



Chemistry 4631

Instrumental Analysis

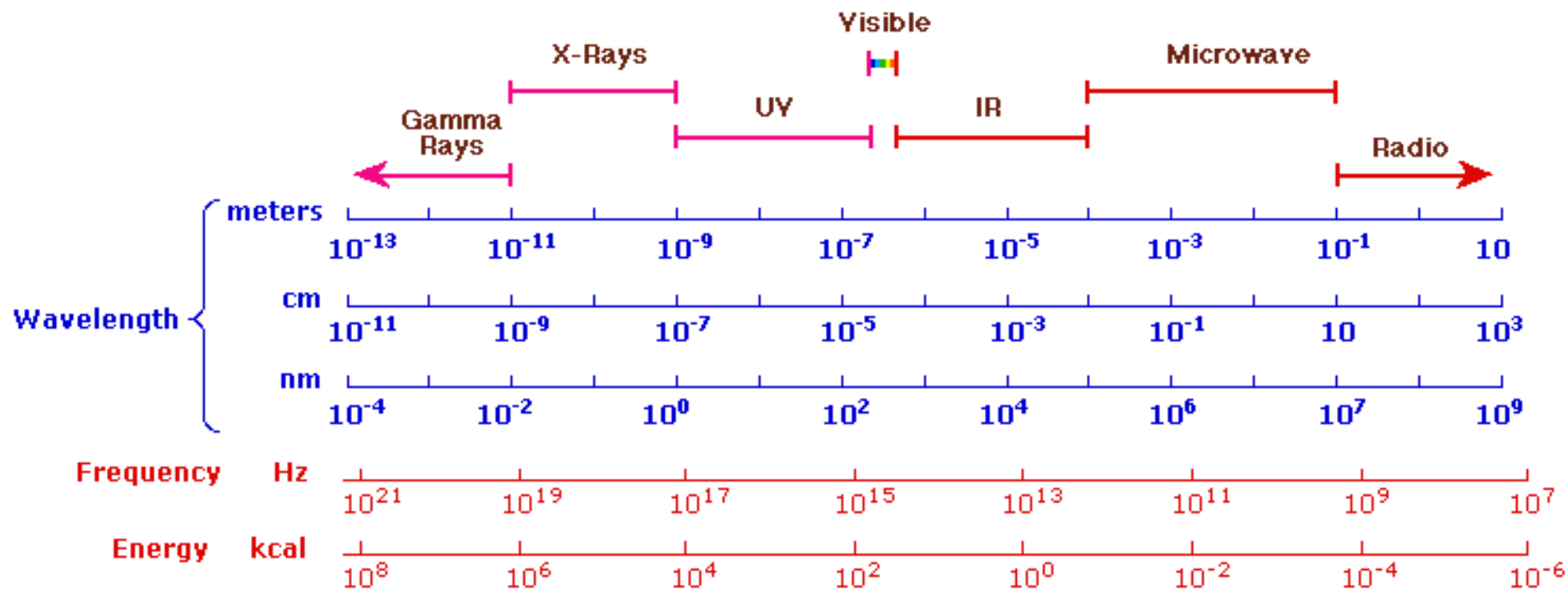
Lecture 5

Atomic Spectroscopy

Electromagnetic Radiation

Electromagnetic Spectrum

The Electromagnetic Spectrum



Components of Optical Instruments

UV-vis

Optical spectroscopy is based on:

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

Components of Optical Instruments

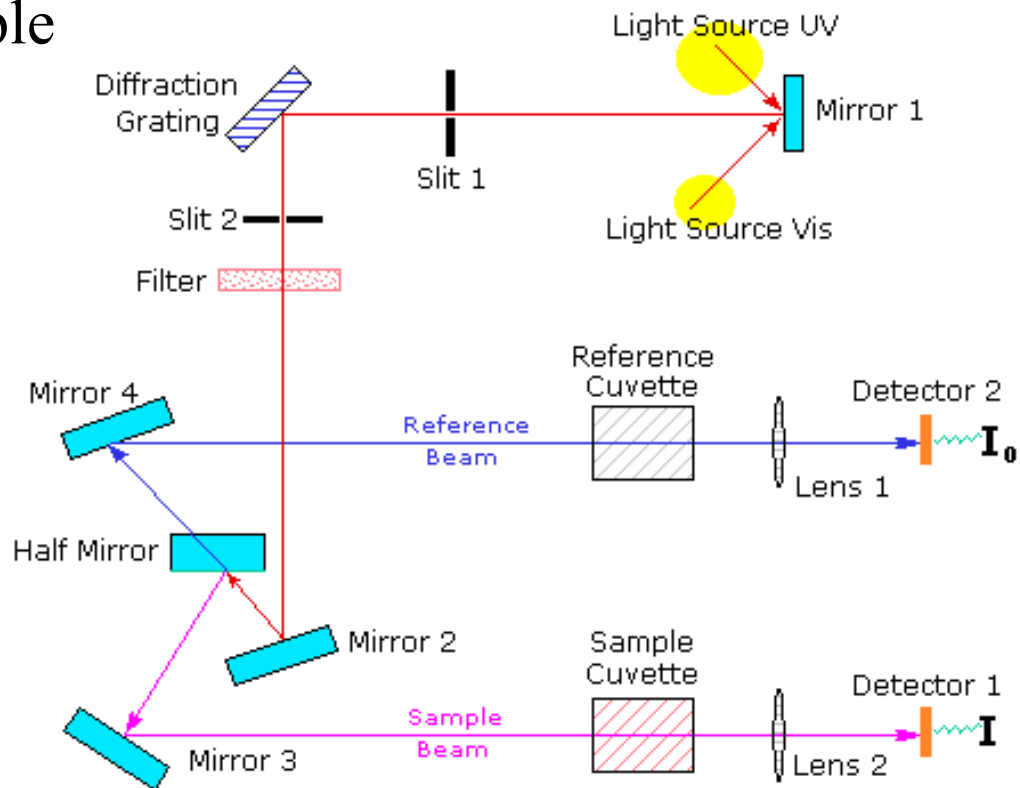
UV-vis

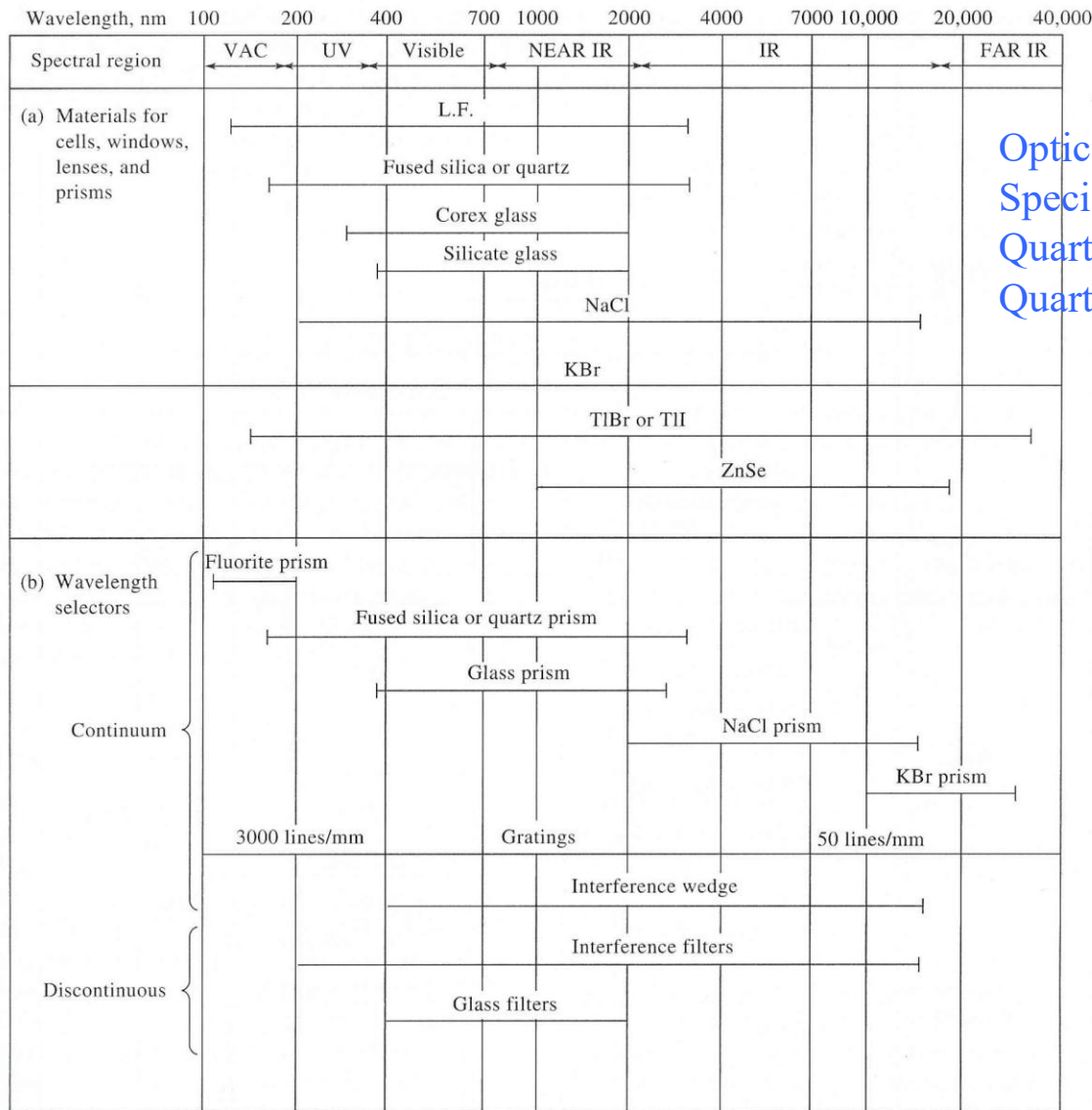
Basic components of spectroscopic instruments:

- 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





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

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

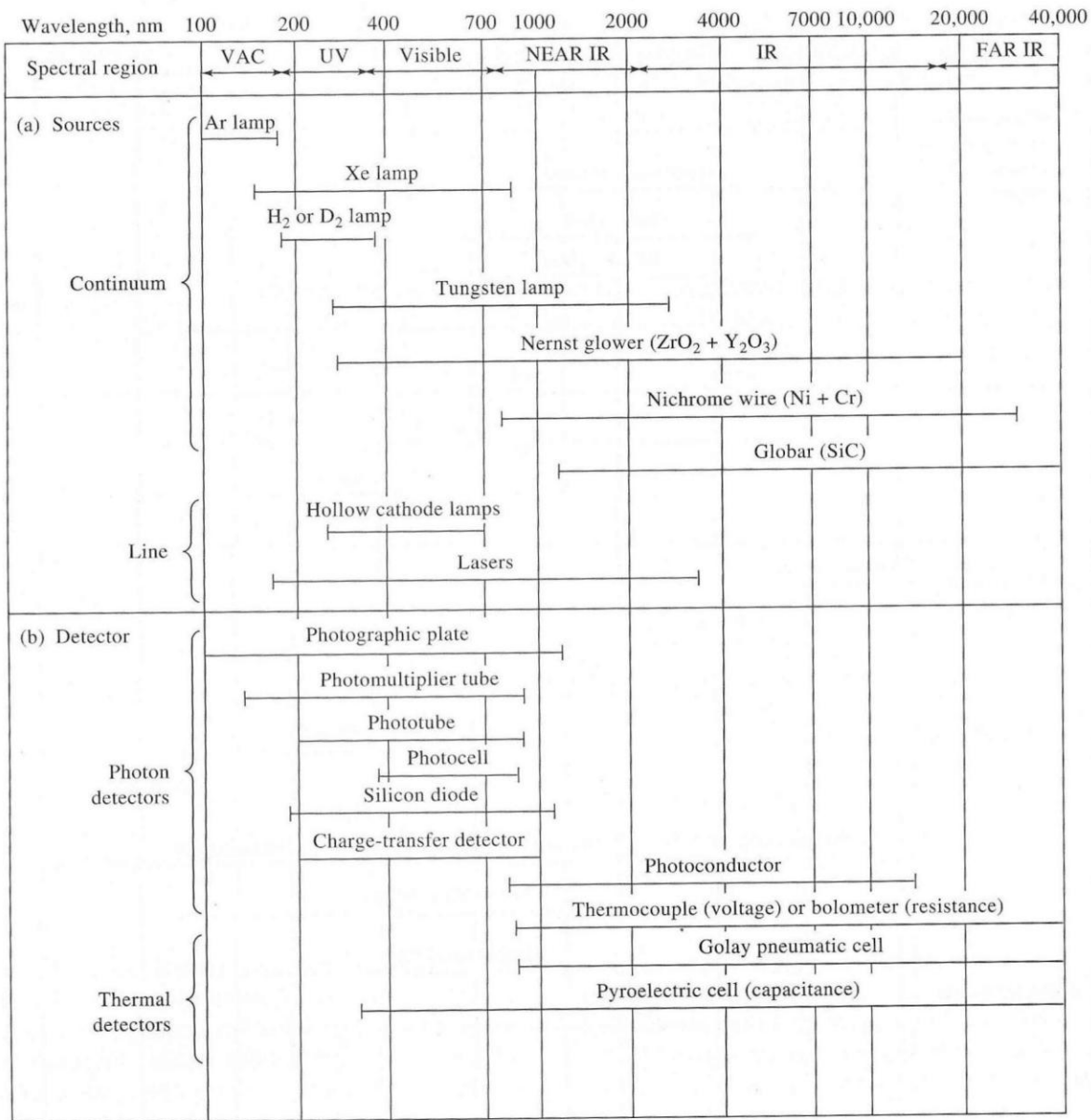


Figure 7-3 (a) Sources and (b) detectors for spectroscopic instruments.

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.

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



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.

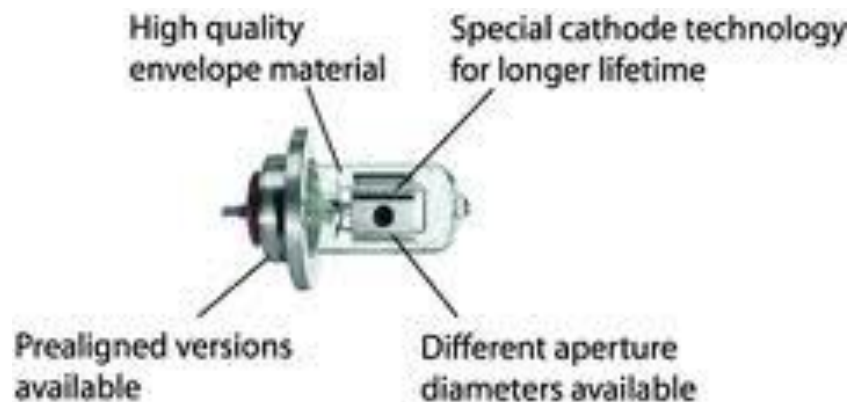
Filament provides a direct current when 40 V is applied.

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

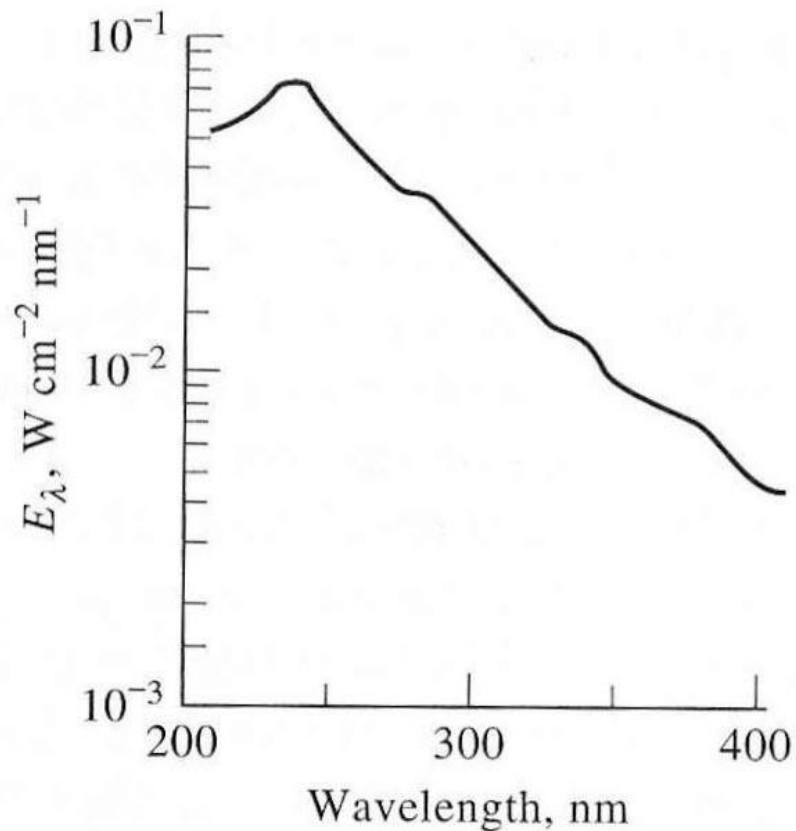


Figure 13-11 Output from a deuterium lamp.

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

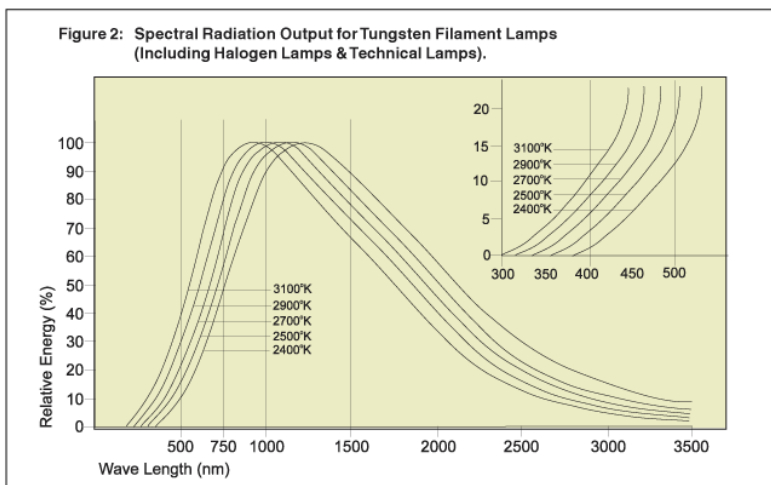
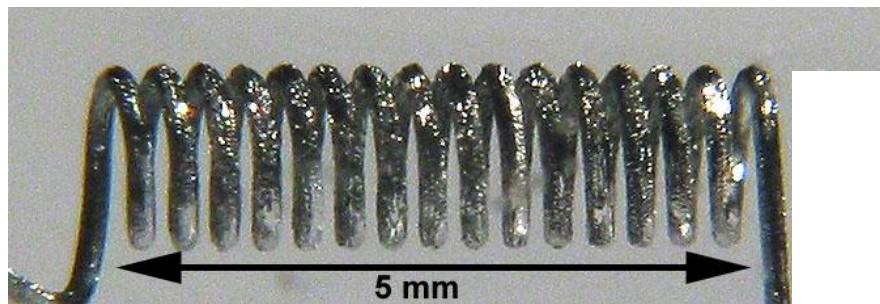
WI_2 strikes the filament

WI_2 decomposes

W redeposits on the filament.

Components of Optical Instruments

Tungsten/halogen lamps



Components of Optical Instruments

Sources of Radiation

Continuum Sources

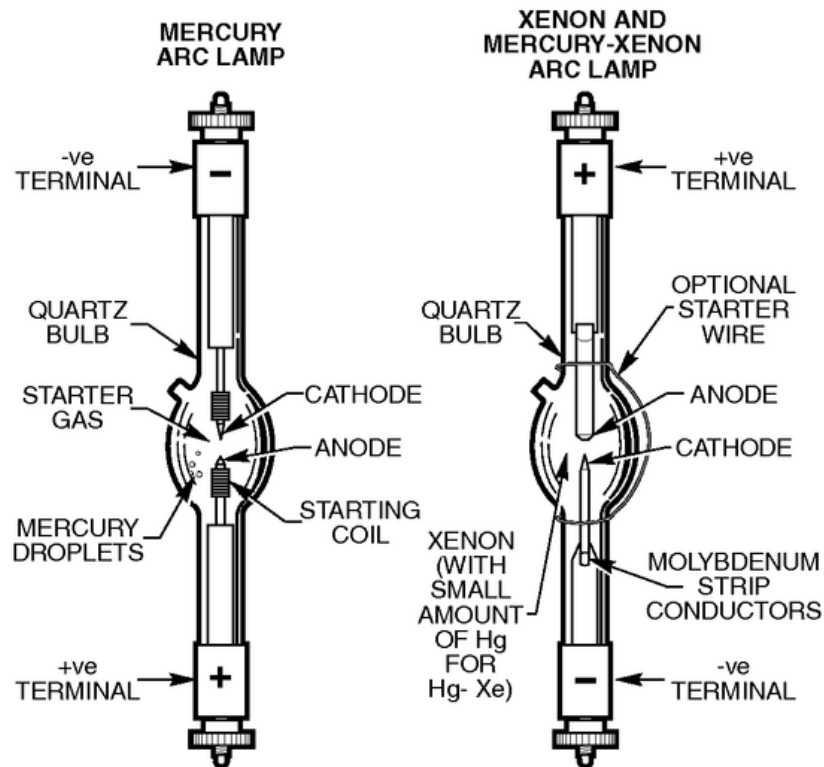
Xenon Arc Lamps

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.

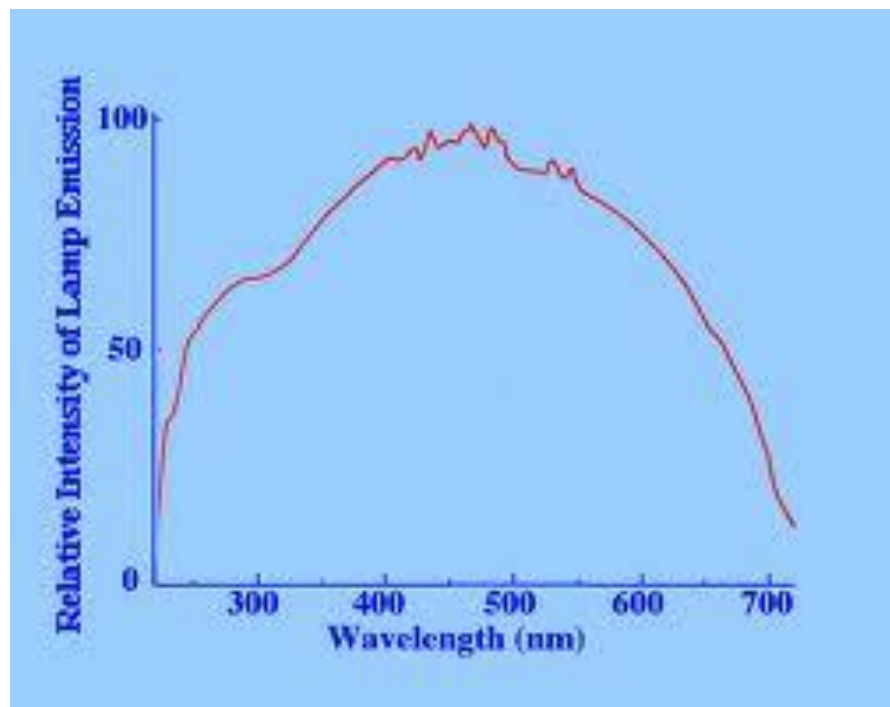
Xenon lamp better for scanning applications. Hg lamp better for a line source (discrete).

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

Sources

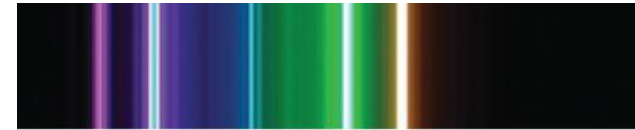
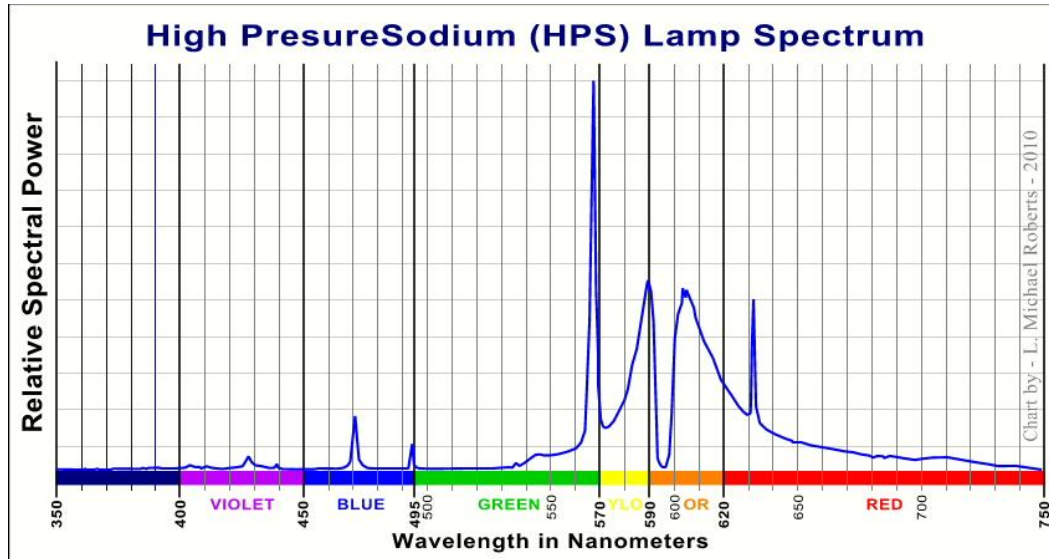
- **Low pressure Hg vapor lamps with a fused silica window.**

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

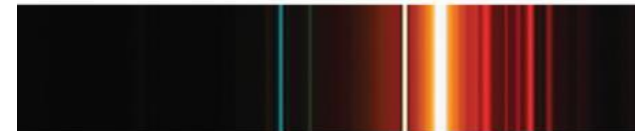
Lines are isolated with filters.

Components of Optical Instruments

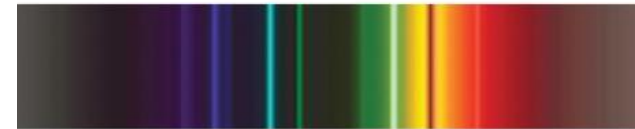
Line Sources



Hg vapor spectrum (350-700 nm)



Low-pressure Na spectrum (350-700 nm)

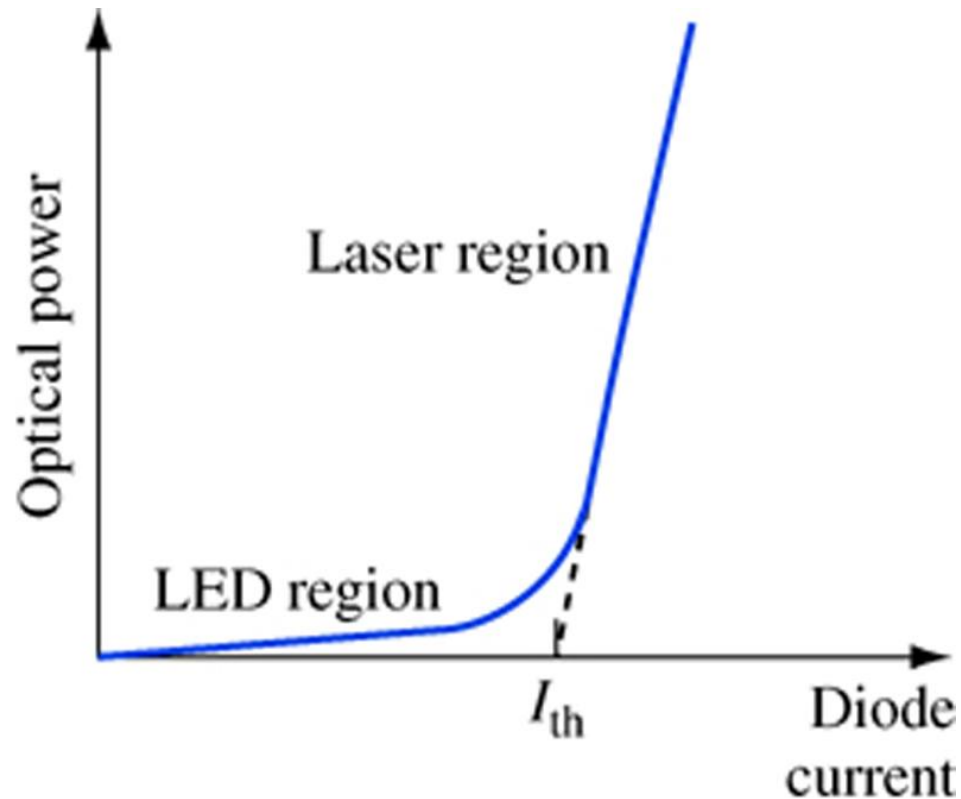


High-pressure Na spectrum (350-700 nm)

Components of Optical Instruments

Sources

Semiconductor LED vs LASER



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

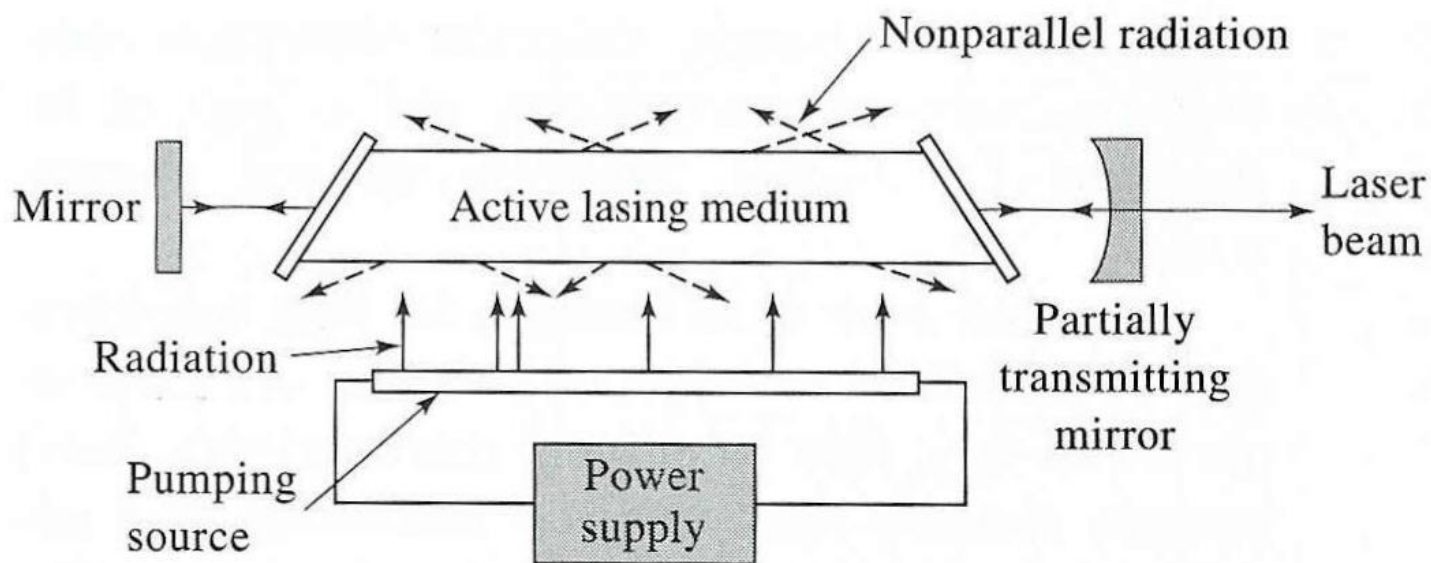
Laser Sources in UV, vis, and IR

Used for

- high resolution spectroscopy
- kinetic studies
- routine analysis

Components of Optical Instruments

Laser Sources



Components of Optical Instruments

Laser Sources

Lasing Medium:

solid crystal (ruby)

semiconductor (gallium arsenide)

solution (organic dye)

gas (argon or krypton)

Components of Optical Instruments

Lasers – Example

- **Lasers tunable dye laser pumped by pulsed N₂ 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.

Assignment

- Read Chapter 6
- Read Chapter 7
- Read Chapter 13
- Go over Lab Lecture 2

- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due today)
- HW3: Ch. 7: 2-4, 8-13, and 16 (Due 1-30)

