Chemistry 4631

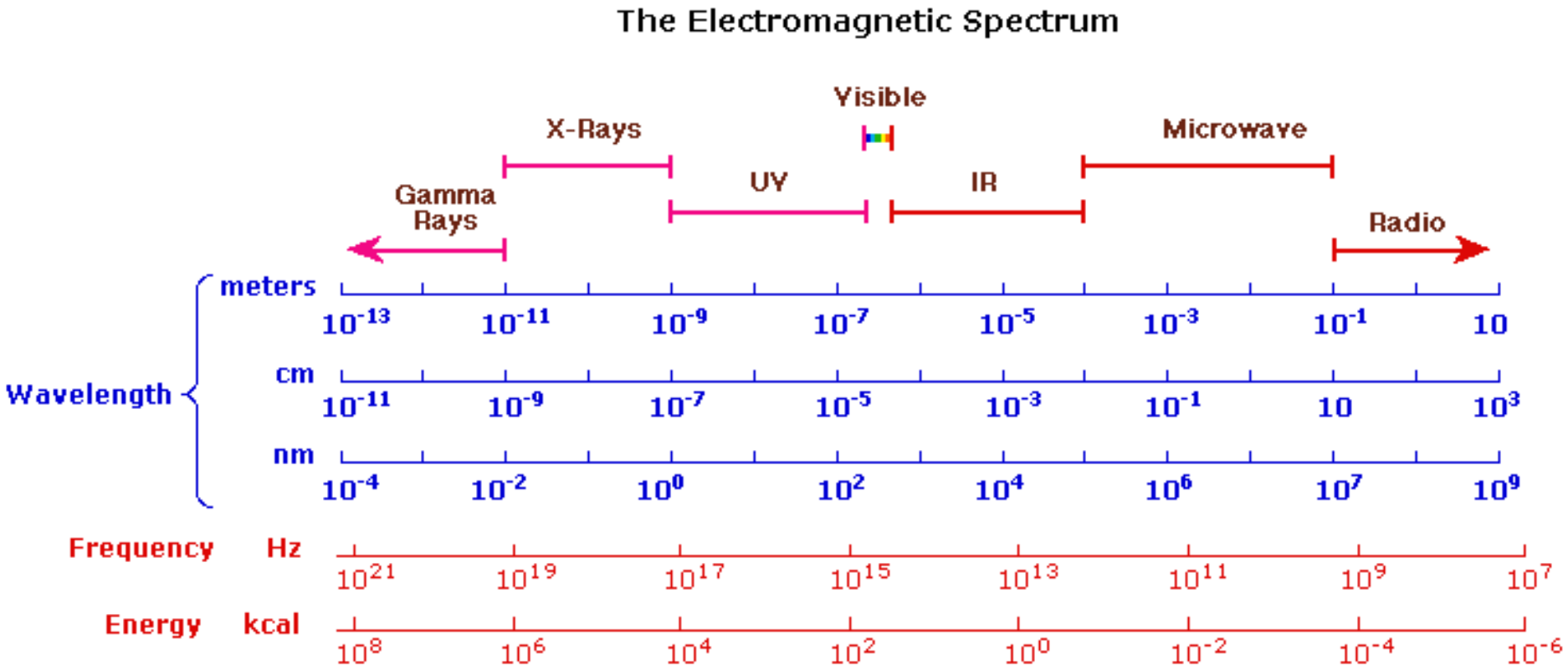
Instrumental Analysis

Lecture 6

Atomic Spectroscopy

Electromagnetic Radiation

Electromagnetic Spectrum



Components of Optical Instruments

UV, Fluorescence to IR

Optical spectroscopy is based on:

- absorption
- fluorescence
- phosphorescence
- scattering
- emission
- chemiluminescence
- transmission

Components of Optical Instruments

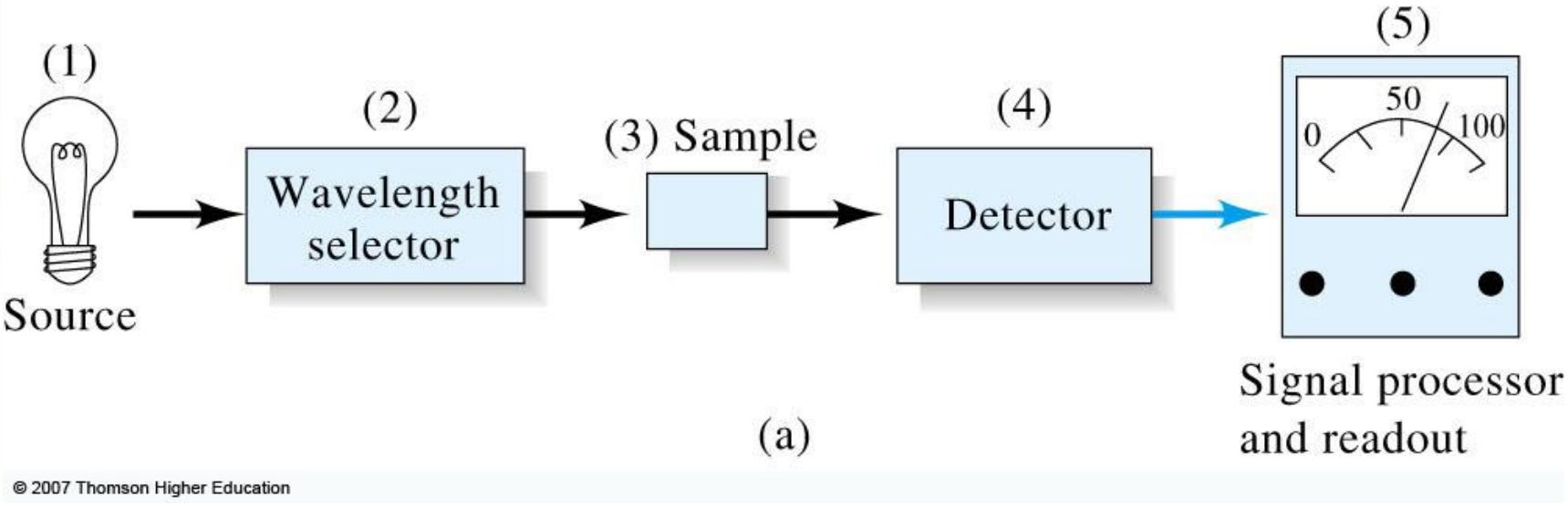
UV, Fluorescence to IR

Basic components of spectroscopic instruments:

- stable source of radiant energy
- transparent container to hold sample
- device to isolate selected region of the spectrum for measurement
- detector to convert radiant energy to a signal
- signal processor and readout
- additional components as needed

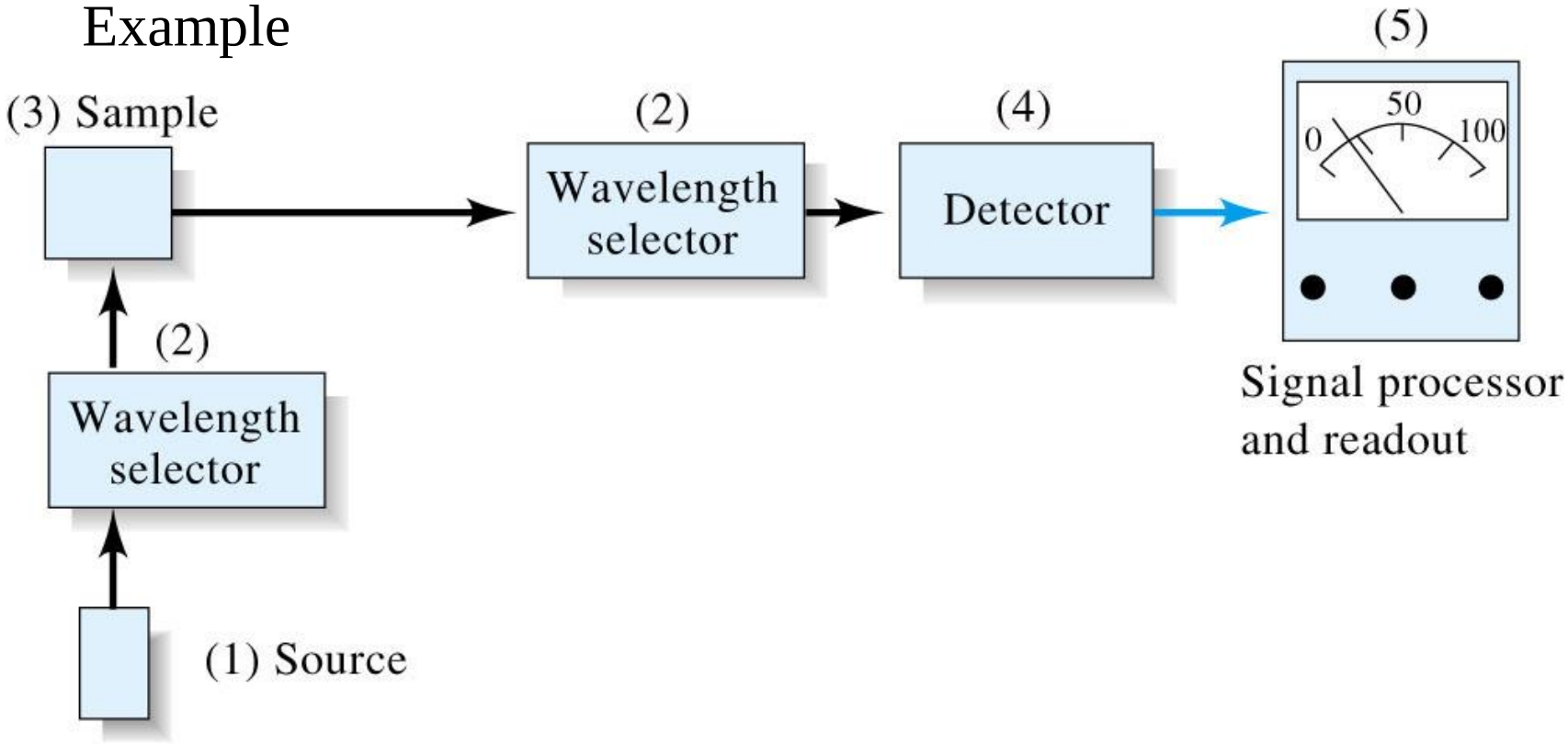
Components of Optical Instruments

Example



Components of Optical Instruments

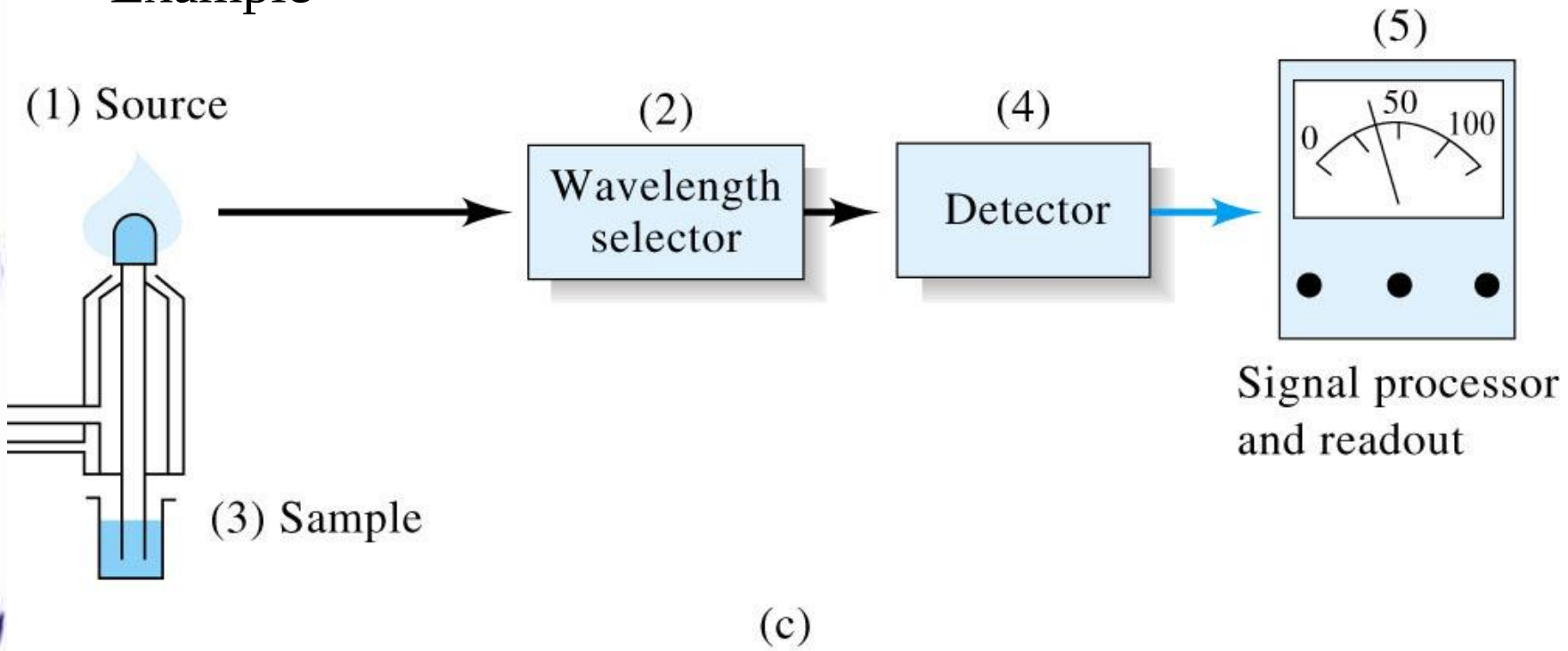
Example



(b)

Components of Optical Instruments

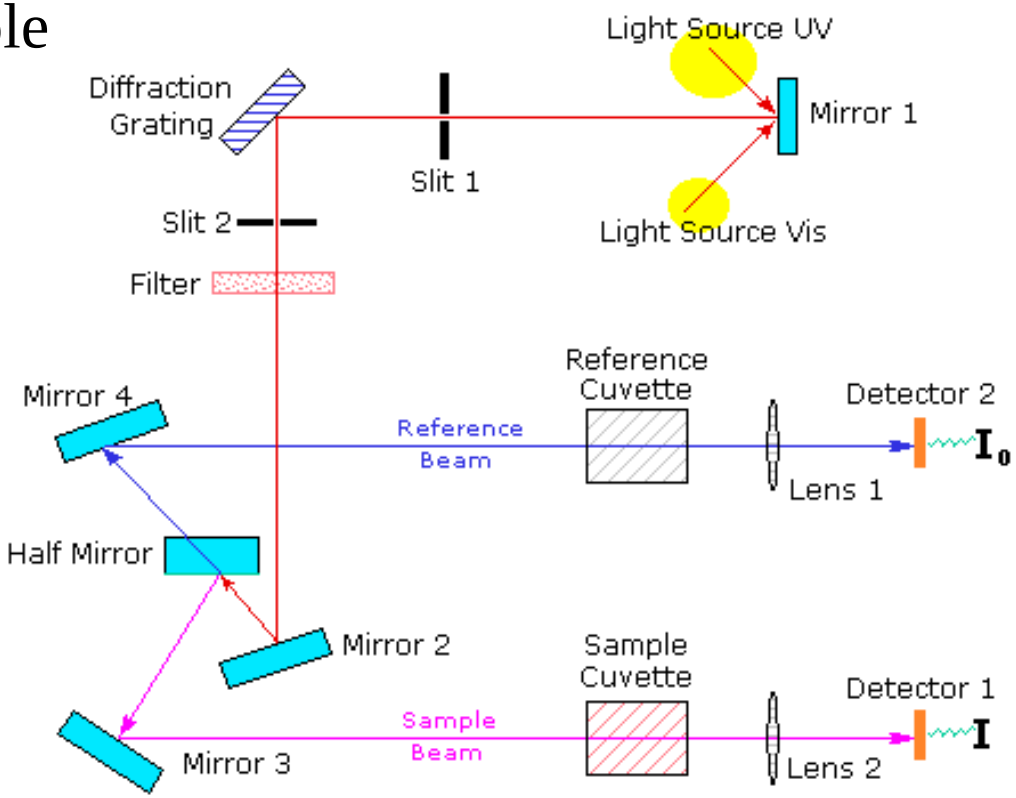
Example



(c)

Components of Optical Instruments

Example



Components of Optical Instruments

Example

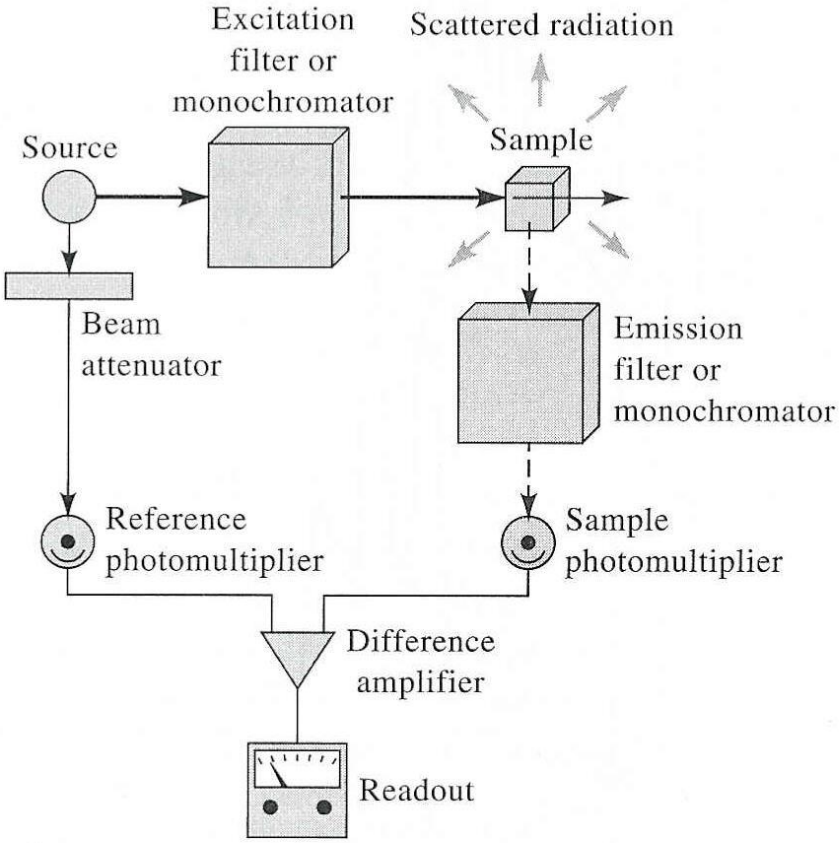
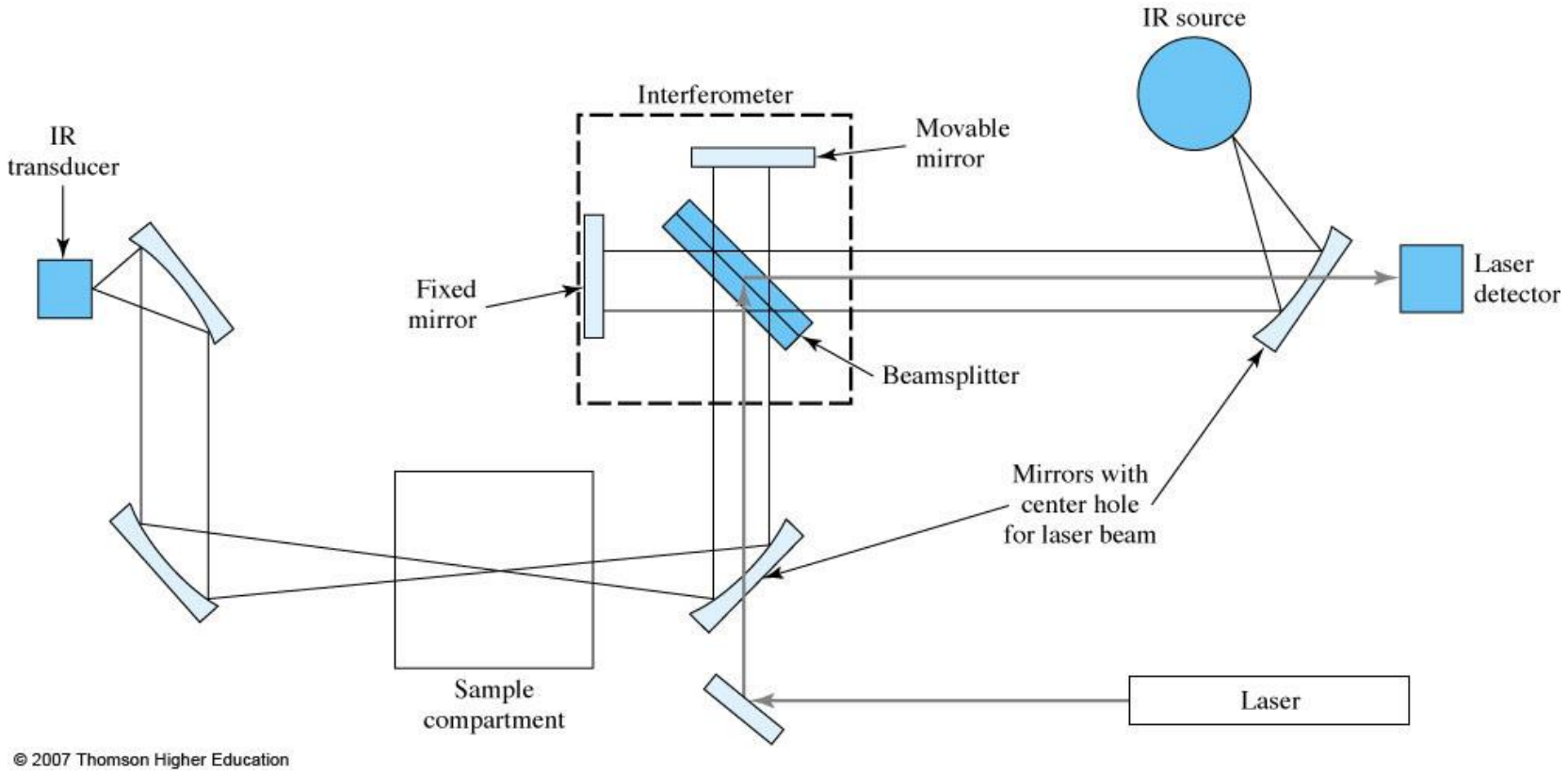


Figure 15-4 Components of a fluorometer or a spectrofluorometer.

Components of Optical Instruments

Example



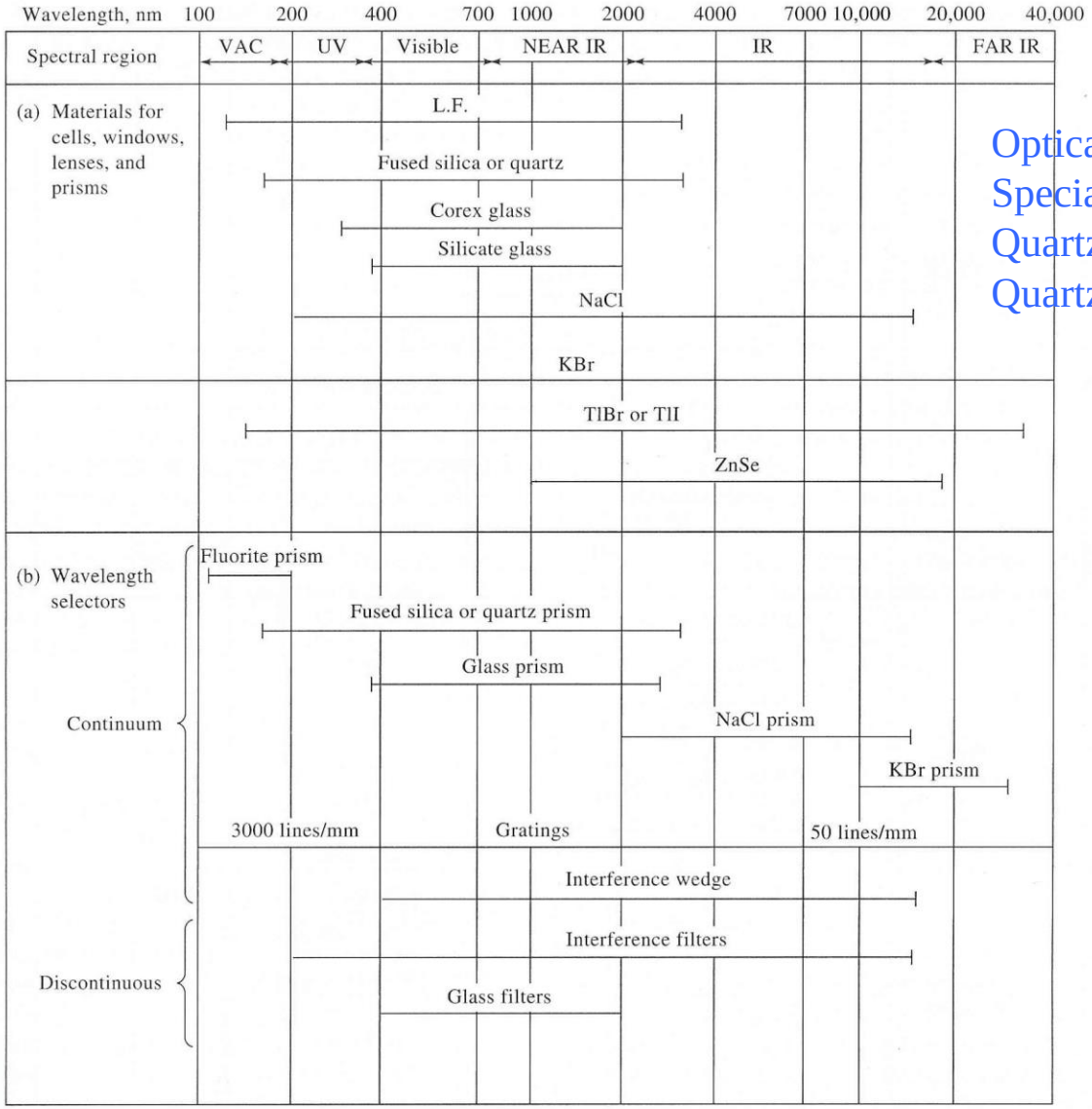


Figure 7-2 (a) Construction materials and (b) wavelength selectors for spectroscopic instruments.

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

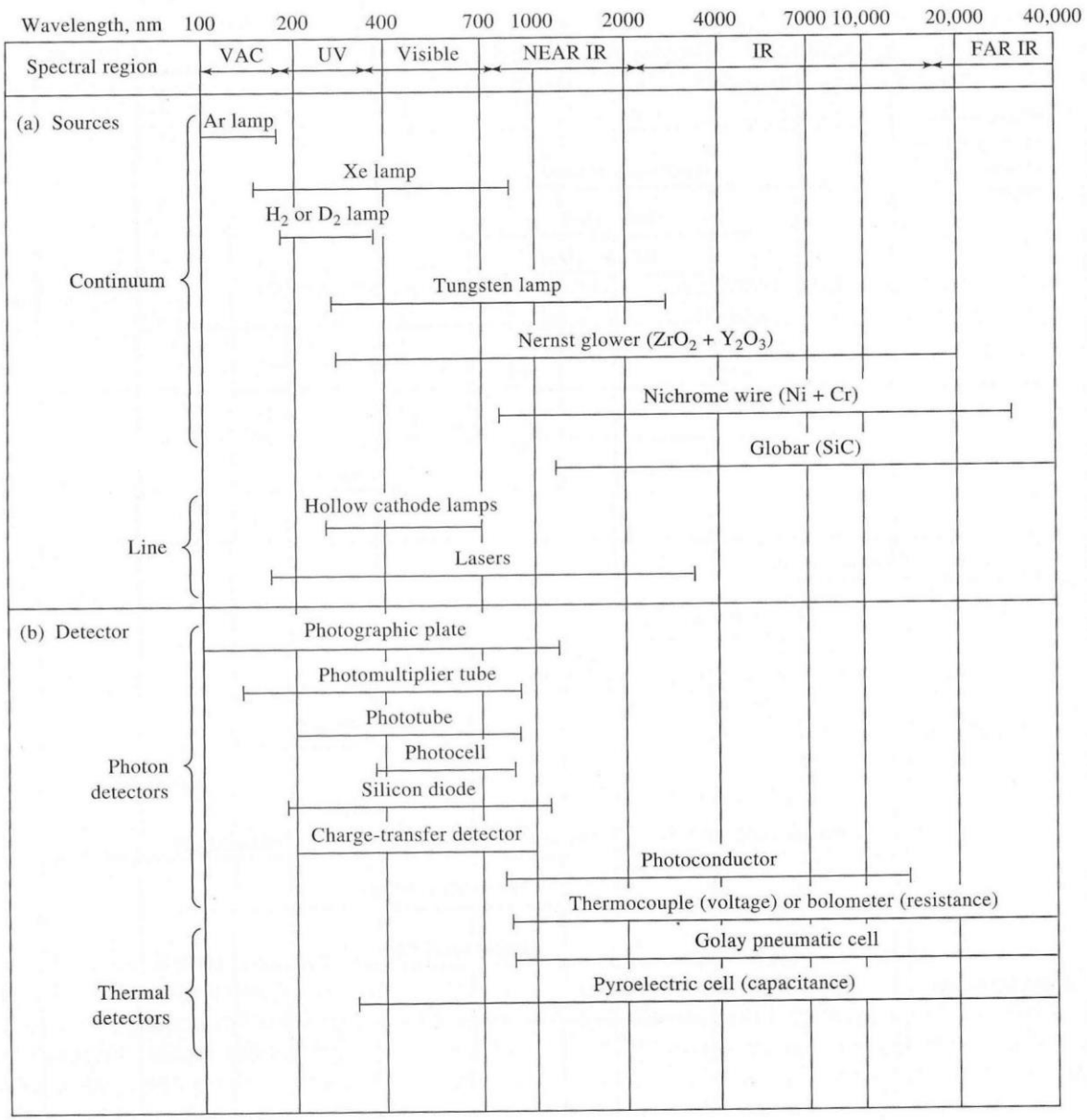


Figure 7-3 (a) Sources and (b) detectors for spectroscopic instruments.

Components of Optical Instruments

Sources of Radiation

Continuum Sources

Used for absorption and fluorescence spectroscopy.

For UV, most common is the deuterium lamp.

For vis, most common is the tungsten filament.

For IR, most common are heated inert solids.

Components of Optical Instruments

Sources of Radiation

Continuum Sources

Deuterium and Hydrogen Lamps

Give continuum spectrum in UV region by electrical excitation of D_2 or H_2 to form an excited molecular species.

The excited molecular species dissociates to two atomic species and a photon.

Components of Optical Instruments

Deuterium and Hydrogen Lamps

$D_2 + E_e \rightarrow D_2^* \rightarrow D' + D'' + h\upsilon$

E_e – electrical energy absorbed by molecule.

Components of Optical Instruments

Deuterium and Hydrogen Lamps

The lamp has a heated filament which forms an arc with a metal electrode.

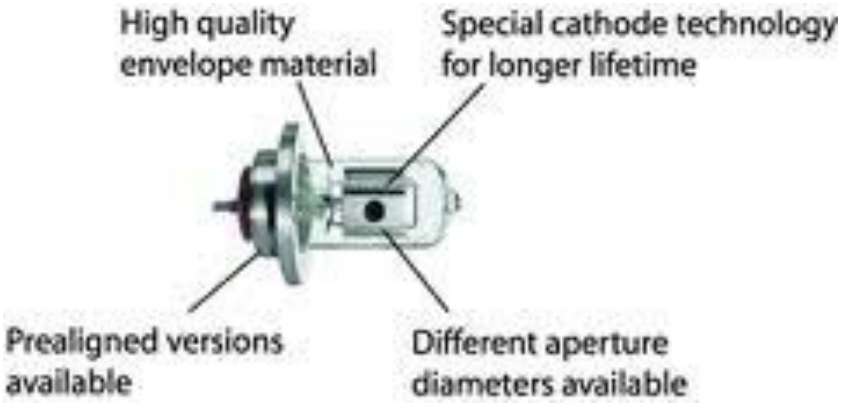
Filament provides a direct current when 40 V is applied.

Spectrum range 160 – 375 nm

Must use quartz windows with these lamps since glass absorbs strongly at wavelengths below 350 nm.

Components of Optical Instruments

Deuterium and Hydrogen Lamps



Components of Optical Instruments

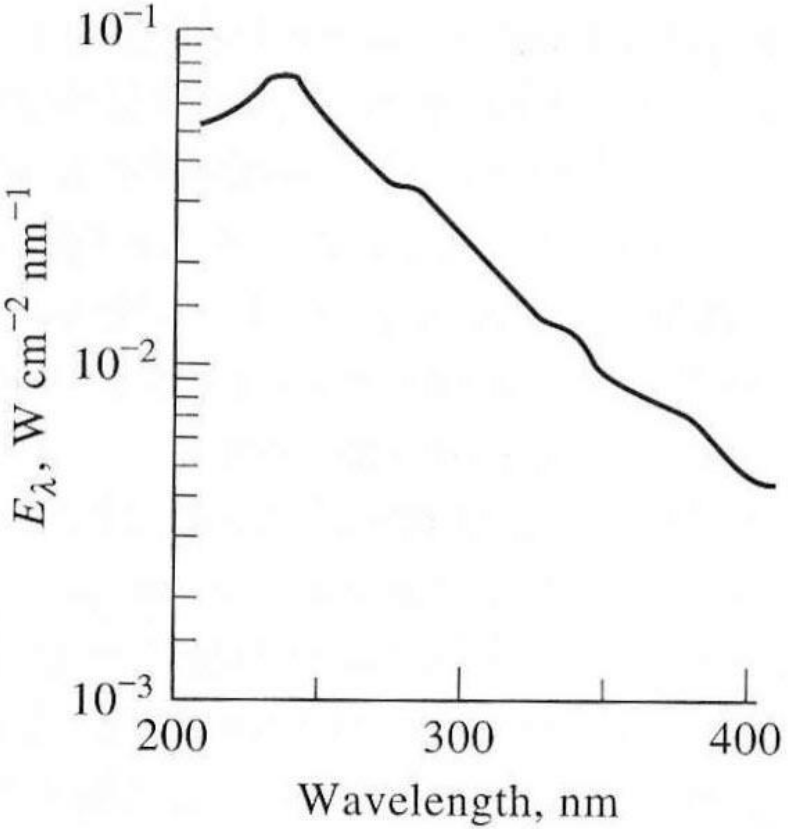


Figure 13-11 Output from a deuterium lamp.

Components of Optical Instruments

Sources of Radiation

Continuum Sources

Tungsten Filament Lamp

- Source for vis and near IR
- Wavelength range 350 – 2500 nm

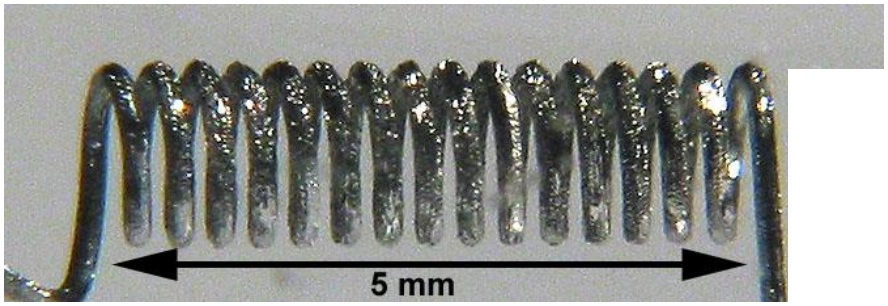
Components of Optical Instruments

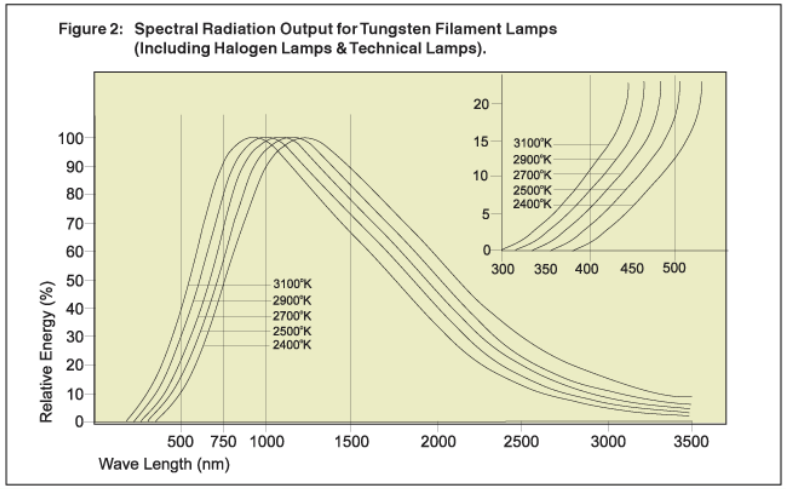
Tungsten/halogen lamps

- **Add a small amount of iodine**
- **Lifetime 2x of regular lamp**
- **I_2 reacts with gaseous W to form WI_2**
- **WI_2 strikes the filament**
- **WI_2 decomposes**
- **W redeposits on the filament.**

Components of Optical Instruments

Tungsten/halogen lamps





Components of Optical Instruments

Sources of Radiation

Continuum Sources

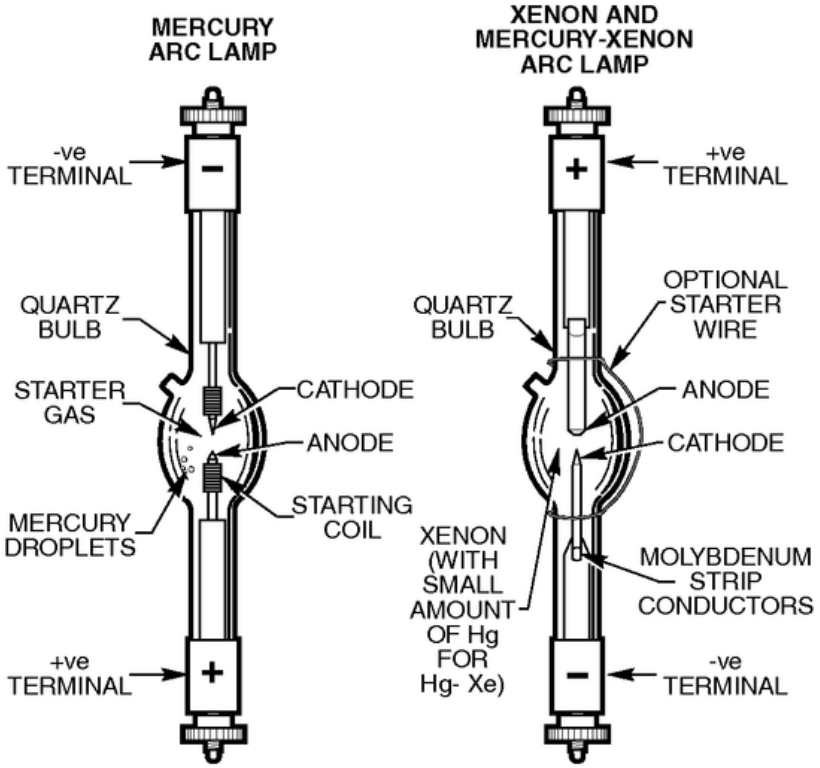
Xenon Arc Lamps

Produces intense radiation by passing current through gaseous Xe.

Gives continuum spectrum between 200-1000 nm

Components of Optical Instruments

Xenon and Mercury Arc Lamps



Components of Optical Instruments

Xenon and Mercury Arc Lamps

The anode and cathode are made of tungsten and sealed in a clear quartz envelope.

Arc lamps are filled with either rare gas at several atmospheres pressure, or a little rare gas and an exact amount of mercury.

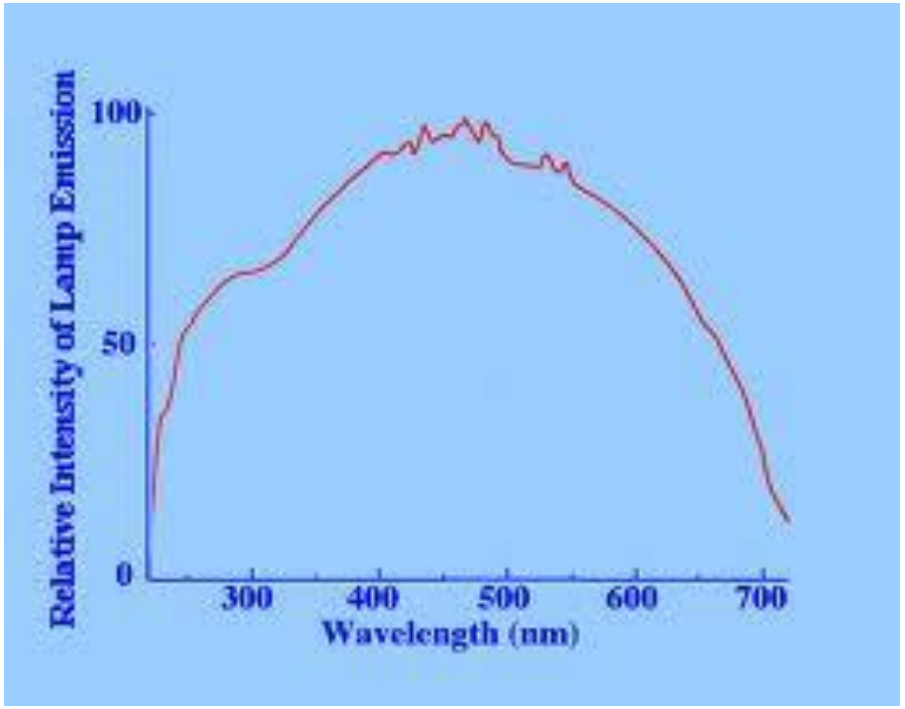
Xenon lamp better for scanning applications. Hg lamp better for a line source (discrete).

Components of Optical Instruments

Sources of Radiation

Continuum Sources

Xenon Arc Lamps



Components of Optical Instruments

Sources of Radiation

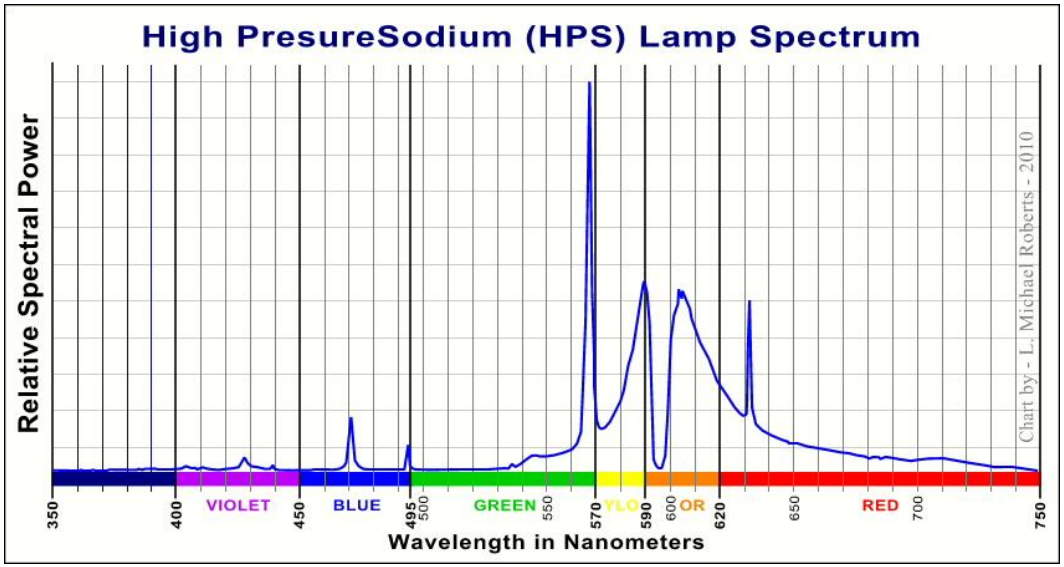
Line Sources

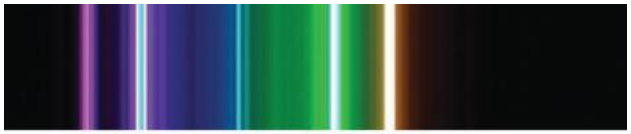
Emit a few discrete lines.

Hg and Na vapor lamps have a few sharp lines in the UV and vis region.

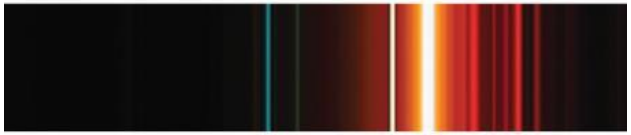
Components of Optical Instruments

Line Sources

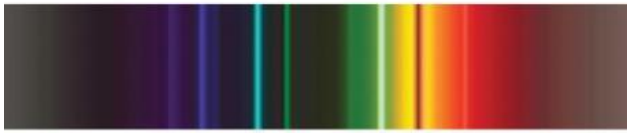




Hg vapor spectrum (350-700 nm)



Low-pressure Na spectrum
(350-700 nm)



High-pressure Na spectrum
(350-700 nm)

Components of Optical Instruments

Laser Sources

Light **A**mplification by **S**timulated **E**mission of **R**adiation

- High Intensities
- Narrow Bandwidths
- Coherent Outputs

Components of Optical Instruments

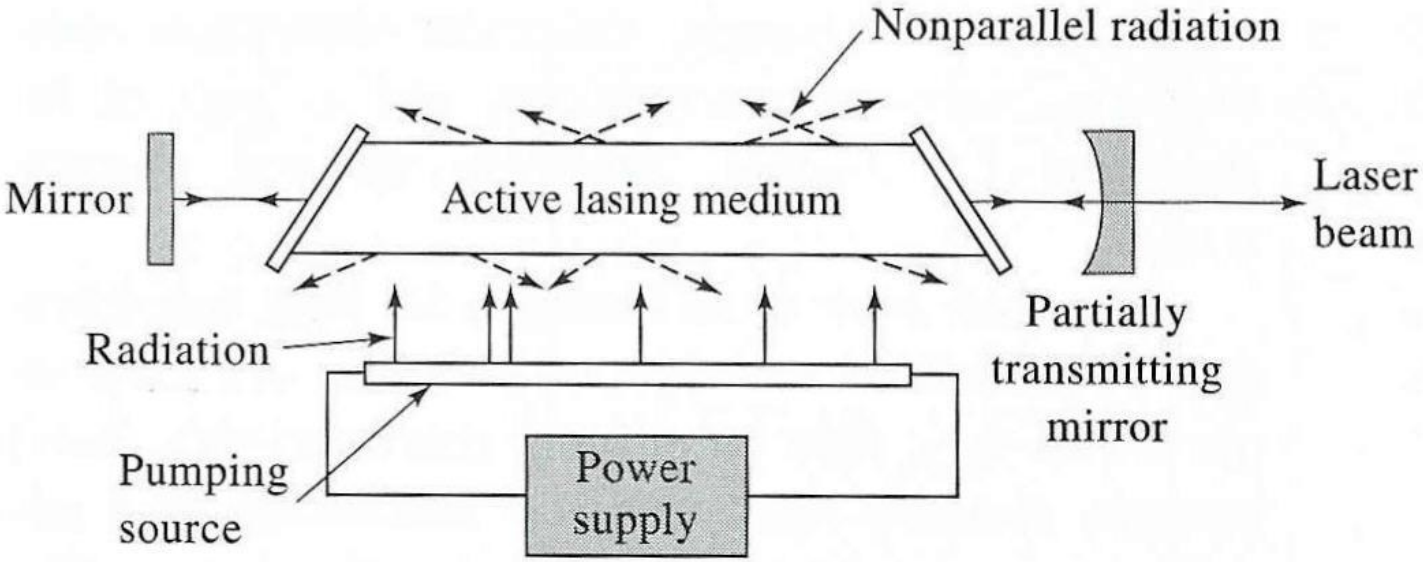
Laser Sources
in UV, vis, and IR

Used for

- **high resolution spectroscopy**
- **kinetic studies**
- **routine analysis**

Components of Optical Instruments

Laser Sources



Components of Optical Instruments

Fluorescence Instrument

Components are very similar to those for absorbance.

Fluorescence instruments incorporate double-beam optics to compensate for fluctuations in radiant power.

Components of Optical Instruments

Fluorescence Instrument

Fluorescence is emitted in all directions but best observed at 90^{o}.

The right-angle geometry minimizes contributions from scattering and the intense source radiation.

Fluorescence Spectrometry

Instrumentation

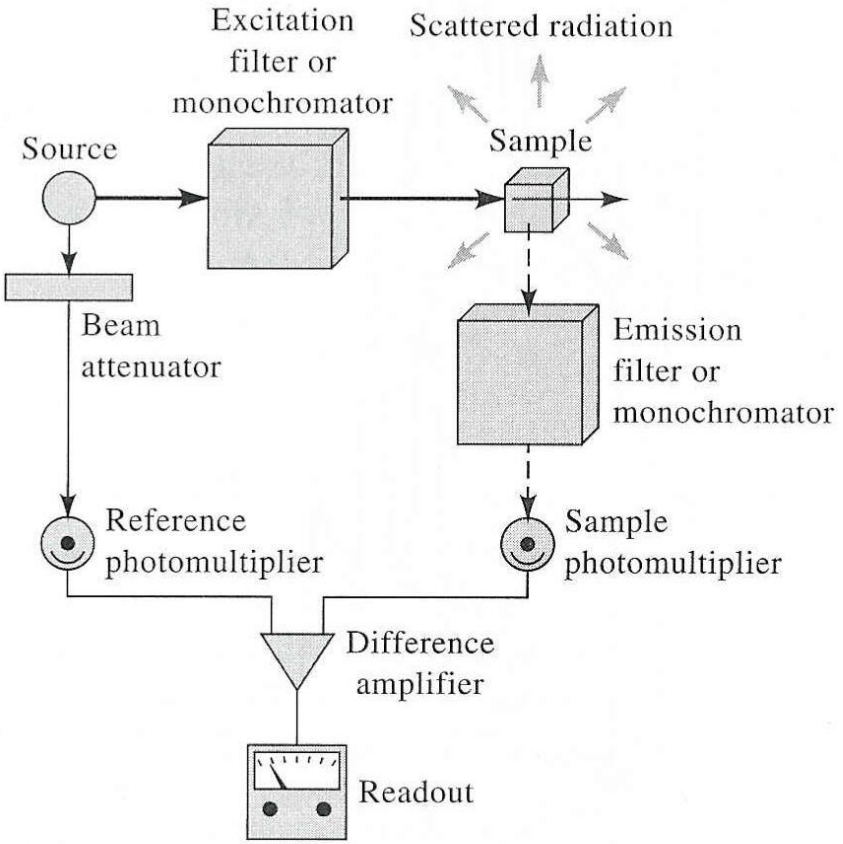


Figure 15-4 Components of a fluorometer or a spectrofluorometer.

Components of Optical Instruments

Fluorescence Instrument

Sources

Need to be more intense than for absorbance - since the magnitude of the output signal is directly proportional to the source radiant power Po.

Components of Optical Instruments

Fluorescence Instrument

Sources

- Low pressure Hg vapor lamps with a fused silica window.

  Has excitation lines at 254, 302, 313, 546, 578, 691, and 773 nm.

  Lines are isolated with filters.

Components of Optical Instruments

Fluorescence Instrument

Sources

- **High pressure xenon arc lamps**

  75 to 450 W gives continuum from 300 - 1300 nm approximates that of a blackbody, weaker radiation produced down to 200 nm. Can pulse at constant frequency to get higher peak intensities.

Components of Optical Instruments

Fluorescence Sources

- **Blue light-emitting diodes (LEDs)**

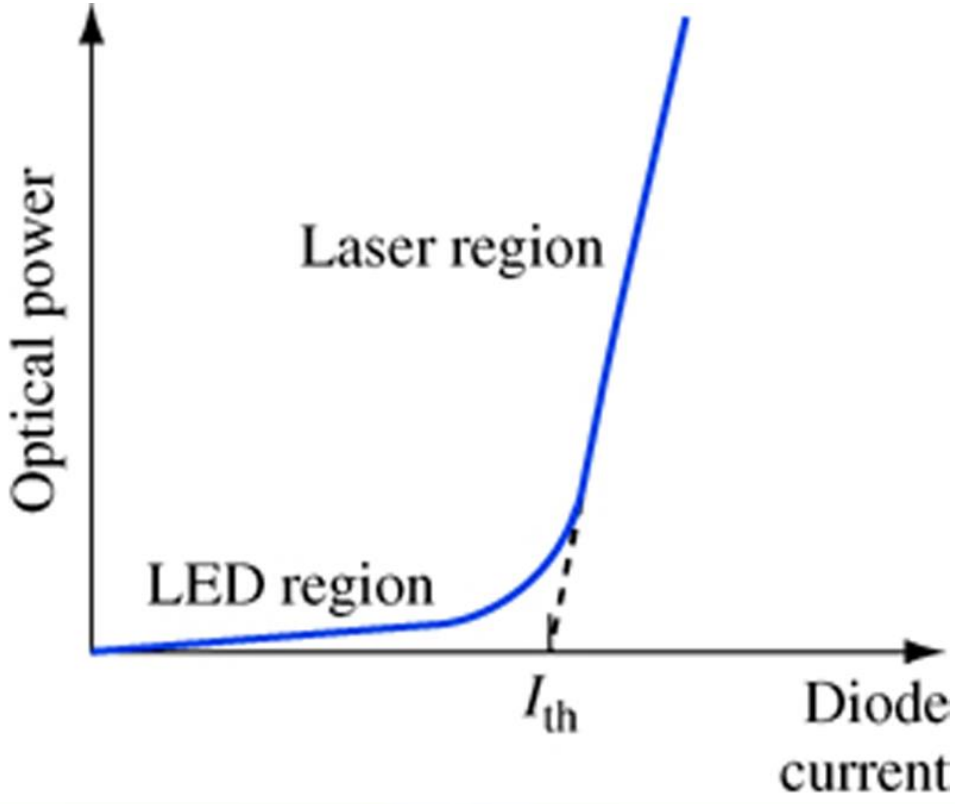
  Emit at 450-475 nm

  - **Use a pn junction under forward bias to produce radiant energy**
  - **The diodes are made from gallium nitride (λ = 465 nm) or indium gallium nitride (λ = 450 nm)**

Components of Optical Instruments

Sources

Semiconductor LED vs LASER



Components of Optical Instruments

Fluorescence Instrument

Sources

- **Lasers tunable dye laser pumped by pulsed N_2 gas or Nd:YAG laser– minimize interferences.**

Components of Optical Instruments

Instrument

- **Lasers**

  Advantages:

  For microbore chromatography or CE which use only mL or less of sample.

  In remote sensing where the collimated nature of the laser beam is needed.

  To minimize the effects of fluorescing interferences by using highly monochromatic excitation.

Components of Optical Instruments

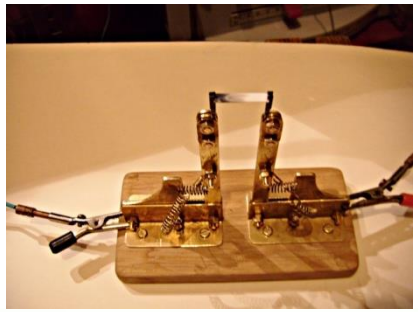
Instrument

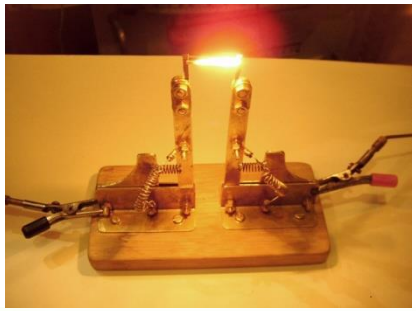
IR Sources

Inert solid heated electrically to a temperature between 1500-2200 K, to give continuum radiation.

Nernst Glower

Composed of rare earth oxides in the shape of a cylinder (diameter – 1 to 2 mm, length – 20 mm). Platinum leads connected to ends of cylinder.





Components of Optical Instruments

IR Sources

Globar Source

A SiC rod (diameter – 5 mm, length – 50 mm) that has a positive coefficient of resistance. Contacts must be water cooled to prevent arcing.

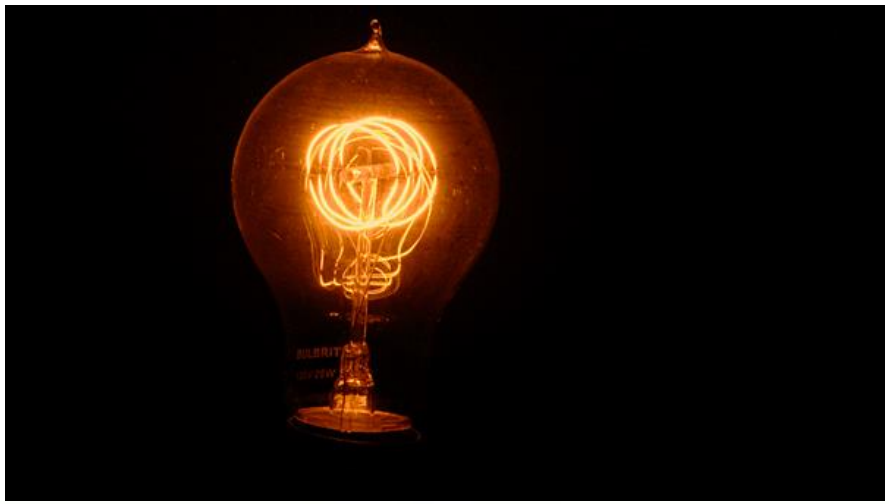
Components of Optical Instruments

IR Sources

Incandescent wire source

Spiral of nichrome wire heated to about 1100K.

Intensity lower but longer life.



Components of Optical Instruments

IR Sources

Mercury Arc

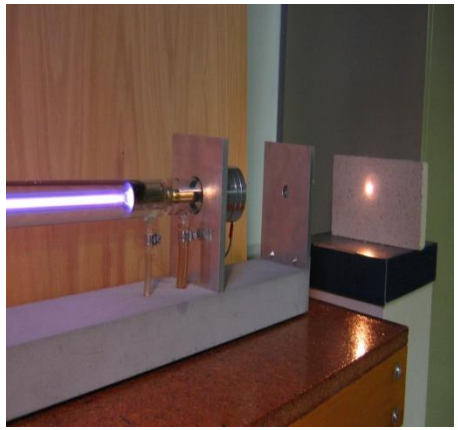
- **Quartz-jacketed tube containing mercury vapor.**
- **Electrical current passed through vapor to give radiation in far-infrared region ($\lambda > 50\ \mu m$).**

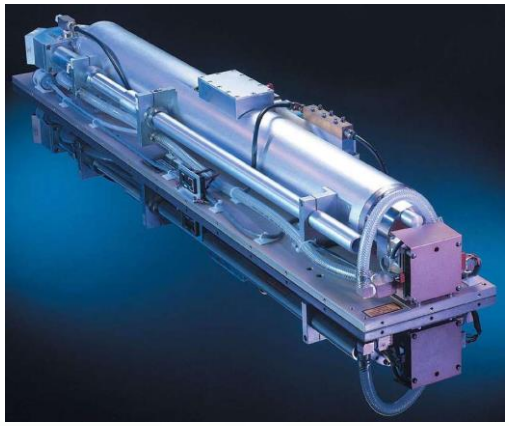
Components of Optical Instruments

IR Sources

Carbon Dioxide Laser Source

Tunable laser produces band of radiation in 900-1100 cm^{-1} range. This region is sensitive for CO_2 stretching and for determination of ammonia, benzene, ethanol, NO_2, etc…





Assignment

- Read Chapter 6 & 7 & 13
- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due today)
- Read Chapter 15
- Read Chapter 16 & 17
- HW 3: Ch. 16: 7, 8, 11 and Ch. 17: 2, 4, 5 (Due 1-31)
- HW4: Ch. 15: 1, 2, 4, 5, 9, 13 (Due 2-02)
- HW5: Ch. 7: 2-4, 8-13, and 16 (Due 2-05)