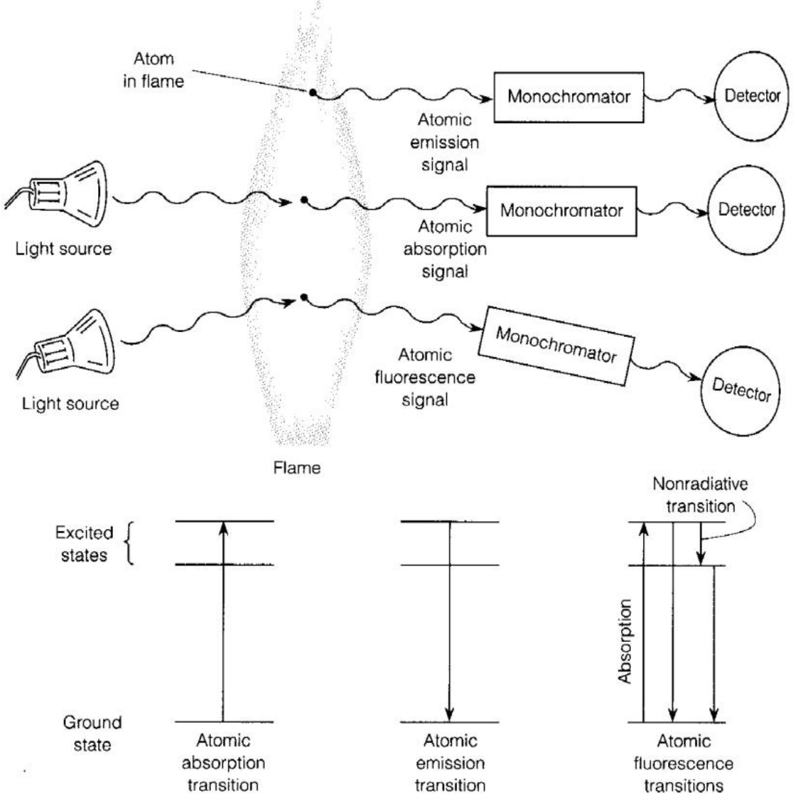
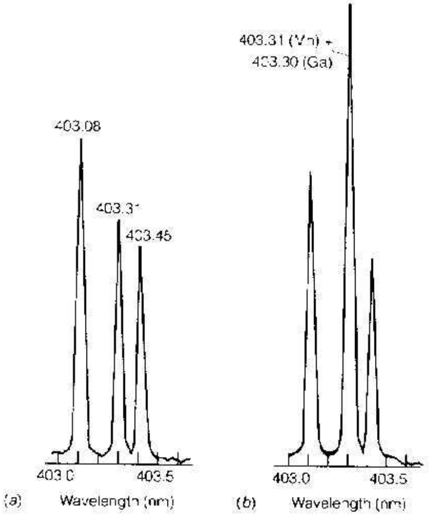
Chapter 8 - Atomic Spectroscopy
Chapter 9 – Atomic Absorption

$$A(\lambda) = \varepsilon(\lambda)bC$$



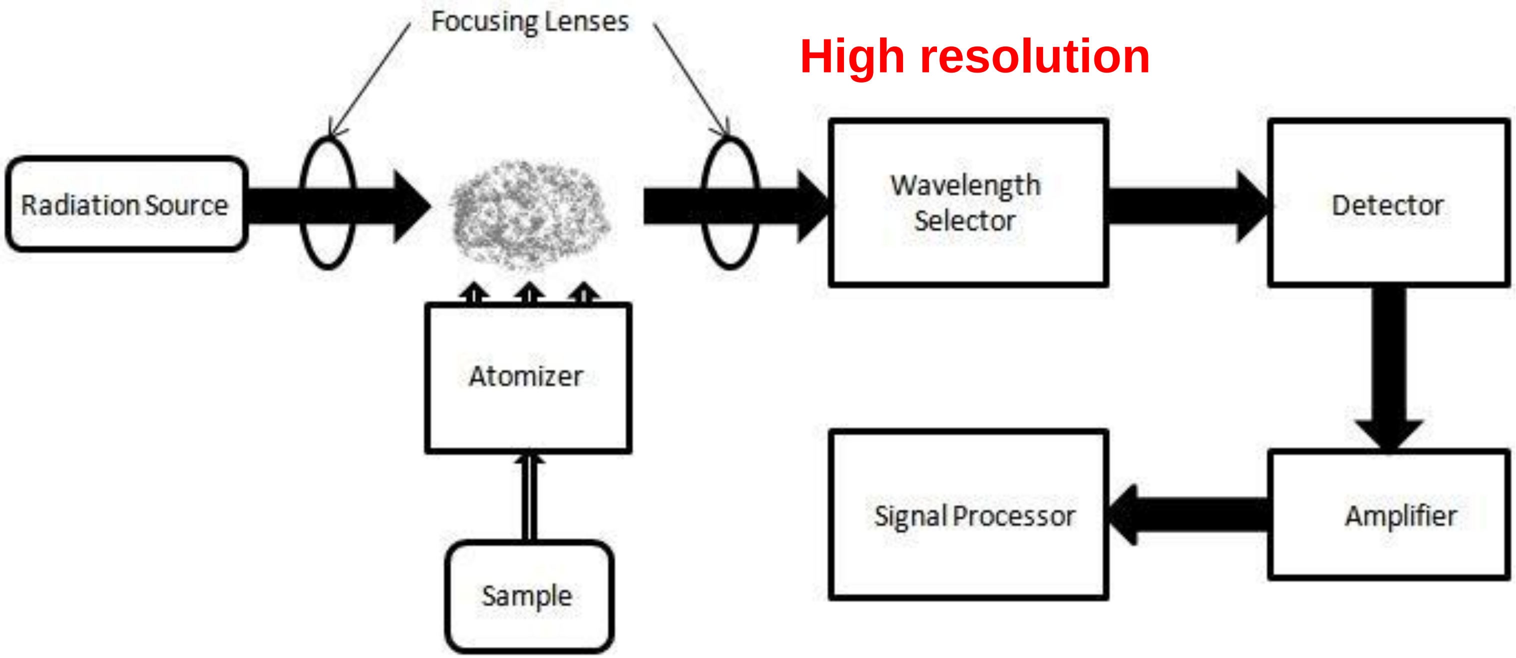


For Problem 14: Fluorescence excitation of solution containing (*a*) 1 μg Mn/mL and (*b*) 1 μg Mn/mL plus 5 μg Ga/mL. [From S. J. Weeks, H. Haraguchi, and J. D. Winefordner, *Anal. Chem.* 1978, *50*, 360.]

Notice high resolution!

Excellent series of methods for determining the elemental composition in environmental samples, foods and drinks, potable water, biological fluids, and materials.

Atomic Absorption Spectrophotometer



High resolution

Sample – aerosol mist, desolvation, atomization – atoms in gas phase!
Flame – sample holder – creates atoms to absorb wavelengths from lamp.
Radiation source – hollow cathode lamp, emission lines for the element being analyzed

An Example of Material Characterization

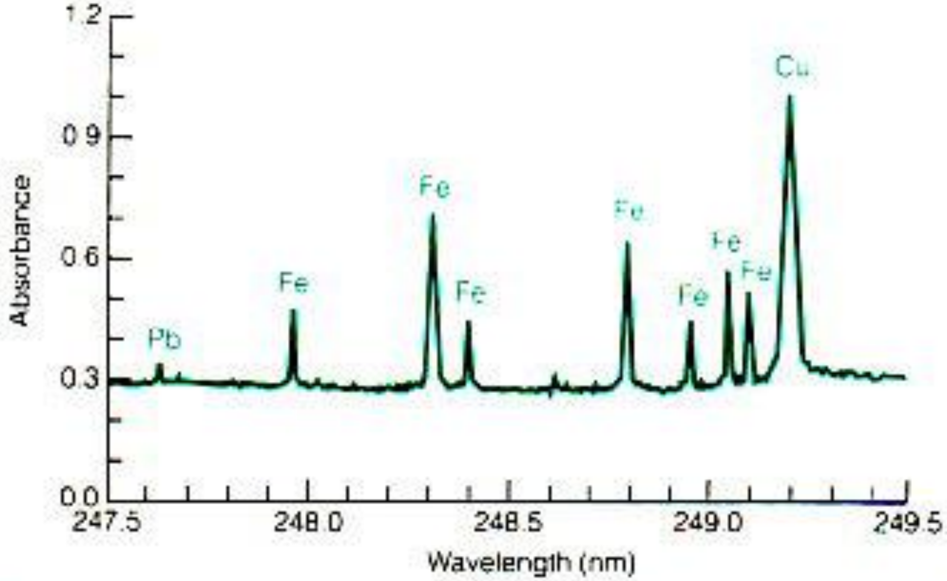


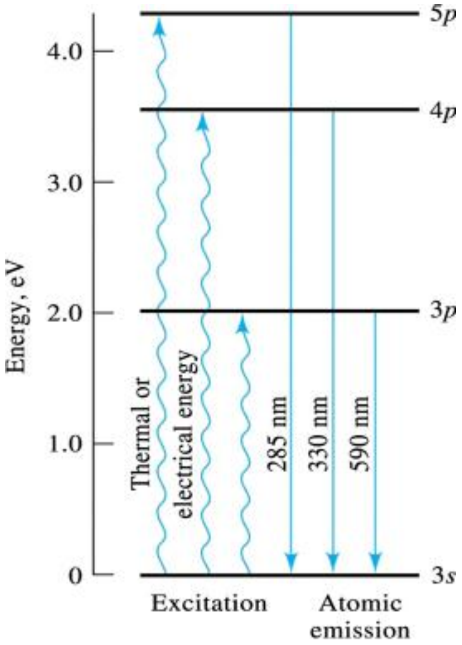
Figure 20-14 Graphite furnace absorption spectrum of bronze dissolved in HNO_3. Notice the high, constant background absorbance of 0.3 in this narrow region of the spectrum. [From B. T. Jones, B. W. Smith, and J. D. Winefordner, *Anal. Chem.* **1989**, *61*, 1670.]

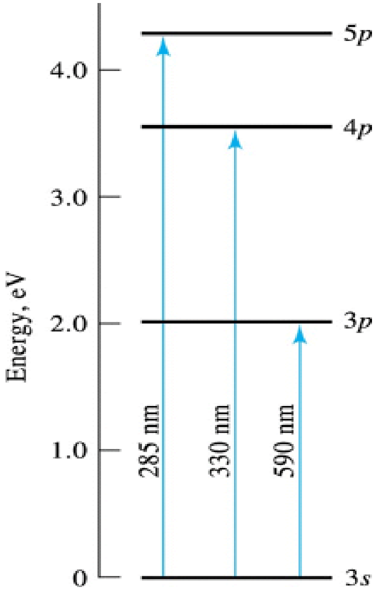
An absorption measurement was used to determine the levels of different metals in bronze. Measurement made by oxidizing the metal sample (dissolving) and then measuring the solution concentrations of the different metal ions.

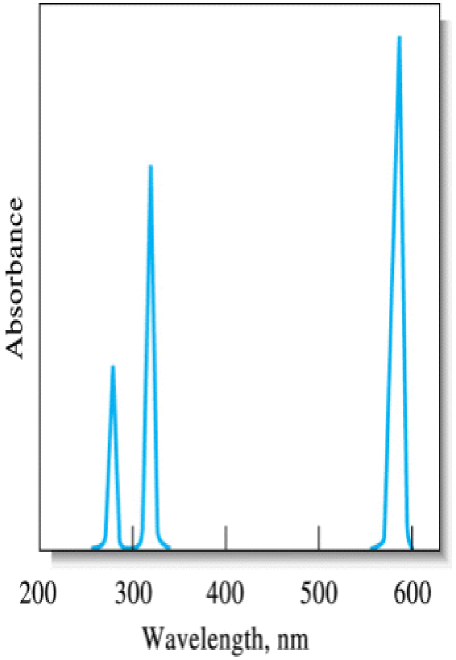
Origins of Atomic Spectra

Spectroscopy of atoms or ions do not involve vibrational or rotational transitions. Transition involves promoting an electron from a ground state to a higher empty atomic state orbital, this state is referred to as the excited state.

Shown to the right is the three absorption and emission lines for Na. Atomic p-orbitals are in fact split into two energy levels for the multiple spins of the electron. The energy level is so small however that a single line observed. A high resolution would show the line as a doublet.







Chemical Problem

The first excited state of Ca is reached by absorption of 422.7 nm light. Calculate the energy difference (kJ/mole) between the ground and excited states.

$E = h\upsilon = hc/\lambda$

$$E = \frac{(6.62 \text{ x } 10^{-34} \text{ J-s})(3.00 \text{ x } 10^{8} \text{ m/s})}{(422.7 \text{ nm})(1.00 \text{ x } 10^{-9} \text{ m/nm})} = 4.69 \text{ x } 10^{-19} \text{ J/photon}$$

$(4.69 \text{ x } 10^{-19} \text{ J/photon})(6.02 \text{ x } 10^{23} \text{ photons/mol}) = 2.83 \text{ x } 10^{5} \text{ J/photon}$

$(2.83 \text{ x } 10^{5} \text{ J/photon}) (1 \text{ kJ/1000 J}) = 283 \text{ kJ/mol}$

Optical Atomic Spectra

- Outer shell or valence electrons are promoted to unoccupied atomic orbitals by incident radiation.

- **$\Delta E = h\upsilon = hc/\lambda$**

- Small energy differences between the different transitions – excited states, therefore, high resolution instruments are needed.
- Transitions are observed only between certain energy states.

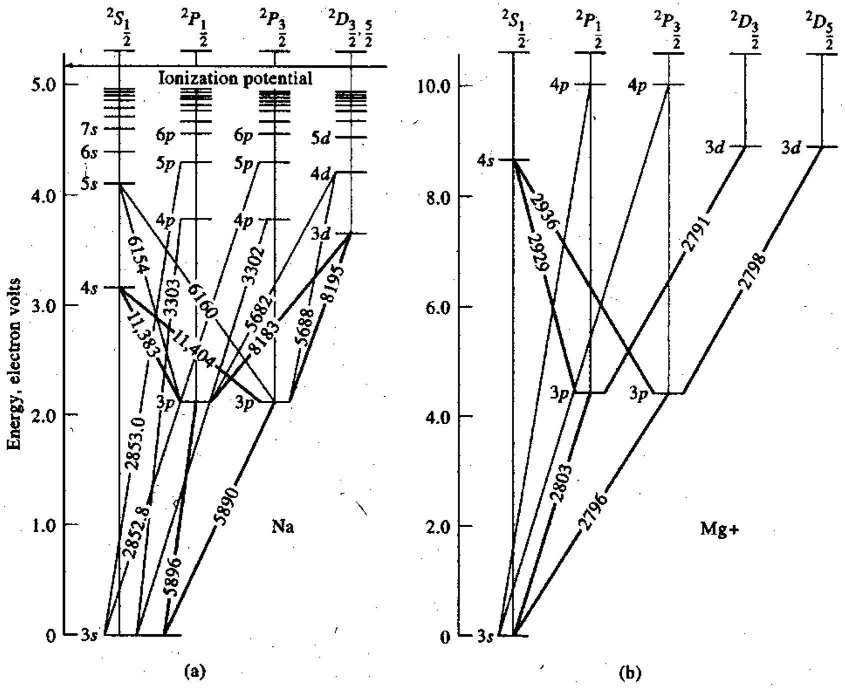


Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

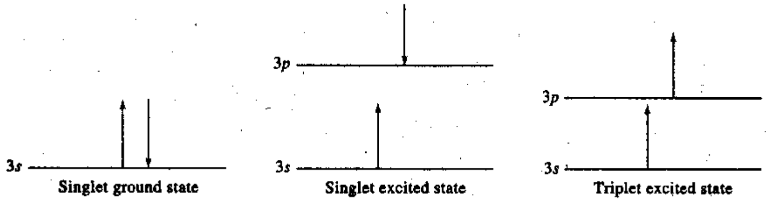


Figure 8-3 Spin orientations in singlet ground and excited states and triplet excited state.

Excitation Wavelengths and Detection Limits

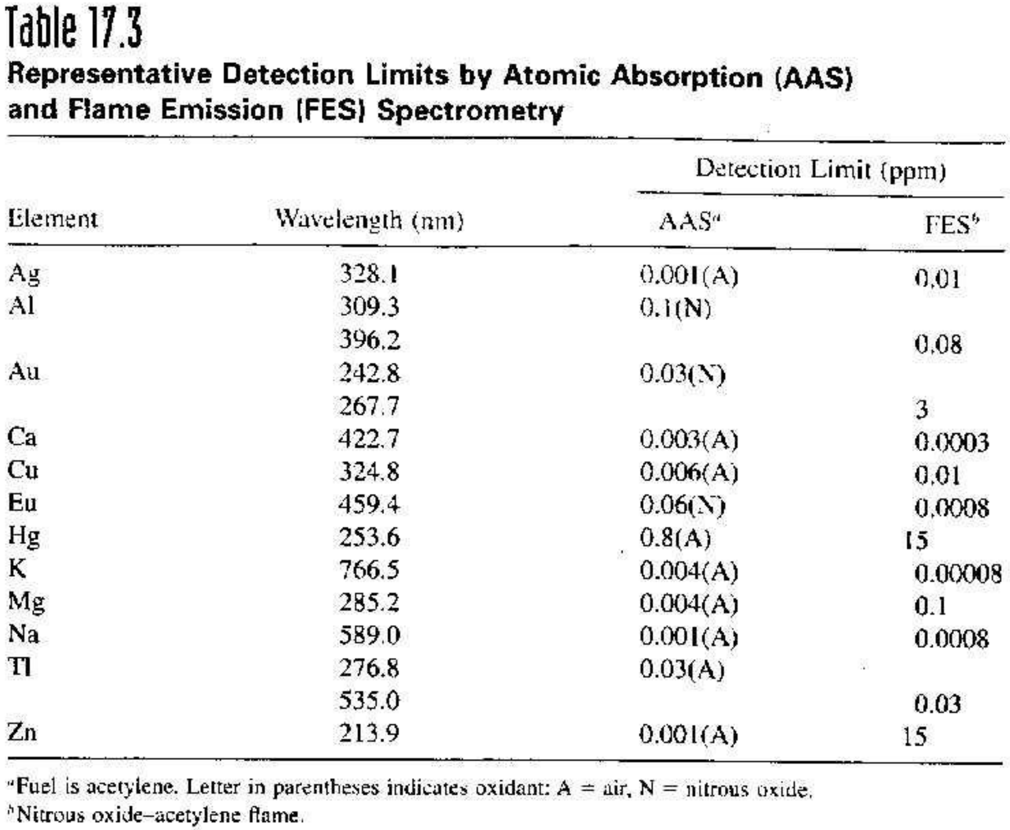


Table 17.3

Representative Detection Limits by Atomic Absorption (AAS) and Flame Emission (FES) Spectrometry

Element	Wavelength (nm)	Detection Limit (ppm)	
		AAS[a]	FES[b]
Ag	328.1	0.001(A)	0.01
Al	309.3	0.1(N)	
	396.2		0.08
Au	242.8	0.03(N)	
	267.7		3
Ca	422.7	0.003(A)	0.0003
Cu	324.8	0.006(A)	0.01
Eu	459.4	0.06(N)	0.0008
Hg	253.6	0.8(A)	15
K	766.5	0.004(A)	0.00008
Mg	285.2	0.004(A)	0.1
Na	589.0	0.001(A)	0.0008
Tl	276.8	0.03(A)	
	535.0		0.03
Zn	213.9	0.001(A)	15

[a] Fuel is acetylene. Letter in parentheses indicates oxidant: A = air, N = nitrous oxide.

[b] Nitrous oxide–acetylene flame.

These are wavelengths with relatively large ε(λ) values so signals are good to use for quantitation.

Chemical Problem

Calculate the emission wavelength (nm) of excited atoms that lie 3.371×10^{-19} J per molecule above the ground state.

$E = hc/\lambda$ or $\lambda = hc/E$

$$\lambda = \frac{(6.62 \times 10^{-34}\ \text{J-s})(3.00 \times 10^{8}\ \text{m/s})}{3.371 \times 10^{-19}\ \text{J}} = 5.89 \times 10^{-7}\ \text{m}$$

$$\frac{(5.89 \times 10^{-7}\ \text{m})\ (1)}{1.00 \times 10^{-9}\ \text{m/nm}} = 589\ \text{nm}$$

Visible light!!

Atomic Line Widths

Sources of Line Broadening

1. Uncertainty effect
2. Pressure effects due to collisions
3. Doppler effect
4. Electric and magnetic field effects

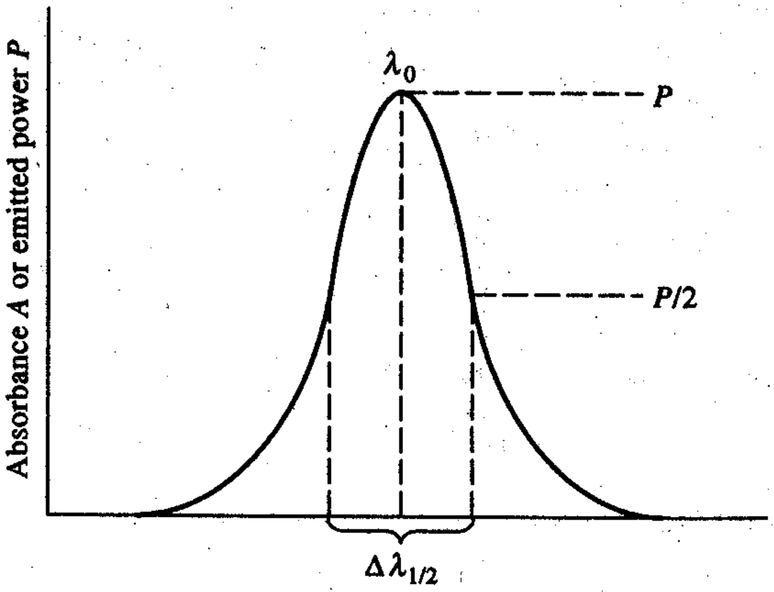


Figure 8-6 Profile of an atomic line showing definition of the effective line width $\Delta\lambda_{1/2}$.

Spectral line widths are typically 0.01 nm or so.

The Uncertainty Effect

- Spectral lines always have finite widths because the lifetimes of one or both of the transitions states are finite, which leads to uncertainties in the transition times.

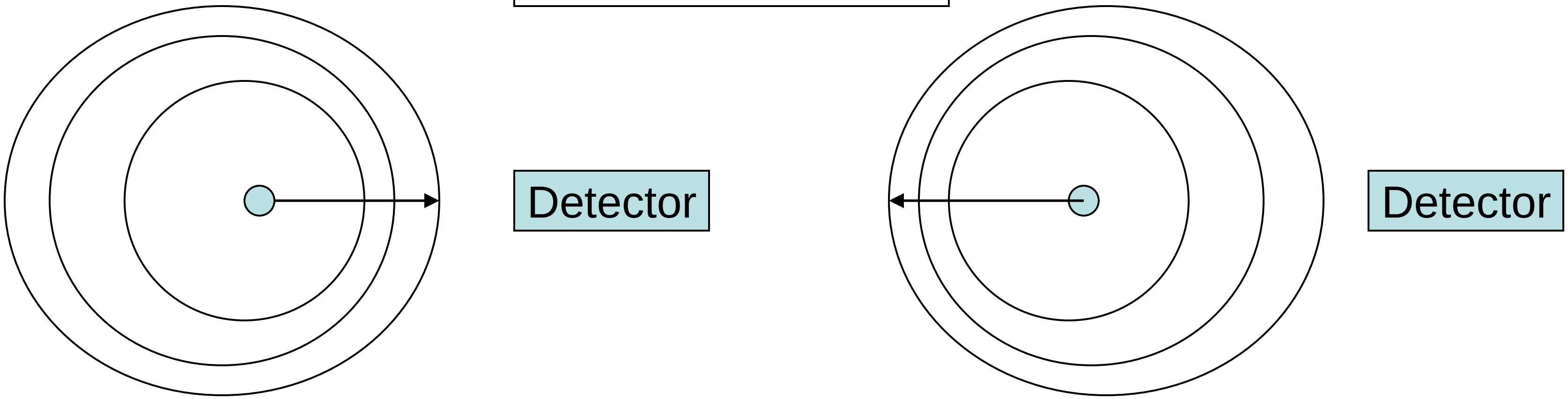
$$\Delta\upsilon \bullet \Delta t > 1$$

- Lifetime of the ground state is long but the lifetime of the excited state is brief, 10^{-8} s.
- If one wants to know $\Delta\upsilon$ with high accuracy, then the time of the measurement, Δt, must be very long!
- Line widths due to uncertainty broadening are sometimes called natural line widths, and are about 10^{-4} Å.

Doppler Broadening

$$\Delta\lambda/\lambda_o = \upsilon/c$$

υ = velocity of an emitting and moving atom


Detector

Detector

Doppler Broadening - When molecules are moving towards a detector or away from a detector the frequency will be offset by the net speed the radiation hits the detector. This is also known as the Doppler effect and the true frequency will ether be red shifted (if the chemical is moving away from the detector) or blue shifted (if the chemical is moving towards the detector)

- Wavelength of radiation emitted or absorbed by rapidly moving atom **decreases** if motion is toward the detector and **increases** if motion is away from the detector.
- 10^{-2} to 10^{-1} Å **Situation is the same for an absorbing atom moving toward or away from the source.**

Pressure Broadening

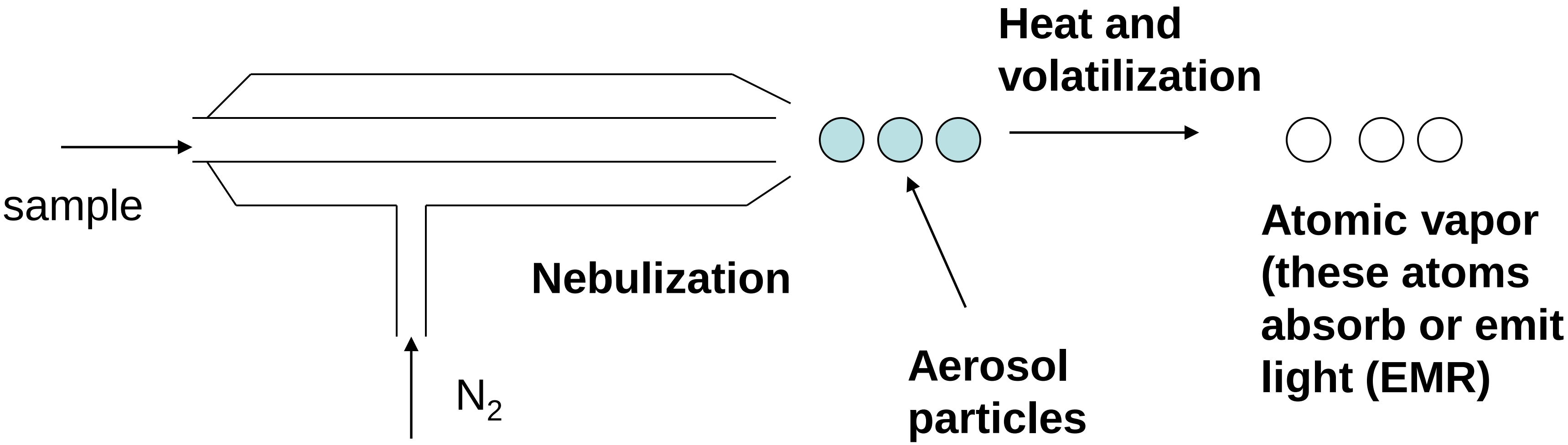
- Broadening that arises from collisions of the emitting or absorbing species with other atoms or ions in the heated medium.
- Collisions cause small changes in the ground state energy levels and hence a range of absorbed or emitted wavelengths.
- ~ 10^{-1} Å or so

Atomization Process

- Temperature effects are significant

$$N_j/N_o = P_j/P_o \exp(-E_j/kT)$$

- The process by which a sample is converted into atomic vapor is called *atomization*.



sample

N_2

Nebulization

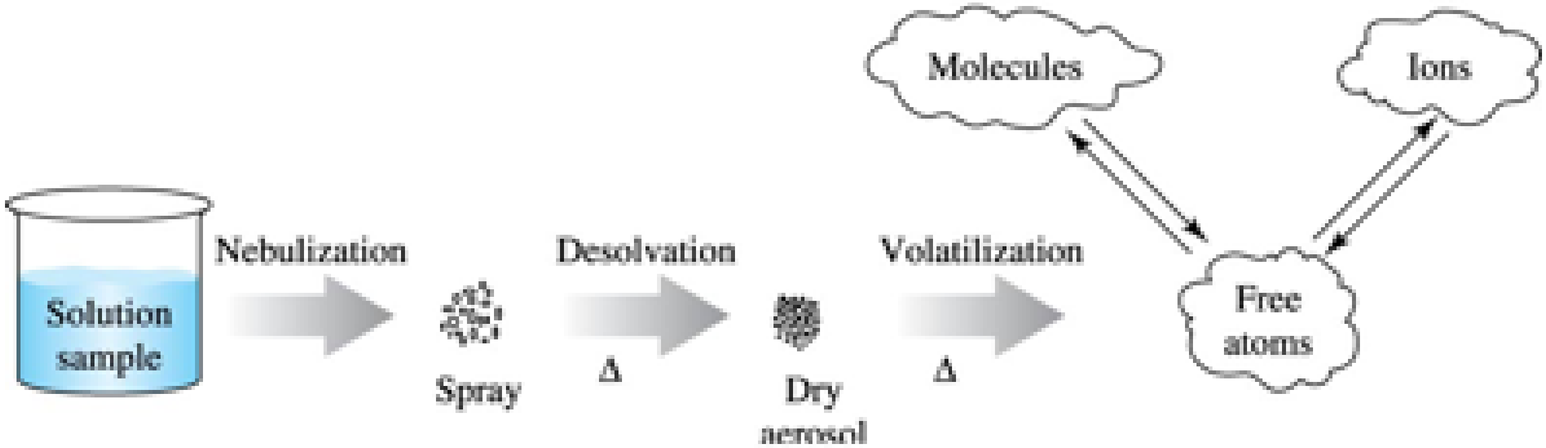
Aerosol particles

Heat and volatilization

Atomic vapor (these atoms absorb or emit light (EMR)

Nature of the Sample in AAS

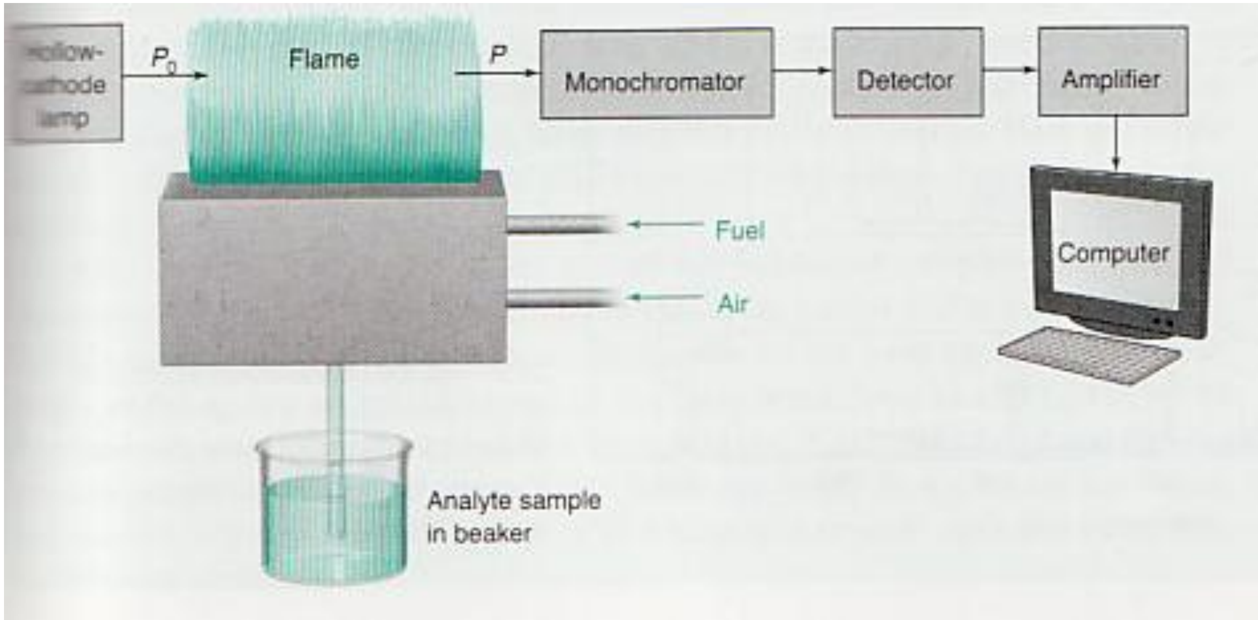
Neutral atoms in the gas phase are desired!!



Process of sample introduction into the flame where absorption occurs. It is the “sample”holder”.

Atomic Spectroscopy

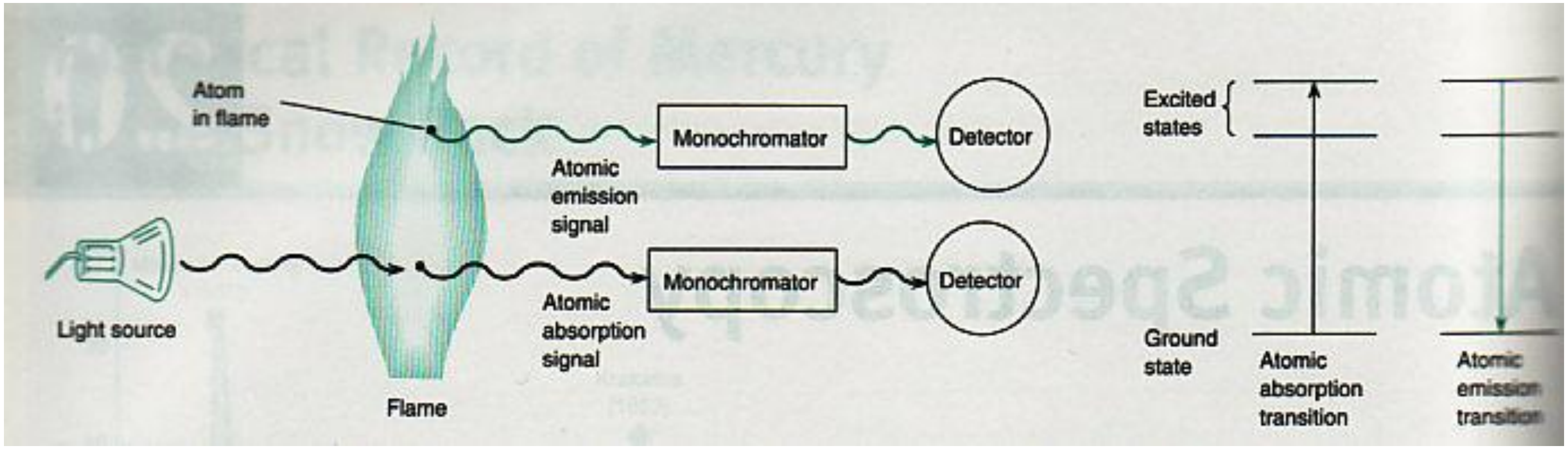
Atomic spectroscopy is a principal tool for measuring metallic elements at trace levels in industrial and environmental laboratories.



Atomic absorption = requires a lamp with light absorbed by atoms

Atomic emission = luminescence from excited atoms – no lamp required.

Sample Holder is the Flame

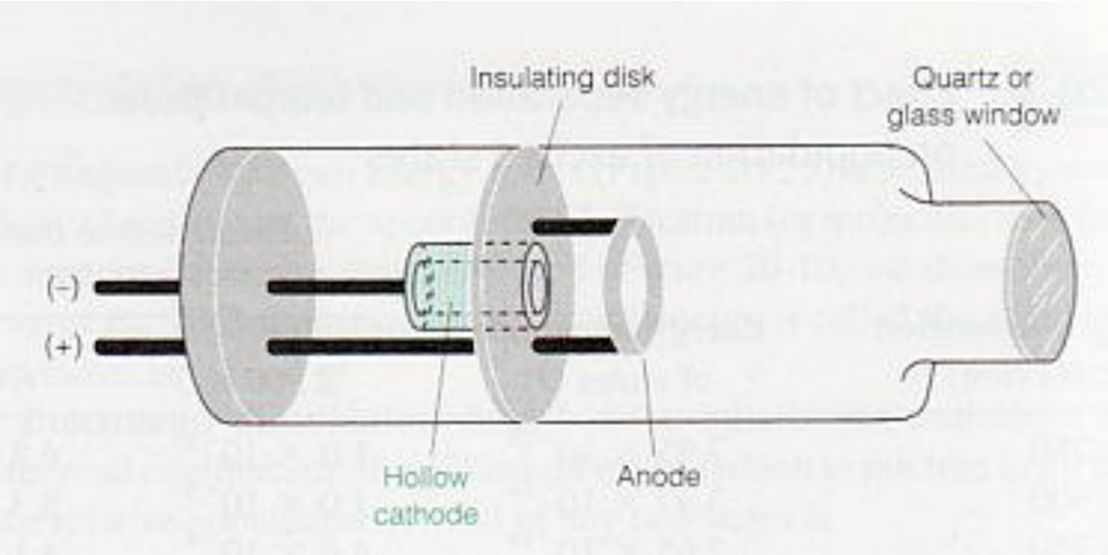


Neutral atom in gas phase

Atoms have no vibrations and rotations (energy levels associated with molecules), therefore, spectral bands are more narrow so high resolution instrument

Hollow Cathode Lamp (Line Source)

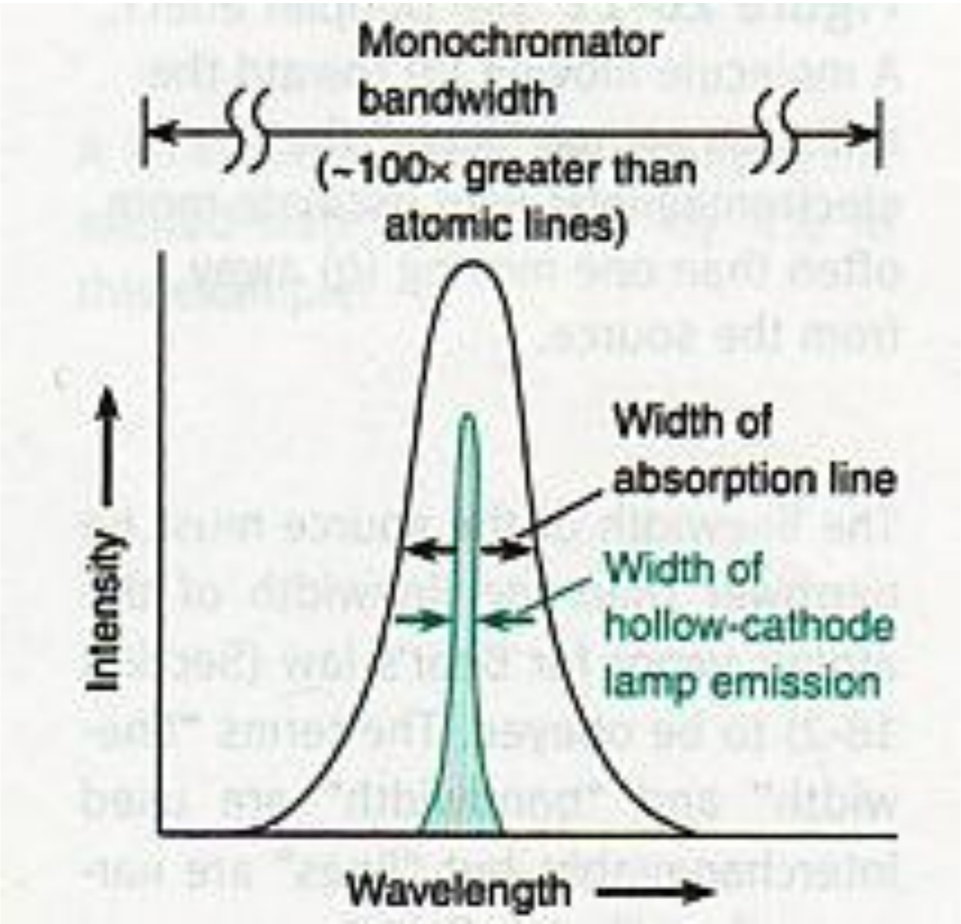
A lamp with a <u>matching</u> cathode material is required for each element.



Gaseous metal atoms sputtered from cathode by impacting Ar+ in an excited state. They release this “extra energy” by emitting photons and return to ground state.

Atomic radiation emitted by the lamp has the same frequencies at that absorbed by atoms in the flame or furnace.

Narrow Absorption Lines from Source



High resolution instruments needed. Monochromator with a longer focal length, more narrow slit widths and a higher resolution grating are needed.

Flame = Sample Holder

Acetylene – air

(2400 -2700 K)

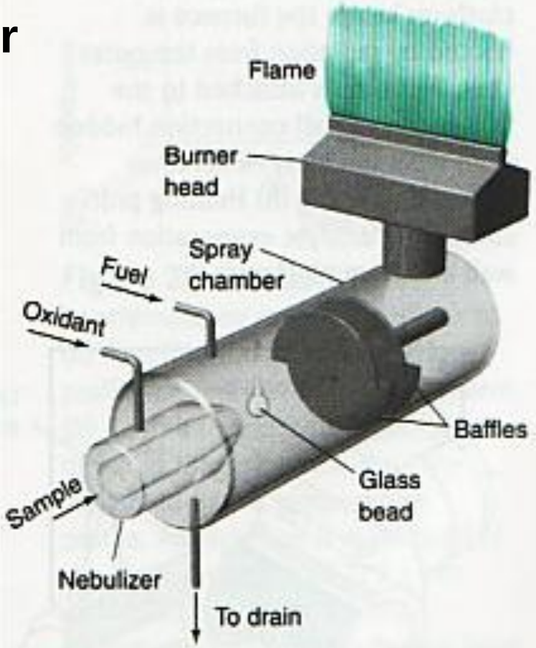


Figure 20-4 Premix burner with a pneumatic nebulizer. The slot in the burner head is typically 10 cm long and 0.5 mm wide.

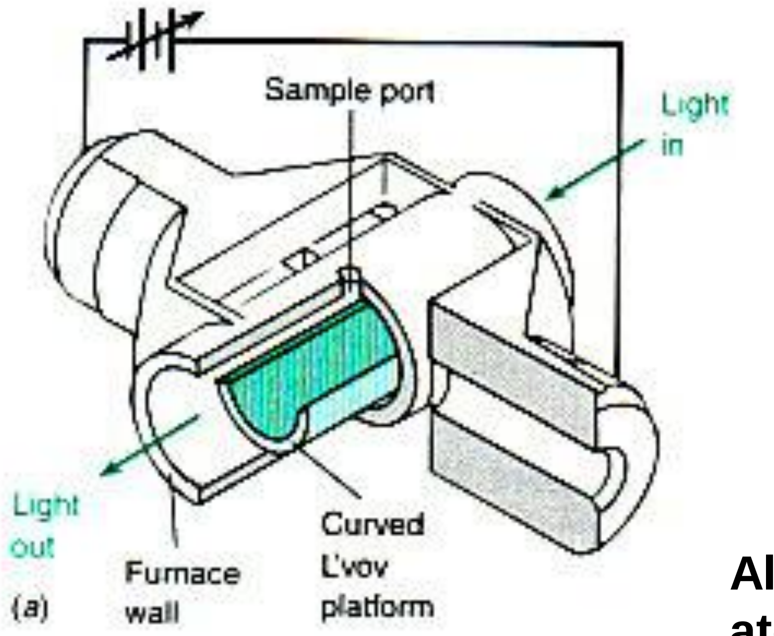
1. Nebulization

2. Desolvation

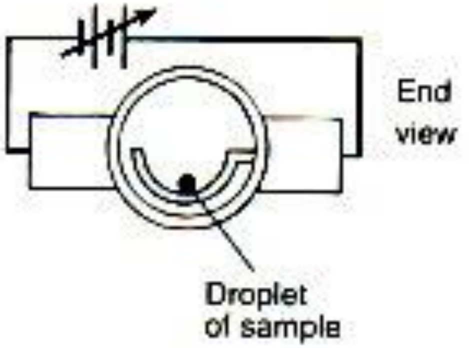
3. Atomization

Atomization is the process of breaking analyte into gaseous atoms, which are then measured by their absorption or emission of radiation.

Graphite Tube Furnace



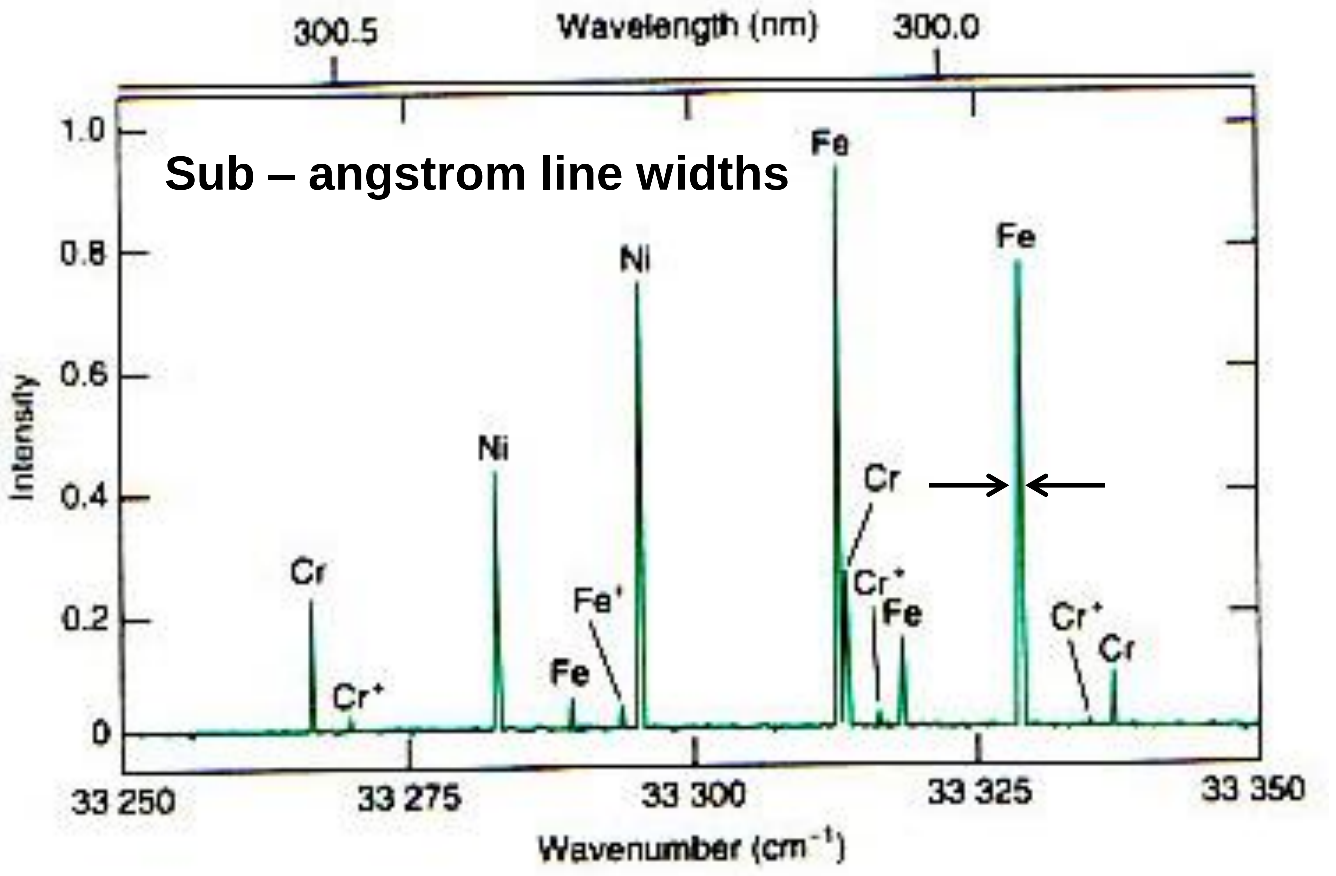
1 – 100 µL sample volume



All sample is atomized and all atoms remain in optical path for several seconds.

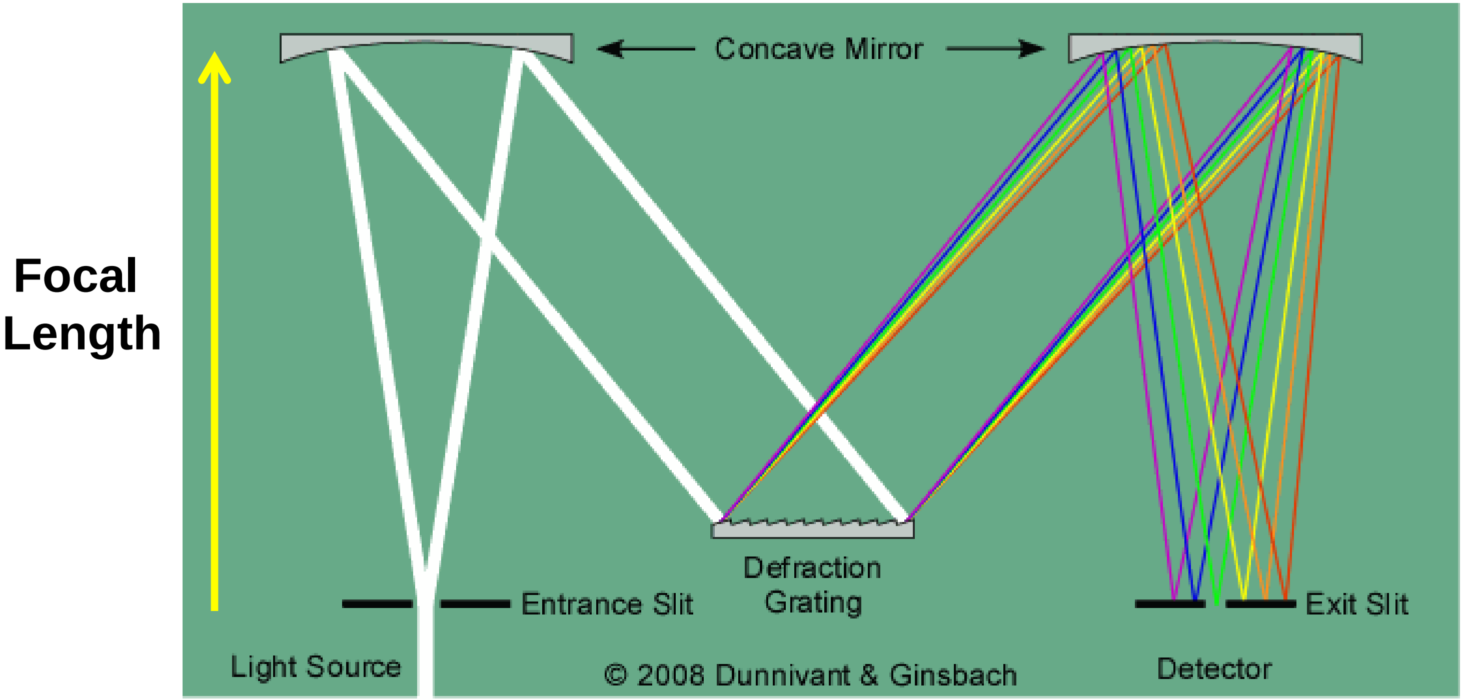
Furnaces offer increased sensitivity (significantly lower detection limits) and require less sample than a flame.

Typical Spectrum



Multiple narrow bands are typical for atomic absorption or emission spectra. Gaseous atoms absorbing or emitting light.

Monochromator or Wavelength Selector



Key component properties: (i) good stray light rejection, (ii) high resolution ($\Delta\lambda/\lambda = nN$), (iii) good light gathering power (F = f (focal length)/d (diameter of mirror)

Photomultiplier Tube (Single Channel)

A photomultiplier tube, useful for light detection of very weak signals, is a photoemissive device in which the absorption of a photon results in the emission of an electron. These detectors work by **amplifying** the electrons generated by a photocathode exposed to a photon flux.

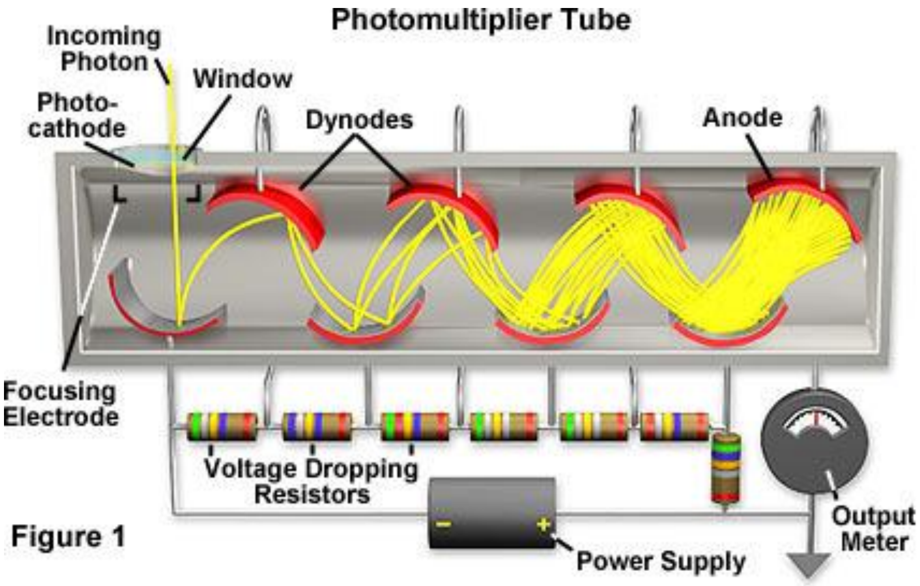

Photomultiplier Tube

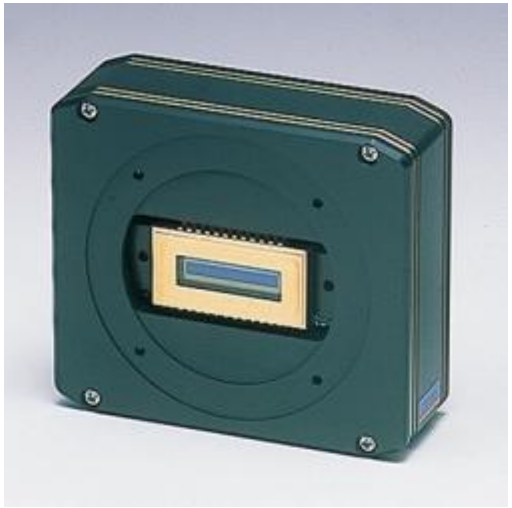
Figure 1

Each dynode is + 90 V more positive that the previous one

$$\boxed{I_{ph} = kP}$$

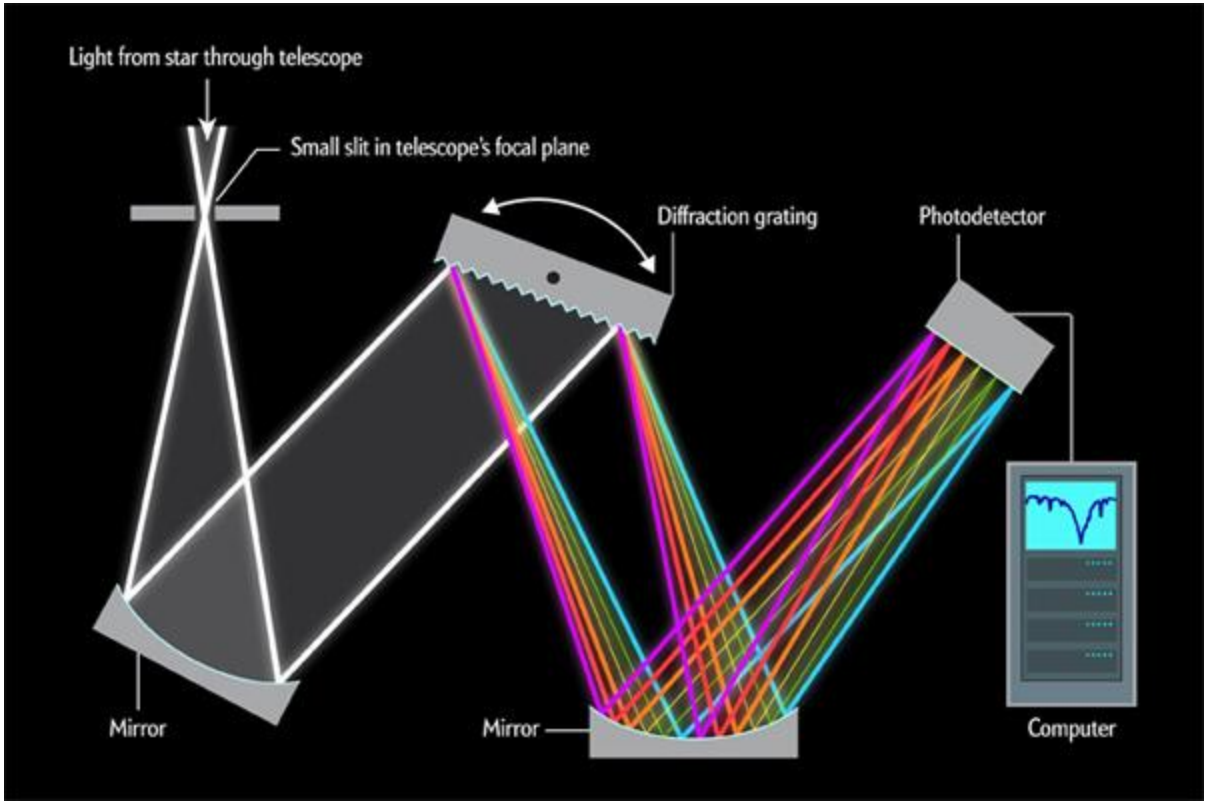
I_{ph} = photocurrent
P = incident power of light

Spectrograph - Multichannel Detector



Hamamatsu

$$\boxed{I_{ph} = kP}$$



All wavelengths detected simultaneously, fast scanning instruments, signal averaging possible to improve S/N

Types of Interferences

- ***Spectral*** – signals from other elements overlap signals for analyte of interest.

Analyte signal overlaps signals from other species or from flame.

- ***Chemical***– chemical reactions decrease the concentration of analyte atoms.

$Ca^{2+} + SO_4^{2-} \longrightarrow CaSO_4$

(nonvolatile)

(*Releasing* and *protecting* agents)

- ***Ionization*** – ionization of analyte atoms decreases the concentration of neutral atoms.

$M(g) \longrightarrow M^+(g) + e^-$

(*Ionization suppressor*)