

## Atomic Emission Spectroscopy (Chapter 9/10):

Identification of **elements** but not **compounds**

### **Excitation and Atomization:**

Traditionally based on

- flame

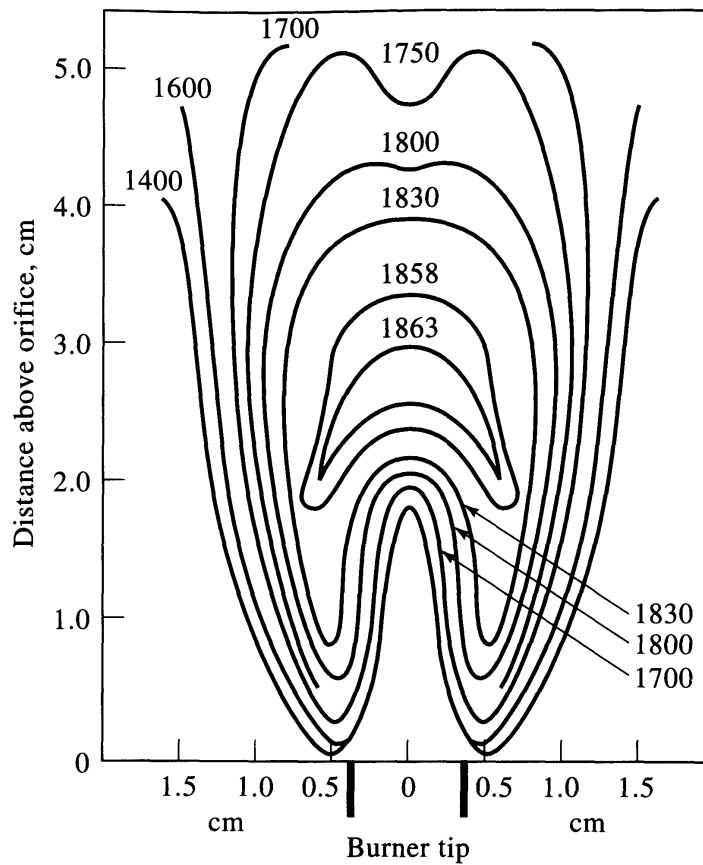
but

- 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

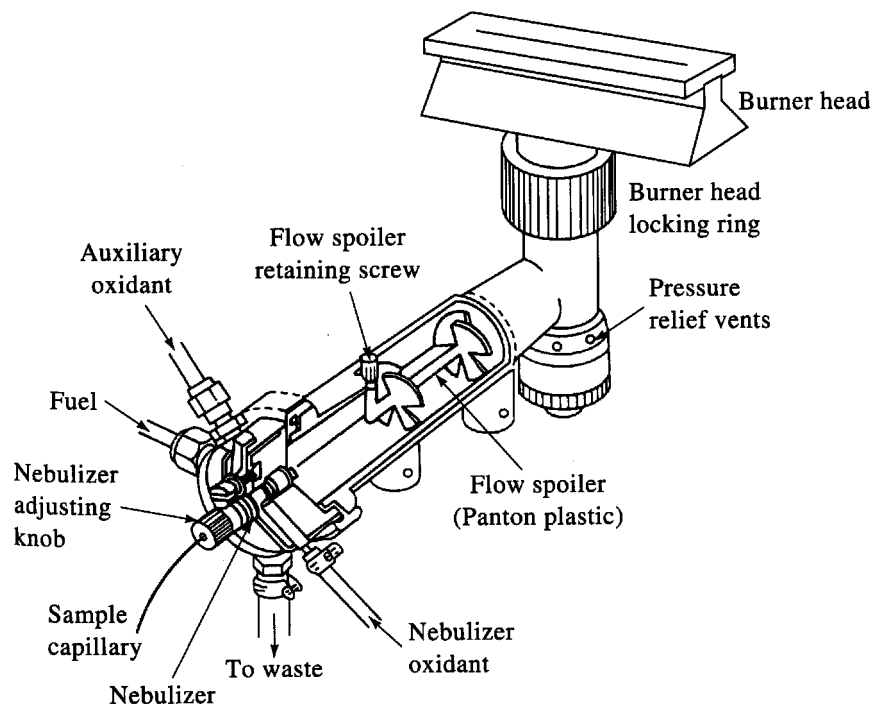
Interzonal Region

Secondary Combustion Zone

Flame Temperatures:

Fuel	Oxidant	Temperature
Gas	Air	~1800 °C
H <sub>2</sub>	O <sub>2</sub>	~2600 °C
Acetylene	O <sub>2</sub>	~3000 °C

## Laminar Flow Burner: (Fig 9-5)

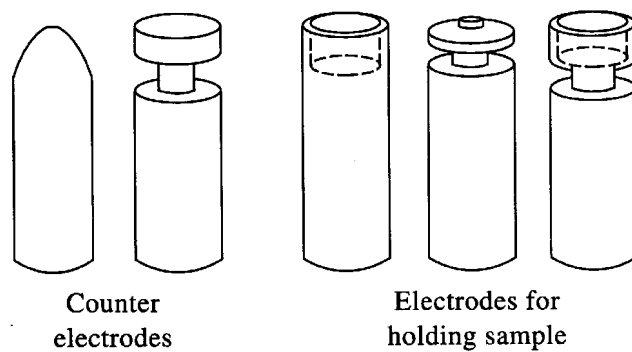


- Cheap
- Simple
- Flame stability
- Low temperature

## 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"

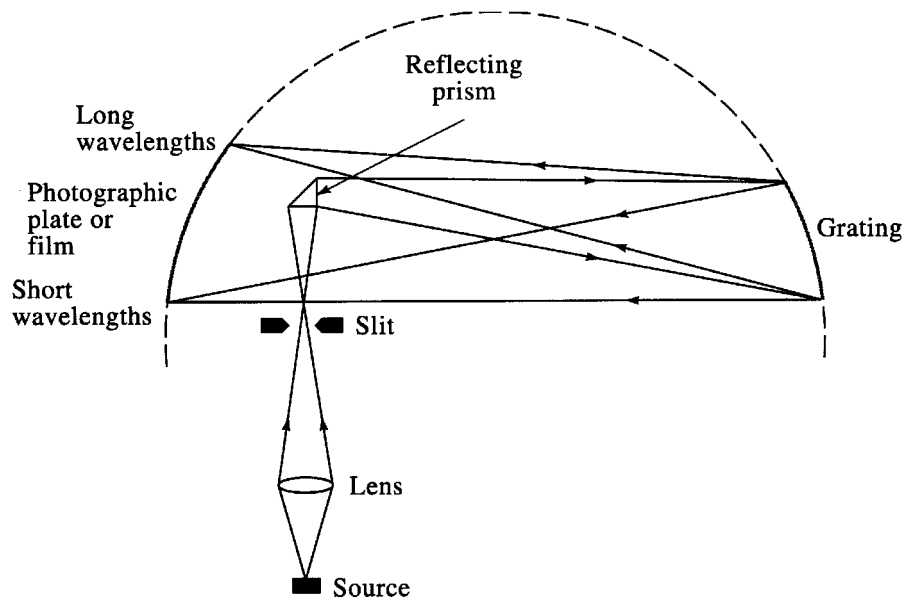


Fig 10-17

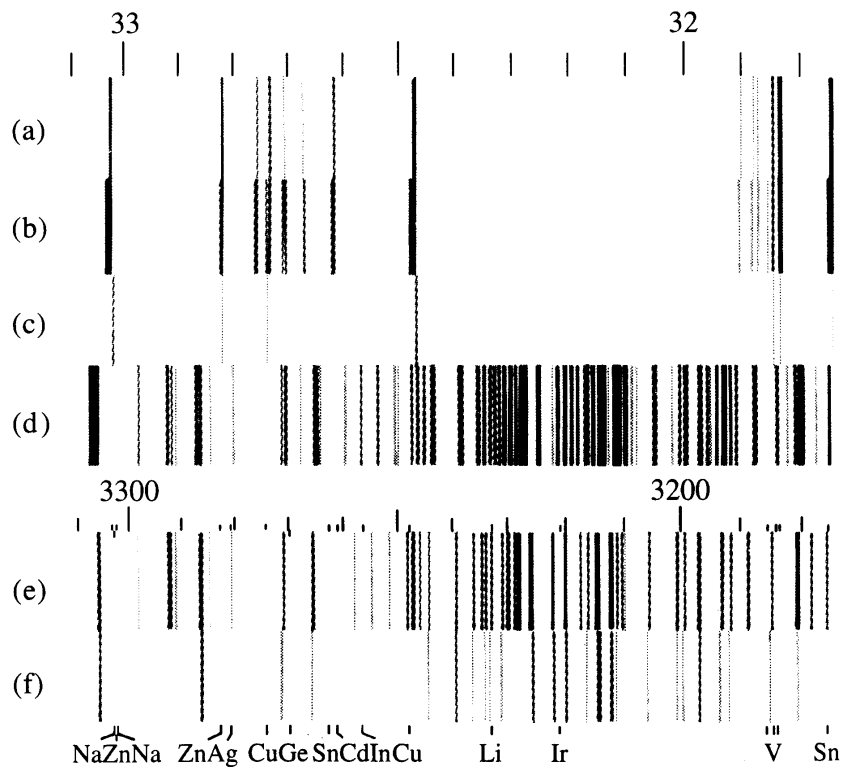


Fig 10-18

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)

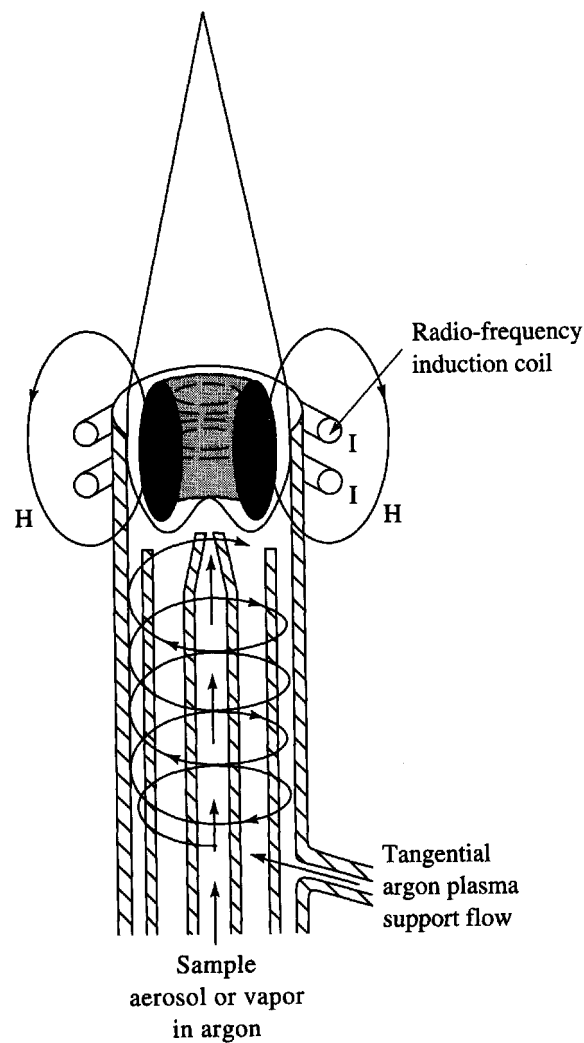
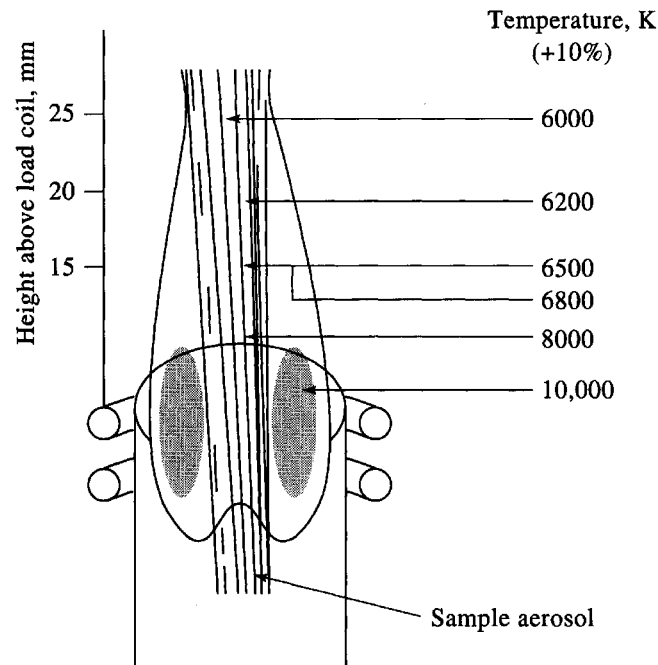


Fig 10-1

- **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

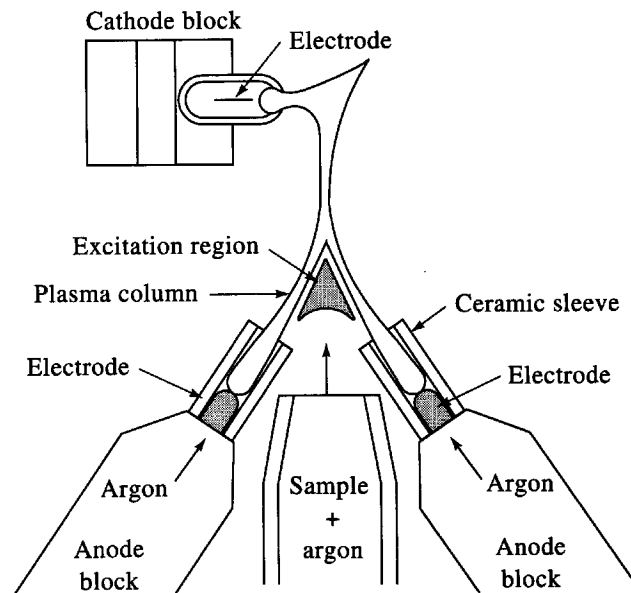
## Plasma Structure: (Fig. 10-4)



- 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 ( $<1 \text{ \AA}$ ) on continuum

Need

- high resolution ( $<0.1 \text{ \AA}$ )
- 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

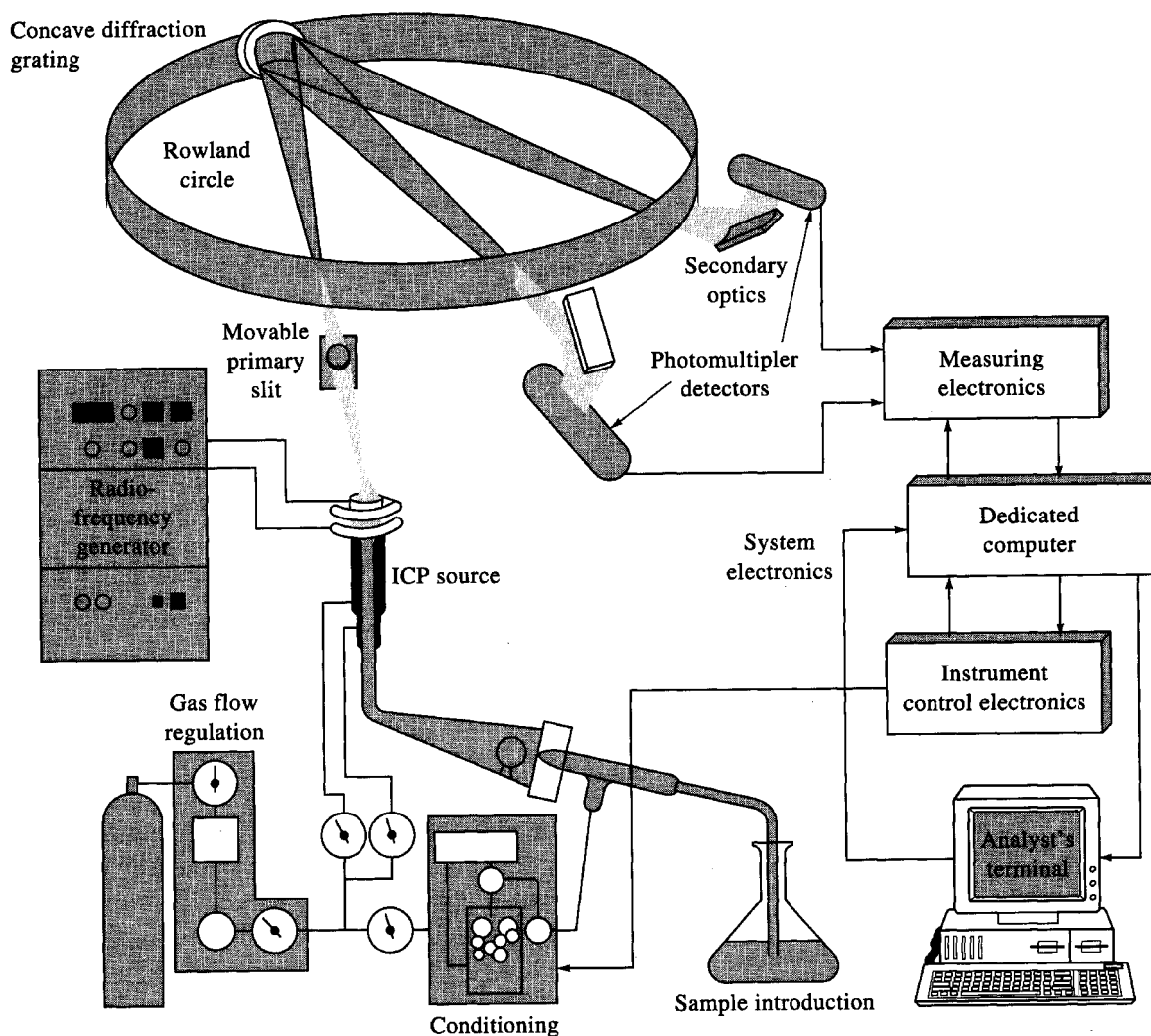
(Fourier transform FT-AES)

## 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  $\lambda$  on exit slit

- Cheaper
- Slower
- Pre-configured exit slits to detect up to 20 lines, slew scan

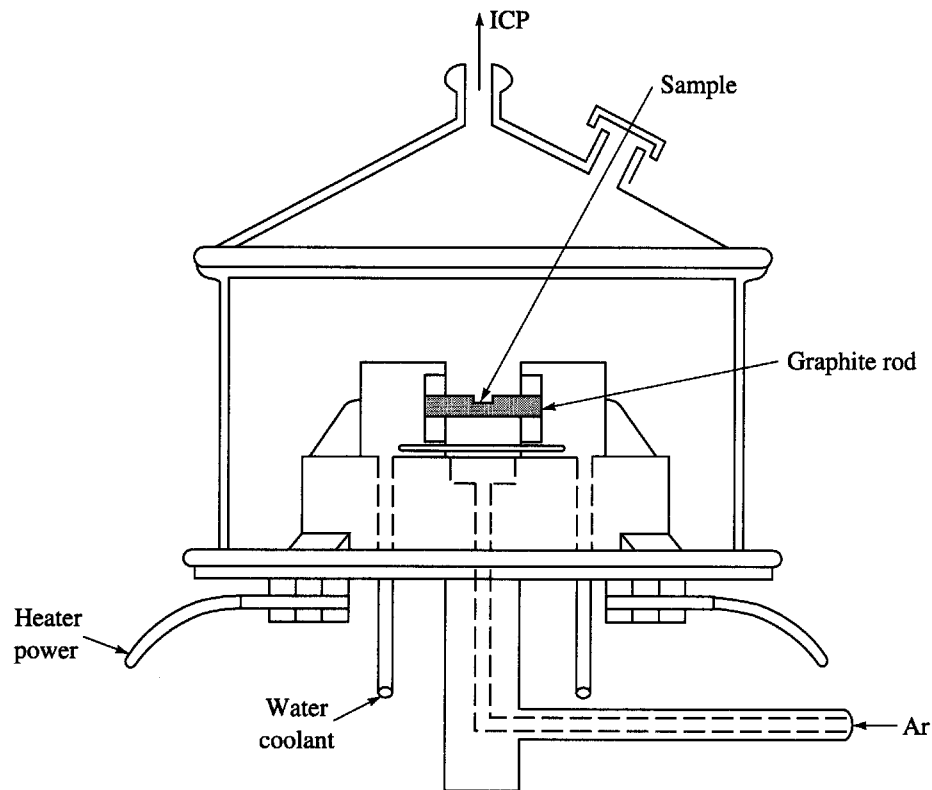
Multichannel instrument - multiple PMT's

- 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

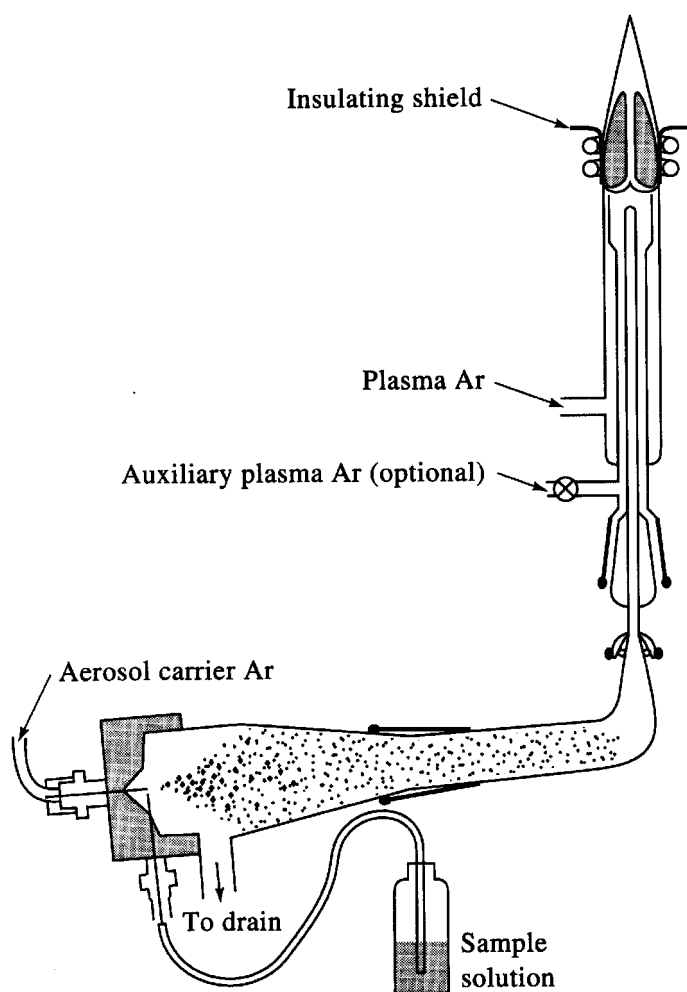


Fig 10-2

## 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

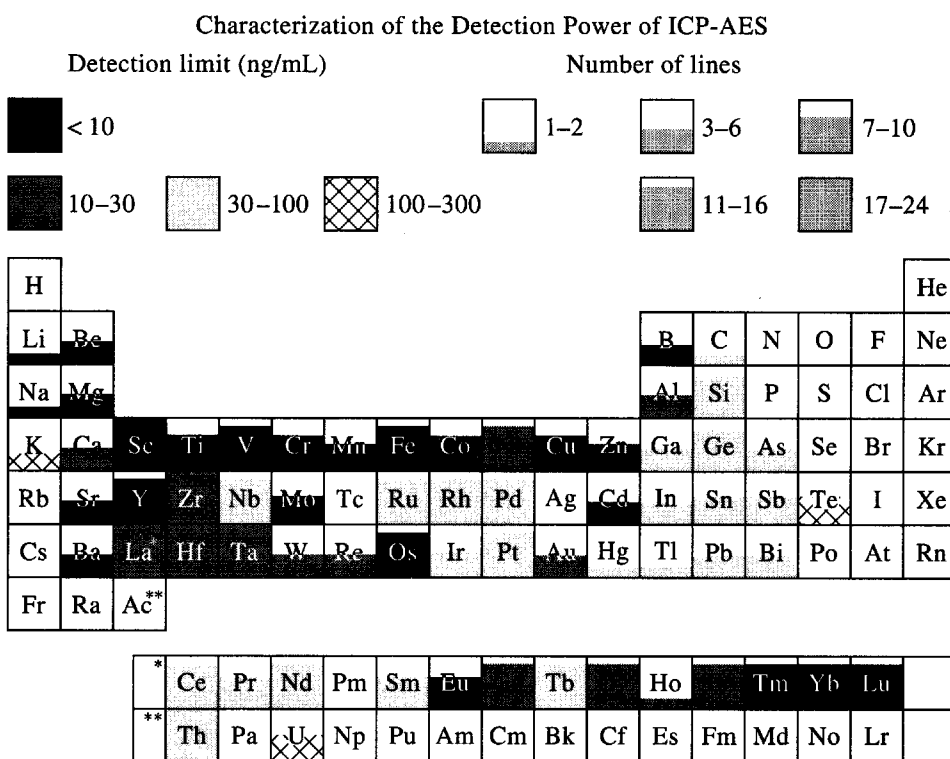


Fig 10-13



