Chapter 8: An Introduction to Optical Atomic Spectrometry

Sample is atomized (gaseous atoms/ions)
absorption or emission measured

- Optical Atomic Spectra
- Atomization Methods
- Sample Introduction Methods
- Optical Spectrometry as opposed to MS
- Optics are similar to Molecular Absorption and Fluorescence Spectrometry
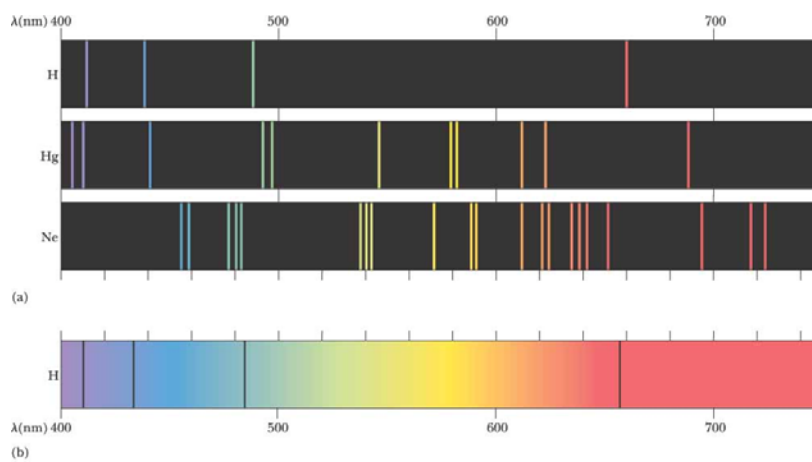

Basics

- Generally solution samples (sometimes solids)

- Aspirate sample into flame or plasma

- Or heat sample to atomize

- Observe emission from excited state (AE)

- Or use light source to measure atomic absorption (AA)

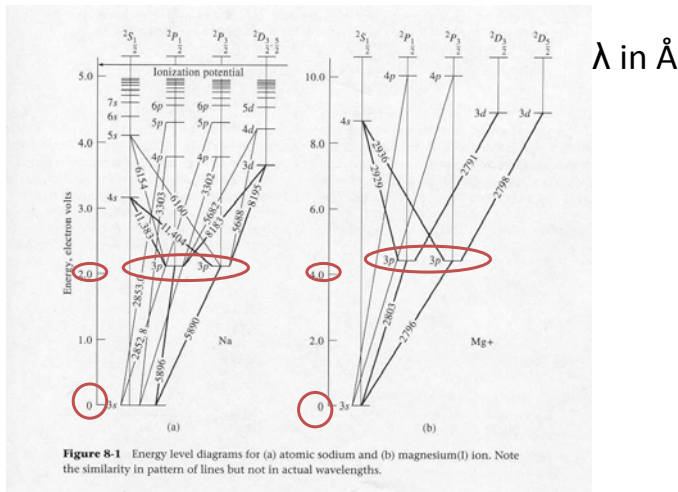- Or use light source to generate atomic fluorescence (AF)

Atomic spectra are line spectra
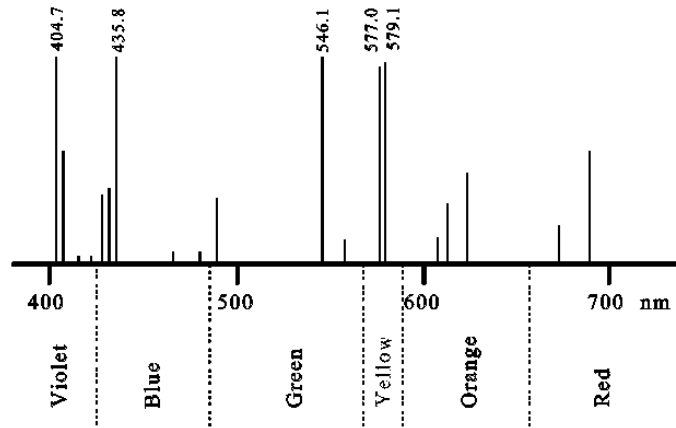
Some prominent lines in the atomic spectrum of mercury (Hg)

Other atomic spectra – many lines per spectra, lines are very narrow

©2004 Thomson - Brooks/Cole

Periodic Table of the Elements

IA																	0
1 **H**	IIA											IIIA	IVA	VA	VIA	VIIA	2 **He**
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
11 **Na**	12 **Mg**	IIIB	IVB	VB	VIB	VIIB	——— VII ———			IB	IB	13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	57 ***La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89 **+Ac**	104 **Rf**	105 **Ha**	106 **106**	107 **107**	108 **108**	109 **109**	110 **110**								

* Lanthanide Series

58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**

+ Actinide Series

90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

Energy Level Diagrams

Every elements has unique set of atomic orbitals

p,d,f... levels split by spin-orbit coupling

Spin (s) and orbital (l) motion create magnetic fields that perturb each other (couple)

   if fields parallel - slightly higher energy

   if fields antiparallel - slightly lower energy

$$\boxed{\begin{matrix} N \\ \\ S \end{matrix}} \quad \boxed{\begin{matrix} N \\ \\ S \end{matrix}} \qquad vs. \qquad \boxed{\begin{matrix} N \\ \\ S \end{matrix}} \quad \boxed{\begin{matrix} S \\ \\ N \end{matrix}}$$

Define SO coupling by J (total angular momentum)

$$J = L + S \quad (L = \Sigma l \quad S = \Sigma s) \text{ (positive values only)}$$

λ in Å

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.

• Similar pattern between atoms but different spacing
• Spectrum of ion different to atom
• Separations measured in electronvolts (eV) $1eV = 1.602 \times 10^{-19}C' \; 1V(J/C) = 1.602 \times 10^{-19}$ J $= 96.484$ kJ $\times$ mol-1
• As # of electrons increases, # of levels increases
Emission spectra become more complex
Li 30 lines, Cs 645 lines, Cr 2277 lines

Resonance fluorescence lines involve the ground state

Others involve a two step process
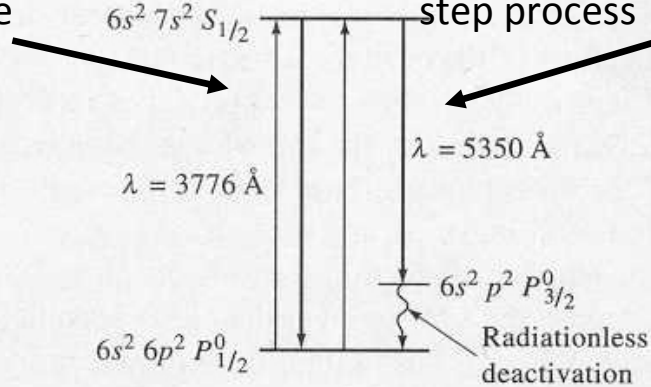
Figure 8-5 Energy level diagram for thallium showing the source of two fluorescence lines.

Atomic line widths are important when considering spectral resolution, absorption experiments, etc.

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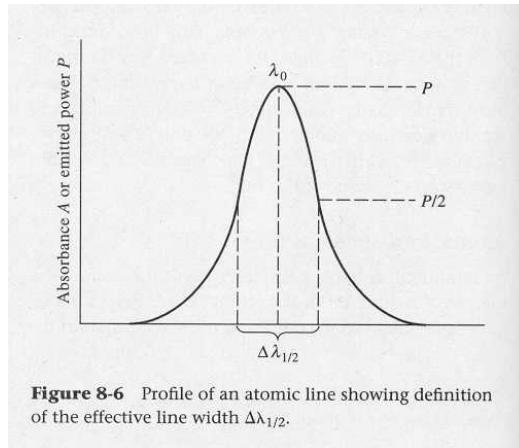
Desire narrow lines for accurate identification

Broadened by

    (i) uncertainty principle

    (ii) pressure broadening

    (iii) Doppler effect

    (iv) (electric and magnetic fields)

(i) Uncertainty Principle:

Quantum mechanical idea states must measure for some minimum time to tell two frequencies apart

$$\Delta t \cdot \Delta E \geq h$$

$$\underbrace{\Delta t}_{\substack{\text{minimum} \\ \text{time for} \\ \text{measurement}}} \cdot \underbrace{\Delta\nu}_{\substack{\text{minimum} \\ \text{detectable} \\ \text{difference in} \\ \text{frequencies}}} \geq 1$$

Shows up in lifetime of excited state

- if lifetime infinitely long, ΔE infinitely narrow

- if lifetime short, ΔE is broadened

sometimes called **natural linewidth**

About 10^{-5} nm or 10^{-4} Å

(ii) Pressure broadening:

Collisions with atoms/molecules transfers small quantities of vibrational energy (heat) - ill-defined ground state energy

Effect worse at high pressures

- For low pressure hollow cathode lamps (1-10 torr) 10^{-1}-10^{-2} Å

- For high pressure Xe lamps (>10,000 torr) 100-1000 Å (turns lines into continua!)

Doppler broadening occurs due to the observed compression and expansion of light waves as an atom moves toward or away from the radiation source

Photon detector

Photon detector

In gas, broadens line symmetrically

Doppler broadening increases with $\sqrt{T}$

- At room T ~10^{-2}-10^{-3} Å

Total linewidth typically 0.01-0.1 Å
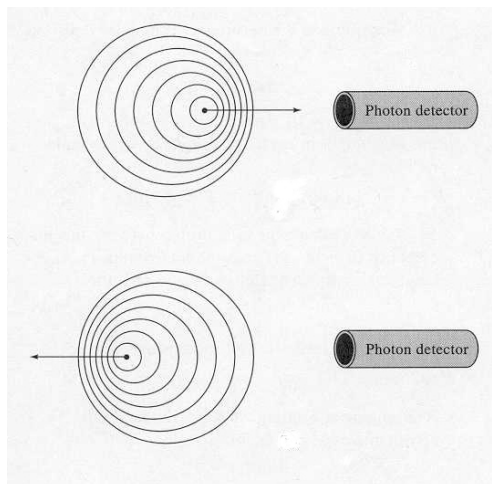
Other broadening effects include

- pressure or collisional broadening (10^{-4} Å)
- broadening from uncertainty effects
- electric & magnetic field effects

Temperature effects from Boltzmann equation

$$\frac{N_1}{N_0} = \frac{P_1}{P_0} \exp\left(-\frac{\Delta E}{kT}\right)$$

N = population of state   P = statistical factor

E_j = energy difference   k = Boltzmann constant

T = temp   o & j signify ground & excited states

Important in emission measurements relying on thermal excitation

Na atoms at 2500 K, only 0.02 % atoms in first excited state!

Less important in absorption measurements - 99.98 % atoms in ground state!

Molecular emission in flames & plasmas is generally unwanted may obscure part of the spectrum & cause interference

Note similarity of spectra

CaOH emission

CaOH absorption

Wavelength of Ba resonance line

5536

Wavelength, Å
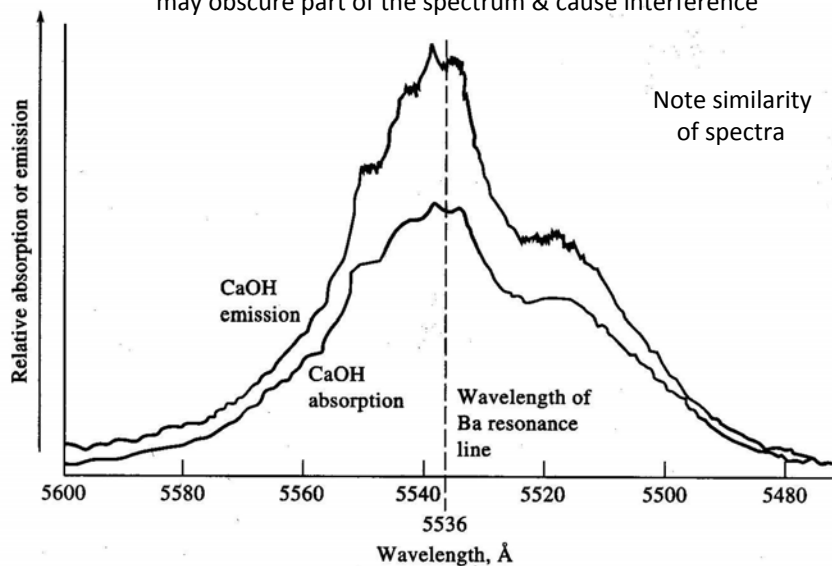
Figure 8-8 Molecular flame and flame absorption spectra for CaOH and Ba.

The sample must be converted to its atomic state which can be done at high temp. in a flame, furnace, plasma, arc or spark

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 (?)

Introducing the sample to the high temperature source can be tricky

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, 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
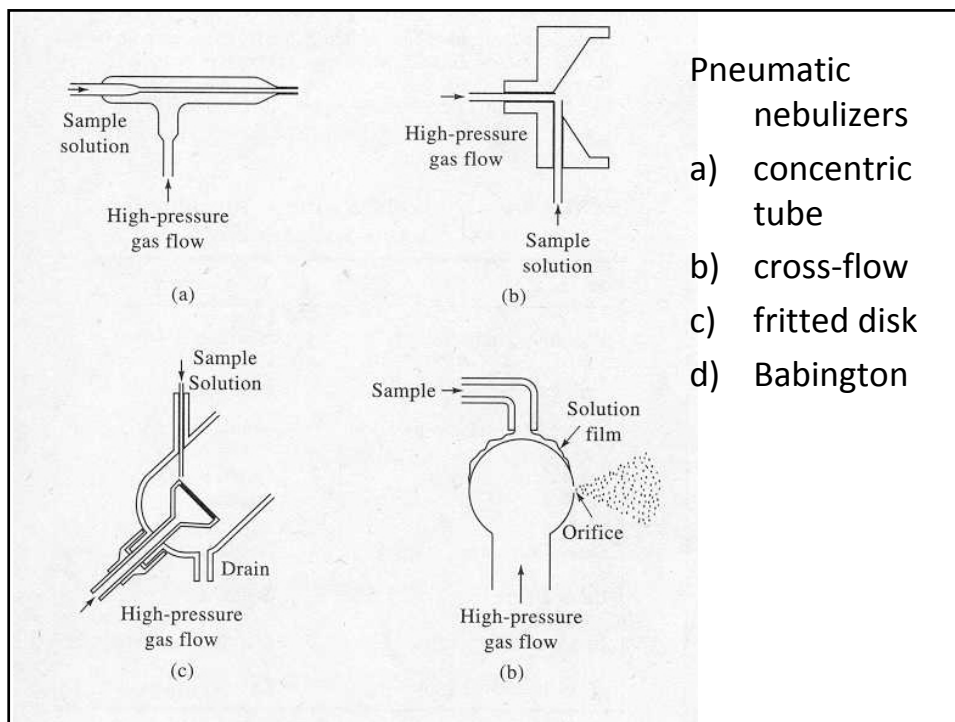
Pneumatic nebulizers

a) concentric tube
b) cross-flow
c) fritted disk
d) Babington

Sample introduction for solutions:

1) Pneumatic nebulizers
2) Ultrasonic nebulizers
3) Electrothermal vaporizers
4) Hydride generation

$$3\ BH_4^- + 3\ H^+ + 4\ H_3AsO_3 \rightarrow$$
$$3\ H_3BO_3 + 4\ AsH_3 + 3\ H_2O$$

5) Cold vapor generation

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^o + Sn^{4+}$$
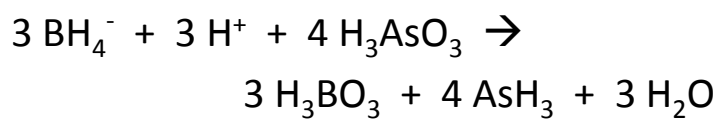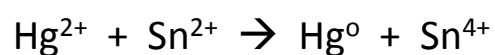
Solid sample introduction:

1) Laser ablation – zap sample with laser and sweep atoms into flame/plasma

2) Direct sample insertion – place sample directly in atomizer (e.g. furnace)

3) Electrothermal atomizers – electrically heat graphite or tantalum boat

4) Arc/Spark ablation – coat sample on electrode or place in electrode well or cup

5) Glow discharge technique – see p 227

Chapter 9: Atomic Absorption & Atomic Fluorescence Spectrometry

- Atomic Absorption (AA)
- Atomic Fluorescence (AF)
- Sample Atomization (Both AA and AF)

- Both AA and AF require a light source
- Like Molecular Absorption & Fluorescence, in AA high intensity is NOT required, in AF high intensity results in greater sensitivity

Figure 9-1 Processes occurring during atomization.

occurs in flame, plasma, etc.

Molecular emission is generally unwanted & can cause interference

---
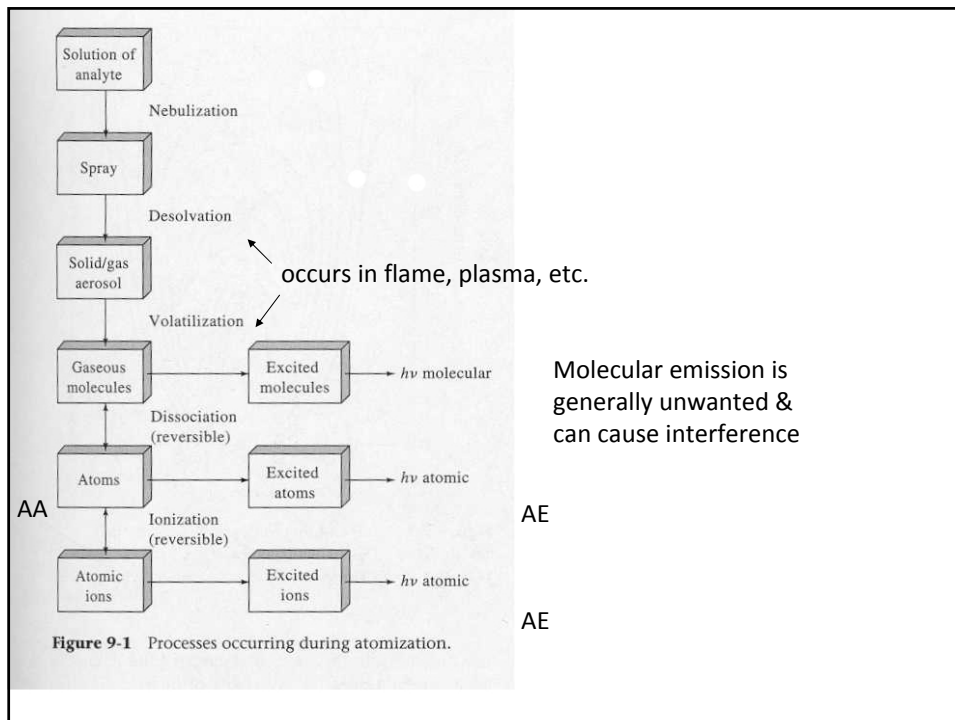
• AAS intrinsically more sensitive than AES

• similar atomization techniques to AES

• addition of radiation source

• high temperature for atomization necessary

flame and electrothermal atomization

• very high temperature for excitation not necessary

generally no plasma/arc/spark AAS

TABLE 9-1 Properties of Flames   They're HOT !

Fuel	Oxidant	Temperatures, °C	Maximum Burning Velocity (cm s^{-1})
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

Very important
Low rate: flashback
Higher rate: Blows off
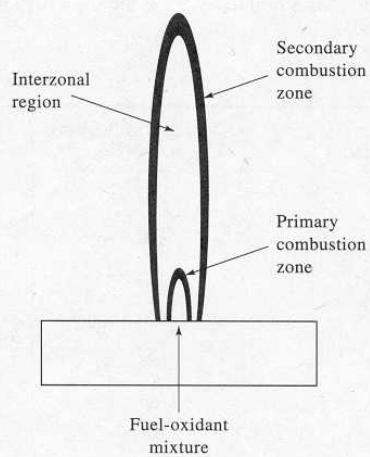
Figure 9-2 Regions in a flame.

Primary combustion zone - initial decomposition, molecular fragments, cool

Interzonal region - hottest, most atomic fragments, used for emission/fluorescence

Secondary combustion zone - cooler, conversion of atoms to stable molecules, oxides
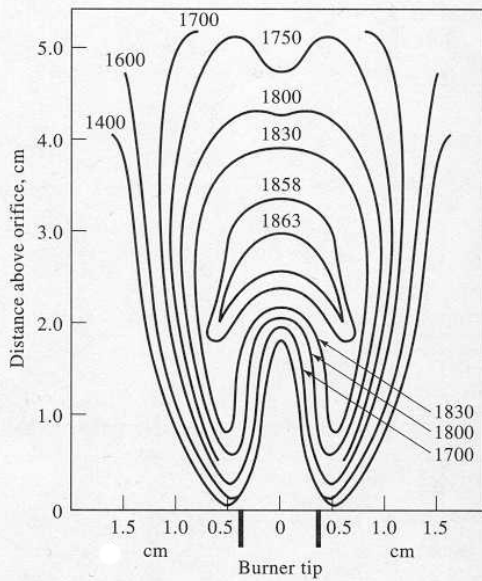
Figure 9-3 Temperature profiles in °C for a natural gas/air flame. *(From B. Lewis and G. vanElbe, J. Chem. Phys., 1943, 11, 94. With permission.)*
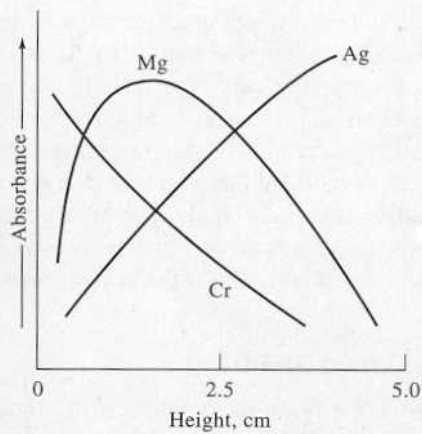
Figure 9-4 Flame absorbance profile for three elements.

Consequences?

sensitivity varies with element

must maximize burner position

makes multielement detection difficult

Burner head

Burner head locking ring

Pressure relief vents

Auxiliary oxidant

Flow spoiler retaining screw

Fuel

Nebulizer adjusting knob

Sample capillary

To waste

Nebulizer

Nebulizer oxidant

Flow spoiler (Panton plastic)
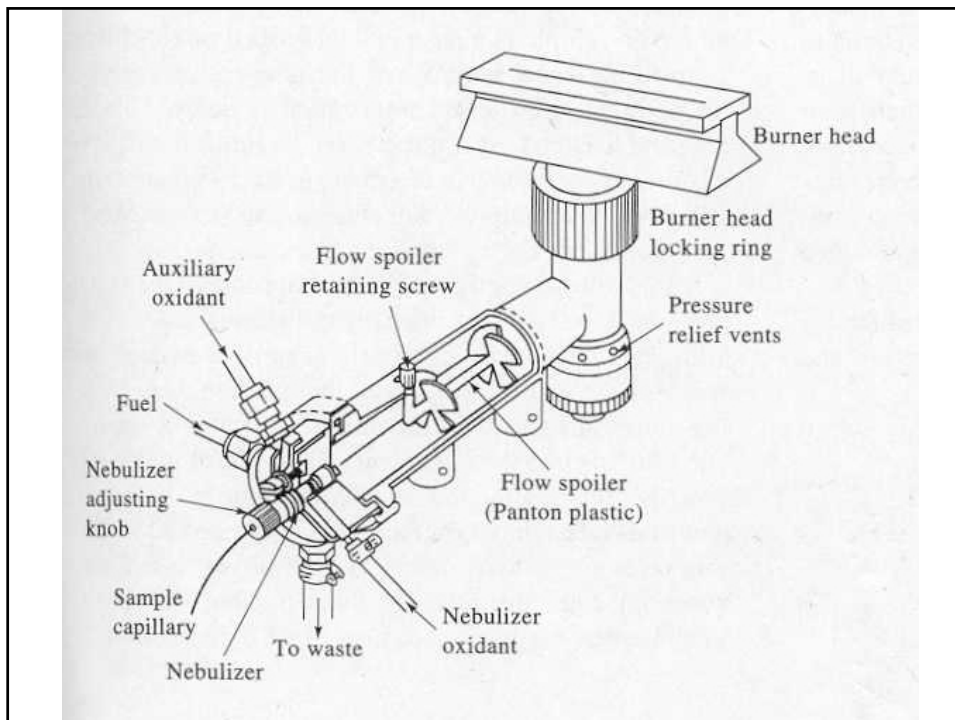
AA Slot Burner and Flame

Figure 9-6 (a) Cross-sectional view of a graphite furnace. *(Courtesy of the Perkin-Elmer Corporation, Norwalk, CT.)* (b) The L'vov platform and its position in the graphite furnace.

• external Ar gas prevents tube destruction

• internal Ar gas circulates gaseous analyte

Electrothermal Atomizers:

• entire sample atomized short time (2000-3000 ° C)

• sample spends up to 1 s in analysis volume

• superior sensitivity (10^{-10}-10^{-13} g analyte)

• less reproducible (5-10 %)

Three step sample preparation for graphite furnace:

(1) Dry - evaporation of solvents (10->100 s)

(2) Ash - removal of volatile hydroxides, sulfates, carbonates (10-100 s)

(3) Fire/Atomize - atomization of remaining analyte (1 s)

Figure 9-7 Typical output from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 μL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively. *(Courtesy of Varian Instrument Division, Palo Alto, CA.)*

Figure 9-9 A hydride generation and atomization system for atomic absorption spectrometry.

There are many possible variations for the hydride generation apparatus

Sample introduction for solutions:

1) Pneumatic nebulizers
2) Ultrasonic nebulizers
3) Electrothermal vaporizers
4) Hydride generation

$$3\ BH_4^- + 3\ H^+ + 4\ H_3AsO_3 \rightarrow$$
$$3\ H_3BO_3 + 4\ AsH_3 + 3\ H_2O$$

5) Cold vapor generation

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^0 + Sn^{4+}$$
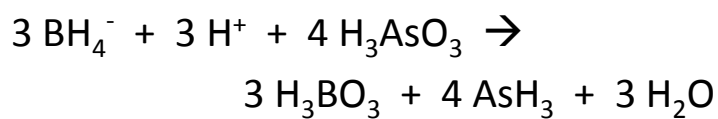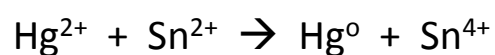
Atomic Absorption Instrumentation:

• AAS should be very selective - each element has different set of energy levels and lines very narrow

• BUT for linear calibration curve (Beers' Law) need bandwidth of absorbing species to be broader than that of light source

difficult with ordinary monochromator

Solved by using very narrow line radiation sources

• minimize Doppler broadening

• pressure broadening

• lower P and T than atomizer

and using resonant absorption

• Na emission 3p→2s at 589.6 nm used to probe Na in analyte

Figure 9-10 Absorption of a resonance line by atoms.
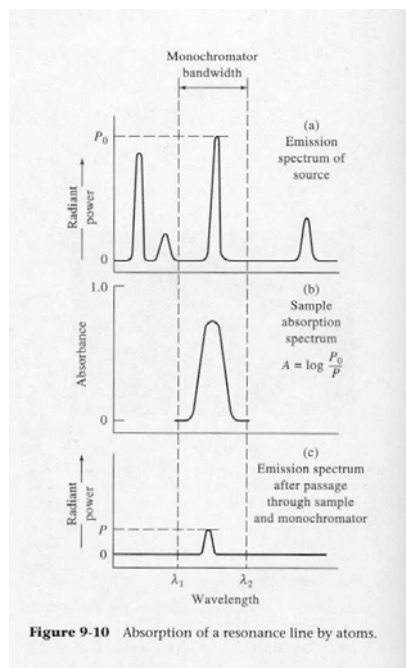
Normal or idealized situation for the absorption of source radiation in AA

Problems arise if the sample absorption is interfered with by a matrix component
- sloped baseline
- overlapping molecular band

Background correction is then needed

Hollow Cathode Lamp:
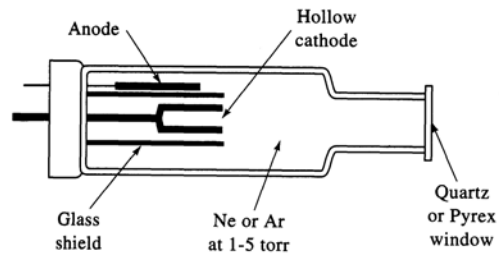
- 300 V applied between anode (+) and metal cathode (-)
- Ar ions bombard cathode and sputter cathode atoms
- Fraction of sputtered atoms excited, then fluoresce
- Cathode made of metal of interest (Na, Ca, K, Fe...)

different lamp for each element

restricts multielement detection

- Hollow cathode to

maximize probability of redeposition on cathode

restricts light direction

Electrodeless Discharge Lamp:
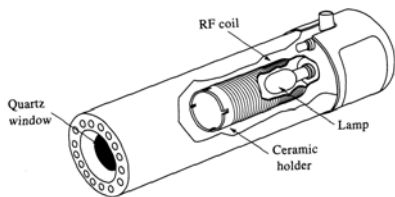
Electrodeless discharge lamp

An alternative to the hollow cathode lamp.

A salt containing the metal of interest is sealed in a quartz tube along with an inert gas.

An RF field is used to excite the gas which in turn causes the metal be be ionized.

Light intensity is about 10-100 times greater but are not as stable as HC lamps.

EDLs provide greater light output and longer life than corresponding HCLs.

EDLs will also provide improved sensitivity and lower detection limits.

AAS Spectrophotometers:

(a)
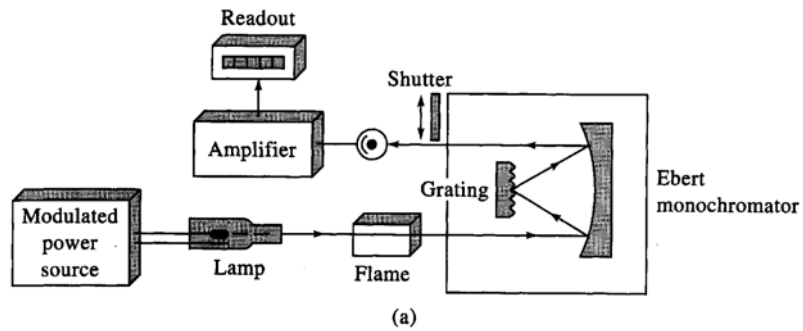
Signal at one wavelength often contains luminescence from interferents in flame

(b)
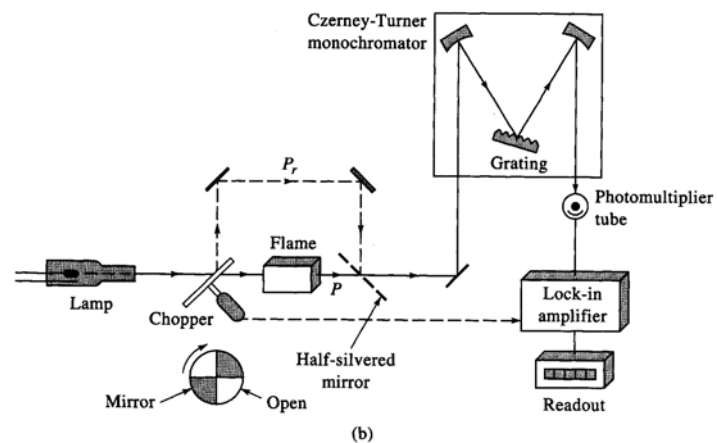
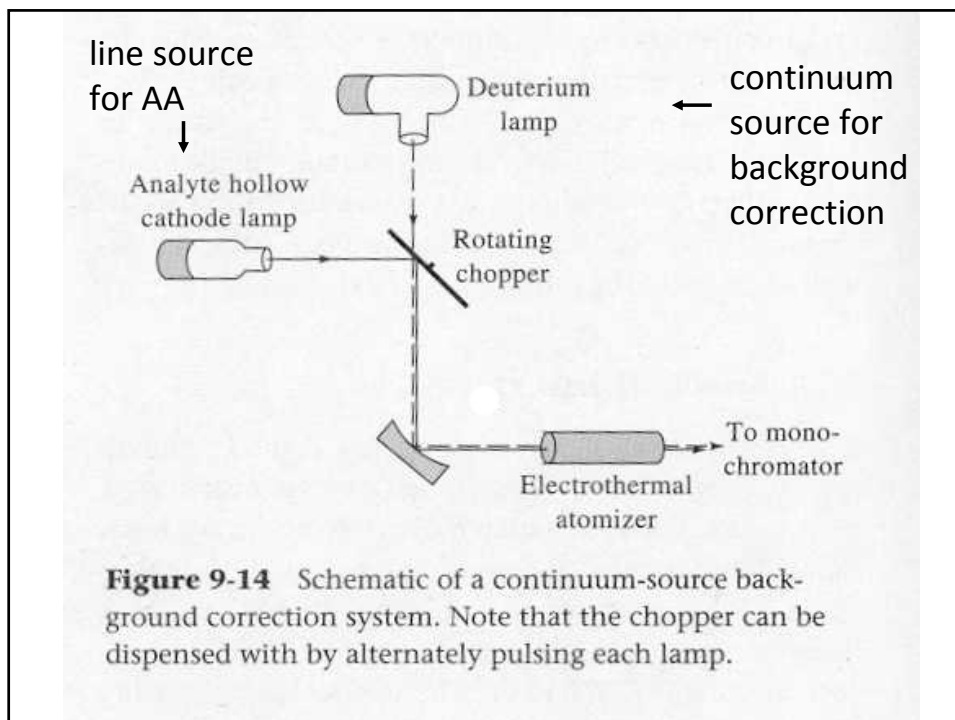Beam usually *chopped* or *modulated* at known frequency

Signal then contains constant (background) and dynamic (timevarying) signals
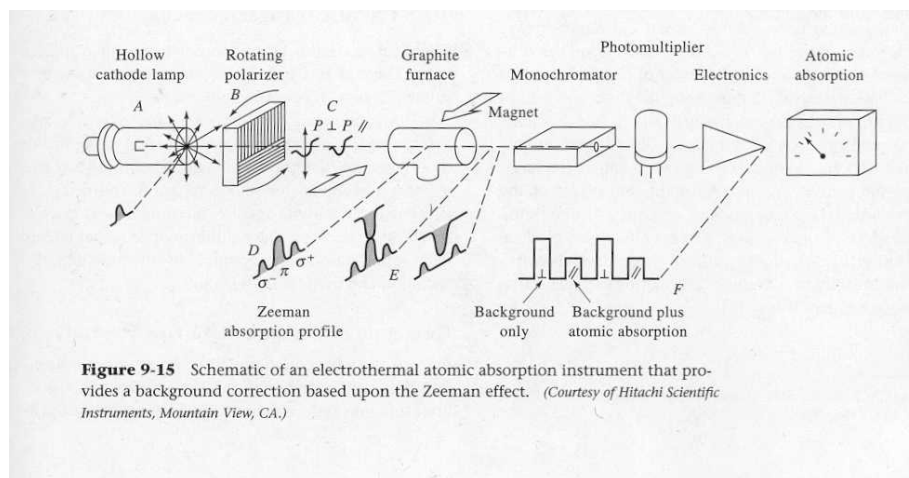
Interferences in AA can be

- Spectral – atomic spectral lines overlap or are too close to resolve – these are rare & generally well known or characterized
- Matrix – scattering of radiation during atomization (smoke), enhancement by matrix elements, structured background – handled by background correction
- Chemical – reactions that take place to alter the analyte (like Ca atoms reacting with PO_4 to form a new species) – change conditions

Background Correction in AA

- Two-Line correction (not very common)
- Continuous source correction (very common)
- Zeeman background correction (common for graphite furnace instruments)
- Smith-Hieftje correction (relatively new '83)

line source
for AA
↓

Analyte hollow
cathode lamp

Deuterium
lamp

continuum
source for
background
correction

Rotating
chopper

To mono-
chromator

Electrothermal
atomizer

Figure 9-14 Schematic of a continuum-source background correction system. Note that the chopper can be dispensed with by alternately pulsing each lamp.

The Zeeman effect splits the absorption peak in a magnetic field & shifts absorption to higher & lower wavelength. The new absorption peaks interact differently with polarized light allowing analyte & background absorbance to be measured

Hollow cathode lamp   Rotating polarizer   Graphite furnace   Photomultiplier   Atomic absorption

A   B   C   Monochromator   Electronics

$P \perp P \parallel$ Magnet

D $\sigma^- \pi \sigma^+$ E

Zeeman absorption profile   Background only   Background plus atomic absorption   F

Figure 9-15 Schematic of an electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect. *(Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)*

The Smith-Hieftje technique splits the HCL line
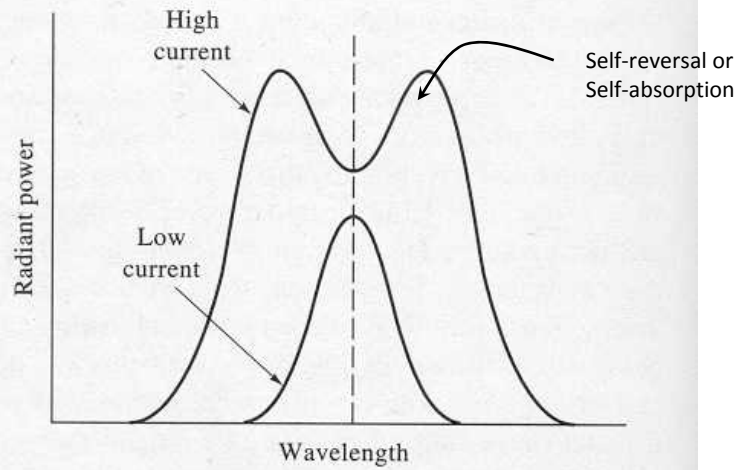
Figure 9-16 Emission line profiles for a hollow-cathode lamp operated at high and low currents.
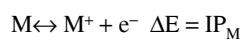

Chemical interference:

(i) reverses atomization equilibria

(ii) reacts with analyte to form low volatility compound

       releasing agent - cations that react preferentially with interferent - Sr acts as releasing agent for Ca with phosphate

       protecting agent - form stable but volatile compounds with analyte (metal-EDTA formation constants)

(iii) ionization

$$M \leftrightarrow M^+ + e^- \quad \Delta E = IP_M$$

$$N_{M+} = N_M \times \exp(IP_M/kT)$$

Another type of matrix interference not alleviated by background correction involves variable amounts of analyte ionization in flames or plasmas

TABLE 9-2 Degree of Ionization of Metals at Flame Temperatures*

Element	Ionization Potential, eV	Fraction Ionized at the Indicated Pressure and Temperature			
		$p = 10^{-4}$ atm		$p = 10^{-6}$ atm	
		2000 K	3500 K	2000 K	3500 K
Cs	3.893	0.01	0.86	0.11	>0.99
Rb	4.176	0.004	0.74	0.04	>0.99
K	4.339	0.003	0.66	0.03	0.99
Na	5.138	0.0003	0.26	0.003	0.90
Li	5.390	0.0001	0.18	0.001	0.82
Ba	5.210	0.0006	0.41	0.006	0.95
Sr	5.692	0.0001	0.21	0.001	0.87
Ca	6.111	3×10^{-5}	0.11	0.0003	0.67
Mg	7.644	4×10^{-7}	0.01	4×10^{-6}	0.09

*Data from B. L. Vallee and R. E. Thiers, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 6, p. 3500. New York: Interscience, 1965. Reprinted with permission of John Wiley & Sons, Inc.

hotter atomization means: more ionization

emission from interferents
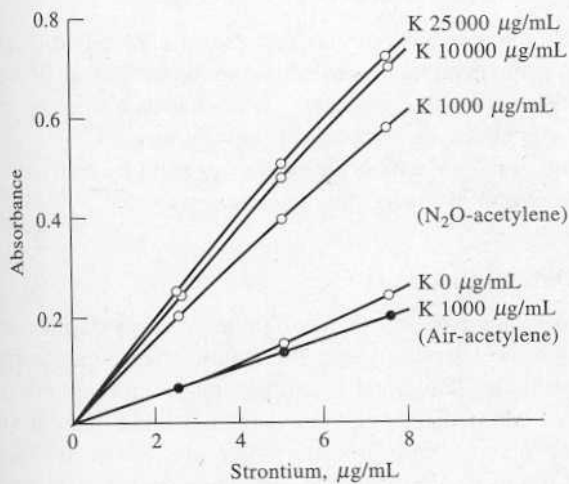
Figure 9-17 Effect of potassium concentration on the calibration curve for strontium. *(Reprinted with permission from J. A. Bowman and J. B. Willis, Anal. Chem., 1967, 39, 1220. Copyright 1967 American Chemical Society.)*

One other factor (other than temp.) that influences degree of ionization is the presence of another easily ionized species. Here K enhances the Sr AA signal by suppressing Sr ionization

Detection limits for AAS/AES?

• AA/AE comparable (ppb in flame)

• AAS less suitable for

weak absorbers (forbidden transitions)

metalloids and non-metals (absorb in UV) metals with low IP (alkali metals)

TABLE 9-3 Detection Limits (ng/mL)* for Selected Elements†

Element	AAS‡ Flame	AAS§ Electrothermal	AES‡ Flame	AES‡ ICP	AFS‡ Flame
Al	30	0.005	5	2	5
As	100	0.02	0.0005	40	100
Ca	1	0.02	0.1	0.02	0.001
Cd	1	0.0001	800	2	0.01
Cr	3	0.01	4	0.3	4
Cu	2	0.002	10	0.1	1
Fe	5	0.005	30	0.3	8
Hg	500	0.1	0.0004	1	20
Mg	0.1	0.00002	5	0.05	1
Mn	2	0.0002	5	0.06	2
Mo	30	0.005	100	0.2	60
Na	2	0.0002	0.1	0.2	—
Ni	5	0.02	20	0.4	3
Pb	10	0.002	100	2	10
Sn	20	0.1	300	30	50
V	20	0.1	10	0.2	70
Zn	2	0.00005	0.0005	2	0.02

*Nanogram/milliliter = 10^{-3} µg/mL = 10^{-3} ppm.

Atomic Fluorescence – use an intense light source to excite AF of elements in a flame or plasma.

Chapter 10: Emission Spectroscopy Using Plasmas, Arcs or Sparks

Identification of elements but not compounds

Excitation and Atomization:

Traditionally based on
• flame
but
• arc and spark
• plasma
　　Inductively Coupled Plasma (ICP) Direct Current Plasma (DCP)

excitation offers
(i) increased atomization/excitation
(ii) wider range of elements
(iii) emission from multiple species simultaneously
(iv) wide dynamic range

Arc and Spark Excitation Sources:
• Limited to semiquantitative/qualitative analysis (arc flicker)
• Usually performed on solids
• Largely displaced by plasma-AES

Arc/spark unstable - each line measured >20 s (needs multichannel detection)
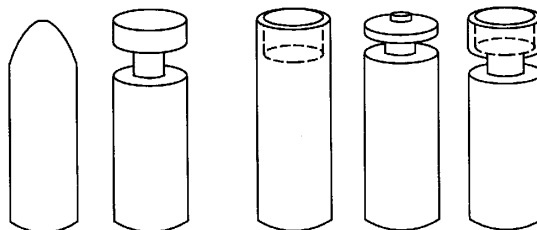
Counter electrodes　　　Electrodes for holding sample

Sample pressed into electrode or mixed with Cu powder and pressed - briquetting
Cyanogen bands (CN) 350-420 nm occur with C electrodes in air - He, Ar atmosphere

Eagle Mount

photographic film:
- Cheap
- Long integration times
- Difficult to develop/analyze
- Non-linearity of line "darkness"

multichannel PMT instruments:
- for rapid determinations (<20 lines) but not versatile
- routine analysis of solids - metals, alloys, ores, rocks, soils
- portable instruments

Figure 10-18 Projected spectra by a comparator-densitometer: (a), (b), and (c) spectra of sample at three different exposures; (d) iron spectrum on the sample plate; (e) and (f) iron spectra on the master plate.

Plasma Excitation Sources:
gas containing high proportion of cations and electrons
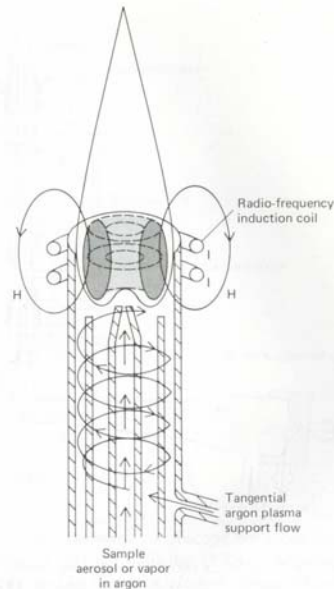
Inductively Coupled Plasma (ICP)

- Torch up to 1" diameter
- Ar cools outer tube, defines plasma shape
- Radio-frequency (RF) up to 2 kW
- Ar flow up to 20 L/min

Solution Sample Introduction:

(1) Electrothermal vaporizer* (ETV)
- electric current rapidly heats crucible containing sample
- sample carried to atomizer by gas (Ar, He)
- only for introduction, not atomization (Fig 10-3)
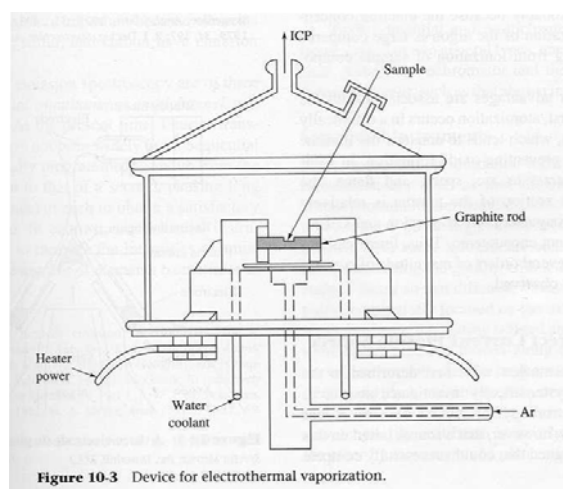
Figure 10-3 Device for electrothermal vaporization.

(2) Nebulizer - convert solution to fine spray or aerosol

• **(a) Ultrasonic nebulizer uses ultrasound waves to "boil" solution** flowing across disc

• **(b) Pneumatic nebulizer uses high pressure gas to entrain** Solution

ICP Torch with sample introduction system (nebulizer and spray chamber)

Insulating shield

Plasma Ar

Auxiliary plasma Ar (optional)

Aerosol carrier Ar

To drain

Sample solution

Cross-flow Nebulizer
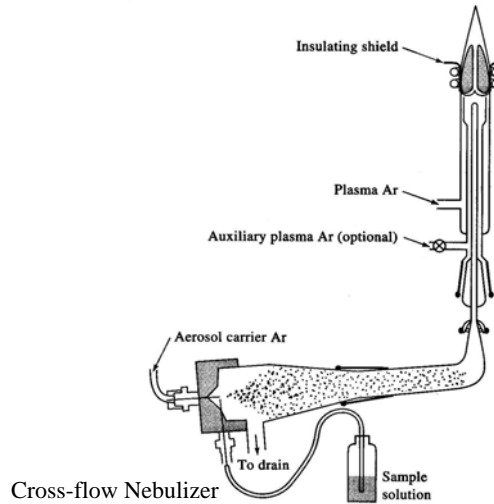
Solid Sample Introduction:

(1) Electrothermal vaporizer*
(2) Direct Insertion(*) uses powder placed inside flame, plasma, arc or spark atomizer (atomizer acts as vaporizer)
Coating on electrode in atomizer
(3) Ablation uses coating of electrodes in discharge cell and sample entrained in Ar or He gas
Laser ablation uses laser to vaporize sample

ICP Temps.

The viewing area for each element is typically reported as mm above the load coil

• Brilliant white core - Ar continuum and lines
• Flame-like tail up to 2 cm
• Transparent region - measurements made
• Hotter than flame (10,000 K) - more complete atomization/excitation
• Atomized in "inert" atmosphere
• Little ionization - too many electrons in plasma
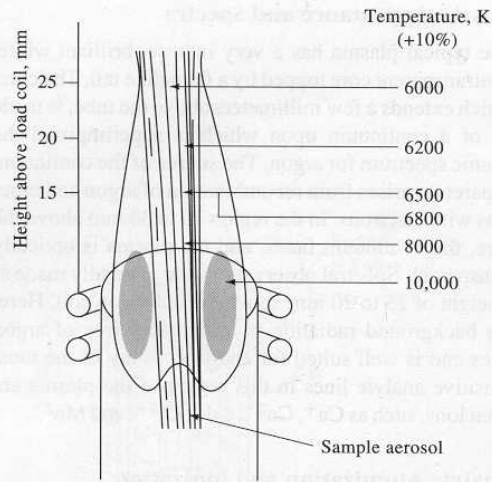
Figure 10-4 Temperatures in a typical inductively coupled plasma source. *(From V. A. Fassel, Science, 1978, 202, 186. With permission. Copyright 1978 by the American Association for the Advancement of Science.)*
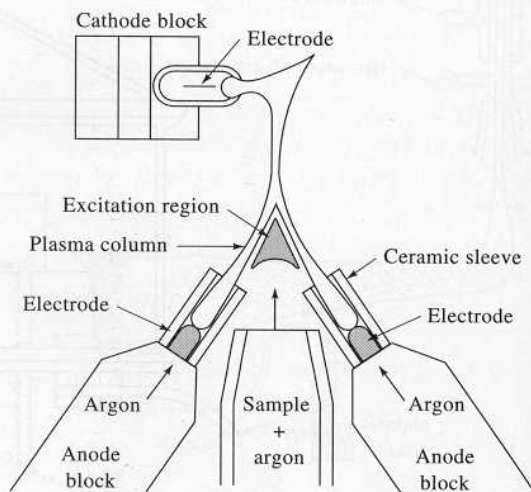
Figure 10-5 A three-electrode dc plasma jet. *(Courtesy of Spectra Metrics, Inc. Haverhill, MA.)*

Direct Current Plasma (DCP) Torch

Lab will involve use of DCP for multielement analysis

• DC current (10-15 A) flows between C anodes and W cathode

• Plasma core at 10,000 K, viewing region at ~5,000 K

• Simpler, less Ar than ICP - less expensive

Atomic Emission Spectrometers:

May be >1,000 visible lines (<1 Å) on continuum
Need
• high resolution (<0.1 Å)
• high throughput
• low stray light
• wide dynamic range (>10^6)
• precise and accurate wavelength calibration/intensities
• stability
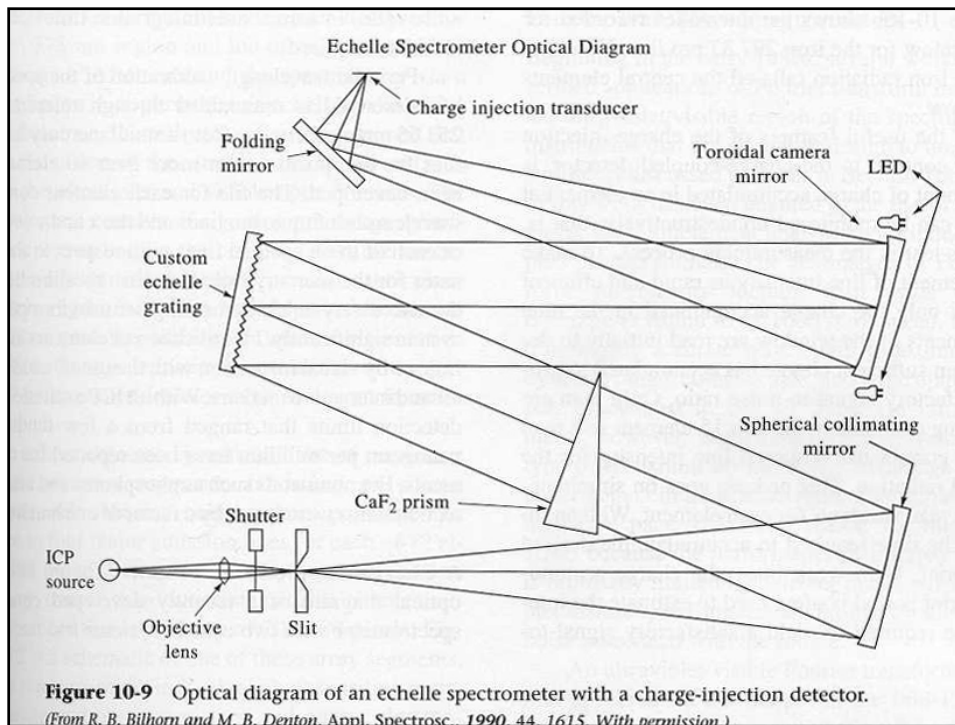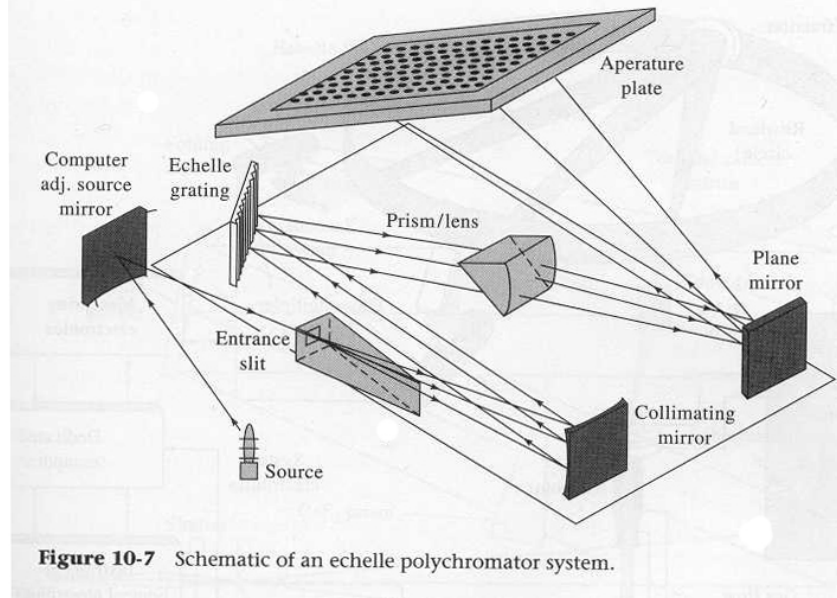• computer controlled

Three instrument types:
sequential (scanning and slew-scanning)
multichannel
(Fourier transform FT-AES)

• **Sequential monochromators:**

• Slew-scan spectrometers - even with many lines, much spectrum

• contains no information

• rapidly scanned (slewed) across blank regions

• slowly scanned across lines

• computer control/preselected lines to scan

Multichannel AES:

Figure 10-7 Schematic of an echelle polychromator system.

Labels: Aperature plate; Computer adj. source mirror; Echelle grating; Prism/lens; Plane mirror; Entrance slit; Collimating mirror; Source

Echelle Spectrometer Optical Diagram

Labels: Charge injection transducer; Folding mirror; Toroidal camera mirror; LED; Custom echelle grating; Spherical collimating mirror; CaF$_2$ prism; Shutter; ICP source; Objective lens; Slit

Figure 10-9 Optical diagram of an echelle spectrometer with a charge-injection detector.
(From R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., 1990, 44, 1615. With permission.)

Figure 10-10 (a) Schematic representing the surface of a charge-injection device. The short horizontal lines represent the "read windows." A magnified image of one of the read windows is also shown. The nine central elements form the "examination window" where a line is positioned. (b) Intensity profile for an iron line. All of the radiation from the line falls on the 3 × 3 examination window. *(From R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., 1990, 44, 1540. With permission.)*
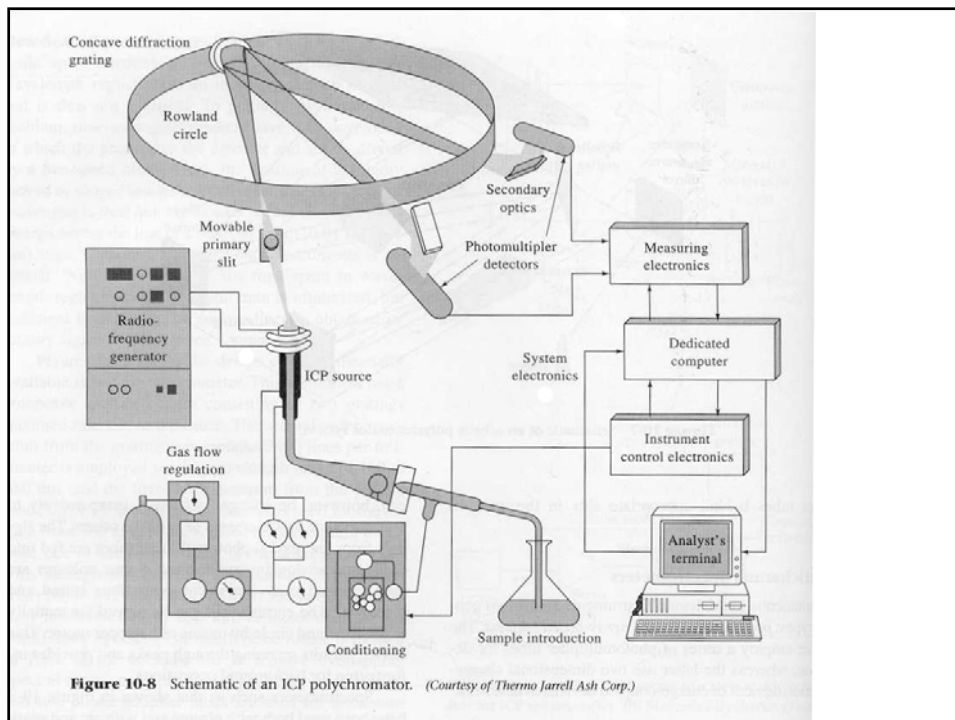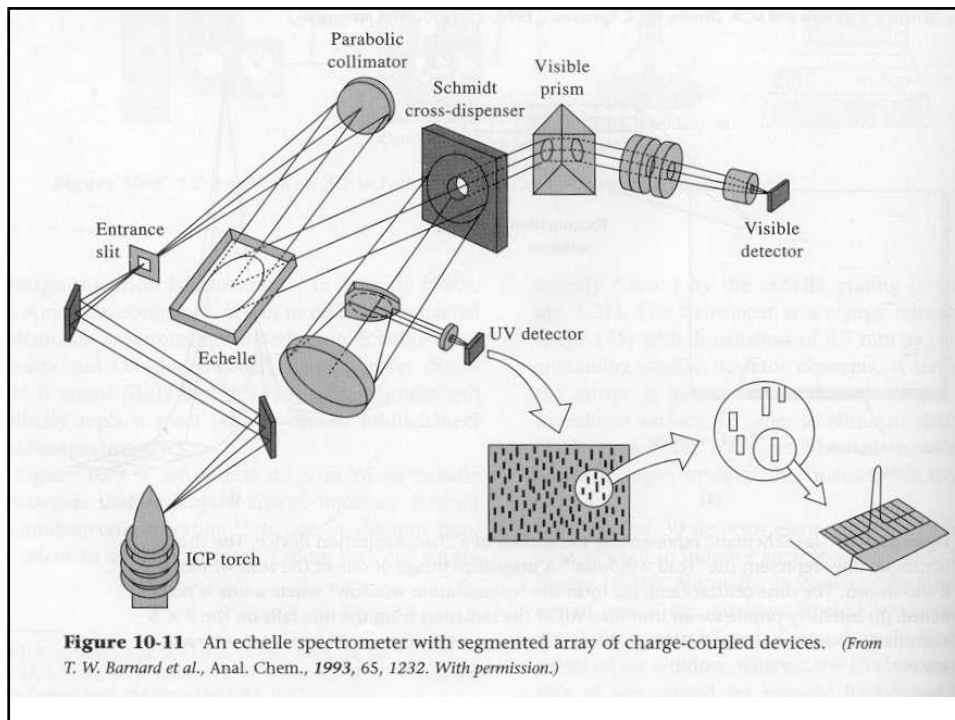

Figure 10-8 Schematic of an ICP polychromator. *(Courtesy of Thermo Jarrell Ash Corp.)*

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.)*

Sequential instrument - PMT moved behind aperture plate, or
grating+prism moved to focus new λ on exit slit
• Cheaper
• Slower
• Pre-configured exit slits to detect up to 20 lines, slew scan

Multichannel instrument - multiple PMT's
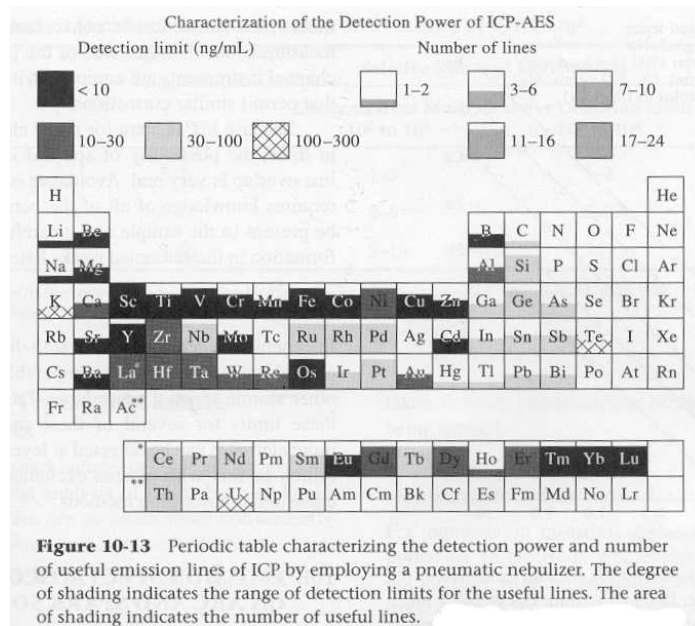• Expensive
• Faster

Applications of AES:

AES relatively insensitive (small excited state population at moderate temperature)

AAS still used more than AES
(i) less expensive/complex instrumentation
(ii) lower operating costs
(iii) greater precision

In practice ~60 elements detectable
• 10 ppb range most metals
• Li, K, Rb, Cs strongest lines in IR
• Large # of lines, increase chance of overlap

Figure 10-13 Periodic table characterizing the detection power and number of useful emission lines of ICP by employing a pneumatic nebulizer. The degree of shading indicates the range of detection limits for the useful lines. The area of shading indicates the number of useful lines.
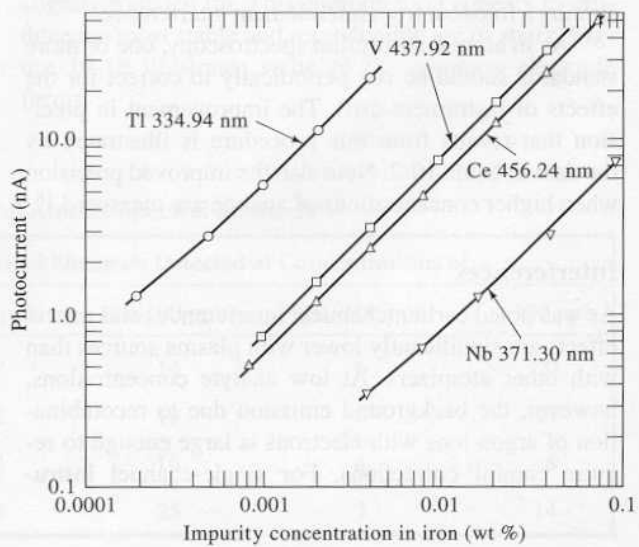
Figure 10-14 Typical calibration curves. *(From V. A. Fassel and R. N. Kniseley, Anal. Chem., 1974, 46, 1117A. With permission.)*
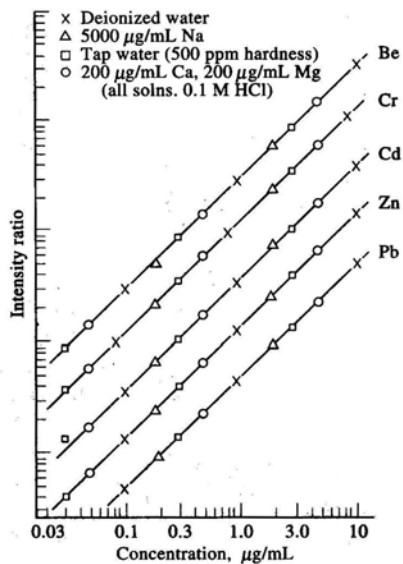
Figure 10-15 Calibration curves with an inductively coupled plasma source. Here, an yttrium line at 242.2 nm served as an internal standard. Notice the lack of interelement interference. *From V. A. Fassel, Science, 1978, 202, 187.*
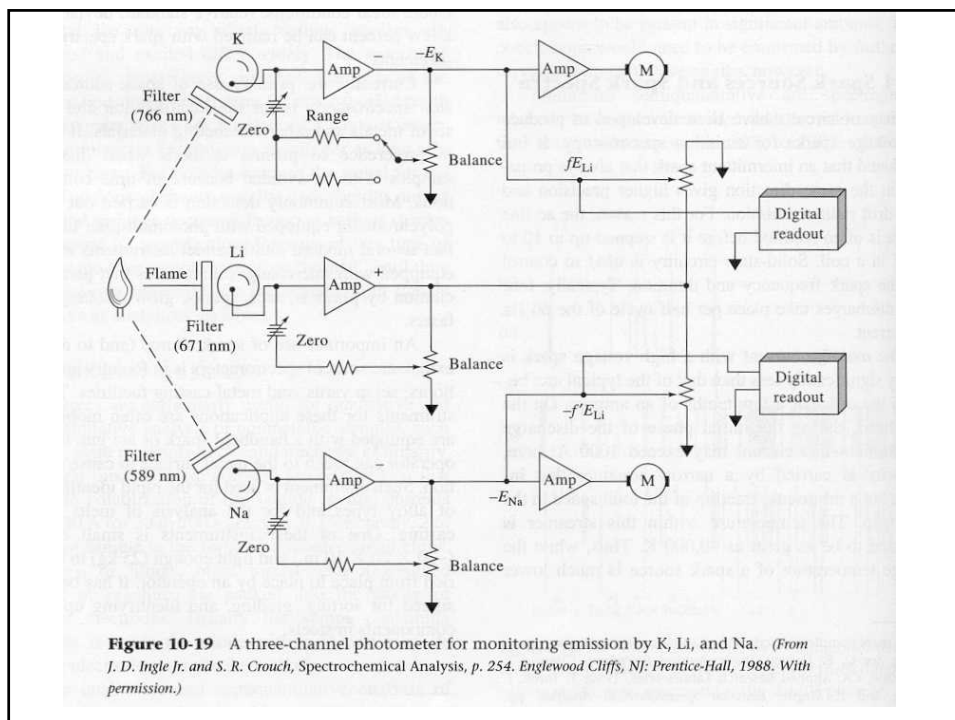
Figure 10-19 A three-channel photometer for monitoring emission by K, Li, and Na. *(From J. D. Ingle Jr. and S. R. Crouch, Spectrochemical Analysis, p. 254. Englewood Cliffs, NJ: Prentice-Hall, 1988. With permission.)*

TABLE 10-1 Desirable Properties of an Emission Spectrometer

1. High resolution (0.01 nm or $\lambda/\Delta\lambda > 100,000$)

2. Rapid signal acquisition and recovery

3. Low stray light

4. Wide dynamic range ($>10^6$)

5. Accurate and precise wavelength identification and selection

6. Precise intensity readings ($<1\%$ RSD at $500 \times$ the detection limit)

7. High stability with respect to environmental changes

8. Easy background corrections

9. Computerized operation: readout, storage data manipulation, etc.

TABLE 10-2 Effect of Standardization Frequency on Precision of ICP Data*

| Frequency of Recalibration, hr | Relative Standard Deviation, % | | | |
| | Concentration Multiple above Detection Limit | | | |
	10^1 to 10^2	10^2 to 10^3	10^3 to 10^4	10^4 to 10^5
0.5	3–7	1–3	1–2	1.5–2
2	5–10	2–6	1.5–2.5	2–3
8	8–15	3–10	3–7	4–8

*Data from: R. M. Barnes, in *Applications of Inductively Coupled Plasmas to Emission Spectroscopy*, R. M. Barnes, Ed., p. 16. Philadelphia: The Franklin Institute Press, 1978. With permission.

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods*

| Method | Number of Elements Detected at Concentrations of | | | | |
	<1 ppb	1–10 ppb	11–100 ppb	101–500 ppb	>500 ppb
Inductively coupled plasma emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	19
Flame atomic fluorescence	4	14	16	4	6
Flame atomic absorption	1	14	25	3	14

*Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise. Data abstracted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, **1974**, *46*(13), 1111A. Copyright 1974 American Chemical Society.

Chapter 11: Atomic Mass Spectrometry (Inorganic MS)

- Mass Spectrometers
- ICP-MS
- Spark Source MS
- Glow-Discharge MS
- Elemental Surface Analysis by MS
- Laser Ablation ICP-MS

Atomic Mass Spec processes

- Atomization (sample intro)
- Conversion to ions, singly charged positive ions
- Separation based on m/z ratio
- Detection ion current

In other forms of MS (GC-MS or MS of organic compounds), sample introduction does not involve making atoms, just getting molecules into the high vacuum system

Atomic Mass Spec has been around for a long time but one of the most significant advances in this field occurred recently, the development of ICP-MS

TABLE 11-1 Types of Atomic Mass Spectrometry

Name	Acronym	Atomic Ion Sources	Typical Mass Analyzer
Inductively coupled plasma	ICPMS	High-temperature argon plasma	Quadrupole
Direct current plasma	DCPMS	High-temperature argon plasma	Quadrupole
Microwave-induced plasma	MIPMS	High-temperature argon plasma	Quadrupole
Spark source	SSMS	Radio-frequency electric spark	Double-focusing
Thermal ionization	TIMS	Electrically heated plasma	Double-focusing
Glow discharge	GDMS	Glow-discharge plasma	Double-focusing
Laser microprobe	LMMS	Focused laser beam	Time-of-flight
Secondary ion	SIMS	Accelerated ion bombardment	Double-focusing

Basic MS design components

Note high vacuum
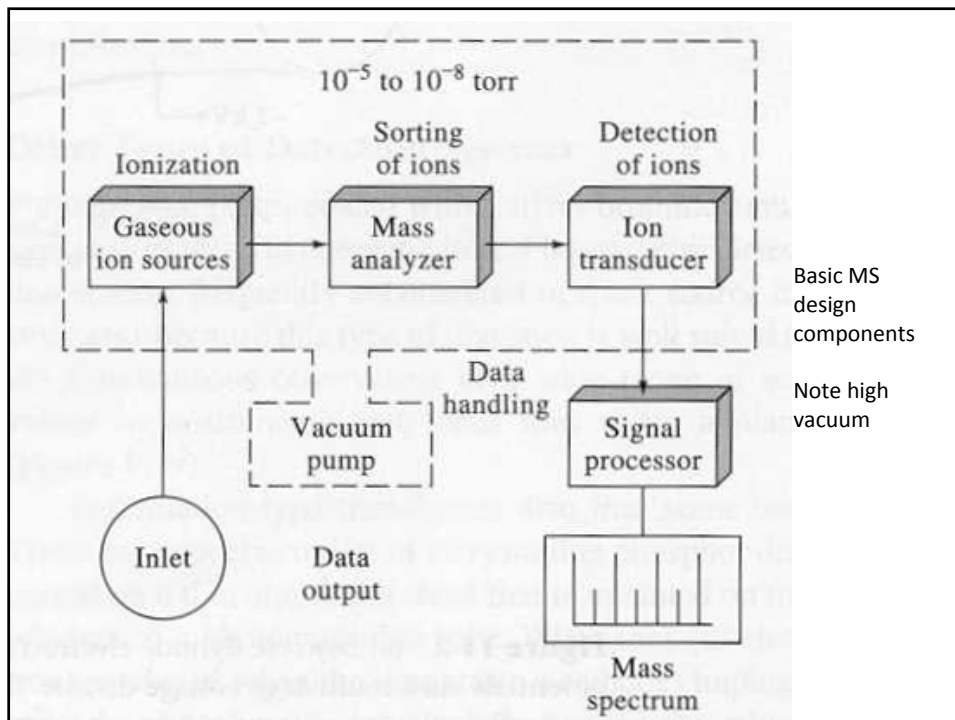
Advantages of Atomic Mass Spec over Optical
Atomic Spectrometry

1) Detection limits are better, sometimes
   several orders of magnitude better

2) Very simple spectra

3) Ability to measure isotope ratios

Disadvantages

1) Equipment cost

2) Instrument drift
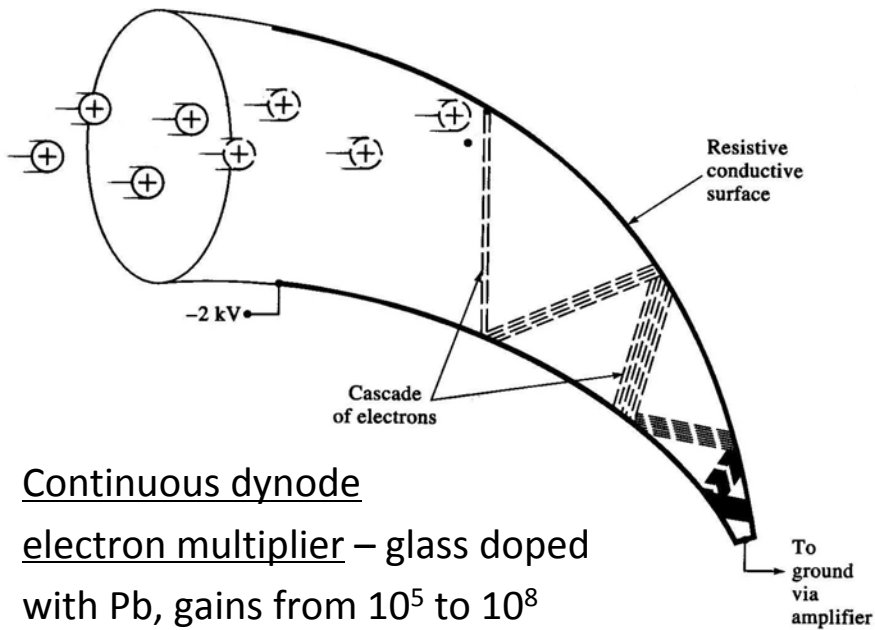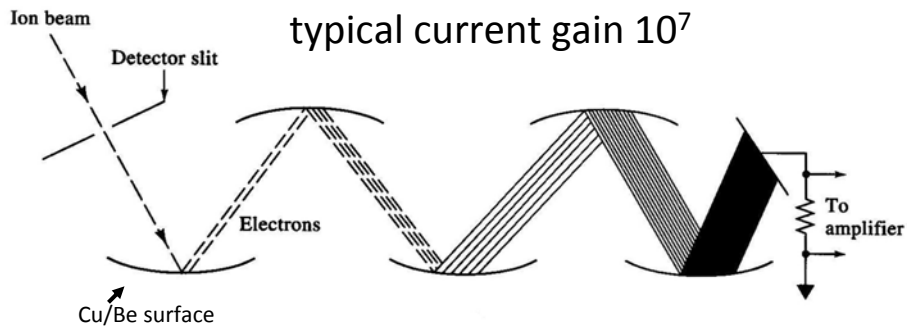
3) Isotopic interferences

- Mass Spectrum of Li
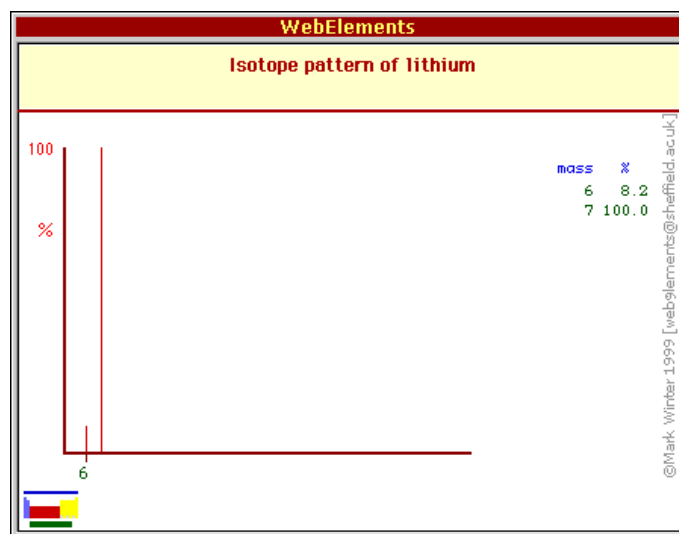
Detectors = Transducers for Mass Spec

1) Electron Multipliers – transducer of choice

<u>Discrete dynode electron multiplier</u> works like a photomultiplier tube

ions → electrons → many electrons

typical current gain 10^7

Ion beam

Detector slit

Electrons

To amplifier

Cu/Be surface

<u>Continuous dynode</u>
<u>electron multiplier</u> – glass doped
with Pb, gains from 10^5 to 10^8

Resistive conductive surface

−2 kV

Cascade of electrons

To ground via amplifier

2) Faraday Cup – historically important, not extremely sensitive, slow
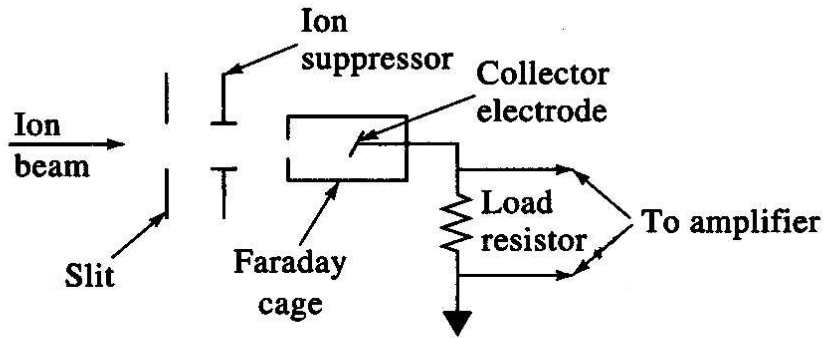
Figure 11-3 Faraday cup detector. The potential on the ion suppressor plates is adjusted to minimize differential response as a function of mass.

Separation of ions = Mass Analyzers

1) Quadrupole Mass Analyzers
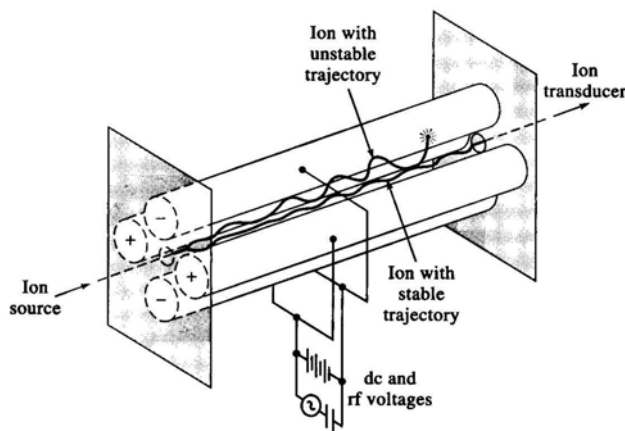
Important device that acts as a mass filter passing only ions of certain m/z

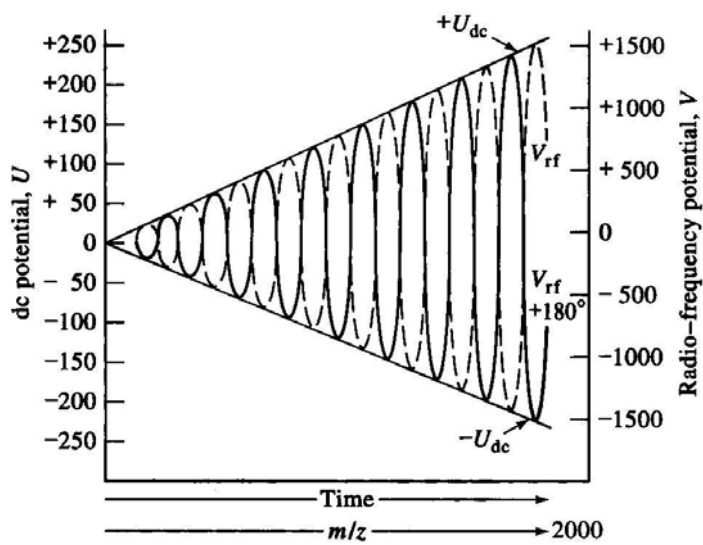**Figure 11-4** A quadrupole mass spectrometer.

Figure 11-7 Voltage relationships during a mass scan with a quadrupole analyzer.

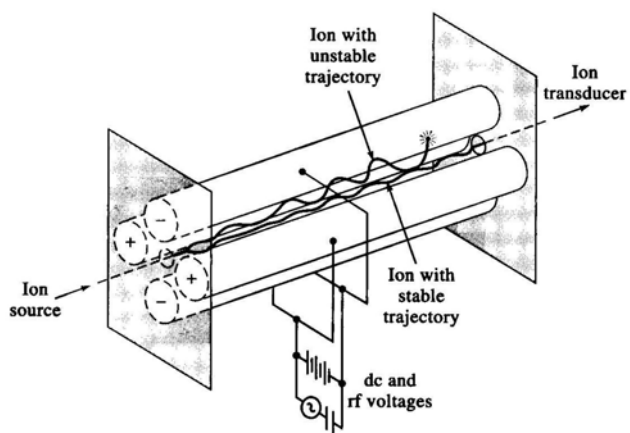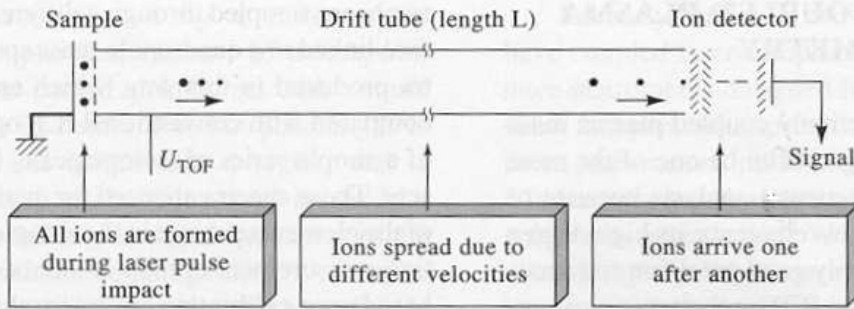Separation of ions = Mass Analyzers
1) Quadrupole Mass Analyzers


**Figure 11-4** A quadrupole mass spectrometer.

2) Time of Flight Mass Analyzers

Ions are accelerated into a field-free drift tube approximately 1 m long & separated based on kinetic energy (1 – 30 µs)

3) Double-Focusing Mass Analyzer
employs electrostatic analyzer & magnetic sector analyzer

ICP-MS showing various sample introduction modes, ICP torch, mass analyzer & detector
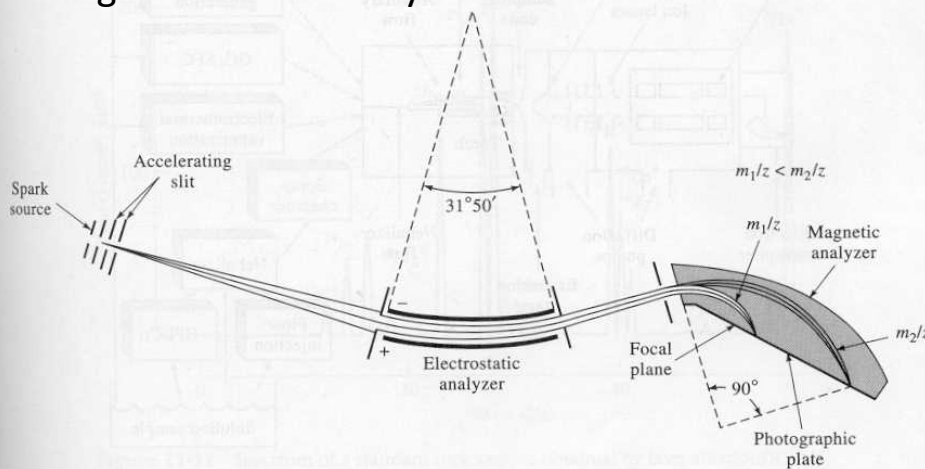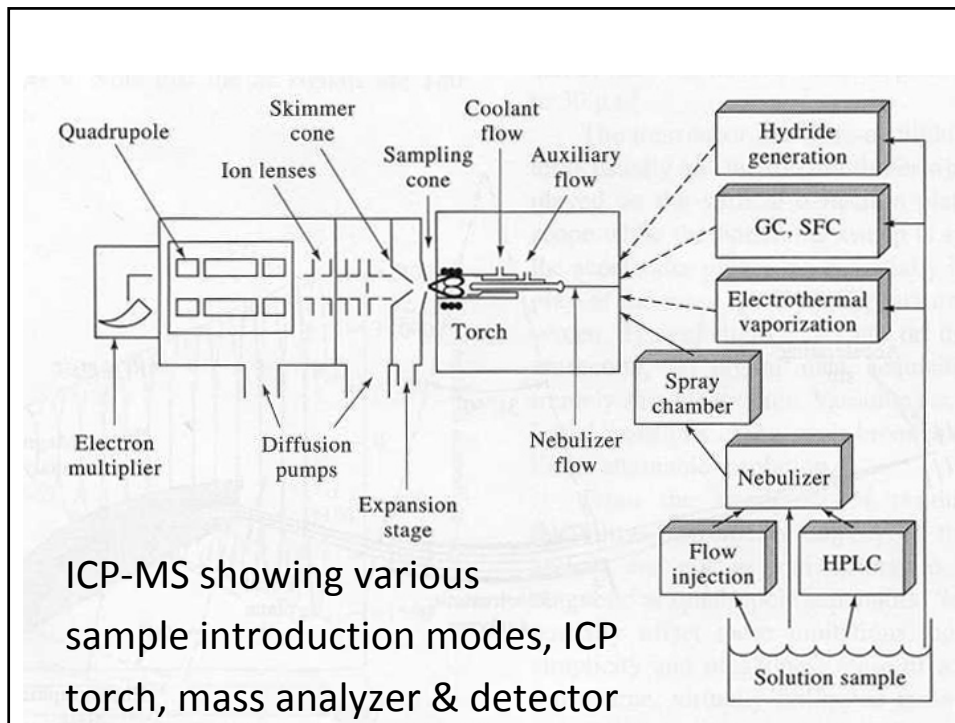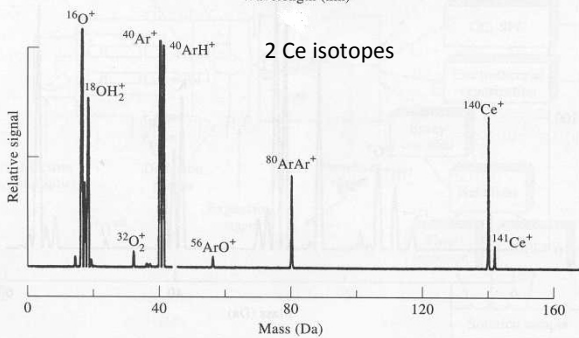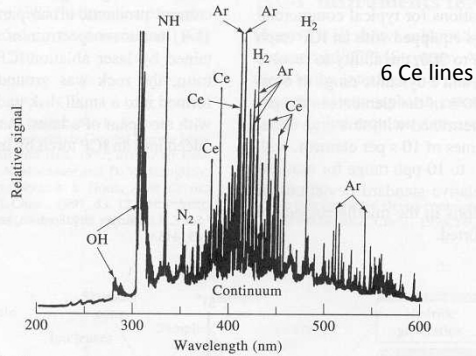
ICP-MS

- Developed early 1980's
- Low detection limits (0.1 to 10 ppb)
- High selectivity
- Good precision (2 - 4%) & accuracy
- m/z range 3 - 300 = 90% of periodic table
- Resolution 1 m/z
- Dynamic range 10^6
- Approximately 10 sec measurement time
- Various sample introduction methods

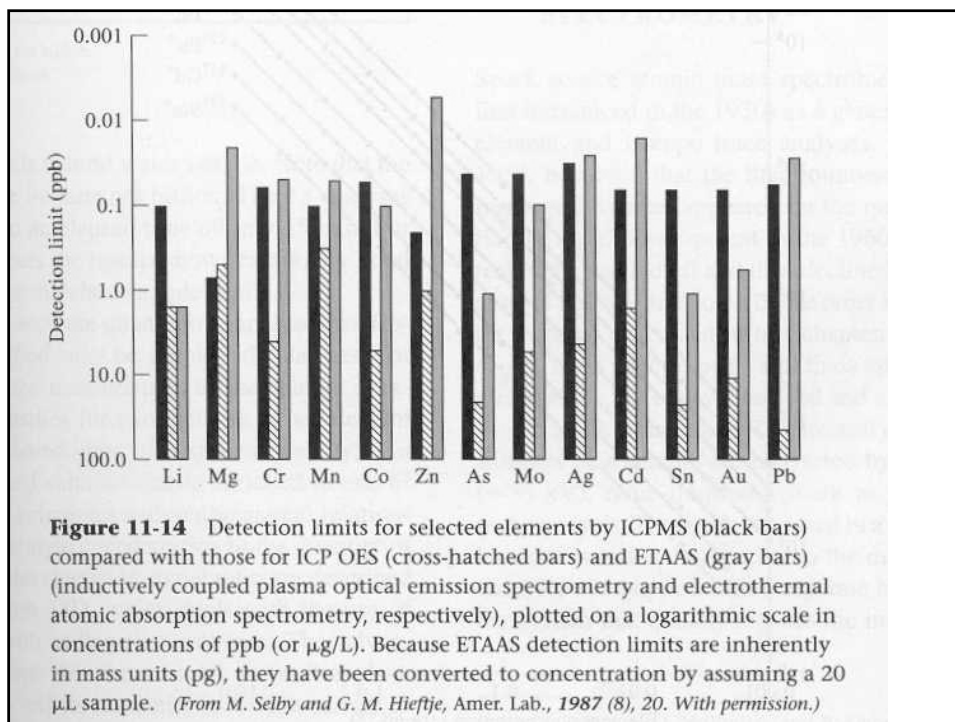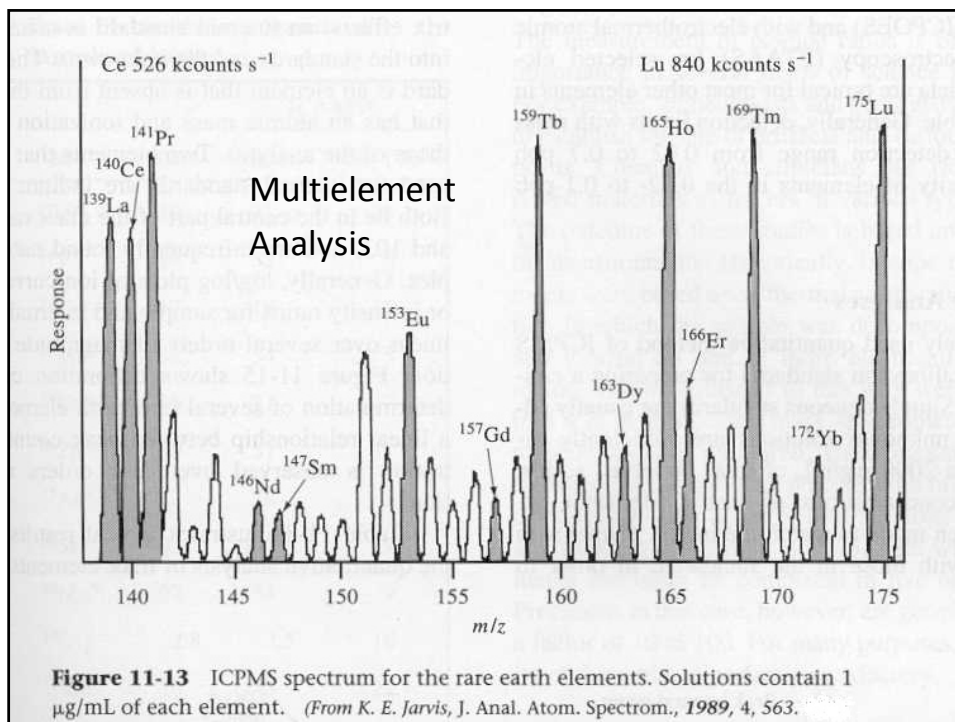ICP Mass Spectrum of rock sample produced
by Laser Ablation
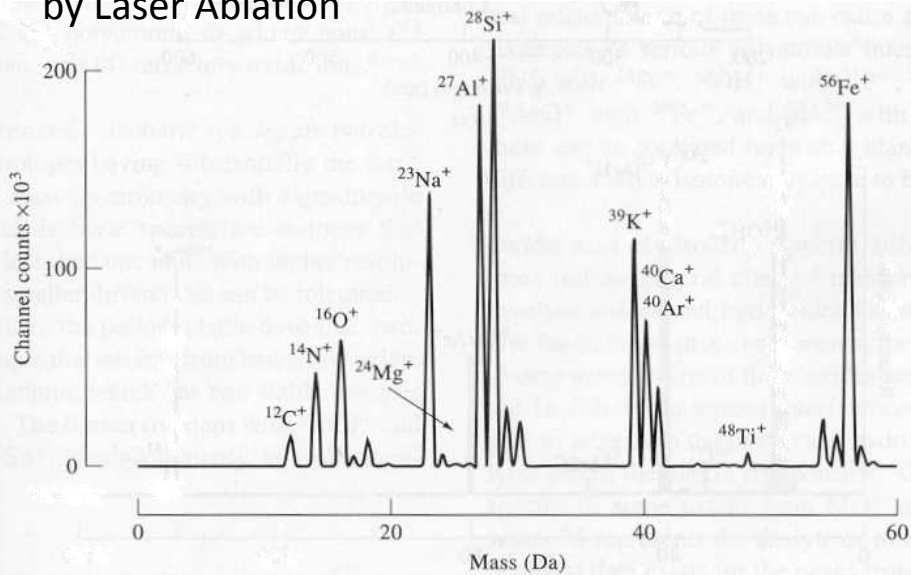
Comparison of ICP optical emission spectrum & ICP-MS spectrum for 100 ppm cerium (Ce)

Spectroscopic Interferences

1) Isobaric interferences – element isotopes with same m/z (e.g. $^{113}In^+$ & $^{115}In^+$ overlap with $^{113}Cd^+$ & $^{115}Sn^+$)

2) Polyatomic ion interferences – formed from interactions of species in plasma

3) Oxide & Hydroxide species interference – MO^+ or MOH^+ formed in plasma

4) Matrix effects – similar to optical atomic spectrometry

TABLE 11-2 Calcium Oxide and Hydroxide Species and Other Potential Interferences in the Mass Region for Ni Determination

m/z	Element	Interferences
56	Fe(91.66)	^{40}ArO, ^{40}CaO
57	Fe(2.19)	$^{40}ArOH$, $^{40}CaOH$
58	Ni(67.77), Fe(0.33)	^{42}CaO, NaCl
59	Co(100)	^{43}CaO, $^{42}CaOH$
60	Ni(26.16)	$^{43}CaOH$, ^{44}CaO
61	Ni(1.25)	$^{44}CaOH$
62	Ni(3.66)	^{46}CaO, Na_2O, NaK
63	Cu(69.1)	$^{46}CaOH$, $^{40}ArNa$
64	Ni(1.16), Zn(48.89)	$^{32}SO_2$, $^{32}S_2$, ^{48}CaO
65	Cu(30.9)	$^{33}S^{32}S$, $^{33}SO_2$, $^{48}CaOH$

Multielement Analysis

Figure 11-13 ICPMS spectrum for the rare earth elements. Solutions contain 1 µg/mL of each element. *(From K. E. Jarvis, J. Anal. Atom. Spectrom., 1989, 4, 563.*

Figure 11-14 Detection limits for selected elements by ICPMS (black bars) compared with those for ICP OES (cross-hatched bars) and ETAAS (gray bars) (inductively coupled plasma optical emission spectrometry and electrothermal atomic absorption spectrometry, respectively), plotted on a logarithmic scale in concentrations of ppb (or µg/L). Because ETAAS detection limits are inherently in mass units (pg), they have been converted to concentration by assuming a 20 µL sample. *(From M. Selby and G. M. Hieftje, Amer. Lab., 1987 (8), 20. With permission.)*

Figure 11-15 ICPMS calibration curves for several rare earth elements.

Good linearity

TABLE 11-3 Quantitative Determination of Trace Elements in a Standard Sample of Water

Element	Ion	NBS[a]	ICP-MS[a] Mean	ICP-MS[a] RSD (%)[b]
Beryllium	$^9Be^+$	19	21	20
Vanadium	$^{51}V^+$	54	52	6
Chromium	$^{52}Cr^+$	17	18	12
Manganese	$^{55}Mn^+$	32	34	5
Cobalt	$^{59}Co^+$	19	21	7
Zinc	$^{66}Zn^+$	69	57	11
Arsenic	$^{75}As^+$	77	76	5
Strontium	$^{88}Sr^+$	243	297	7
Molybdenum	$^{98}Mo^+$	97	134	9
Silver	$^{107}Ag^+$	2.8	3.5	16
Cadmium	$^{114}Cd^+$	10	13	22
Barium	$^{138}Ba^+$	47	74	17
Lead	$^{208}Pb^+$	27	31	8

[a]Concentration in parts per billion.
[b]Based on 10 determinations.

Isotope Ratio Measurements – ICP-MS makes measurement of isotope ratios for a sample become relatively easy in many cases. This is a powerful technique that can identify elements from different sources, allow use of tracers, etc.