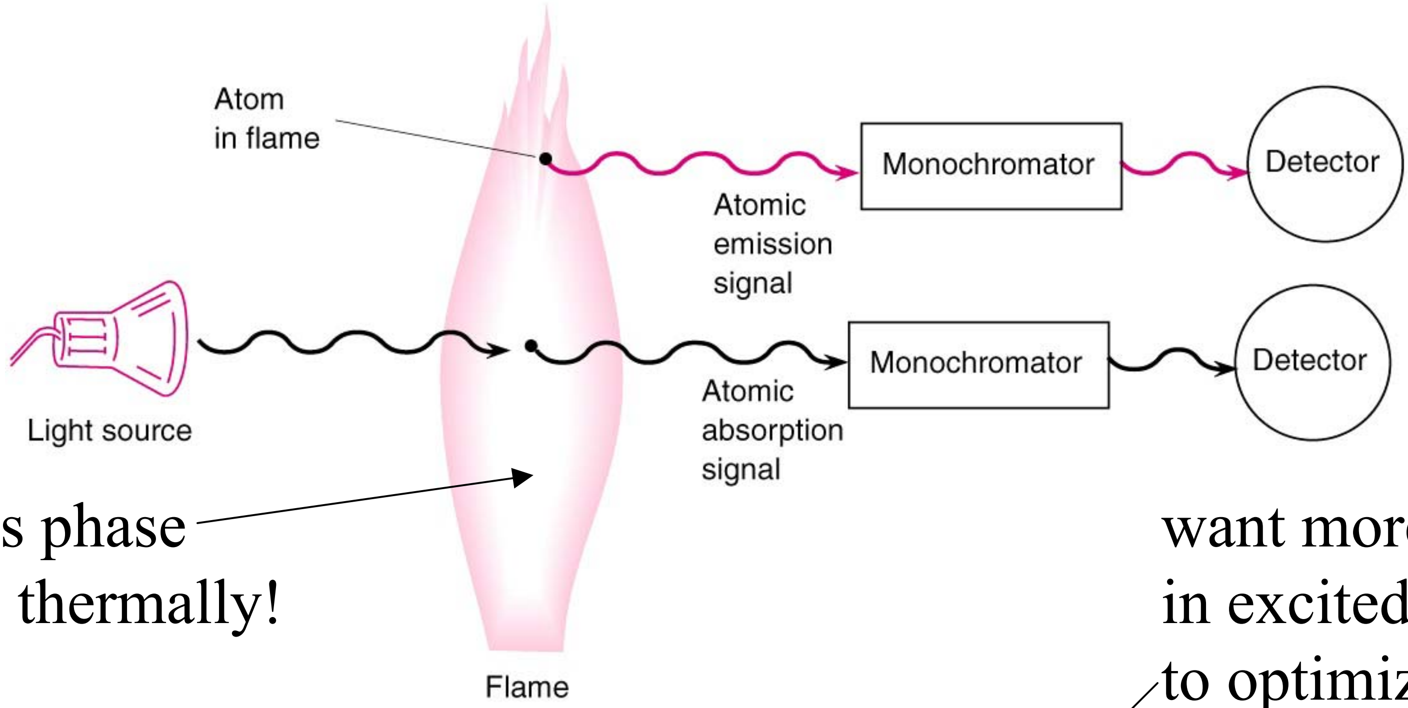
Optical Atomic Spectroscopy

- Methods to measure conentrations of primarily metallic elements at < ppm levels with high selectivity!

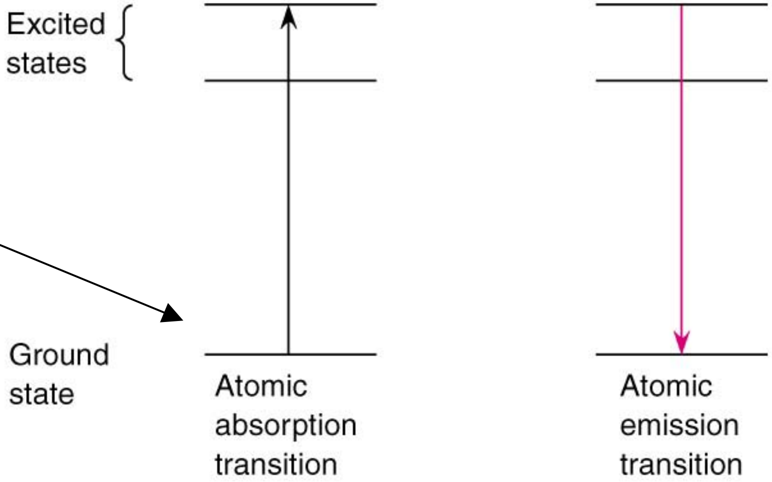
- Two main optical methodologies-
  - -Atomic Absorption--need ground state atoms
  - -Atomic Emission--need excited state atoms

- Also---type of hybrid methods--ICP-MS (inductively coupled plasma with mass spectrometry detection)



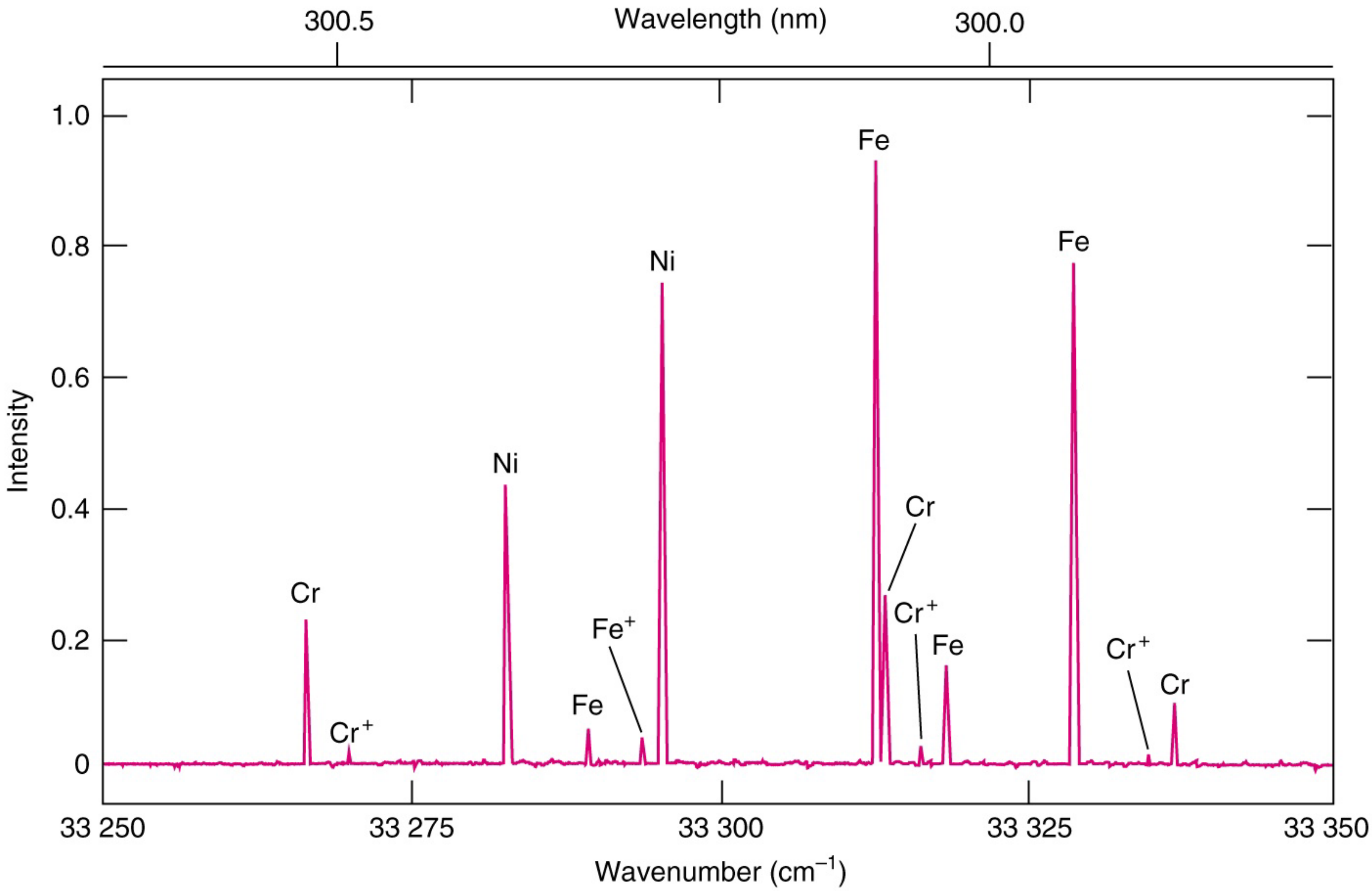
for gas phase atoms thermally!

want more atoms in excited state to optimize sensitivity!



want more atoms in ground state to optimize sensitivity

energy levels of atoms are quantized-very finite energy difference between orbitals--thus absorption and emission lines are very narrow--10^{-2} - 10^{-3} nm



part of emission spectrum from atomization of steel--note how narrow the lines are --expressed in cm^{-1} ; λ= 1/wavenumber

Ways to form gas phase atoms (called atomization)

1. **Flames---**aspirate liquid sample into flame!--Heat of the flame desolvates species, creates salts of ions, and then further heating in flame decomposes these particles into gas phase atoms

   ---Temperature of flame is critical---for atomic absorption--want cooler flame---but still hot enough to get good atomization efficiency;

   ---For atomic emission--want hotter flame--to get more gas phase atoms in excited state!

Boltzmann Distribution:

$$\frac{N^*}{N_o} = \left(\frac{g^*}{g_o}\right) e^{-\frac{\Delta E}{kT}}$$

k = 1.381 x 10^{-23} J/K

N^* = # atoms in excited state

N_o = # atoms in lower energy level

Ratio--relative population

g^* and g --degeneracies--effective # of possible states at each energy level sample values---from Boltzmann equation;

for Na^0 (for 3.371 J/atom energy difference)($g^*/g_o = 2$):
@ 2600^o K; $N^*/N_o = 0.000167$
@ 2610^o K; $N^*/N_o = 0.000174$

% difference = 4% ; small change in temperature significantly changes the ratio of N^*/ N_o ---and since emission intensity would depend on N^* value---then atomic emission techniques would be most influenced by this change in temperature.

However, if you were doing AA (atomic absorption)---this small change in temperature would have very little effect---since 99.8% of the sodium atoms are in ground state and small change in temperature may change this to 99.7%---but this would not effect the AA absorbance signal measured!

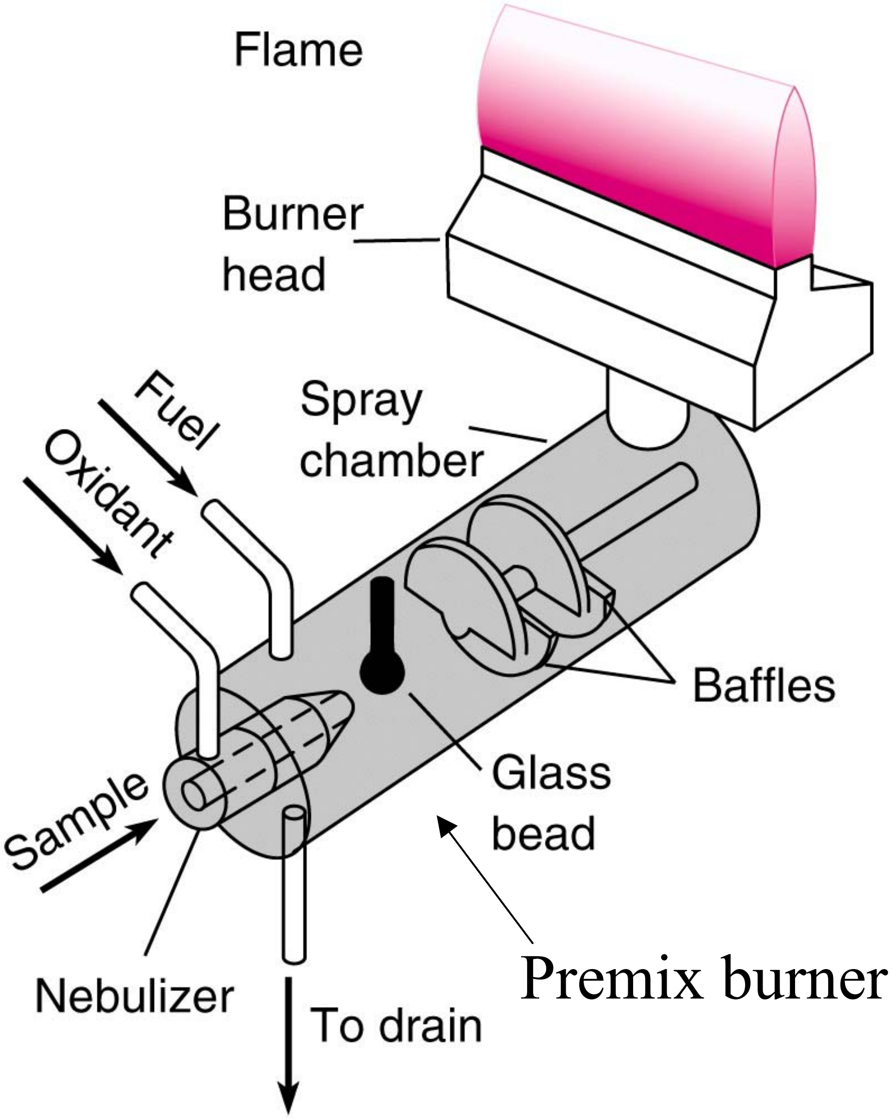
more example data from boltzmann (assuming $g^*/g_o=1$)--

N^*/N_o values

	2500° K	6000° K
250 nm	1.0×10^{-10}	6.8×10^{-5}
500 nm	1.0×10^{-5}	8.3×10^{-3}
750 nm	4.6×10^{-4}	4.1×10^{-2}

note--even at high temperatures----always more species in ground state---however, 100 fold or greater increase in N^*/N_o values---**means that emission spectroscopy at high temperatures will be much more sensitive**!!--(lower detection limits).

Flames--Con’t ; temperature depends on **fuel** and **oxidant** used!

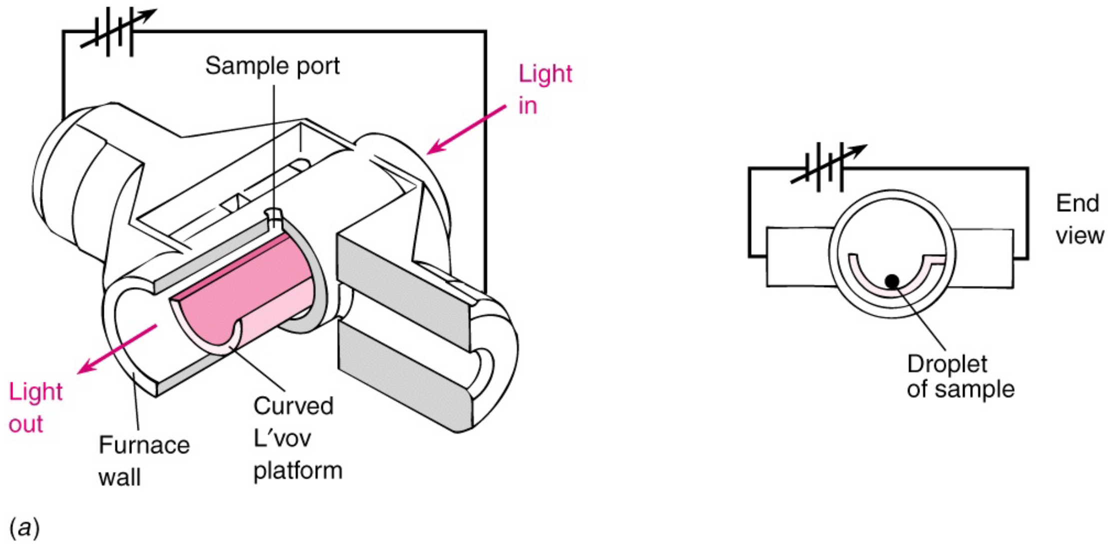


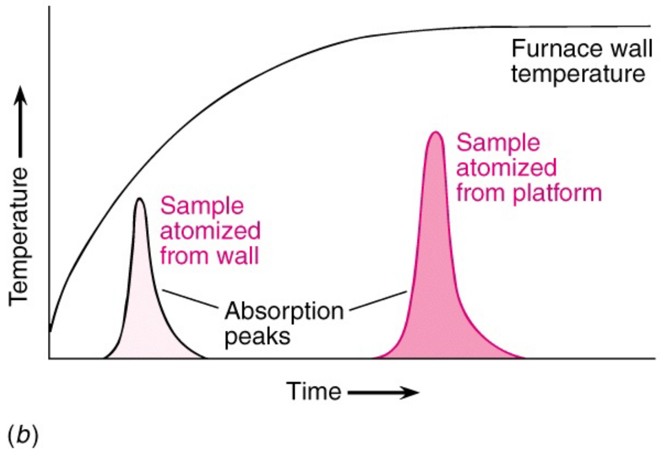
Premix burner

Acetylene/air- 2400-2700 K
H_2/O_2 --2300-2400 K
Acetylene/O_2 -3300-3400 K

nebulizer----fine (tiny) droplets of sample ----allows fast desolvation when small droplets enter flame!
--Residence time in flame is very short---so time for desolvation and atomization is very short!--<u>THIS LIMITS ATOMIZATION EFFICIENCY</u>

Graphite Furnace----Second way to form gas phase atoms---used exclusively for AA (flameless AA).





- small volume of sample deposited within graphite tube or on graphite platform

- wall of tube is made hotter and hotter in 3 steps by flowing current through the wall-- with external power supply (ohmic heating).

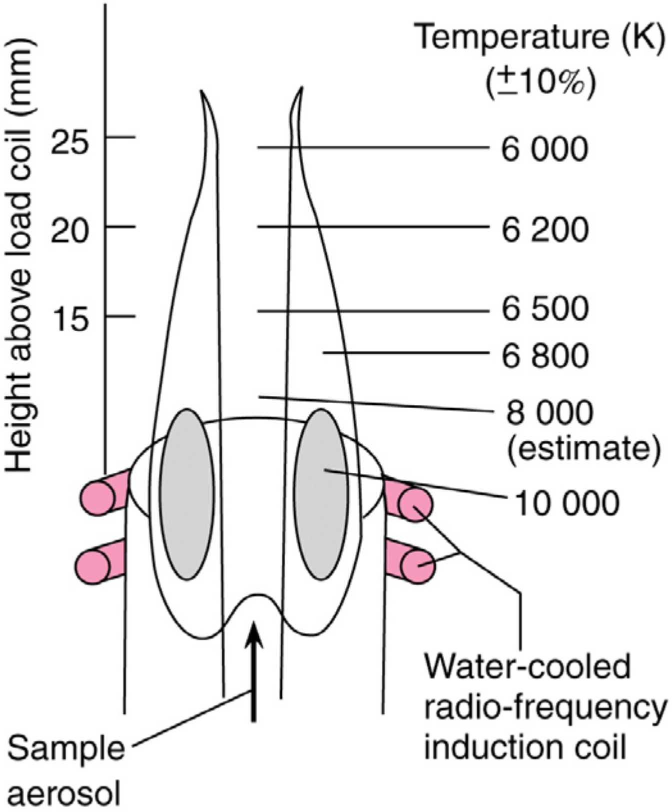
- first use low temp to dry the sample---then heat the wall to 1400 K for short period to ash/char--then up to 2550 ^{o}K for few seconds---to form gas phase atoms

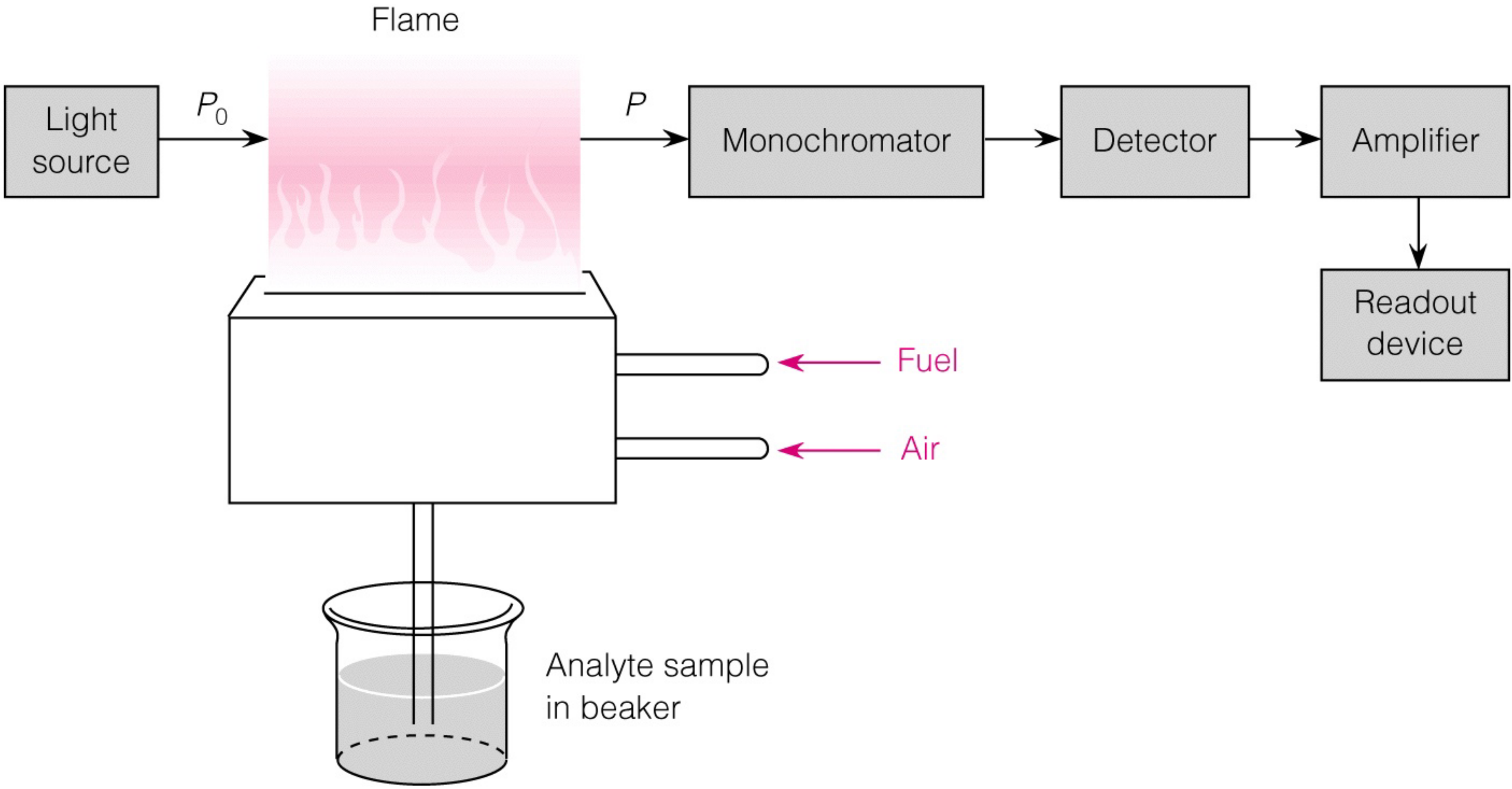
Furnace gives better detection limits than flame for AA--because you get much great atomization efficiency---(I.e., greater fraction of what you put in as sample is actually converted to gas phase atoms-you control time of desolvation, ashing, etc.---entire plume of analyte atoms comes off wall into path of light beam!

Inductively Coupled Plasma----3rd and Hottest Source---used for ICP-emission, ICP-MS

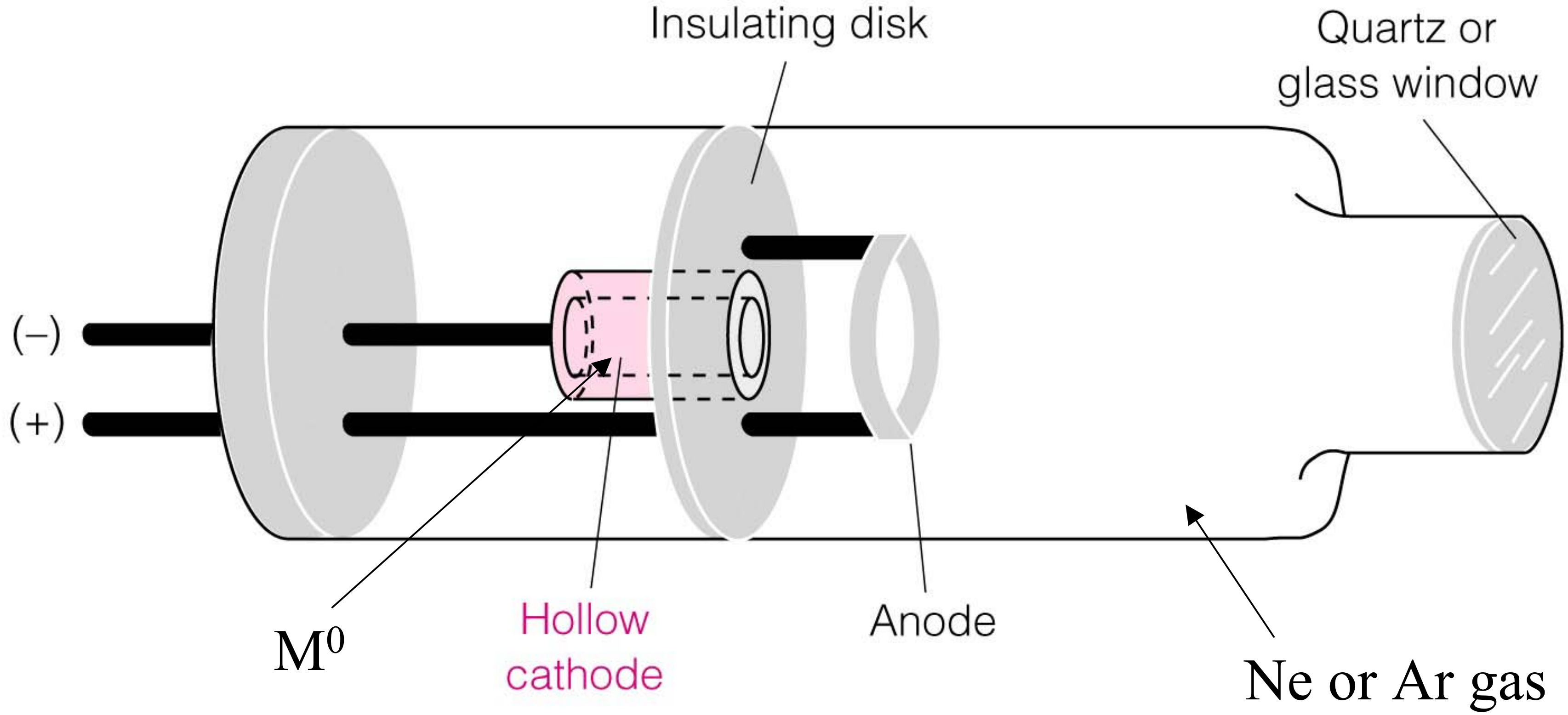
use Ar gas---and ionize it ---to create He^{+} + e^{-} --then use oscillating magnetic field produced by induction coil to cause hot plasma of ionized gas!

Very expensive to, both to purchase and operate!!



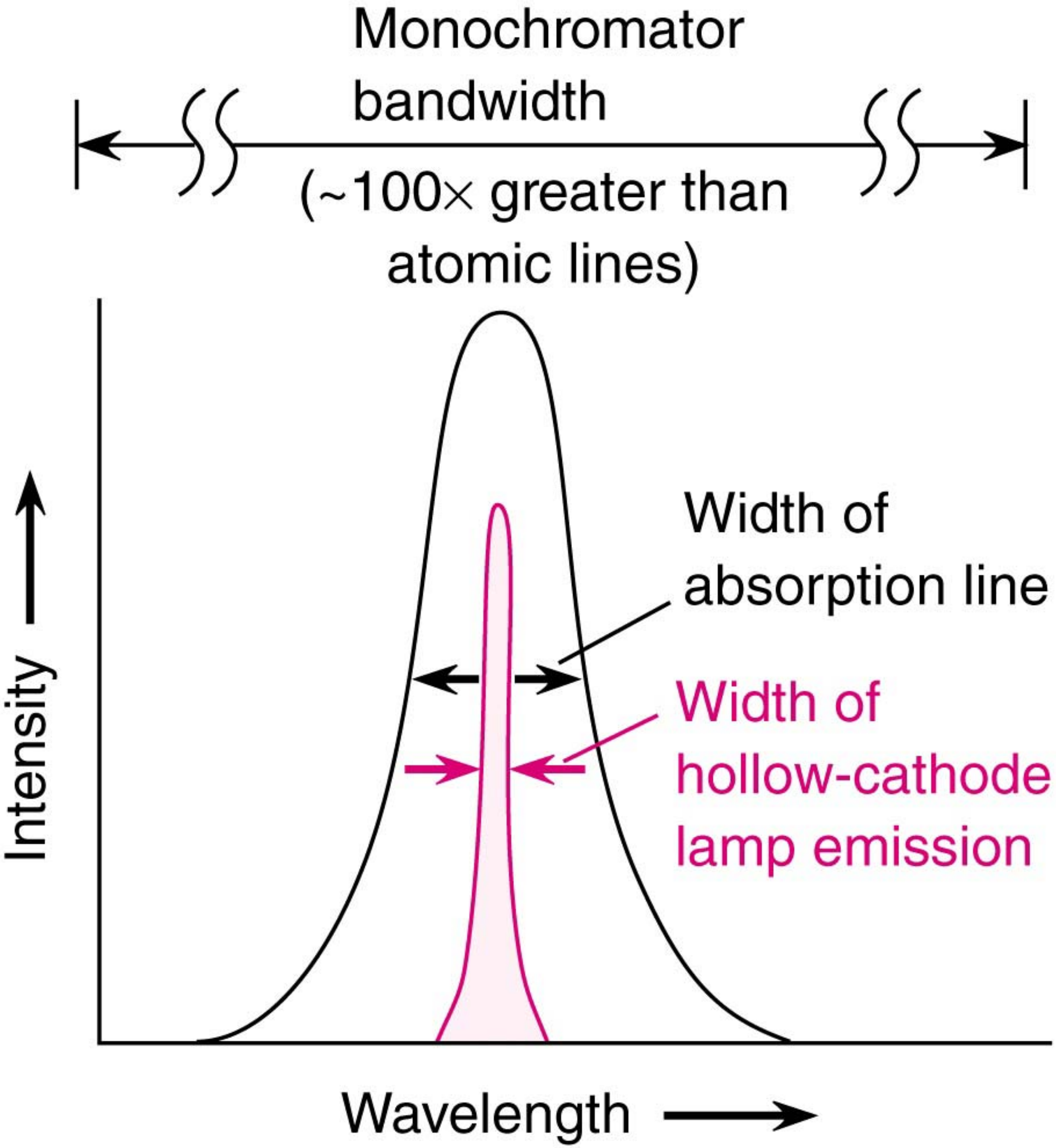


schematic of typical “Flame” AA instrument!--note that monochromator is place after flame---to get rid of large background of white light from flame itself--



Hollow Cathode lamp (HCL)---used only for AA---as source of radiation of given element being detemined. Solid element is present on cathode (M^o)

High voltage ionizes gas in tube---creates Ar^+ or Ne^+ ions at anode; these are accelerated to cathode surface--and “sputter” element off of the cathod when the strike surface---creates gas phase M^o* and excited state atom---that relaxes and give off photon that is unique in wavelengths for that given element!


Monochromator bandwidth (~100× greater than atomic lines)
Width of absorption line
Width of hollow-cathode lamp emission
Intensity
Wavelength

ICP-MS; most sensitive of all atomic methods---not strictly a spectroscopy--since we do not measure the emission of radiation from excited state atoms!

In ICP-MS---we use high temperature of an ICP-torch to actually ionize a small fraction of the analyte species--(e.g., Cu, Pb, Hg, Zn, etc.). ----by ionizing---we create M^+ species in gas phase!

then these ions are accelerated into a Mass Spectrometer----
and ions with different mass/charge ratios are separated and detected.

Detection limits (ng/mL)

Fe
0.7 — Inductively coupled plasma emission
5 — Flame atomic absorption
0.02 — Graphite furnace atomic absorption
0.008 — Inductively coupled plasma-mass spectrometry

Li 0.7 2 0.1 0.0002	**Be** ▨ 0.07 1 0.02 0.0009											**B** ▨ 🟥 1 500 15 0.0008	**C** 10 — —	**N**	**O**	**F**	**Ne**
Na 🟥 3 0.2 0.005 0.0002	**Mg** 0.08 0.3 0.004 0.0003											**Al** ▨ 🟥 2 30 0.01 0.0002	**Si** ▨ 5 100 0.1 <0.0001	**P** 🟥 7 40 000 30 <0.0001	**S** 🟥 3 — — 0.0001	**Cl**	**Ar**
K 🟥 20 3 0.1 0.0002	**Ca** 0.07 0.5 0.01 0.007	**Sc** ▨ 0.3 40 — 0.0002	**Ti** ▨ 0.4 70 0.5 0.004	**V** ▨ 0.7 50 0.2 0.0003	**Cr** 2 3 0.01 0.0003	**Mn** 0.2 2 0.01 0.0002	**Fe** 0.7 5 0.02 0.008	**Co** 1 4 0.02 0.0002	**Ni** 3 90 0.1 0.001	**Cu** 0.9 1 0.02 0.0005	**Zn** 0.6 0.5 0.001 0.003	**Ga** 10 60 0.5 0.006	**Ge** ▨ 20 200 — 0.002	**As** 7 200 0.2 0.003	**Se** 10 250 0.5 0.05	**Br** — — — 0.02	**Kr**
Rb 🟥 1 7 0.05 0.0003	**Sr** 🟥 0.2 2 0.1 0.0003	**Y** ▨ 🟥 0.6 200 — 0.0003	**Zr** ▨ 2 1000 — 0.0006	**Nb** ▨ 5 2000 — 0.0008	**Mo** ▨ 3 20 0.02 0.002	**Tc**	**Ru** 10 60 1 0.001	**Rh** 20 4 — 0.0003	**Pd** 4 10 0.3 0.001	**Ag** 0.8 2 0.005 0.0007	**Cd** 0.5 0.4 0.003 0.0008	**In** 🟥 20 40 1 0.0003	**Sn** 9 30 0.2 0.0009	**Sb** 9 40 0.1 0.001	**Te** 4 30 0.1 0.02	**I** — — — 0.002	**Xe**
Cs 40 000 4 0.2 0.0003	**Ba** ▨ 🟥 0.6 10 0.04 0.0003	**La** ▨ 🟥 1 2000 — 0.0003	**Hf** ▨ 4 2000 — 0.0008	**Ta** ▨ 10 2000 — 0.0005	**W** ▨ 8 1000 — 0.002	**Re** 3 600 — 0.0007	**Os** ▨ 0.2 100 — 0.002	**Ir** ▨ 7 400 — 0.0004	**Pt** 7 100 0.2 0.001	**Au** 2 10 0.1 0.0009	**Hg** 7 150 2 0.0009	**Tl** 10 20 0.1 0.0004	**Pb** 10 10 0.05 0.0006	**Bi** 7 40 0.1 0.0005	**Po**	**At**	**Rn**

Ce 🟥 2 — — 0.0003	**Pr** ▨ 🟥 9 6000 — 0.0002	**Nd** ▨ 10 1000 — 0.001	**Pm**	**Sm** ▨ 🟥 10 1000 — 0.001	**Eu** 🟥 0.9 20 0.5 0.0004	**Gd** ▨ 🟥 5 2000 — 0.001	**Tb** ▨ 🟥 6 500 0.1 0.0002	**Dy** ▨ 2 30 1 0.0009	**Ho** ▨ 2 40 — 0.0002	**Er** ▨ 0.7 30 2 0.0007	**Tm** 2 900 — 0.0002	**Yb** 0.3 4 — 0.001	**Lu** 0.3 300 — 0.0002
Th 🟥 7 — — 0.0003	**Pa**	**U** ▨ 🟥 60 40 000 — 0.0005	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

▨ Requires N_2O/C_2H_2 flame and is therefore better analyzed by inductively coupled plasma

🟥 Best analyzed by emission