CEE 772: Instrumental Methods in Environmental Analysis

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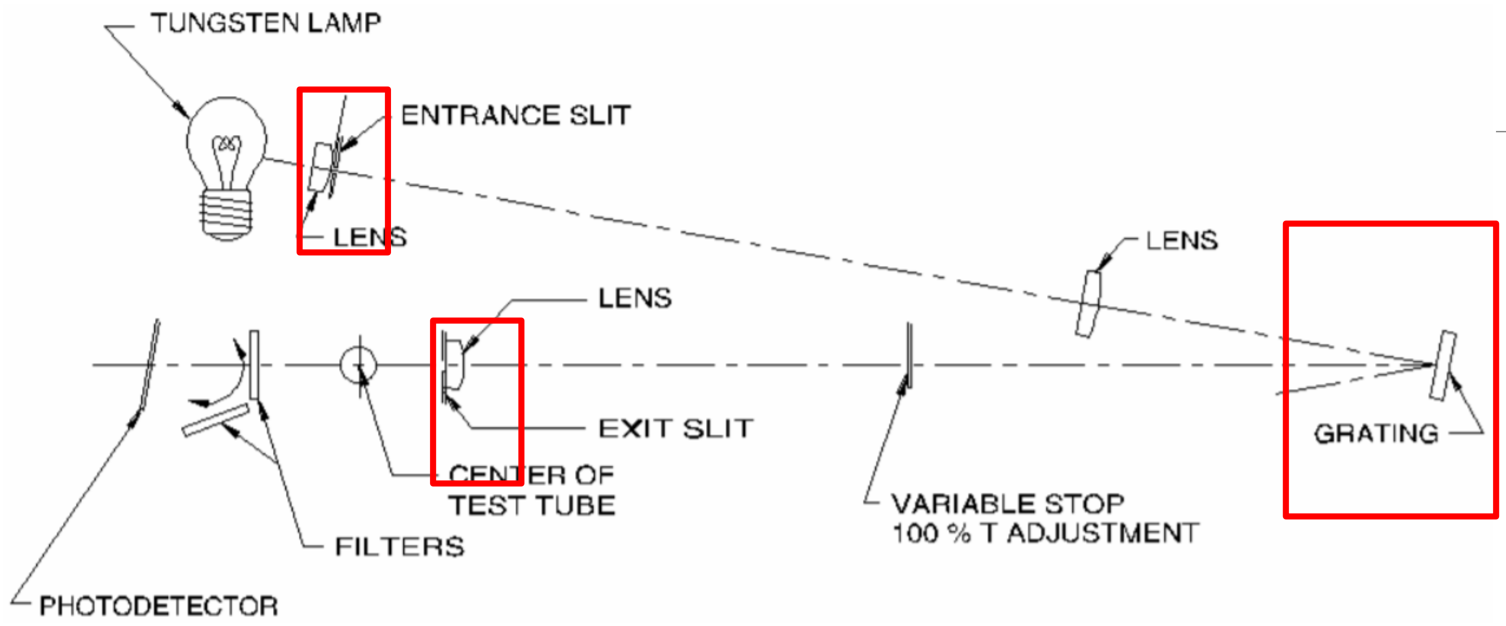
OPTICAL SPECTROSCOPY (CONTD.),SKOOG (4^{TH} ED.), CHA 7

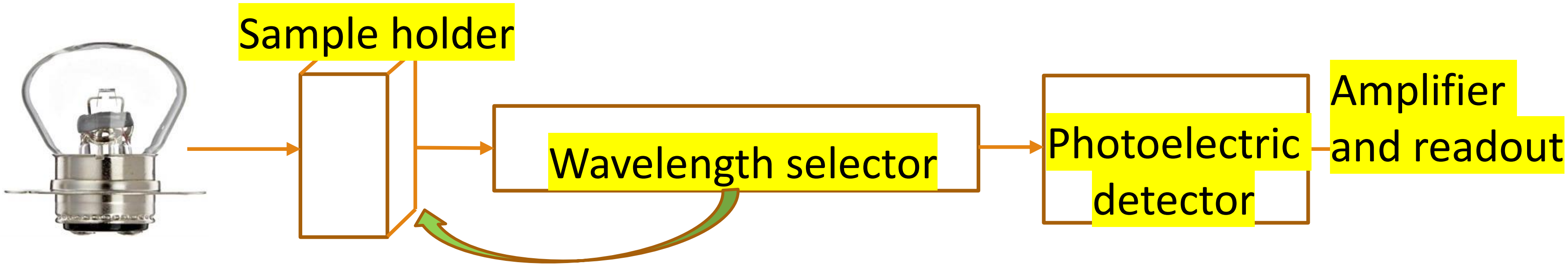
Example of a Simple Spectrophotometer



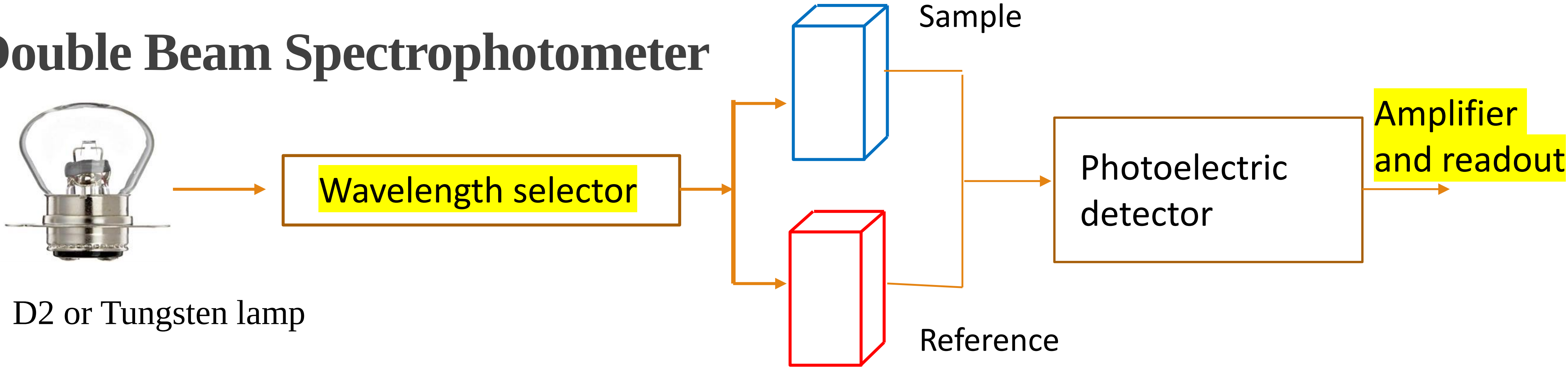
Spectronic 20

340-950 nm (visible range)
Single beam
Spectral bandpass 20 nm
Quantitative at single wavelengths

Single Beam Spectrophotometer

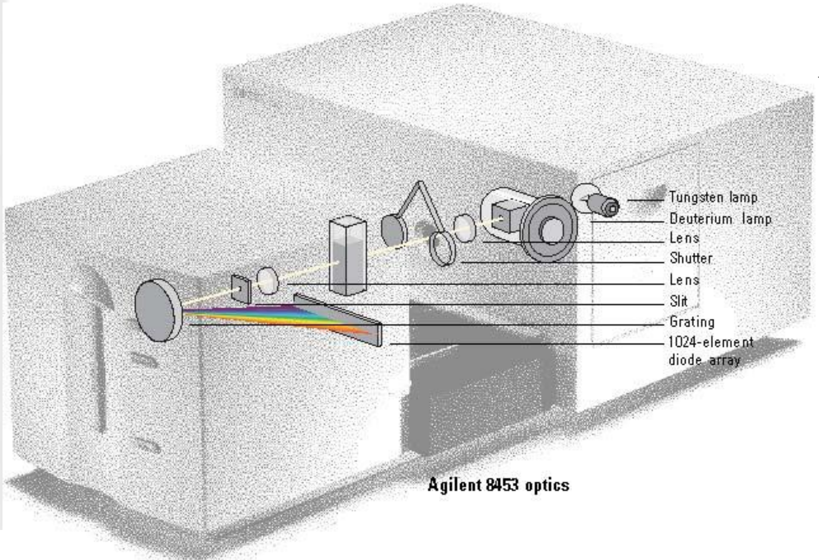


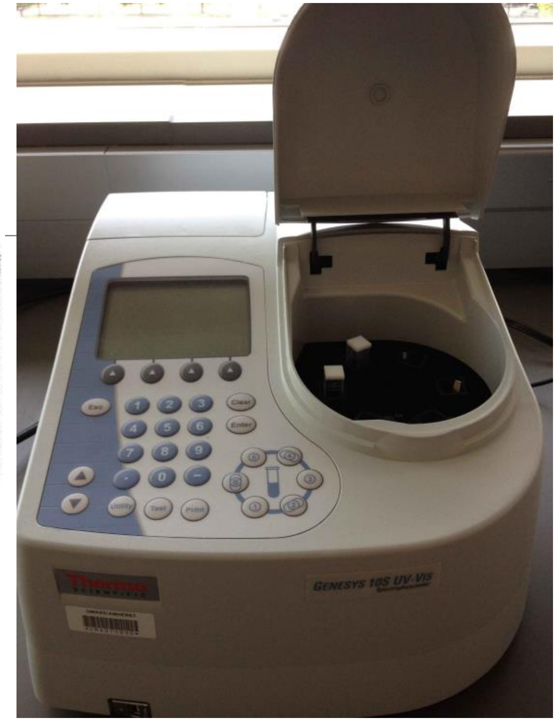
Double Beam Spectrophotometer



D2 or Tungsten lamp

Shimadzu





Shimadzu UV 1900
UV/ Vis- 190-1100 nm
Double beam
1nm bandwidth

Agilent 8453 (~2008)
UV- deuterium
Vis- Tungstan filament lamp

Thermo Fisher, Genesys 10s
UV-Vis

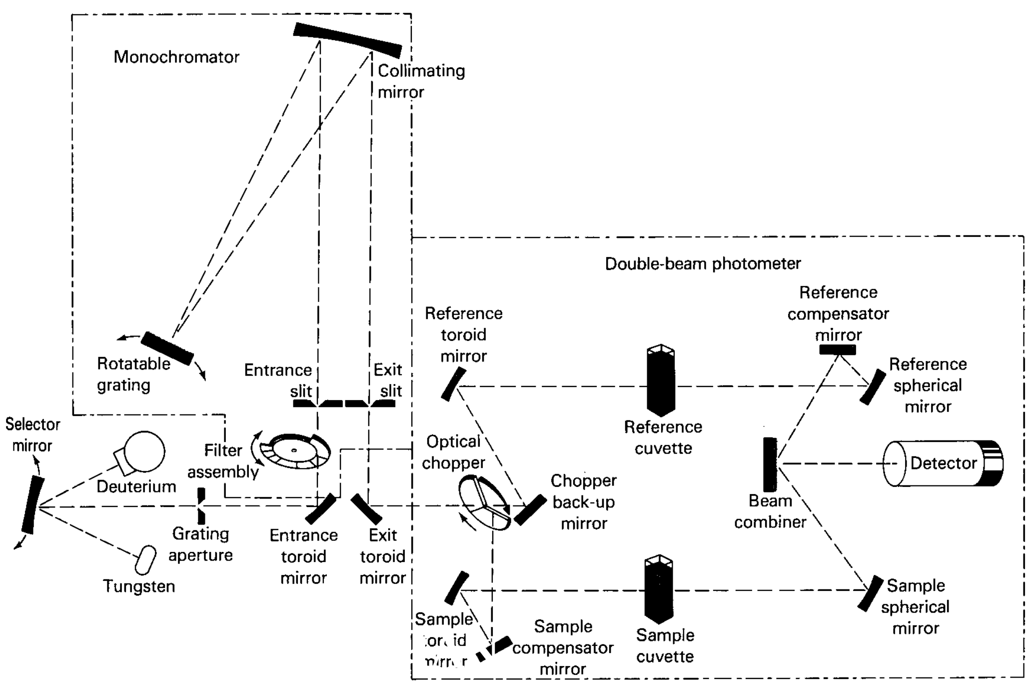
Cary 100 UV-Vis Spectrophotometer
0.2 nm bandwidth
Single, Double or Dual-Single Beam Modes

Features

- **Versatile set of accessories** including temperature control, liquid and solid sample holders, multicell holders, specular reflectance, diffuse reflectance, and fiber optics
- **Large sample compartment** with built-in accessory controller
- **Working range past 3.5 absorbance units** eliminates sample dilution
- **WinUV software** – modular design provides a wide range of applications via a simple interface
- **Variable slit widths** for optimum control over spectral resolution
- **Phase-locked wavelength drive** prevents peak shifts and peak suppression at high scan speeds
- **Sealed optics** with quartz overcoating prevents exposure to corrosive environments and simplifies cleaning
- Software and Informatics

https://www.agilent.com/en/products/uv-vis-uv-vis-nir/uv-vis-uv-vis-nir-systems/cary-100-uv-vis

	Single - beam	Dual - beam
Advantages	-less expensive -High energy throughput (no source splitting, hence better sensitivity)	-Modern improvements permit high level of automation and offer the same or even better level of detection as compared to earlier single beam systems. -Instability factors due to lamp drift, stray light, voltage fluctuations do not affect the measurement in real-time. -Little or no lamp warm up time is required. -Improved results and lamp life
Disadvantages	Instability (no corrections for disturbances like circuit fluctuations, voltage fluctuations, mechanical component's instability or drift in energy of light sources)	Old dual beam instruments re complicated, difficult to align, and expensive to service.

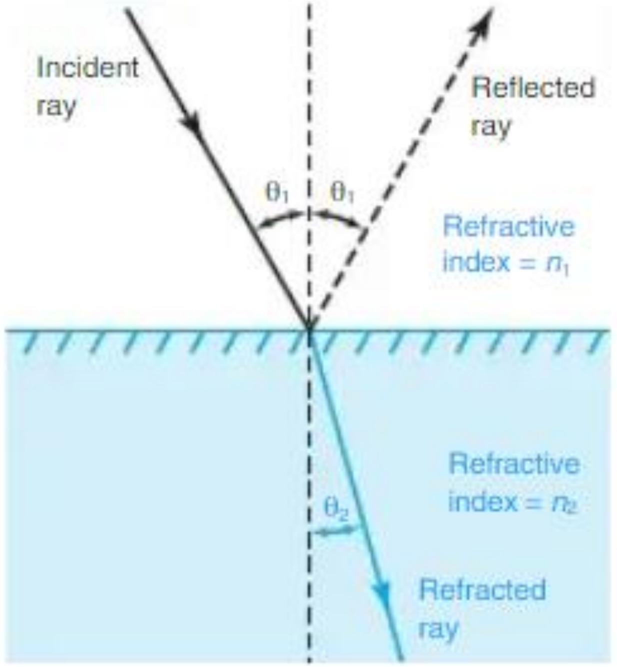


Optodes (Harris, 7th ed., pg. 437; Skoog, 4th ed., pg. 108)

Refraction- Snell's Law

Angle of incidence=angle of reflection

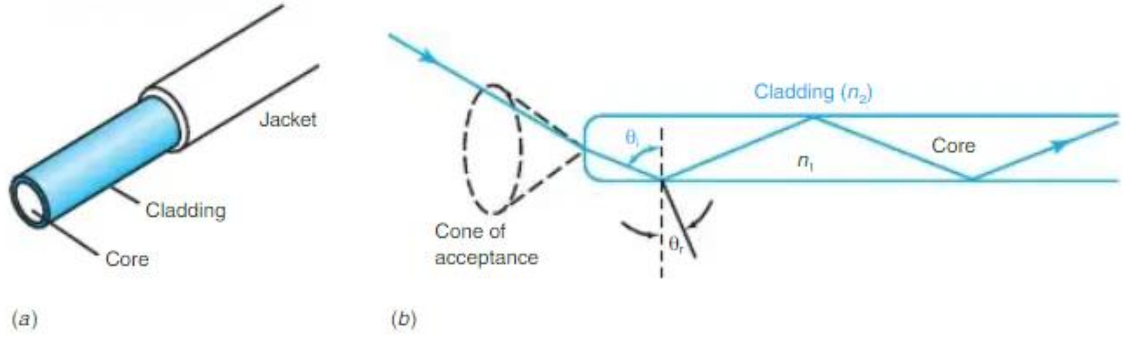
$n_1 \sin \Theta = n_2 \sin \Theta$



Chemical sensor based on optical fiber construction

Constructed by placing a chemically sensitive layer at the end of the fibre (photosensor)

E.g. Sulfites in food, nitric oxide in cells, explosives in GW.



Considerations for selecting a spectrophotometer

Detection limits

Nature of analyte you wish to measure

Wavelength range

Analytical working range

Sample throughput (single sample vs. multi-sample)

Data quality

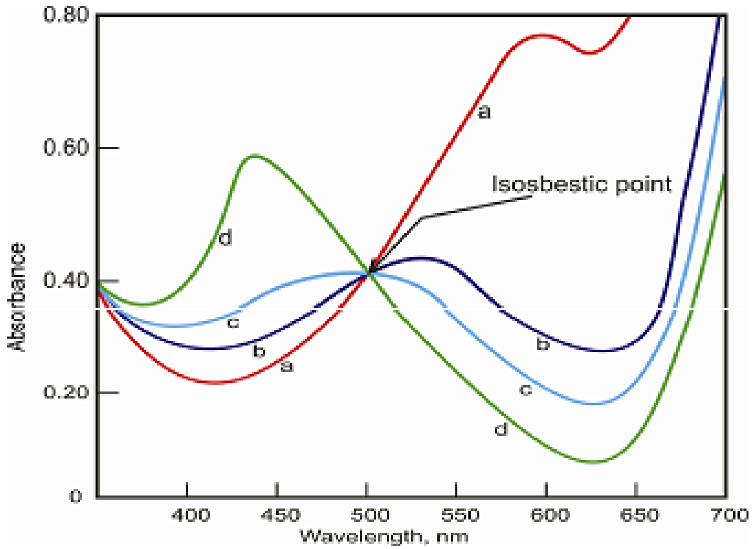
Cost (and footprint) of instrument and associated consumables

Customizable and/or pre-configured method options

Measurement time

https://www.coleparmer.com/tech-article/spectroscopy-selection-guide

Errors and deviations in linearity



Deviations

Real

Instrumental

Chemical

-Beer Lambert only applies to dilute solutions (mM) (A vs C linear)
At high concentrations, ϵ not constant- deviation from law-

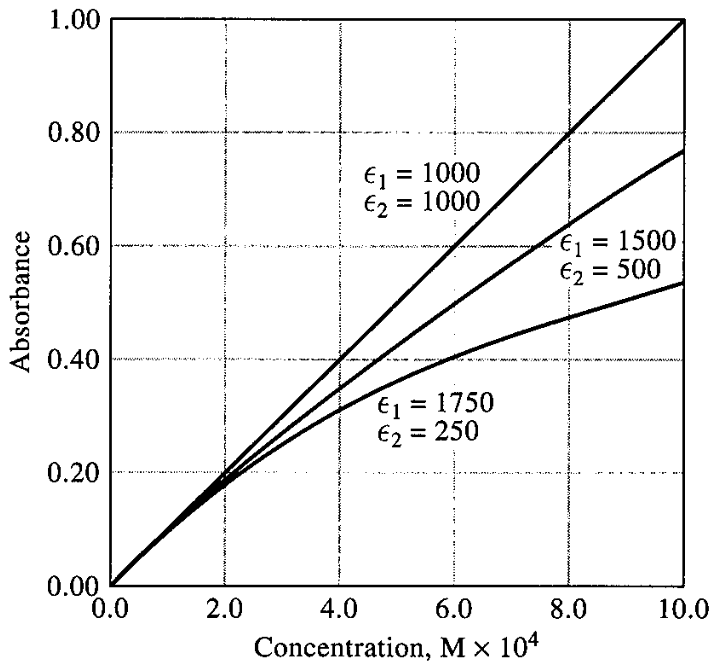
-Polychromatic radiation
-Stray light
-Bandpass

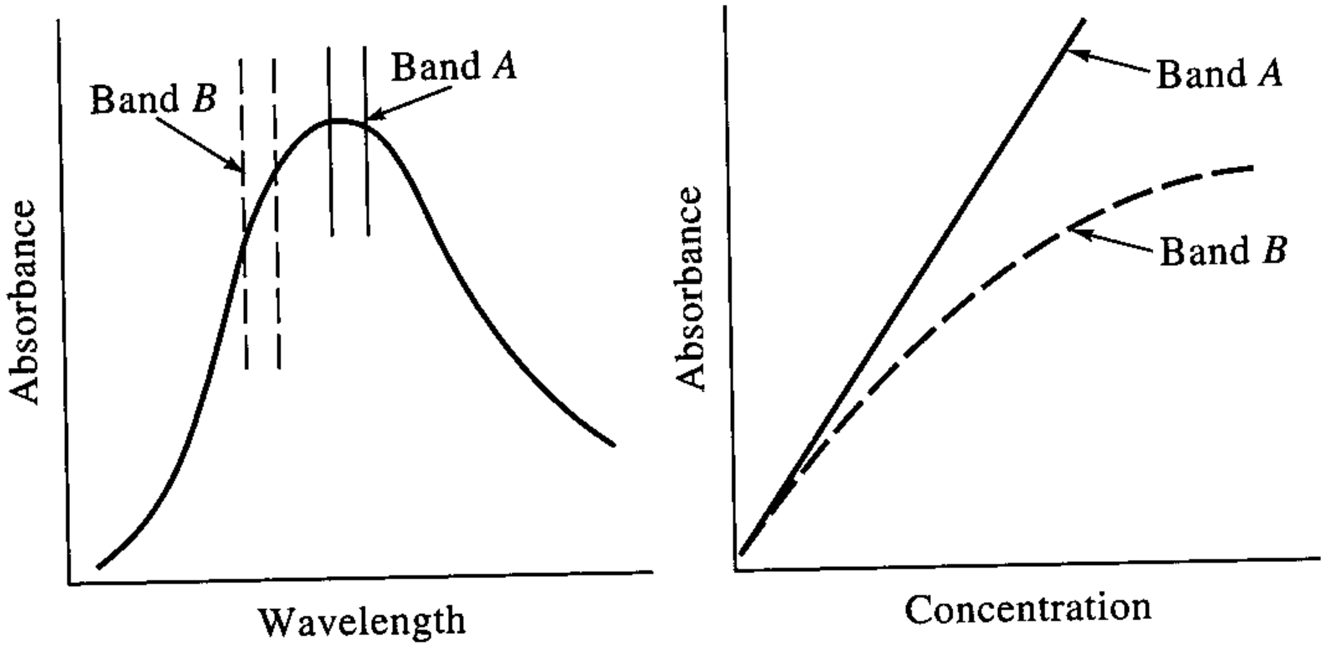
-As position of equilibrium changes, concentration of absorber changes.
-Equilibrium can be affected by association/dissociation/complexation.
-Corrected by using isobestic point at which absorbance of all equilibria components are similar.

Errors and deviations in linearity -Instrumental (polychromatic)

-due to band pass of measurement

-narrow slit and wide bandpass gives changing ϵ





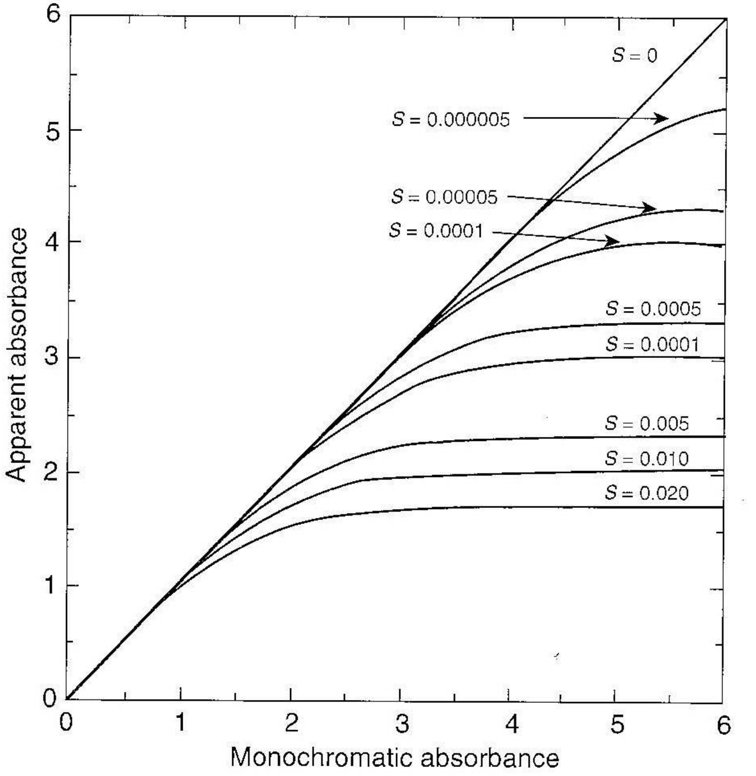
Errors and deviations in linearity -Instrumental (stray light)

-Increased light reaching detector

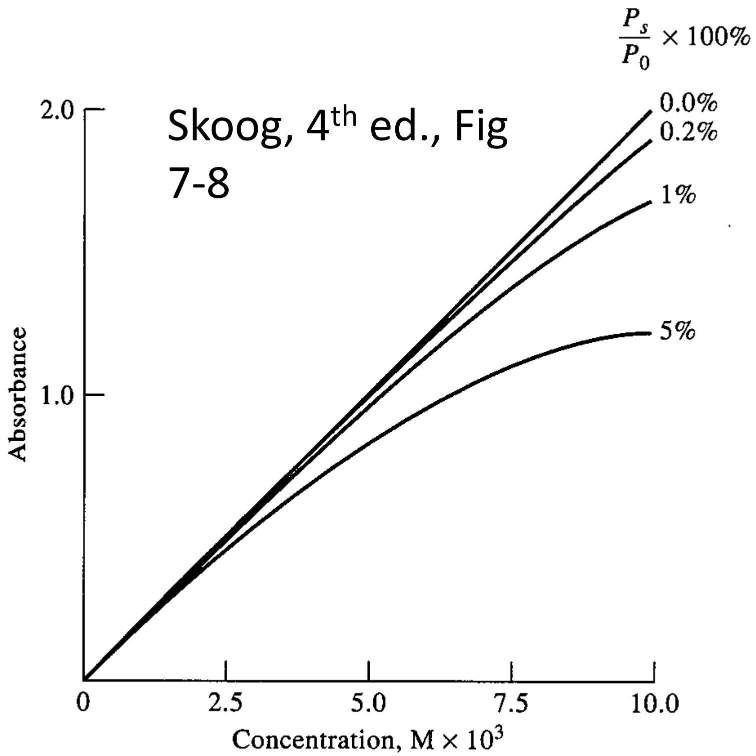
-Occurs when I<<Io

-Negative error or deviation

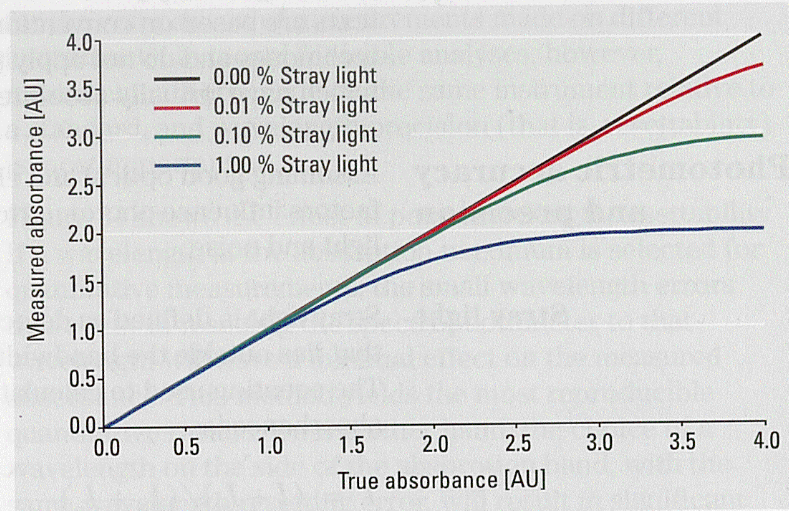
-Improved by decreasing bandpass



Thomas & Burgess, 2007

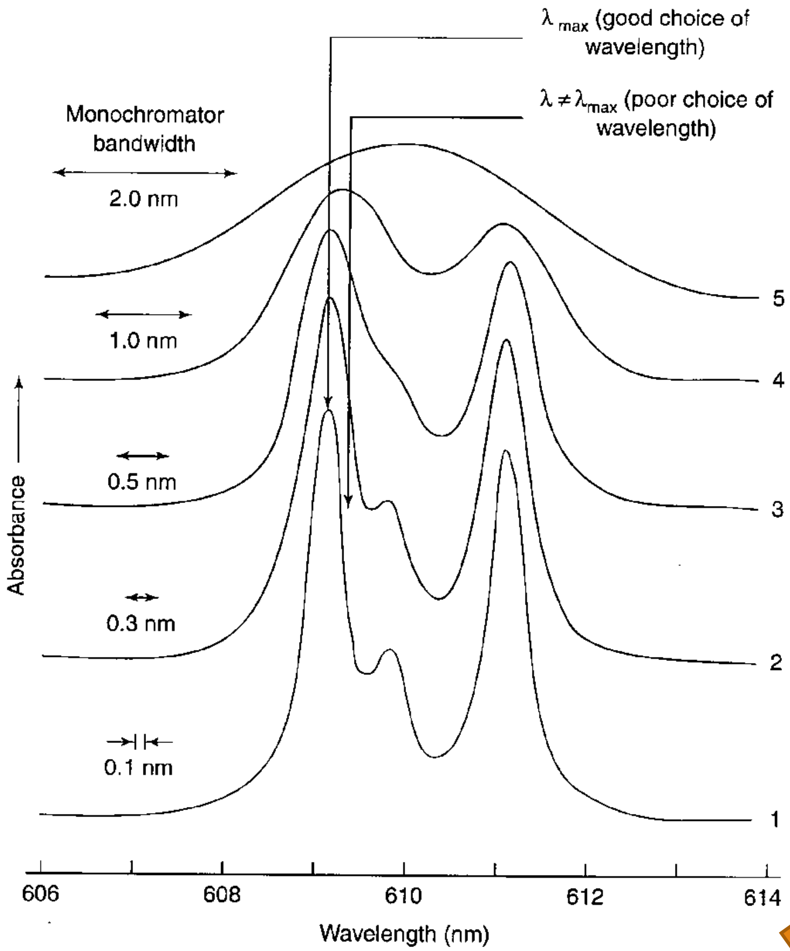


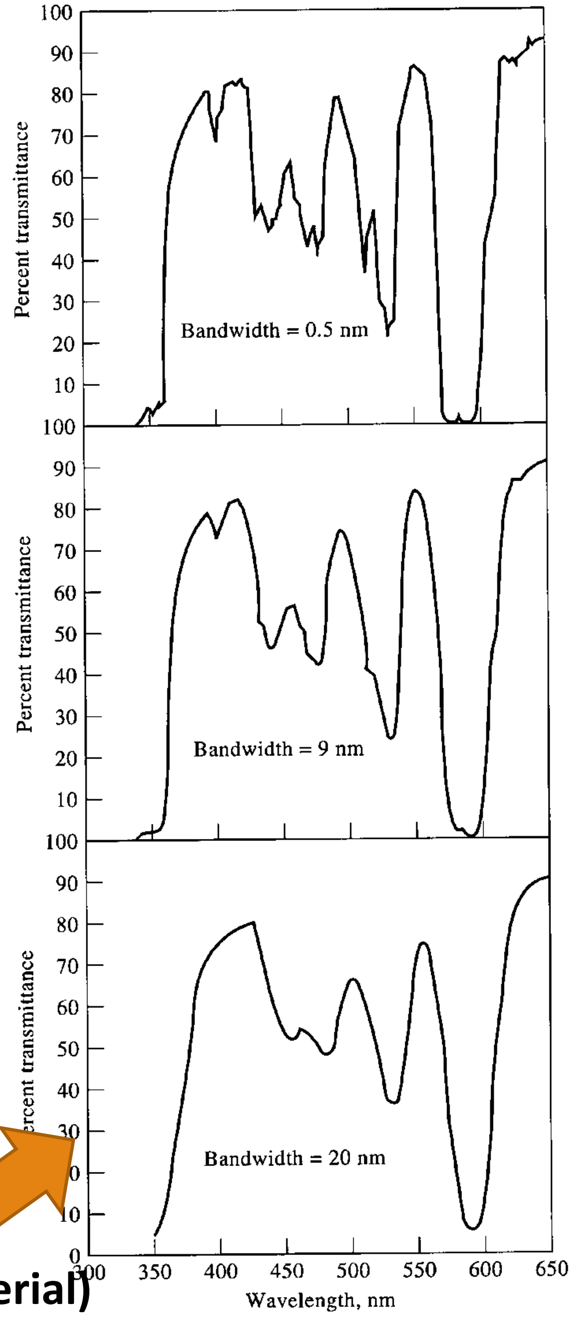
Skoog, 4th ed., Fig 7-8



Errors and deviations in linearity -Instrumental (slit width)

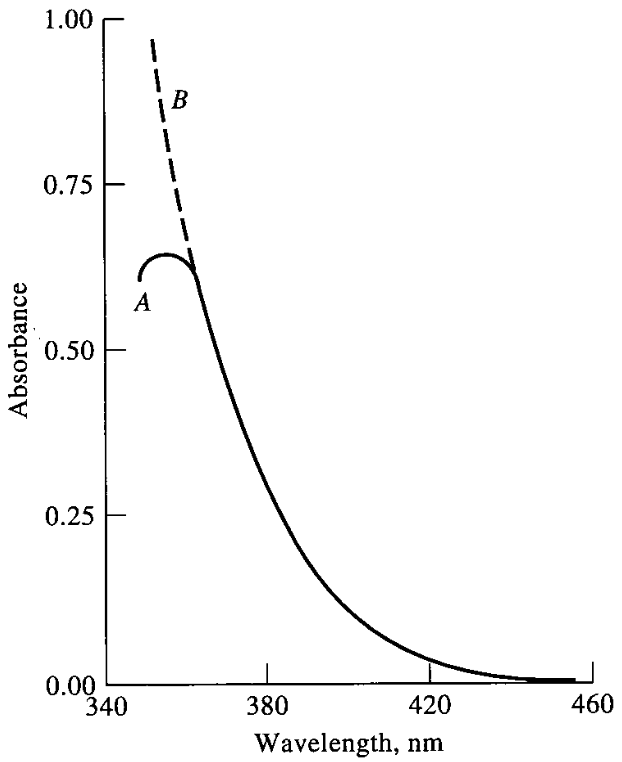
-Narrower the slit width, better resolved the spectra.
-Loss of details dur to wider slit width shown in figures.





DIDYMIUM GLASS (safety glass material)

Errors and deviations in linearity -Instrumental (Stray light)

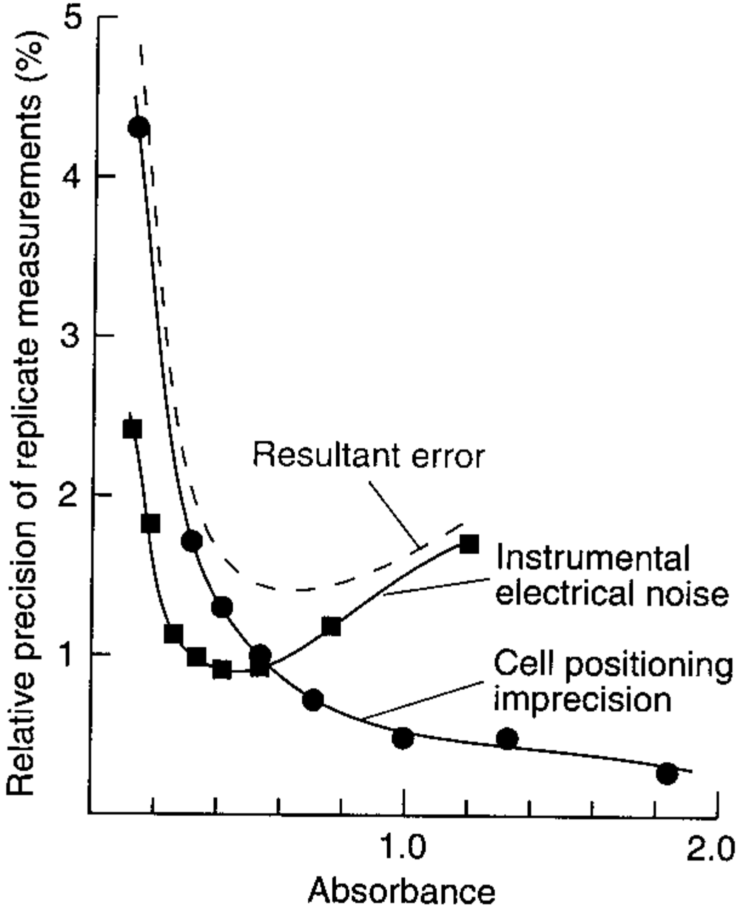


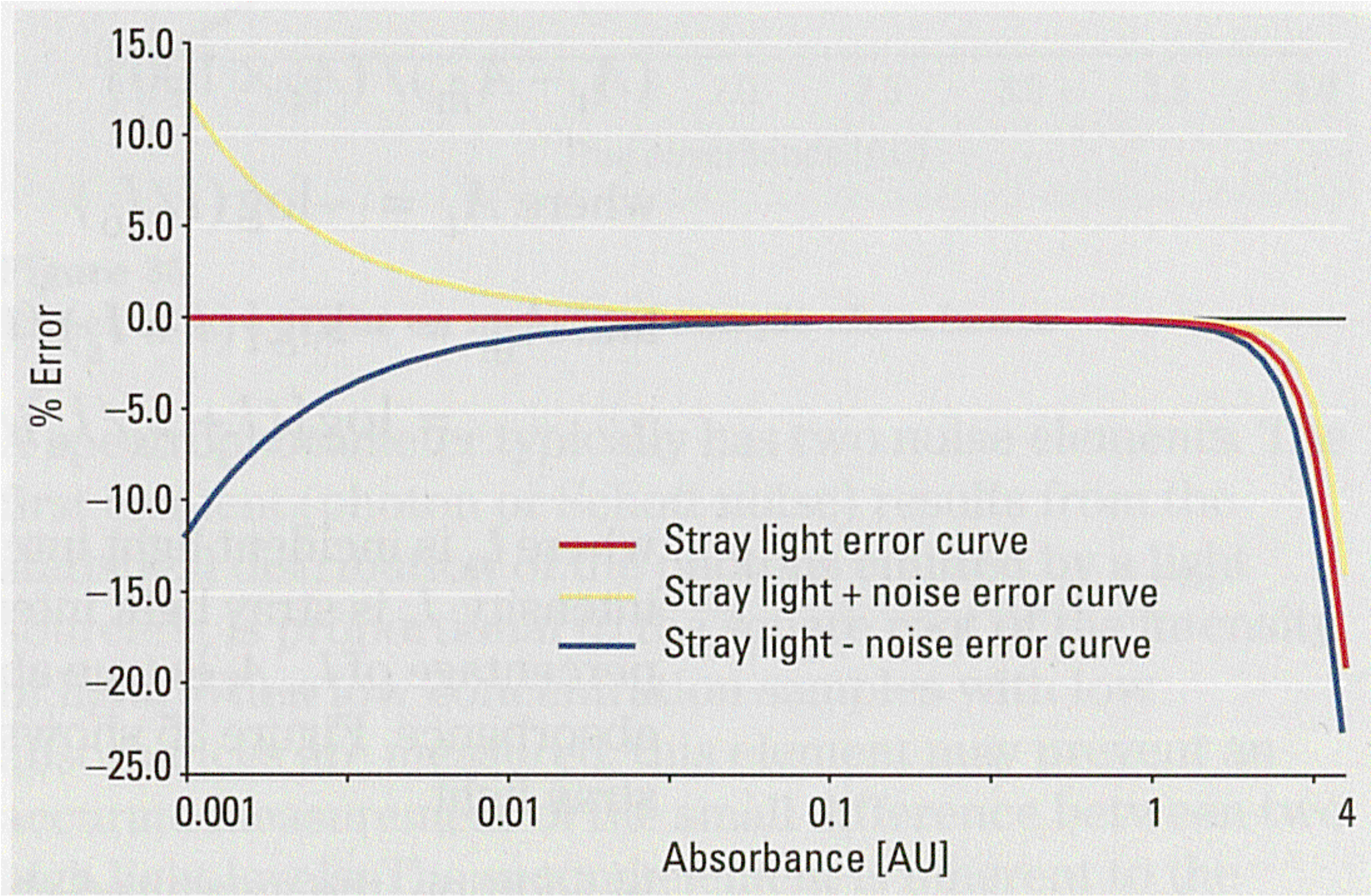
-Spectra of cerium (IV) obtained in a glass optics (A) and quartz optics (B) cell.

-Note false peak at A

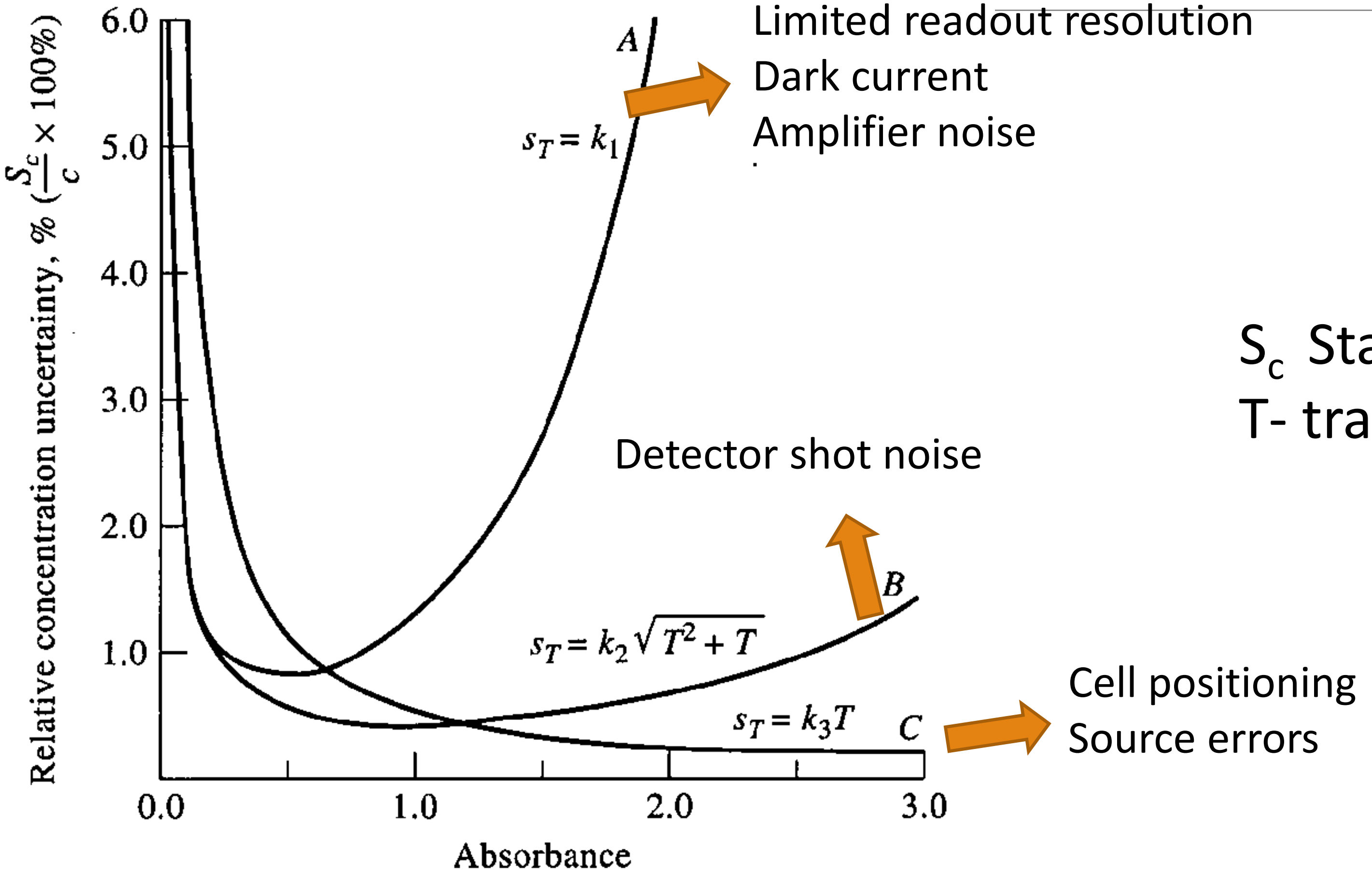
This occurs due to transmission of stay at longer wavelengths. (Skoog, 4th ed., Fig 7-12)

Accuracy is dependant on the instrument!





Errors impacting precision (Ref Table 7-3, Sec 7B-4,Skoog, 4th ed.)



$$\frac{S_c}{c} = \frac{0.434\, S_T}{T \log T}$$

S_c Standard deviation in concentration c

T- transmittance