact design



Problem with quartz prisms is that quartz is optically active (optically anisotropic). With the Littrow prism or any reflecting prism, the light travels essentially the same path in both directions and this effect is eliminated.

Cornu Prism

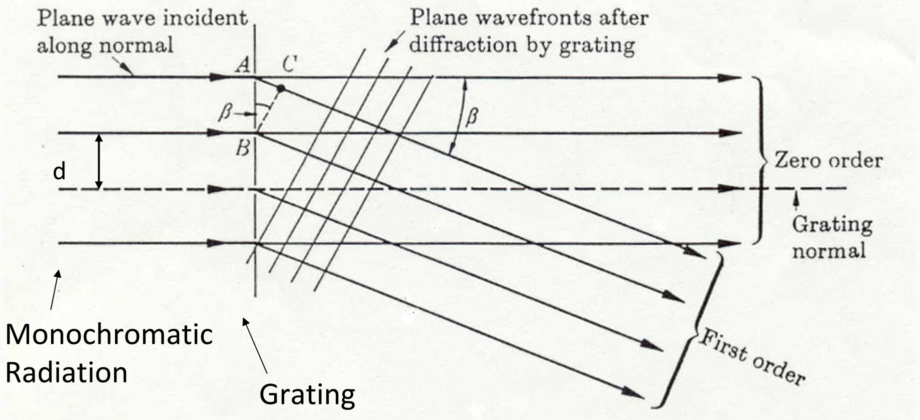




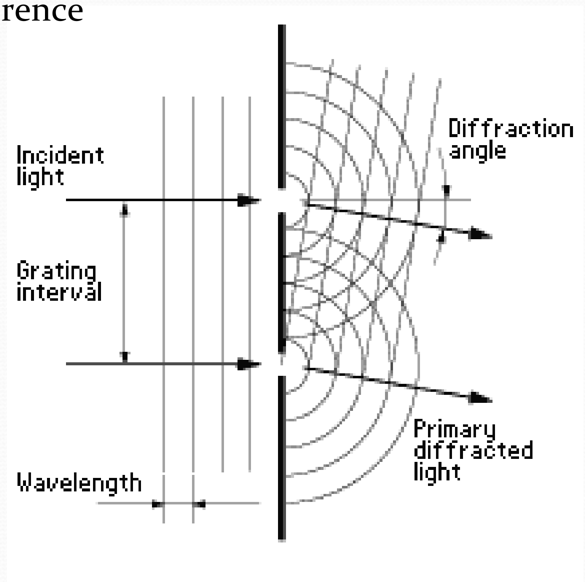
Cornu prism of quartz. The circular double refraction (not shown) produced by the first half is just offset by the equal and opposite effect in the second half. Two overlapping spectra would result if the prism were all of one kind of crystalline quartz.

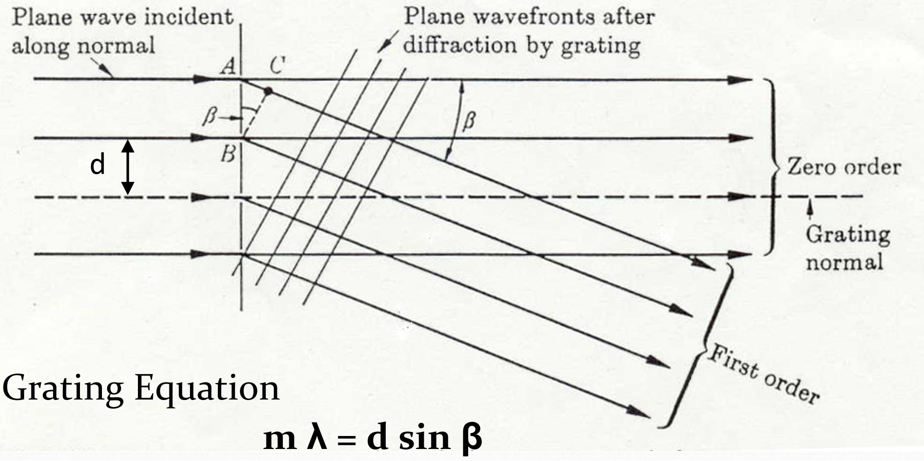
Gratings – based on diffraction & interference

Transmission Gratings & Reflection Gratings consist of a series of grooves in glass or quartz or a mirror (usual kind)



Gratings work on the principles of diffraction & interference





Grating Equation

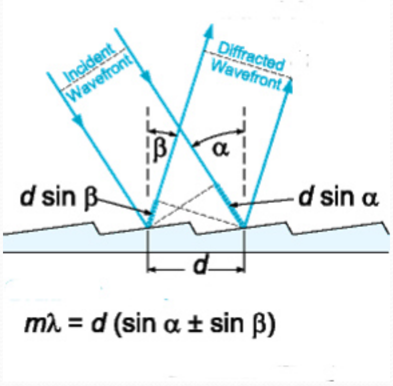
$$m\,\lambda = d \sin \beta$$

Condition for constructive interference

AC = extra distance light travels for first order = d sin β

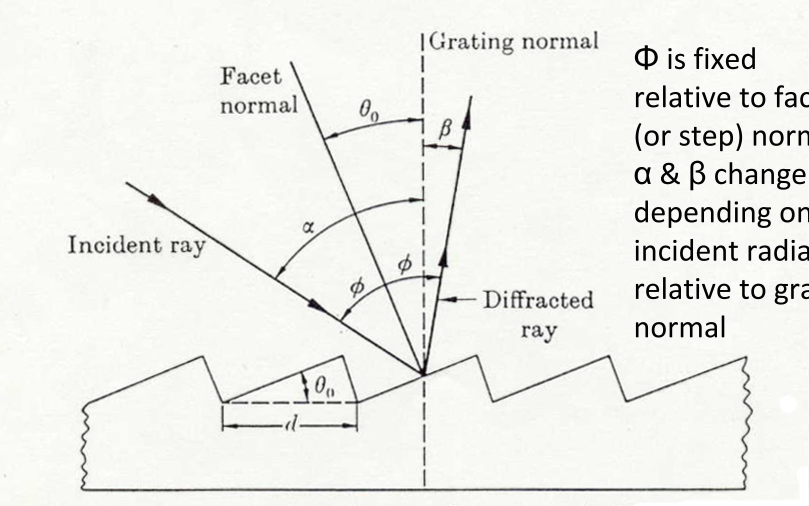
For higher orders the distance gets longer

Reflection grating with non-normal incidence



$m\lambda = d(\sin\alpha \pm \sin\beta)$

Reflection grating with non-normal incidence (another view)



Φ is fixed relative to facet (or step) normal, α & β change depending on incident radiation relative to grating normal

Preparation of reflection gratings – a master grating is prepared by ruling grooves in a reflective aluminum surface on glass (from 20 – 3000 grooves/mm or 10,000 lines/inch)

Replicate gratings can be prepared from master grating which brings down the cost

fraction of monochromatic light

diffracted in a particular order

Grating Efficiency = -------------------------------------
---

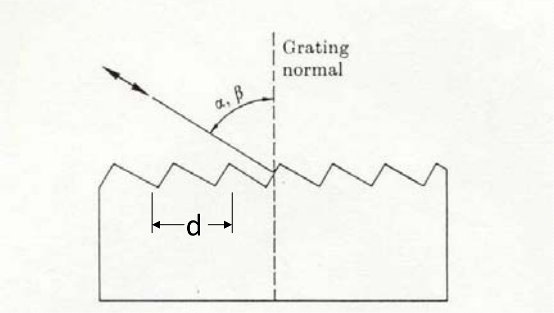
fraction specularly reflected

Efficiency is maximum for situation where diffracted ray & specularly reflected ray coincide = blaze wavelength = λ_B = λ of maximum efficiency

---

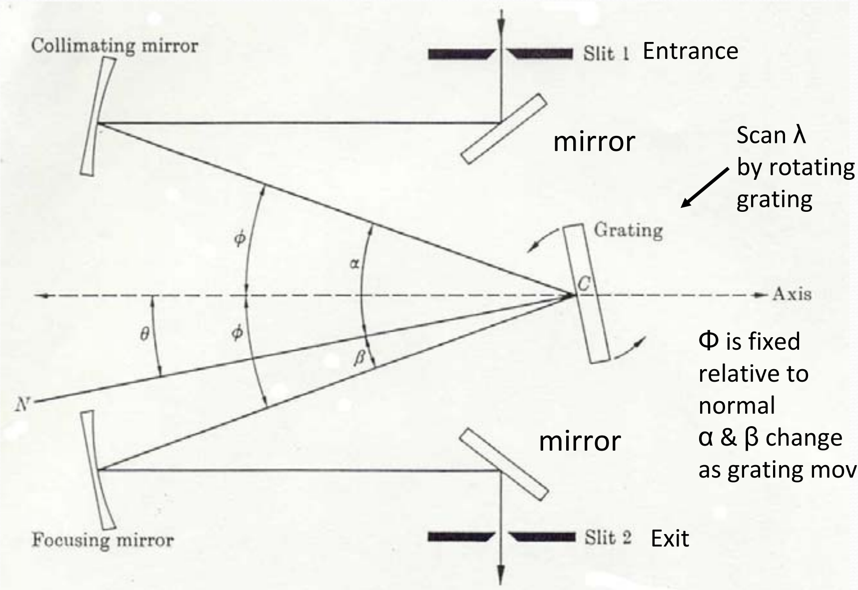
Efficiency is maximum for situation where diffracted ray & specularly reflected ray coincide = blaze wavelength = λ_B = λ of maximum efficiency

An Echelle type reflection grating has a coarse ruling (i.e. large d) and produces good spectral efficiency in higher orders making very high resolution possible



- The echellette grating concentrates most of the intensity in the first few orders
- First order efficiency at λ_B is 60 - 70 % and typically falls off by about half at $2/3\ \lambda_B$ and $2\lambda_B$
- Choose angle for λ region of interest
- Echellette is the normal grating for UV, vis, IR
- Echelle grating used for atomic emission
  - Concentrates intensity in higher orders
  - Uses steeper steps

Mountings for Gratings – Czerny-Turner



Entrance

mirror

Scan λ by rotating grating

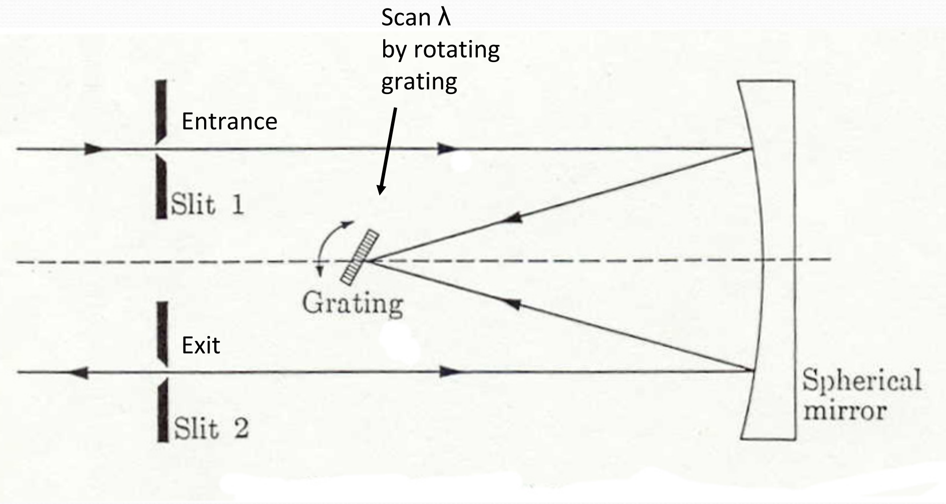
Φ is fixed relative to normal

α & β change as grating moves

mirror

Exit

Mountings for Gratings – Ebert Mounting



Littrow mounting is the same as for prism except use grating in place of prism

Grating Characteristics – Resolution & Dispersion are very high for a long, finely ruled grating

Resolution (theoretical)

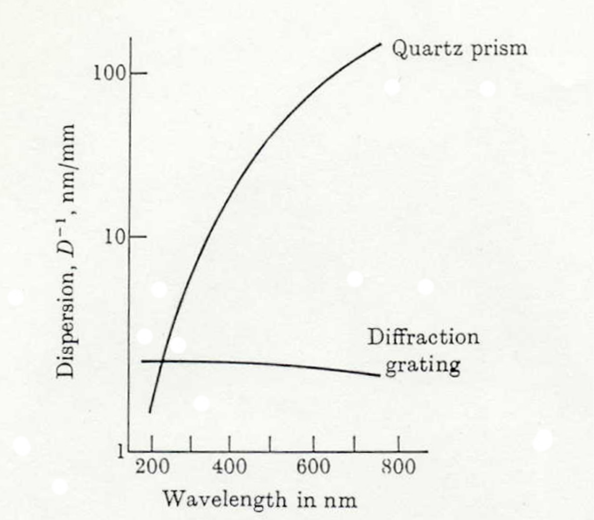
$$R = \overset{\text{order}}{m}\ \overset{\text{number of rulings illuminated}}{N}$$

Combine with grating equation (given previously)

$$R = W\,(\sin \beta)\,/\,\lambda$$

where W (length of ruled area) = N d

The length of ruled area is important



Dispersion - almost constant with wavelength for grating (an advantage over prisms)

Don’t have to change slits to get constant bandpass across spectrum

---

Disadvantages of gratings relative to prisms:

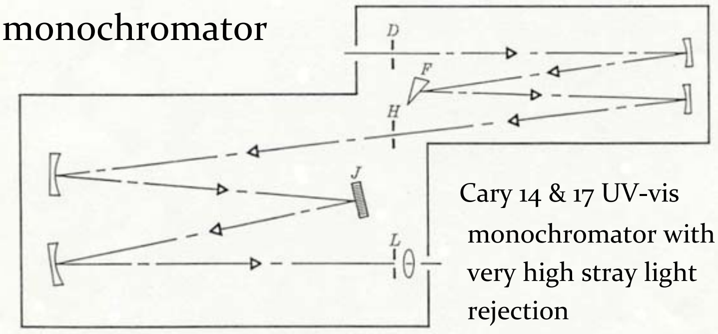
1) they are less rugged
2) they generate slightly more scattered light which is stray light → radiation present at unwanted orders
3) order overlap → multiples of λ present

Stray Radiation sources:

1) Diffracted from grating at unwanted angle
2) Diffracted from slit edges
3) Reflected from interior surfaces of filters, lenses, prisms & other components of system
4) Scattered by imperfections in optical components

Methods of reducing stray light:

1) Paint interior black
2) Use baffles to obstruct stray radiation
3) Use high quality components
4) Keep out dust and fumes
5) Can also use double monochromator



Cary 14 & 17 UV-vis monochromator with very high stray light rejection

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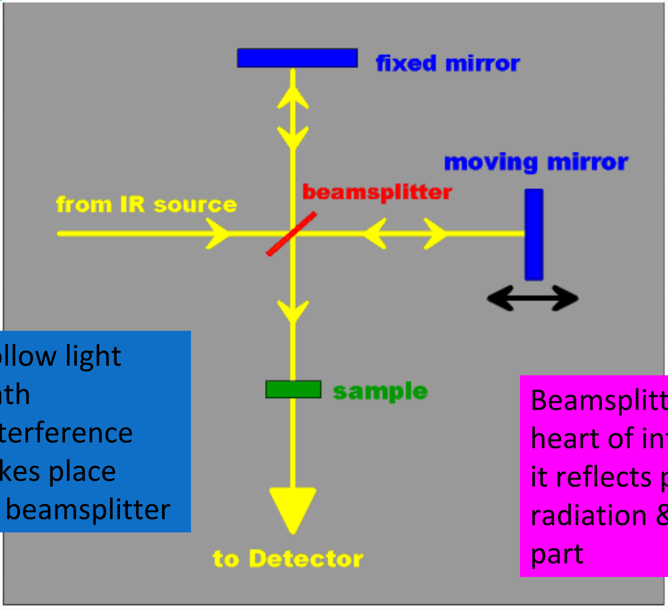
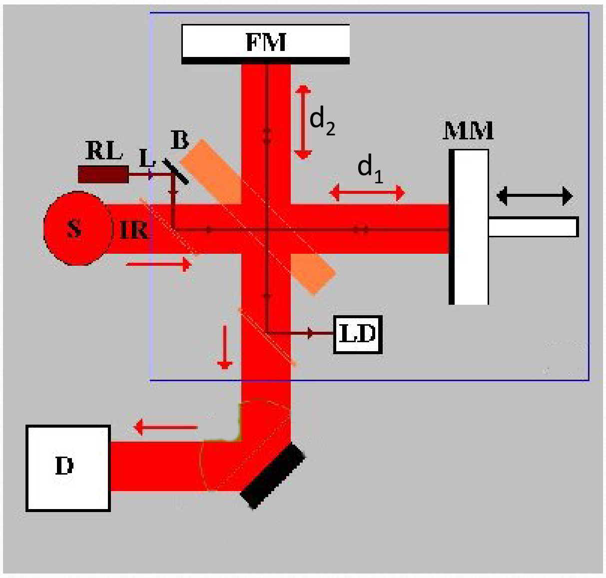
Basic diagram of a Michelson Interferometer



Follow light path
Interference takes place at beamsplitter

Beamsplitter is at the heart of interferometer, it reflects part of the radiation & transmits part

Michaelson Interferometer as commonly used in an FTIR



Where:

S = IR source

IR = infrared beam

D = detector

B = beamsplitter

FM = fixed mirror

MM = moving mirror

RL = reference laser

L = laser beam

LD = laser detector

d_1 = distance to moving mirror

d_2 = distance to fixed

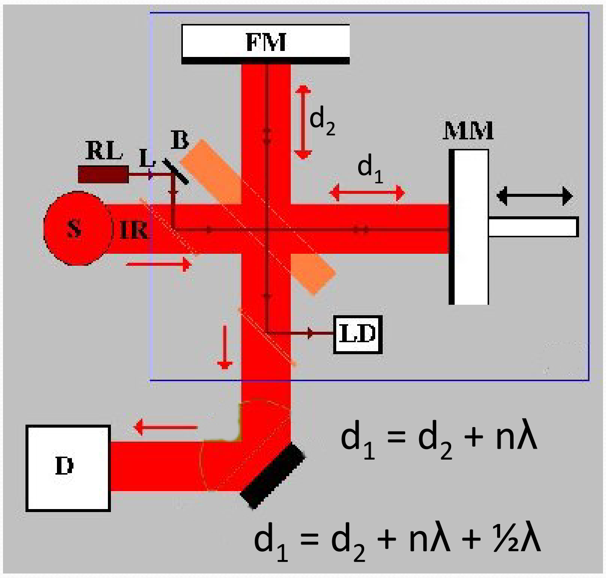
Interferometers have no slits so a wide beam of radiation can be used

Assuming monochromatic radiation

$d_1 = d_2 + n\lambda$ → for constructive interference

$d_1 = d_2 + n\lambda + \frac{1}{2}\lambda$ → destructive interference

Michaelson Interferometer as commonly used in an FTIR



$d_1 = d_2 + n\lambda$

$d_1 = d_2 + n\lambda + \frac{1}{2}\lambda$

Where:

S = IR source

IR = infrared beam

D = detector

B = beamsplitter

FM = fixed mirror

MM = moving mirror

RL = reference laser

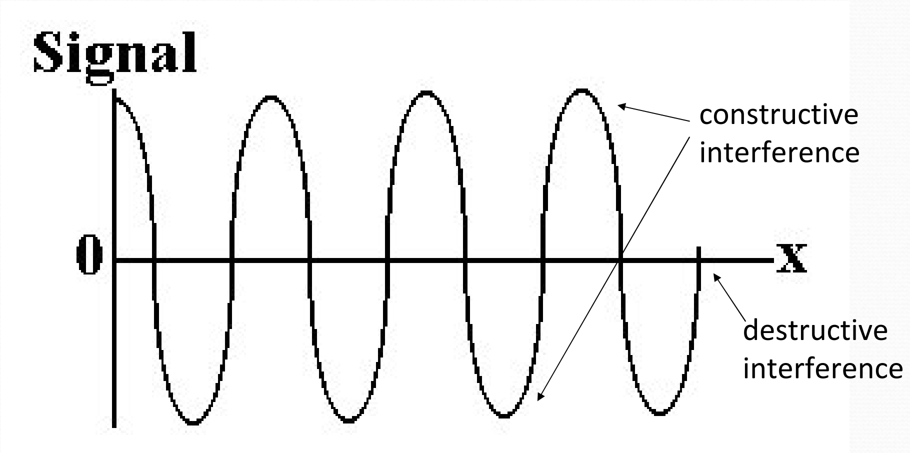
L = laser beam

LD = laser detector

d_1 = distance to moving mirror

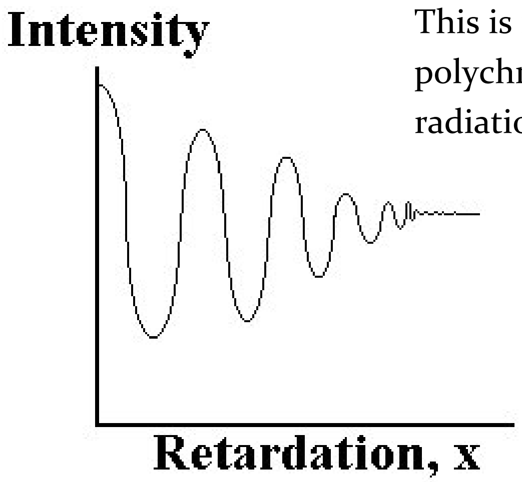
d_2 = distance to fixed

Reference laser signal as it passes through the interferometer



This allows the position of the moving mirror to be determined accurately

Interferogram is a plot of energy vs mirror displacement from zero (i.e. $d_1 = d_2$)



This is for polychromatic radiation

Mechanical specifications for mirror movement are very exacting → gets worse as λ gets shorter, therefore interferometers are used in the IR region but are not very feasible in the visible and UV regions

Extracting a conventional spectrum (i.e. I vs λ) from interferogram involves the complex mathematics of the Fourier integral also known as Fourier Transform → need computer to do calculations

Advantages of Interferometers:

1) Energy throughput is much grater than for monochromators → better signal to noise ratio because there are no slits – this is particularly important in IR where the sources are relatively weak
2) High resolution
3) Multiplex Advantage – all signals are viewed simultaneously, obtain data in 1s or less

Disadvantage: Mechanical tolerance for mirror movement is severe – can't do interferometry in the UV-vis region, λ too short

---

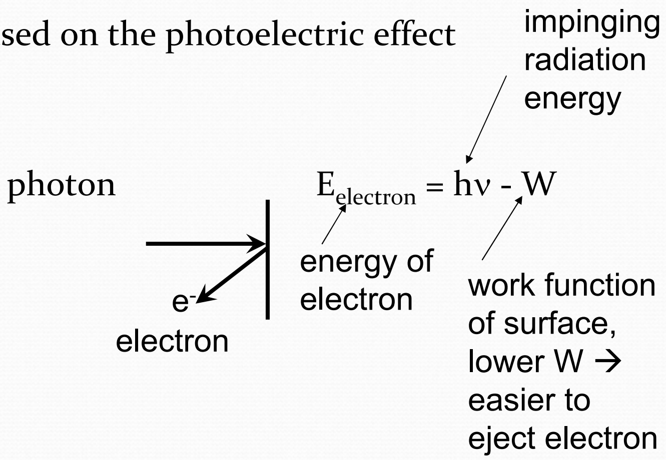
DETECTORS

Important characteristics:

1) Wavelength response
2) Quantum response – how light is detected
3) Sensitivity
4) Frequency of response (response time)
5) Stability
6) Cost
7) convenience

Photoelectric detectors – main detectors in visible and UV

Based on the photoelectric effect



photon

e$^-$ electron

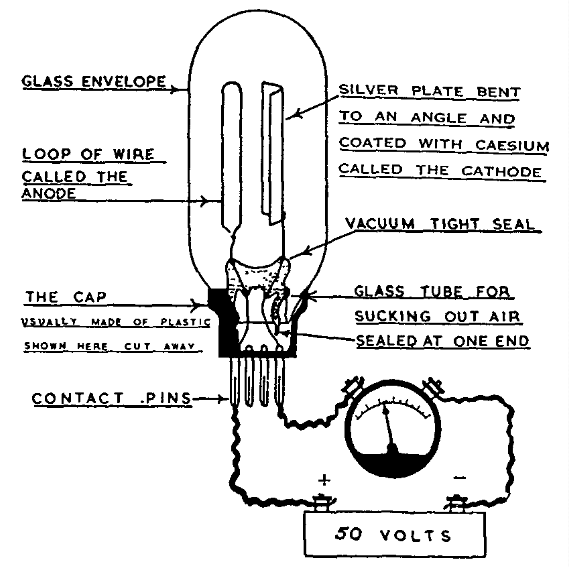
$E_{electron} = h\nu - W$

impinging radiation energy

energy of electron

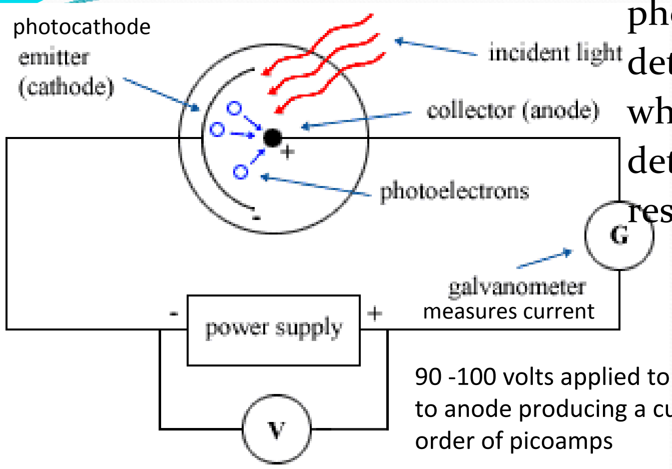
work function of surface, lower W → easier to eject electron

Primitive Phototube



Phototube or photodiode

Composition of photocathode determines W which in turn determines λ response



90 -100 volts applied to draw electrons to anode producing a current on the order of picoamps

photons → electrons → current

Usually need current to voltage converter to display signal as voltage proportional to # of photons

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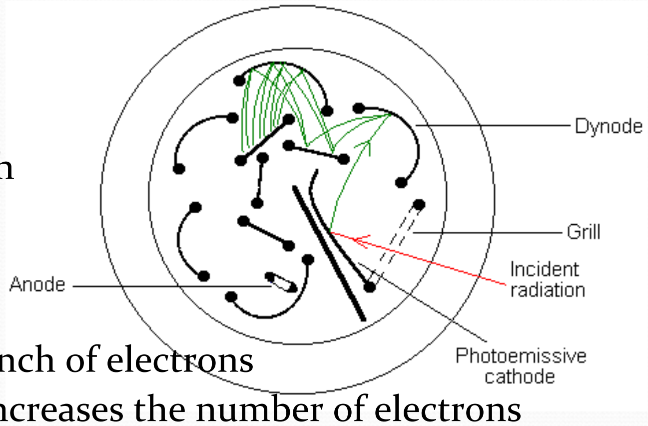
Photomultiplier Tube or multiplier phototube (PMT) → essentially a phototube with built in amplifier

90 – 100 volts between photocathode & 1st dynode & between each successive dynode



1 photon → bunch of electrons

Each dynode increases the number of electrons

Typically 10-20 dynodes

Photomultiplier Tubes (PMTs)

Standard PMT
Normal device for
UV-vis absorption

End-On PMT
Typically used where required by
space or geometry constraints

Characteristic Parameters of PMTs:

(typically specified by manufacturers)

a) Quantum efficiency = $\mathbf{f}(\lambda)$

$$= \frac{\text{photoelectrons ejected}}{\text{photons striking photocathode}}$$

b) Cathode sensitivity = µ A/lumen or µA/watt

have to specify λ and use a standard source at known temperature

c) Gain = $f\,(g\,\delta)^n$

number of dynodes

collector efficiency

transfer efficiency dynode to dynode

Typical gain 10^6 electrons/photon in

$$g\,\delta = 4.5$$

$$\frac{\text{\# of electrons emitted}}{\text{electron striking dynode}}$$

d) Spectral response – depends on photocathode work function (sensitivity as a function of wavelength) *Very Important*- must be corrected for when scanning e.g. in fluorescence spectrum

e) Dark current – current when photomultiplier is operated in complete darkness. Lower limit to the current that can be measured → dark current needs to be minimized if low intensities are to be measured

---

Thermionic emission is an important source of dark current → this thermal dark current is temperature dependent

Therefore, cooling the photomultiplier tube reduces dark current (-40 °C is sufficient to eliminate the thermal component of dark current for most photocathodes

Smaller w → higher dark current (smaller W's are associated with photocathodes that respond at longer λ's i.e. red sensitive cathodes) → low energy photons

If photocathode is exposed to bright daylight without power, it traps energy and it takes 24 – 48 hrs in the dark with high voltage on in order for dark current to go back to equilibrium value

Long term exposures to bright light leads to sensitivity loss particularly at longer λ

Noise – due to random fluctuations in:

1) Electron current (shot noise)
2) Thermal motion of conducting electrons in the load resistor (Johnson noise)
3) Incident photon flux (quantum noise) – flux of photons varies statistically

---

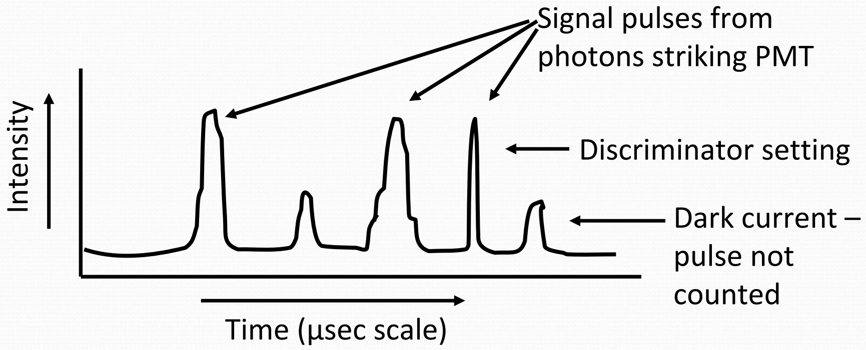
Advantages of PMTs

1) Stable except after exposure to high light levels
2) Sensitive
3) Linear over several orders of magnitude
4) Reasonable cost
    1) Simple PMT for visible region = $200
    2) Quartz jacketed PMT for UV & red sensitive tubes for near IR can be more expensive
5) Long lifetime
6) Rapid response (on the order of nanoseconds)

IR detectors not nearly as good as PMTs

Normally measure DC level of current resulting from all electrons generated in PMT. However, at low light levels it is possible to do **photon counting**

Each photon gives rise to a pulse of electrons



Signal pulses from photons striking PMT

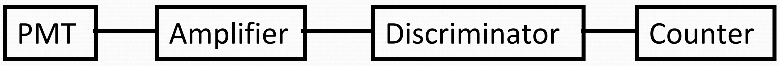
Intensity

Discriminator setting

Dark current – pulse not counted

Time (μsec scale)

Block Diagram of Photon Counting System



PMT

Amplifier

Discriminator

Counter

Discriminator sets the level for counting. Pulses exceeding the discriminator level are counted. Pulses below the discriminator level are not counted.

Dead Time – after each pulse, electronics need some time to recover = dead time. Any pulse arriving during the dead time interval will not be counted (typically 0.1 to 0.01 µsec)

Dead Time Loss – decrease in signal because of uncounted pulses arriving during the dead time. This becomes significant at count rates somewhere between 10^5 & 10^6 counts/sec = upper limit to intensities measured by photon counting

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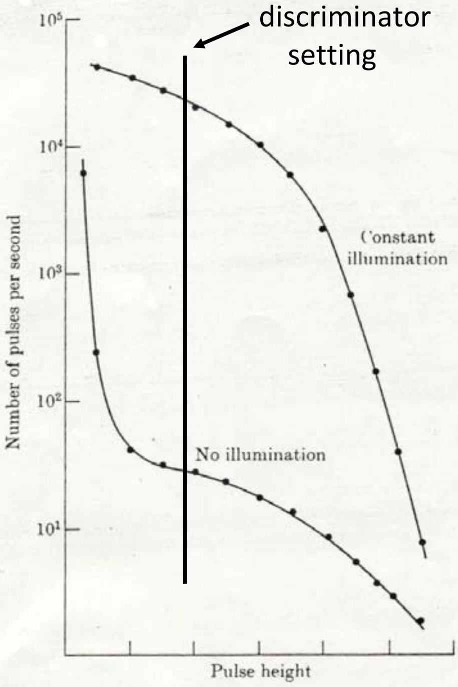


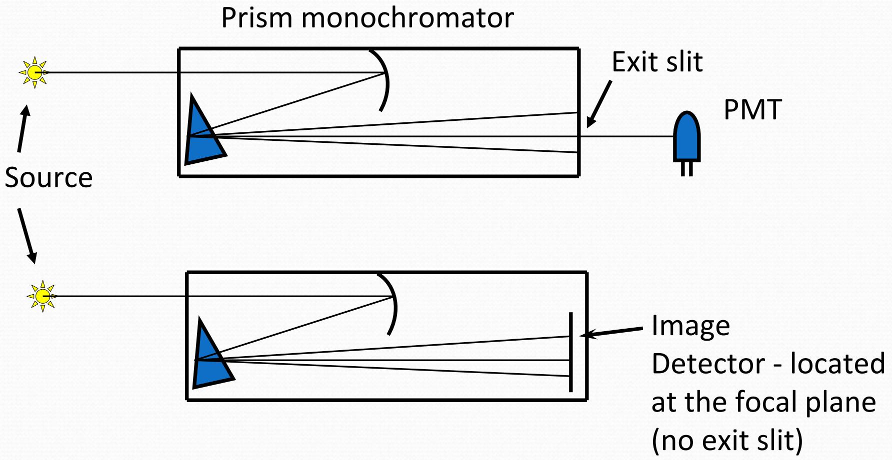
discriminator setting

Plot of number of photon counting pulses observed vs pulse heights for 2 conditions, constant light (top) & no light (lower)

If discriminator is set too high → get too few pulses counted (see upper curve)

If set too low → get too many pulses counted (lower curve)

Image Detectors – powerful detectors used instead of PMTs to detect a complete spectrum or part of a spectrum



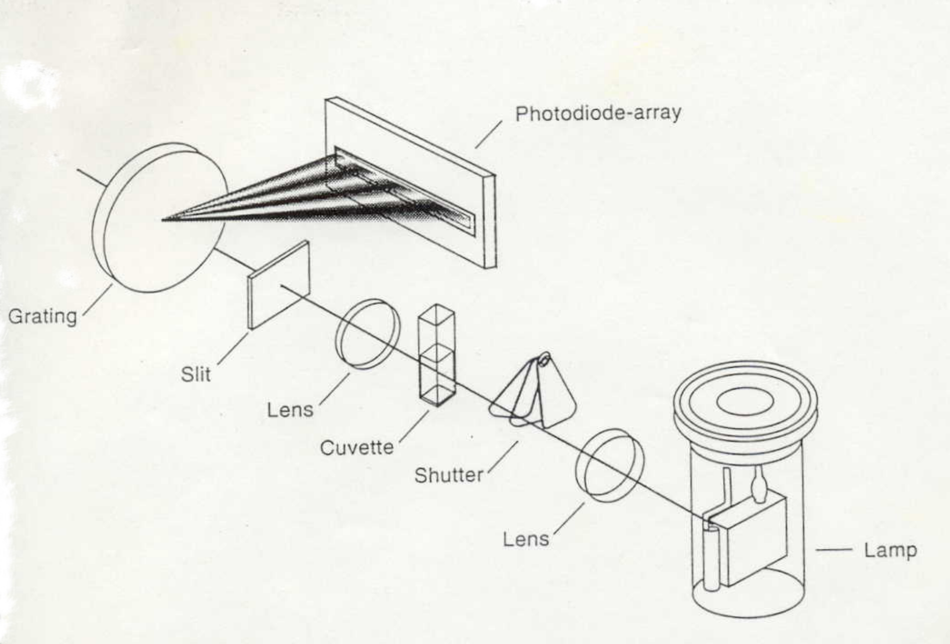
Prism monochromator

Exit slit

PMT

Source

Image Detector - located at the focal plane (no exit slit)



Common Image Detectors

1) Electron Image Intensifiers
2) Image Dissectors
3) Solid-State Imaging Systems
    a) Vidicon tubes
    b) Optical Multichannel Analyzers (OMAs)
    c) Photo Diode Arrays (PDAs)
4) Charge Coupled Devices (CCDs)

These are often used with intensifiers – device to increase sensitivity

Photodiodes, Linear Diode Array & Two Dimensional Arrays

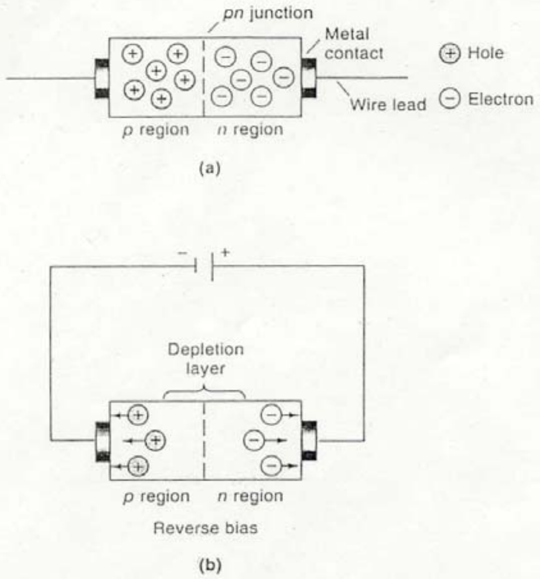
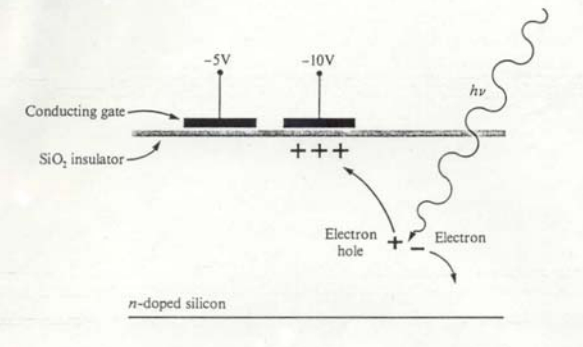
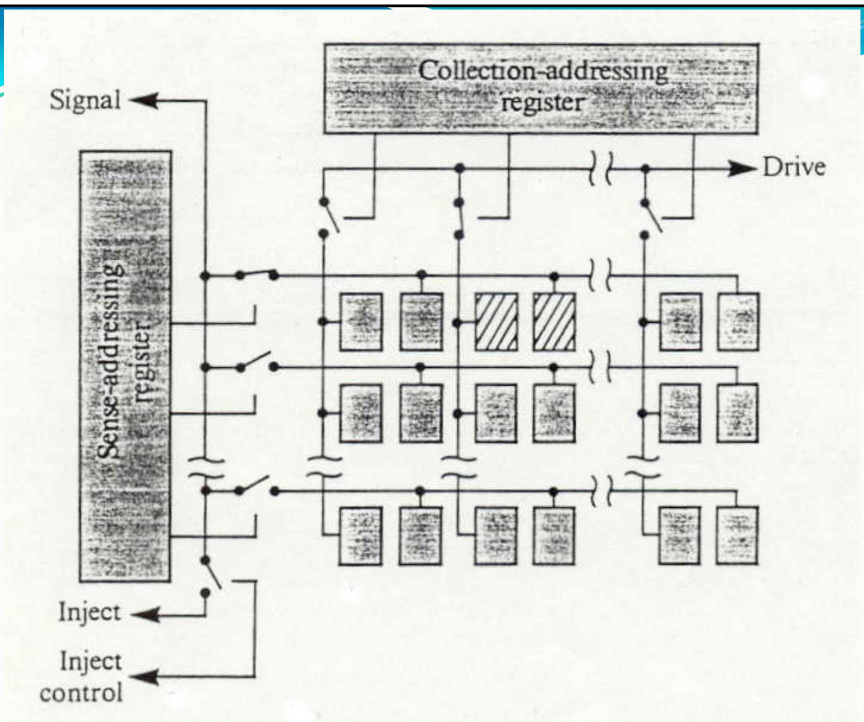


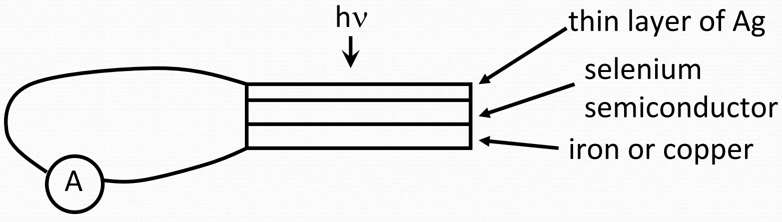
FIGURE 6–24 (a) Schematic of a silicon diode. (b) Formation of depletion layer, which prevents flow of electricity under reverse bias.

Charge Coupled Device (CCD)





Photovoltaic Cell

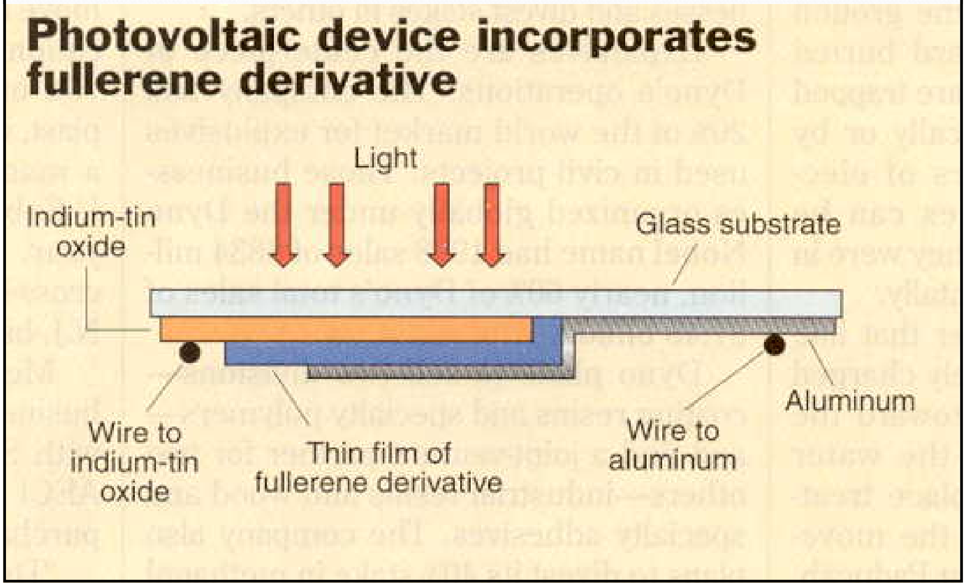


Light excites electrons in Se at Se-Ag interface into “conduction band” and to metal conductor → current

Good only for high light levels

Subject to fatigue effects

Another example of a Photovoltaic cell



Photovoltaic device incorporates fullerene derivative

Photoconductive detector – semiconductor used with voltage applied across it

Photons → electrons promoted to conduction band → high conductivity (lower resistance)

PbS, PbSe, InSb good for 0.7 to 4.5 μm (near IR)

Ge activated with Cu, Au or Zn good from 2 to 15 μm – operated at ~5 °K

Considerably less sensitive than PMTs

Better than thermal detectors in IR

Photographic detection – place film at focal plane and expose (integrating detector)

Advantages:

1) good resolution
2) fairly sensitive
3) covers entire spectral region

Disadvantages:

1) very old technique
2) quantitatively very bad (can use densitometer)

Thermal Detectors for IR – in IR region photons have lower energies → necessary to resort to <u>thermal detectors</u> – radiation absorbed and temperature change is detected

Response time is limited by rate of heat transfer → slow

Sensitivity is also much poorer

Three types of thermal detectors:

1) Thermocouples (most common) – junction between dissimilar metals often covered with black substance to increase absorption

Voltage difference across junction is a function of temperature

Amplify signal and detect

Response time ~60 msec (i.e. slow)

Sensitivity is greater using a thermopile = a bundle of many thermocouples

2) Bolometer (thermistor) – resistance is a function of temperature

Different kinds → Ni or Pt metal or oxides like NiO, CoO or MnO

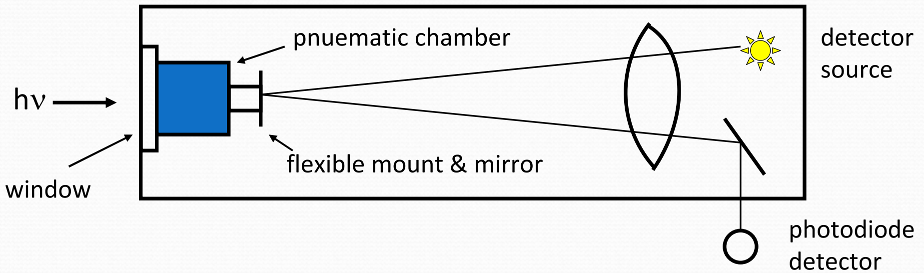
Many have black coating on side toward source and a heat shield around them

Typically connected to a bridge circuit

Johnson noise is important

Requires stable power supply

3) Golay Pneumatic Detector (best performance characteristics)



Heat from radiation → gas expands → mirror position changes → amount of light reflected to photodiode changes

Best sensitivity

Response time ~4 msec → heat transfer in gas phase faster than in solid

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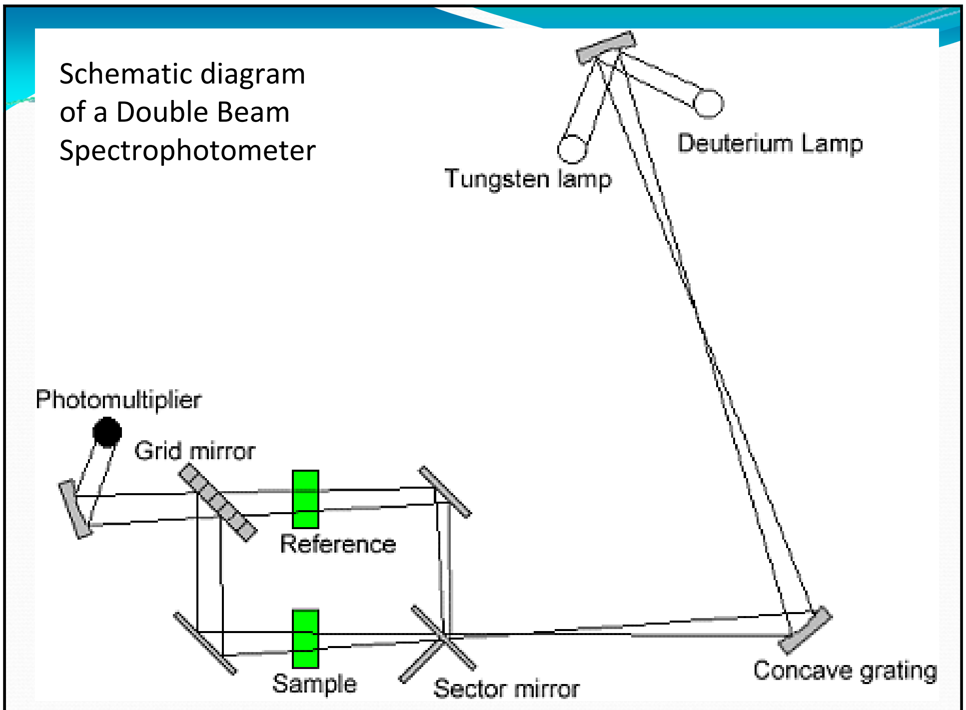
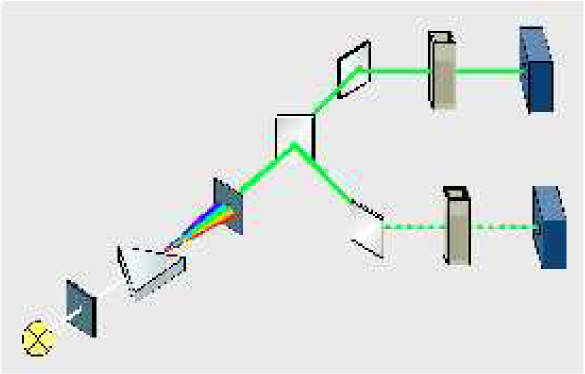
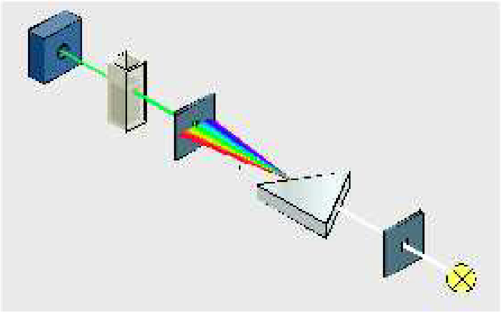
Schematic diagram of a Double Beam Spectrophotometer

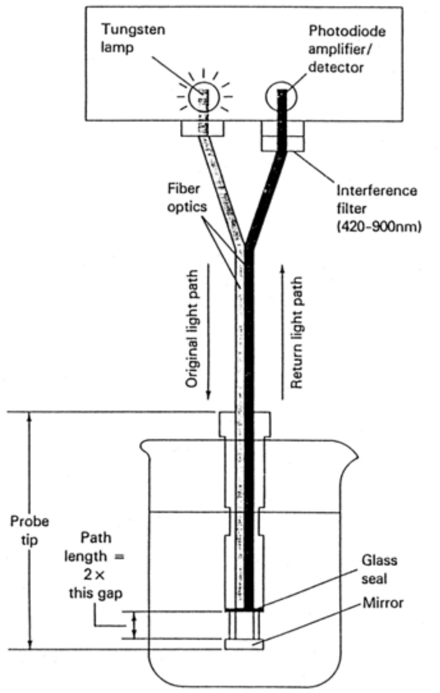


Schematic diagram of a Double Beam Spectrophotometer



Schematic diagram of a Single Beam Spectrophotometer





Spectrophotometric system using a Fiber Optic Probe for UV-vis absorption measurements

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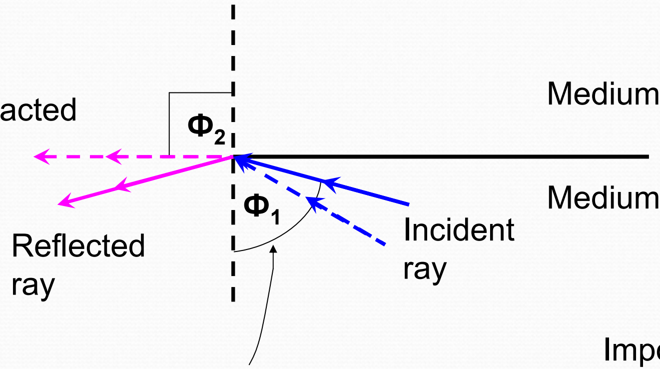
Critical Angle (Φ_C)

At angles greater than the Critical angle, 100 % reflection occurs or **Total Internal Reflectance**



Normal to surface

Medium 2 (air)

Refracted ray

Φ_2

Medium 1 (glass)

Φ_1

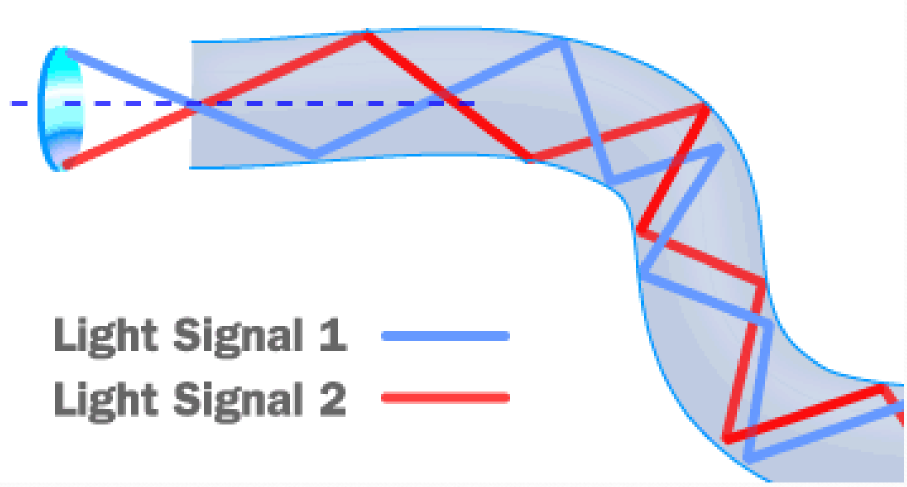
Incident ray

Reflected ray

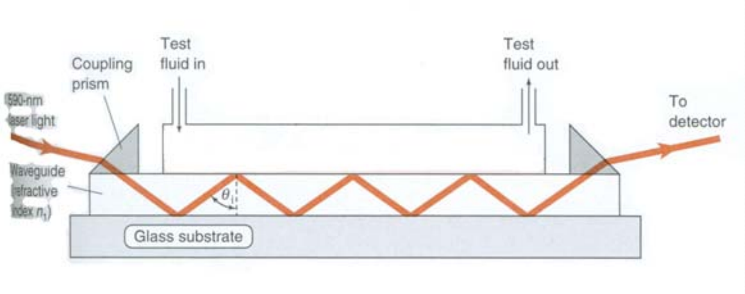
New value of Φ_1 for Reflection $\Phi_1 > \Phi_C$

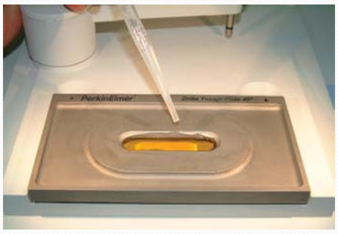
Important for:
1) Refractometers
2) Fiber Optics

Light propagation down a Fiber Optic Cable – based on Total Internal Reflectance



Attenuated Total Reflectance (ATR) Cell for IR Spectroscopy





HW3

- 7-9
- 7-12
- 7-13
- 7-16
- 7-17
- 7-18
- 7-22
- 7-23