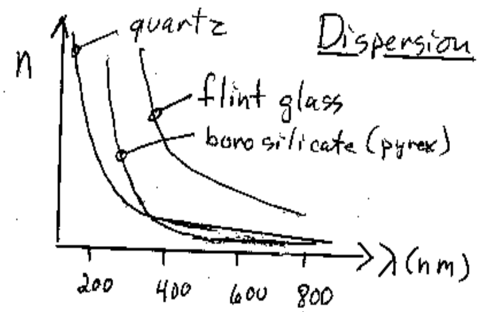
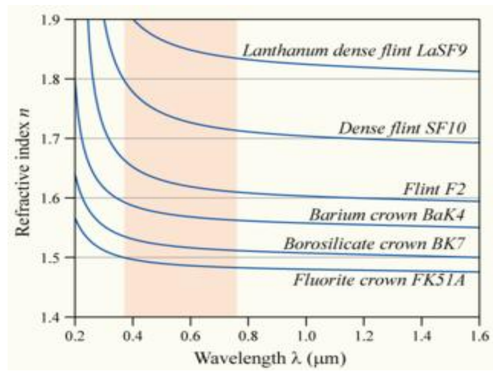
Chem 524-- Outline (Sect. 6) – 2013

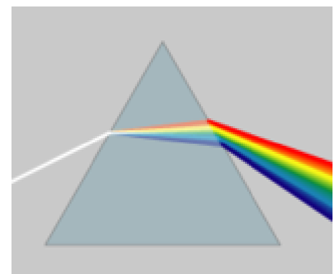
IV. Wavelength discriminators (Read text Ch. 3.5)

A. Monochromators work by dispersing wavelength, λ, in space

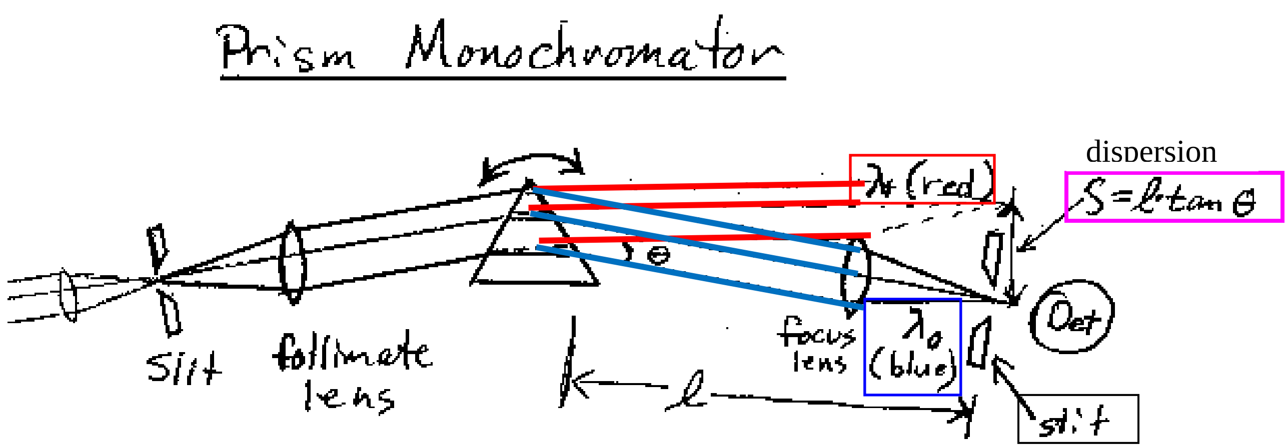
1. Prism - dispersion of wavelengths due to refractive index, n, dispersion, $dn/d\lambda$







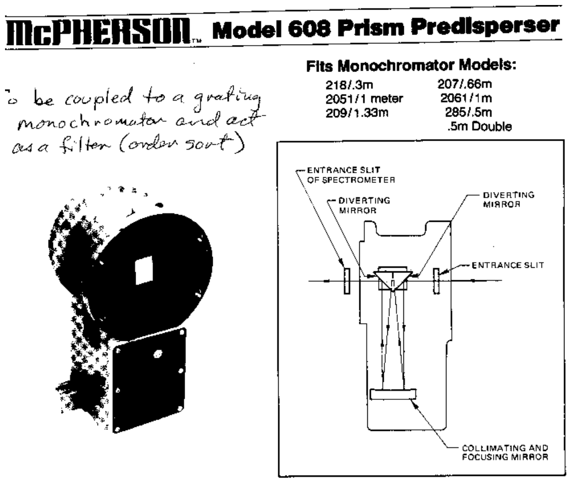
- material dependent--all index, n, values increase as λ go to uv, with different penetration of uv, n correlate to A, at absorbance band, index disp. has anomaly (derivative shape, complex n)
- very non-linear — fast change in uv, slow in IR (poor λ separation) - not a simple function of λ
- monochromator — collimate beam in, parallel at prism, focus refracted output (f is focal length) onto dispersed detector (film or CCD → spectrograph)

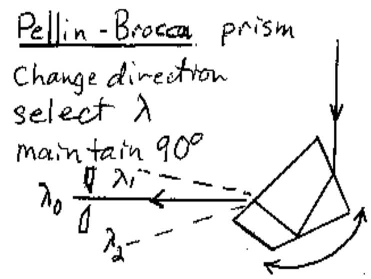


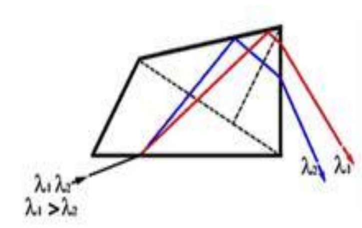
- or rotate prism to focus different λ on slit, whose width ΔS gives $\Delta\lambda$ or resolution--bandpass
- angular dispersion: $d\theta/d\lambda$ → linear separation/dispersion: $S = l \cdot \tan\theta$

uses

-- predisperser – Prism has no orders, non-linear dispersion, restricts grating range (Cary 14)



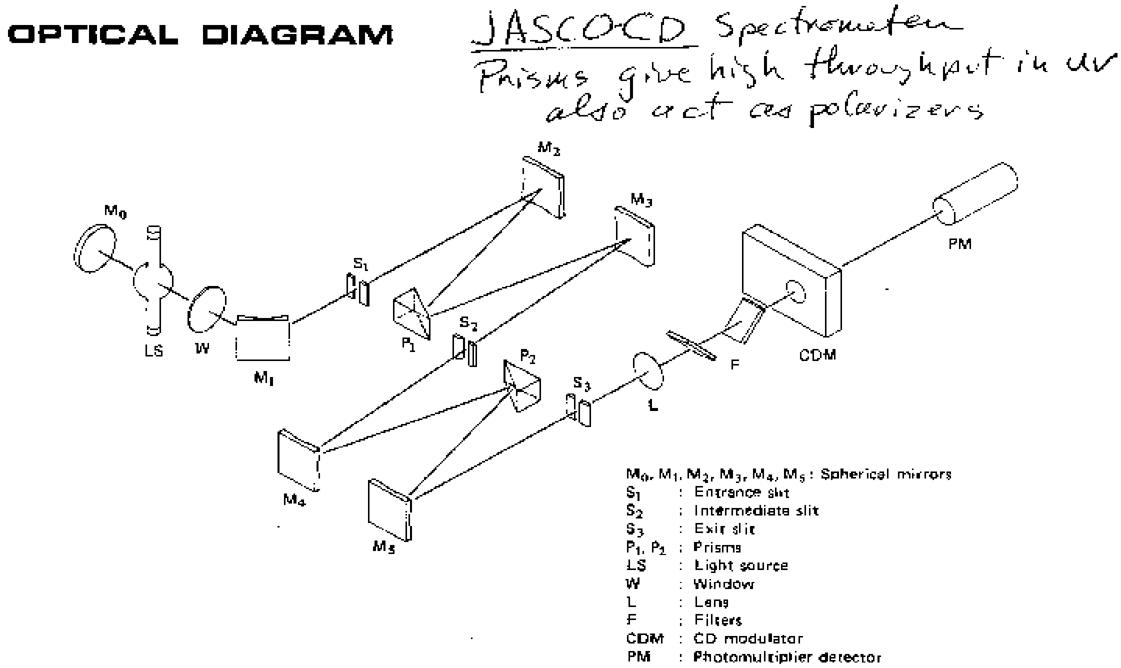


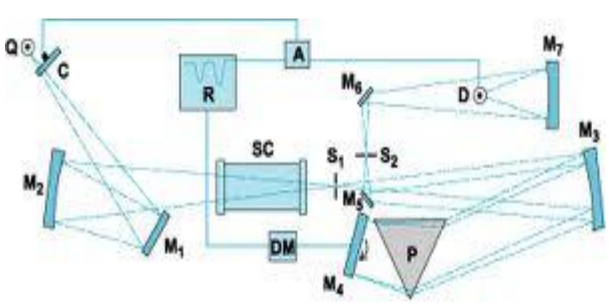


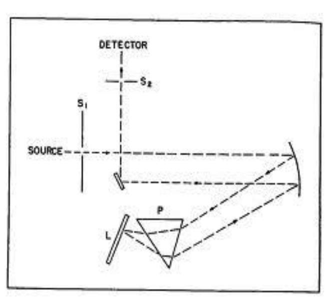
--Laser turn/sort—Pellin-Brocca low loss, rotate - freq. select λ with no beam angle change

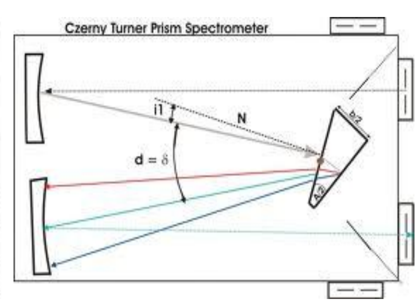
ex. Output Raman shifter, laser line sort / cleanup in Raman

—for uv (higher throughput/good dispersion--e.g. CD spectrometer)

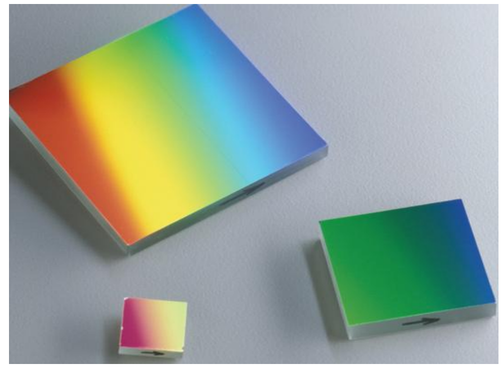








2. [Grating] transmission or reflection—
[diffraction cause interference] for different λ
at different angles:



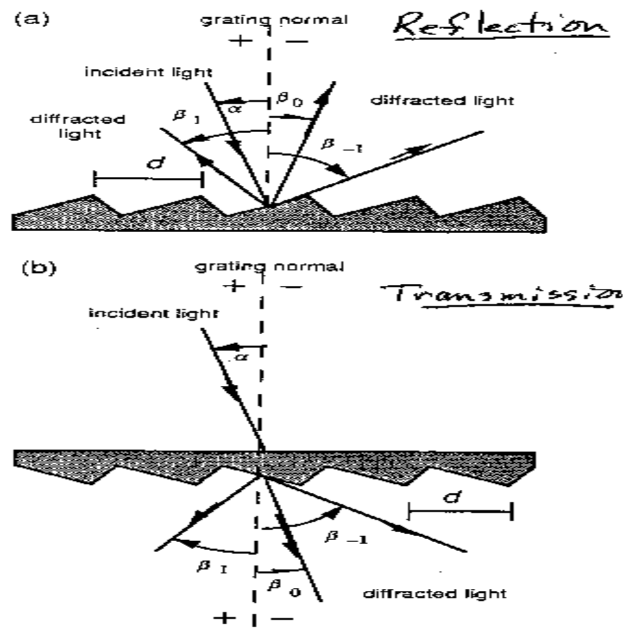


Figure II-1. Diffraction by a plane grating. A beam of monochromatic light of wavelength λ is incident on a grating and diffracted along several discrete paths. The triangular grooves come out of the page; the rays lie in the plane of the page. The sign convention for the angles α and β is shown by the + and − signs on either side of the grating normal. (a) A *reflection grating*: the incident and diffracted rays lie on the same side of the grating. (b) A *transmission grating*: the incident and diffracted rays lies on opposite sides of the grating.

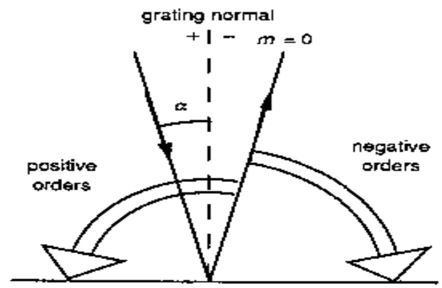


Figure II-4. Sign convention for the spectral order m. In this example α is positive.

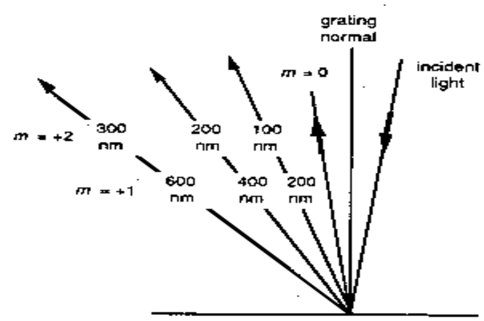
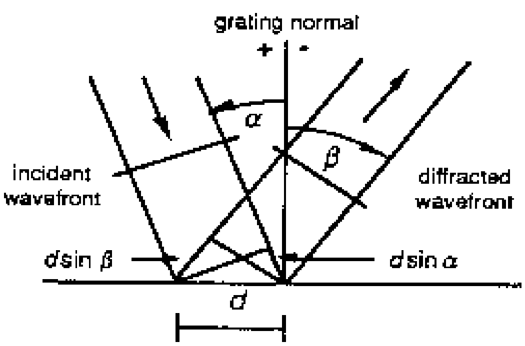


Figure II-5 - Overlapping of spectral orders. The light for wavelengths 100, 200 and 300 nm in the second order is diffracted in the same direction as the light for wavelengths 200, 400 and 600 nm in the first order. In this diagram, the light is incident from the right, so $\alpha < 0$.

- **$d(\sin\alpha + \sin\beta) = m\lambda$** , $m = 0, \pm1, \pm2, \ldots$ (m = order) –**this is critical equation**



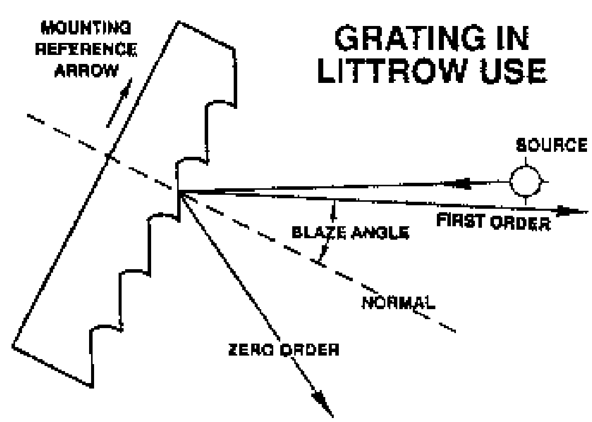


Figure II-2. Geometry of diffraction, for planar wavefronts. The terms in the path difference, $d \sin\alpha$ and $d \sin\beta$, are shown.

- Note ***β is negative*** *so difference in path* is **d(sin |α| –sin |β|)** which creates interference/diffraction
- In **Littrow**, incident & diffracted light same direction, *blaze make mirror-like* for one angle/wavelength

- orders need to be sorted out, reason for prism ***predisperser or filter*** system:

  m>0 (positive order) $\beta > -\alpha$, **m<0** (neg) $\beta < -\alpha$ and $\beta = -\alpha$, m=0

- - free spectral range: $\Delta\lambda = \lambda/(m + 1)$ - at given diffraction angle, get λ, and $\Delta\lambda$

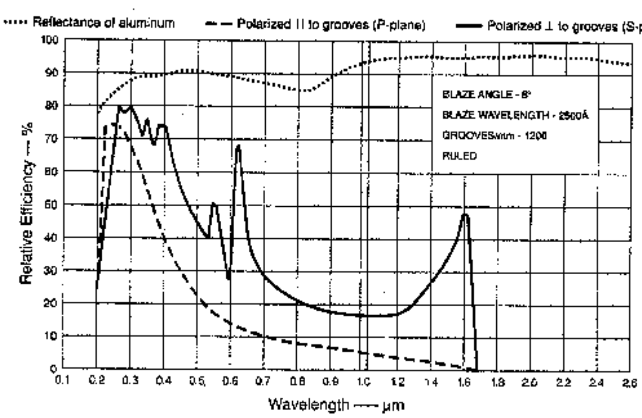
  extent of wavelength range before higher order interfere with a lower order

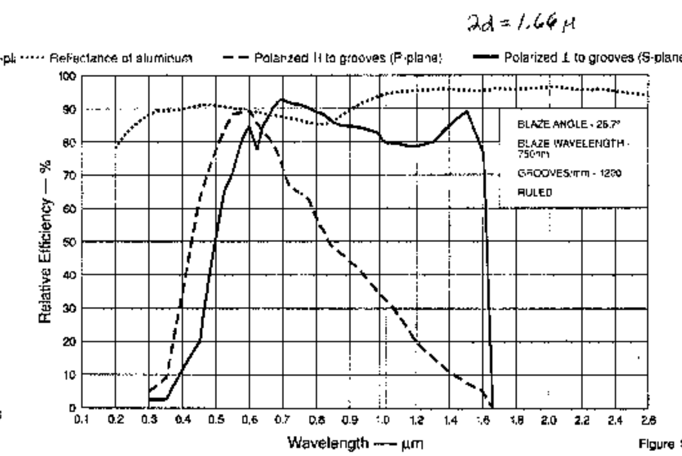
- zero order (top fig) → $\alpha = -\beta$ i.e. no solution *or* all wavelengths→*grating acts like mirror*

- Blaze — maximum λ efficiency: $\lambda_\beta = d \sin\beta$ (defined for $\alpha = 0$, Littrow condition)

useful range (2/3 λ_B→ 3/2 λ_B) , from shaping groove as a triangle so wide faces mirror-like

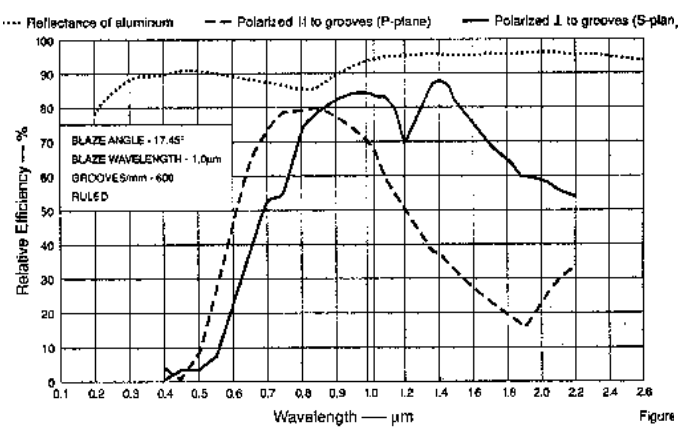
cut-off $\lambda > 2d$ no diffraction (eg. 1200 gr/mm → d = 833 nm)—(can't get path diff. of nλ)

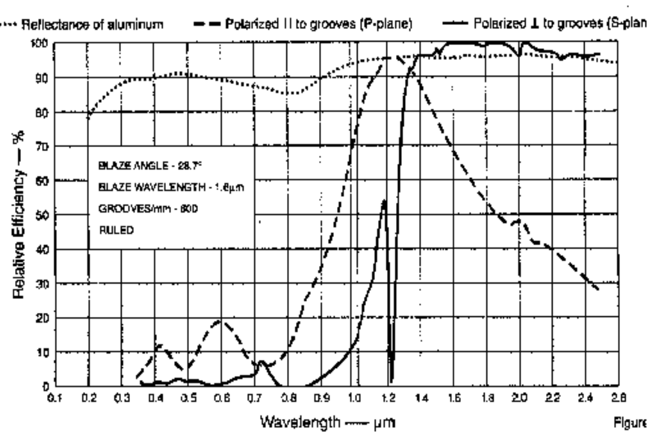




--Compare blazes –250 nm (8°) – left, and 750 nm (25.7°) – right

--also polarized, ⊥ to grooves → more intensity to red of maximum, **||** → more intensity to blue,





anomalies occur as function of λ blaze, result in extreme polarization

– sharp changes in diffraction efficiency – scanning λ intensity variation, can look like peak

Dispersion: $D_a = d\beta/d\lambda = |m|/d \cos\beta = (\sin\alpha + \sin\beta)/\lambda \cos\beta$

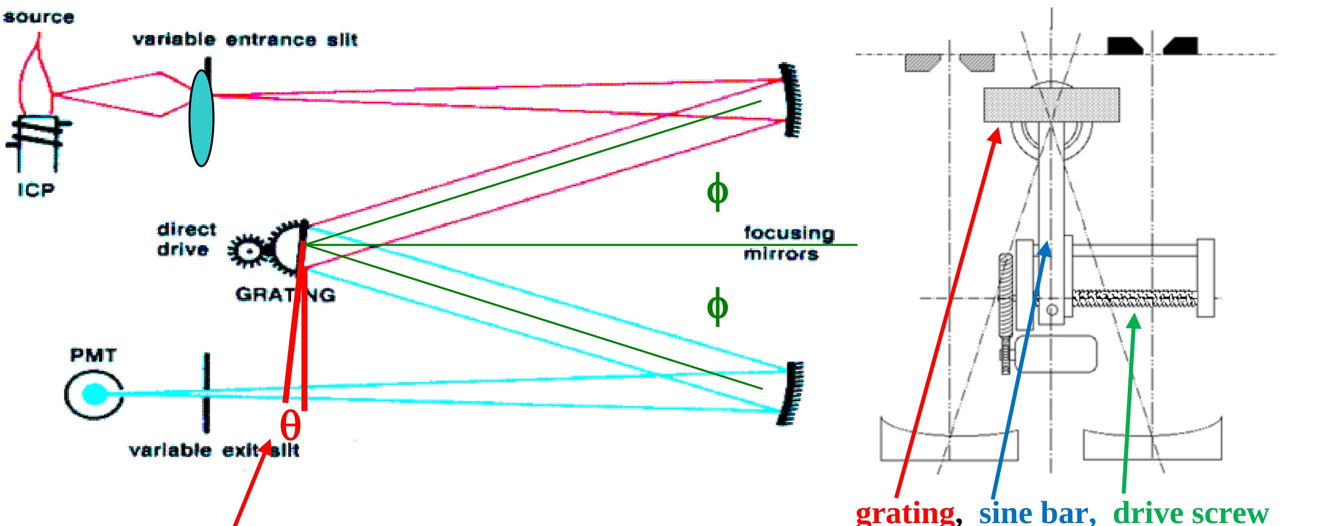
-- closer spaced grooves (small d) — more angular dispersion (*depend on grating*)

-- higher *order*, larger |m|, more dispersion, (large diffraction angles → denom: cos β)

-- linear dispersion: $D_l = f\, D_a = dx/d\lambda = f\, |m|/d \cos\beta$ f - focal length (instr. effect)

Common model system:-- (Czerny Turner, ϕ-fixed, λ~sinθ): often has *Sine bar drive*

$$d\,(\sin\alpha + \sin\beta) = 2d\,(\sin\theta \cos\phi) = m\lambda$$

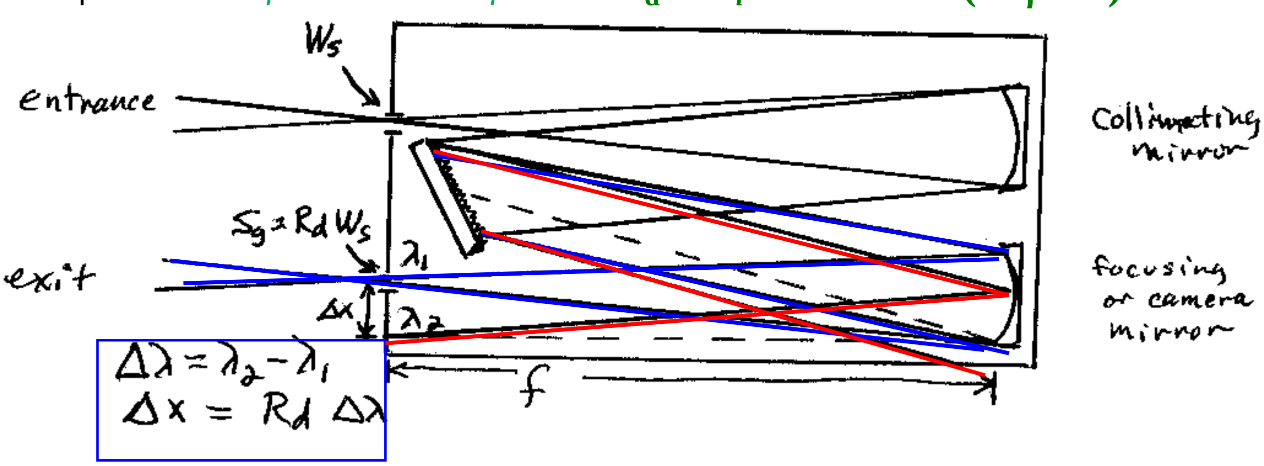


i.e.: $\lambda \sim \sin\theta$ --normal design, turn screw move nut (linear motion, ⊥ grating plane)

this is coupled to arm that rotates (θ) grating, arm will be variable length (hypotenuse)

so linear *motion creates* $\sin\theta$ and is *proportional to* λ

--practical: *reciprocal linear dispersion*: $R_d = D_l^{-1} = d\lambda/dx = (f\, d\beta/d\lambda)^{-1}$

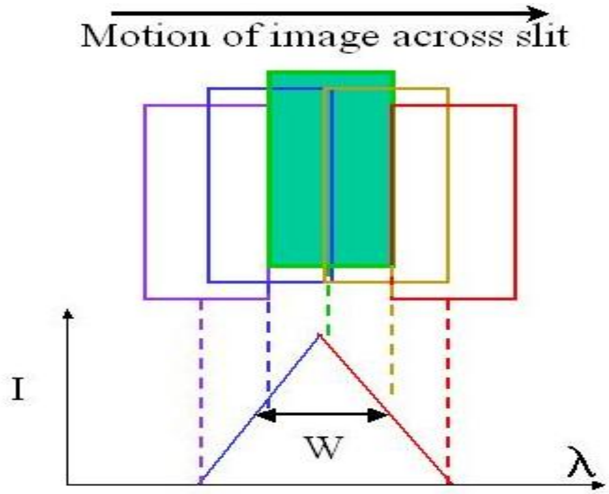


Refocused λ values separate in space by linear dispersion, depends on focal length, f

--*spectral band pass* $s_g = R_d W$ -- W = slit width

-- move image of entrance slit across the exit slit (slide rectangles over each other) result will be a triangle representing the amount of open area vs. the distance moved, i.e.

--triangular slit function: $\Delta\lambda = s_g = R_d W$, *full width at half height*



(text good diagram: fig 3-48)

--normal conditions, get instrument limited triangle shape for spectral line narrow compared to S (e.g. atomic line); for molecule, get broad bandshape

- ideal resolution, separate line (bands) to baseline, $\Delta\lambda = 2s_g = 2R_d W$
- realistic, separate bands to distinguish (sense separate contribution, 2 overlap peaks)
- common statement of resolution, **FWHH ~ s_g**
- very high resolution, can get *Rayleigh dispersion:* $\Delta\lambda_D = \lambda / D_a W_D$, $W_D = W_G \cos\beta$

--Resolving power (theoretical): $R_{th} = \lambda/\Delta\lambda = W_G|m|/d = |m|\, N$

-- Depends on order, m, and # of grooves, N

– consider, more grooves → more interfering wave differences, so more selection between wavelengths to be in phase

- Throughput — aperture diameter: $D_p = [4A_p/\pi]^{1/2}$ where $A_p = A_G \cos\theta$

1. $F/n = f/D_p$ solid angle $\Omega = A_p/f = (\pi/4)\,(F/n)^{-2}$
2. *Limiting aperture* normally is the **grating**—*most expensive component*

– effective size reduced by angle θ, since as turns have less cross section to beam

- *Broadband output*: $B_x W^2 H \Omega T_{op} R_d$ -- varies like W^2 or $\Phi = B T_{op} R_d\, \Omega\, H W^2$
- \- so increased resolution (smaller W) costs light throughput
- *Stray radiation* an important consideration in design (multiple mono better, but sharply reduce throughput) hard to quantify, usually given as $\Phi_{SR}/\Phi_{\lambda o}$

- Solving problems:
- A. if Littrow mount, then $\alpha = -\beta$, β comes back on top of α, but the grating is turned, reference to normal, so values are not zero ($\sin(-\beta) = \sin\alpha$) so: $m\lambda = 2d \sin \beta$
- B. If Czerny Turner, then convert form α,β to ϕ,θ and use: $2d (\sin\theta \cos\phi) = m\lambda$
  - C. Resolution questions will use: $D_l = f D_a = f |m|/d \cos \beta$ **or** $R_d = D_l^{-1}$
  - D. spectral width / bandpass also will show up as : $s_g = R_d W$

Examples — monochromator problems to learn to solve

Imagine an 1800 g/mm grating

$d = 0.555\ \mu = 0.555 \times 10^{-6}$ m

assume $\alpha = 0$, $m = 1$ (1st order)

$m\lambda = d \sin\beta$

for 500 nm (green-blue)

$\sin\beta = 500\text{ nm}/555\text{ nm} = 0.9$

$\beta = 64.2°$

$D_a = d\beta/d\lambda = \frac{|m|}{d\cos\beta} = 1/555(\text{nm}) \cdot 0.436 = 0.00413\ \text{nm}^{-1}$

Solve for a $f = 0.5$ m focal length Czerny-Turner

$D_e = f D_a = 0.00206\ \text{m/nm}^{-1} = 2.06\ \text{mm/nm}^{-1}$

$R_d = D_e^{-1} = 0.484\ \text{nm/mm}$

So if you want a resolution of 0.1 nm at 500 nm

$\frac{0.1}{500} = \frac{\Delta\nu}{20000\ \text{cm}^{-1}} \Rightarrow \Delta\nu = \frac{2000}{500} = \frac{20}{5} = 4\ \text{cm}^{-1}$

Slit: $S = 0.1\text{ nm}/0.484\ \text{nm/mm} = 0.206$ mm

Spectral Bandpass $\boxed{S_g = R_d W}$ W = width of slit

ex: if W = 0.1 mm

$S_g = 0.484 \cdot 0.1 = 0.048$ nm

at 500 nm (20000 cm^{-1}) ~ 2 cm^{-1}

Holographic grating production, interfering, parallel monochormatic laser beams

requires imaging optics, stable conditions

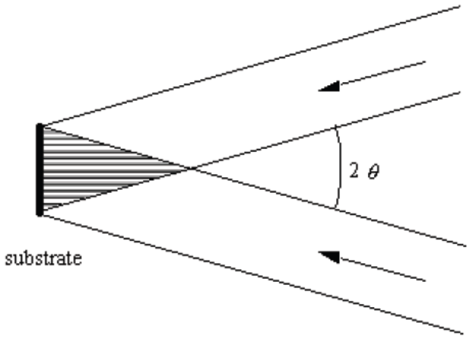


Figure 4-1. Formation of interference fringes. Two collimated beams of wavelength λ form an interference pattern composed of straight equally spaced planes of intensity maxima (shown as the

fringe separation d = λ/(2 sinθ)

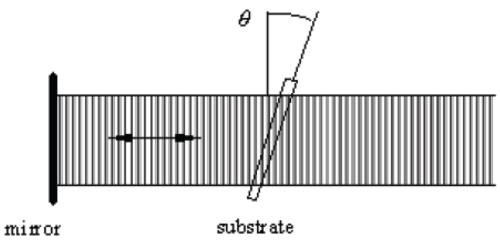


Figure 4-2. Sheridon recording method. A collimated beam of light, incident from the right, is retroreflected by a plane mirror, which forms a standing wave pattern whose intensity maxima are shown. A transparent substrate, inclined at an angle θ to the fringes, will have its surfaces exposed to a sinusoidally varying intensity pattern.

depth of groove: h = λ/2n

λ wavelength recording light, n index of photoresist,

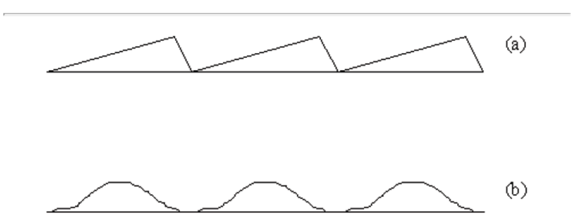


Figure 4-4. Ideal groove profiles for ruled and holographic gratings.. (a) Triangular grooves, representing the profile of a mechanically ruled grating. (b) Sinusoidal grooves, representing the profile of a holographic grating.

can enhance holographic profile to blaze, and can subsequently ion etch, at an angle to ablate just part of groove

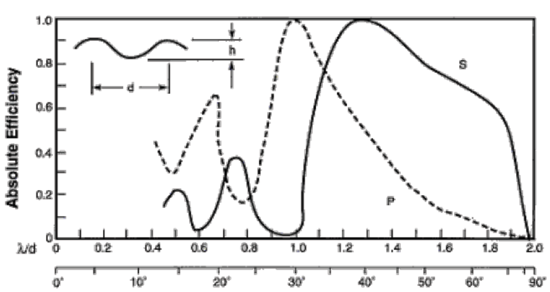
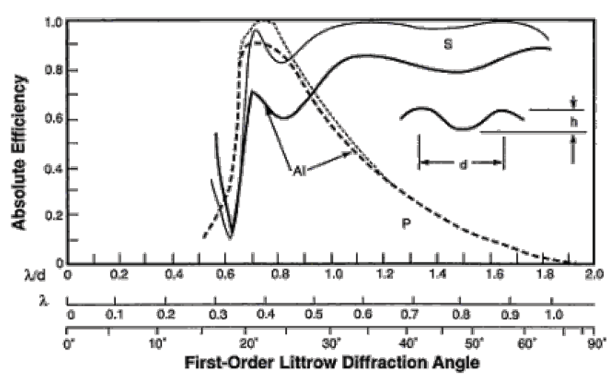
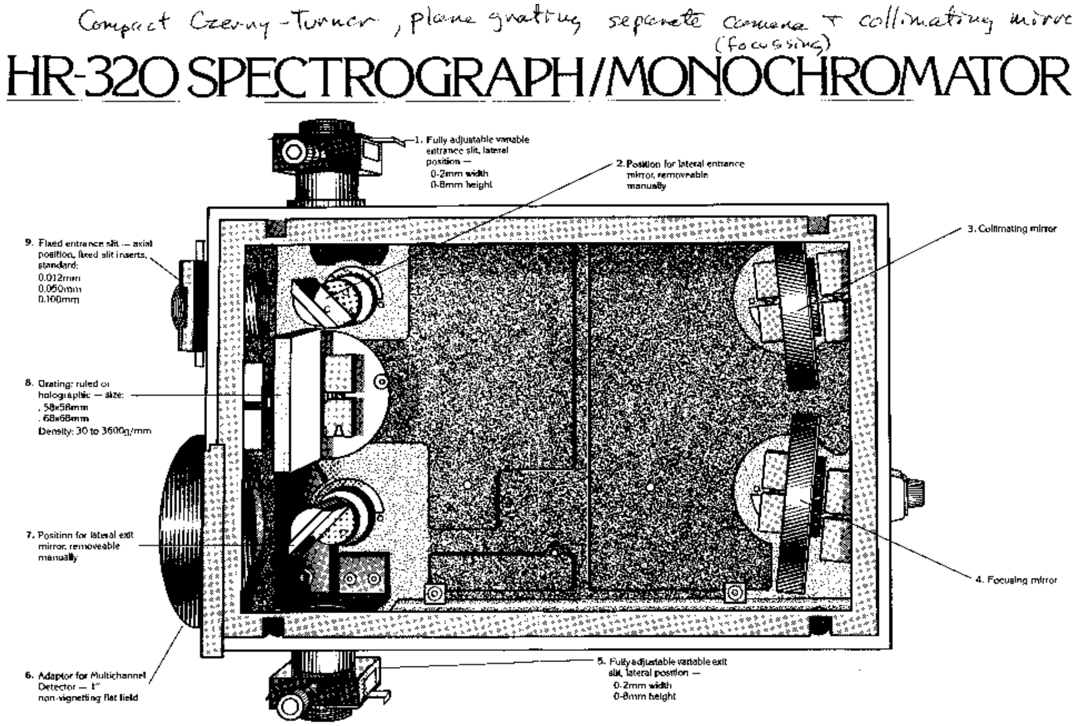


Figure 9-18. Second-order theoretical efficiency curve: sinusoidal grating, μ = 0.36 and Littrow mounting. Solid curve, S-plane; dashed curve, P-plane.



“blaze” of holographic grating, more evident in second order (left)

Models/designs (not all links work, see text for old designs, **see links below to instrument companies for newer ones**): Czerny Turner, Ebert, Littrow, Roland Circle, Echelle, Concave gratings, transmission gratings, multiple grating, double monochromators (subtractive and additive dispersion)--often used additively for Raman spectra to reduce scattered light. and increase resolution in visible

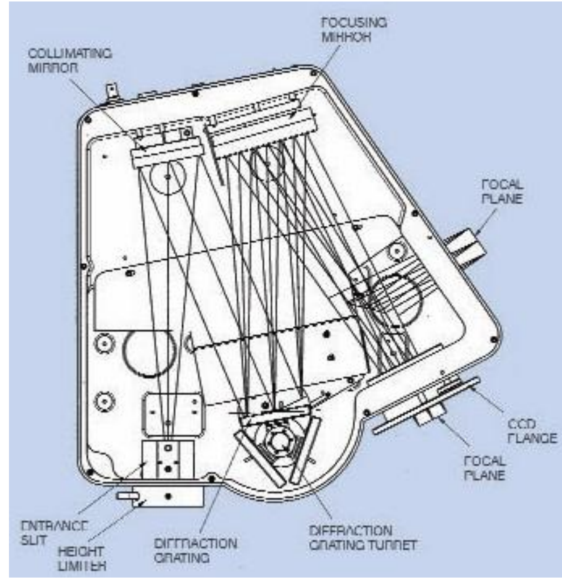


Compact Czerny-Turner, plane grating, collimating mirror illuminates grating, focusing (camera) mirror puts image of entrance slit but dispersed by wavelength light at exit slit, *extra mirrors* let you choose slit, out → front or in → side (J-Y/Horiba)

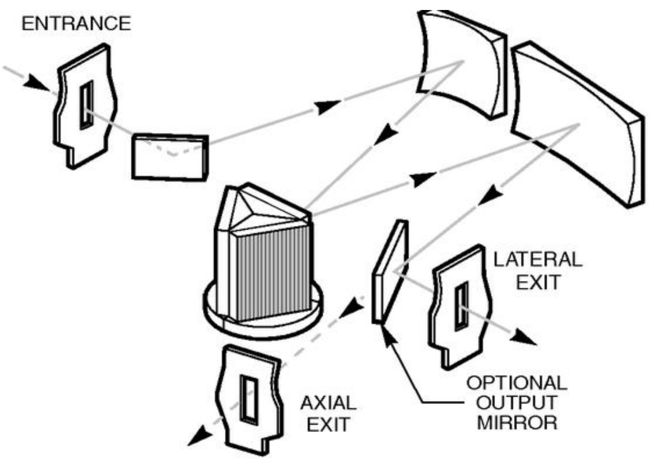
- Computer controlled, interchangeable multi-grating turrets for extended spectral coverage
- Image corrected optics provide superior imaging quality for multi-track applications
- Stepping motor scanning system with microprocessor control provides superior precision and repeatability of wavelength positioning

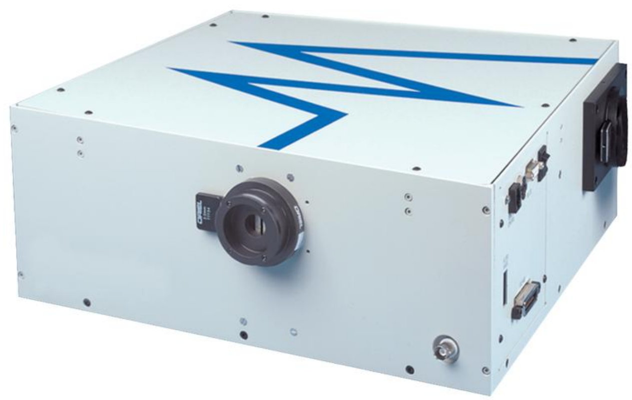
(Acton Research – Princeton Instr.)

with turret, one can interchange gratings to get better or worse resolution
– requires larger separation entrance and exit which can create risk of astigmatism.
--So J-Y series have corrected optics

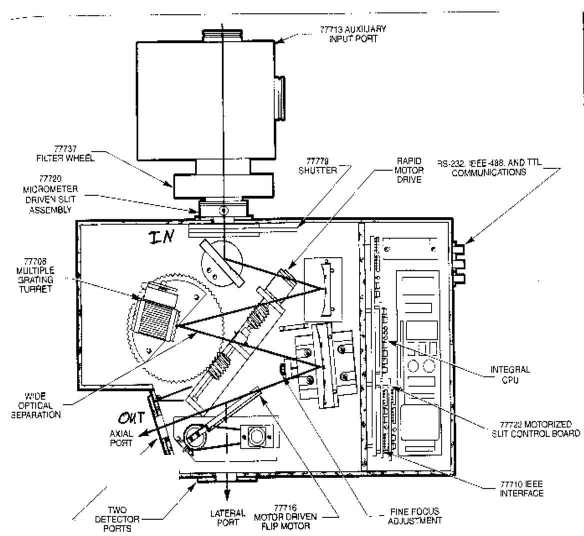


Newport selection includes Czerny-Turner with turret, at ¼ m focal length— compact design





Can be very long – this J-Y goes up to 1.25 m



ig. 1 MS257™ Monochromator/Spectrograph with selected optional accessories.

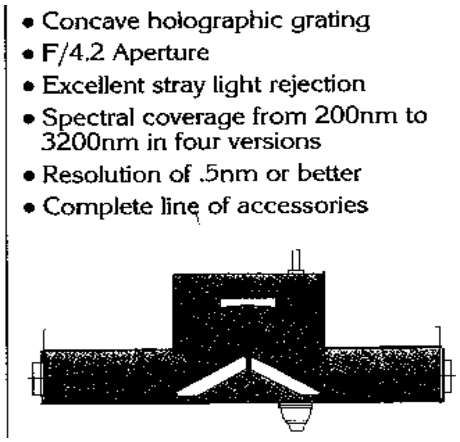
FULL FEATURED SYSTEM...
MS257™ is a generation ahead of the traditional 1/4 m ıonochromator. Look at what you can get with the standard and optional accessories...

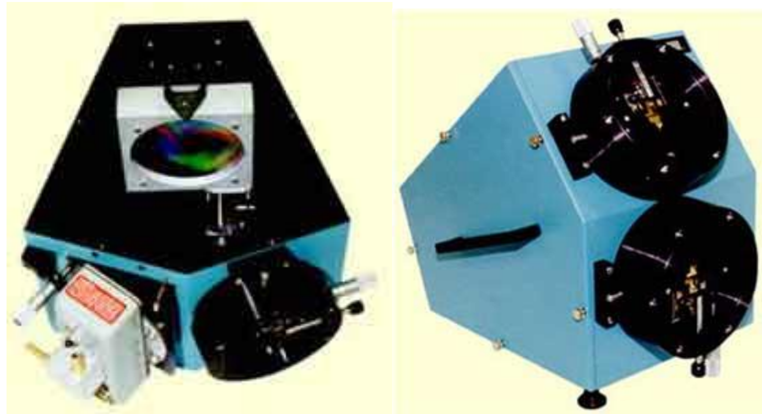
itandard Accessories

APPLICATIONS
- UV to IR measurements
- Absorption, Reflection and Transmission
- Radiometry and Photometry
- Emission and Fluorescence
- Multichannel Spectroscopy (PDAs and CCDs)

to right is an alternate turret design,

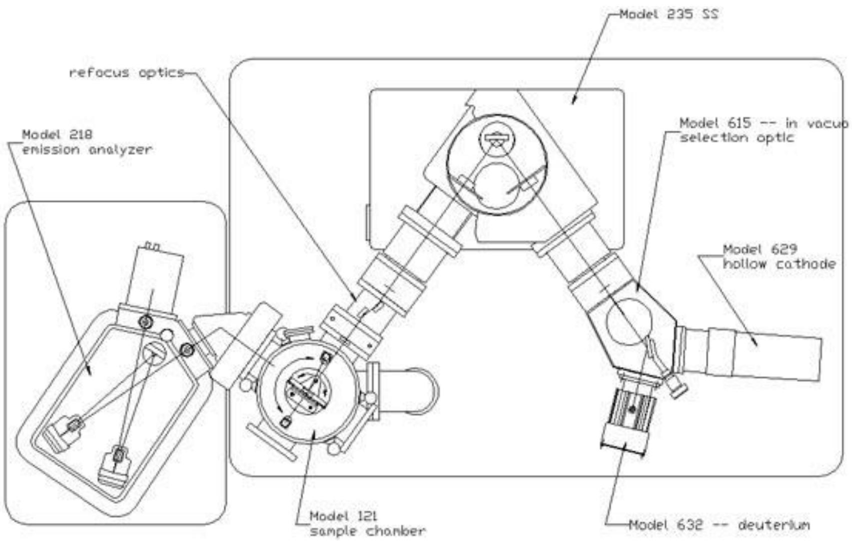
4 gratings with vertical rotation





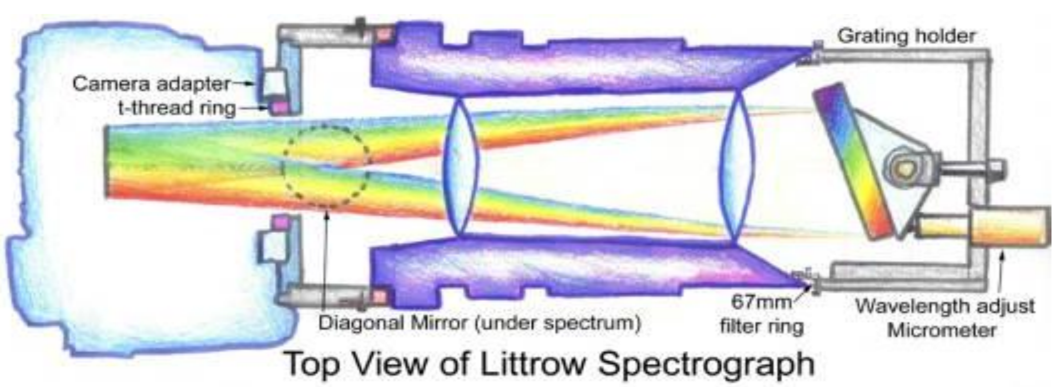
(Jobin-Yvon/Horiba) (McPherson)

Concave grating focuses, not Czerny Turner,(left) mirrors steer beam, (right) just use grating



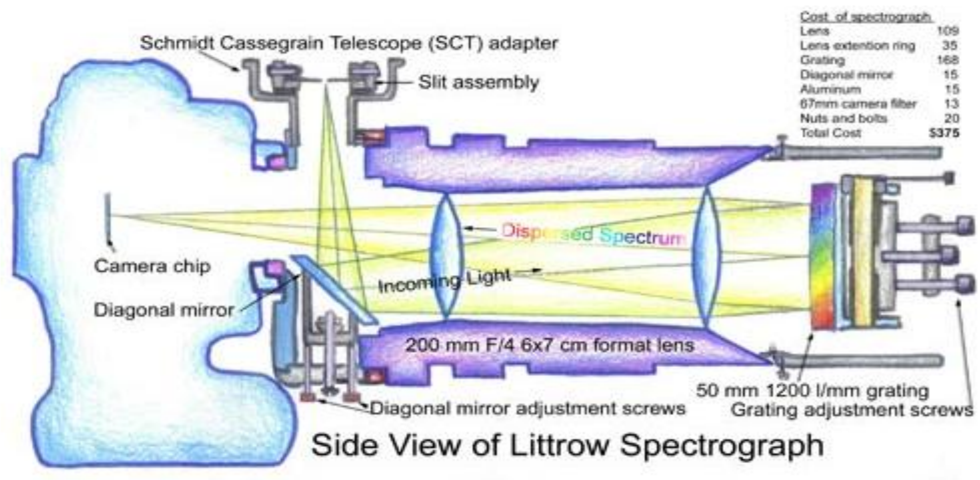
Seya Namioka design -- Vacuum UV, minimize reflections, vacuum enclosure (McPherson)

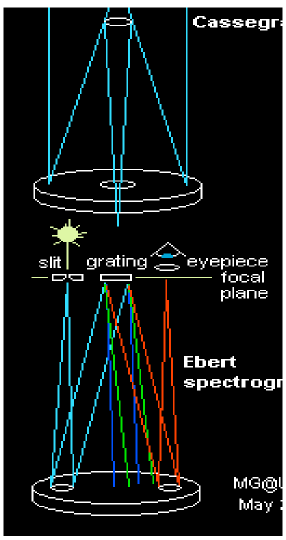
Classic designs

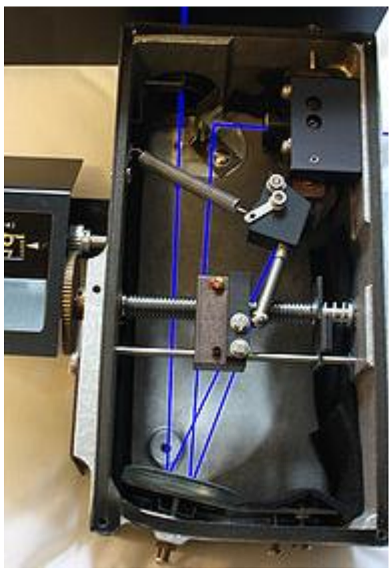


As grating turns, beam comes back on itself for selected λ, so offset vertically to detect,

Light comes in from below and out over input to camera, see side-view below







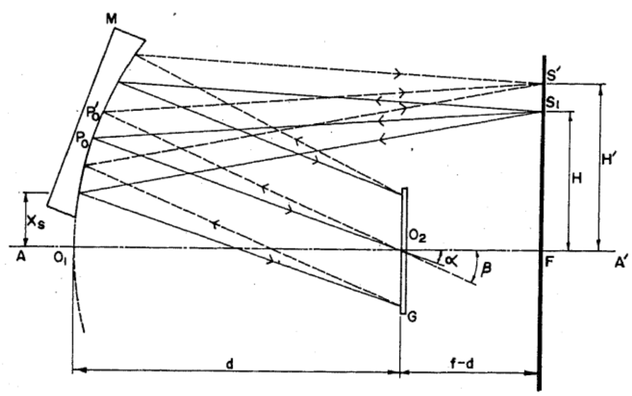
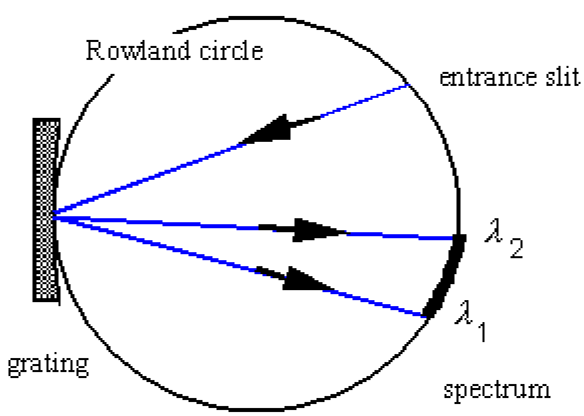
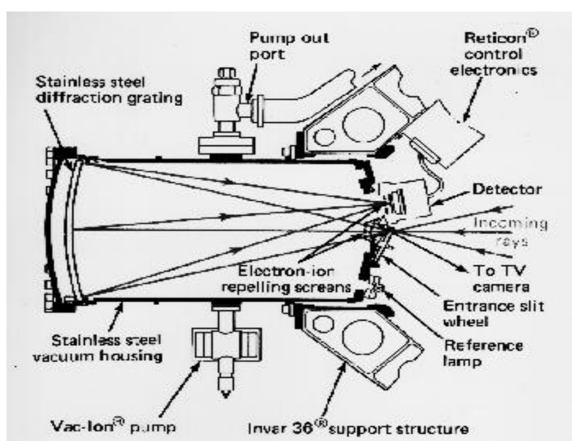


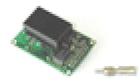
Figure 7. Schematic diagram of the practical spectrograph using the off-axis concave *M* and the holographic grating *G*.

Ebert design uses one focusing mirror, can be a Littrow setup (center, right), or can be two parts of the same mirror (left, sort of like Cassegrain) for collimating and for focusing

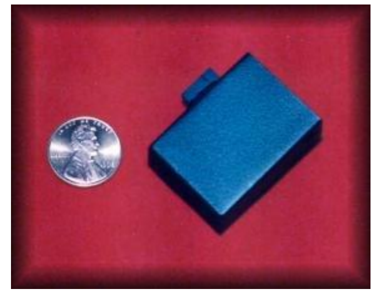




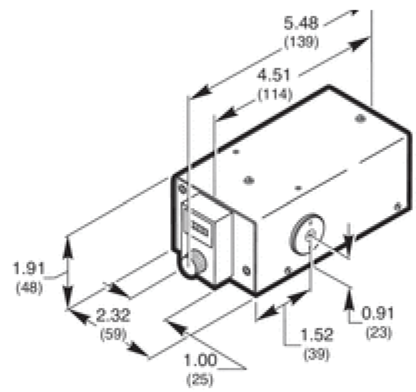
Rowland Circle is a classic idea where entrance slit is focused at different points along a circle. So detector must move of be spatially sensitive (like film can curve). Some are super high resolution, size of a room.



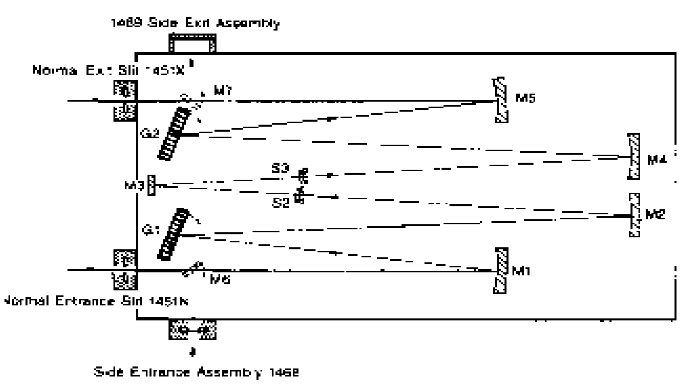
Miniaturization is a big thing now (top left J-Y) (Ocean optics and others)



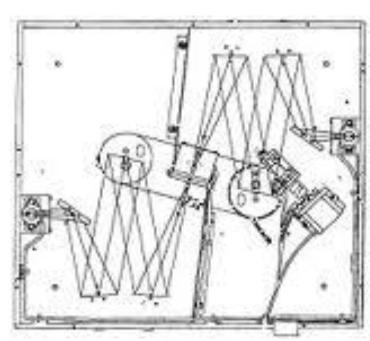
Compact design 60 x 140 mm (Oriel/Newport)



Or they can be very large, like a double 1 m from J-Y / SPEX



Double C-T monochromator, reduce stray light, (add) increase resolution or (subtr) makes a bandpass filter



Double monochormators, increase resolution, reduce scatter light, or filter (old Raman)

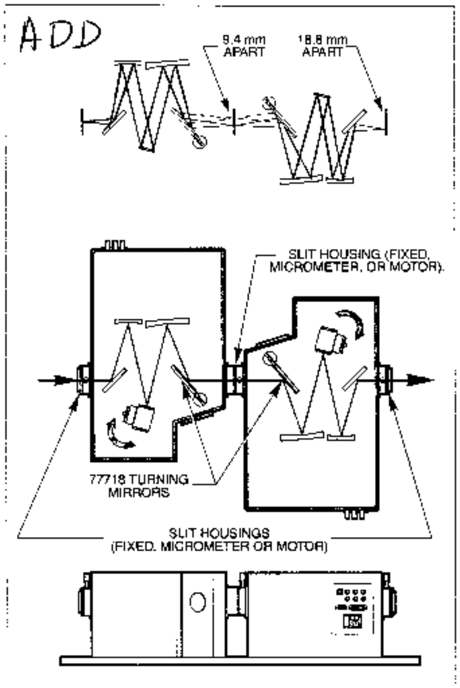


Fig. 14 Simulated ray trace and schematic diagram for Double MS257™ in additive configuration, model 77719.

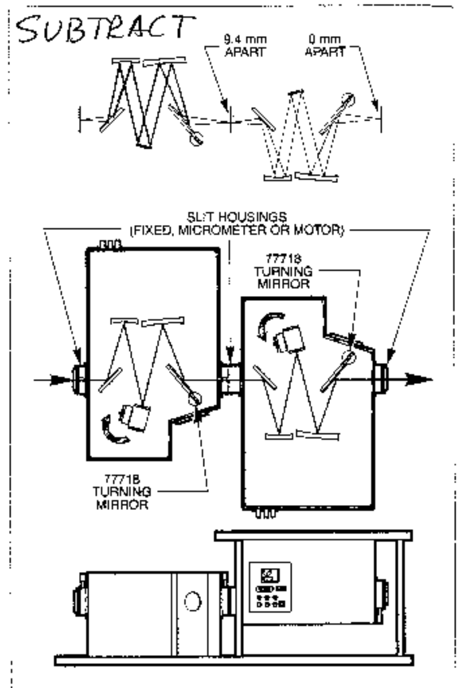


Fig. 15 Simulated ray trace and schematic diagram for Double MS257™ in subtractive configuration, model 77715

ADDITIVE CONFIGURATION

The resolution limit of an additive double monochromator is slightly better than a single monochromator. The additive configuration is illustrated in Fig. 14. In this case, the output spectral band from the first monchromator is dispersed again by the second monochromator. Ignoring all aberrations, an additive double monochromator should provide twice the dispersion of each single monochromator. That is to say, a double 1/4 m monochromator should have dispersion equivalent to a 1/2 m monochromator using the same grating. In practice this is never quite possible because system aberrations, alignment, and synchronization slightly deteriorate the resolution of a double monochromator.

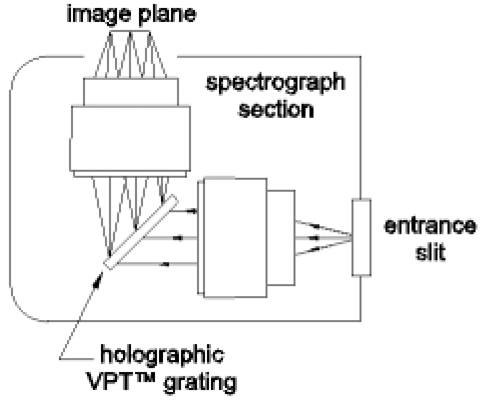
SUBTRACTIVE CONFIGURATION

Subtractive dispersion refers to the homogenizing of the spectrum which occurs within the second monochromator. Usually, the output band of a monochromator is a narrow slice of spectrum, changing slightly in wavelength from one side of the band to the other. In a subtractive dispersion configuration the spectrum passed through the central slit by the first monochromator is mixed at the exit slit of the double system. Theoretically, double monochromator instruments in subtractive configuration have only the dispersion of the first single monochromator. Again, there is some deterioration from this theoretical limit due to system aberrations, alignment, and synchronization. The resolution limit of a subtractive double monochromator is slightly worse than a single monochromator.

Lens based focusing, imaging spectrographs:

-
- Easy wavelength adjustment for 650nm to 830nm laser excitations
- Unique f/2 lenses with proprietary coatings from Acton Optics, providing > 99% throughput
- Optional integrated Raman filter for effective laser line filtering
- 5 cm^{-1} resolution accommodates most NIR Raman applications (Princeton Instr.)

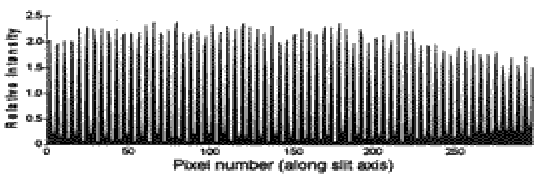
Transmission grating based design, (Kaiser Optical)



The HoloSpec™ *ƒ*/1.8 holographic imaging spectrograph provide high throughput due to aperture ratio of *ƒ*/1.8 - well-suited to visible or fluorescence spectroscopy, or Raman with filtering of Rayleigh scatter

The optics employed in the HoloSpec™ spectrograph achieve thorough aberration correction across a large field along both the slit axis and the wavelength axis.

HoloSpec *ƒ*/1.8i



Typical 0.25 m Czerny-Turner Spectrograph

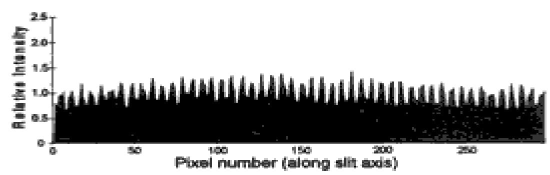


Image Data graphically illustrating the superior image quality achievable by the HoloSpec *ƒ*/1.8i over the entire area of a commonly used CCD camera.
Graphs are image cross-sections of a 250 line/inch Ronchi ruling taken at the edge of a 26 mm x 6.7 mm CCD having 23 micron pixels, illuminated at 543.5 nm.

Homework, part of set #2 – read Chap. 3-5,6 as a minimal start. Read from the Richardson Grating book, see links below, and the web sites by JY and/or wikipedia

Discussion: Chap 3--#9,25,28, 30

1. why are prism monochromators not used in general spectroscopy?
2. why do prism monochormators have an advantage in the far UV?
3. Why do you want high density (small d spacing) gratings for UV but low density ones for IR?
4. What advantages do holographic gratings have over ruled ones? why?

Problems to hand in: Chap 3: 3 (previously assumed $\phi=7^o$), 20-21-22
practice: (#s : 15-16-17 and 20-21-22 are very similar, hand in only the second one)

Link to grating manufacturers (not checked)

Richardson Grating Lab, formerly Bausch and Lomb, now apparently part of Newport Optical
Historically they have produced a ***very useful book*** on grating use and design, worth reading, download at:

http://gratings.newport.com/information/handbook/handbook.asp

Jobin-Yvon (French) now with Horiba (Japanese)

http://www.jobinyvon.com/usadivisions/gratings/gratings.htm

Check out their explanatory grating tutorial page

http://www.jobinyvon.com/usadivisions/OOS/oos1.htm

Gratingworks, smaller sizes

http://www.gratingworks.com/

Grating Calculator

http://xraysweb.lbl.gov/SCIrick/QuickCheck/Mono/mono.html

Brief explanatory web site with lots of links to physics principles

http://en.wikipedia.org/wiki/Diffraction_grating

Links to monochromator topics

Tutorials:

Nice page on "Heath" monochromator, point being what were the design considerations used to build it

http://www.stolaf.edu/people/walters/narrative/mono.html

Brief explanatory page on monochromators

http://en.wikipedia.org/wiki/Monochromator

Companies

McPherson—higher specs, vacuum capability avalable

http://www.mcphersoninc.com/

Jobin-Yvon, Spex, Instruments ISA

http://www.jobinyvon.com/usadivisions/OSD/currentmonos.htm

Acton Research

http://www.acton-research.com/catalog/list.php?s=i&c=SpectraPro

Oriel, now Newport, has spectrometers and monochromators

http://www.newport.com/Spectroscopy%20Instruments/1/productmain.aspx

OLIS makes spectrometers for specific purposes, but some use the clever rapid scan DeSa monochromator

http://www.olisweb.com/products/rsm/components.php

Simple monochromator used in a PTI fluorimeter, links to a very nice manual

http://www.pti-nj.com/obb_5.html

Mini-monochromator, 74 mm, with Fastie-Ebert mount, from Optometrics

http://www.optometrics.com/prod/fr_mono_sys.html

Ocean Optics, mini monochromators

http://www.oceanoptics.com/