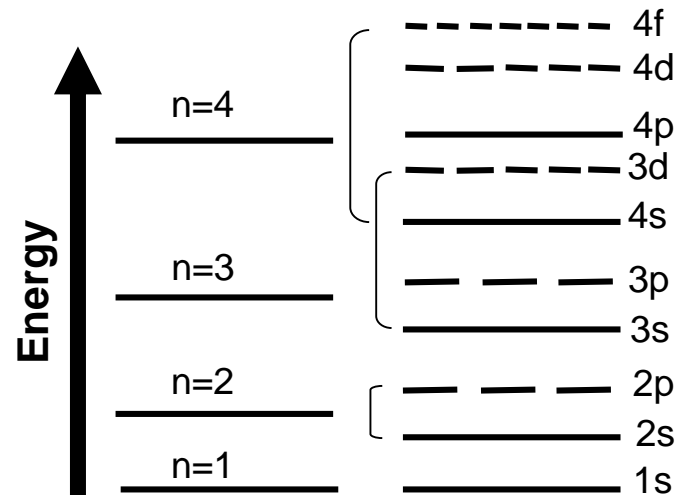
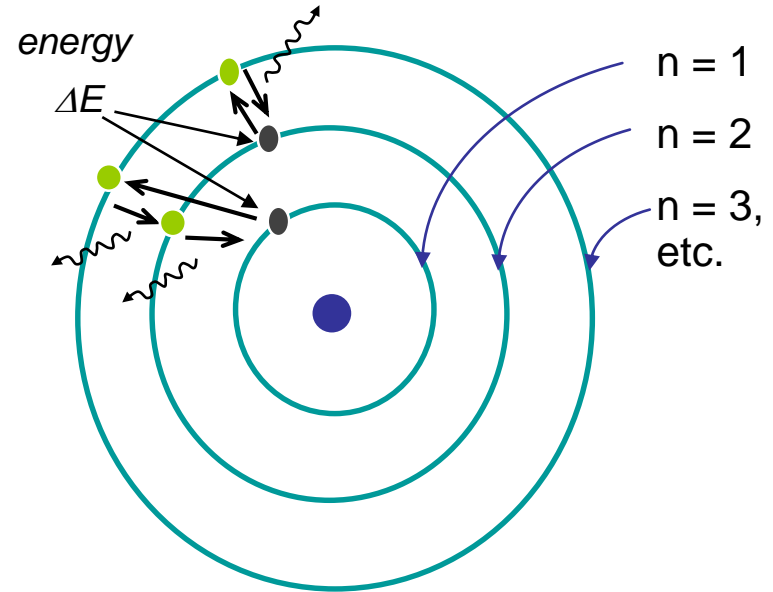


Atomic Spectroscopy

Atomic Spectra

• Electron excitation

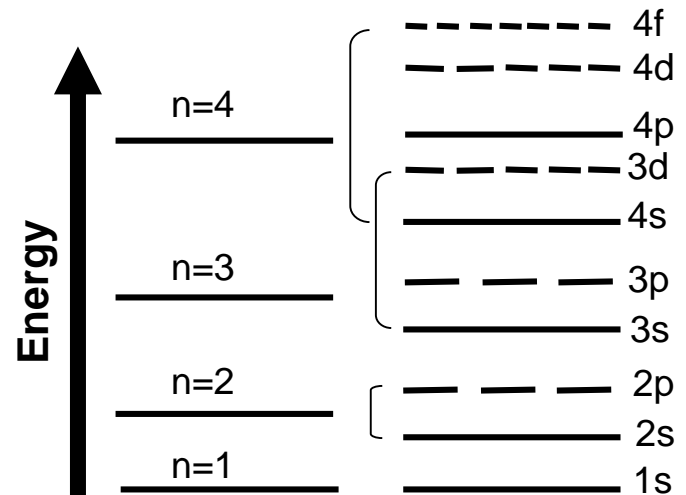
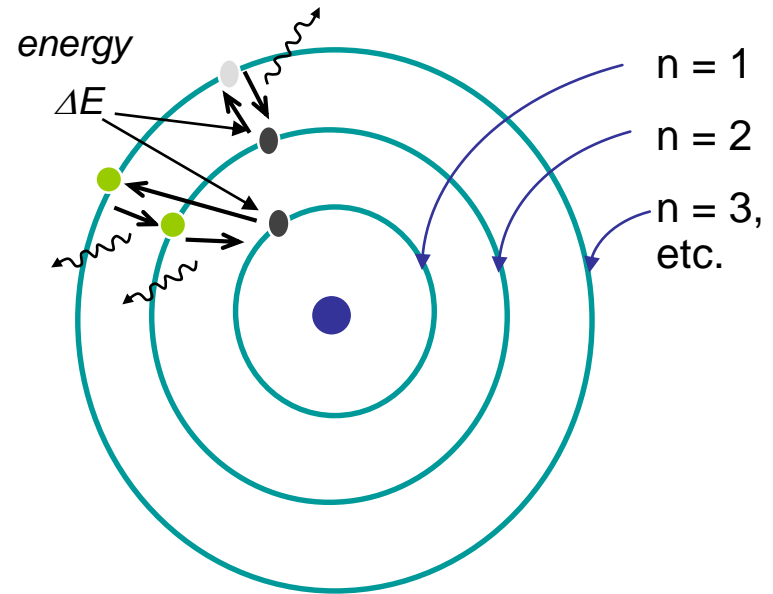
- The excitation can occur at different degrees
 - low E tends to excite the outmost e⁻'s first
 - when excited with a high E (photon of high ν) an e⁻ can jump more than one levels
 - even higher E can tear inner e⁻'s away from nuclei
- An e⁻ at its excited state is not stable and tends to return its ground state
- If an e⁻ jumped more than one energy levels because of absorption of a high E, the process of the e⁻ returning to its ground state may take several steps, - i.e. to the nearest low energy level first then down to next ...



Atomic Spectra

- **Atomic spectra**

- The level and quantities of energy supplied to excite e⁻'s can be measured & studied in terms of the frequency and the intensity of an e.m.r. - the **absorption spectroscopy**
- The level and quantities of energy emitted by excited e⁻'s, as they return to their ground state, can be measured & studied by means of the **emission spectroscopy**
- The level & quantities of energy absorbed or emitted (ν & intensity of e.m.r.) are specific for a substance
- Atomic spectra are mostly in UV (sometime in visible) regions

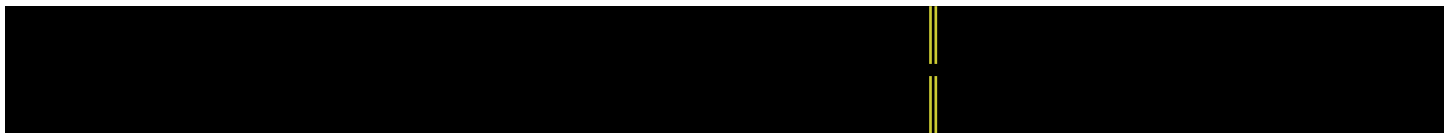


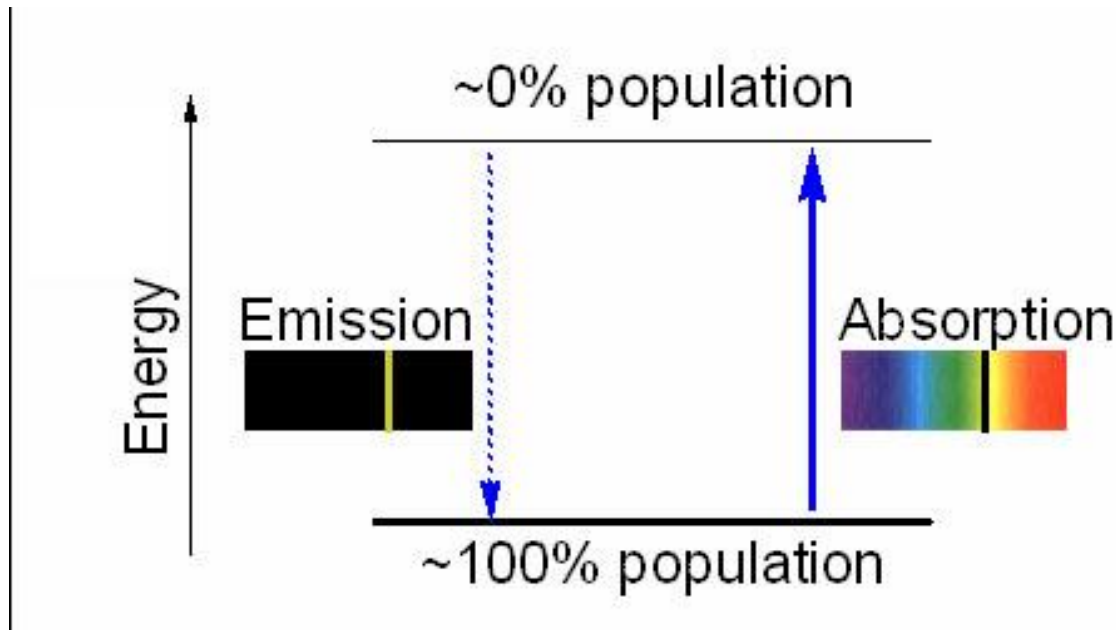
Atomic spectroscopy

- Atomic emission
 - Zero background (noise)



- Atomic absorption
 - Bright background (noise)
 - Measure intensity change
 - More signal than emission
 - Trace detection





Signal is proportional to number of atoms
AES - low noise (background)
AAS - high signal

The energy gap for emission is exactly the same as for absorption.

All systems are more stable at lower energy. Even in the flame, most of the atoms will be in their lowest energy state.

Boltzmann Distribution

$$\frac{\text{population}(j)}{\text{population}(0)} = \frac{N_j}{N_0} = \exp\left\{\frac{-E_j}{kT}\right\} = \exp\left\{\frac{-E_j}{RT}\right\}$$

Atomic energy
Molecular energy

Atom	Wavelength	N_j/N_0 at 3000 K
Cs	852.1 nm	7.24×10^{-3}
Na	589.0 nm	5.88×10^{-4}
Ca	422.7 nm	3.69×10^{-5}
Zn	213.9 nm	5.58×10^{-10}

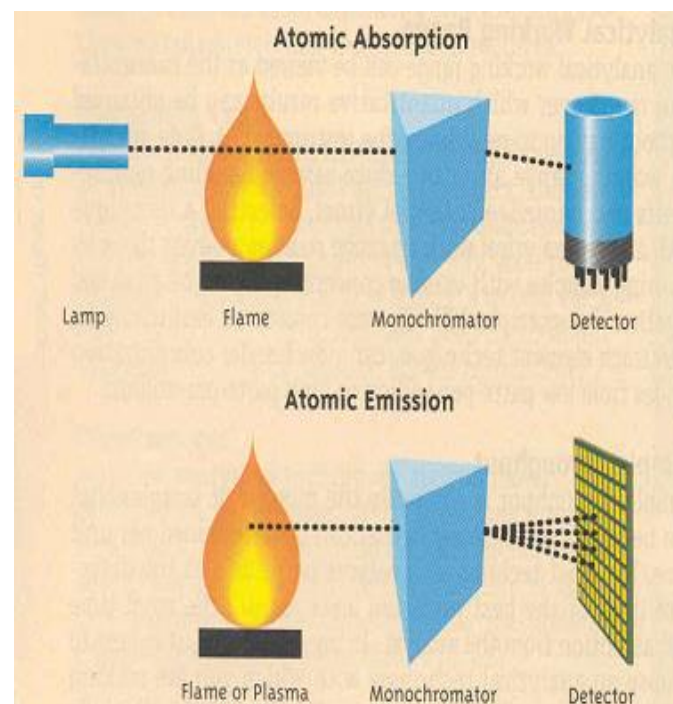
All systems are more stable at lower energy. Even in the flame, most of the atoms will be in their lowest energy state.

At 3000K, for every 7 Cs atoms available for emission, there are 1000 Cs atoms available for absorption.

At 3000 K, for each Zn available for emission, there are approximately 1 000 000 000 Zn atoms available for absorption.

Atomic Absorption/Emission Spectroscopy

- Atomic absorption/emission spectrometers involve e⁻'s changing *energy* states
 - Most useful in quantitative analysis of elements, especially metals
- These spectrometers are usually carried out in optical means, involving
- conversion of compounds/elements to gaseous atoms by atomisation. Atomization is the most critical step in flame spectroscopy. Often limits the precision of these methods.
 - excitation of electrons of atoms through heating or X-ray **bombardment**
 - **UV/vis absorption, emission or fluorescence** of atomic species in vapor is measured
- Instrument easy to tune and operate
- Sample preparation is simple (often involving only dissolution in an acid)



Source: R. Thomas, "Choosing the Right Trace Element Technique," *Today's Chemist at Work*, Oct. 1999, 42.

- A. Walsh, "The application of atomic absorption spectra to chemical analysis", *Spectrochimica Acta*, 1955, 7, 108-117.

Spectrochimica Acta, 1955, Vol. 7, pp. 108 to 117. Pergamon Press Ltd., London

The application of atomic absorption spectra to chemical analysis

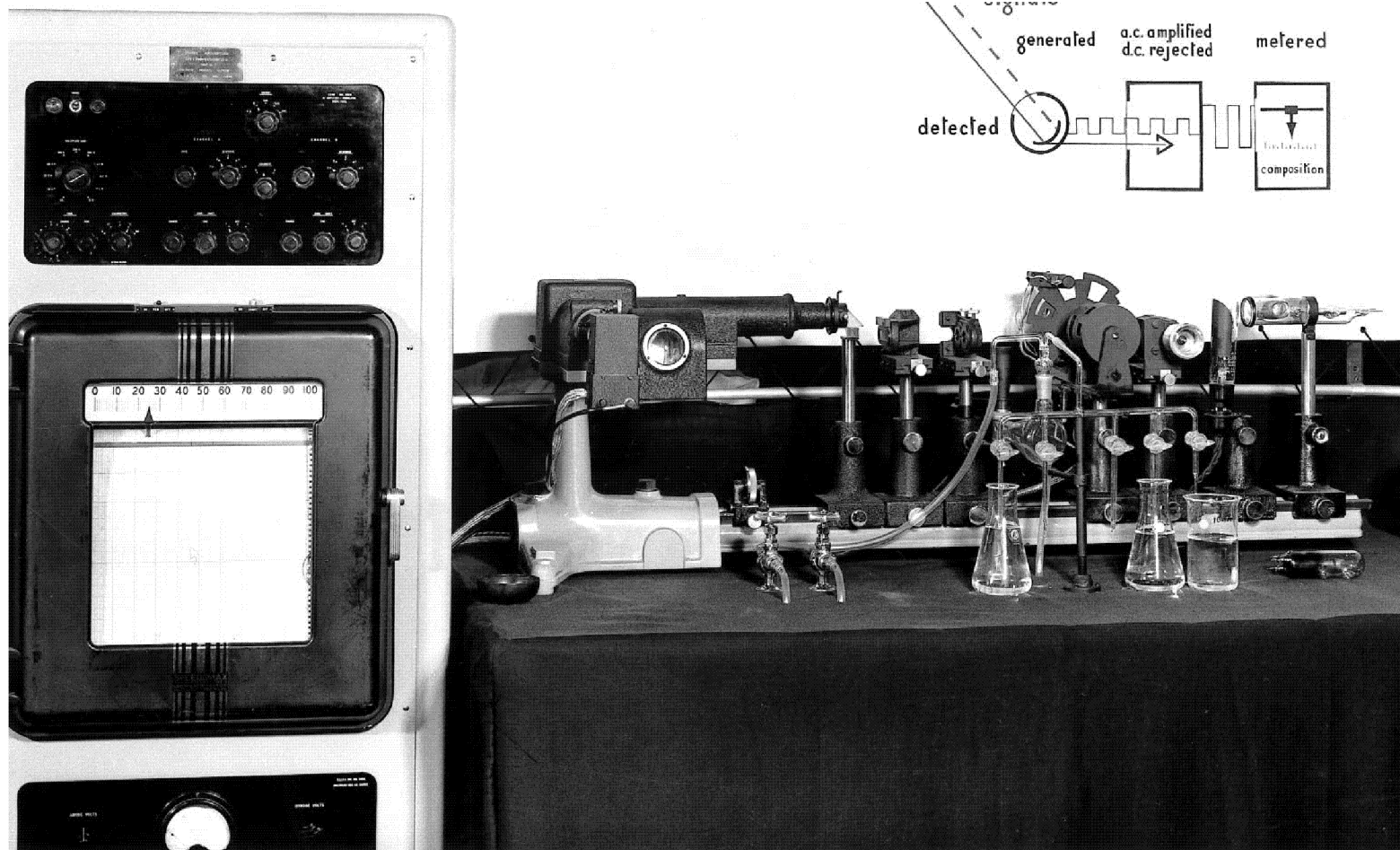
A. WALSH

Chemical Physics Section, Division of Industrial Chemistry,
Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

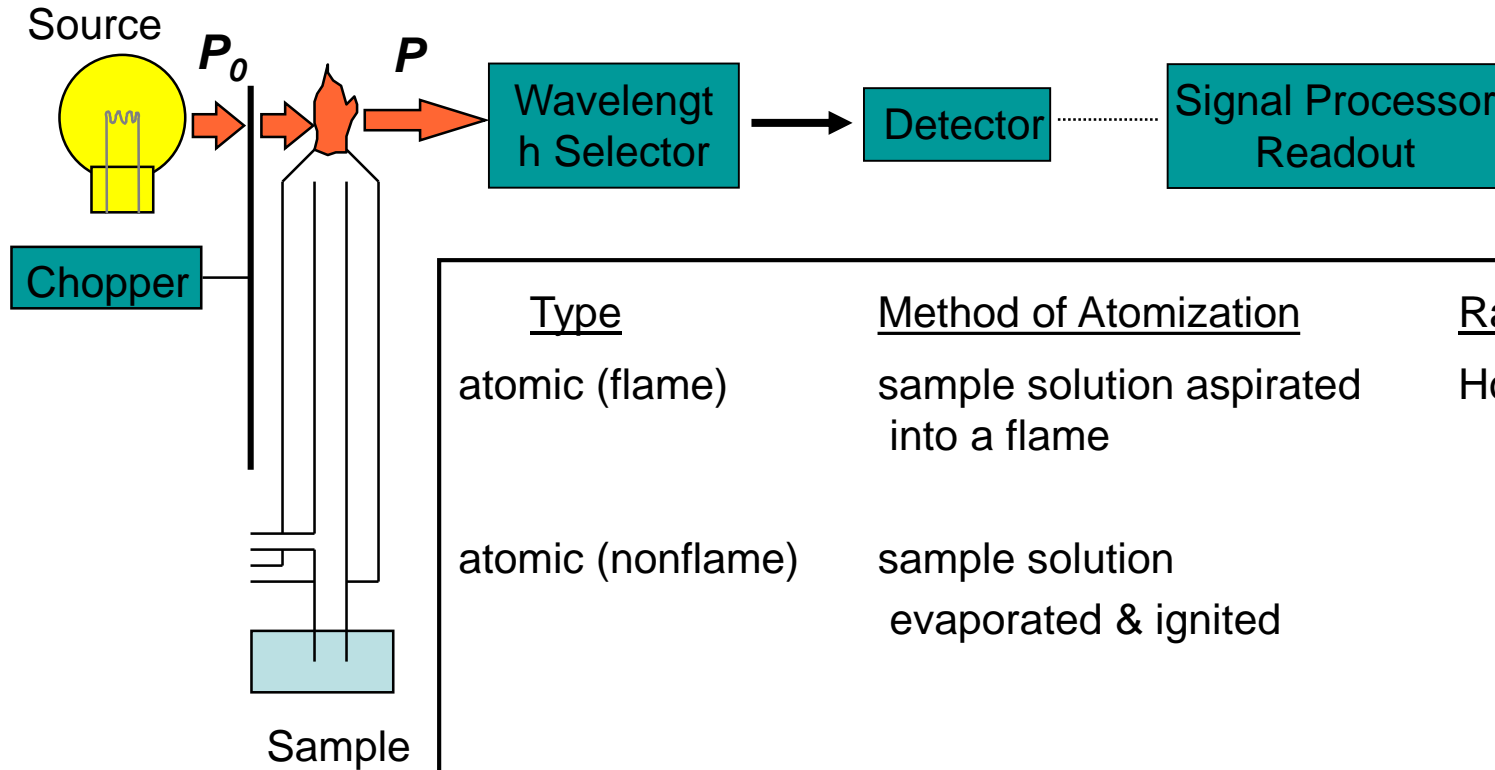
(Received 18 January 1955)

Summary—The theoretical factors governing the relationship between atomic absorption and atomic concentration are examined and the experimental problems involved in recording atomic absorption spectra are discussed. On the basis of the discussions, it is shown that such spectra provide a promising method of chemical analysis with vital advantages over emission methods, particularly from the viewpoint of absolute analysis. It is also suggested that the absorption method offers the possibility of providing a simple means of isotopic analysis.

The original 1954 AAS instrument

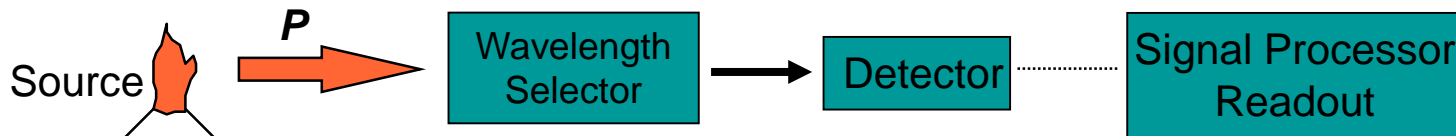


Atomic Absorption Spectrometer (AA)



<u>Type</u>	<u>Method of Atomization</u>	<u>Radiation Source</u>
atomic (flame)	sample solution aspirated into a flame	Hollow cathode lamp (HCL)
atomic (nonflame)	sample solution evaporated & ignited	HCL

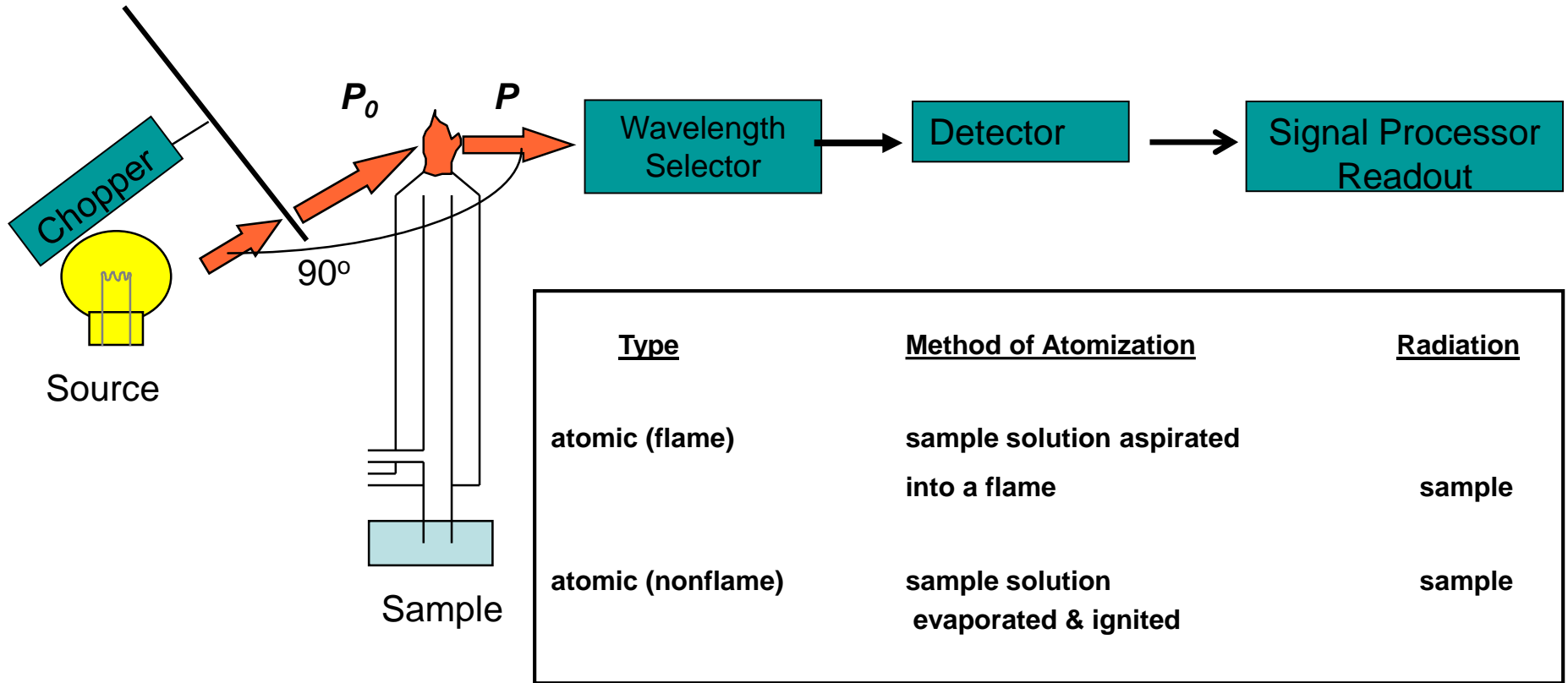
Atomic Emission Spectrometer (AES)



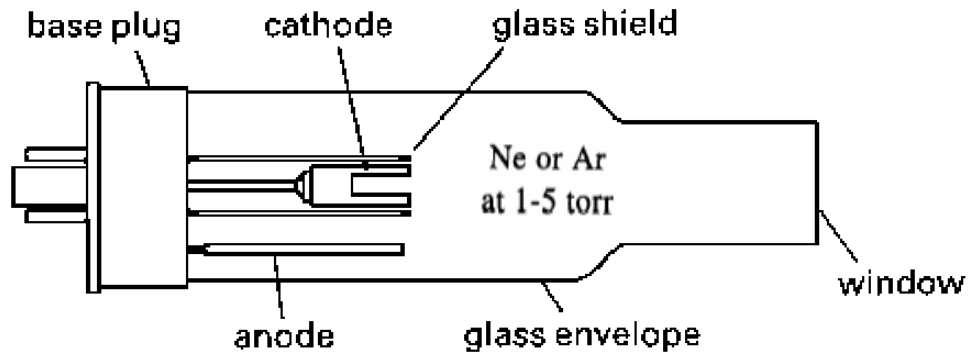
<u>Type</u>	<u>Method of Atomization</u>	<u>Radiation Source</u>
arc	sample heated in an electric arc	sample
spark	sample excited in a high voltage spark	sample
argon plasma	sample heated in an argon plasma	sample
flame	sample solution aspirated into a flame	sample

Atomic Fluorescence Spectrometer (AFS)

optical emission from gas-phase atoms that have been excited to higher energy levels



Hollow cathode lamp



- Electron and ionic impact on cathode
- $M(s) \rightarrow M(g)$
- $M(g) \rightarrow \rightarrow \rightarrow M^*(g)$
- $M^*(g) \rightarrow M(g) + h\nu$

- The hollow cathode lamp is an example of a metal vapour lamp emits light at the characteristic wavelength(s) of the metal in the cathode.
- The lamp gas is under near-vacuum conditions. Electron flow ionises the gas. The cations bombard the cathode to vaporise the metal. Combination of ion-atom collisions, electron-atom collisions, and other processes excite the electrons inside the metal vapour atoms, which emit light.



Thin lay of cathode material

Types of Atomizers

Flame

Electrothermal

Special

- Glow Discharge

- Hydride Generation

- Cold-Vapor

A. Flame Atomization

Flame Atomizers: Superior method for reproducible liquid sample introduction for atomic absorption and fluorescence spectroscopy. Other methods better in terms of sampling efficiency and sensitivity.

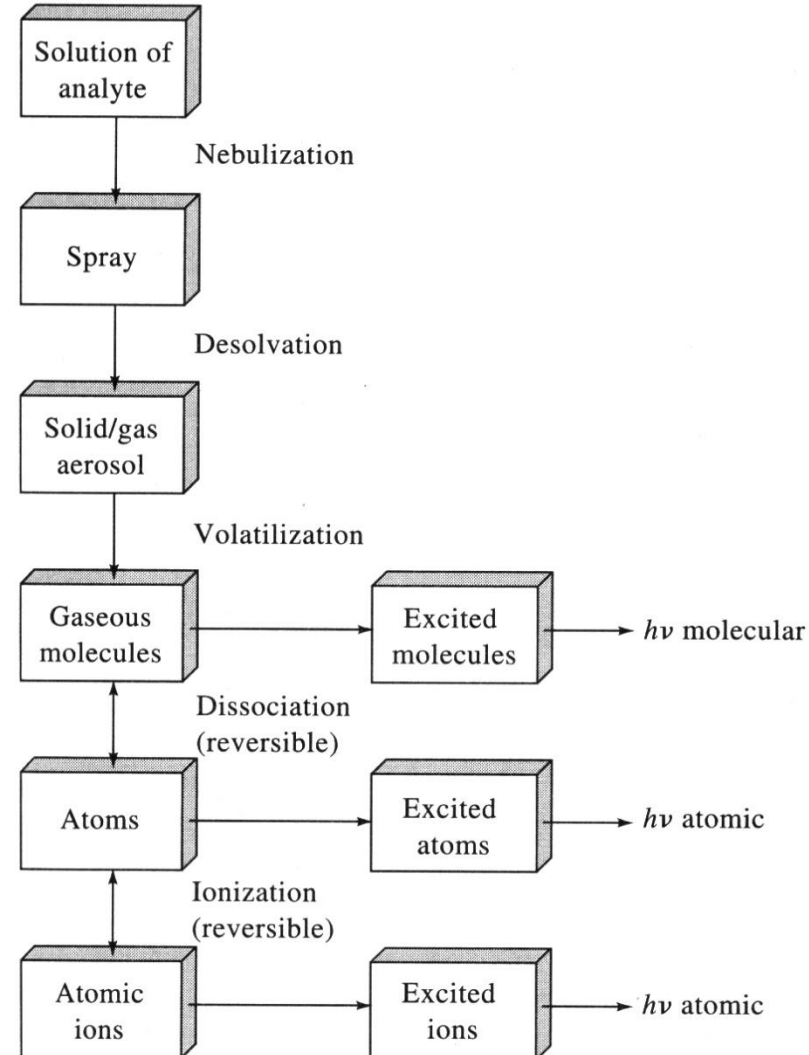
Nebulization - Conversion of the liquid sample to a fine spray.

Desolvation - Solid atoms are mixed with the gaseous fuel.

Volatilization - Solid atoms are converted to a vapor in the flame.

- There are three types of particles that exist in the flame:

- 1) Atoms
- 2) Ions
- 3) Molecules



1. Types of Flames

<u>Fuel / Oxidant</u>	<u>Temperature</u>	
acetylene / air	2100 °C – 2400 °C	(most common)
acetylene / N ₂ O	2600 °C – 2800 °C	
acetylene / O ₂	3050 °C – 3150 °C	

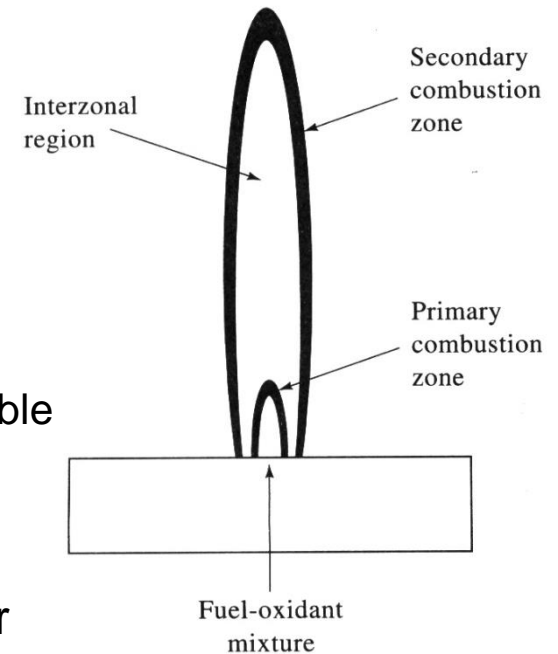
- Selection of flame type depends on the volatilization temperature of the atom of interest.

2. Flame Structure

- Primary combustion zone - initial decomposition, molecular fragments, cool,
- Interzonal region is the hottest part of the flame, most atomic fragments and used for emission/fluorescence
- Secondary combustion zone - cooler, conversion of atoms to stable molecules, oxides.

element rapidly oxidizes - largest [atom] near burner

element poorly oxidizes - largest [atom] away from burner



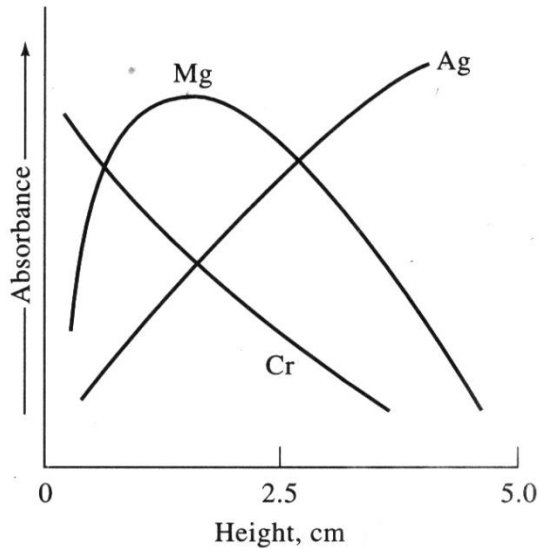
- Fuel rich flames are best for atoms because the likelihood of oxidation of the atoms is reduced.

3. Temperature Profiles

- It is important to focus the entrance slit of the monochromator on the same part of the flame for all calibration and sample measurements.

4. Flame Absorption Profiles

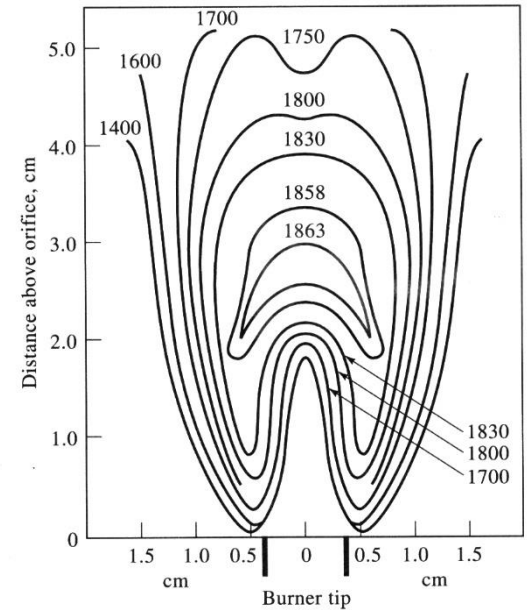
most sensitive part of flame for AAS varies with analyte



- Mg - atomized by longer exposure to flame, but is eventually oxidized.
- Ag - slow to oxidize, the number of atoms increases with flame height.
- Cr - oxidizes readily, highest concentration of atoms at the base of the flame.

Consequences?

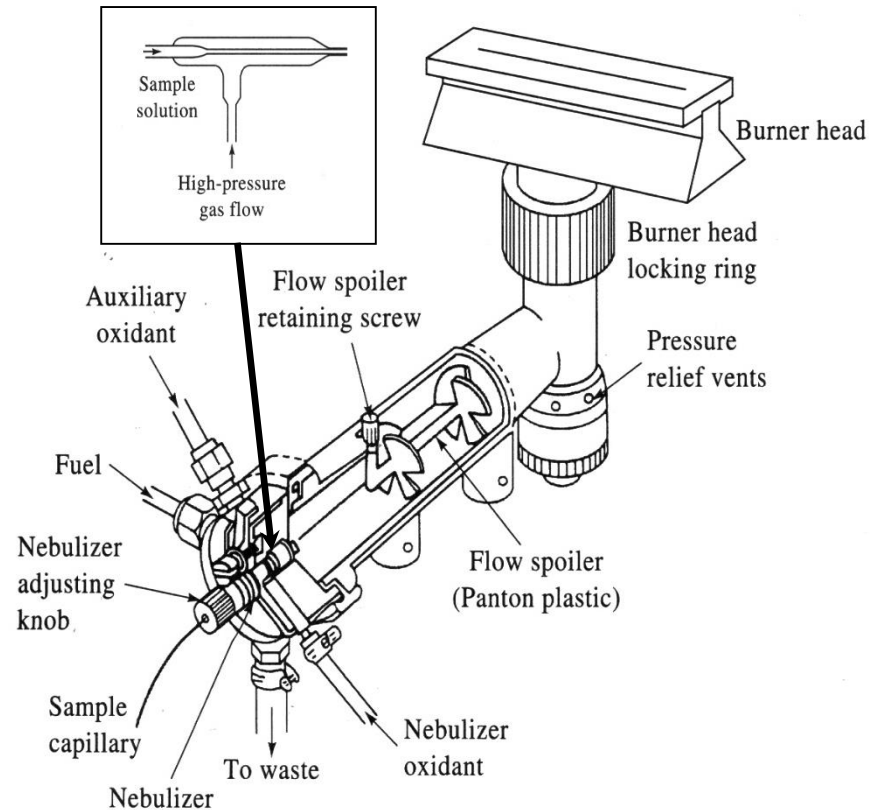
- sensitivity varies with element
- must maximize burner position
- makes multielement detection difficult



5. Flame Atomizers

Laminar Flow Burners

- Sample is “pulled” into the nebulization chamber by the flow of fuel and oxidant.
- Contains spoilers (baffles) to allow only the finest droplets to reach the burner head.
- Burner head has a long path length and is ideal for atomic absorption spectroscopy.



Detection limits (ppm = ng mL⁻¹)

Element	Flame AAS	Flame AES
Ag	3	20
Ca	1	0.1
Cd	1	2000
Fe	6	50
K	2	3
Mg	0.2	5
Mn	2	15
Na	0.2	0.1
Ni	3	600
Pb	5	200
Zn	1	200

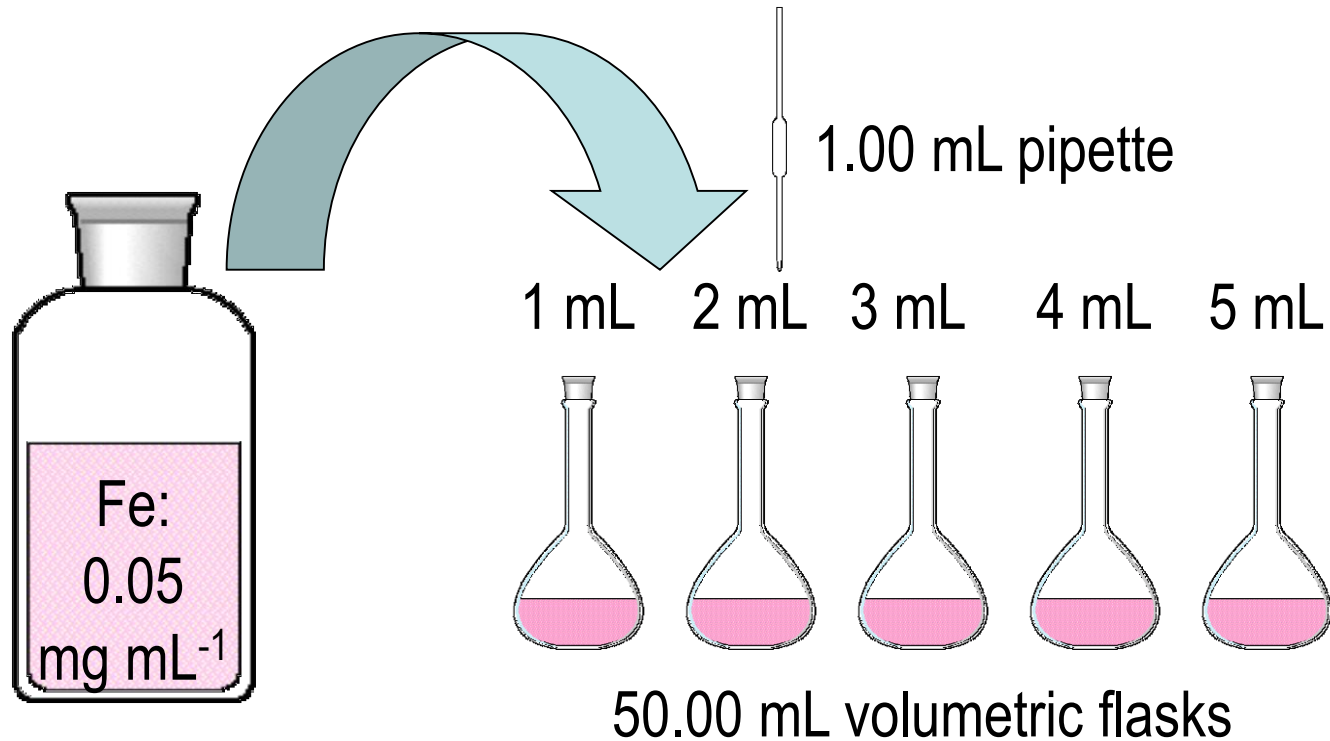
The detection limit is the smallest amount of an element that can be reliably measured.

Smaller limits of detection (LODs) are better.

Some common light metals have a lower LOD using flame atomic emission.

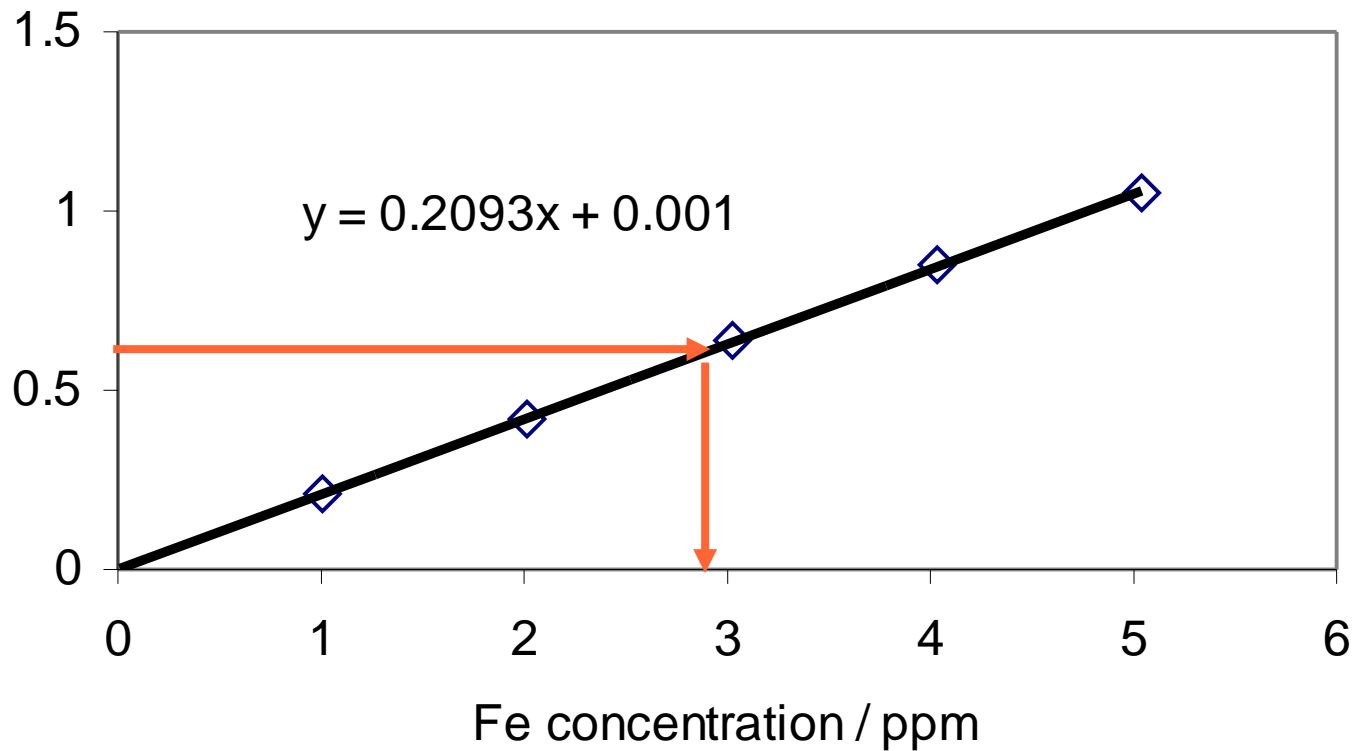
Most transition elements have a significantly lower LOD using AAS.

Student determination of Fe

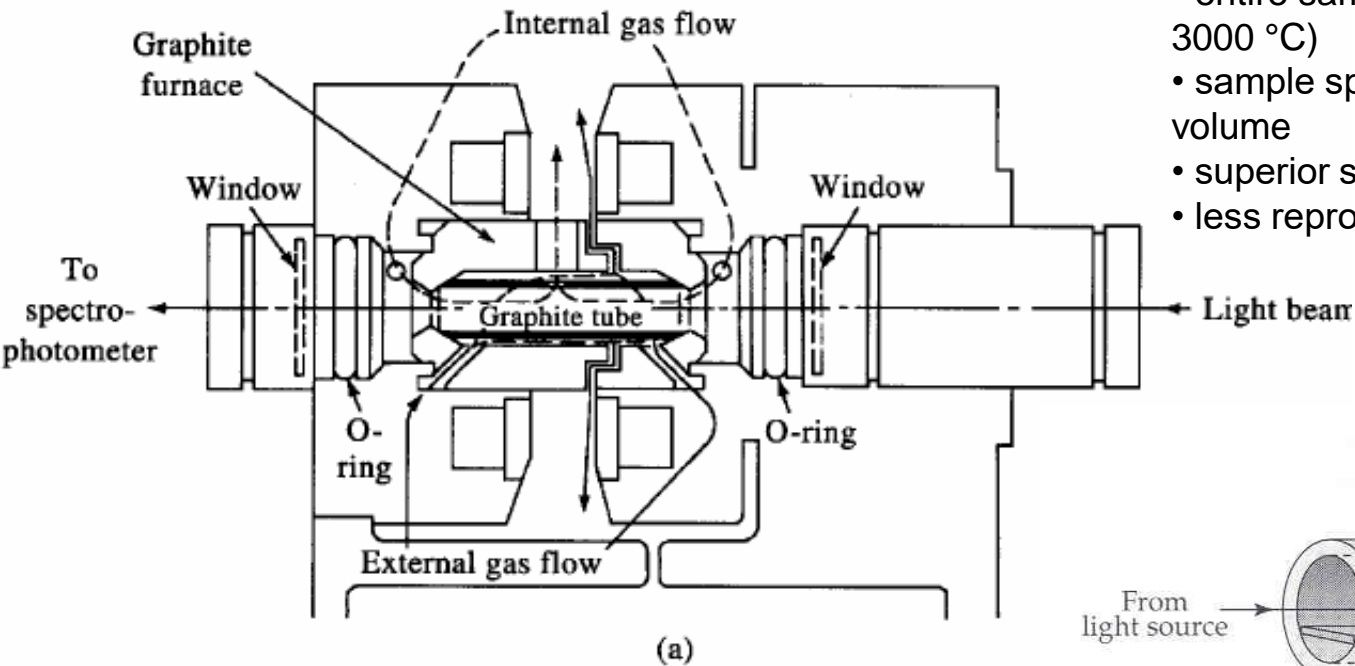


Determination of Fe

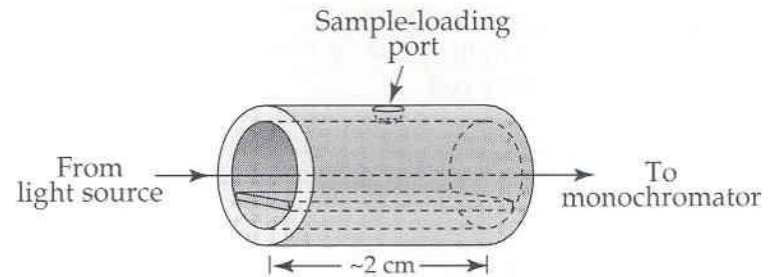
Calibration curve for absorbance of Fe



Electrothermal Atomization



- 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 %)



-0.5-10 mL of sample evaporated at low temperature, then ashed at higher temperature in electrically heated graphite furnace.

-Finally, current rapidly increased causing temperature increase (to 2000-3000 °C) and rapid atomization.

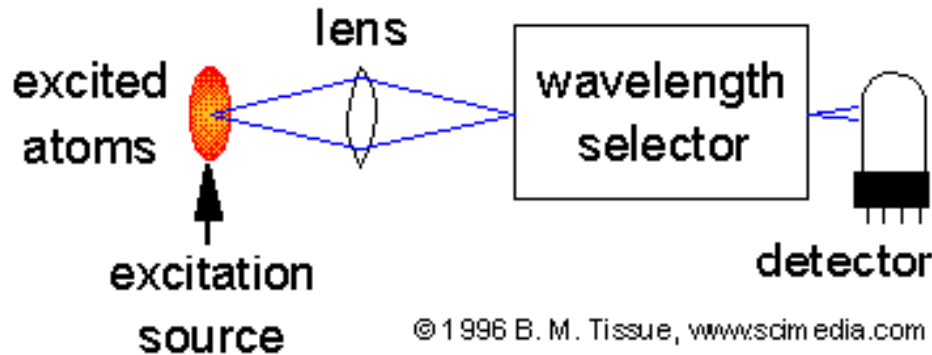
- Usually used only when flame or plasma atomization provides inadequate detection limits.

Atomic Emission Spectroscopy (AES, OES)

Introduction:

- Atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical [emission](#) from excited atoms to determine analyte concentration.
- Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma.
- These high-temperature atomization sources provide sufficient energy to promote the atoms into high energy levels.
- The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow.
- The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer.
- Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to [atomic-absorption \(AA\) spectroscopy](#).

Instrumentation:



As in AA spectroscopy, the sample must be converted to free atoms, usually in a high-temperature excitation source

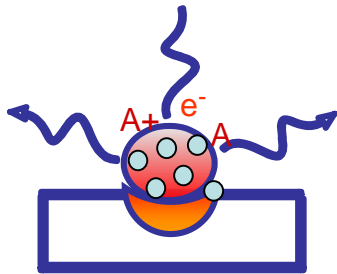
- Sample Introduction:
- Liquid samples are nebulized and carried into the excitation source by a flowing gas.
- Solid samples can be introduced into the source by a slurry or by laser ablation of the solid sample in a gas stream. Solids can also be directly vaporized and excited by a spark between electrodes or by a laser pulse.

Excitation:

- The excitation source must desolvate, atomize, and excite the analyte atoms. A variety of excitation sources are described in separate documents:
 - Flame
 - Arc / Spark
 - Inductively-coupled plasma (ICP)
 - Direct-current plasma (DCP)
 - Microwave-induced plasma (MIP)
 - Laser-induced plasma, Laser-induced breakdown (LIBS)

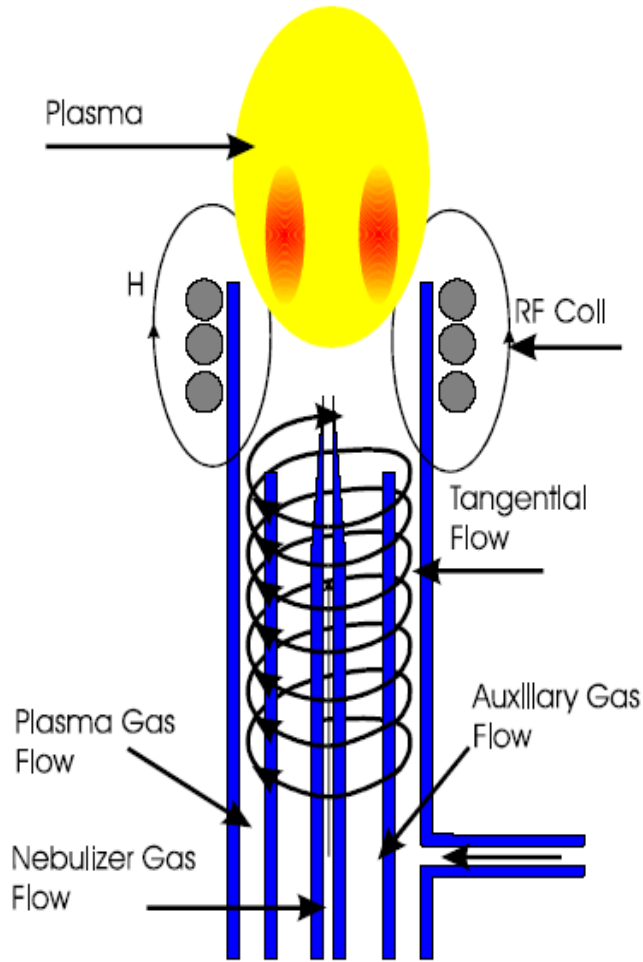
AES based on Plasma Sources:

- **Plasma** is an electrical conducting gaseous mixture containing significant amounts of cations and electrons (net charge approaches zero)
- **Plasmas** have sufficiently high energy to atomize, ionize, and excite virtually all elements in the periodic table, which are intentionally introduced into it for the purpose of elemental chemical analysis.



- 1) **increased** atomization/excitation
- 2) wider range of elements
- 3) simultaneous multielement analysis
- 4) wide dynamic range

1) ICP-OES:



-Inductively coupled plasmas are formed by coupling energy produced by a RF generator to the plasma support gas with an electromagnetic field.

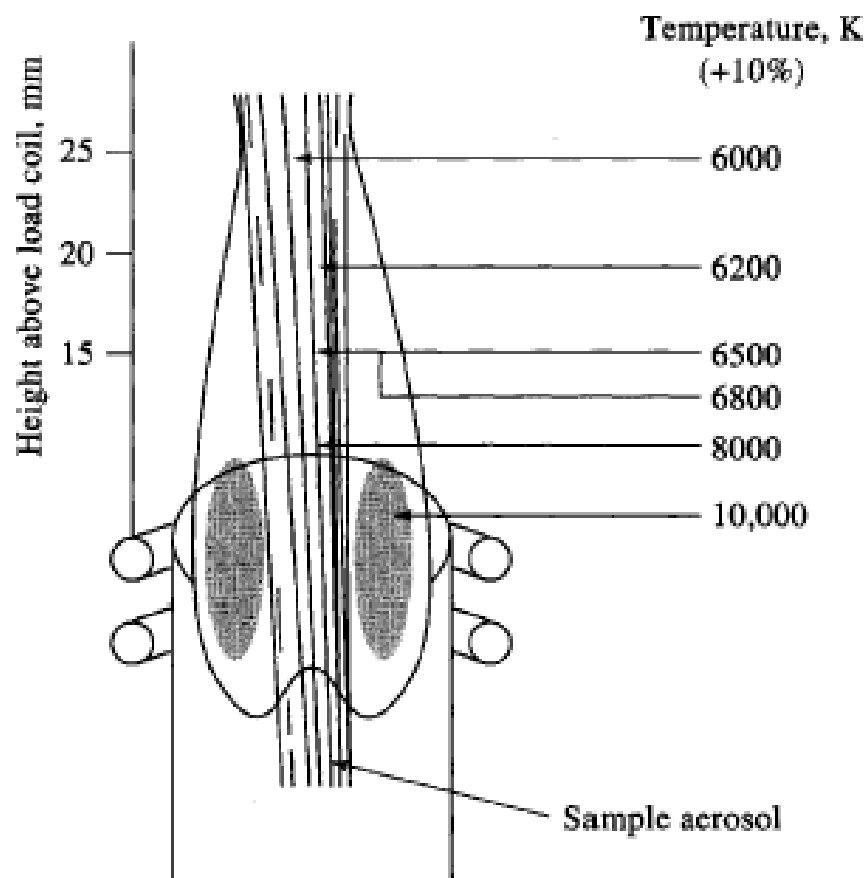
- The field is produced by applying an RF power (typically 700-1500 W) to an antenna (load coil) constructed from 3-mm-diameter copper tubing wrapped in a two- or three-turn 3-cm-diameter coil, positioned around the quartz torch assembly designed to configure and confine the plasma.

- An alternating current field is created that oscillates at the frequency of the tuned RF generator. The plasma is initiated by the addition of a few "seed" electrons, generated from the spark of a Tesla coil or a piezoelectric starter, to the flowing support gas in the vicinity of the load coil

- After the plasma is initiated it is sustained by a process known as inductive coupling. As these seed electrons are accelerated by the electromagnetic RF field, collisions with neutral gas atoms create the ionized medium of the plasma.

- 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

ICP Plasma Structure



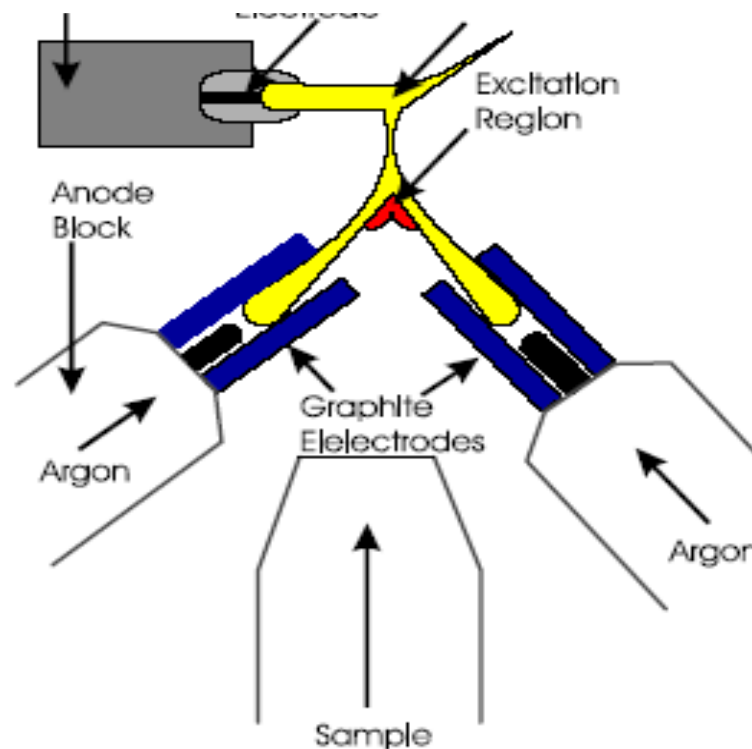
- Brilliant **white core** - Ar continuum and lines
- **Flame-like tail** up to 2 cm
- **Transparent region** - measurements made
- **Hotter than flame** (10,000 K) - more complete atomization/excitation
- **Atomized in "inert" atmosphere**
- **Little ionization** - too many electrons in plasma

2) Direct Current DC-Plasma

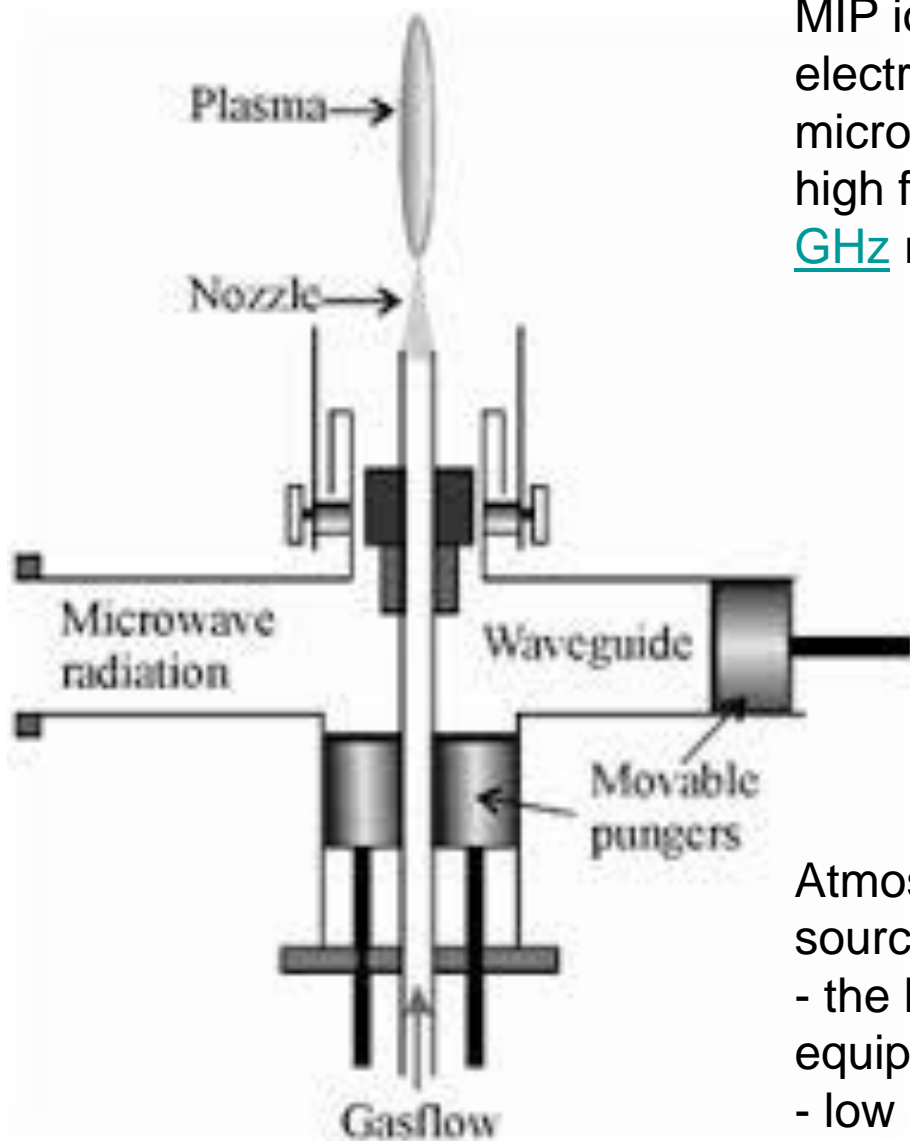
Direct current plasma (DCP) is obtained when a direct current field is established across electrodes,

- 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**

DCP was the first described and commercialized plasma, however, the ICP is currently the most commonly used plasma because of some unique properties.



3) Microwave Induced Plasma, MIP



MIP ion sources are capable of exciting electrodeless gas discharges to create ions. A microwave plasma is a type of [plasma](#), that has high frequency [electromagnetic radiation](#) in the [GHz](#) range.

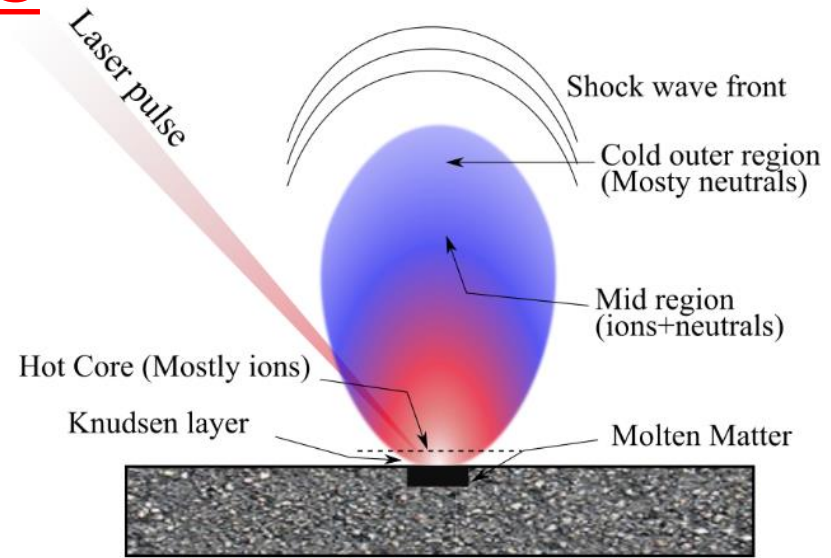


Atmospheric microwave induced plasma, MIP sources have many advantages, such as

- the lack of the necessity for expensive vacuum equipment,
- low cost and simple systems, and
- easy operation.

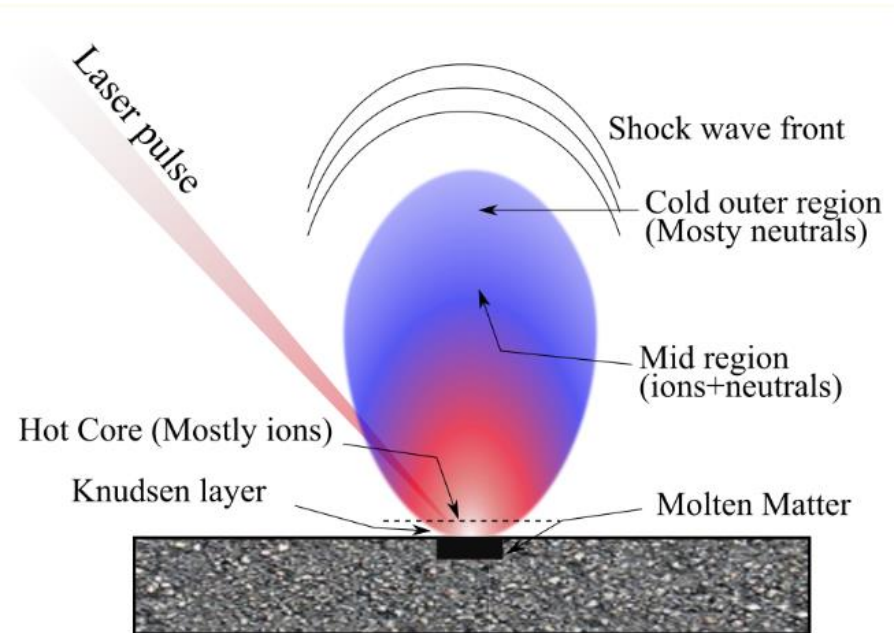
4) Laser Induced Plasma, LIBS

- LIBS is an optical emission technique using a high peak power pulsed laser beam to form a small spark (i.e., breakdown) directly in/on the sample.
- This spark creates a plasma state hot enough to dissociate molecules into their constituent atoms and to excite the electrons in the neutral atoms and ions formed in the plasma out of the ground state and into excited electronic states.



- Near the target surface is the hottest and the densest part of the plasma called the core; in this region, the material is mostly found in the ionized state because of high temperatures.
- Within the core adjacent to the target surface there exists a so-called *Knudsen layer* having a thickness equal to a few mean free paths. *Knudsen layer* is defined as the region in which a particle achieves an equilibrium velocity distribution from non-equilibrium distribution within a few mean-free paths. (*mean free path* is the average distance over which a moving [particle](#) (such as an [atom](#), a [molecule](#), or a [photon](#)) travels before substantially changing its direction or energy, typically as a result of one or more successive [collisions](#) with other particles.

- In the mid-region of plasma, ions and neutrals (atoms + molecules) coexist due to the ongoing ionization and recombination processes.
- The outermost region of the plasma is relatively cold, where the population of neutrals dominates and may absorb the radiations coming out of the core and mid-regions of the plasma.
- Beyond it, there is a shock wave front produced due to the explosive expansion of the plasma, and travels ahead of the plasma plume.
- As the plasma cools, excited electrons and ions relax back into their ground states, emitting light at characteristic atomic wavelengths.
- Material identification is accomplished by detecting the atomic emission using a spectrometer. Concentrations can be determined through relative light intensities.
- Multielemental analysis can be applied to different types of samples and matrices, i.e. gas, solids, liquids



Advantages:

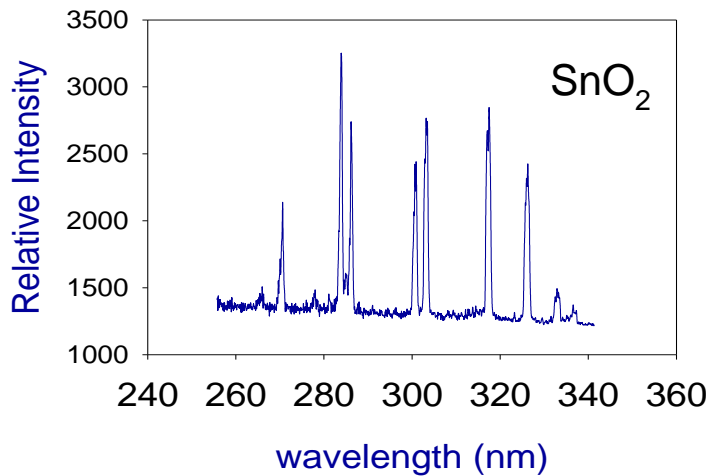
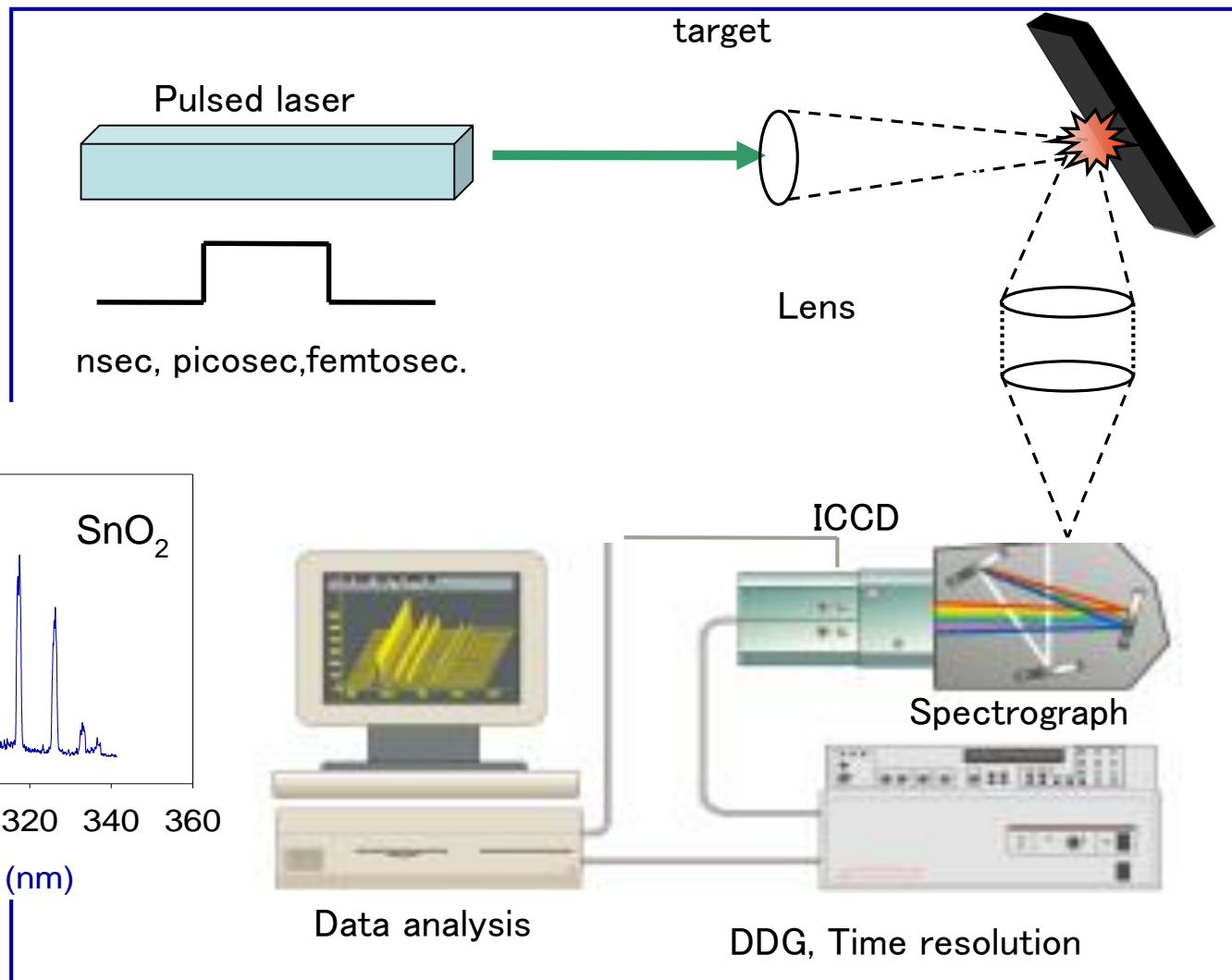
- No or only minor sample preparation is needed
- small amount of material is consumed during the LIBS process; non-destructive
- Spatially and depth-resolved analysis is possible with resolution in the μm range
- LIPS can be used for many process analytical applications for a fast and on-line analysis of various raw materials such as minerals, ores, clays, chalk
- Remote sensing is possible using mirror- or fibre-optical interfaces

LIBS is the only technology that can provide distinct spectral signatures characteristic of all chemical species in all environm

Disadvantages:

- Difficulty in obtaining suitable standards (semi-quantitative)
- Relatively high detection limits (high ppb- low ppm)
- Surface composition can be different than bulk composition
- Variations in laser puls energy, shot to shot variation
- Low analytical performances,
 - The **accuracy** of LIBS measurement is typically better than 10%
 - and **precision** is often better than 5%

Instrumentation



Laser Induced Breakdown Spectroscopy

LIBS Applications:

- Metallurgy (solid or molten metals, alloy composition, process monitoring etc ...)
- Pharmaceutical (active agent, lubricant, in tablets, etc...)
- Mining and mineral industry (detection, mineral composition)
- Microanalysis (by sharp laser focusing composition measurement at the micron scale;
- measurement of composition below the surface: 3D- composition profile
- Recycling (sorting of alloys or various grades...)
- Security: detection of explosives
- Polymers (rubber, pigments, stabilizing additives..)
- Soil contamination
- Papers (pigment distribution, homogeneity)
- Art and archeology
- Biological samples(classification of bacteria: anthrax)

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 MC

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

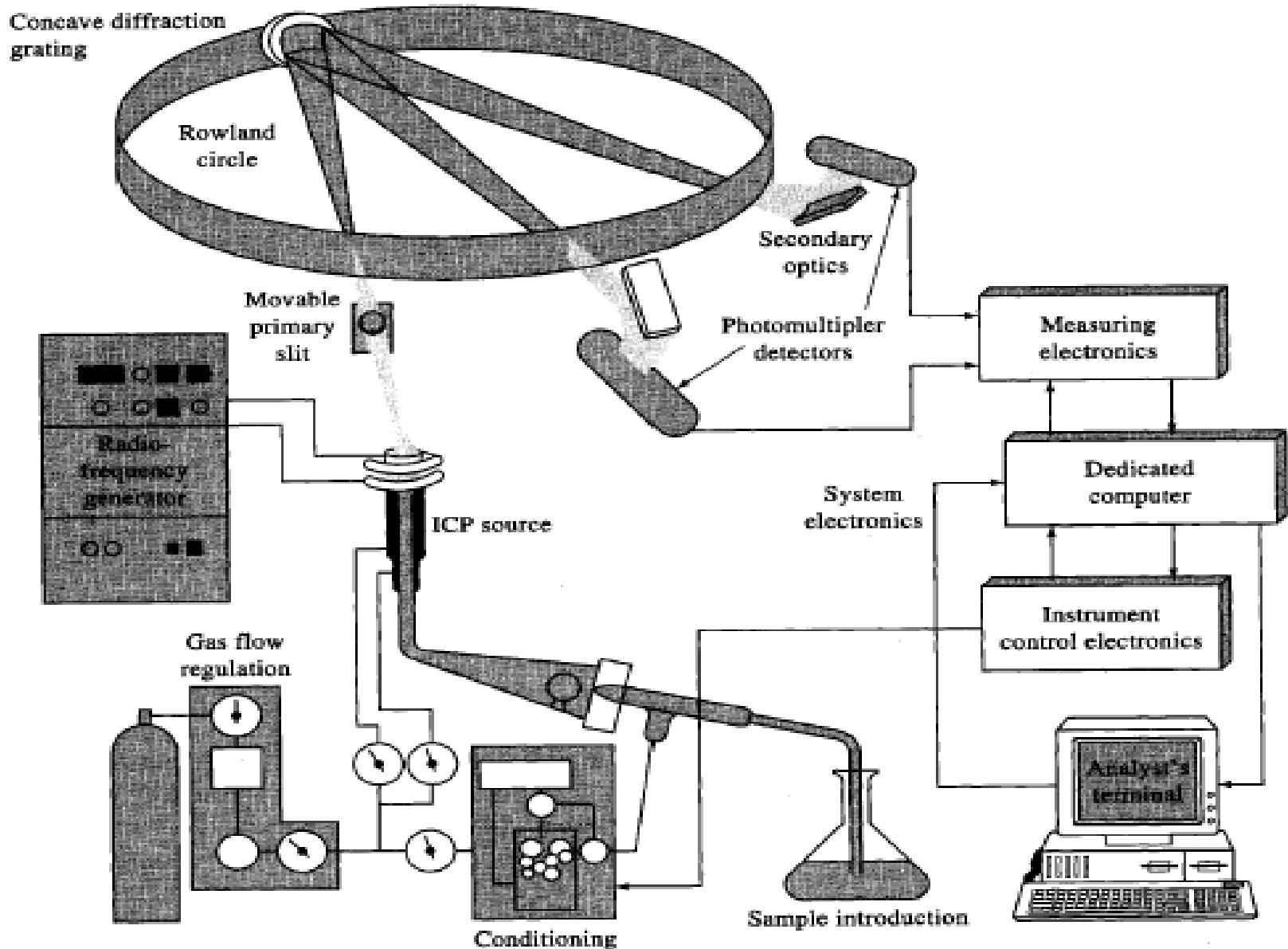
Sequential instrument - PMT moved behind aperture plate, or grating+prism moved to focus new λ on exit slit

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

Multichannel Spectrometers

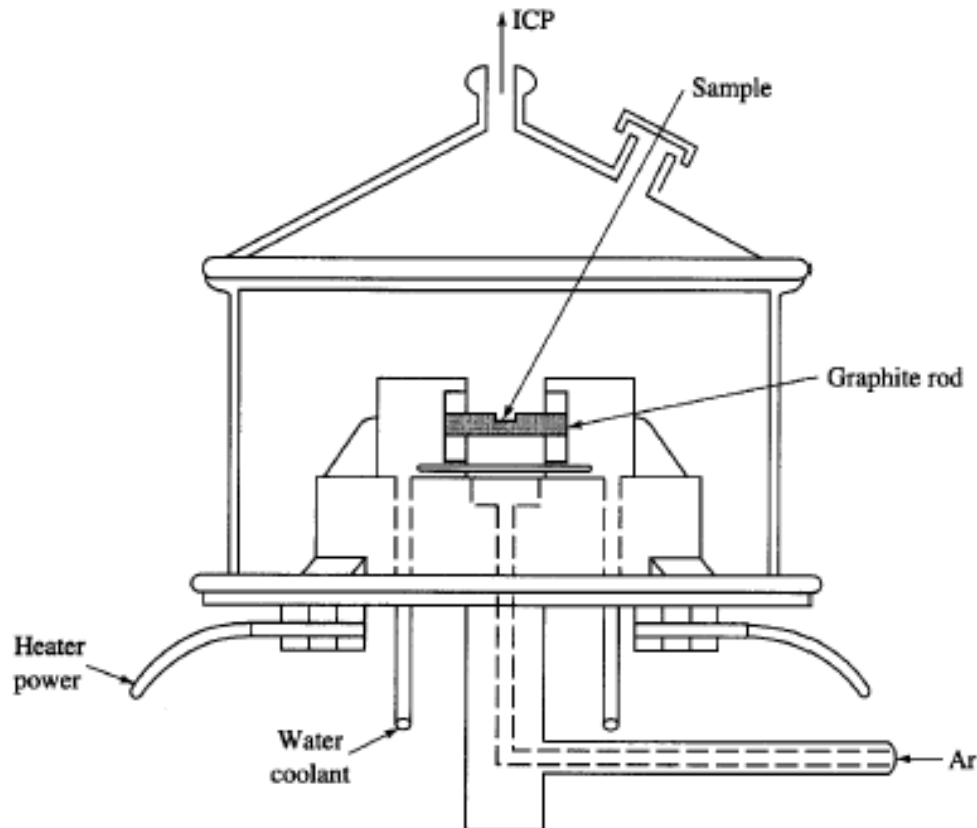
Multichannel instrument - multiple PMT's

- Expensive



Solution Sample Introduction:

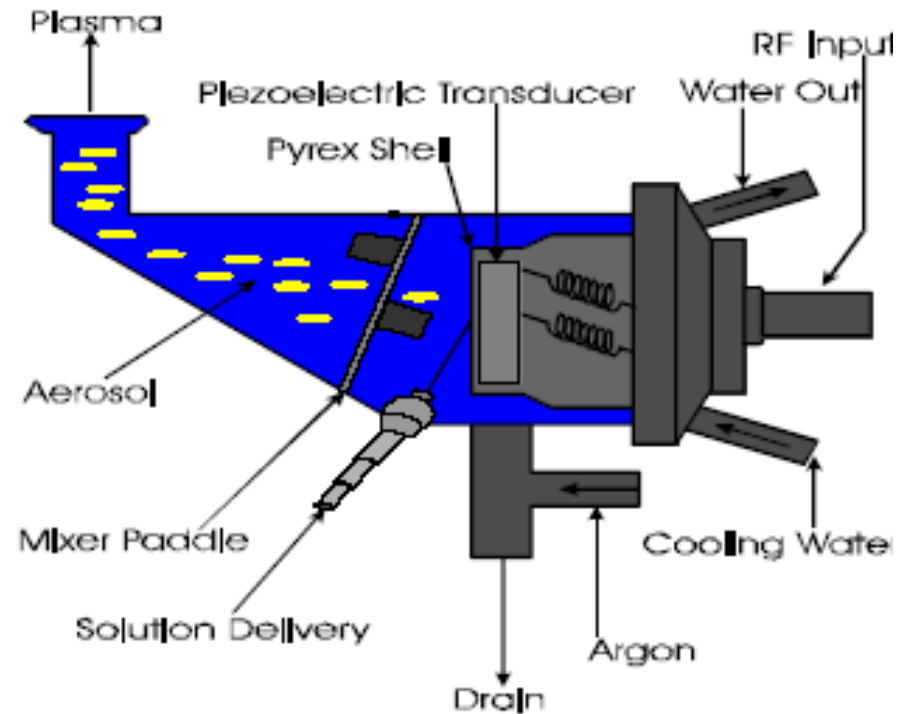
- (1) **Electrothermal vaporizer*** (ETV)
 - electric **current** rapidly heats **crucible containing sample**
 - **sample carried to atomizer** by gas (Ar, He)
 - only for **introduction**, not atomization (Fig 10-3)



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

(a) **Ultrasonic nebulizer**,

- uses ultrasound waves to boil solution flowing across disc.
- The apparatus consists of a piezoelectric crystal transducer, which is driven by an ultrasonic generator operating at a frequency of 200 kHz to 10 MHz.
- Sample is delivered to the front surface of the transducer through tubing from a peristaltic pump at a flow rate of up to 1 mL/min.



(b) Pneumatic nebulizer uses high pressure gas to entrain solution.

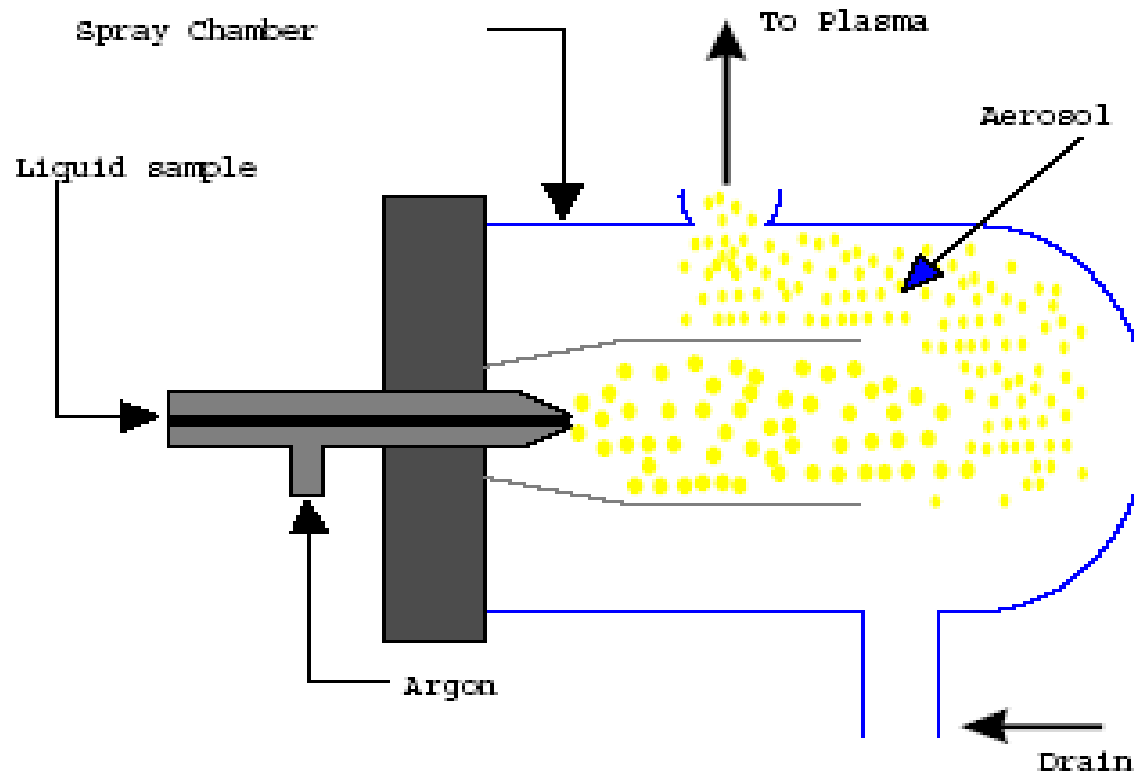
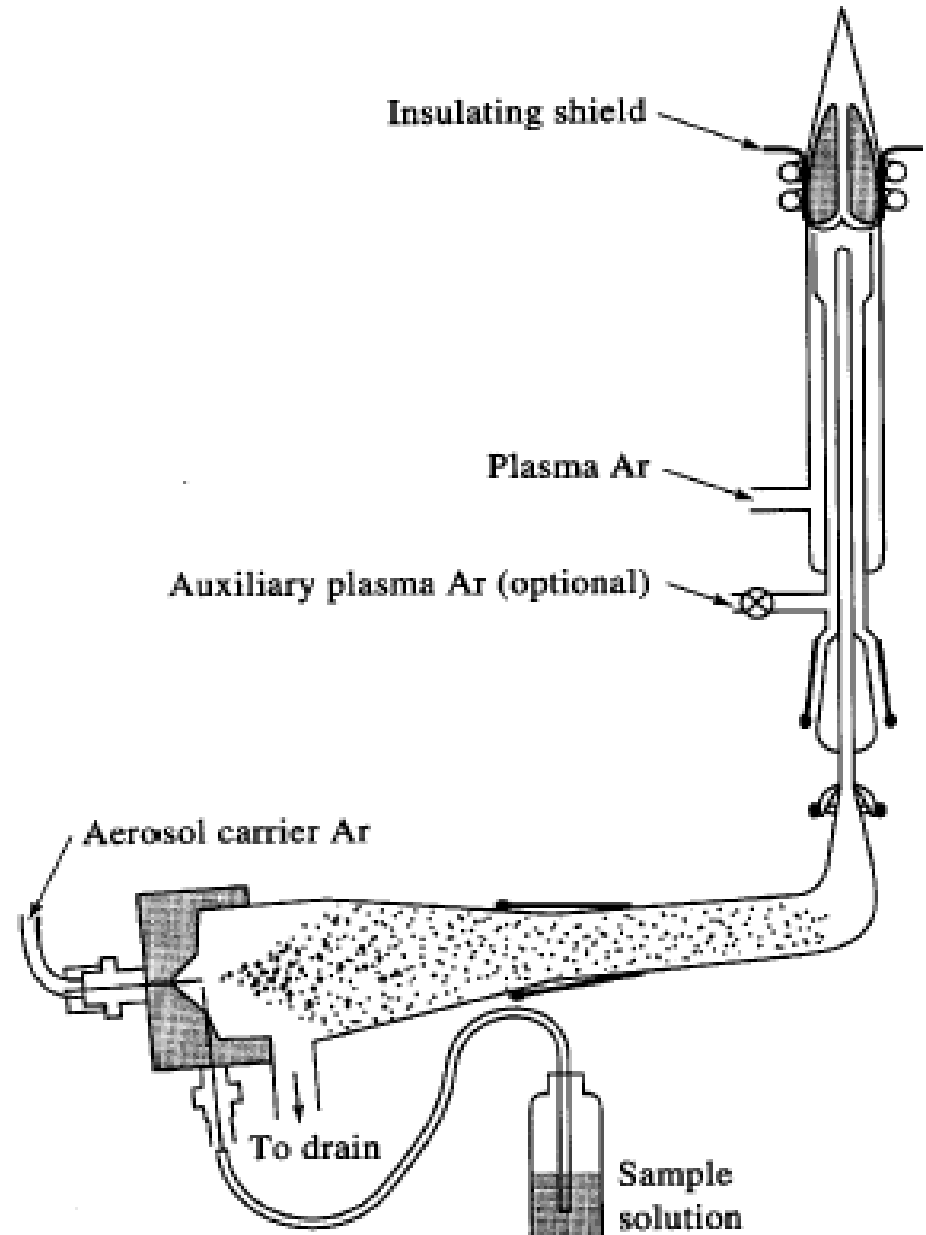


FIGURE 5. A PNEUMATIC NEBULIZER THAT USES THE BERNOULLI EFFECT FOR SAMPLE UPTAKE.

Cross-flow nebulizer

This type of nebulizer consists of two capillary tubes, usually made of glass or quartz, positioned at right angles to each other so that gas flowing through one capillary creates a pressure differential at the tip, which naturally aspirates solution from the other capillary tube at about 3 mL/min.



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

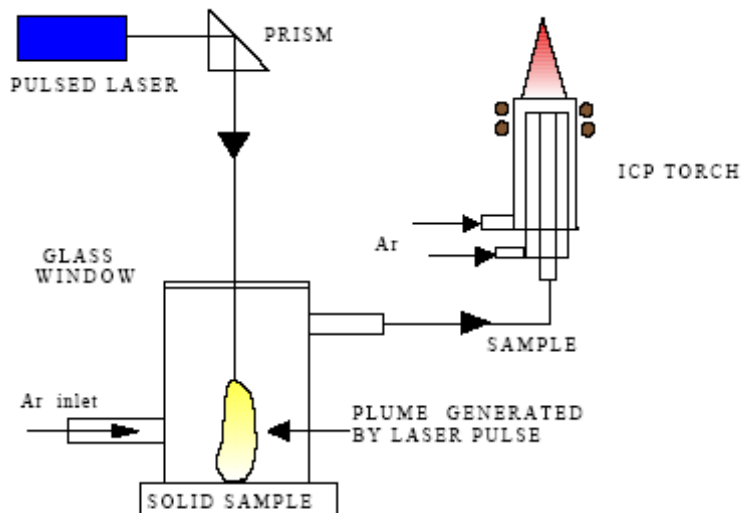


FIGURE 11. SAMPLE INTRODUCTION BY LASER ABLATION.

Applications of AES:

AES relatively **insensitive** (small excited state population at 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

Characterization of the Detection Power of ICP-AES

Detection limit (ng/mL)

Number of lines



H																			He
Li	Be											B	C	N	O	F			Ne
Na	Mg											Al	Si	P	S	Cl			Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br			Kr
Rb	Sr	Y	Zr	Nb	Mu	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At			Rn
Fr	Ra	Ac**																	

*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Dispersion and Detection Methods

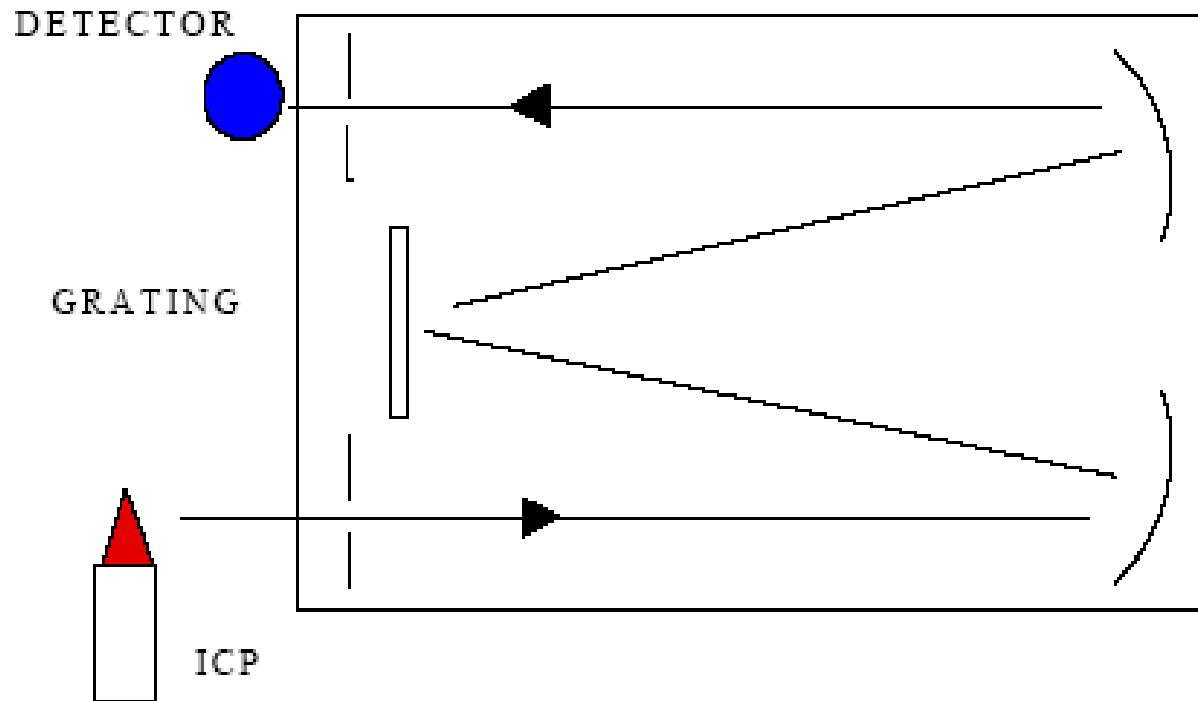


FIGURE 12. A MONOCHROMATOR FOR SEQUENTIAL ANALYSIS OF RADIATION.

Since the atomic emission lines are very narrow, a high-resolution [polychromator](#) is needed to selectively monitor each emission line.

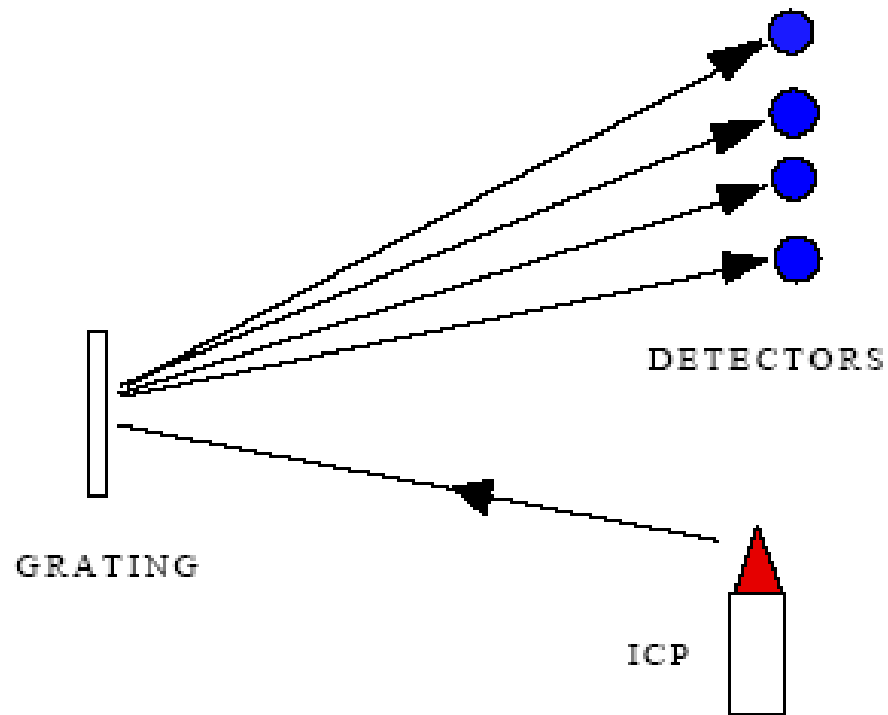


FIGURE 13. A POLYCHROMATOR FOR SIMULTANEOUS ANALYSIS OF RADIATION.

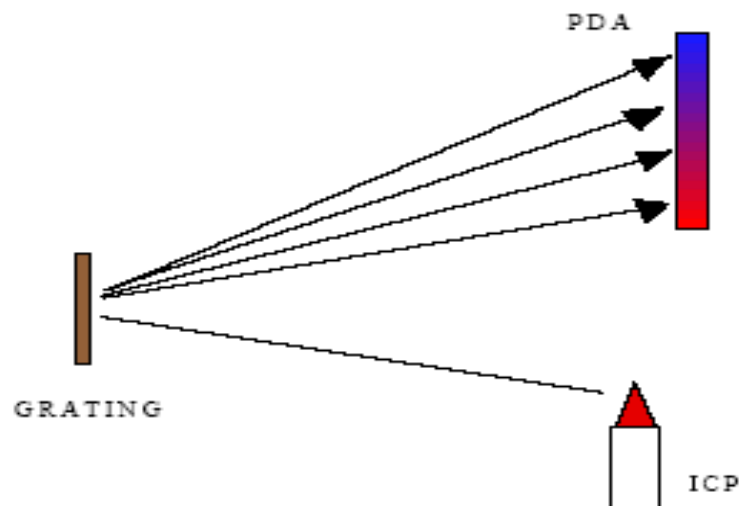


FIGURE 14. A PHOTODIODE ARRAY FOR SIMULTANEOUS ANALYSIS OF RADIATION.

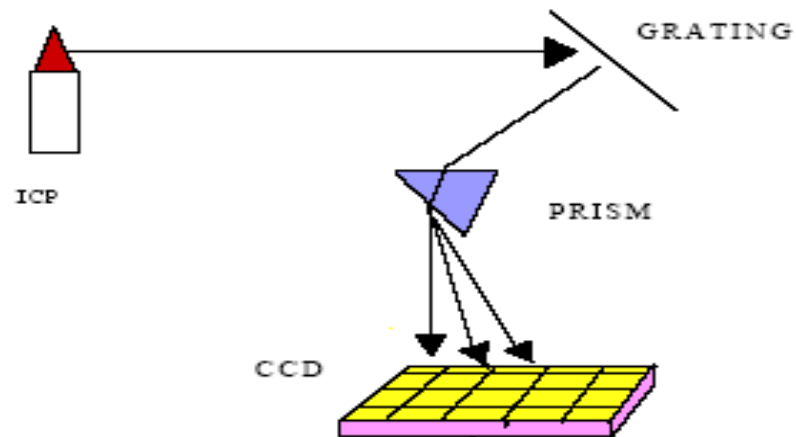


FIGURE 15. TWO-DIMENSIONAL DISPERSION AND DETECTION OF RADIATION USING A CHARGE-COUPLED DEVICE (CCD).

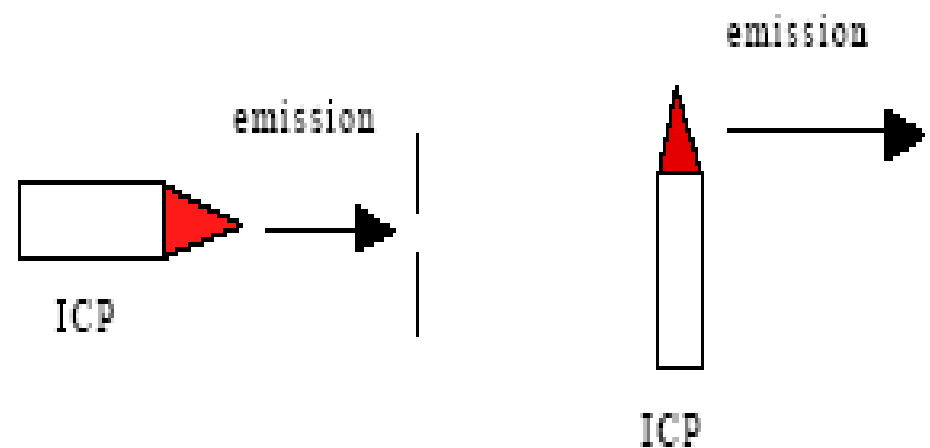


FIGURE 16. ICP TORCH POSITIONS INCLUDE A HORIZONTAL MOUNT (LEFT) AND THE MORE TRADITIONAL VERTICAL MOUNT (RIGHT).

