Atomic Emission Spectroscopy (Chapter 9/10):

Identification of elements but not compounds

Excitation and Atomization:

Traditionally based on

- flame

but

- arc and spark
- plasma

excitation offers

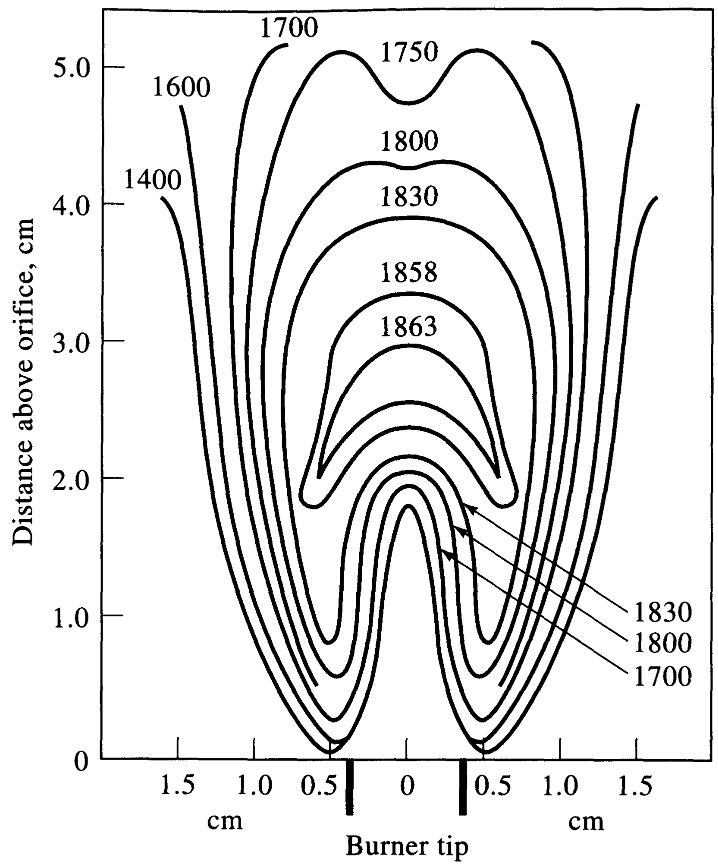
(i) increased atomization/excitation

(ii) wider range of elements

(iii) emission from multiple species simultaneously

(iv) wide dynamic range

Flame Excitation Sources:



(Fig 9-3)

Primary Combustion Zone

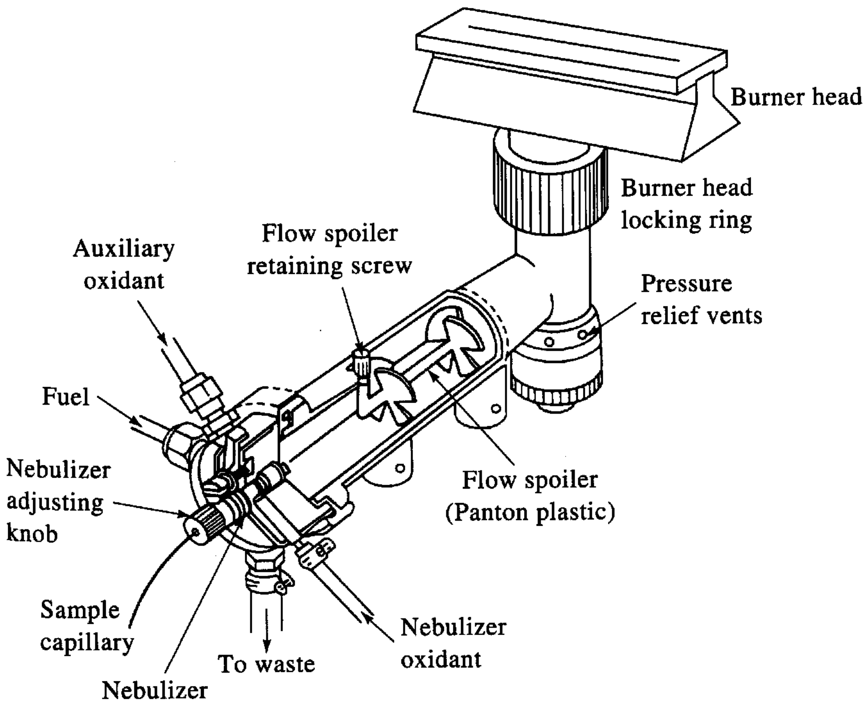
Interzonal Region

Secondary Combustion Zone

Flame Temperatures:

Fuel	Oxidant	Temperature
Gas	Air	~1800 °C
H_2	O_2	~2600 °C
Acetylene	O_2	~3000 °C

Laminar Flow Burner: (Fig 9-5)

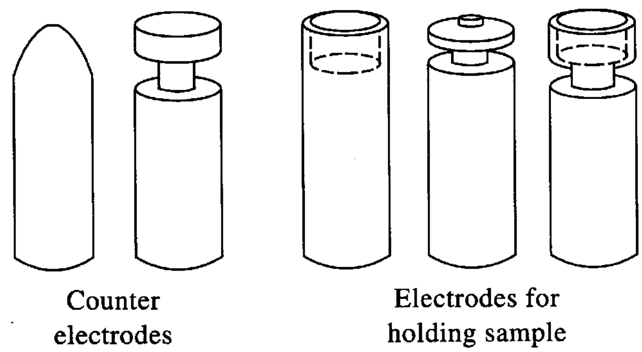


- Cheap
- Simple
- Flame stability
- Low temperature

Arc and Spark Excitation Sources:

- Limited to semiquantitative/qualitative analysis (arc flicker)
- Usually performed on solids
- Largely displaced by plasma-AES

Electric current flowing between two C electrodes (Fig 10-16)



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

Arc/spark unstable - each line measured >20 s (needs multichannel detection)

photographic film:

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

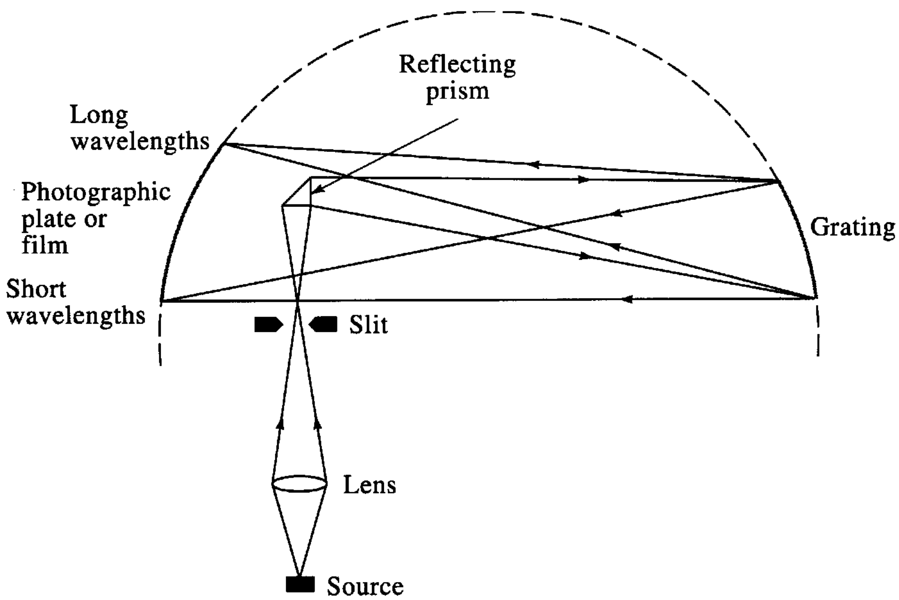


Fig 10-17

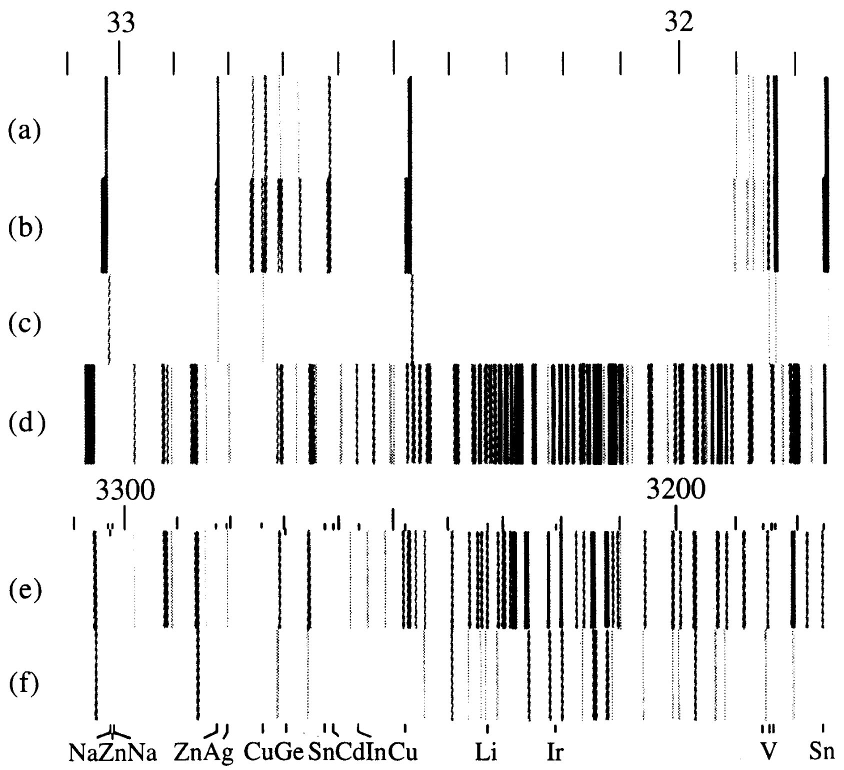


Fig 10-18

multichannel PMT instruments:

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

Plasma Excitation Sources:

gas containing high proportion of cations and electrons

(1) Inductively Coupled Plasma (ICP)

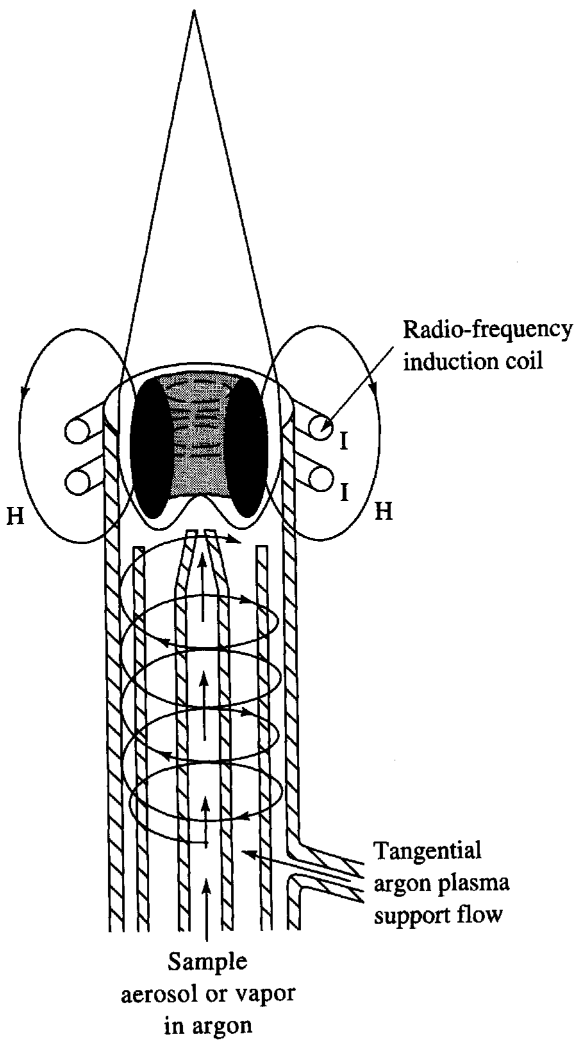
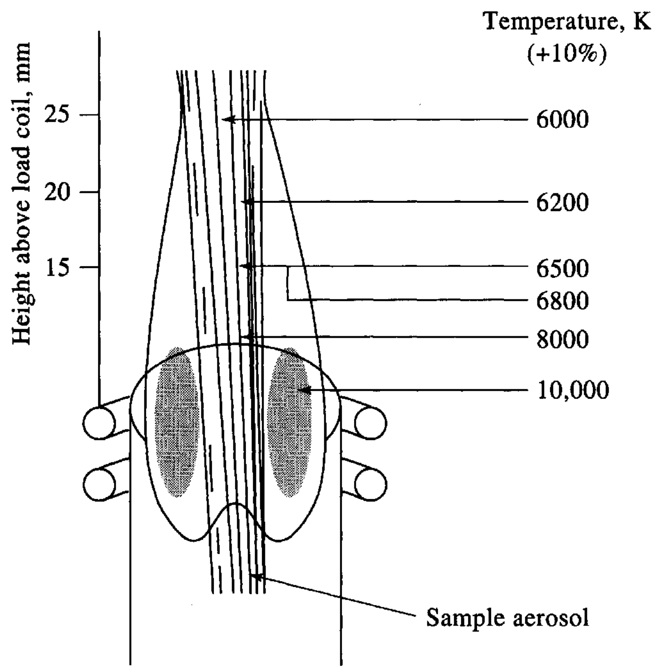


Fig 10-1

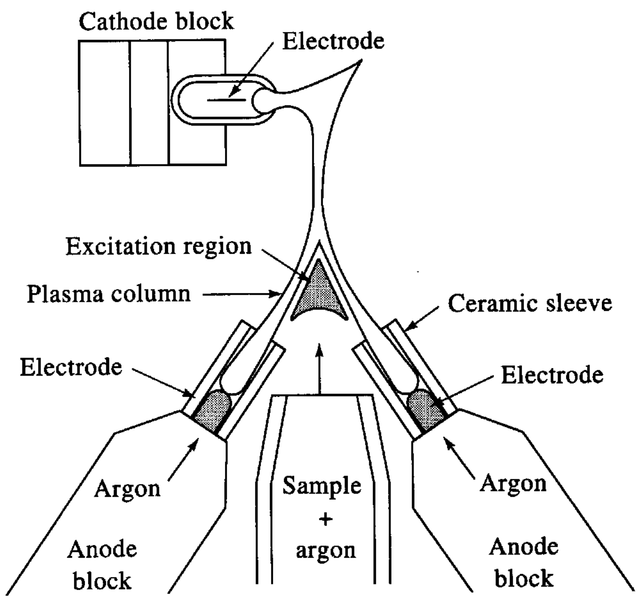
- Torch up to 1" diameter
- Ar cools outer tube, defines plasma shape
- Radio-frequency (RF) up to 2 kW
- Ar flow up to 20 L/min

Plasma Structure: (Fig. 10-4)



- 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

(2) Direct Current (DC) Plasma (Fig 10-5)



- 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

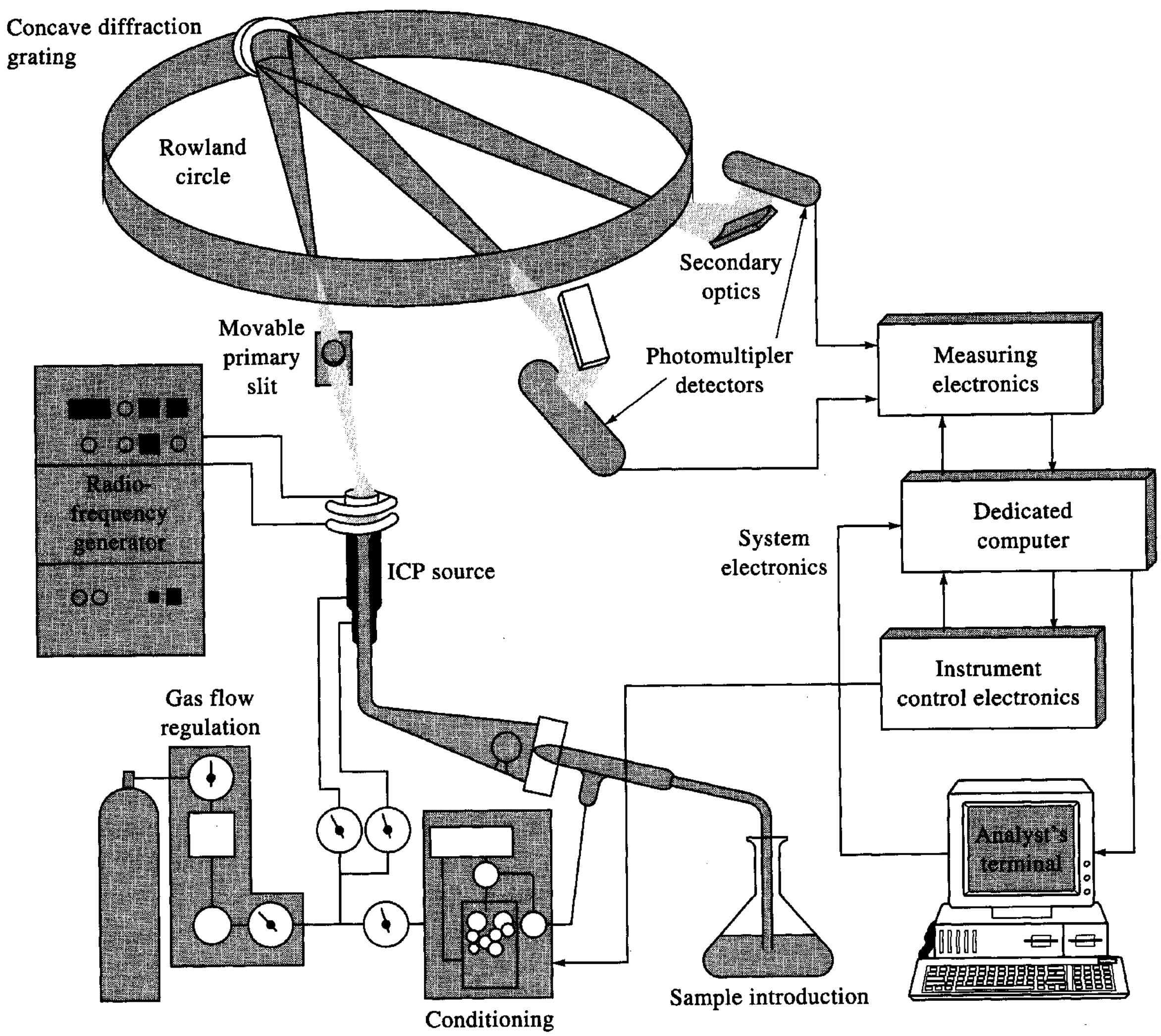
(Fourier transform FT-AES)

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: (Fig. 10-8)



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

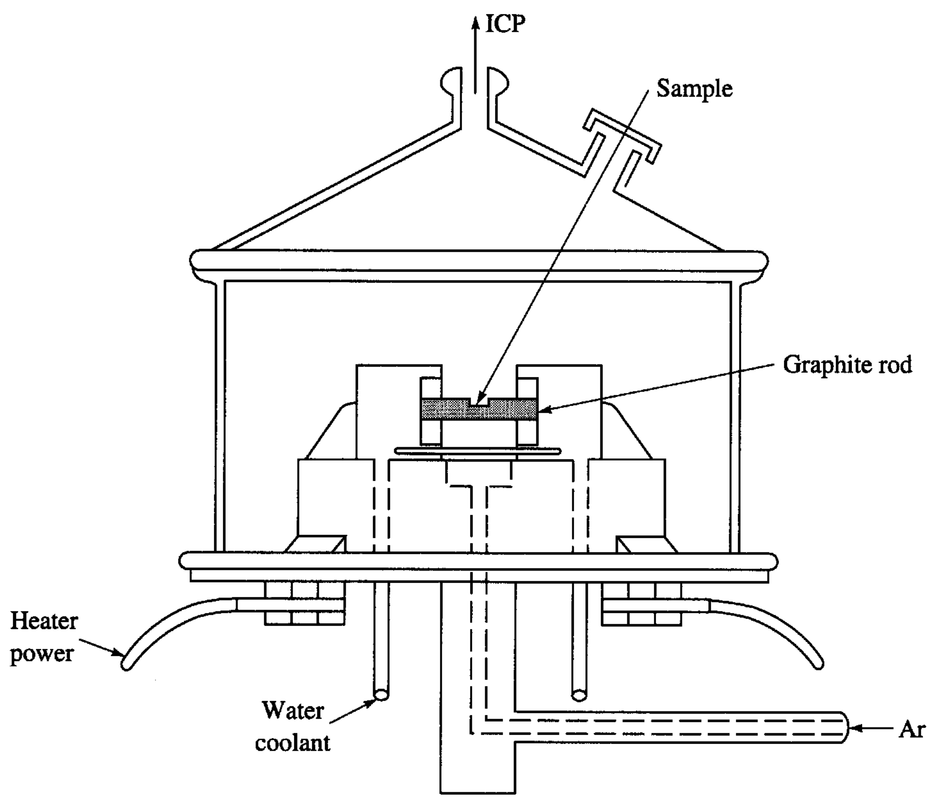
Multichannel instrument - multiple PMT's

- Expensive
- Faster

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)



(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

Cross-flow Nebulizer

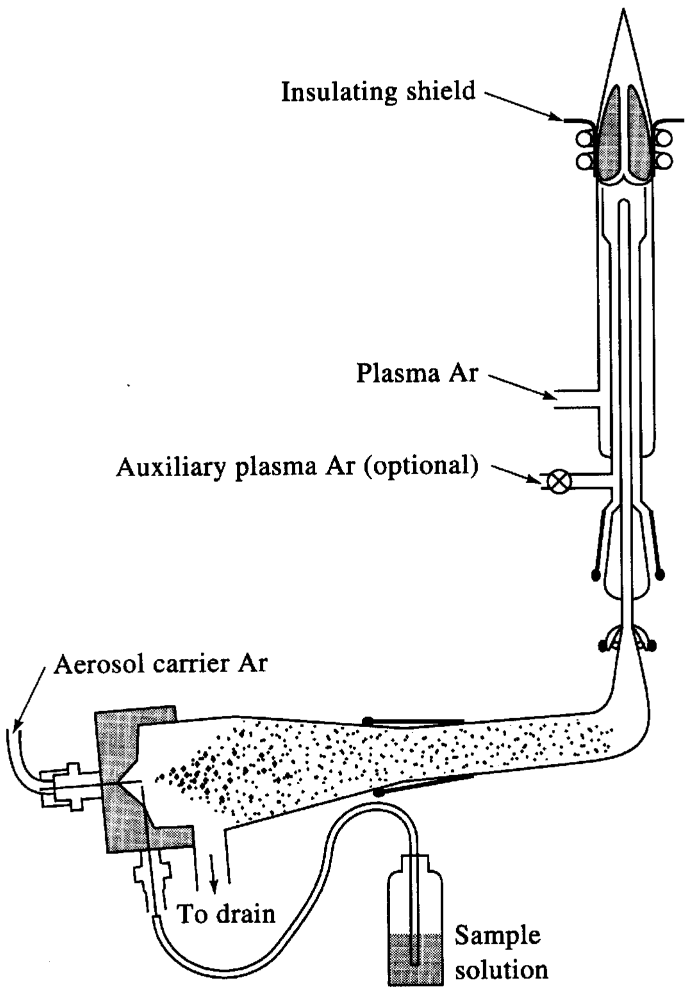


Fig 10-2

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

* intermittent

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

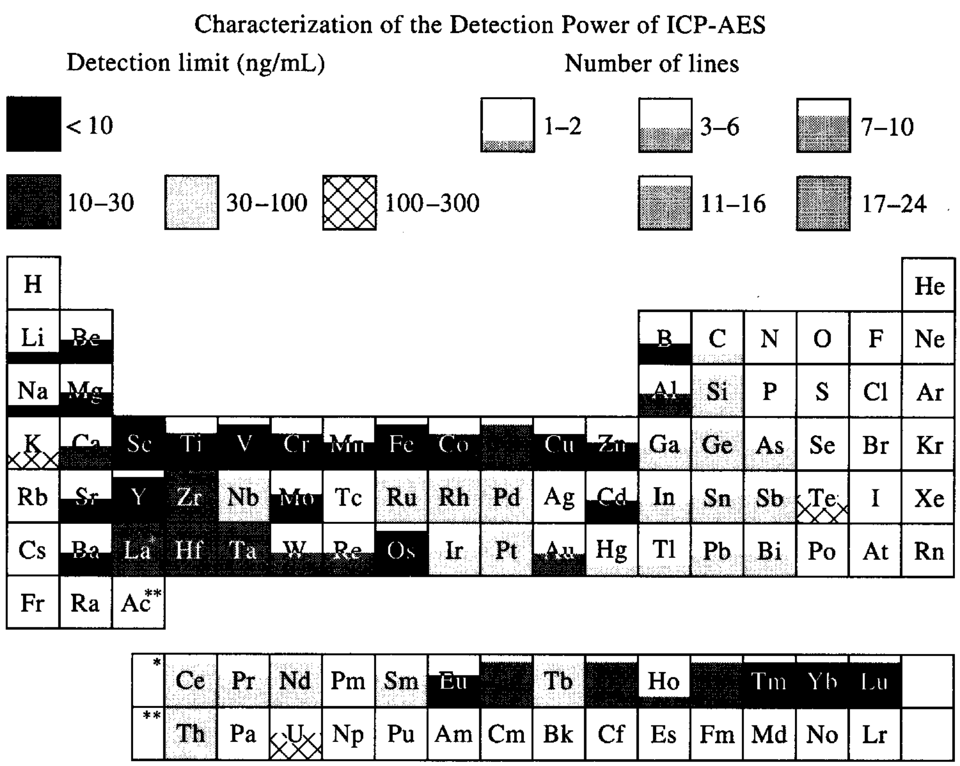


Fig 10-13