

The background of the slide is a blue, spiral-bound notebook. The spiral binding is visible at the top edge. The text is centered on the notebook page.

CHEM*3440

Chemical Instrumentation

Topic 8

Ultraviolet/Visible Absorption Spectroscopy

UV-Visible Electronic Transitions

This technique is mainly a study of molecules and their electronic transitions.

Molar absorptivity (ϵ) ranges from 0 to 10^5 .

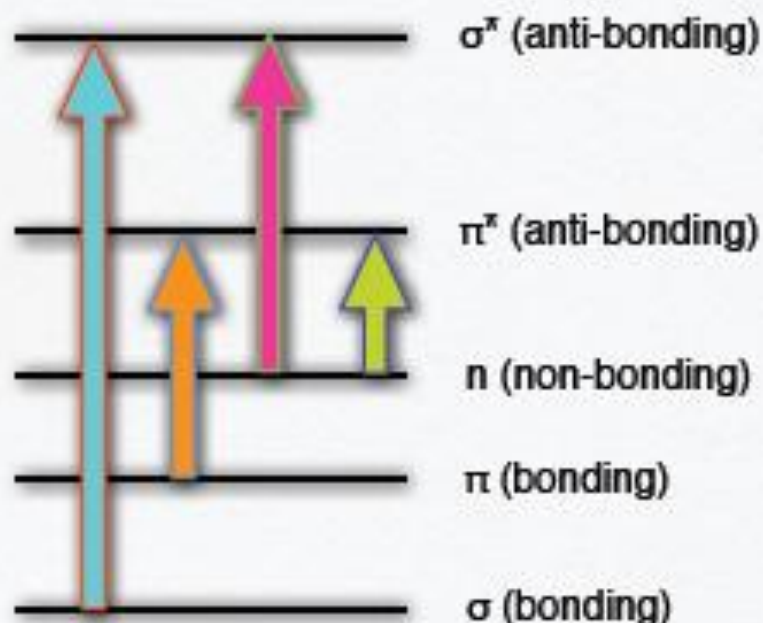
Transitions with $\epsilon < 10^3$ are considered to be of low intensity.

In organic molecules, most bonds are excited by $\lambda < 185$ nm (vacuum UV).

Most functional groups have lone pairs whose energies place them in the near UV and visible range. These groups are called "chromophores".

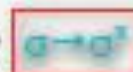
Valence Electronic Structure

The valence electrons are the only ones whose energies permit them to be excited by near UV/Visible radiation.

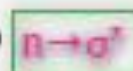


Four types of transitions

Too high energy (VUV)



High energy but accessible



Most common transitions
in UV/Visible range



$n \rightarrow \sigma^*$ Transitions

Still quite high in energy; λ is between 150 and 250 nm.

Not many molecules with $n \rightarrow \sigma^*$ transitions in UV/Visible region.

	λ_{max}	ϵ_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(\text{CH}_2)_2\text{S}$	229	140
$(\text{CH}_2)_2\text{O}$	184	2520
CH_3NH_2	215	600
$(\text{CH}_3)_3\text{N}$	227	900

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most UV/Visible spectra involve these transitions. $\pi \rightarrow \pi^*$ are generally more intense than $n \rightarrow \pi^*$.

	λ_{max}	ϵ_{max}	Type
$\text{C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	177	13000	$\pi \rightarrow \pi^*$
$\text{C}_5\text{H}_{11}\text{C}\equiv\text{C}-\text{CH}_3$	178	10000	$\pi \rightarrow \pi^*$
$(\text{CH}_3)_2\text{C}=\text{O}$	186	1000	$n \rightarrow \pi^*$
CH_3COOH	204	41	$n \rightarrow \pi^*$
CH_3NO_2	280	22	$n \rightarrow \pi^*$
$\text{CH}_3\text{N}=\text{NCH}_3$	339	5	$n \rightarrow \pi^*$

Solvent Effects - Position

Solvents can interact with analyte molecules and shift the position and intensity of their absorbance peaks.

- Red Shift (Bathochromic) - Peaks are shifted to longer wavelength.
- Blue Shift (Hypsochromic) - Peaks are shifted to shorter wavelength.

$n \rightarrow \pi^*$ transitions are generally blue shifted; arises from the solvation of and hydrogen bonding to the lone pair of electrons making the non-bonding level more stable). Shifts are large (up to 30 nm).

Both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are red shifted; arises from attractive polarization forces and it increases with increasing solvent polarity. Shifts are small (less than 5 nm).

Solvent Effects - Intensity

Solvents can also induce significant changes in the intensity of peaks.

- Hyperchromic - Increase in absorption intensity
- Hypochromic - Decrease in absorption intensity

Absorption Characteristics of 2-methylpyridine		
Solvent	λ_{max}	ϵ_{max}
Hexane	260	2000
Chloroform	263	4500
Ethanol	260	4000
Water	260	4000
Ethanol/HCl (1:1)	262	5200

Auxochrome

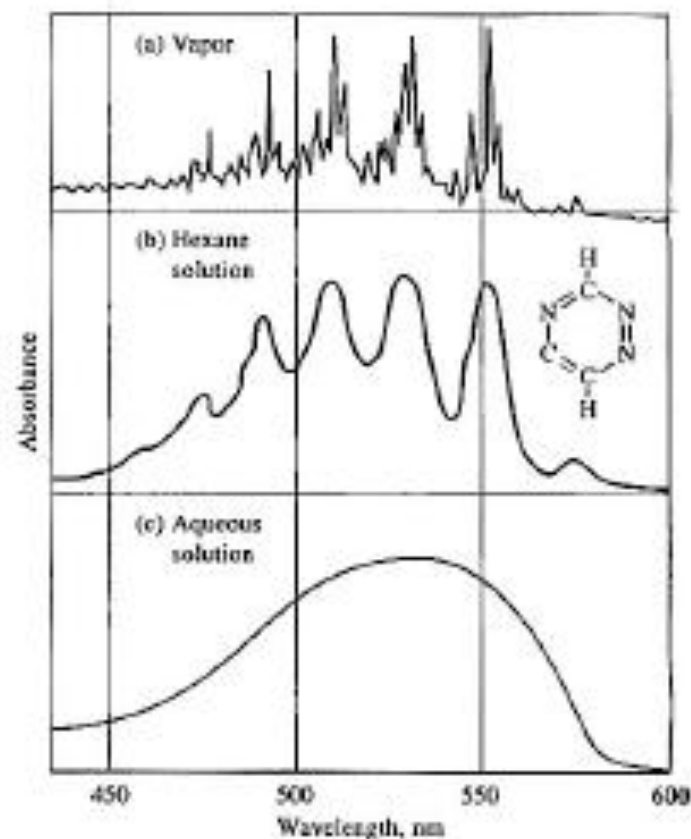
Substituent groups which are not themselves optically active in this energy range but who interact with other chromophores and shifts both intensity and position.

Absorption Characteristics of Pyridine Derivatives

Derivative	λ_{\max}	ϵ_{\max}
pyridine	257	2750
2-CH ₃	262	3560
3-CH ₃	263	3110
4-CH ₃	255	2100
2-F	257	3350
2-Cl	263	3650
2-I	272	400
2-OH	230	10000

Typical Organic UV/Vis Spectra

Note how the same molecule displays markedly different spectral features depending upon the environment in which it finds itself.



Inorganic - Transition Metals

Spectra from transition element ions arise from the 3d and 4d electrons. These spectra are quite broad, often in the visible (solutions are brightly coloured), and are significantly affected by ligands and solvents.

Ligand Field Theory is a molecular orbital approach to understand these effects. Essentially it asserts that the d-orbital energies are split in solution (or with ligands) and transitions between these split levels are at the source of their UV/Vis spectroscopy.

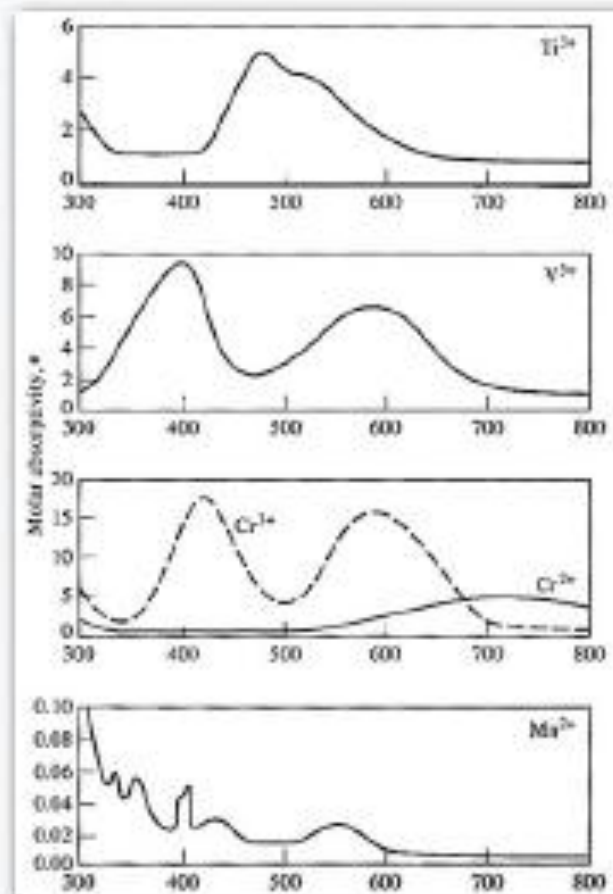


Fig. 14-7 in Skoog, Holler, Nieman.

Inorganic - Lanthanides

UV/Vis spectra of lanthanide ions arise from 4f levels (5f for the actinides). These are rather well-screened from outside influences and as such the spectra are comparatively sharp, and only weakly influenced by ligands and solvents.

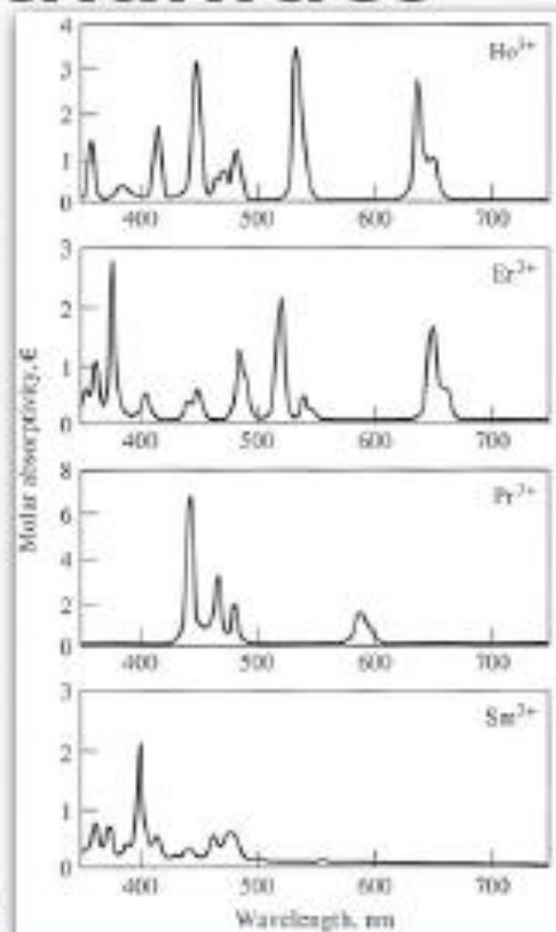
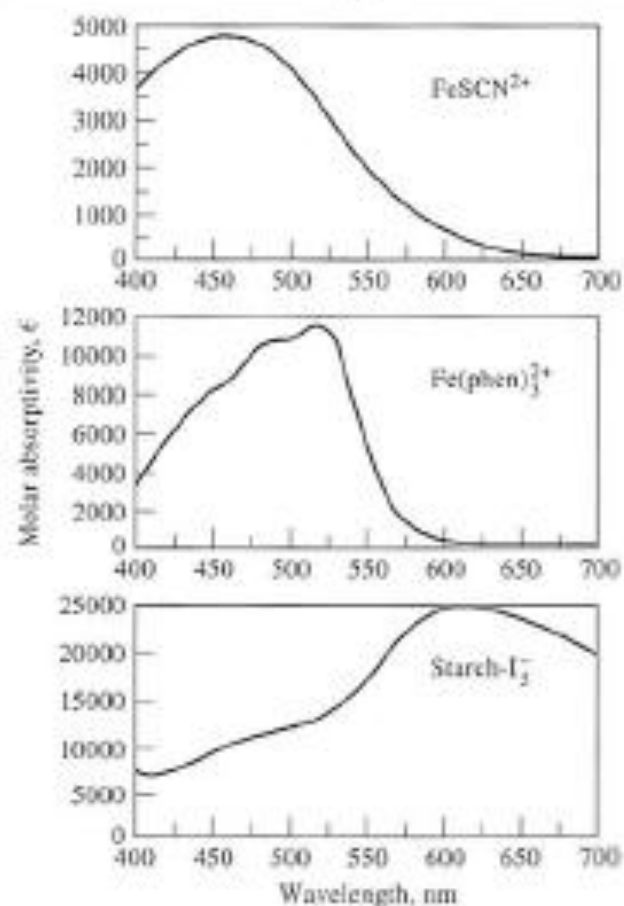


Fig. 14-6 in Skoog, Holler, Nieman.

Inorganic - Charge Transfer



Inorganic complexes – metal ions with surrounding ligands – can undergo absorption processes where the electron jumps from an orbital mostly centered on the ligand to an orbital mostly centered on the metal ion (the opposite can occur, but less frequently). Transitions are intense.

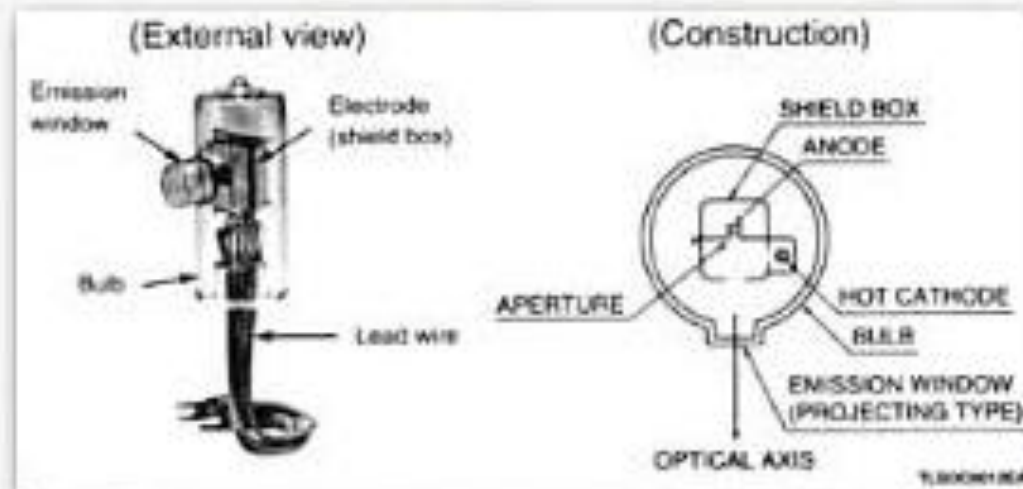
Fig. 14-10 in Skoog, Holler, Nieman.

Instrumentation

Spectrometric instruments have a common set of general features. Often, one technique is distinguished from another by differences in these features. Here we look at specific features for the UV/Visible experiment.

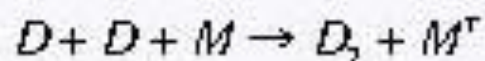
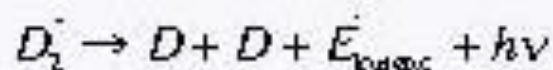
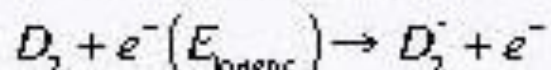
- **Sources:** D₂ lamp, W filament (halogen lamp), and Xe arc lamp.
- **Wavelength Selectors:** Filters and Monochromators.
- **Sample Containers:** Fused silica, quartz, and glass.
- **Detectors:** Phototube, PMT, photodiode, photodiode array, CCD array

Sources - Deuterium Lamp



Strike a low voltage DC arc in a lamp filled with D_2 . Gives continuum emission from 160 to 400 nm.

Reaction Scheme



An L2 D2 deuterium lamp from Hamamatsu.

Sources - Tungsten Filament

Reflecting/Focusing Assembly

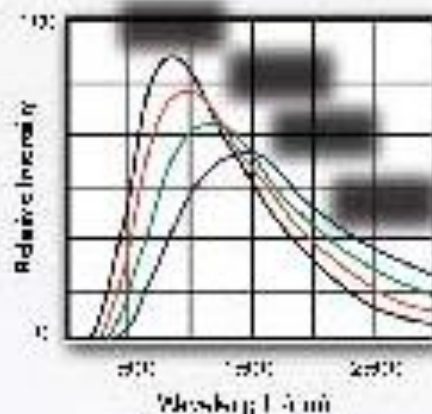


Lamp

Condenser Lens



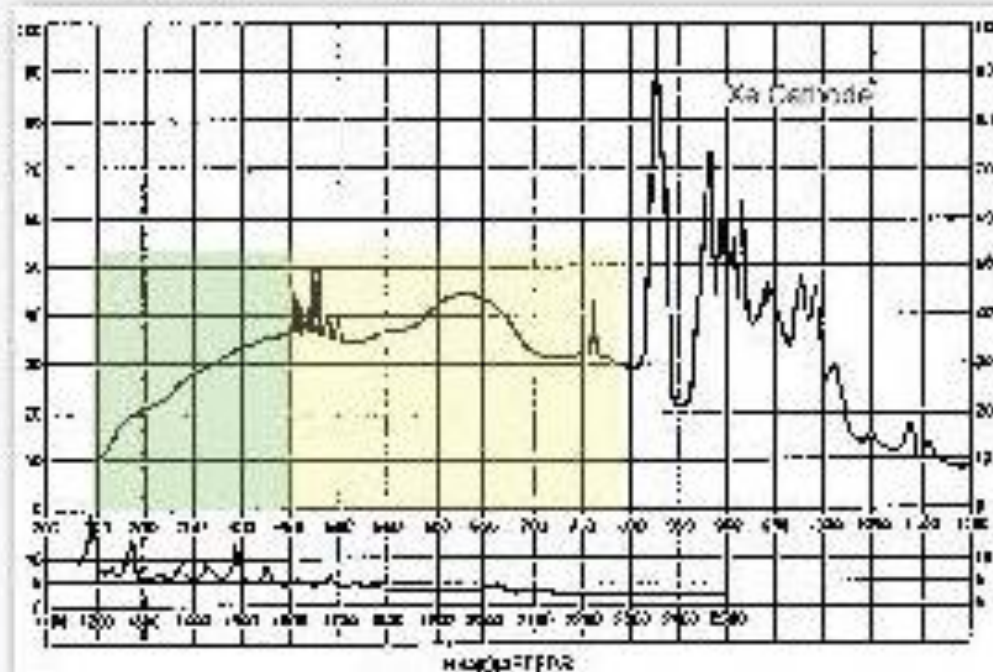
A heated W filament, gives off blackbody radiation. Add a small amount of a halogen gas (usually Br_2). Sublimated W reacts with halogen to form tungsten halide; does not deposit on quartz cover (no blackening) but does redeposit on filament (extends life).



Sources - Xe Lamp

Tube filled with Xe (or sometimes a mixture of Hg and Xe). Pass a low voltage DC current to excite Xe.

UV Region Visible Region



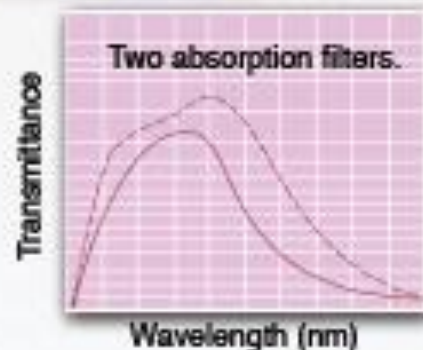
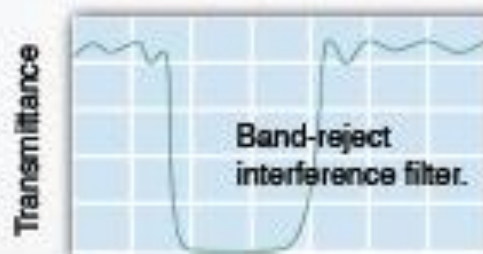
Xe lamp from Hamamatsu.

Filters

Filters can absorb light with dye molecules incorporated into the glass or gel. They can also pass or reject bands of light because of interference effects with multiple layers of materials. Dye or interference filters can select a more narrow region of light to allow through to a detector. Useful in non-scanned situations and when a specific, known band of radiation needs to be monitored.



A filter set from Andover Corp.



Monochromator

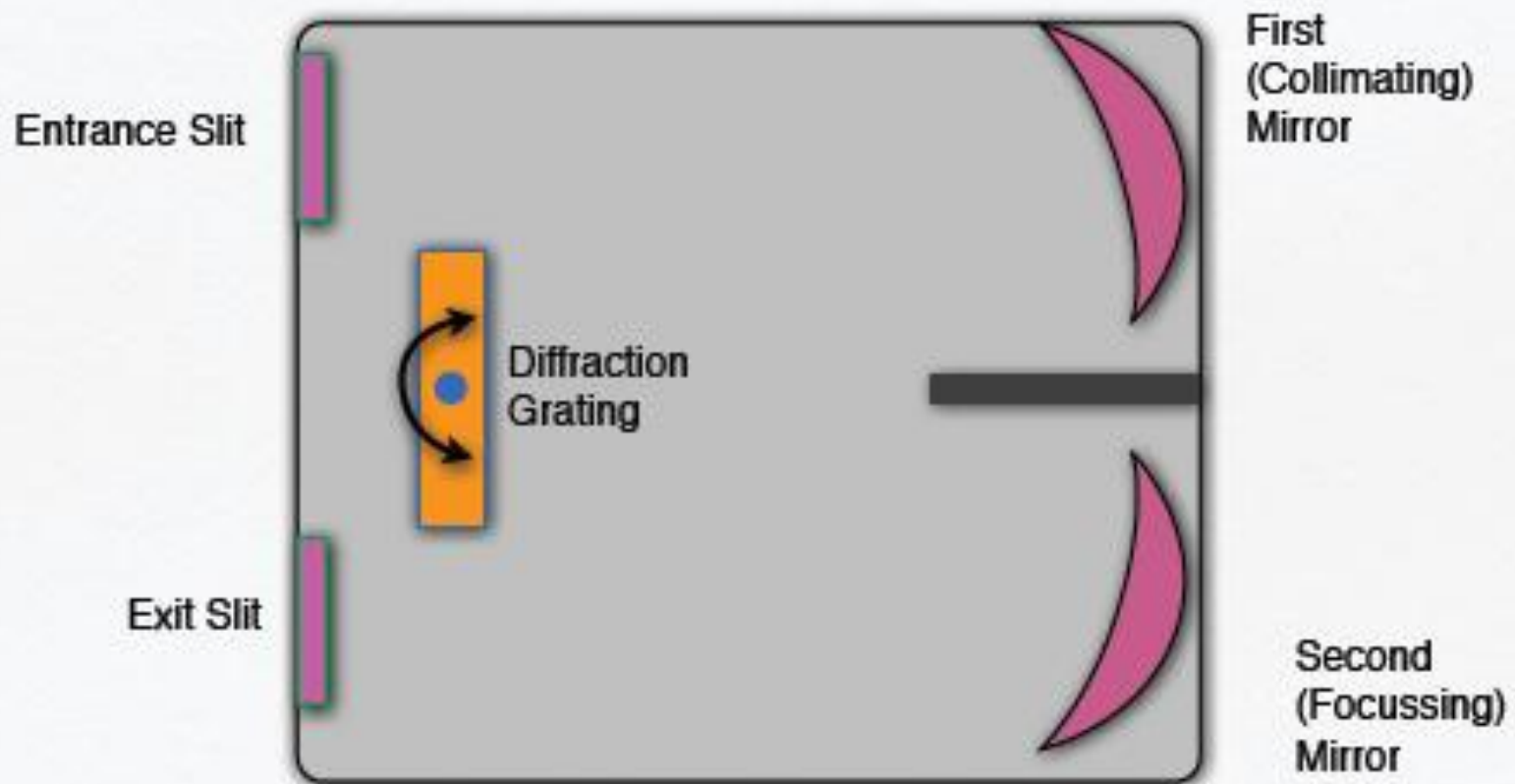
A monochromator disperses the light in order to select a narrow bandwidth. Both gratings and prisms can be used for this dispersion. Numerous instrumental designs available to account for various optical aberrations.



The 500M monochromator from Jobin-Yvon.

A couple of informative sites regarding monochromators.
<http://www.shsu.edu/~chemistry/primers/mono.html>
http://www.monochromator.com/jy/pos/pos_ch1.htm#1.1

Monochromator con't



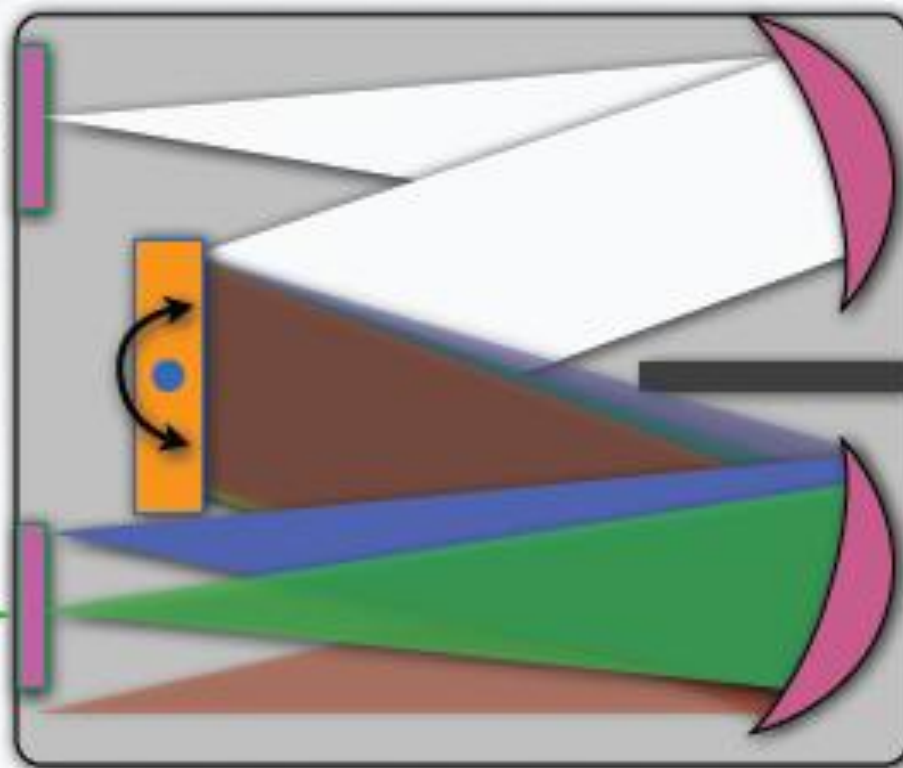
Monochromator con't

White light enters

The light is collimated to fill the grating

Only one colour passes through the exit slit

Only one colour reflects at the right angle to fall upon the exit slit

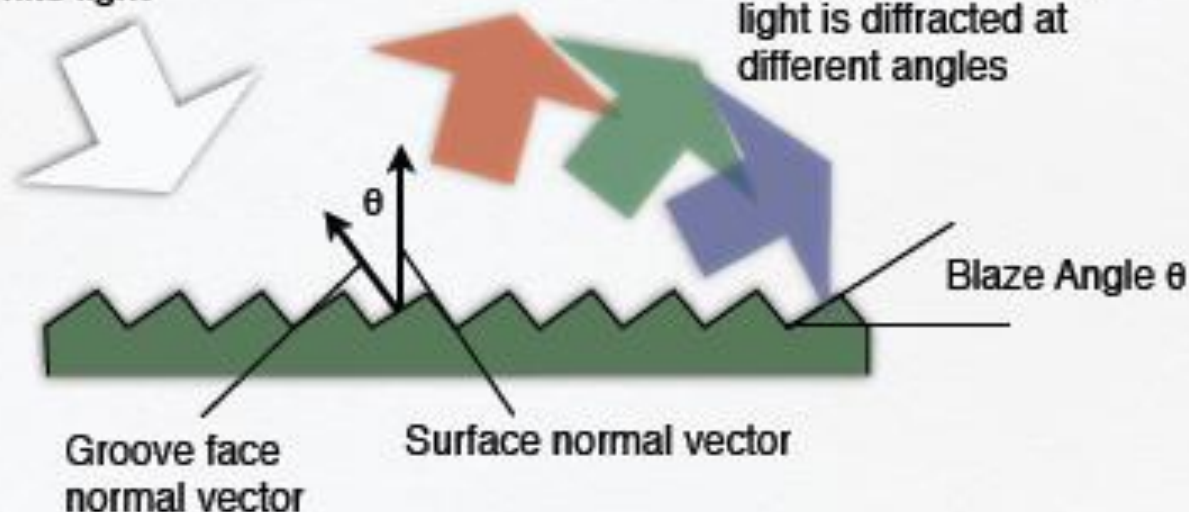


Echelle Grating

Has been most common grating. Ruling engine cuts sawtooth grooves in a master. Replicas are cast from the master.

Incident white light

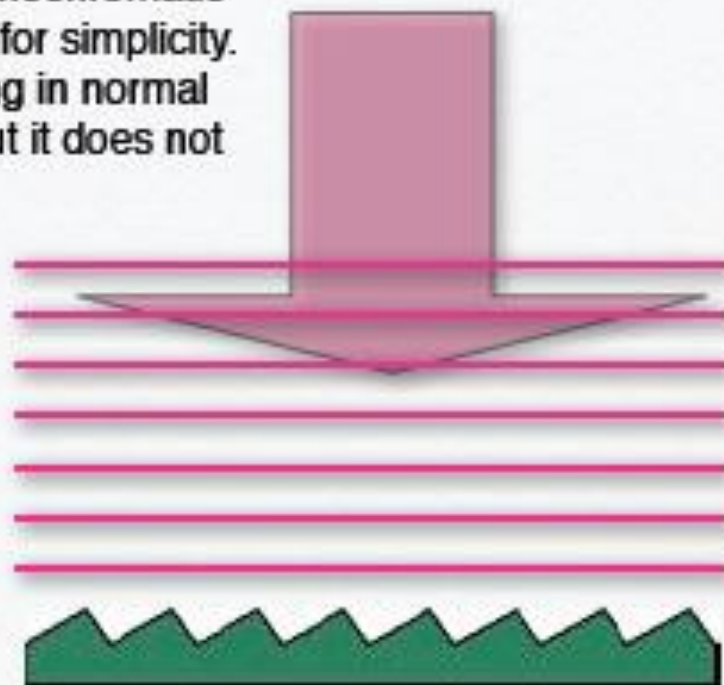
Different wavelength
light is diffracted at
different angles



Two main defining parameters are grooves/mm and the blaze angle.

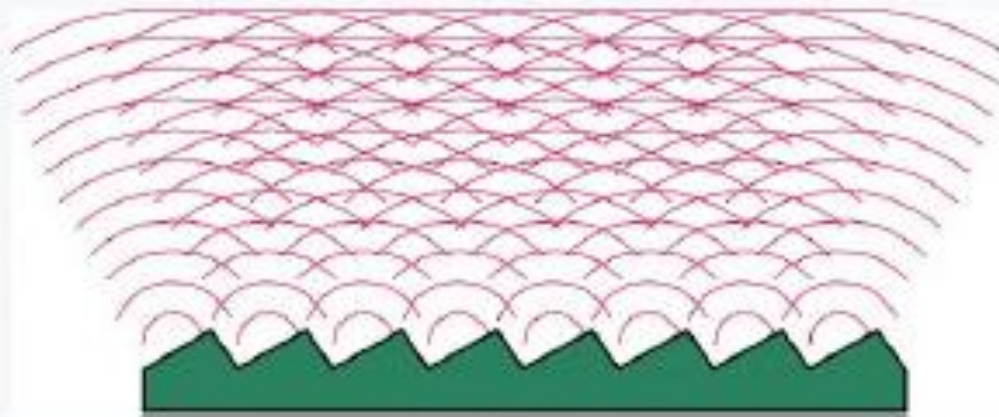
How A Grating Works - 1

Here I am showing monochromatic light (one wavelength) for simplicity. Also, it is shown coming in normal to the grating plane, but it does not have to.



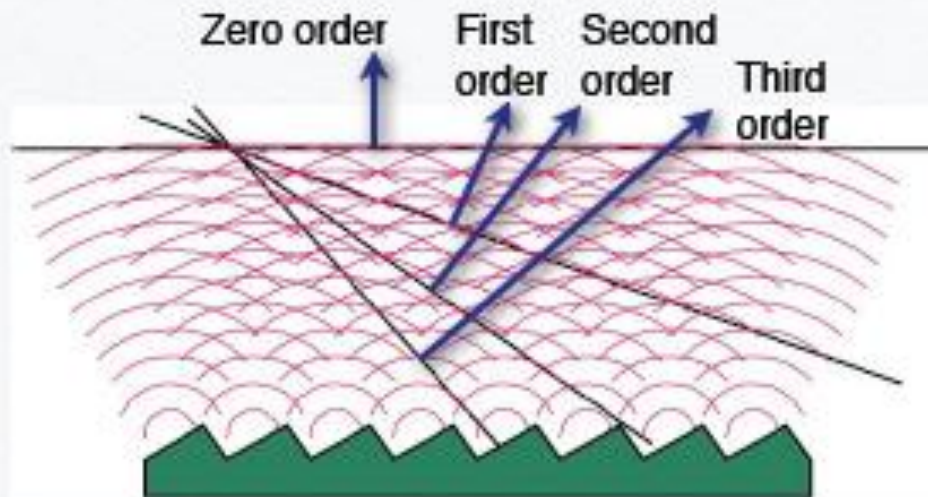
Collimated (light rays all travelling parallel to each other) white light irradiates the grating surface.

How A Grating Works - 2



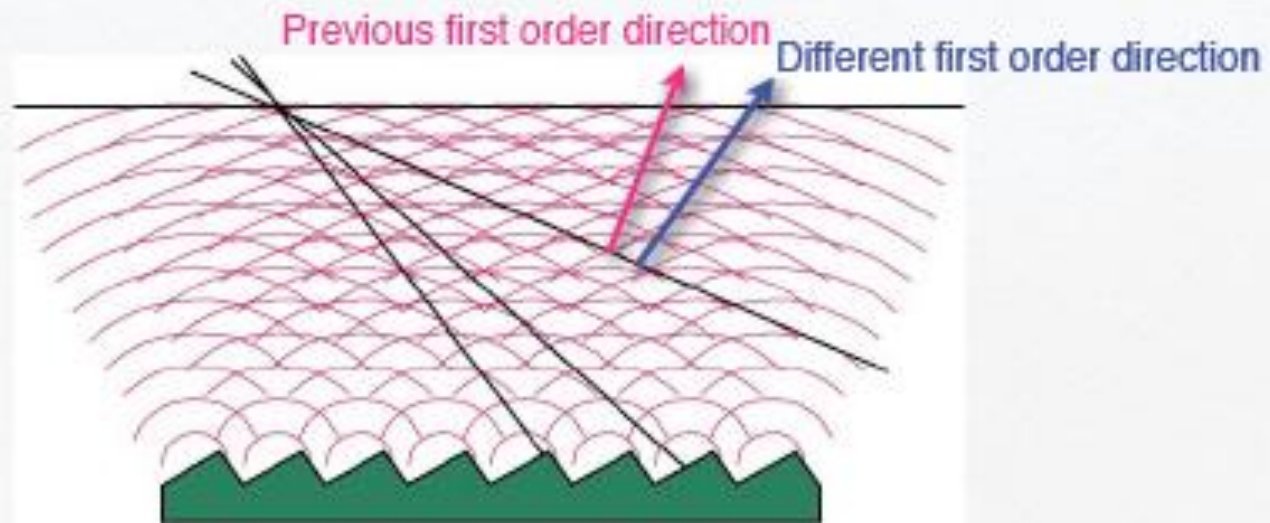
Each facet of the grating becomes a source of spherical re-emission of all of the scattered light. These spherical "wavelets" look like plane waves over small arcs when far enough away from surface.

How A Grating Works - 3



In the far field (many wavelength's distance from the surface) the light only travels in directions where there is constructive interference between wavelets. Different directions are called "diffraction orders". This depends upon the spacing between grooves (groove density).

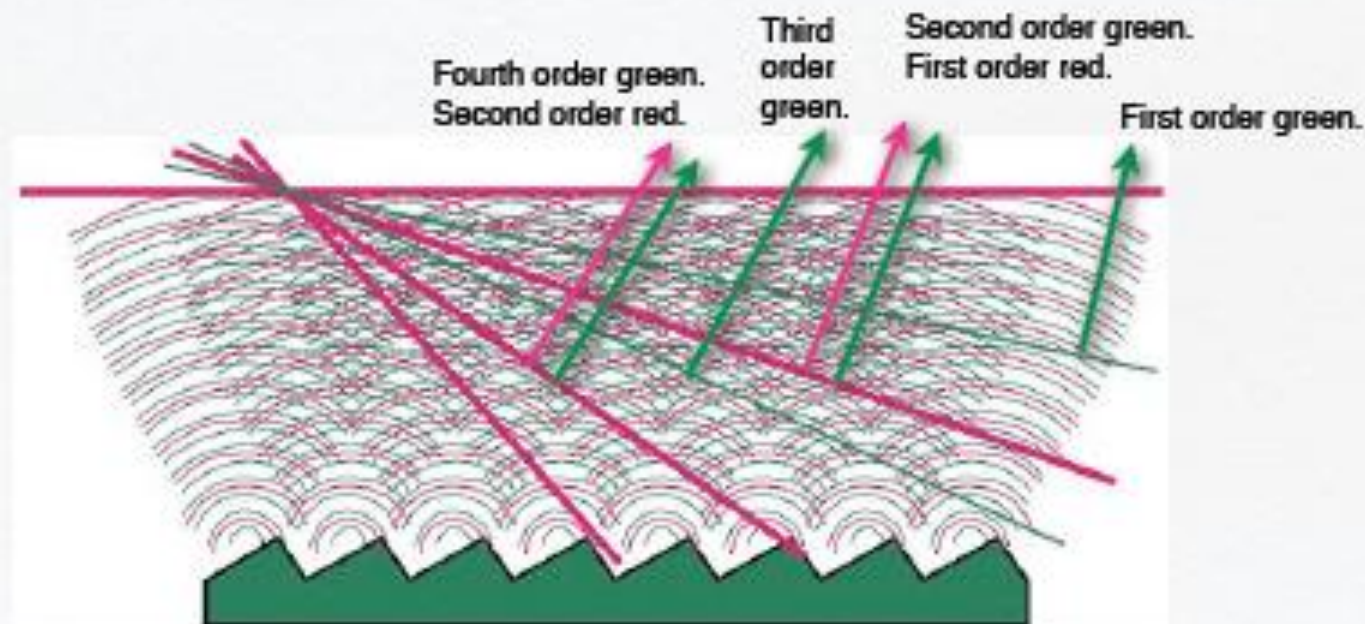
How A Grating Works - 4



When light of a different wavelength impinges upon the grating, its diffraction direction changes for all non-zero order diffraction processes. It is this difference that leads to the dispersion of light of different wavelengths.

How A Grating Works - 5

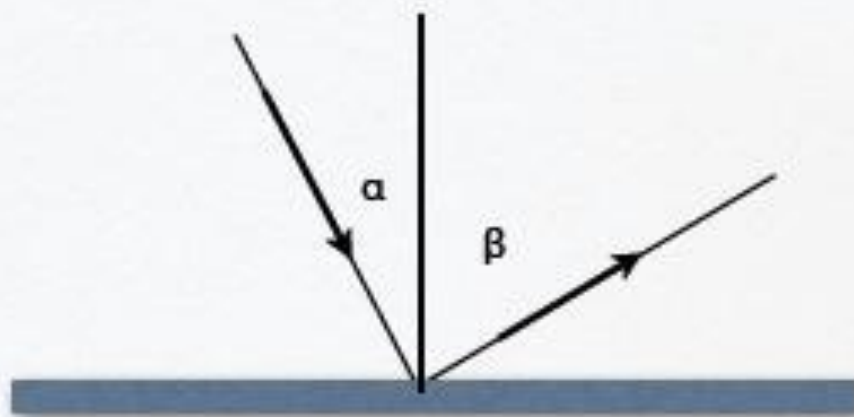
When the incident light contains two wavelengths, one exactly half the wavelength of the other, their orders overlap – scattering into the same angle.



Grating Equation

Most fundamental equation for gratings is

$$\sin(\alpha) + \sin(\beta) = kN\lambda$$



k = diffraction order

N = groove density

λ = radiation wavelength

Angular Dispersion

A grating's effectiveness is in its ability to have two different wavelengths leave its surface at different angles. A direct measure of that property is its angular dispersion, the range of angles into which a range of wavelengths are distributed.

$$\frac{d\beta}{d\lambda} = \frac{kN}{\cos \beta}$$

The larger the angular dispersion, the better is the grating.

Linear Dispersion

Most monochromators scan a grating's output across a fixed slit at some fixed distance from the grating. In this case, the more direct measure of grating effectiveness is linear dispersion – what is the distance at the slit over which a range of wavelengths are distributed.

$$\frac{d\lambda}{dx} = \frac{\cos \beta}{k N L_{\text{exit}}}$$

Distance to the exit slit (the last mirror's focal distance).

Note how linear dispersion can be improved by either increasing the groove density, increasing the diffraction order, or increasing the focal length.

Resolving Power

The resolving power further shows how the size of a grating can impact on the resolution of a grating.

$$R = \frac{\lambda}{d\lambda} = k N W_{\text{grating}}$$

← illuminated width of the grating.

As an example, for a grating with $N = 1200$ lines/mm and a grating width of 110 mm, and working in 1st order:

$$R = 1 \times 1200 \times 110 = 132,000$$

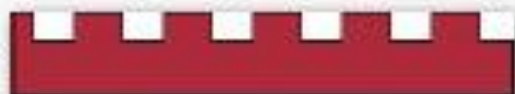
Therefore, at 500 nm, $d\lambda = 500/132,000 = 0.0038$ nm for the bandpass of the grating.

Holographic Gratings

There are ruling errors made with gratings cut using a ruling engine. They produce "ghosts", very weak replicas of intense lines at unexpected wavelengths.

We can expose a photoresist layer to a diffraction pattern from laser. This, followed by chemical and/or ion etching can imprint a grating pattern onto a substrate, making a holographic grating which is ghost free.

Rectangular (non-blazed) grating



Sinusoidal profile grating

Many different shapes can be formed which can help to refine the performance of the grating. Sawtooth gratings (like the blazed gratings produced by a ruling engine) can still be fabricated in this manner.

Echelle Grating

An echelle grating is just like an echellette grating, except it is irradiated on the short edge of the sawtooth and the grating density is much lower (30 - 200 lines/mm). It is used, however, in very high order (20 - 120th order).

An echelle grating has much higher dispersion than an echellette grating of the same size.

However, it needs an additional dispersion element (often a prism) to help sort out the orders. Scanning through the spectrum can involve moving through 90 consecutive orders of diffracted radiation.

Example with light at 300 nm:

Echellette, 1200 lines/mm, first order, resolution 62,400, linear dispersion 16 Å/mm.

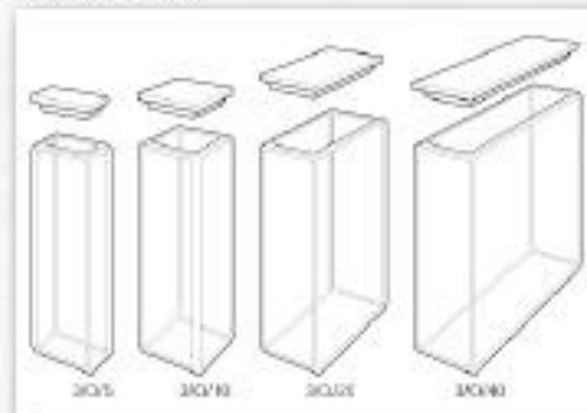
Echelle, 79 lines/mm, 75th order, resolution 763,000, linear dispersion 1.5 Å/mm

Sample Containers

Successful spectroscopy requires that all materials in the beam path other than the analyte should be as transparent to the radiation as possible. Also, the geometries of all components in the system should be such as to maximize the signal and minimize the scattered light.

The material from which a sample cuvette is fabricated controls the optical window that can be used. Some typical materials are:

Optical Glass - 335 - 2500 nm
Special Optical Glass - 320 - 2500 nm
Quartz (Infrared) - 220 - 3800 nm
Quartz (Far-UV) - 170 - 2700 nm

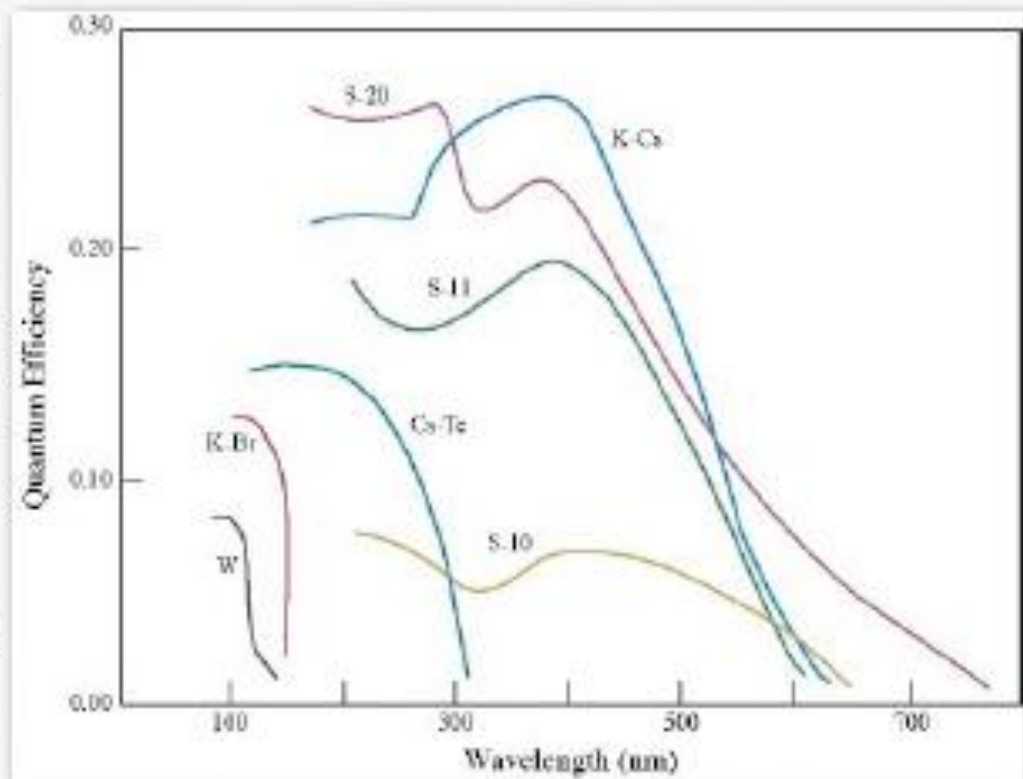


Keep the cuvette clean. Don't clean with paper products (Kim-wipe); use optical paper. Store dry. Don't get finger prints on them. Store carefully and gently.

Detectors - Phototube

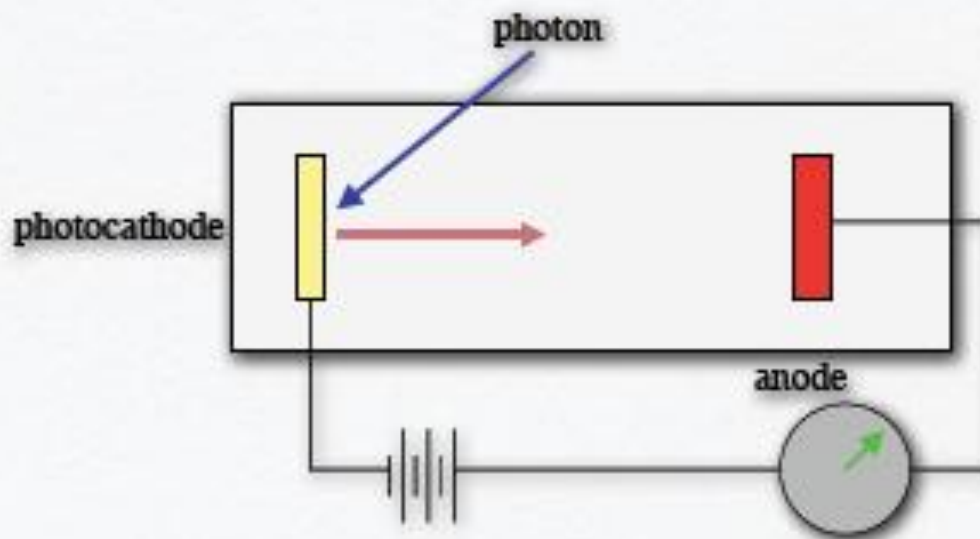
Almost without exception, a photodetector is needed to convert photons into electrons which can be measured and processed electronically.

Different coatings impart different efficiencies to the detection process. Quantum efficiency is the number of electrons produced per absorbed photon.



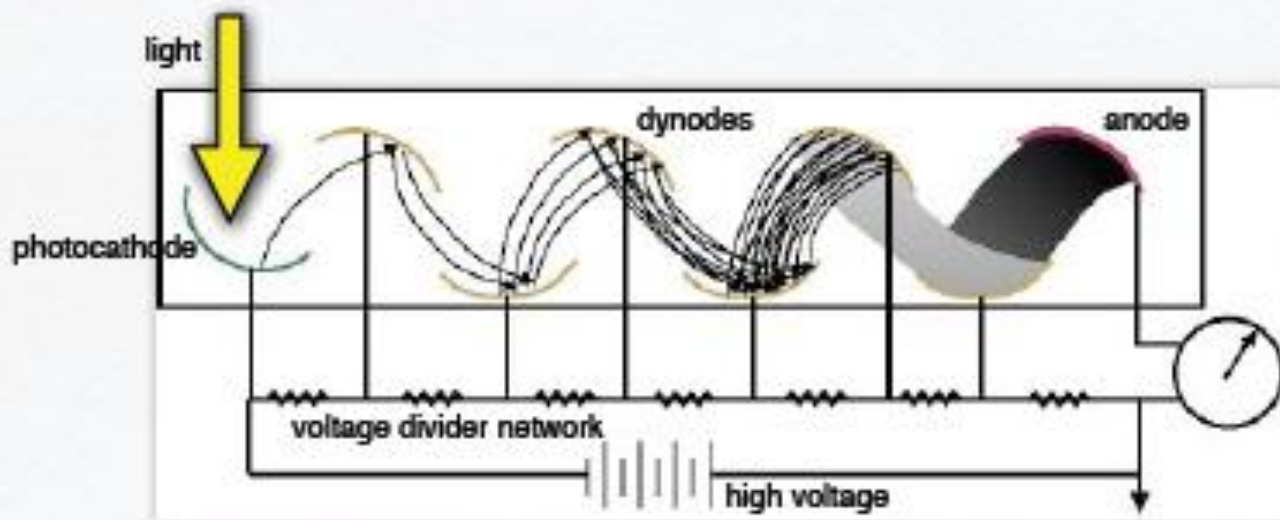
Phototube con't

The basic phototube is packaged in vacuum and presents a photocathode covered with a particular photoemissive material. A biased anode collects the ejected electrons and an external meter measures the current that flows.



Detectors - PMT

A PMT is needed for low light level situations. They provide a significant gain ($10^5 - 10^8$) in electron flow through secondary electron emission at the dynodes. This is a photomultiplier tube (PMT).



Secondary Electron Emissive Materials for Dynodes

BeO (Cs)

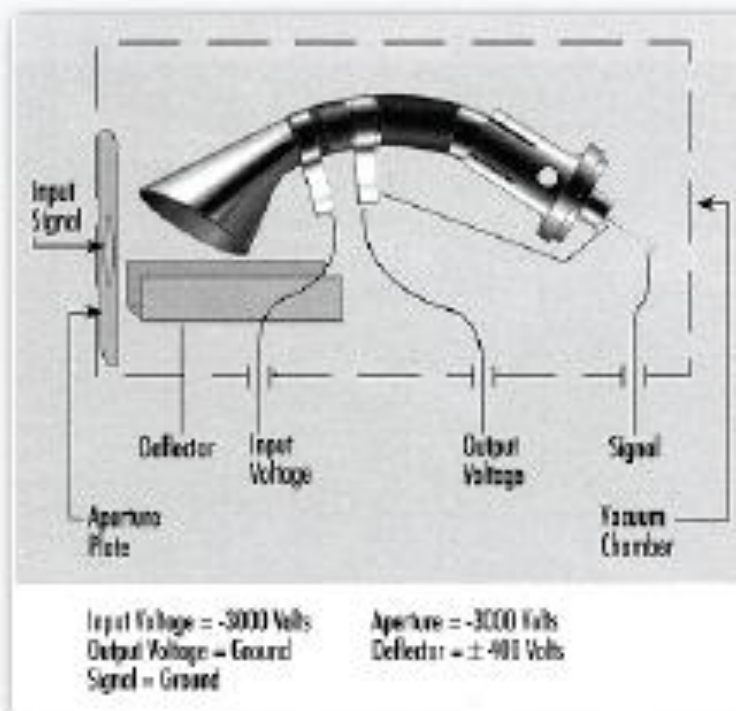
GaP (Cs)

MgO (Cs)

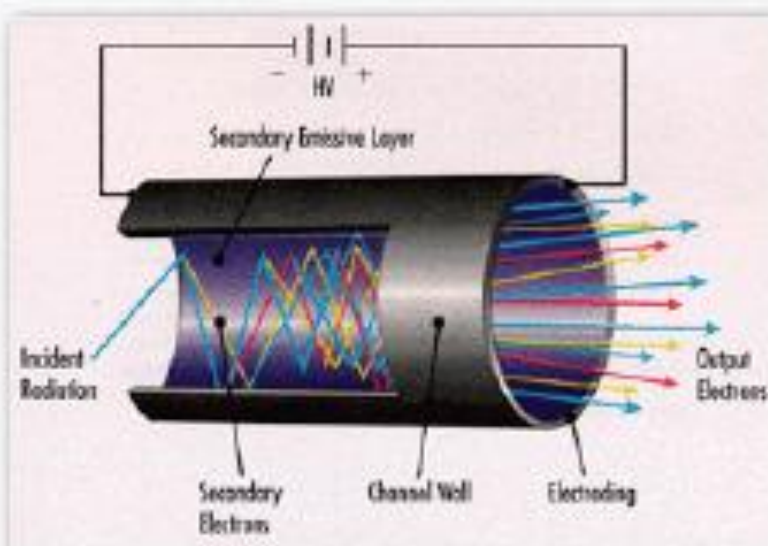
Cs₃Sb

KCl

Detectors - Channeltron

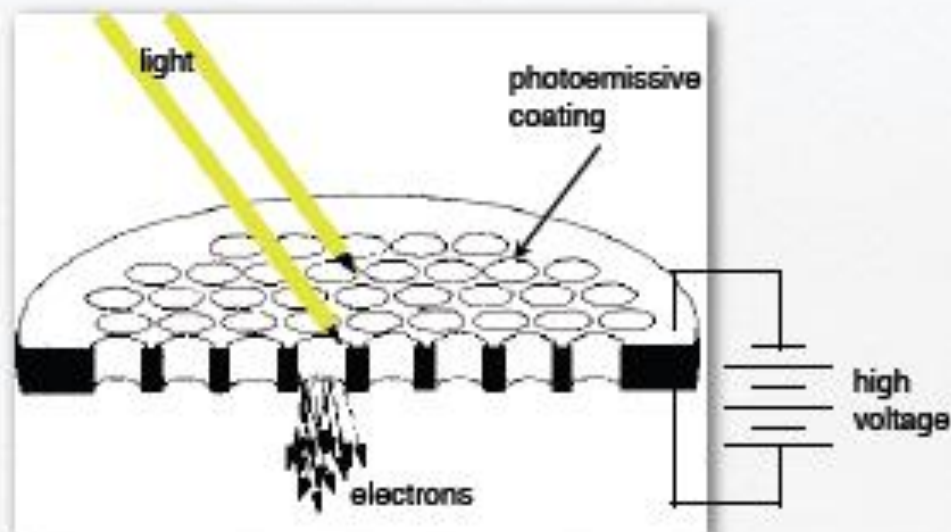


A Channeltron is a continuous dynode chain is built into a single unit. It is an excellent and widely used electron multiplier. Front end it with a photoemissive surface and you have a compact "PMT".



Detectors - Multichannel Plate (MCP)

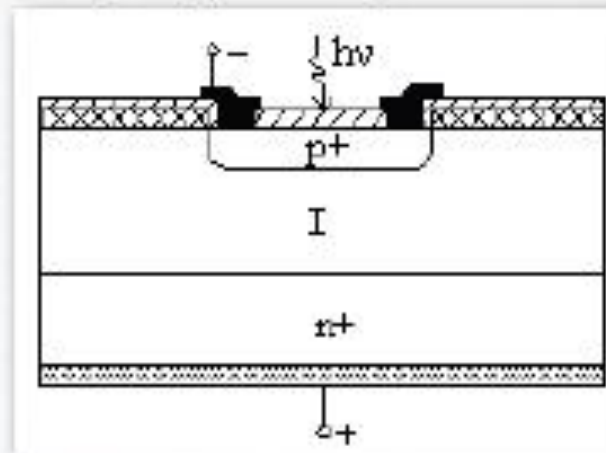
The channeltron concept has been extended to an array of micron-sized holes in a glass plate. Each tunnel functions like its own channeltron.



It is an excellent electron amplifier. The output goes to an anode for recording. A photoemissive front surface makes it a photon detector. It can then be used as an imaging device for low light conditions.

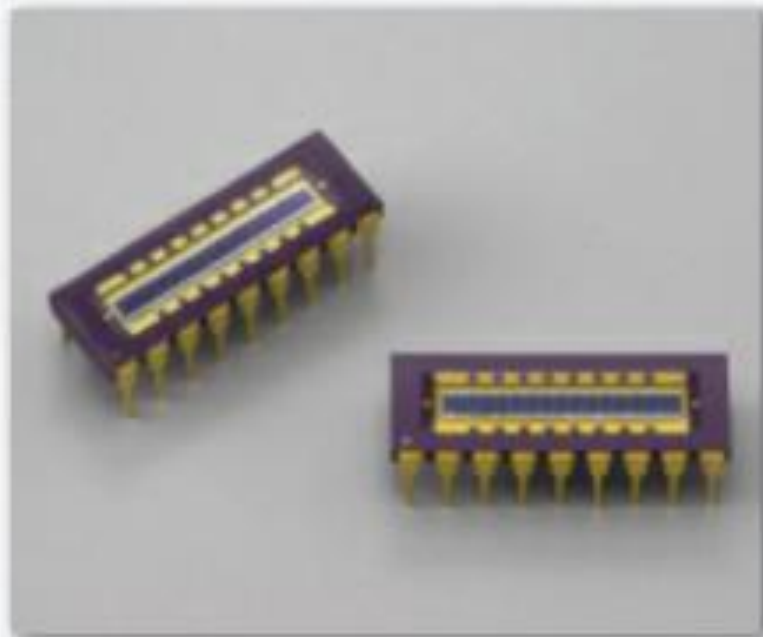
Detectors - Photodiode

A photodiode is formed by sandwiching an undoped layer of Si between a heavily doped p-layer and a heavily doped n-layer. Photons whose wavelength is between 400 nm and 1100 nm can be absorbed in the intrinsic layer, producing an electron-hole pair. The bias potential sweeps these carriers to the opposite regions, producing a current in the external circuit.



Photodiodes are more sensitive than phototubes, but less sensitive than PMT's.

Detectors - Photodiode Array



An array of photodiodes can be made. When this placed in the image plane of a spectrometer, the entire spectrum can be acquired at the same time. This greatly increases the speed of acquisition, enabling longer exposure times and hence improved S/N.

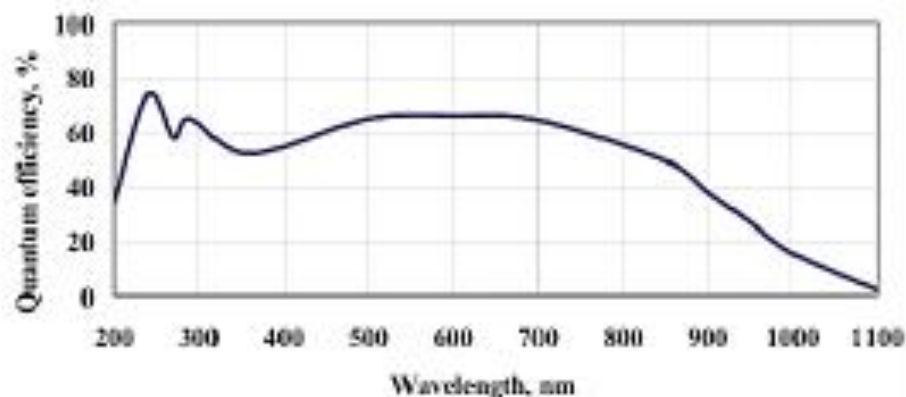
Critical parameters are the number of elements, the size of the device, its sensitivity, spectral range, rise time.

The S4111 series devices from Hamamatsu.

Detectors - CCD Array

Another solid state silicon device. A charged gate collects either the holes or electrons generated by the absorption of a photon. Charge accumulates in the potential well for as long as exposure is maintained. Device is read-out by charge injection (CID) or charge transfer (CCD). Comparable sensitivity to PMT, but functions as array detector also.

Typical spectral response



1024 x 256 back illuminated UV sensitive CCD detector from Jobin Yvon. Pixel size is $26 \times 26 \mu\text{m}$.