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CEE 772: Instrumental Methods in Environmental Analysis

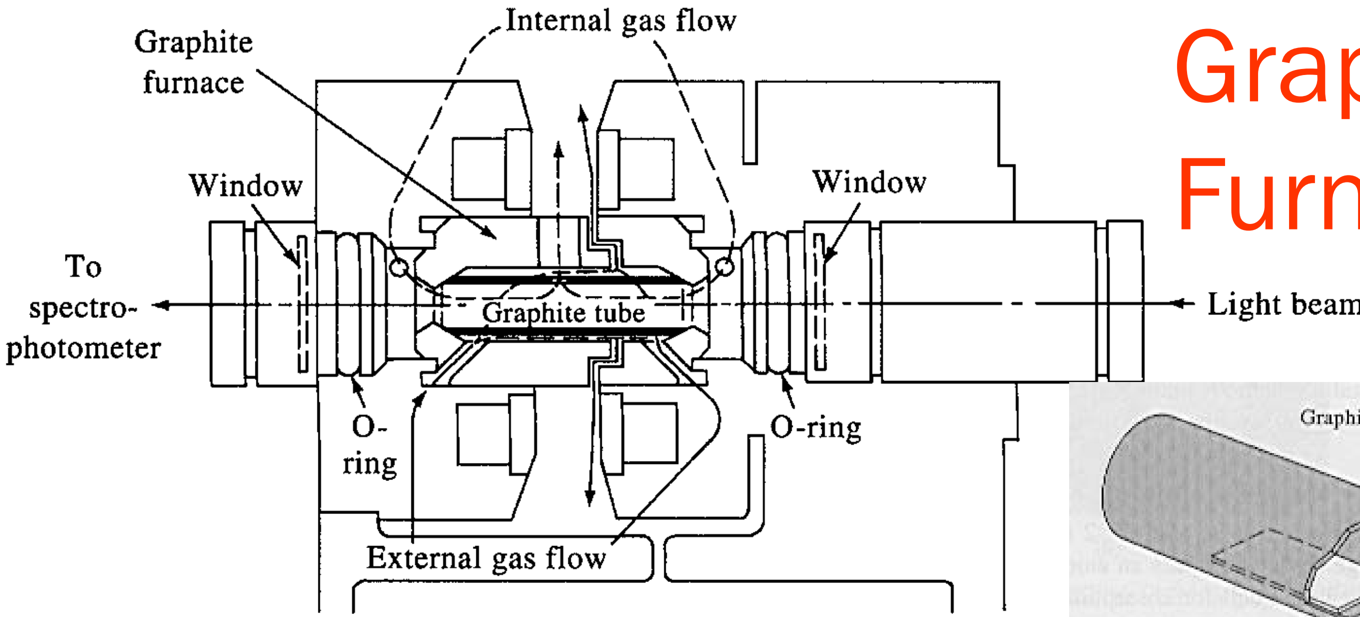
Lecture #7

Atomic Spectroscopy: Sample Treatment and Methodology

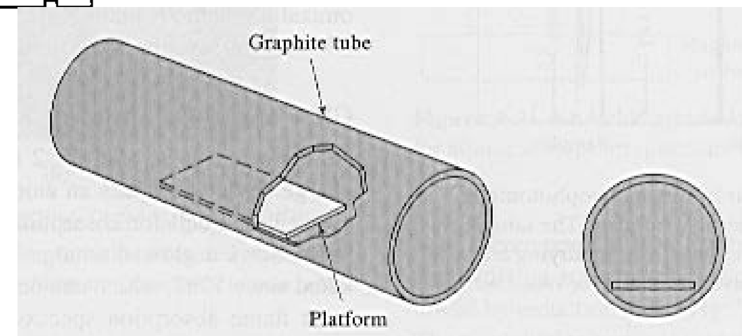
(Skoog, Chapts. 8 & 9; pp.192-203, 206-227)

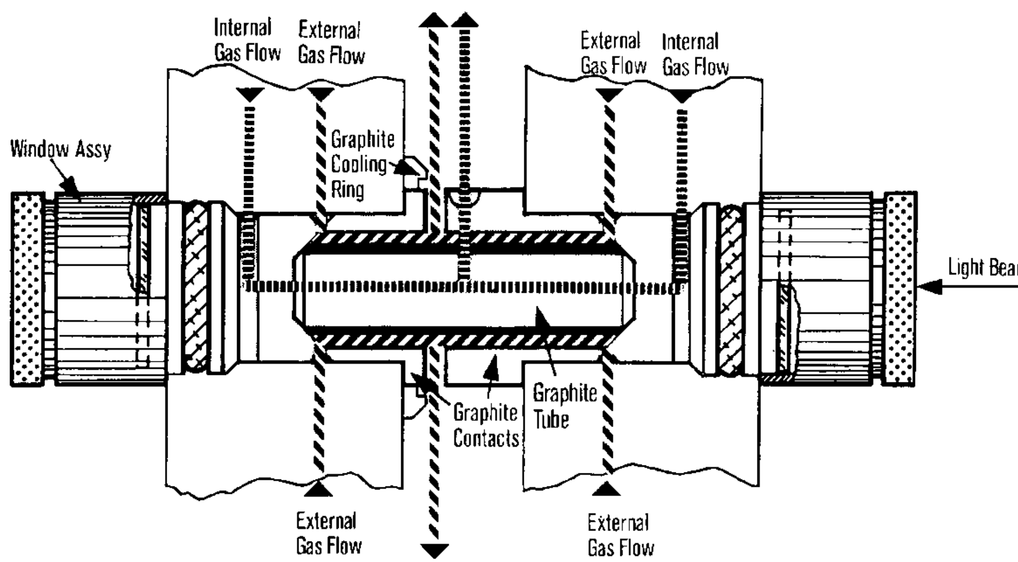
(Harris, Chapt. 22)
(pp.615-635)

Graphite Furnace

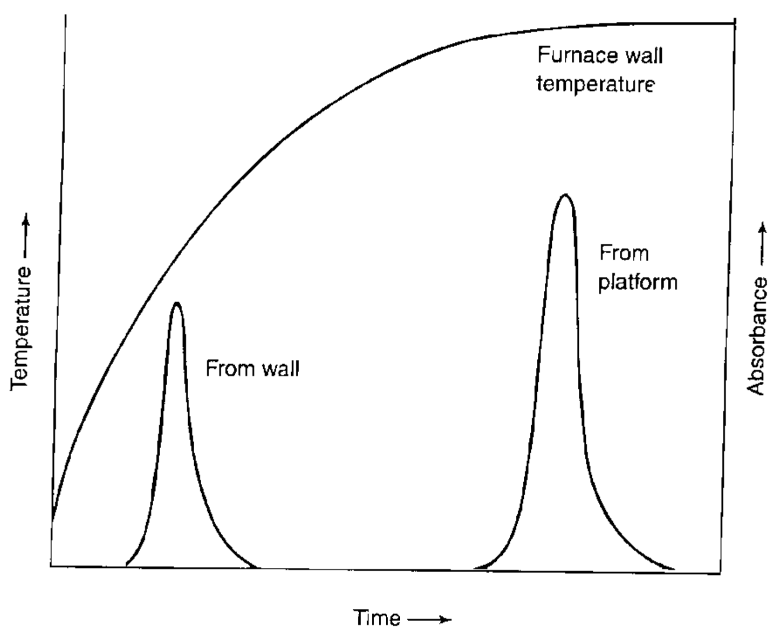


(a)

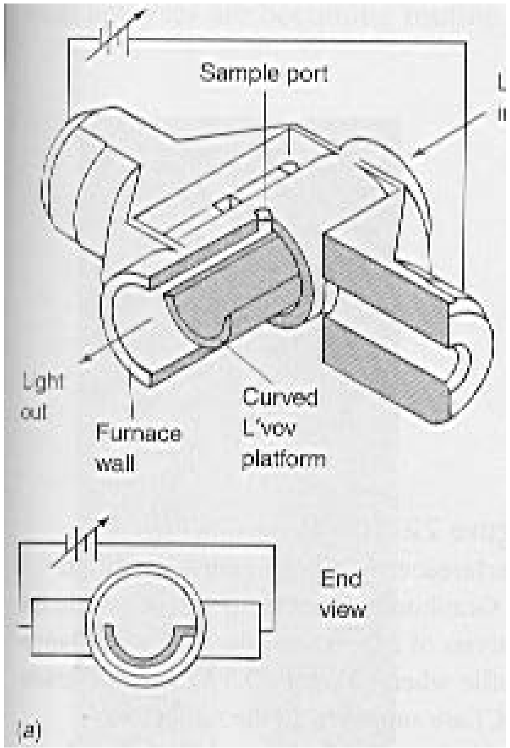




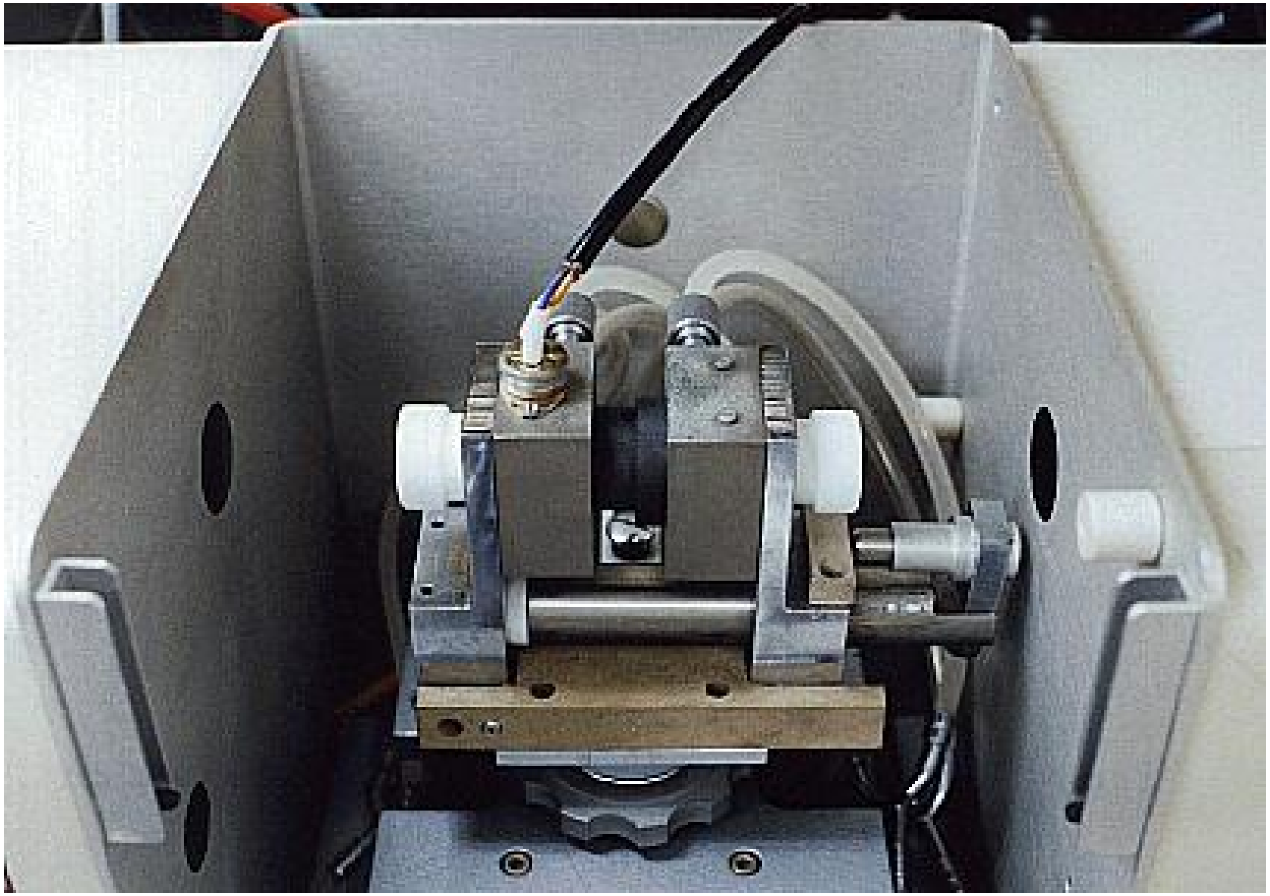
Platform position



(*b*)

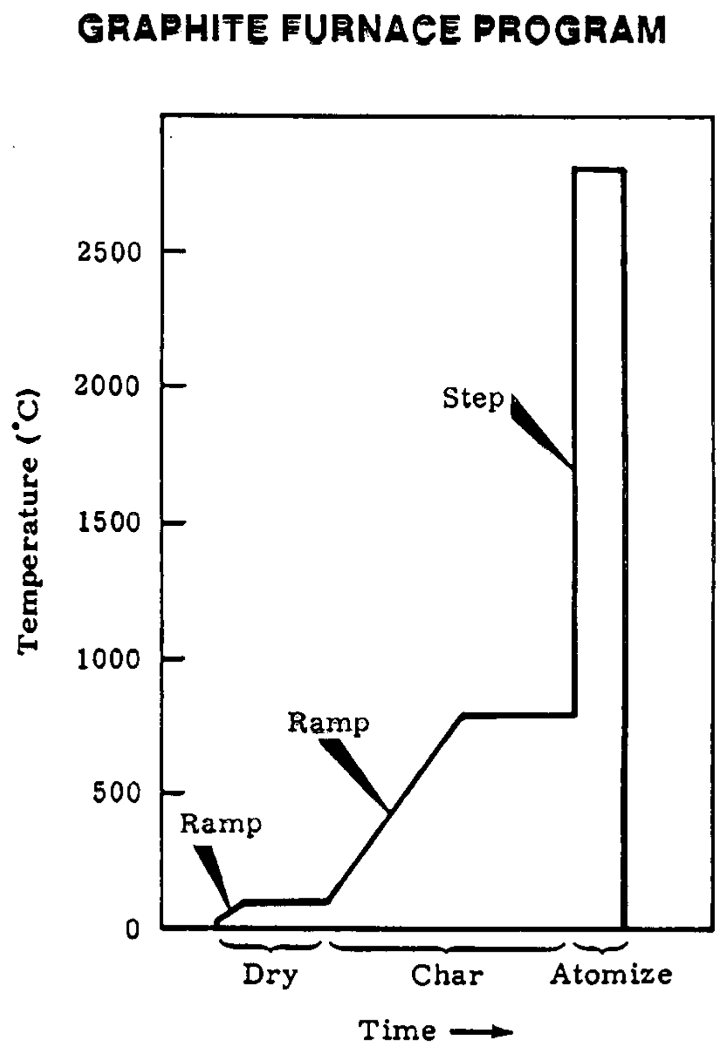


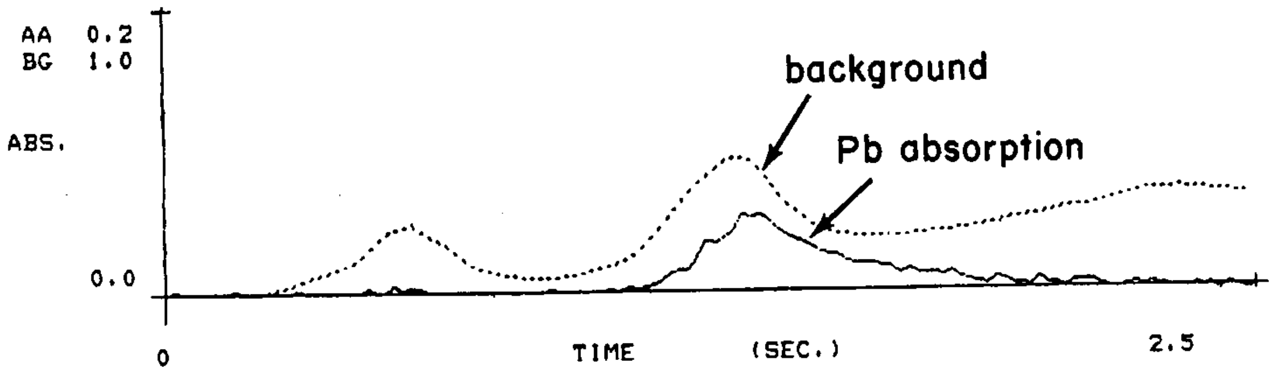
Graphite Furnace

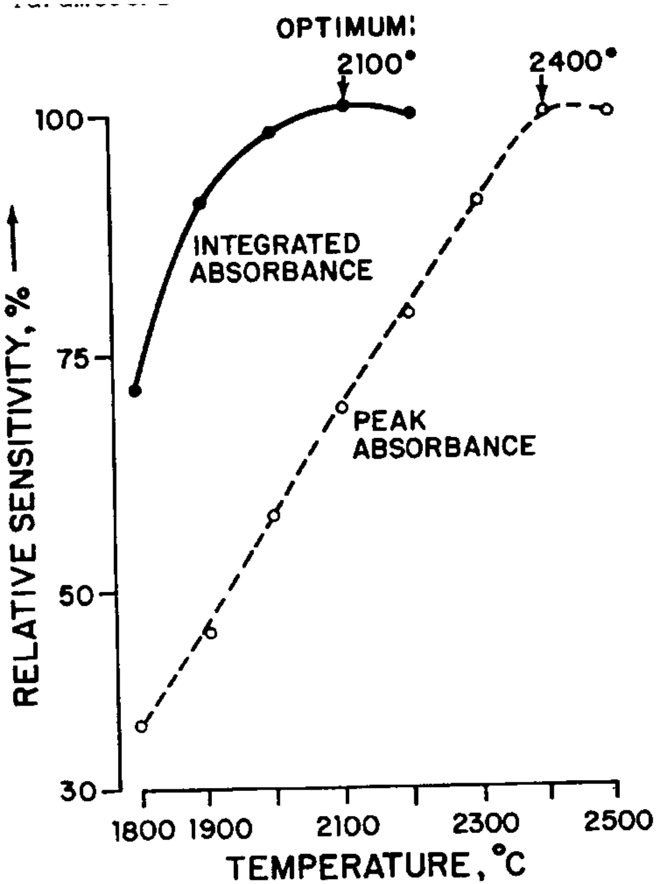


Temperature Programming

- Dry
  - Remove solvent
- Char
  - Remove organic matter and other volatiles
- Atomize
  - Convert analyte to an atom vapor

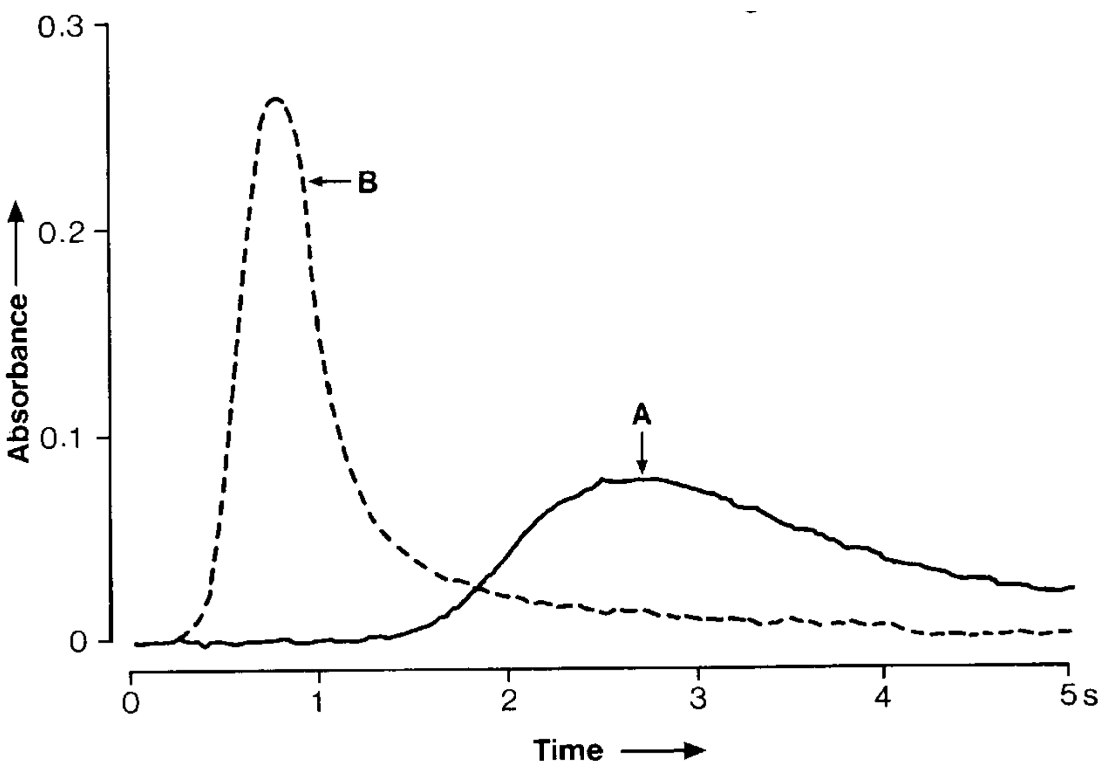



AA 0.2
BG 1.0
ABS.
0.0
background
Pb absorption
0
TIME (SEC.)
2.5


OPTIMUM:
2100°
2400°
100
75
50
30
RELATIVE SENSITIVITY, %
INTEGRATED ABSORBANCE
PEAK ABSORBANCE
1800 1900 2100 2300 2500
TEMPERATURE, °C

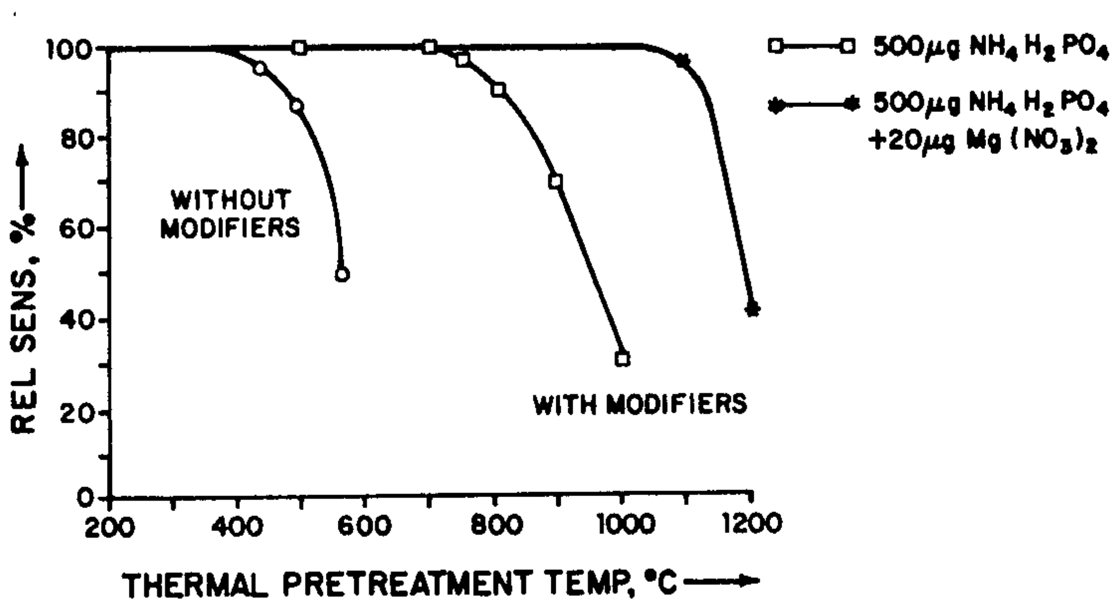
Signals

- Analysis of Molybdenum
  - A: uncoated tube
  - B: pyro-coated tube



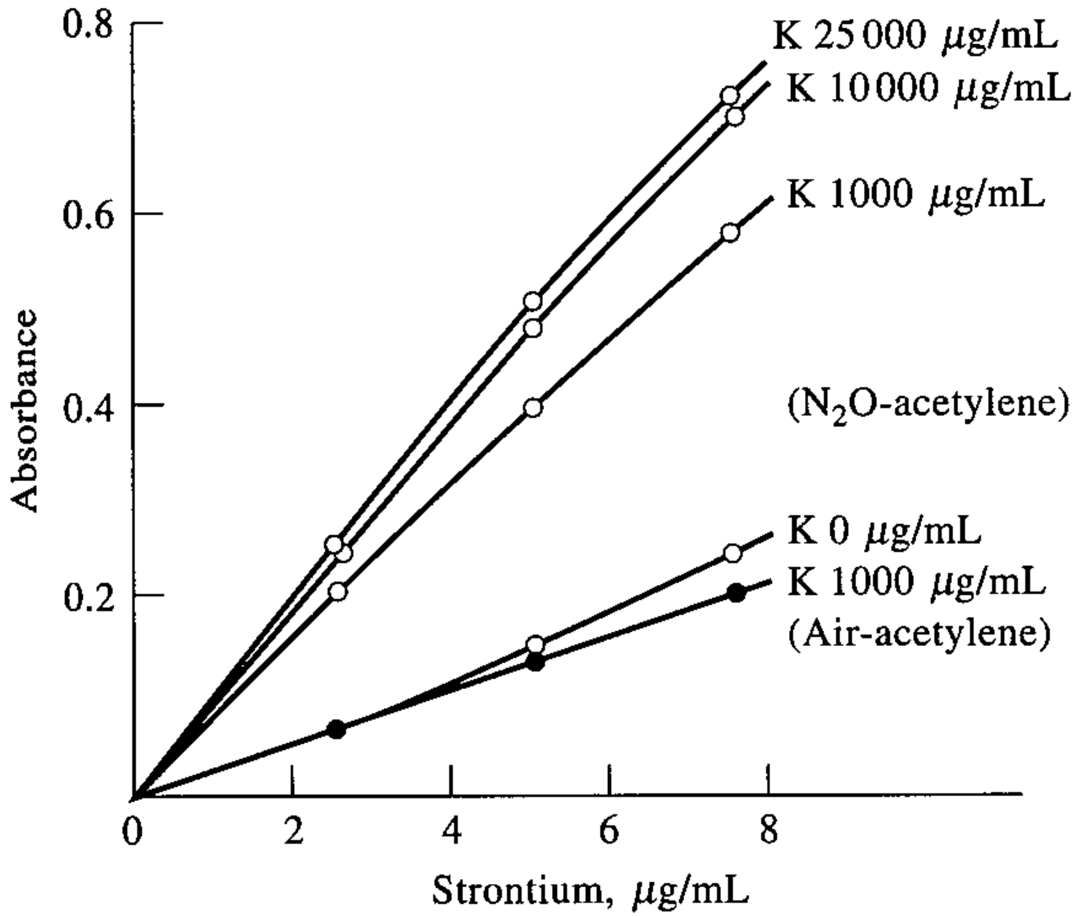
Use of Matrix Modifiers

- Thermal pretreatment for Cd using different matrix modifiers

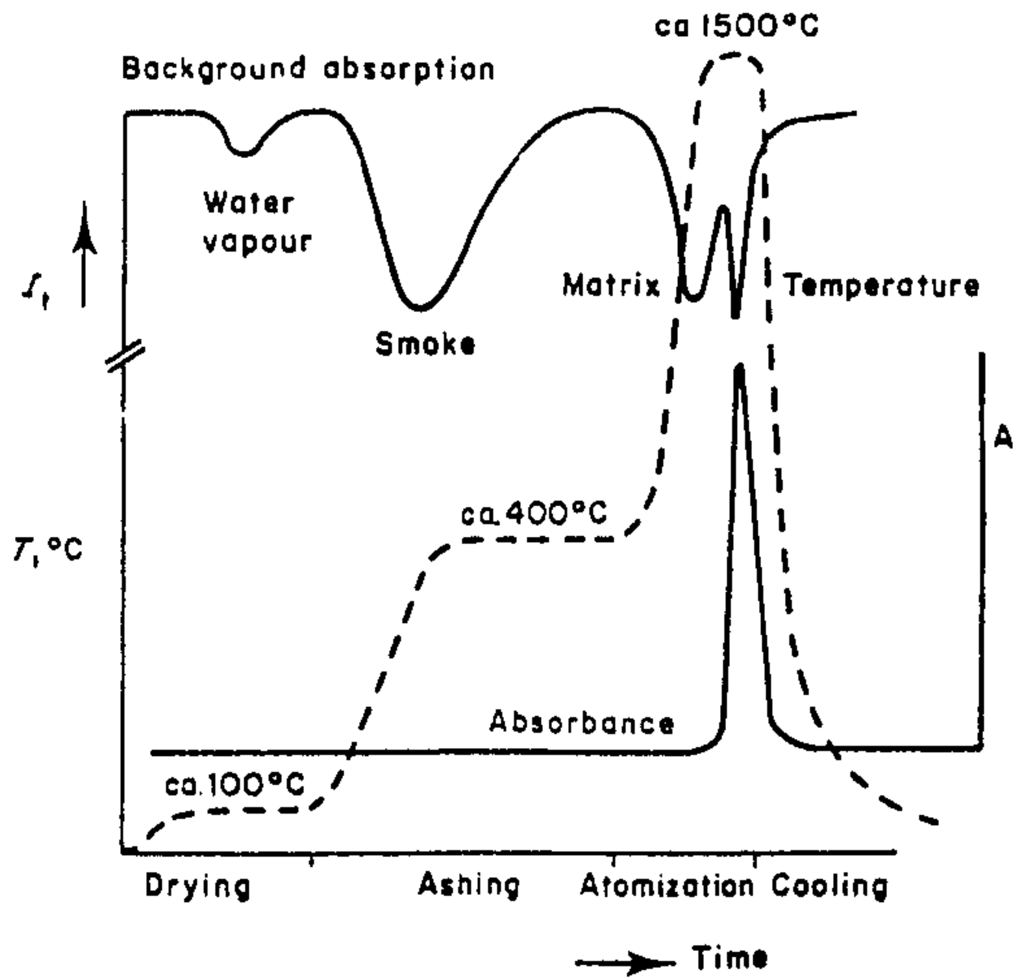


Matrix Modifiers, cont.

- Impact of K on calibration curve for Sr

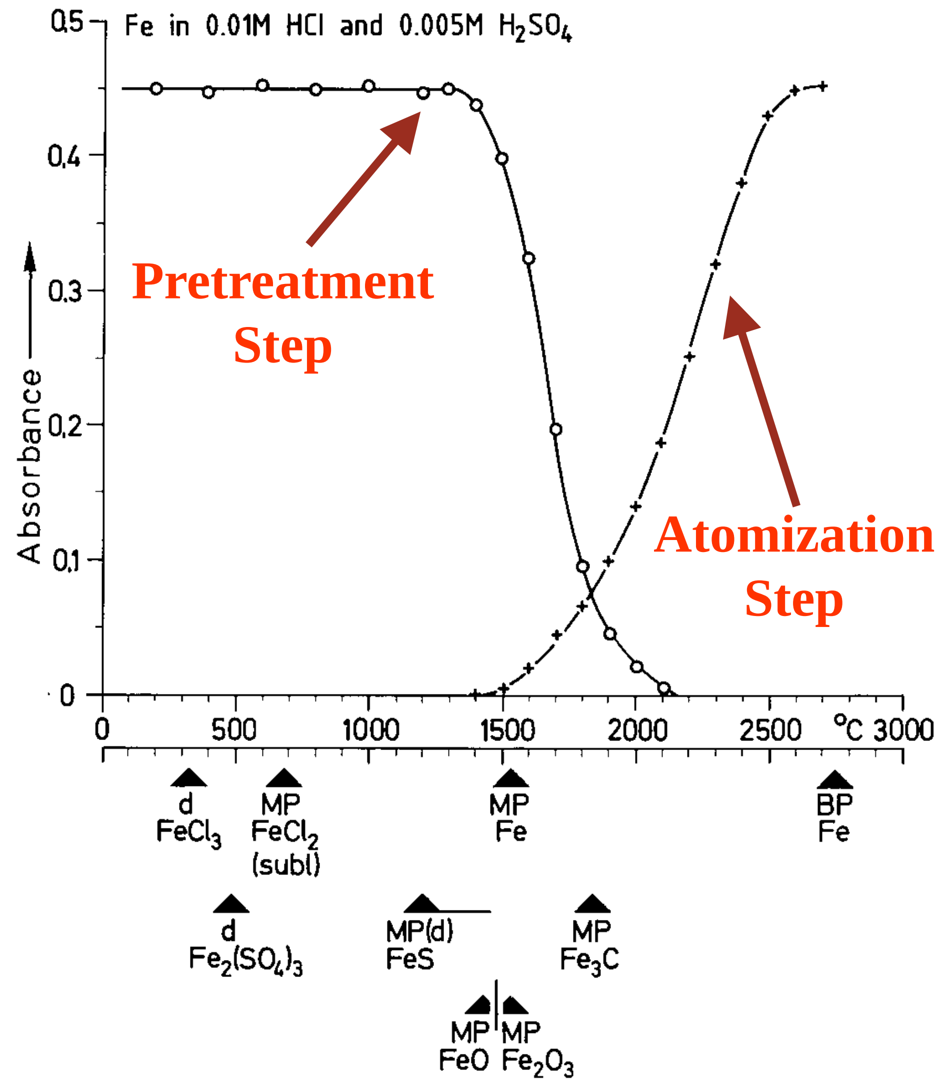


Thermal Progression



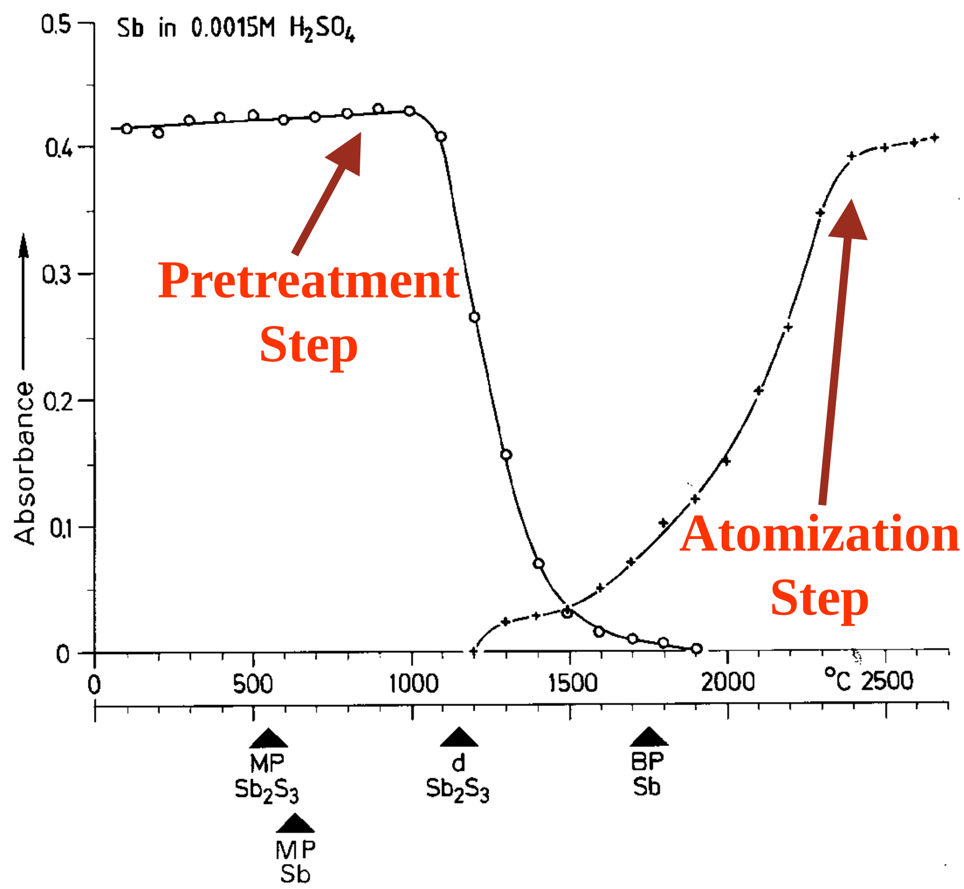
Pretreatment/Atomization 1

- Case for Iron
  - Pretreatment
    - First losses just below melting point
  - Atomization
    - Probably directly from metal as many salts decompose at lower temps



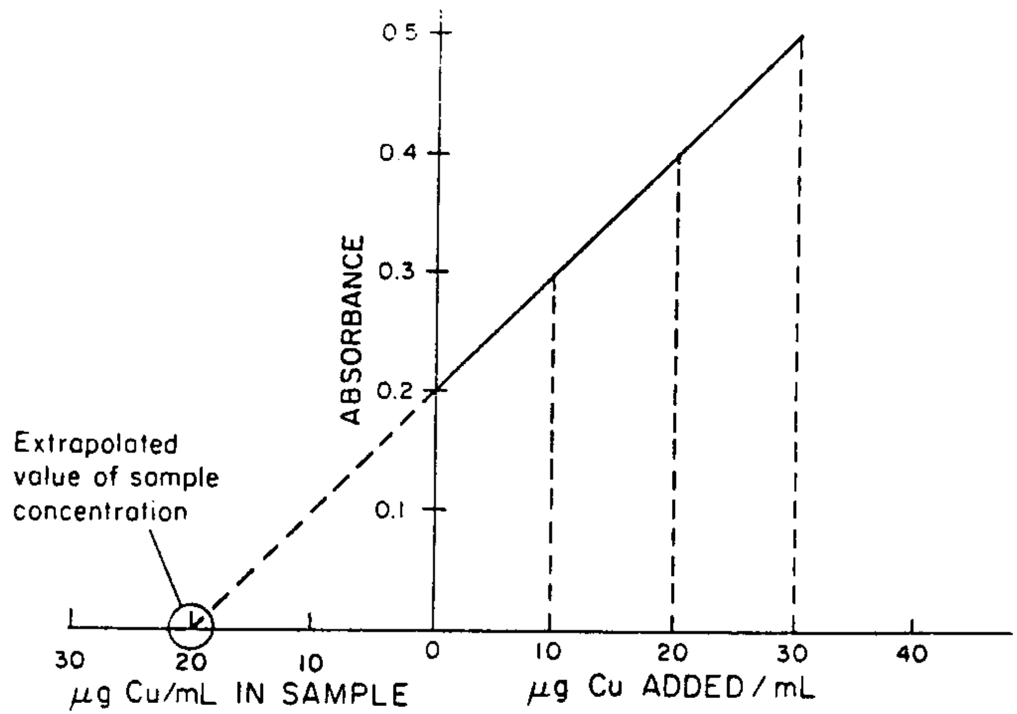
Pretreatment/Atomization 2

- Case for Antimony
  - Pretreatment
    - First losses just below melting point
  - Atomization
    - Probably delayed due to high temp of salt decomposition

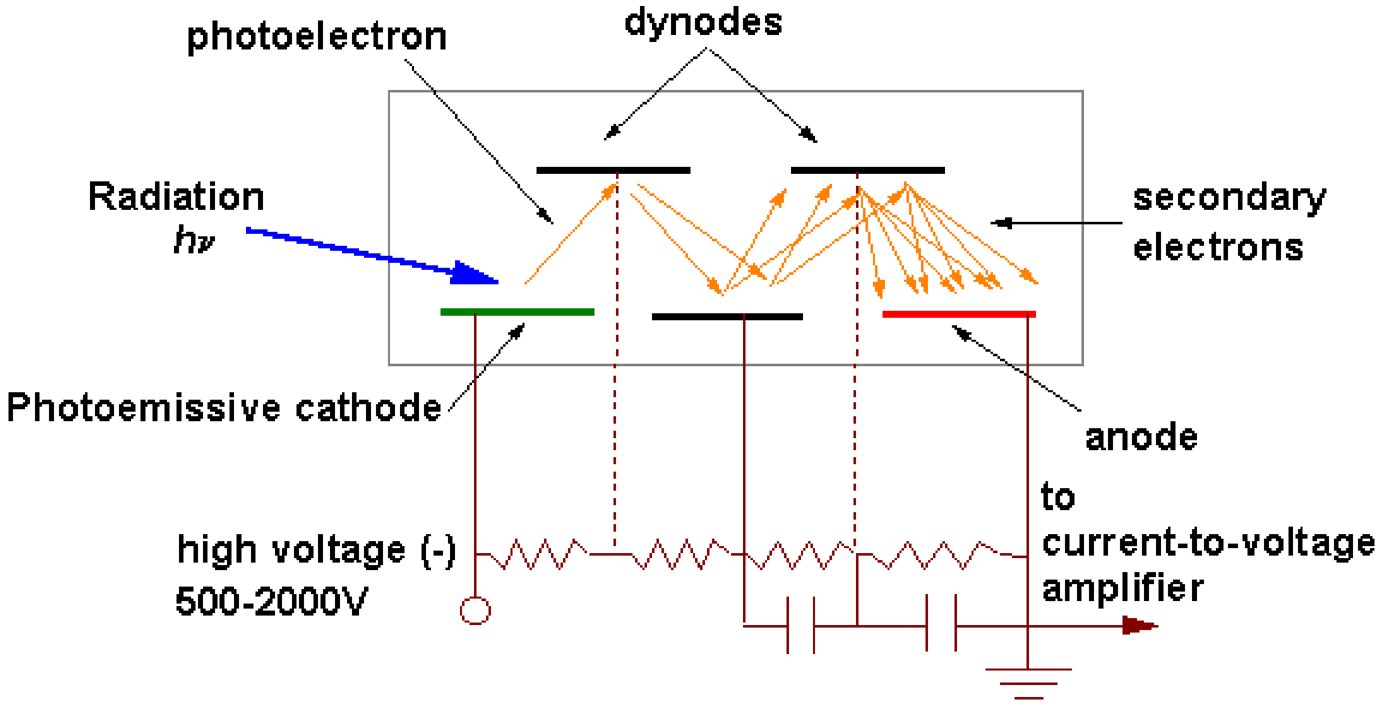


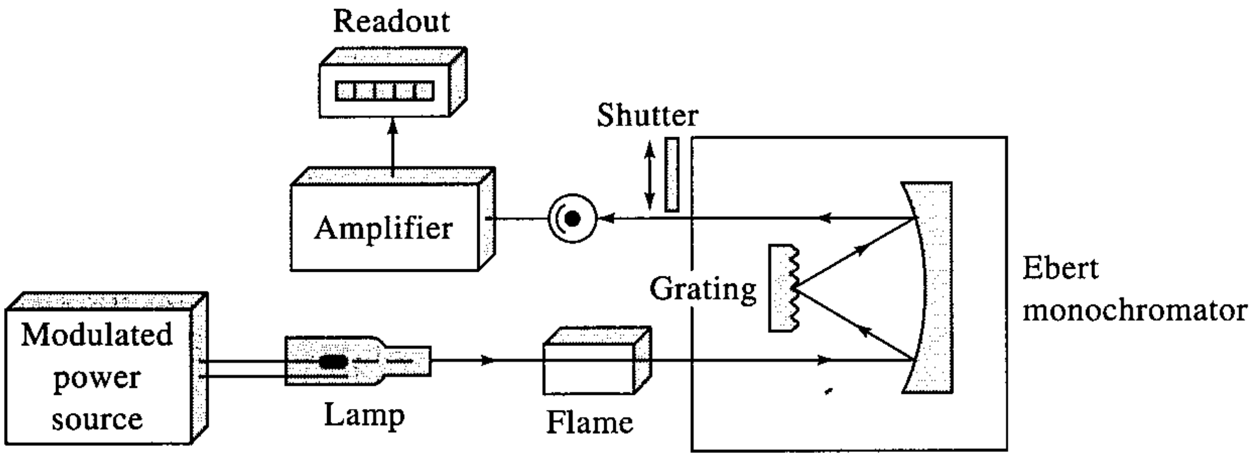
Standard Addition

- Use of standard addition to compensate for matrix effects

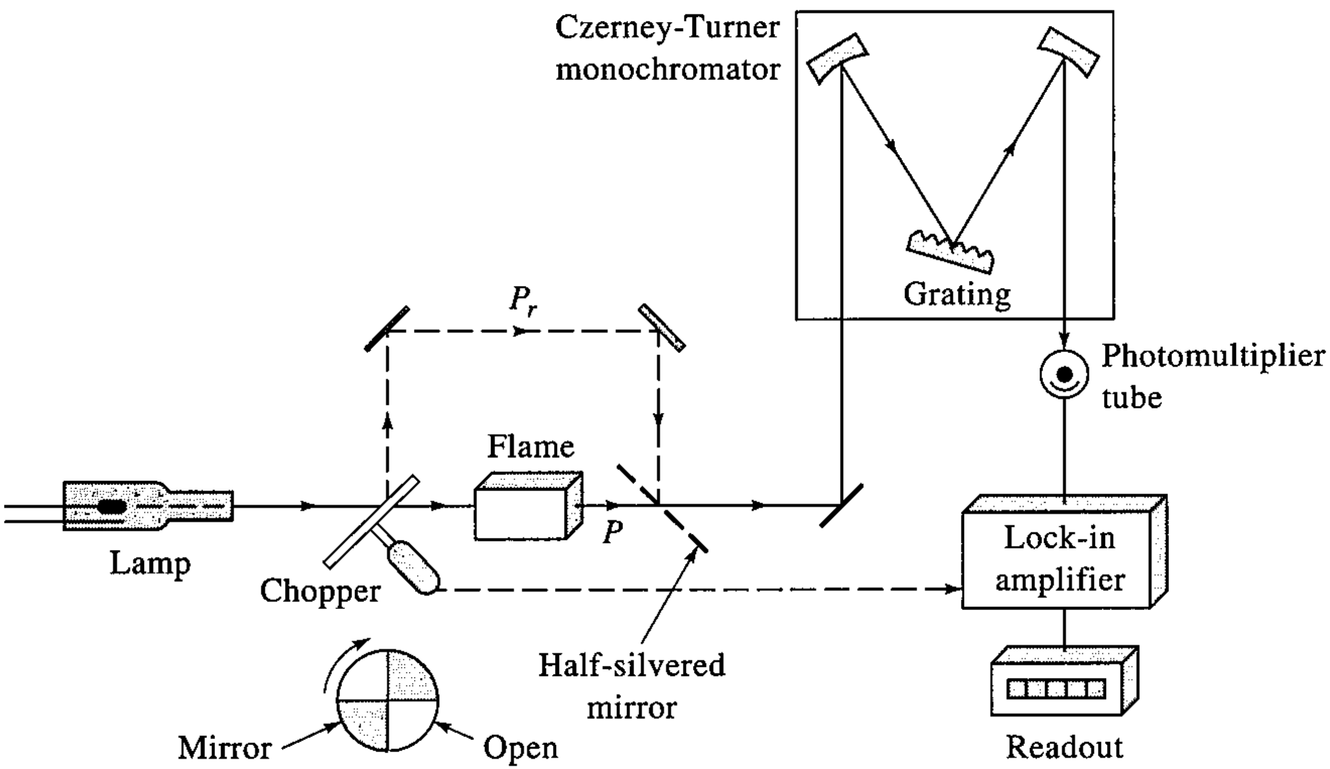


Photomultiplier




Readout
Shutter
Amplifier
Grating
Ebert
monochromator
Modulated
power
source
Lamp
Flame

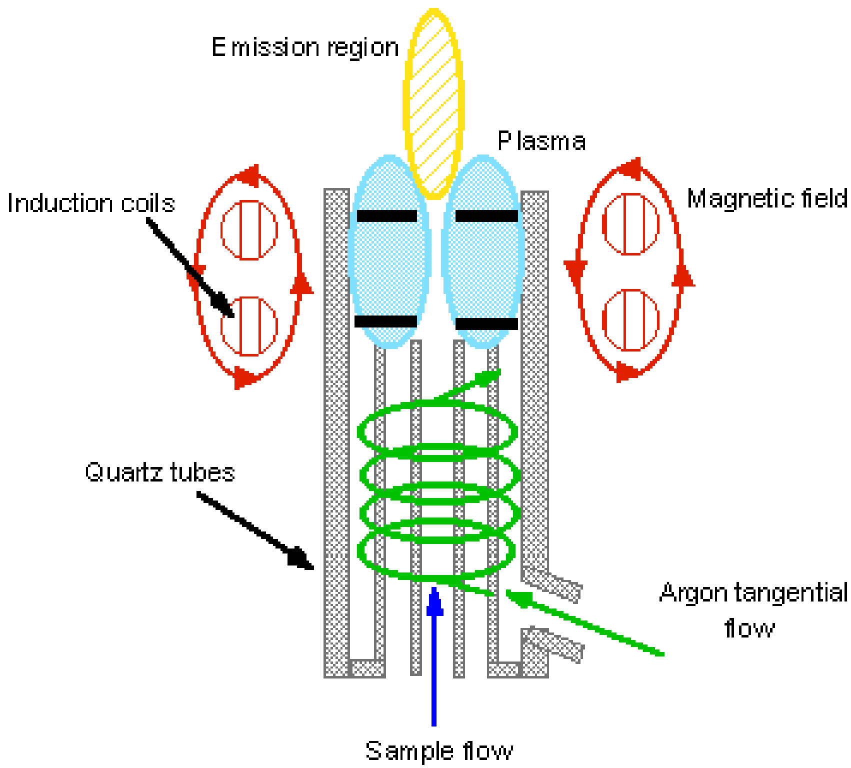
(a)

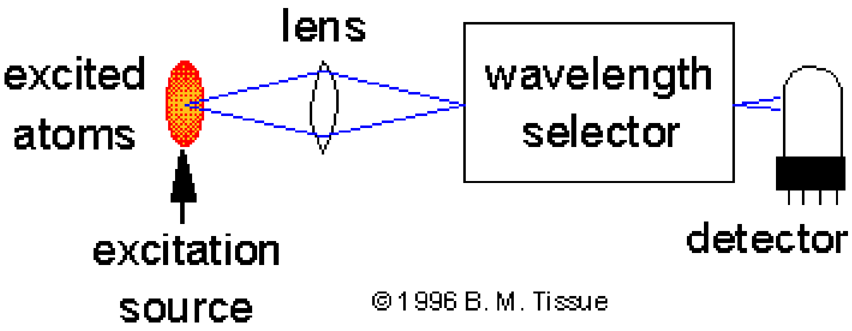

Czerney-Turner
monochromator
Grating
P_r
Photomultiplier
tube
Flame
Lamp
Chopper
P
Lock-in
amplifier
Half-silvered
mirror
Mirror
Open
Readout

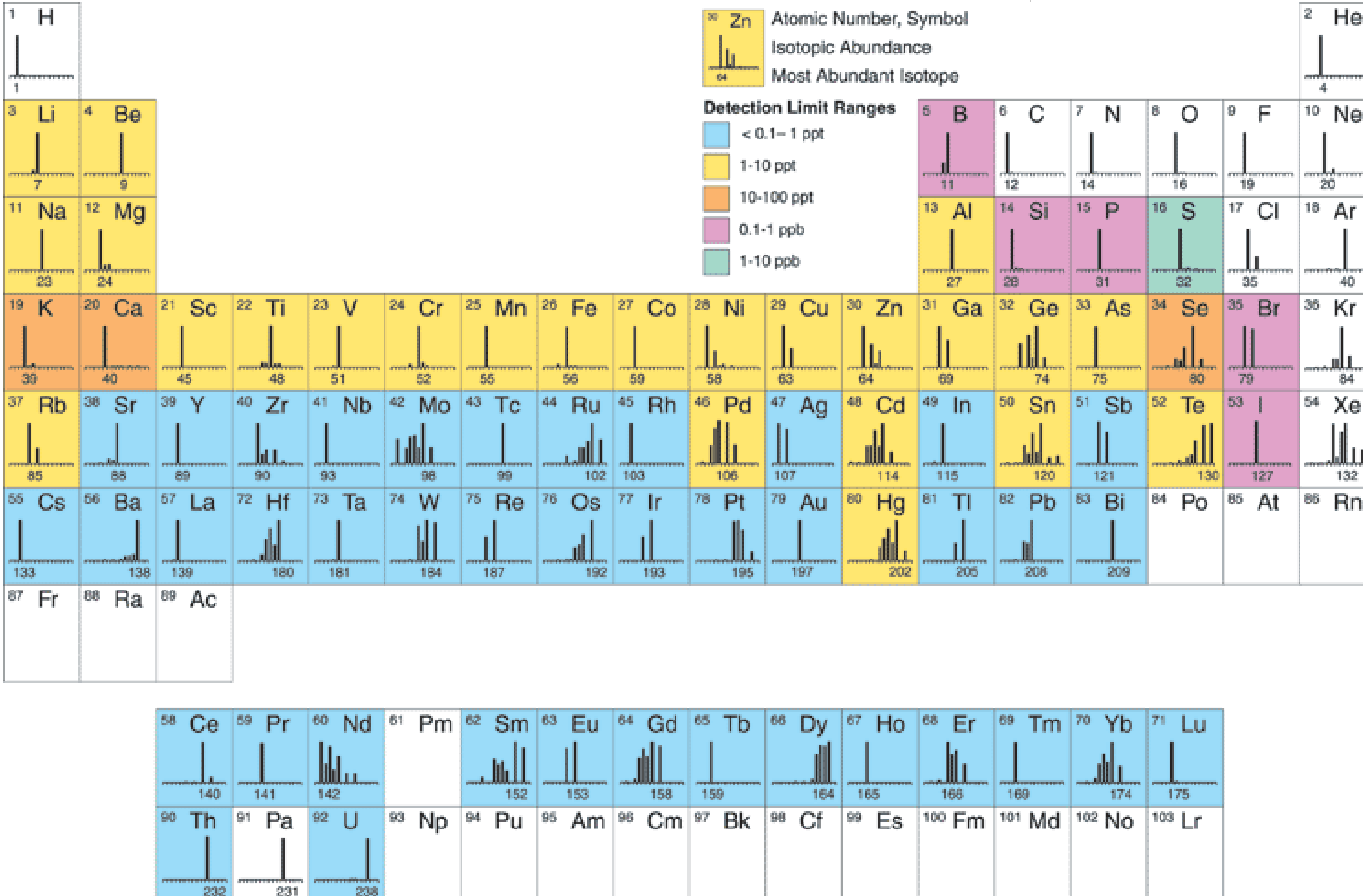
(b)

Plasma source

- The sample is nebulized and entrained in the flow of plasma support gas, which is typically Ar. The plasma torch consists of concentric quartz tubes, with the inner tube containing the sample aerosol and Ar support gas and the outer tube containing an Ar gas flow to cool the tubes (see schematic). A radiofrequency (RF) generator (typically 1-5 kW @ 27 MHz or 41 MHz) produces an oscillating current in an induction coil that wraps around the tubes. The induction coil creates an oscillating magnetic field, which produces an oscillating magnetic field. The magnetic field in turn sets up an oscillating current in the ions and electrons of the support gas. These ions and electrons transfer energy to other atoms in the support gas by collisions to create a very high temperature plasma.




lens
excited
atoms
wavelength
selector
excitation
source
detector
© 1996 B. M. Tissue


30 Zn 64
Atomic Number, Symbol
Isotopic Abundance
Most Abundant Isotope
Detection Limit Ranges
< 0.1– 1 ppt
1-10 ppt
10-100 ppt
0.1-1 ppb
1-10 ppb
1 H 1
2 He 4
3 Li 7
4 Be 9
5 B 11
6 C 12
7 N 14
8 O 16
9 F 19
10 Ne 20
11 Na 23
12 Mg 24
13 Al 27
14 Si 28
15 P 31
16 S 32
17 Cl 35
18 Ar 40
19 K 39
20 Ca 40
21 Sc 45
22 Ti 48
23 V 51
24 Cr 52
25 Mn 55
26 Fe 56
27 Co 59
28 Ni 58
29 Cu 63
30 Zn 64
31 Ga 69
32 Ge 74
33 As 75
34 Se 80
35 Br 79
36 Kr 84
37 Rb 85
38 Sr 88
39 Y 89
40 Zr 90
41 Nb 93
42 Mo 98
43 Tc 99
44 Ru 102
45 Rh 103
46 Pd 106
47 Ag 107
48 Cd 114
49 In 115
50 Sn 120
51 Sb 121
52 Te 130
53 I 127
54 Xe 132
55 Cs 133
56 Ba 138
57 La 139
72 Hf 180
73 Ta 181
74 W 184
75 Re 187
76 Os 192
77 Ir 193
78 Pt 195
79 Au 197
80 Hg 202
81 Tl 205
82 Pb 208
83 Bi 209
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 Ac
58 Ce 140
59 Pr 141
60 Nd 142
61 Pm
62 Sm 152
63 Eu 153
64 Gd 158
65 Tb 159
66 Dy 164
67 Ho 165
68 Er 166
69 Tm 169
70 Yb 174
71 Lu 175
90 Th 232
91 Pa 231
92 U 238
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr

Detection limits (ng/mL)

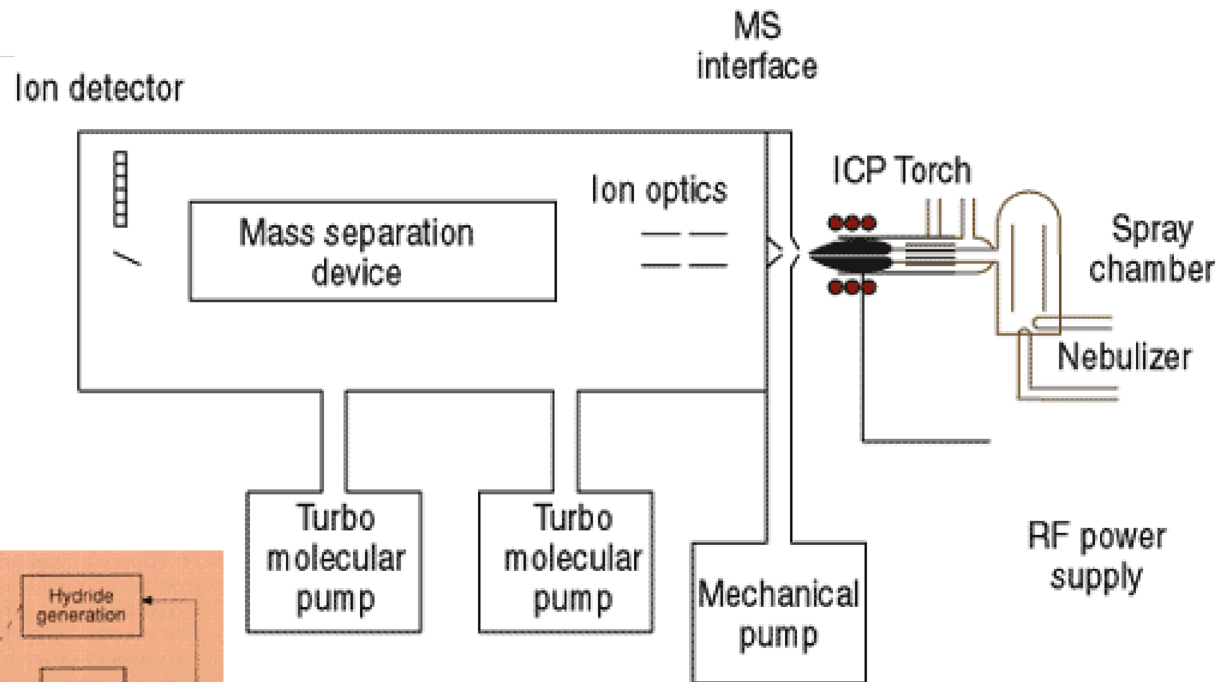
Fe
0.7 — Inductively coupled plasma emission
5 — Flame atomic absorption
0.02 — Graphite furnace atomic absorption

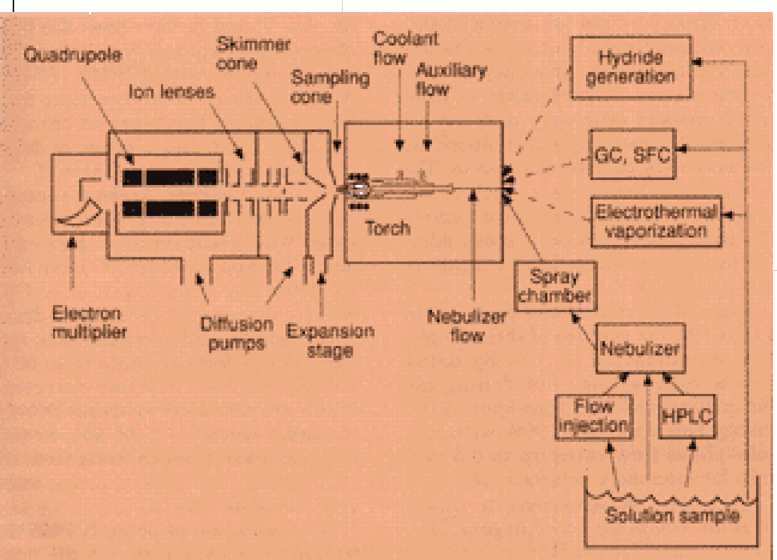
Li 0.7 2 0.1	**Be** 0.07 1 0.02											**B** 1 500 15	**C** 10 — —	**N**	**O**	**F**	**Ne**
Na 3 0.2 0.005	**Mg** 0.08 0.3 0.004											**Al** 2 30 0.01	**Si** 5 100 0.1	**P** 7 40,000 30	**S** 3 — —	**Cl**	**Ar**
K 20 3 0.1	**Ca** 0.07 0.5 0.01	**Sc** 0.3 40 —	**Ti** 0.4 70 0.5	**V** 0.7 50 0.2	**Cr** 2 3 0.01	**Mn** 0.2 2 0.01	**Fe** 0.7 5 0.02	**Co** 1 4 0.02	**Ni** 3 90 0.1	**Cu** 0.9 1 0.02	**Zn** 0.6 0.5 0.001	**Ga** 10 60 0.5	**Ge** 20 200 —	**As** 7 200 0.2	**Se** 10 250 0.5	**Br**	**Kr**
Rb 1 7 0.05	**Sr** 0.2 2 0.1	**Y** 0.6 200 —	**Zr** 2 1000 —	**Nb** 5 2000 —	**Mo** 3 20 0.02	**Tc**	**Ru** 10 60 1	**Rh** 20 4 —	**Pd** 4 10 0.3	**Ag** 0.8 2 0.005	**Cd** 0.5 0.4 0.003	**In** 20 40 1	**Sn** 9 30 0.2	**Sb** 9 40 0.15	**Te** 4 30 0.1	**I**	**Xe**
Cs 40,000 4 0.2	**Ba** 0.6 10 0.04	**La** 1 2000 —	**Hf** 4 2000 —	**Ta** 10 2000 —	**W** 8 1000 —	**Re** 3 600 —	**Os** 0.2 100 —	**Ir** 7 400 —	**Pt** 7 100 0.2	**Au** 2 10 0.1	**Hg** 7 150 2	**Tl** 10 20 0.1	**Pb** 10 10 0.05	**Bi** 7 40 0.1	**Po**	**At**	**Rn**

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

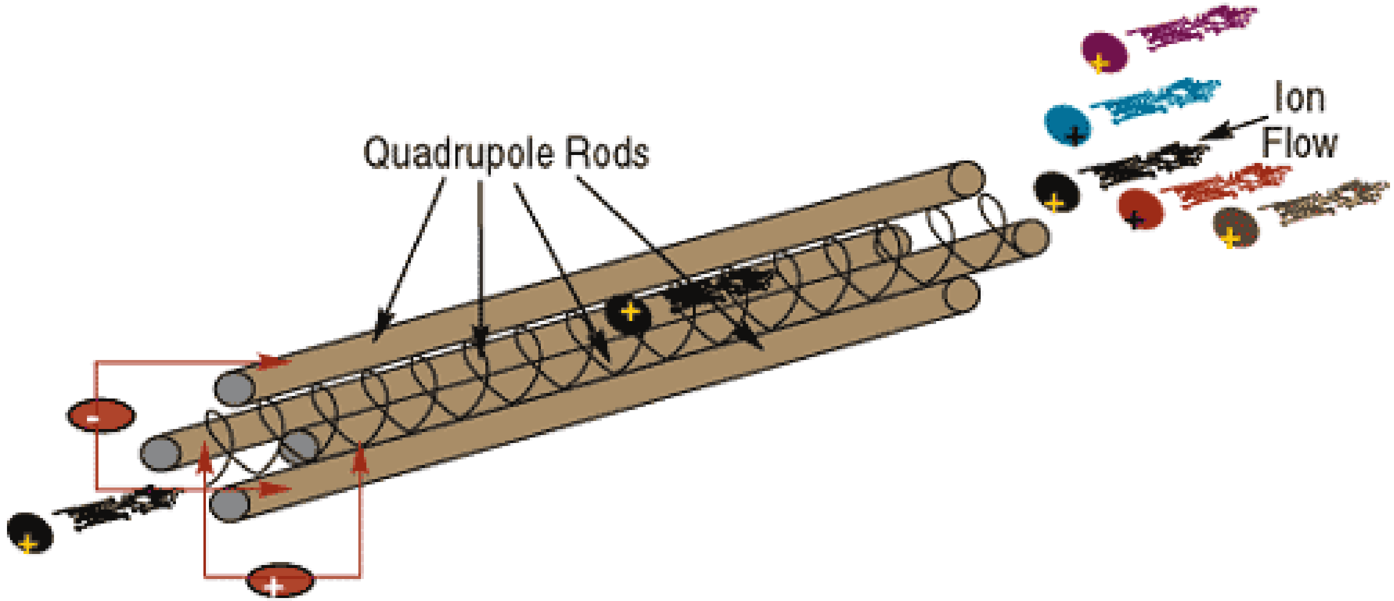
Element	Wavelength (nm)	Estimated Detection Limit (µg/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See note c
Selenium	196.026	75
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

Atomization and MS

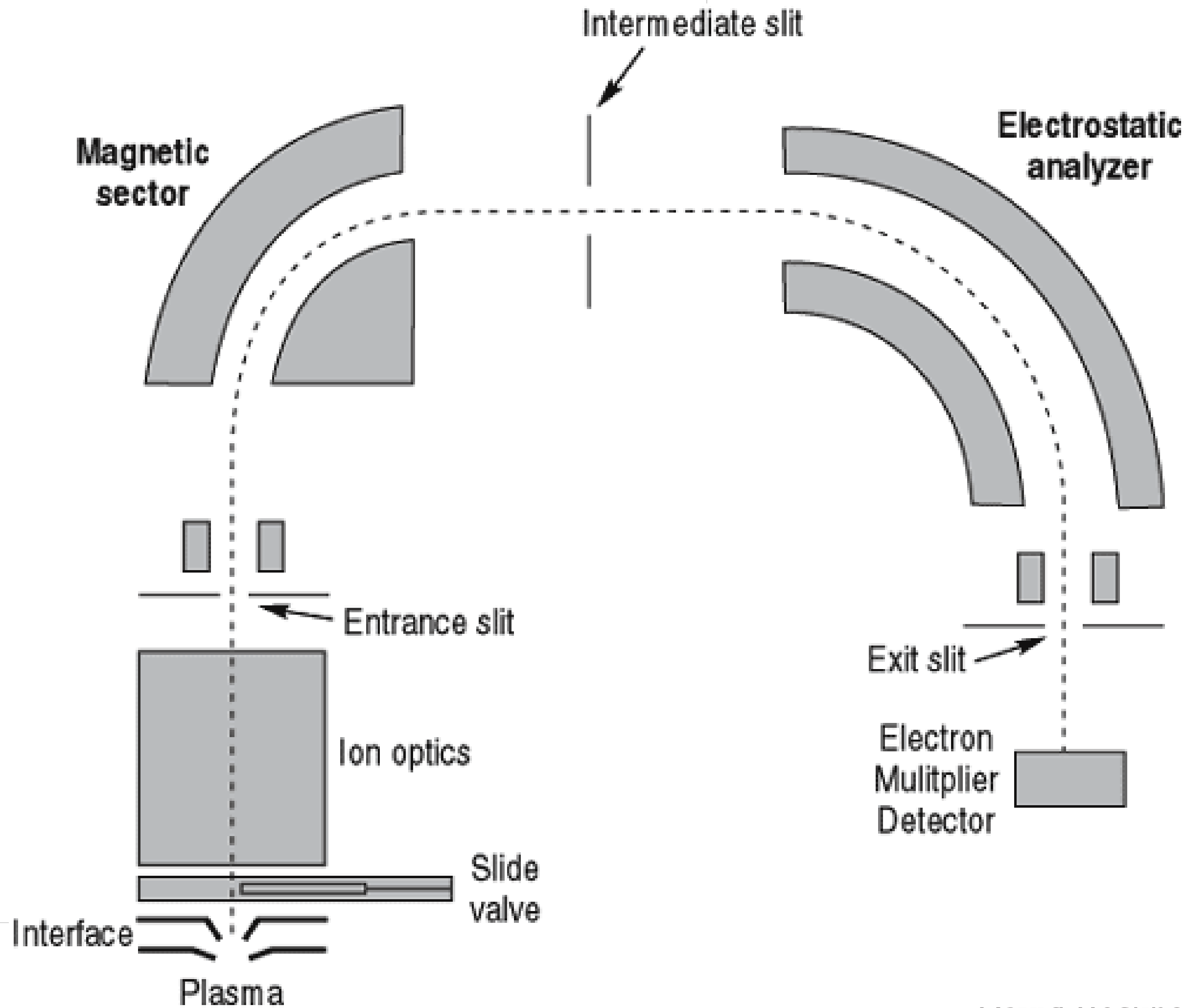




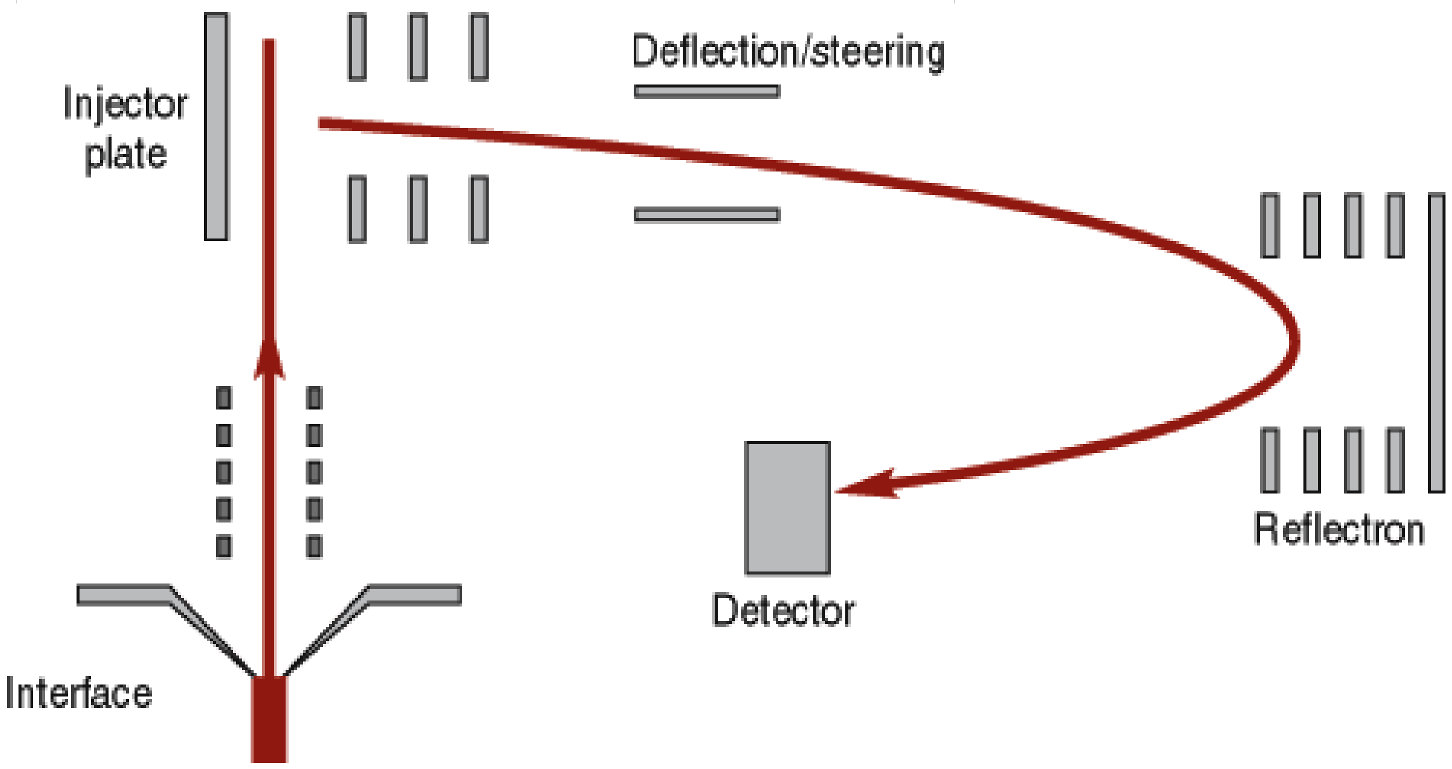
Quadrupole



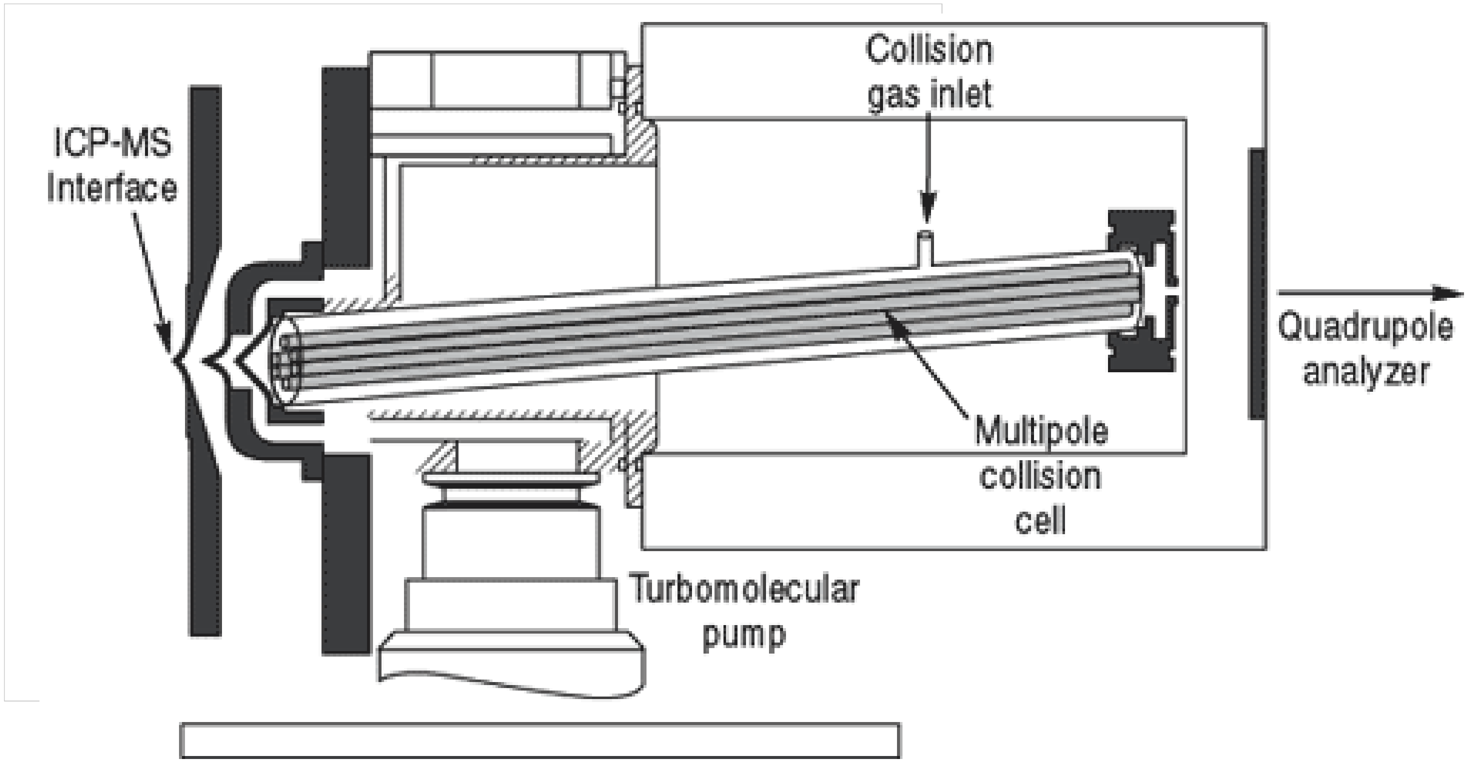
Plasma MS

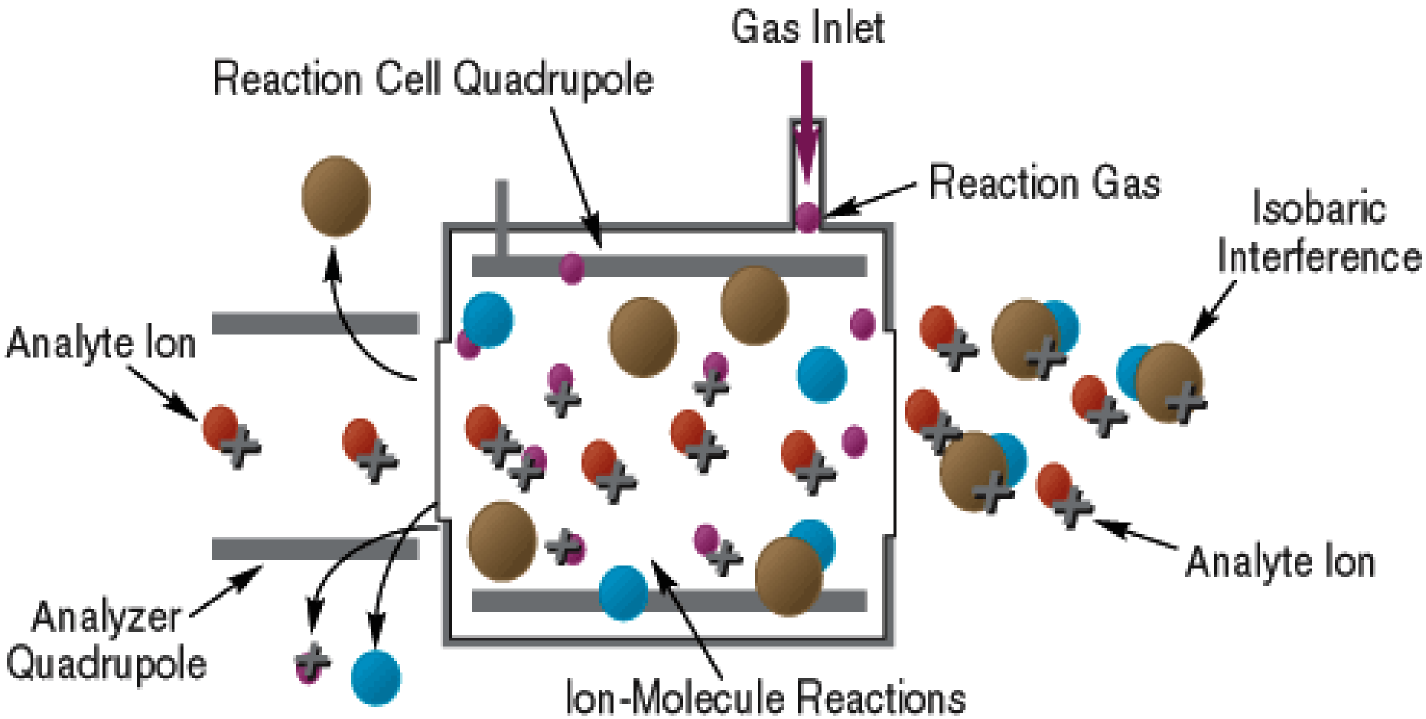


Intermediate slit
Magnetic sector
Electrostatic analyzer
Entrance slit
Exit slit
Ion optics
Electron Mulitplier Detector
Slide valve
Interface
Plasma


Injector
plate
Deflection/steering
Reflectron
Detector
Interface

ICP-MS


Collision
gas inlet
ICP-MS
Interface
Quadrupole
analyzer
Multipole
collision
cell
Turbomolecular
pump


Gas Inlet
Reaction Cell Quadrupole
Reaction Gas
Isobaric
Interference
Analyte Ion
Analyte Ion
Analyzer
Quadrupole
Ion-Molecule Reactions

- To next lecture