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Inspiring Excellence

AA Optics

Spectrometer

- Collimates light from hollow cathode
- Isolates analyte wavelength
 - From other lines
 - From broad band emissions

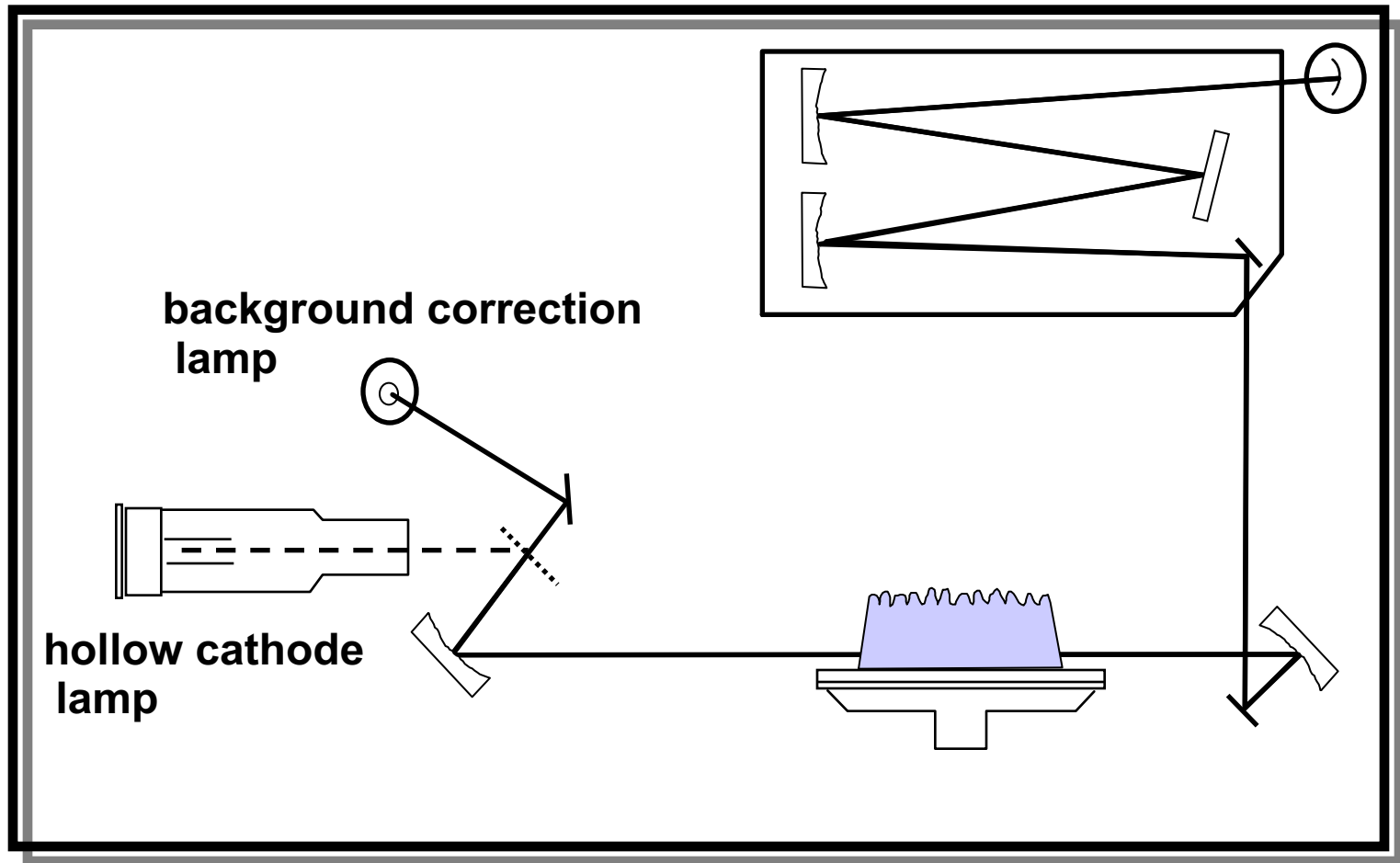
Detector

- Measures light absorbed by analyte atoms
- References absorbed intensity to initial lamp intensity



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Single Beam Optical Layout





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Single Beam Optics

Light from the source traverses ONLY ONE path

Must measure I_0 BEFORE inserting sample

Relies on stable light source

- I_0 does NOT drift while it is measured
- Modern hollow cathode lamps sufficiently stable
 - Appropriate warm Up period
 - Element dependent
 - Typically 10 minutes
 - » Exceptions such as P, Ti, Cu/Zn multi-element
- Change in I_0 = change in baseline



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Single Beam Optics

Aging lamps could drift more

- Use frequent recalibrations and reslopes
- Particularly necessary for graphite furnace

High volume graphite furnace work - Zeeman or double beam optics recommended



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Single Beam Instruments

All of the energy from the source passed through sample cell

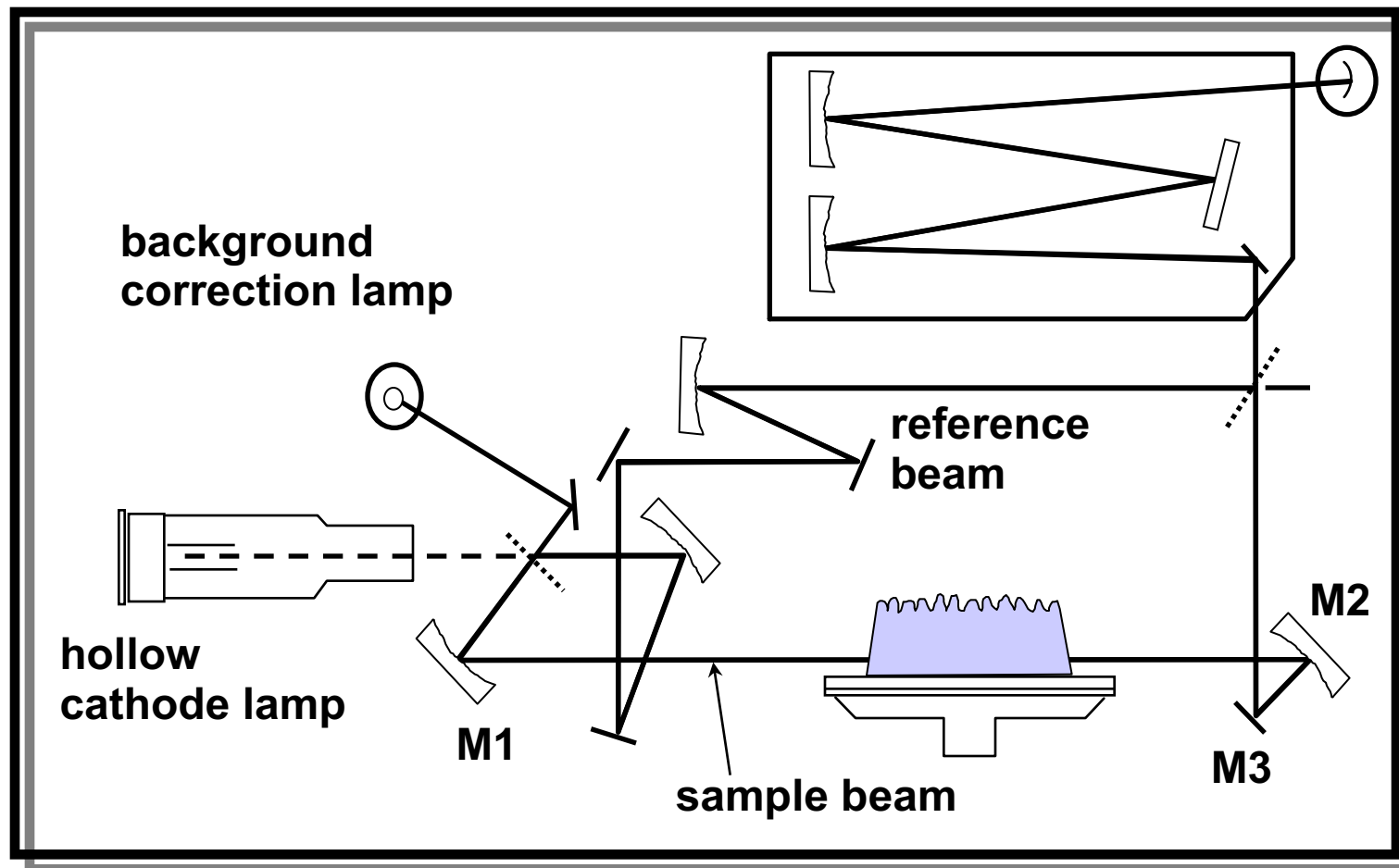
- Good signal to noise ratio
- SLIGHTLY improved detection limits vs double beam

If fitted with deuterium background corrector - same energy as double beam



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Double Beam Optical Layout





Designed to correct for drift in I_0

- NOT LIKE REFERENCE BEAM IN UV-VIS

Light from source is directed at a beam splitter

- Optical component designed to reflect a portion of the light energy and allow the remainder to pass through.
- Normally designed to reflect 50% - pass 50%

Beams recombined before entering monochromator

- Beams must be time separated

Second beam splitter with rotating perforated disk
passing first one beam then the other

- 50% light loss at first beam splitter
- 50% light loss at second beam splitter
- POOR SIGNAL TO NOISE RATIO

Rotating beam combiner (RBC)

- Alternately passes
 - ALL OF REFERENCE BEAM
 - ALL OF SAMPLE BEAM
- BEST POSSIBLE SIGNAL TO NOISE RATIO

Allows intensity (I_0 and I_t) of BOTH reference and sample beam to be measured at high frequency

High frequency monitoring provides near instantaneous corrections for variation in source intensity

Both hollow cathode and deuterium source monitored



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Double Beam Lamp Warm Up

Even with double beam optical design lamp warm up is recommended

- During warm up period emission line profile may change
- Changes in emission profile can cause small changes in the analytical signal



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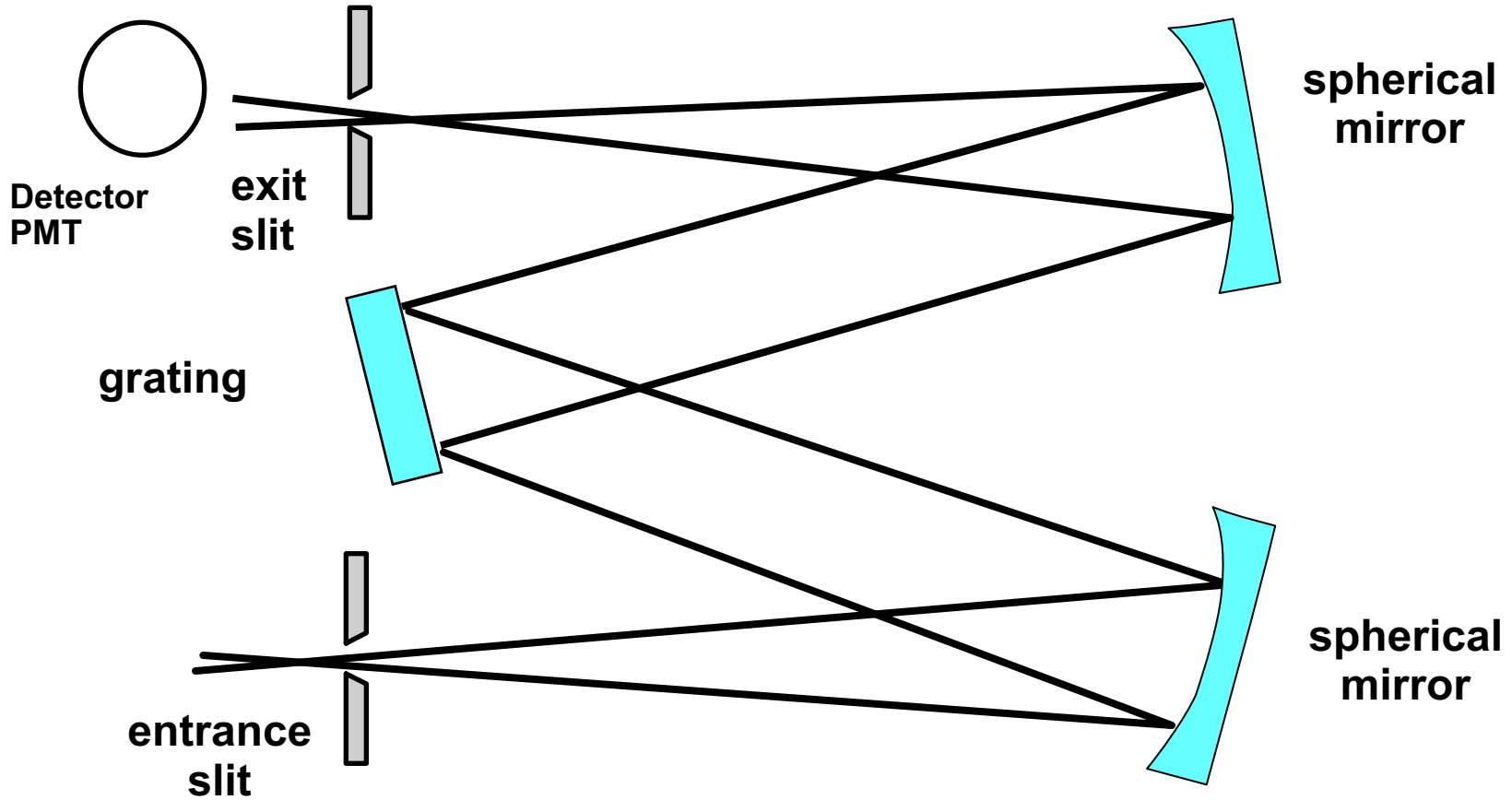
Monochromator Function

Hollow cathode lamp emits many narrow emission lines

Monochromator isolates single resonance emission line from hollow cathode lamp

IDEALLY monochromator isolates **ONLY ONE LINE**

- Sometimes easy – Cu
- Sometimes more difficult - Fe





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Czerny - Turner Monochromator

Uses Two Separate Mirrors

- One to Focus Incoming Light onto Grating
- One to Focus Outgoing Light onto Photomultiplier

Mirrors Have Different Optical Properties

- Reduces Aberrations
- Improves Resolution
- Improves Light Throughput

Mirrors can be Prepared with Great Accuracy



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Diffraction Grating

Heart of monochromator

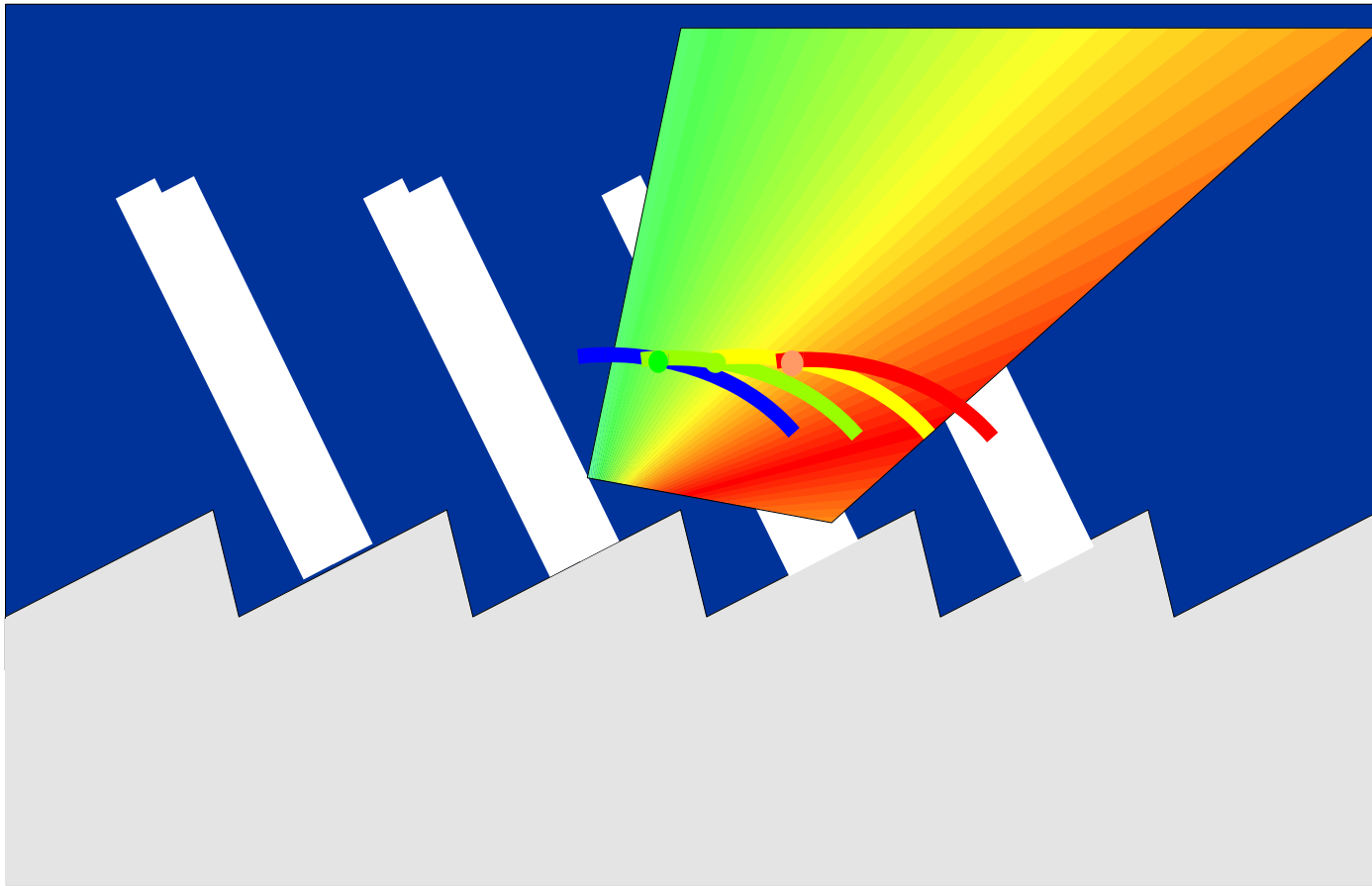
Light focused on grating is dispersed at different angles according to its wavelength

Rotating the grating focuses a specific wavelength on the exit slit



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Spectrum Created by Wave Interference





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Monochromator Resolution

Very important

Very high resolution needed for emission

- Complex spectra generated by high temperature plasma
- < 0.01 nm

“Medium” resolution needed for atomic absorption

- “Simple” spectral output from hollow cathode lamp
- ~ 0.2 nm



Affects spectral isolation of analytical line

- Ability of spectrometer to resolve analytical line from adjacent lines

Normally dictated by nearest adjacent line in spectrum

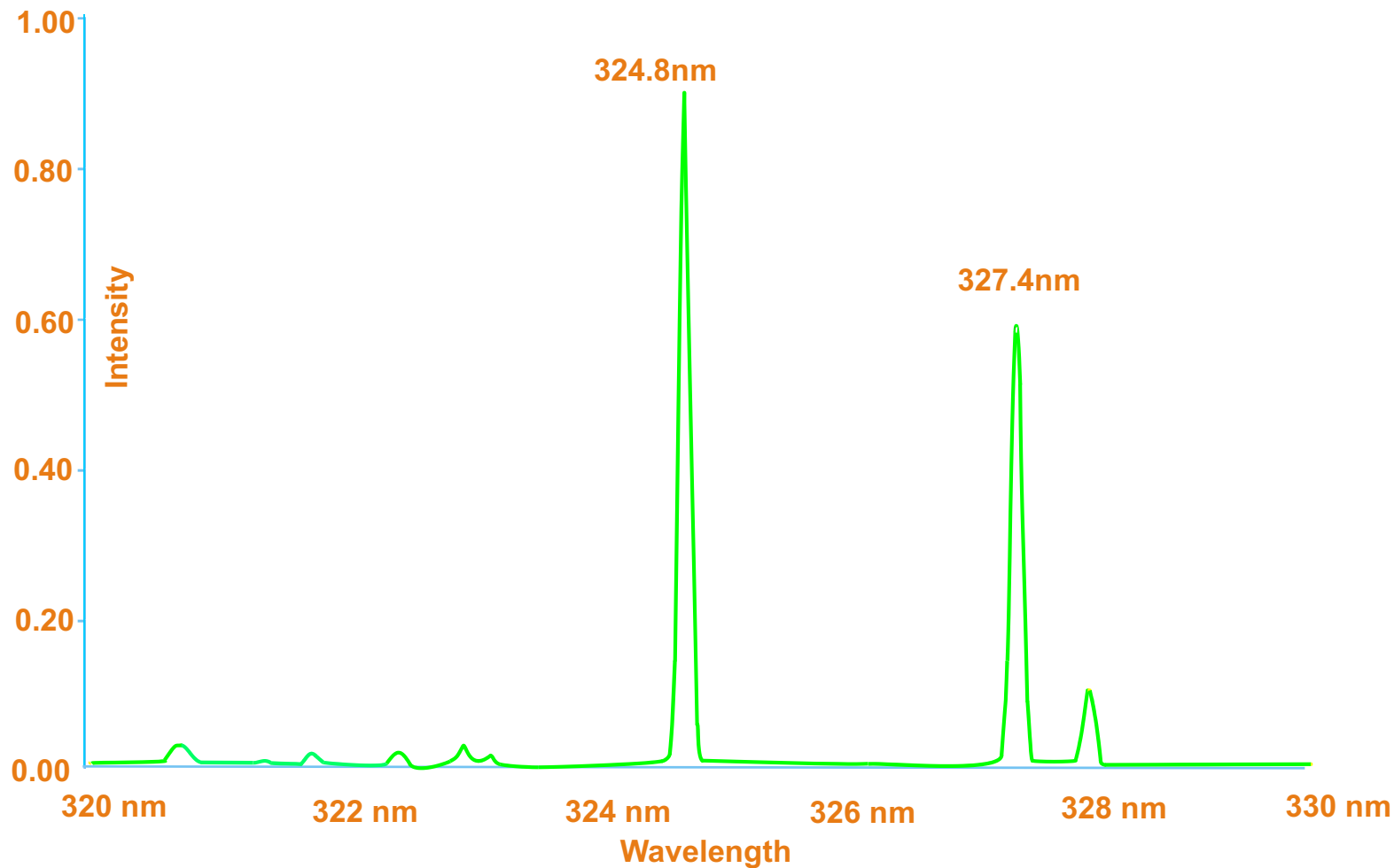
In practice setting slit width is compromise

- Wide slit
 - High energy - good signal to noise
 - Poor spectral resolution - highly curved calibration
- Narrow slit
 - Lower energy - higher noise
 - Good spectral resolution - more linear calibration



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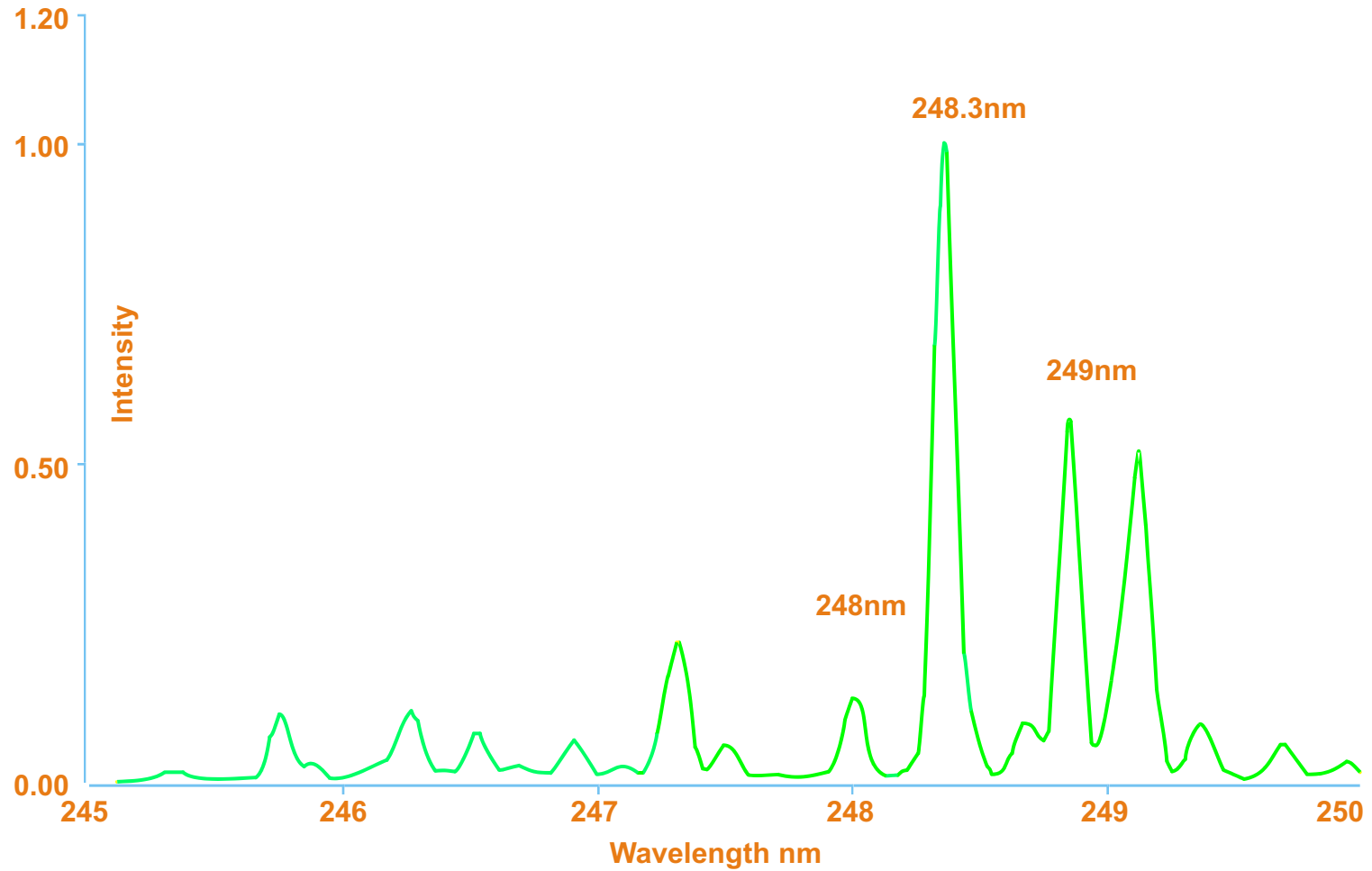
Atomic Spectrum of Cu





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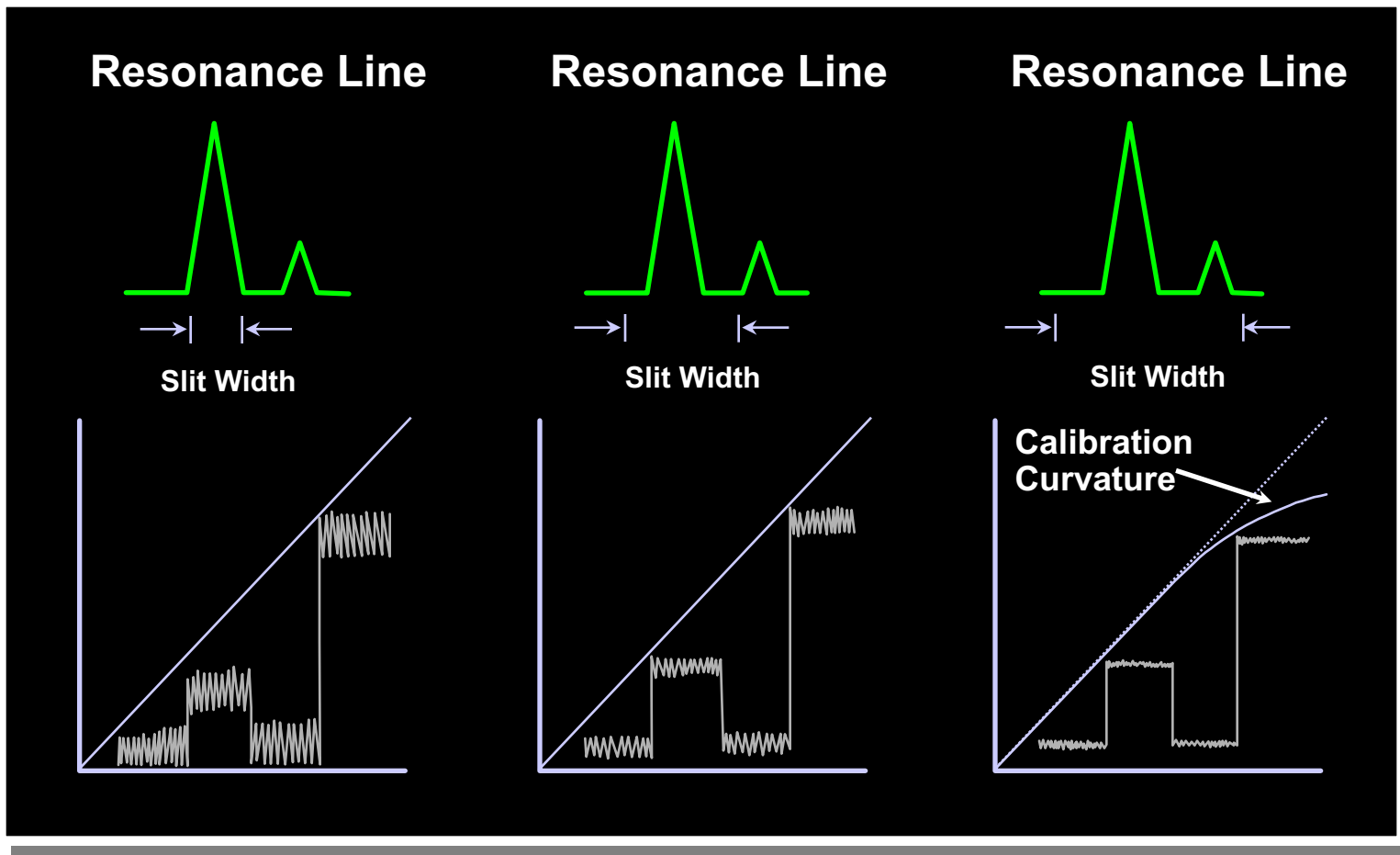
Atomic Spectrum of Fe





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Effect of Spectral Band Width



Detector observes non-analyte emission lines

- Hollow cathode lamp fill gas
- Non-resolved spectral lines



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Detectors - Photomultiplier Tube

Vacuum tube which produces electrical signal proportional to intensity of light reaching it

Light enters a window and falls directly on photoemissive material

Photoemissive material emits electrons

- More light intensity produces more electrons

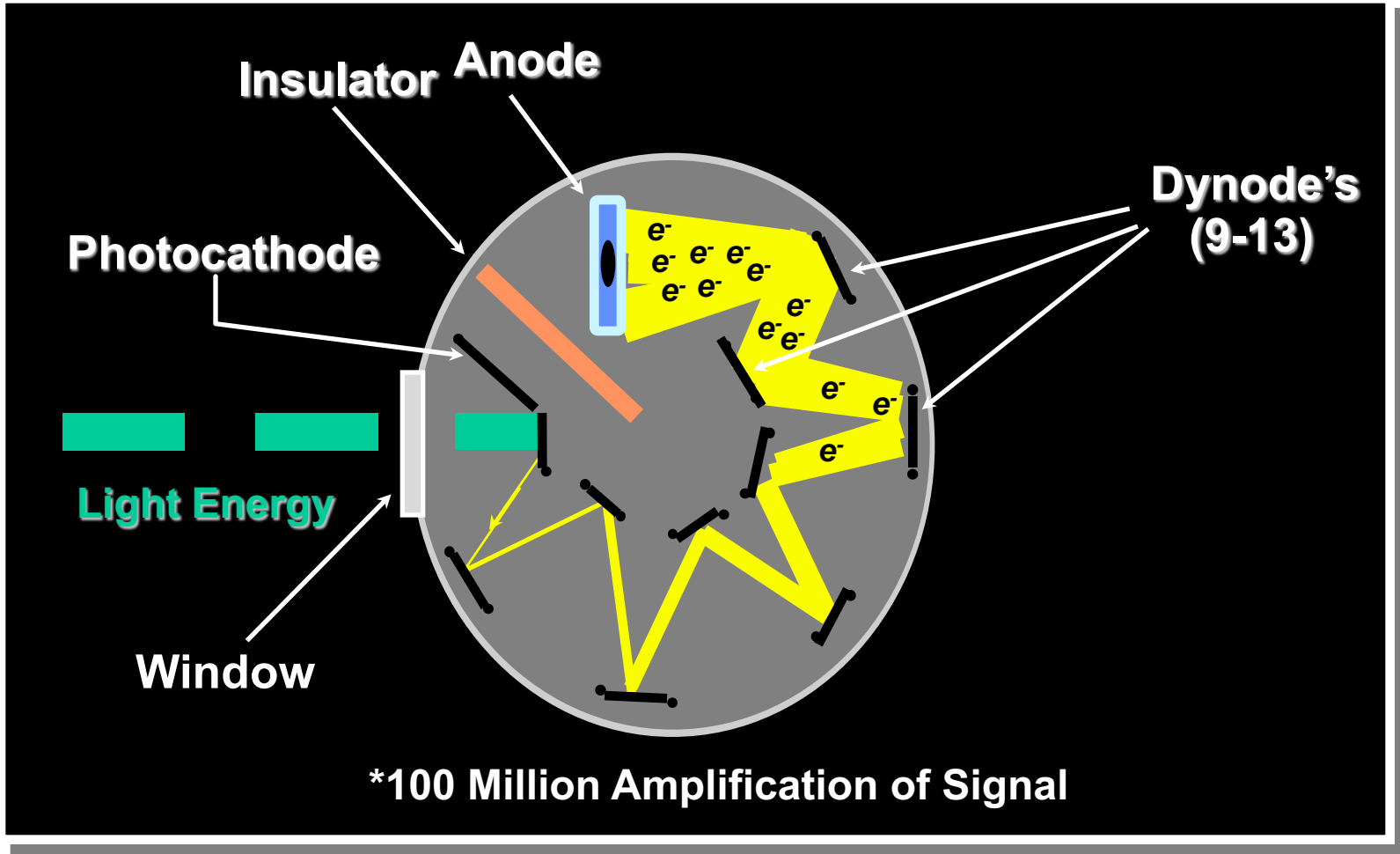
Electrons accelerated to dynodes

Dynodes emit secondary electron for each electron striking it



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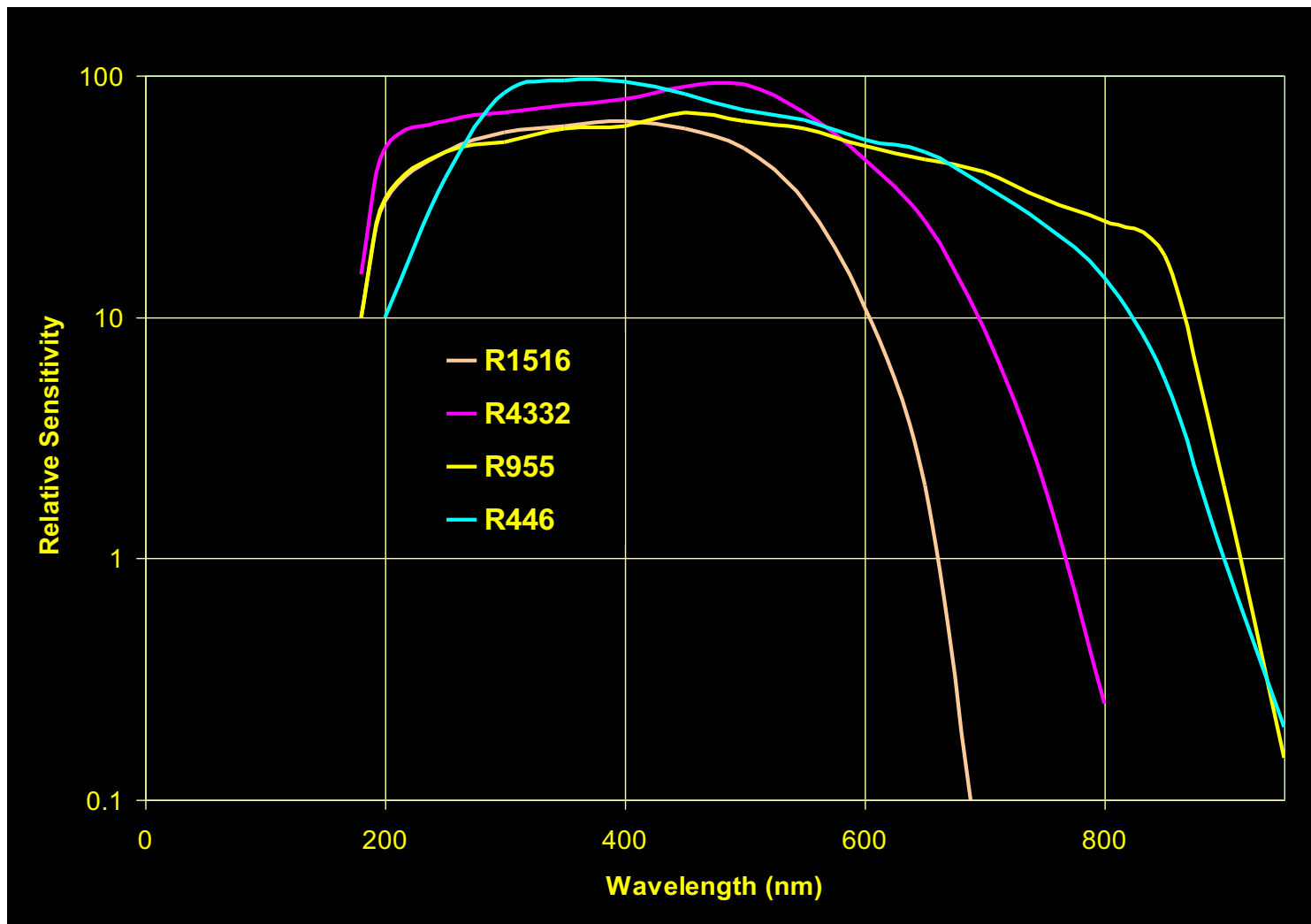
Photomultiplier Tube Operation





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Photomultiplier Response





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Factors Influencing Detection Limits

Detection limit reflects the signal to noise ratio

Factors influencing signal to noise ratio

- Optical design
- Standard deviation of blank
- Analytical sensitivity
- Unlikely to be ANY SIGNIFICANT difference between the detection limits for a double beam and D2 corrected single beam instrument