CHEM 524 -- Course Outline (Part 12) - *Atomic Spectroscopy* —2013

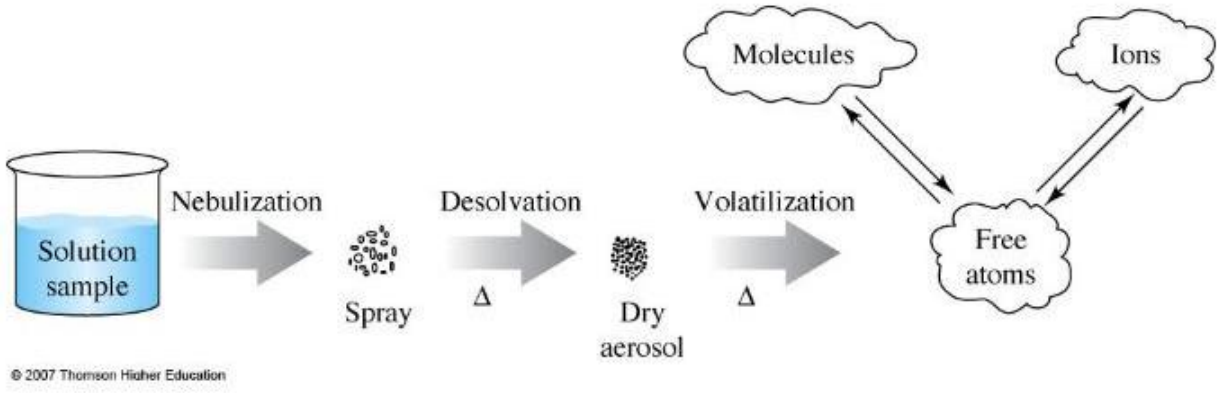
For HTML of 2005 notes with links, click here

VIII. Atomic Spectroscopy (survey text: Chap. 7-11, book is very detailed, we will not do so much)

A. General Purpose— determine trace amounts of metals (usually) in samples, most common

a. Value: trace element sensitivity and selectivity
   i. -- depend on calibration and careful replication of methods used
   ii. —no absolute relationships due to sampling variation

b. Big issue: ***atomize***—strip off all bonds and detect vapor phase atoms by spectra
   but *correlate response to solution concentration* of source of atoms
   i. technique of atomization critical step – efficiency affects detectivity
   ii. **Steps:** solution→nebulize→desolvate→atomize→(ionize possible) – See Chap 7-1



Solution	Nebulizer	Desolvation	Volatilization/atomization
Uniform Anal-	Mechanical	Dry gas (fuel) flow	Key is ***very high heat***
yte dispersal	Break up into	droplet *surface/vol*	furnace, arc, flame
Solid diff.meth.	small droplets	fast evaporate	

iii. Each step is a transient process (flame, arc, spark, furnace) – *not just static sample*

TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy

Type of Atomizer	Typical Atomization Temperature, °C
Flame	1700–3150
Electrothermal vaporization (ETV)	1200–3000
Inductively coupled argon plasma (ICP)	4000–6000
Direct current argon plasma (DCP)	4000–6000
Microwave-induced argon plasma (MIP)	2000–3000
Glow-discharge plasma (GD)	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)

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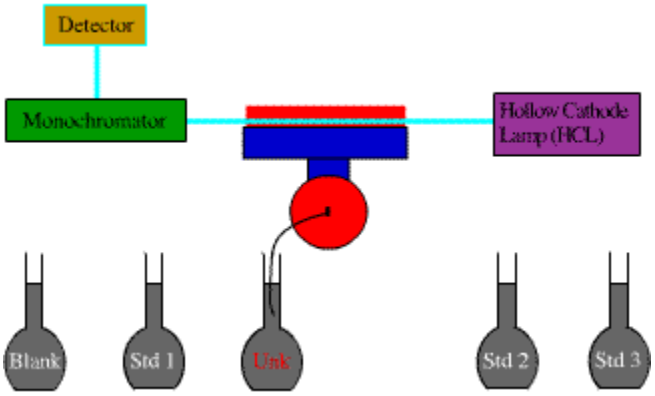
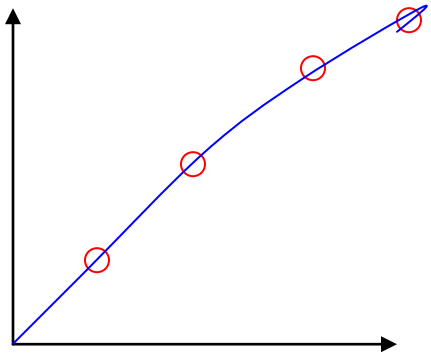
iv. Goal to get absorbance or emission from stable sample reflecting input

v. Lots can go wrong, chemical interactions, burner orientation. . . — *calibrate* to avoid

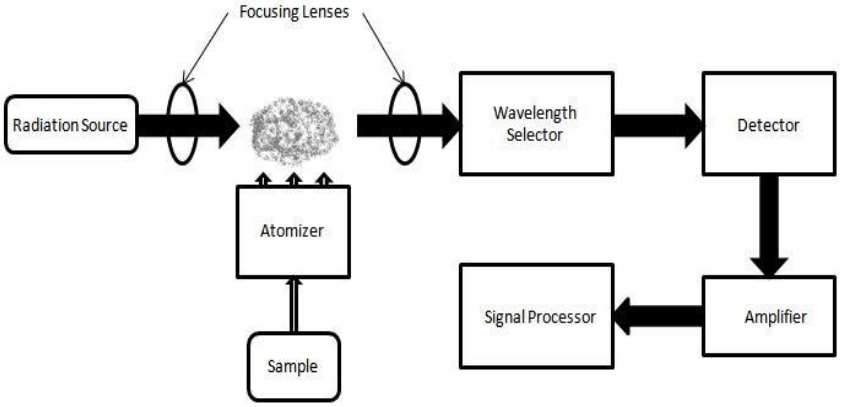
vi. Measure blank, standards, bracket unknown, fit standards to calibration plot





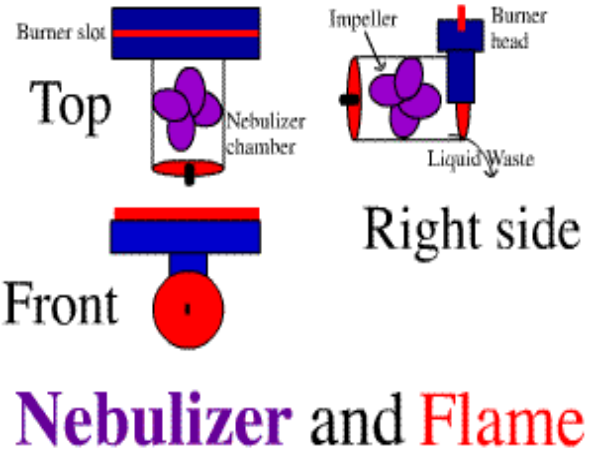
Concentration

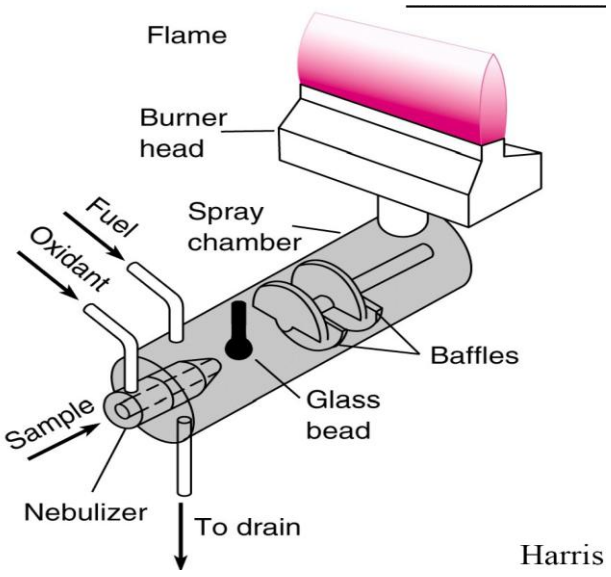
Generic system for Absorption experiment:



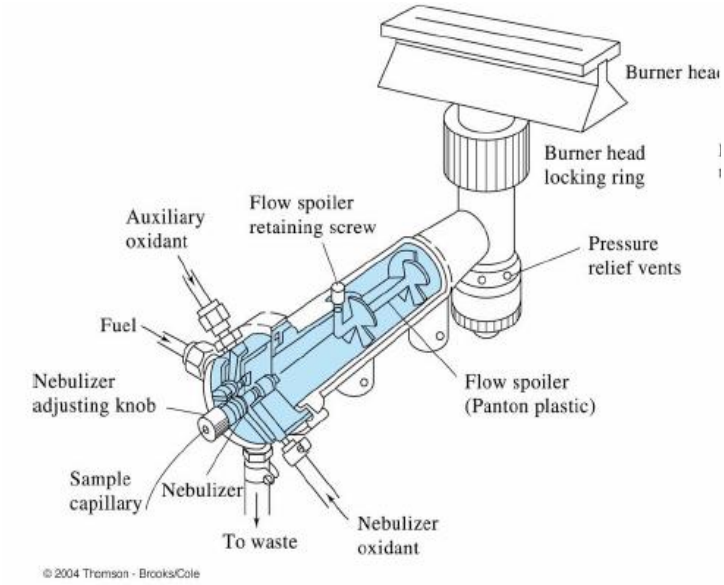
Source is species (atom/ion) specific, selector sorts out lines to use, reduce background

Flame atomizers – slot burner:





Harris

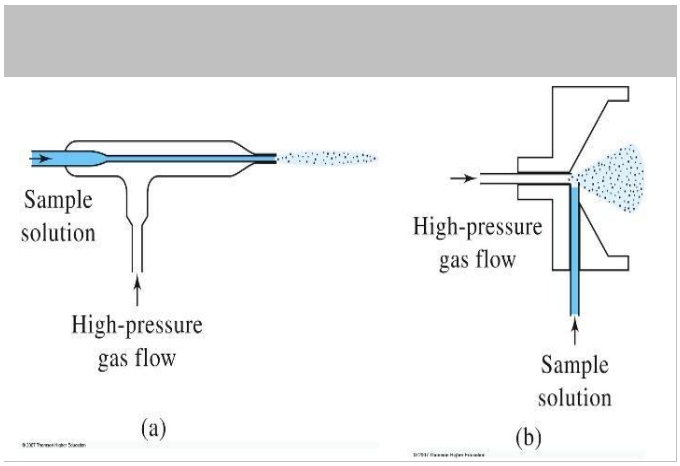


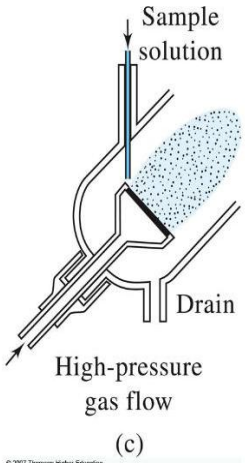
Flames Used in Atomic Spectroscopy

Fuel and Oxidant	Temperature, °C
*Gas/Air	1700–1900
*Gas/O_2	2700–2800
H_2/air	2000–2100
H_2/O_2	2500–2700
†C_2H_2/air	2100–2400
†C_2H_2/O_2	3050–3150
†C_2H_2/N_2O	2600–2800

*Propane or natural gas
†Acetylene

Many designs for nebulizers, volatilizing small droplets so they can dry in gas flow





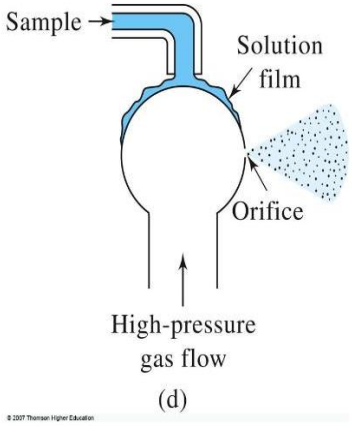
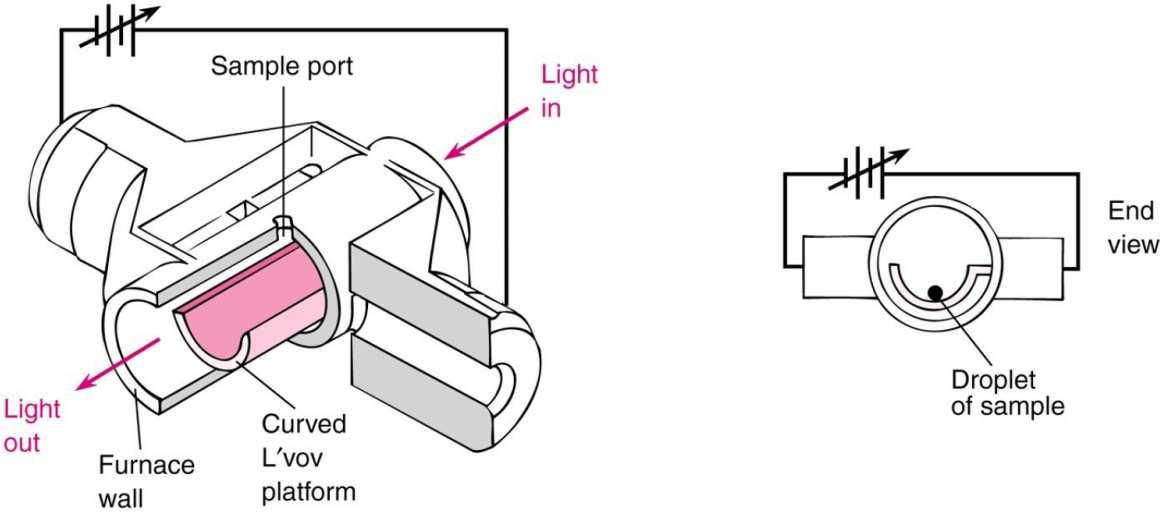
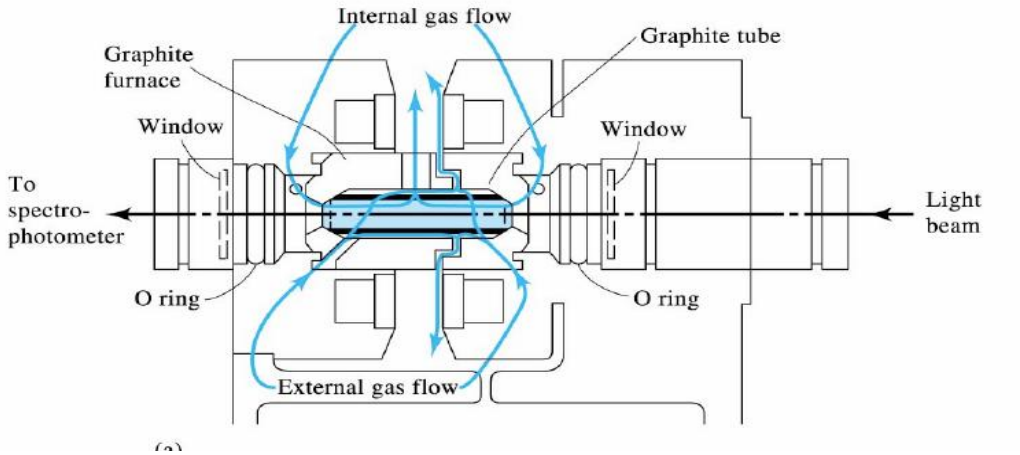


TABLE 8-2 Methods of Sample Introduction in Atomic Spectroscopy

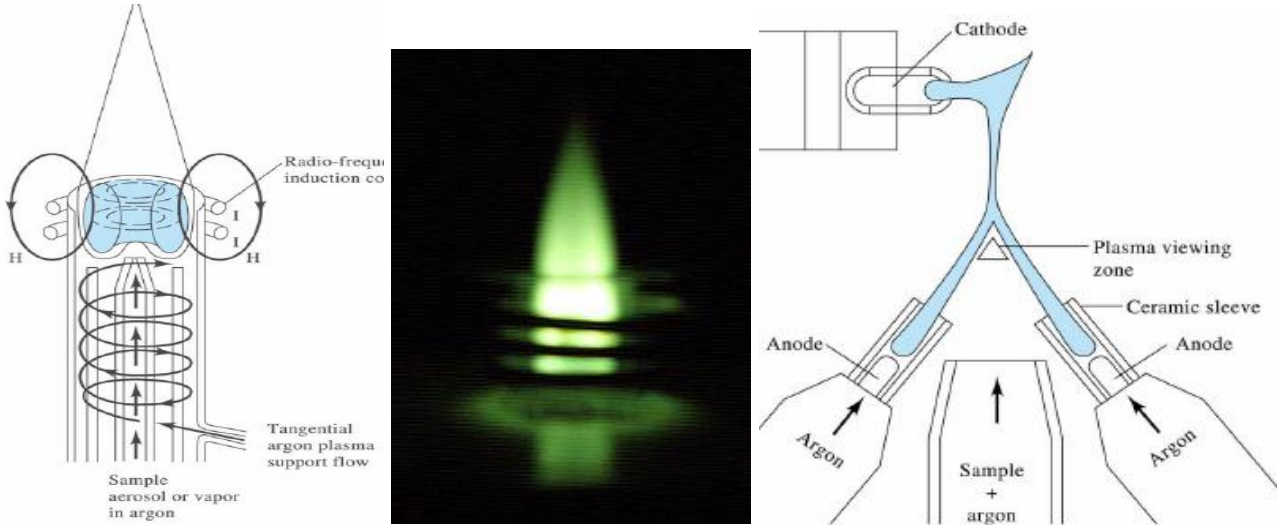
Method	Type of Sample
Pneumatic nebulization	Solution or slurry
Ultrasonic nebulization	Solution
Electrothermal vaporization	Solid, liquid, or solution
Hydride generation	Solution of certain elements
Direct insertion	Solid, powder
Laser ablation	Solid, metal
Spark or arc ablation	Conducting solid
Glow-discharge sputtering	Conducting solid

Alternative: Graphite Furnace, allow *solid sample* introduction, heat in steps –dry, ash, atomize





Emission, often use inductively coupled plasma – ICP



Picture of an analytical ICP viewed through green welder's glass

B. Virtue of *selectivity from high resolution, unique atomic spectra* - suppress interferants

a. -- **emission** - need high resolution optics - separate lines different elements
   i. if other species in mix that emit, could be detected—overlap problem
   ii. careful blank preparation needed

b. -- **absorption** - use hollow cathode lamp to select atomic analyte—very narrow lines
   i. even with low resolution optics interference rare, due to resonance absorbance
   ii. each lamp a different analyte, has other lines (eg Ne) - sort with monochromator

c. –**fluorescence** - more a problem unless tune excitation very precisely, less common

C. Micro-Survey of Principles of Atomic Spectra - *review q.m. course on your own*

a. Atoms are QM problem of multiple particles, but one nucleus, rest are identical/indistinguishable electrons

i. Only electron motion (no vibrations, translation of atom not quantized)

ii. Symmetry is that of a sphere—representations are angular momentum wave functions

iii. States characterized by *Open Shells+Configurations*: n (ℓ^m) –Pauli Principle restricts plus interactions between electrons—repulsion, spin-orbit coupling

1. Term symbols |LSJM> → n (ℓ^m) $^{2S+1}L_J$ $\mathbf{L}=\Sigma\,\boldsymbol{\ell}_i$, $\mathbf{S}=\Sigma\mathbf{s}_i$, $\mathbf{J}=\mathbf{L}+\mathbf{S}$ *(sum over shell - ℓ^m)*
2. These are vector sums, not all values possible,
   - L,S integer separations, if two: $\mathbf{L_{max}}=\boldsymbol{\ell}_1+\boldsymbol{\ell}_2$ $\mathbf{S_{max}}=\mathbf{s}_1+\mathbf{s}_2$ $\mathbf{L_{min}}=|\boldsymbol{\ell}_1-\boldsymbol{\ell}_2|$ etc.
   - $M_L = L_m, L_m - 1, L_m - 2, \ldots - L_m$
   - Same for M_S and M_J based on S_{max} and J_{max}

iv. **Hund's rules**:--relative energies of terms

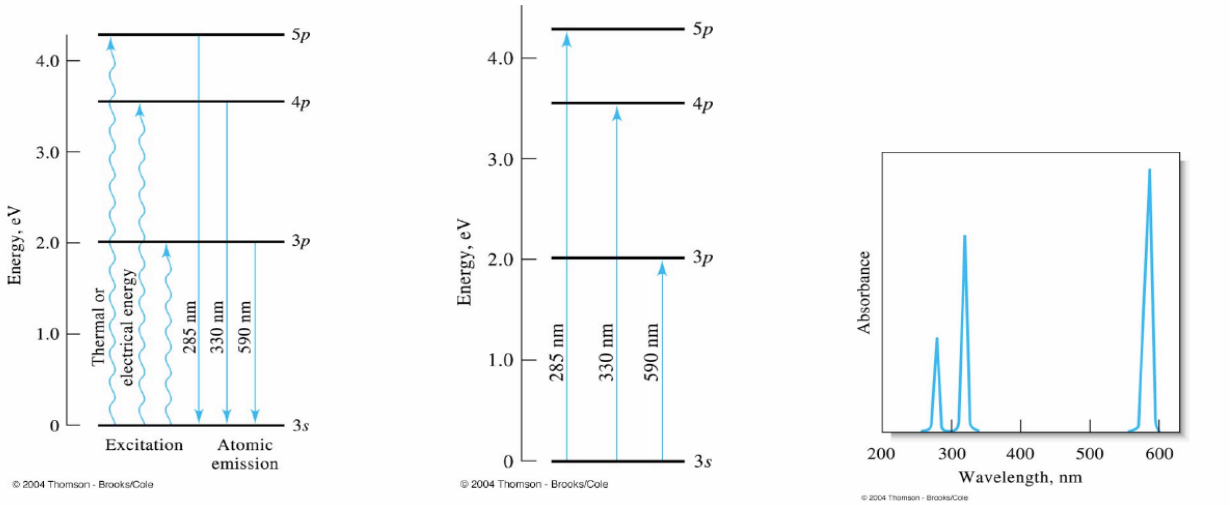
1. **Max S** is lowest energy multiplicity (spin),
2. then of those, **Max L** lowest energy term, ^{2S+1}L
3. Min J lowest level for less than half-filled shell, *or*
4. Max J lowest level for over half-filled shell

v. Properties of open shells -- parity: $\Sigma\ell_i$ -- odd/even,

1. energy operator connect same parity,
2. dipole operator connect opposite parity

Selection rule: Transitions allowed for opposite parity, must change configuration (one ℓ_i change)

Shown to the right is the three sodium absorption and emission process and the emission lines. 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.

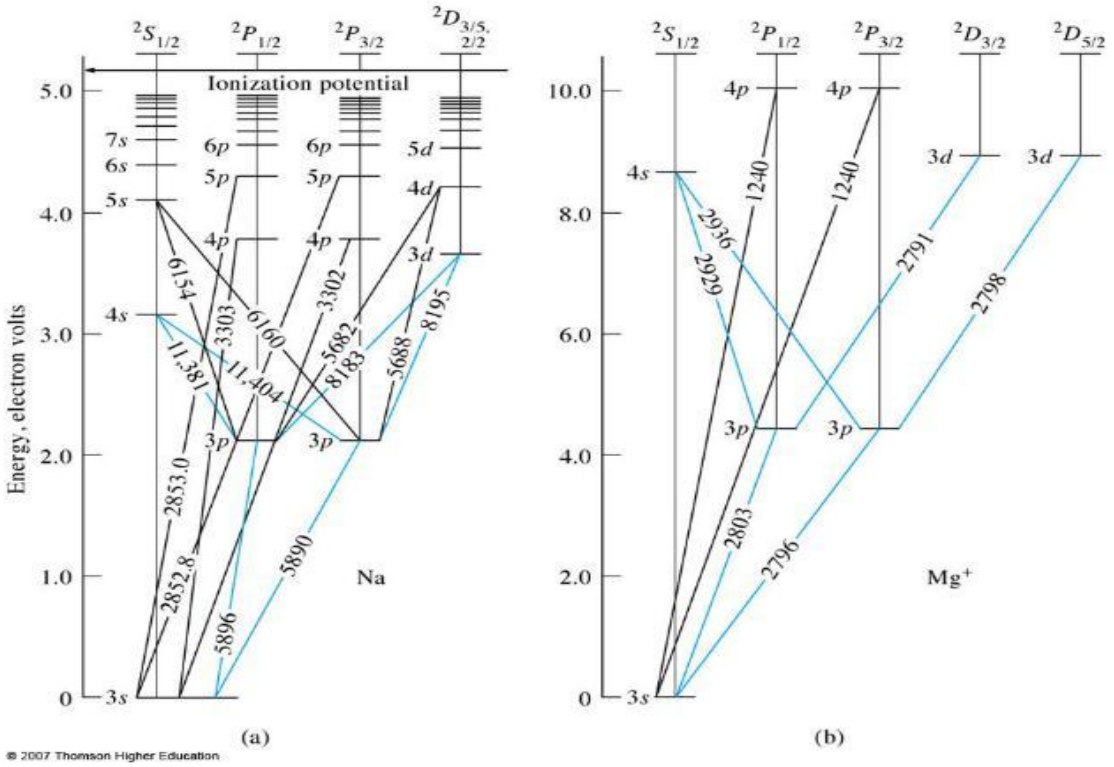


More complete picture, account for all states, and spin-orbit (LS) coupling (J values), see below

a. $\Delta l = \pm 1$; $\Delta J = 0,\pm 1$; J=0-/->J=0

b. LS coupling: $\Delta L = 0,\pm 1$, $\Delta S = 0$

c. Degeneracy: ${}^{2S+1}L_J = (2J+1)$, ${}^{2S+1}L = (2L+1)(2S+1)$



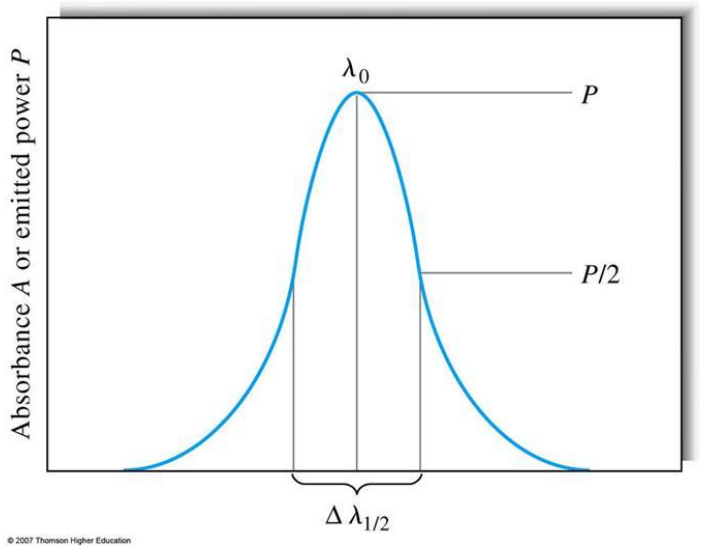
D. Zeeman and Stark effects—split M degeneracy, can use to enhance sensitivity/selectivity

a. Magnetic field, $E_Z \sim \mathbf{B}M_J$
b. Electric field, $E_S \sim \mathbf{E}|M_J|$
c. Selection rule: $\Delta M = \pm 1$

E. Autoionization—increase density can ionize by collision,

a. cause interference or added ion states
b. anomalous intensity

F. Line Broadening— atomic lines normally narrow compared to ordinary spectrometer slit

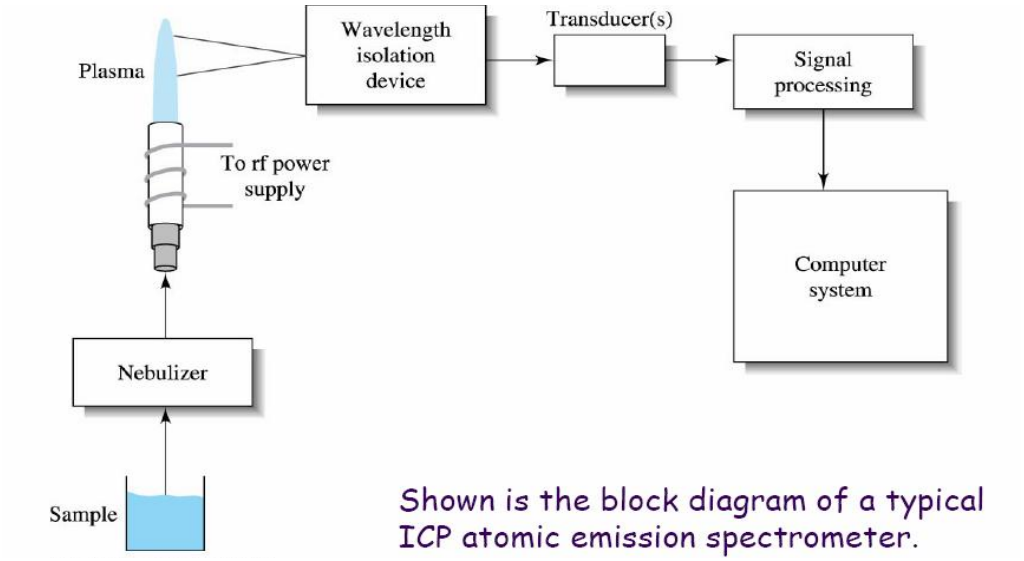


a. natural width—lifetime limited: $\Delta\nu = A_{ij}/2\pi = 1/2\pi\tau_r = k_r/2\pi$
   i. $A_{ij} \sim 10^8\ s^{-1}$ → $t \sim 10^{-8}$ → $\Delta\nu \sim 1.6\times10^7$ Hz ~ $0.5\times10^{-3}\ cm^{-1}$
   ii. Emission lifetime, exponential → FT gives Lorentzian shape

b. Pressure broadening—collision deactivate, shorten life, broaden: $\Delta\nu = (k_c+k_r)/2\pi$
   i. Media dependent, still Lorentzian

c. Doppler—problem of thermal K.E. motion away from or toward detector/source
   i. Gaussian shape: $\Delta\nu_D = 2[2(\ln 2)kT/m]\nu_m/c$ – hotter and lighter → broader

G. AA (absorption) vs. emission



a. Emission – *sample becomes the light source*

i. self absorption in emission—broaden profile, but peak intensity limited
ii. interferents--can use *echelle grating* (high order, 2D) for higher resolutions

1. and array or multiple detector to see various orders (spread 2nd dimen), not overlap
2. Plasma lets use solutions, - with calibration is quantitative
3. Arc or spark can atomize solids, typically qualitative due stability

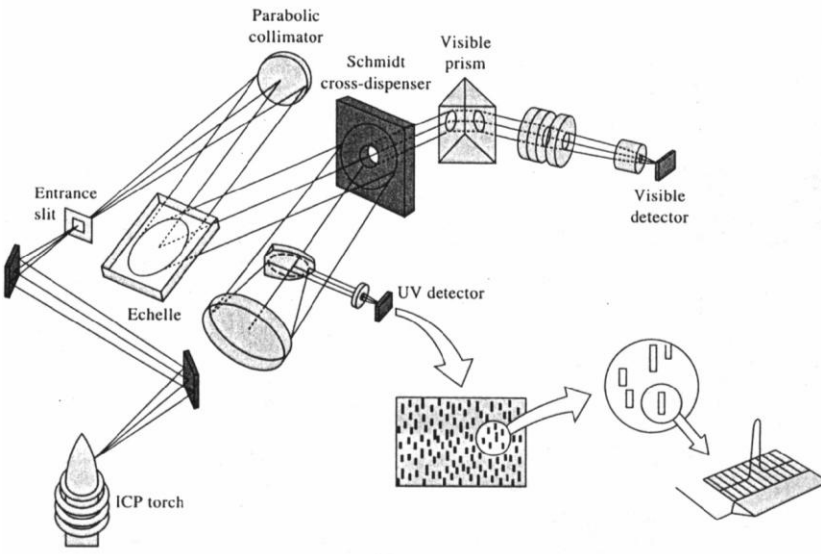
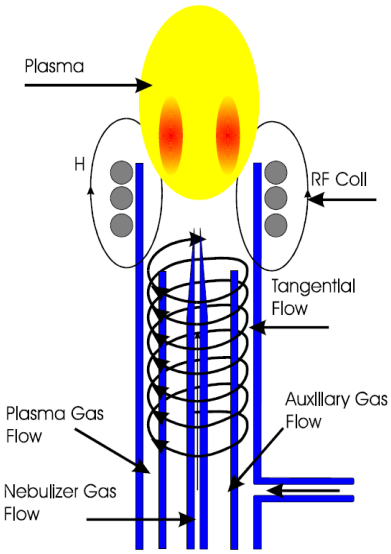
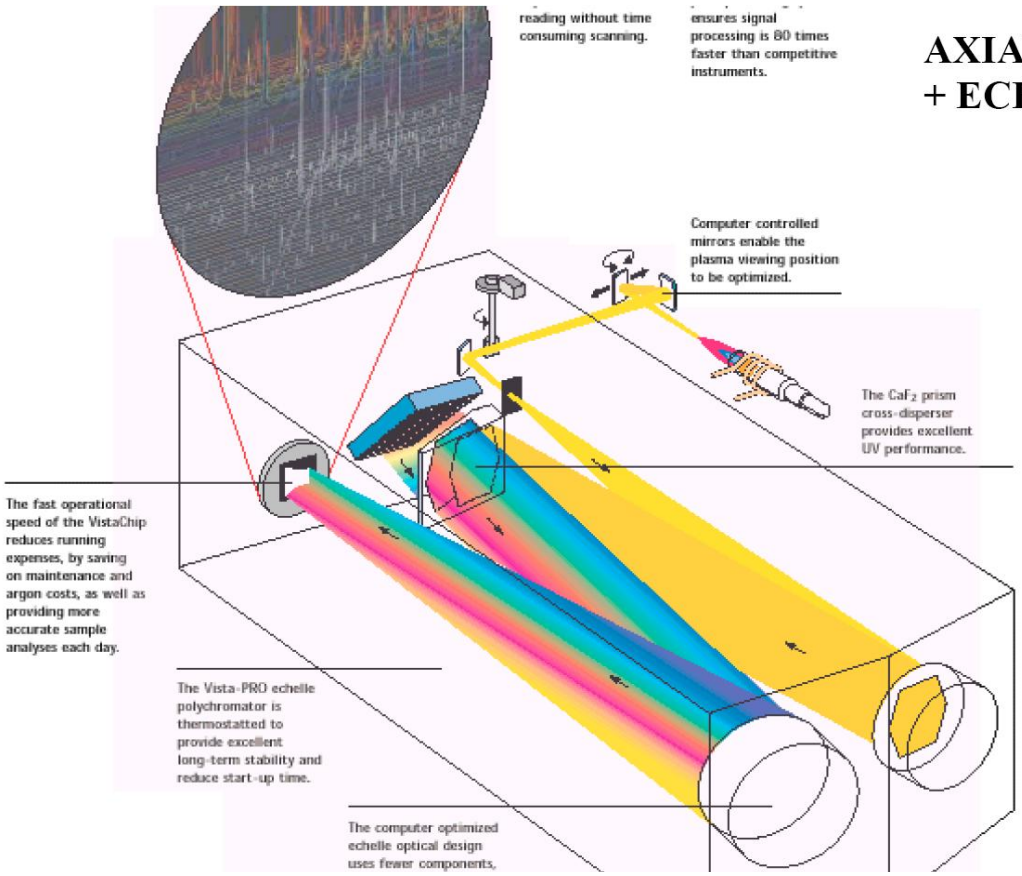


Figure 10-11 An echelle spectrometer with segmented array of charge-coupled devices. *(From T. W. Barnard et al., Anal. Chem., 1993, 65, 1232. With permission.)*



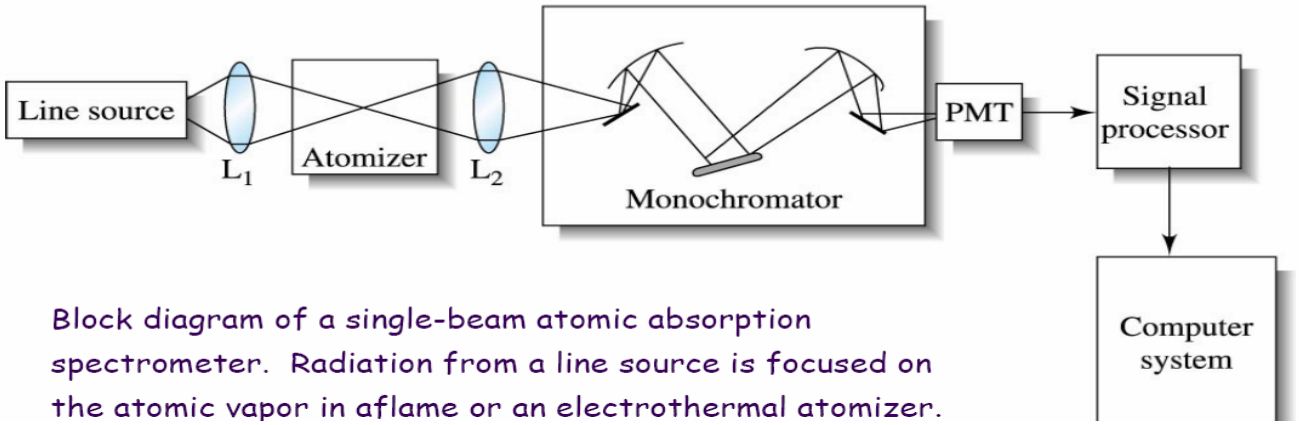
Ecelle grating operates in high order, high resolution, prism separates orders 90° (⊥) to spectrum disp.
Detect with polychromator approach, use of CCD and select out lines atom emits is efficient
Plasma torch has nebulizer surround with carrier Ar gas, that forms plasma - μwave excite (40 MHz)
Get 5000-8000 K, Background Ar + other emission limit sensitivity



b. Absorption—

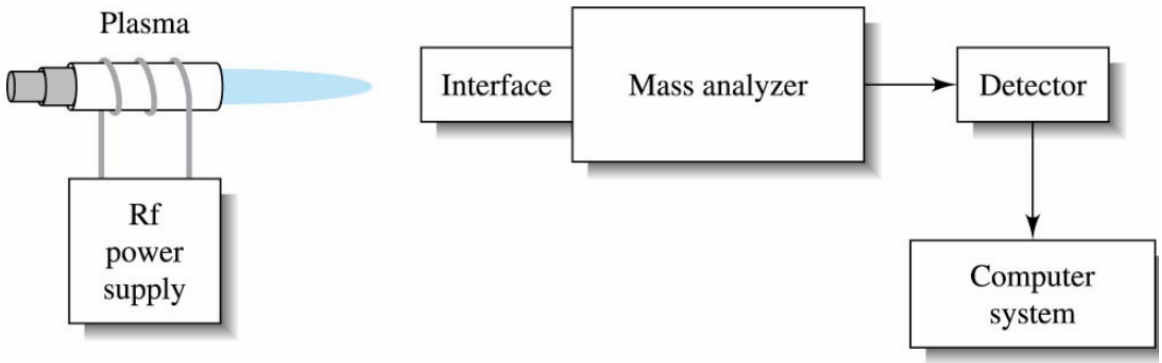
i. non-linear problems due to source (hollow cathode) narrower than absorbance
ii. Can be limited by slit function/extremely sharp resonance lines
iii. Scatter or background absorption could affect signal—use broad band ref channel

Flame atomic absorption spectroscopy (AAS) is the most used of atomic methods.



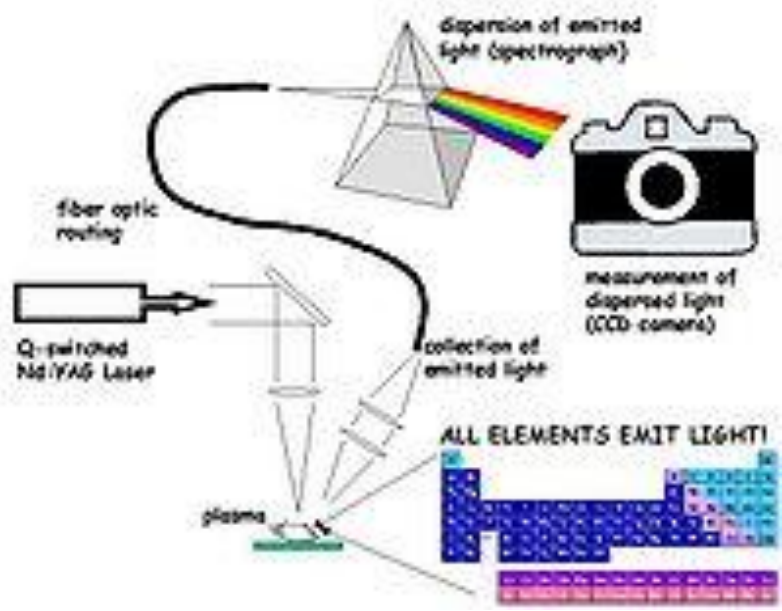
Block diagram of a single-beam atomic absorption spectrometer. Radiation from a line source is focused on the atomic vapor in aflame or an electrothermal atomizer.

Alternative method, use MS detection:



Block diagram of an ICP mass spectrometer system.

Also can atomize by laser ablation, here most often use MS for detection but emission also possible



LIBS – Laser induced breakdown spectra – induce a plasma which dissociates/atomizes surface species where laser is absorbed, can use to feed into MS or collect emission (in principle could do AA)

Rest of Book Chapters:

H. Chap 8-9 address emission,
8 focus on inductively coupled plasma -
   a. most elements can be studied,
   b. actual use is probably limited, expense and problems of standardization.

I. Chap 10 addresses Atomic Absorption, widely used for metals.
   a. Use of a programmed furnace for atomization is strong suit—known sample inserted, conditions relatively reproducible.
   b. Due to hollow cathode lap, optical constants not so high, less expensive

J. Chap. 11 addresses atomic fluorescence,
   a. typically resonance, means excitation and fluorescence at same frequency,
   b. which can be tricky to detect and separate from scatter

Summary

TABLE 1. Summary of common techniques used atomic spectroscopy.

	ICP[1]	FAA[2]	GFAA[3]	MIP[4]	Arc[5]
Temp (K)	4000–8000	1500–2500	2000	1000–2000	3000–8000
e^-/cm^3	5×10^{14}	$3–9 \times 10^{13}$		7×10^{13}	$10^{14}–10^{15}$
gas	argon	air/acetylene	argon	helium	argon
LOD (conc)[6]	2 ppb	10ppb	0.1 ppb		8 ppb
LOD (mass)[7]	4 ng	20 ng	5 ng		16 ng
SME[8]	ME	SE	SE	ME	ME
Heating Method	Induction	combustion	voltage across graphite tube	magnetorn	voltage across graphite tube
λ Range[9]	120–900	190–900	190–900	190–900	190–900
Range[10]	4–6	3–4	2–3	3–4	3–4
AA source		HCL	HCL		
Common Application	ppb of numerous metals in solution	ppm of 1 metal (high volume)	single element low volume (ppb, pg)	halogens (Cl, Br, etc.)	Replaced by ICP
Price[11]	$100,000	$35,000	$55,000	$65,000	
Sample size	Flow (mL)	Flow (mL)	Static (μL)	Flow (mL)	Flow (mL)
Interfer. Instrum. System[12]	argon emis[13] contin.	molecul.[14]	molecul., scatter[15]	He emis[16] contin.	elect[17] Ar emis., contin.
Frequency	27.12, 40 MHz			2450 MHz	DC
Power	1–2 kW			0.2–1 kW	<100 W

[1] Inductively Coupled Plasma-Atomic Emission Spectrometer.
[2] Flame Atomic Absorption.
[3] Graphite Furnace Atomic Absorption.
[4] Microwave Induced Plasma.
[5] DC plasma arc.
[6] The limit of detection for iron by concentration (MIP-AES is used primarily for nonmetals).
[7] The limit of detection for iron by absolute mass (for ICP, FAA, DCP assumes 2 mL volume, GFAA assumes 50 uL).
[8] Single or multielement analysis possible on a single sample. For example, a commercial ICP can simultaneously detect 20 elements but a graphite furnace atomic absorption system is only capable of single element detection with a single "shot."
[9] The linear dynamic range (orders of magnitude).
[10] The wavelength range of the technique. These values can vary with sources, dispersing element, and detector chosen.
[11] Varies with vendor, model, accessories, etc..
[12] Interferences from instrumental system.
[13] Ar emission; continuum background.
[14] Molecular emission; absorbance from gas species (e.g., C_2, N_2, CO, etc.).
[15] Scattering from particulate matter.
[16] Helium emission.
[17] Electrode degradation (e.g., W, WC, emission etc.).

Techniques for elemental analysis

	ICP-MS	ICP-AES	FAAS	GFAAS
• Detection Limits	Excellent	Good	Good	Excellent
• Productivity	Excellent	Very goodGood	Low	
• LDR	10^5	10^6/10^{10} HDD	10^3	10^2
• Precision	1-3 %	0.3-2 %	0.1-1 %	1-5 %
• Spectral interference	Few	Common	Almost none	Very few
• Chemical interference	Moderate	Few	Many	Many
• Ionization	Minimal	Minimal	Some	Minimal
• Mass efffects	High on low	none	none	none
• Isotopes	Yes	none	none	none
• Dissolved solids	0.1-0.4 %	up to 30 %	0.5-3 %	up to 30 %
• No. of elements	~75	~73	~68	~50
• Sample usage	low	medium	high	very low
• Semi-quantitative	yes	yes	no	no
• Isotope analysis	yes	no	no	no
• routine operation	Skill required	easy	easy	skill required
• Method development	skill required	skill required	easy	skill required
• Running costs	high	high	low	medium
• Capital costs	very high	high	low	medium

Homework

Read chap 7. Skim Chaps: 8,9,10,11 to see the various instruments and applications

Discuss: Ch 7 – 3, 4, 13, 14

Hand in : Ch7 - #5, 7, 10, 11 .

Links – check out Casteen animations

Fundamental concepts/freshman physics
http://csep10.phys.utk.edu/astr162/lect/light/absorption.html
Simple AA notes from Korean site:
http://elchem.kaist.ac.kr/vt/chem-ed/spec/atomic/aa.htm
George Mason Univ. Lab tutorial
http://www.gmu.edu/departments/SRIF/tutorial/aas/aas.htm
Slides and Flash module with nice pictures, Univ. Michigan
http://www.umd.umich.edu/casl/natsci/slc/slconline/AA/sld001.htm
http://www.umd.umich.edu/casl/natsci/slc/slconline/AA/AdvAA.swf
Short description of AA by D. Chasteen, Sam Houston Univ. links to a lot of nice animations
http://www.shsu.edu/~chemistry/primers/AAS.html

Companies:

Shimadzu Atomic Absorption:
http://www.ssi.shimadzu.com/products/products.cfm?group=AA
Analytik Jena—AA with Xenon arc lamp—Omega-Biotech supplier
http://www.omega-biotech.ca/
http://www.omega-biotech.ca/fl_contrAA_e_2004-05-01.pdf
Perkin-Elmer AA and ICP-optical Emission pages
http://las.perkinelmer.com/Catalog/default.htm?CategoryID=Atomic+Absorption+%5bAA%5d
http://las.perkinelmer.com/Catalog/default.htm?CategoryID=ICP+Optical+Emission+%5bICP-OES%5d
Thermo elemental analysis page, links to AA ICP etc.
http://www.thermo.com/com/cda/category/category_lp/1,2152,136,00.html?source=google
Aurora Instruments AA
http://www.aurora-instr.com/
Leeman Labs/Teledyne Instr. – Hitachi AA
http://www.leemanlabs.com/spectrometers.asp
Varian AA and links to other techniques (ICP-OES)
http://www.varianinc.com/cgi-bin/nav?products/spectr/aa/index&cid=INKNJKJIFL
http://www.varianinc.com/cgi-bin/nav?products/spectr/icpoes/index&cid=INLOIJNNFI