

# Atomic Absorption Spectroscopy

Spectroscopy is **study of responses** when matter is exposed to various types of radiations

**Atomic Spectroscopy:** Study of interaction of electromagnetic radiation with Atomic species

Atomic Absorption Spectroscopy

Atomic Emission spectroscopy

**Molecular Spectroscopy:** Study of interaction of electromagnetic radiation with molecular species

Molecular Absorption Spectroscopy

U.V/ Visible

IR

NMR

Molecular Emission Spectroscopy(FES)

Fluorimetry

# Atomic Absorption Spectroscopy

- In 1802 phenomenon of Atomic absorption spectroscopy first observed by Woolaston.
- In 1953 Alan Walsh showed that AAS can be used as an analytical tool.
- In atomic absorption spectroscopy measurement of unexcited (ground state) atoms is done by flame method.
- AAS is the most powerful technique of analysis of trace elements.
- Approximately 70 elements can be analyzed by AAS.
- Determination of single element in presence of other elements is possible (no need of their separation)

# Atomic Absorption Spectroscopy

## **Advantages of AAS:**

- 1) High sensitivity
- 2) Can detect approximately 70 elements
- 3) Detection limit is 20 microgram/ml
- 4) Sample required is very small
- 5) Technique is rapid

## **Disadvantages of AAS:**

- 1) Trained person (Expert) is required for analysis
- 2) Instrument is costly

# Atomic Absorption Spectroscopy

## Principle:

In AAS, measurement of unexcited atoms is done by flame method. The ground state atoms in gaseous state absorb energy and excited from ground state to excited state.

When ground state atoms absorb energy, they change their position from lower energy to higher energy and electronic transition of valence electron takes place, this gives rise to narrow lines called as atomic absorption spectra.

When solution containing metal salt /metallic compound is aspirated into the flame, it undergoes vaporization and gaseous atoms are formed. Some atoms gain energy and get excited while large number of atoms remain in ground state.(unexcited)

# Atomic Absorption Spectroscopy

Principle:

In AAS, measurement of unexcited (Ground state) atoms is done by flame method.

When solution containing metal salt /metallic compound is aspirated in to the flame, it undergoes vaporization and gaseous atoms are formed. Some atoms gain energy and get excited while large number of atoms remain in ground state.(unexcited)

# Atomic Absorption Spectroscopy

Ground state atoms are capable of absorbing radiant energy at their resonance wavelength.

When radiation passed through the flame having gaseous state atoms, then part of radiation is absorbed by these atoms.

Extent of absorption is proportional to the number of ground state atom present in the flame.

Total amount of radiation absorbed is given by

$$\nu = \frac{\pi e^2}{m \cdot C} \cdot N f$$

m = mass of electron

C= velocity of light

N= Total number of atoms

$\nu$  =Frequency absorbed by the atoms

e= charge on electron

f= oscillator strength

# Atomic Absorption Spectroscopy

## Comparison between AAS and FES

### Advantages of AAS over FES

- 1) Spectral hindrance is very rare in AAS which is common in FES
- 2) AAS is not affected by temperature
- 3) FES is more sensitive for Al, Ba, Ca, Ho, In, K and Ln, whereas heavy metals are effectively detected by AAS.
- 4) AAS is very rapid technique and concentration less than 1 ppm can be determined by AAS.

# Atomic Absorption Spectroscopy

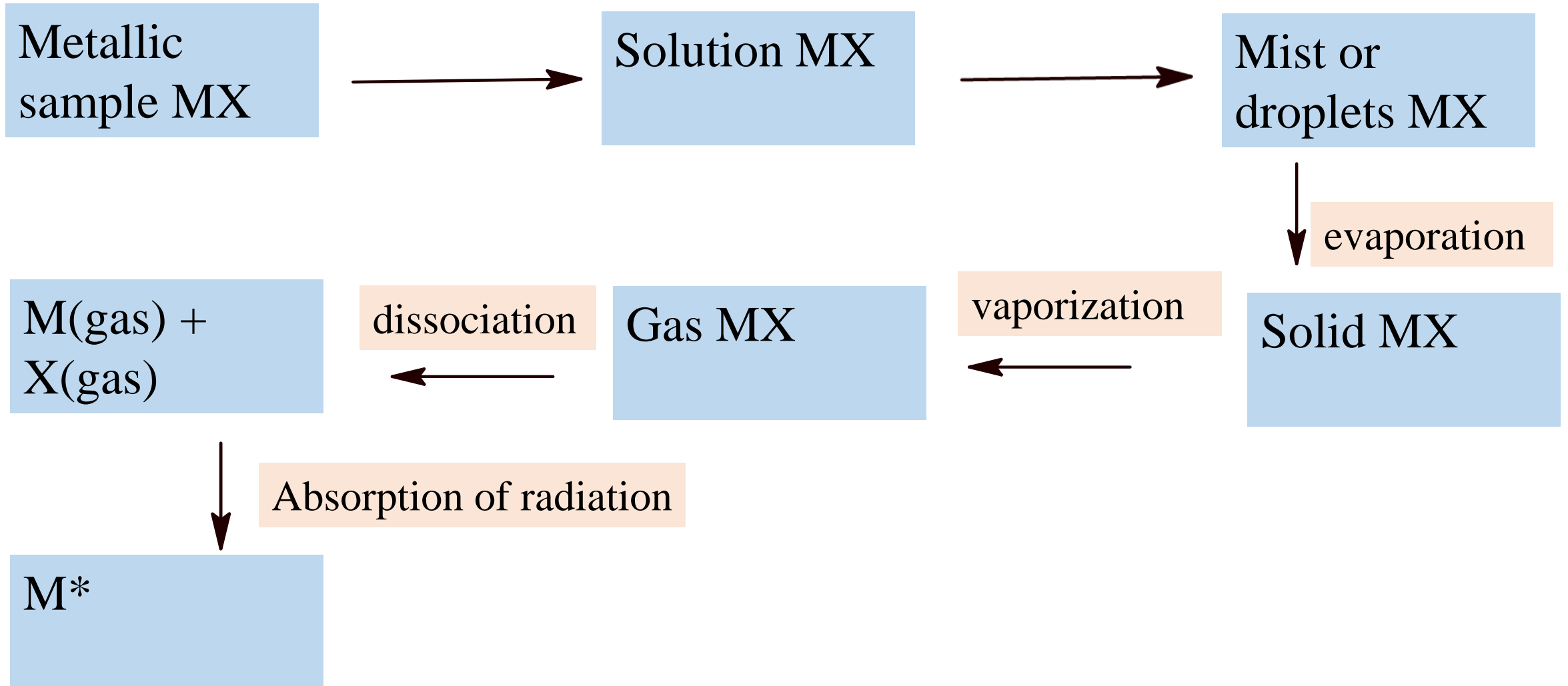
## Disadvantages of AAS

- 1) Different hollow cathode lamps are required for different elements. Thus scope of AAS is limited.
- 2) The elements which form oxide on heating are not effectively estimated by AAS.( Al, W, Mo, Ti, Si, V etc.)
- 3) Sample required is in liquid form.
- 4) Common anions (Chloride, sulphate, carbonate) affect the efficiency of analysis.
- 5) Metal solution in organic solvent is preferred over aqueous solution.



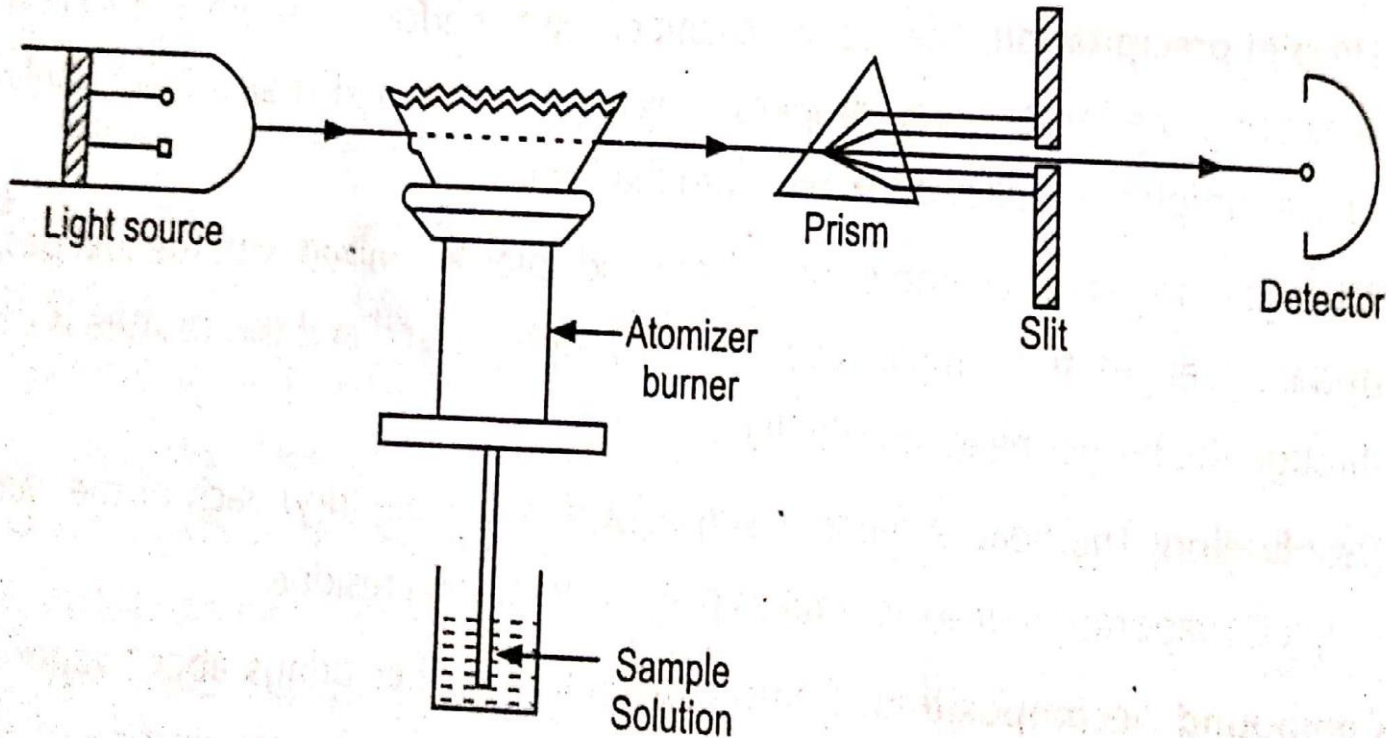
# Atomic Absorption Spectroscopy

## AAS Process



# Atomic Absorption Spectroscopy

## Instrumentation:

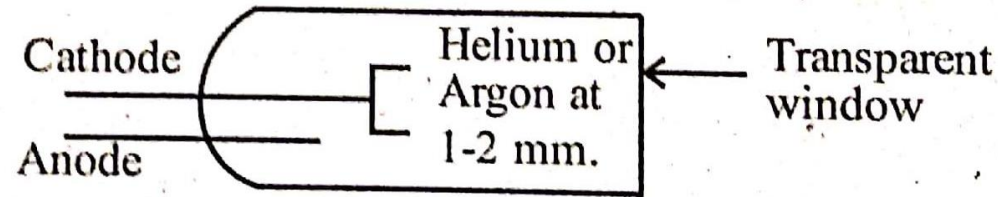


- 1) Radiation source
- 2) Chopper
- 3) Atomizers
- 4) Nebuliser
- 5) Monochromator
- 6) Detector
- 7) Amplifier
- 8) Read out device

# Atomic Absorption Spectroscopy

## Instrumentation:

**1) Hallow cathode lamp:** It is used as a source of intense narrow electromagnetic radiation.



## Construction:-

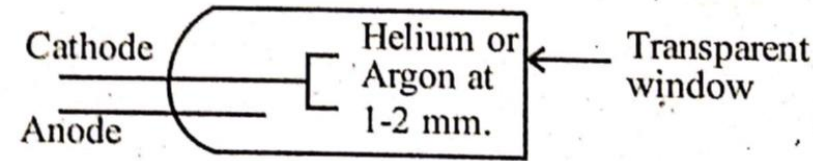
- Hallow cathode lamp consists of two electrodes i.e. anode and cathode.
- Anode is made up of tungsten, nickel or zinc metal ,while cathode is hallow cylinder made up of metal to be analysed.
- Both electrodes are enclosed in glass cylinder containing inert gas like Argon, Neon etc.
- At the end of hallow cathode lamp there is small window made up of quartz ,Silica or glass for transfer of radiation.

# Atomic Absorption Spectroscopy

## Instrumentation:

### 1) Hollow cathode lamp:

#### Working :-

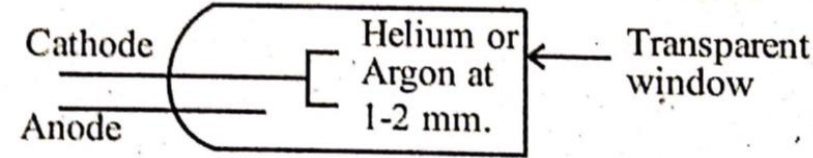


- High potential ( 200 to 600 V ) is applied across the electrodes.
- Due to this ionization of inert gas take place and ions are produced. positive ions are attracted towards negative electrode (Cathode) and strike on the surface of cathode. As a result of this atoms from the surface of the cathode are ejected, this process is called as **sputtering**.
- These gaseous atoms absorb energy by colliding with cations of inert gas and goes to excited state and return to ground state by emitting energy. This radiation is used for further analysis

# Atomic Absorption Spectroscopy

## Instrumentation:

### 1) Hollow cathode lamp:



### Life of Hollow Cathode lamp

Life depends on the current used during operation, Average life time of HCL is two years.

### Multi Element Lamp:

By combining two or more elements for preparation of cathode, it is possible to produce multi elemental HCL

# Atomic Absorption Spectroscopy

## Instrumentation:

### 2) Copper:

A rotating wheel placed in between Hollow cathode lamp and the flame is known as chopper. Function of chopper is to break the steady light from HCL in to intermittent light. This gives alternating current in photocell.

### 3) Atomizer:

Atomizer convert sample solution in to atomic vapour.

Important functions of flame

- 1) To evaporate solvent
- 2) To dissociate sample in to molecule
- 3) To provide ground state atoms for analysis

Temperature of flame is kept low, because at high temperature ionization of atoms take place which do not show absorption

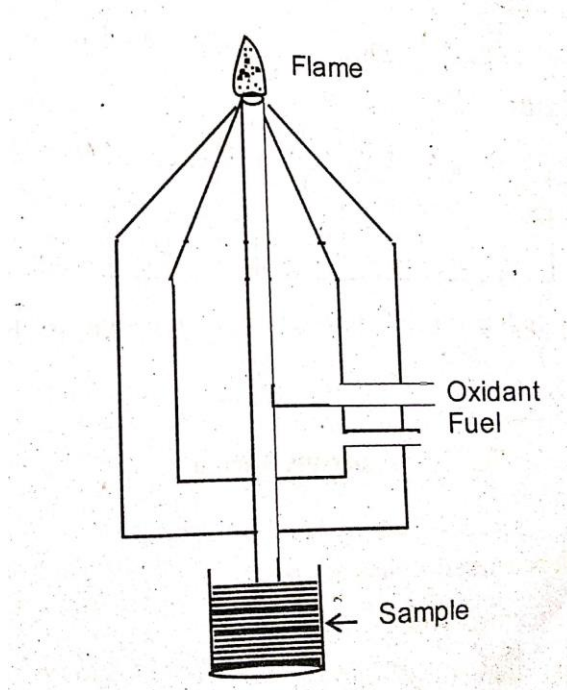
# Atomic Absorption Spectroscopy

## Instrumentation:

### 3) Atomizer:

#### Types of Burners

#### 1) Total consumption burner:



Sample solution, fuel gas and oxidising gas are passed through separate inlet and mixed at the top of the flame.

Sample solution is converted to tiny droplets, which on evaporation form residue and residue finally produce ground state atoms.

#### Advantages:

- 1) High sensitivity
- 2) No risk of explosion

#### Disadvantages:

- 1) Clogging is possible
- 2) Poor reproducibility
- 3) Noisy operation
- 4) Rate of sample introduction depends on viscosity of solution

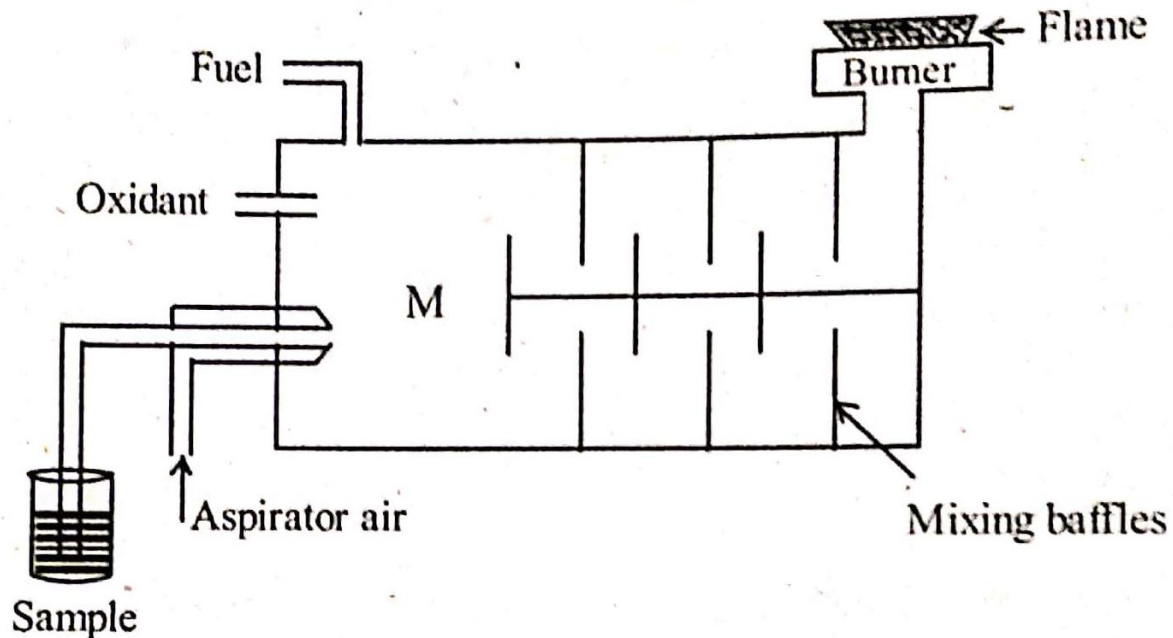
# Atomic Absorption Spectroscopy

## Instrumentation:

### 3) Atomizer:

Types of Burners

### 2) Laminar flow /Premix burner:



Sample solution, fuel gas and oxidising gas are mixed in mixing chamber

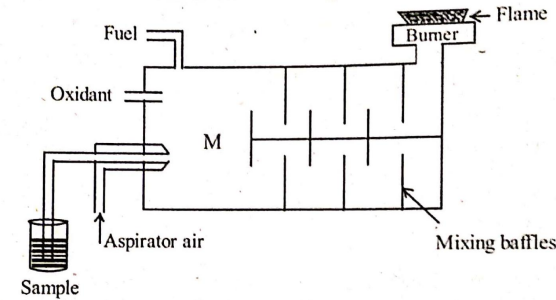
This mixture is then passed through a series of baffles where thorough mixing and formation of uniform droplets of the sample take place.



# Atomic Absorption Spectroscopy

## Instrumentation:

### 2) Laminar flow /Premix burner:



## Advantages:

- 1) Atomization efficiency is high as droplets are finer
- 2) Sensitivity is very high due to mixing baffles.
- 3) Good reproducibility
- 4) Little tendency to clog
- 5) No noisy operation

## Disadvantages:

- 1) Rate of sample introduction is slow
- 2) Possibility of explosion in mixing chamber.
- 3) Selective evaporation of mixed solvent can lead to analytical errors.

# Atomic Absorption Spectroscopy

## Instrumentation:

Total consumption burner	Laminar flow /Premix burner
1) Tiny droplets reach to the flame	1) Uniform sized fine droplets reach to the flame
2) Amount of sample in flame is large, hence less sensitivity	2) Due to Baffle path length is increased and high sensitivity is achieved
3) No risk of explosion	3) Possibility of explosion in mixing chamber
4) Clogging is possible.	4) Little tendency to clog

# Atomic Absorption Spectroscopy

## Instrumentation:

### Types of Flames

#### Fuel / Oxidant

#### Temperature

acetylene / air

2100 °C – 2400 °C (most common)

acetylene / N<sub>2</sub>O

2600 °C – 2800 °C

acetylene / O<sub>2</sub>

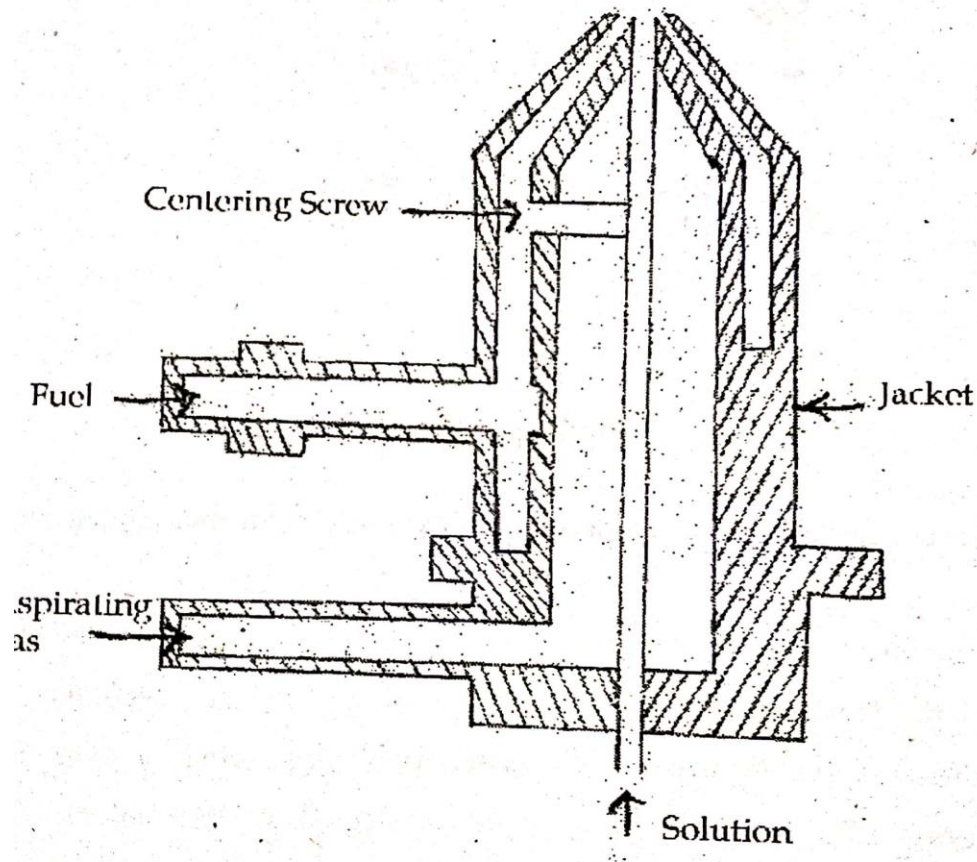
3050 °C – 3150 °C

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

# Atomic Absorption Spectroscopy

## Instrumentation:

### 4) Nebulizer:



In nebulization sample is converted into a fine mist or droplets using a jet of compressed gas.

The flow carries the sample into the atomization region.

- **Pneumatic Nebulizers :**

The liquid sample to be analyzed is sucked by a capillary with high pressure by a gas moving at high velocity.

This process is also called as aspiration. Because of high velocity sample breaks into a fine droplets (mist) and carries it to the atomization region.

# Atomic Absorption Spectroscopy

## Instrumentation:

### 5) Monochromator:

Commonly used monochromators in AAS are **prisms and gratings**.

Monochromator select monochromatic light from polychromatic light emitted by a hollow cathode lamp.

#### i) Prism:

It is triangular shape piece of glass or quartz. It work on refraction phenomenon.

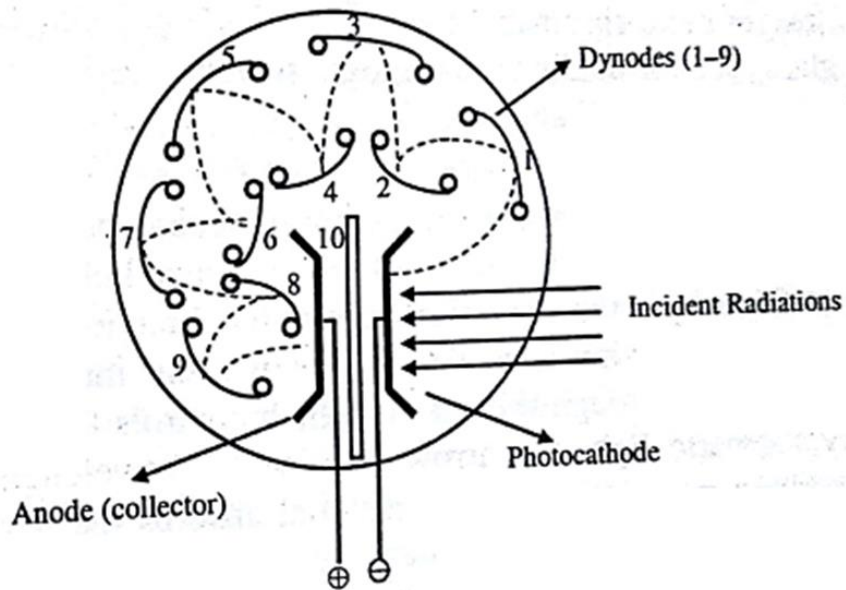
#### ii) Diffraction Grating:

It is dispersing element that can isolate a selected band of wavelength. It is prepared by ruling a large number of parallel equidistance groves upon highly polished metallic surface. Approximately 15,000 to 30,000 groves per square inch are present on diffraction grating, these groves acts as scattering centers.

# Atomic Absorption Spectroscopy

## Instrumentation:

### 6) Detector:



## Photomultiplier tube

### Construction:

It contains a photosensitive half cylinder of metal which acts as a cathode.

The inner surface of the cathode is coated with light sensitive material like  $\text{Cs}_2\text{O}$ ,  $\text{Ag}_2\text{O}$  and  $\text{K}_2\text{O}$ .

It consists of 9 dynodes which have a coating of cesium metal which emits several electrons (2 to 5).

These electrons are collected by the collecting electrode (anode).

# Atomic Absorption Spectroscopy

## Instrumentation:

### 6) Detector:

#### Working:

When light strike on cathode surface, it eject electrons due to photoelectric effect.

These electrons strike on the surface of first dynode and ejection of 2 to 5 electrons take place.

These electrons strike on surface of second dynode and ejection of more electron take place.

This process is continued up to 9<sup>th</sup> dynode. Emitted electrons are collected by collecting electrode and current begin to flow. This current is amplified and measured by read out device.

#### Advantages:

- 1) It is very fast (response time is  $10^{-9}$  second)
- 2) High sensitivity for U.V. and visible region.

# Atomic Absorption Spectroscopy

## **Instrumentation:**

### **7) Amplifier:**

It amplifies the current from photomultiplier tube.

### **8) Read out device:**

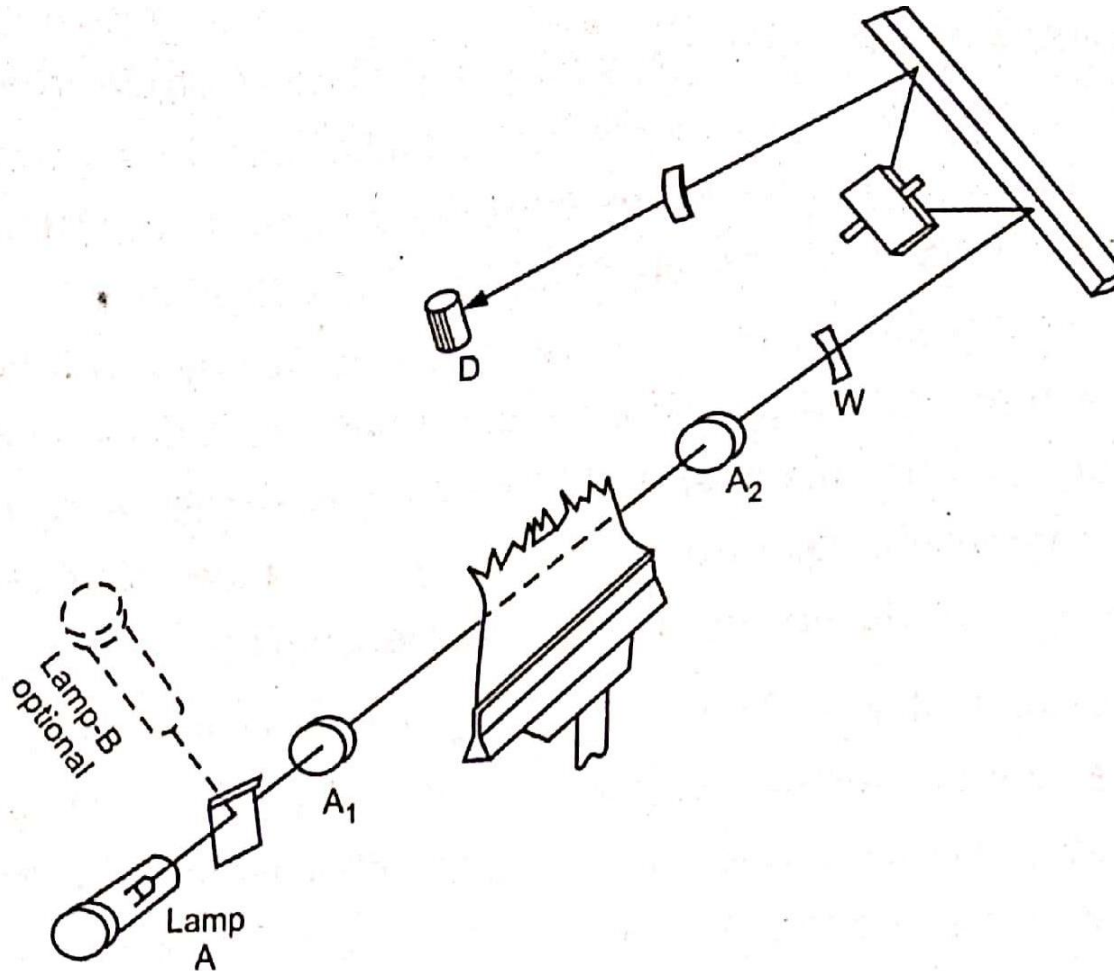
Chart recorder is the most common read out device. Microammeter is the other read out device used in AAS.



# Atomic Absorption Spectroscopy

## Atomic Absorption Spectrophotometer

### Single beam Spectrophotometer



A<sub>1</sub> and A<sub>2</sub> are the lenses located between lamp and monochromator.

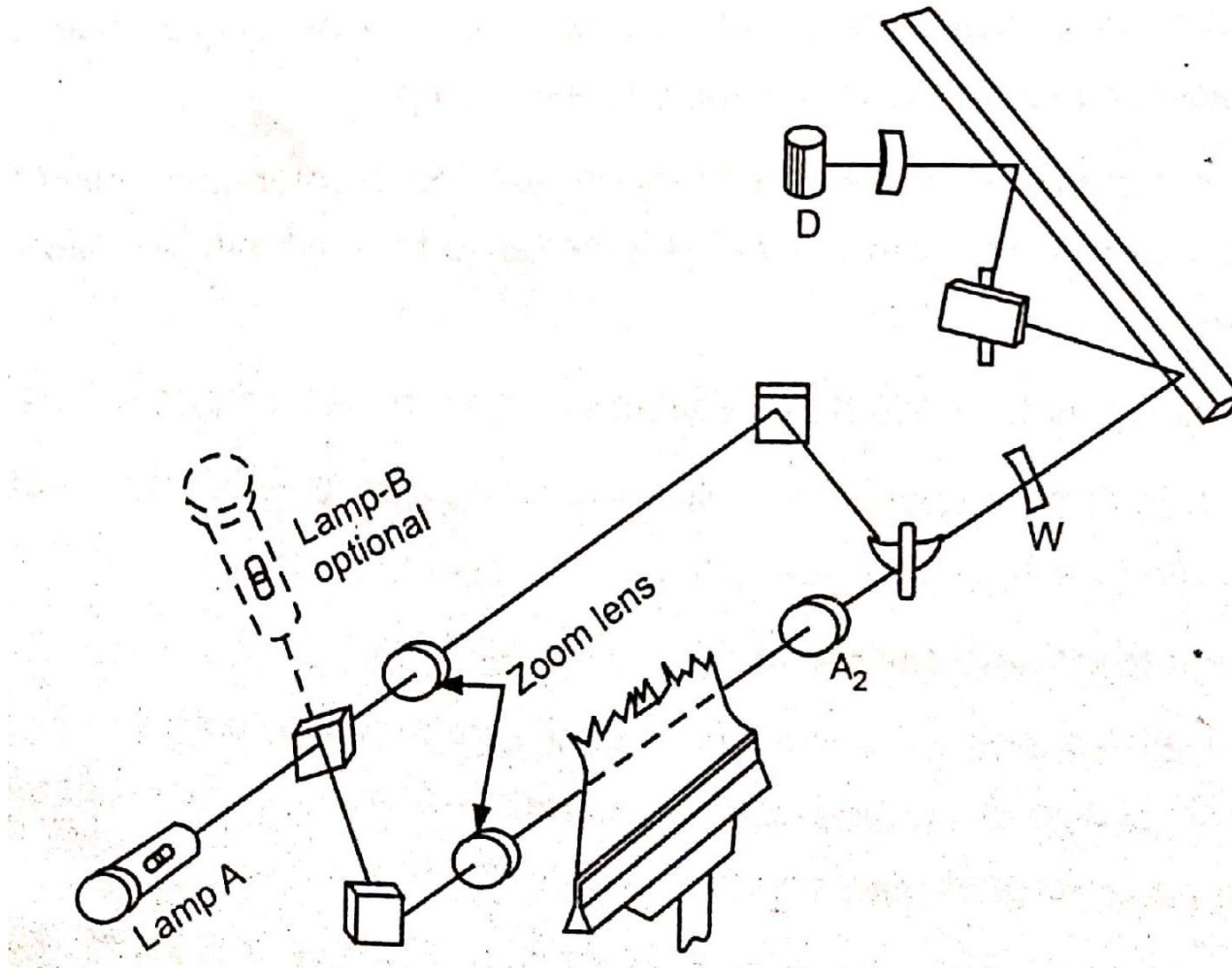
W is wavelength isolation system

B is optional lamp for background correction

# Atomic Absorption Spectroscopy

## Atomic Absorption Spectrophotometer

### Double beam Spectrophotometer



This instrument does not require measurement with blank before use.

Beam of light splits into two parts for the same purpose. One part of beam is passed through the flame while other passes through a reference or standard solution.

#### Advantages:

More accurate detection

No warm up time

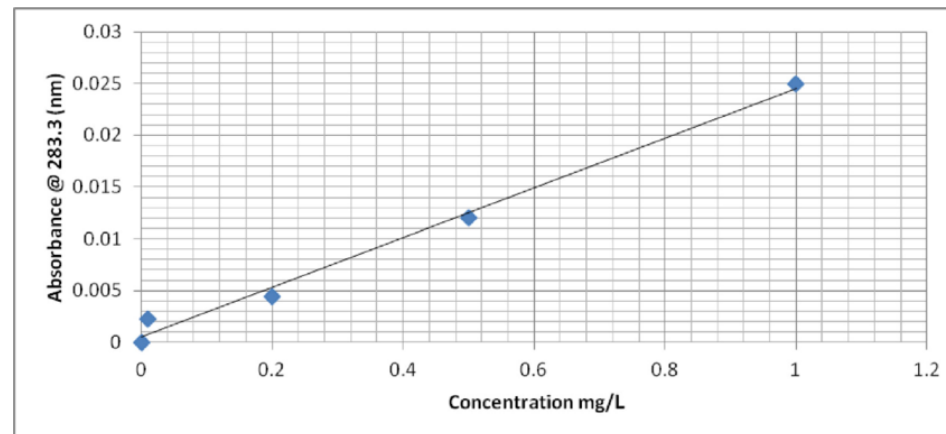
#### Disadvantages:

Cost of instrument is high

# Atomic Absorption Spectroscopy

## Operations of AAS:

- 100 % transmittance or zero absorbance is adjusted by keeping Hollow cathode lamp on,
- Zero transmittance is adjusted by putting Hollow cathode lamp off.
- Standard solutions of element to be analyzed are prepared.
- Absorbance of each standard solution is measured.
- Calibration curve (absorbance vs concentration) is plotted.
- Absorbance of unknown solution is measured and its concentration is find out by using calibration curve.



# Atomic Absorption Spectroscopy

## Sensitivity and detection limit:

**Sensitivity** is defined as the analyte concentration in microgram per milliliter at which absorption is 1% or 0.0044 absorbance unit.

$$\text{Concentration of standard} = \frac{A \times S}{0.0044}$$

A= Absorbance required

S= Sensitivity of an element.

$$\text{Sensitivity} = \frac{\text{Concentration of standard} \times 0.0044}{\text{Measured absorbance}}$$

**Detection limit :** It is defined as concentration in microgram per milliliter that result in the shifting of the absorbance signal to a value which is equal to peak to peak noise of base line.

# Atomic Absorption Spectroscopy

## Interferences in AAS:

### Interference :

Any process which causes error in determination is called interference.

**Interferent** is the substance present in the sample, blank or standard solution which affects the signal of the analyte.

### 1) Chemical Interference:

Because of formation of stable compound which cannot undergo decomposed at flame temperature.

Example Aluminum and magnesium form a thermally stable mixed oxide, thus low results are obtained for magnesium in presence of aluminum..

Chemical interference affect the number of free atoms reaching to the optical path to be absorbed. Precipitation, viscosity ,surface tension and pH are some factors which causes chemical interference.

# Atomic Absorption Spectroscopy

## Interferences in AAS:

### 2) Spectral Interference:

When spectral lines overlap with each other then this kind of interference is observed.

Absorption or emission of an interfering species either overlaps or lies so close to the analyte band that resolution by the monochromator become difficult. In AAS spectral interference is rare.

Element	Wavelength	Interferent	Wavelength
Al	308.33	V	308.21
Cu	324.44	Eu	324.76
Fe	271.90	Pt	271.90
Ga	403.30	Mn	403.31
Hg	253.65	Co	253.65

# Atomic Absorption Spectroscopy

## Interferences in AAS:

### 3) Ionization Interference:

Due to high flame temperature (air -acetylene or nitrous acid-acetylene) ionization of atoms take place.

Atoms with low ionization potential undergo ionization and reduce the population of ground state atom and excited state atoms.

To overcome this effect easily ionizable elements such as K, Na, Cs are added to the sample ( 1000 microgram/ liter)

Due to easily ionizable atoms large number of electrons are produced which suppressed the ionization of analyte atoms.

# Atomic Absorption Spectroscopy

## Interferences in AAS:

### 4) Background Absorption :

It is caused by absorption of the species other than the atoms at resonance wavelength.

This is observed due to scattering of light due to small, un-volatilized particles present in the flame.

It is wavelength dependent phenomenon and gives a positive error in the analysis.

It can be minimized by using Deuterium arc background correction (continuum source)



# Atomic Absorption Spectroscopy

## Applications of AAS:

### Qualitative Analysis:

Different hollow cathode lamp is required for different element. ( It is able to detect only element whose hollow cathode lamp is used) hence scope of AAS in qualitative analysis is limited.

### Quantitative Analysis:

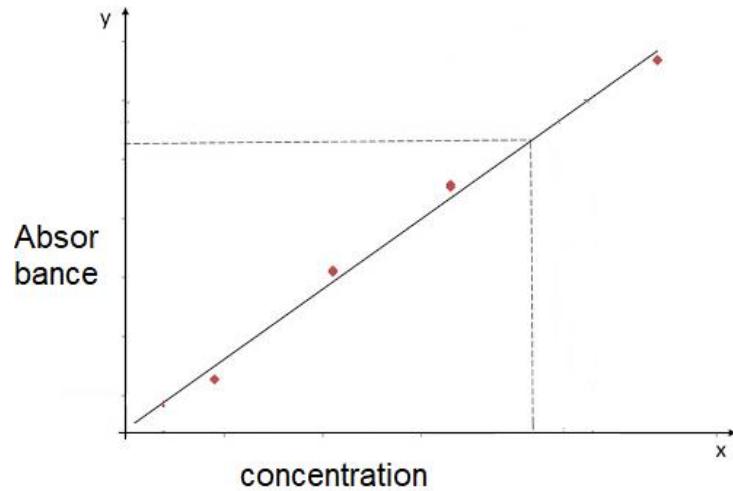
A.A.S is the powerful technique for the quantitative analysis of trace metals.

#### 1) Concentration of unknown sample:

- 100 % transmittance or zero absorbance is adjusted by keeping Hollow cathode lamp on,
- Standard solutions of element to be analyzed are prepared.
- Absorbance of each standard solution is measured.
- Calibration curve (absorbance vs concentration) is plotted.

# Atomic Absorption Spectroscopy

## Applications of AAS:



Slope of calibration line is obtained and it is used in below equation to find out unknown concentration.

$$A = m.C.$$

A= Absorbance of unknown

M= slope

C= concentration

Absorbance of unknown solution can also measured by using calibration curve.(Se

# Atomic Absorption Spectroscopy

## Applications of AAS:

### Qualitative Analysis:

#### 2) Simultaneous multicomponent analysis:

By using multicomponent hollow cathode lamp, elements like Zn, Cd, Ni, Ca, Fe, Mn, Cu and Mg can be detected in spectral region 232 to 328 nm.

#### 3) Analysis of biological material and food material:

Trace metals from biological system, Ni from vegetable oil, Cu from beer, Na and K from blood serum can be analyzed by AAS. It is also used to find out impurities present in food material.

#### 4) Determination of lead in petrol:

Tetra ethyl lead ( $(\text{C}_2\text{H}_5)_4\text{Pb}$ ) and tetramethyl lead ( $(\text{CH}_3)_4\text{Pb}$ ) are two anti knocking agents used in petrol. ( antiknock agent is an additive used for reducing engine knocking property and to increase fuel's octane rating.)

# Atomic Absorption Spectroscopy

## Applications of AAS:

### Qualitative Analysis:

#### 4) Determination of lead in petrol:

##### a) Direct method:

Absorbance of standard solution and sample solution is measured at 283.3 nm. Calibration curve is plotted and concentration of lead in petrol is determined.

##### b) Indirect method:

Standard solutions of lead containing 50,25,10,5  $\mu\text{g/mL}$  are prepared by using deionized water .

Absorbance is recorded at 283.3 nm.

Unknown sample is treated with  $\text{Br}_2$  and Pb is converted to  $\text{PbBr}_2$ ,

It is extracted in dil.  $\text{HNO}_3$  and absorbance is recorded.

Concentration is measured by using below equation

# Atomic Absorption Spectroscopy

## Applications of AAS:

### Qualitative Analysis:

#### 4) Determination of lead in petrol:

Concentration is measured by using below equation

$$Pb \text{ in } \mu\text{g/mL} = \frac{S_2 - S_1}{S_0 - S_2} \times C \times \frac{1}{10 \times \text{specific gravity of sample}}$$

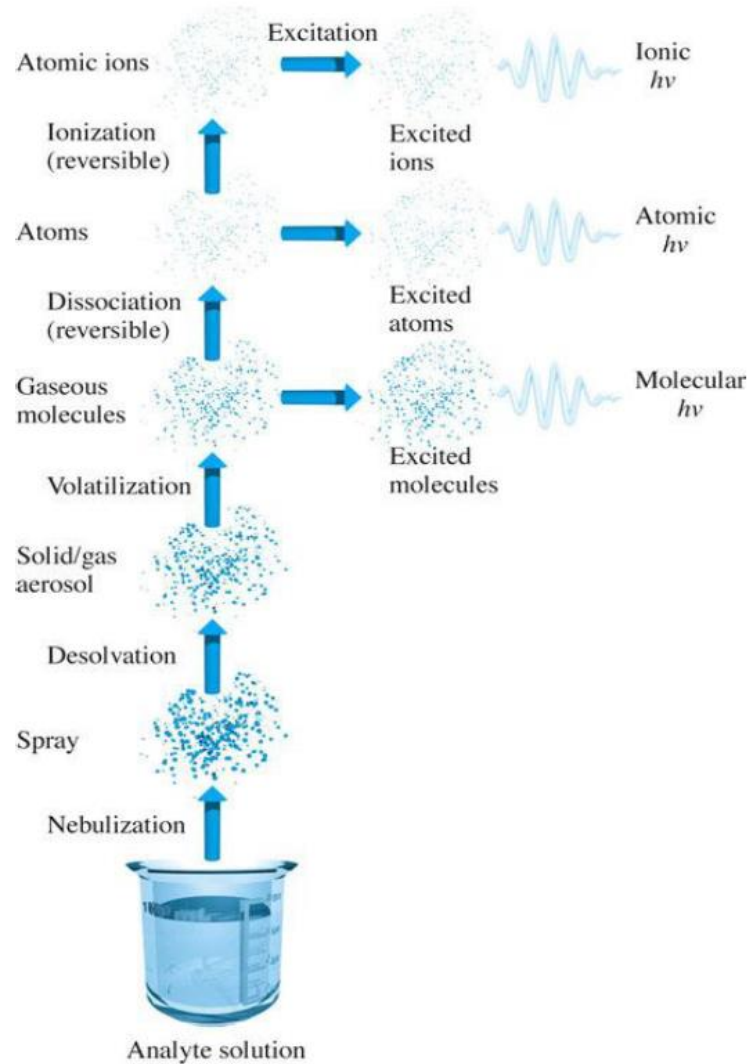
$S_0$  = absorbance for blank (1%  $\text{HNO}_3$ )

$S_1$  = absorbance for unknown solution (sample)

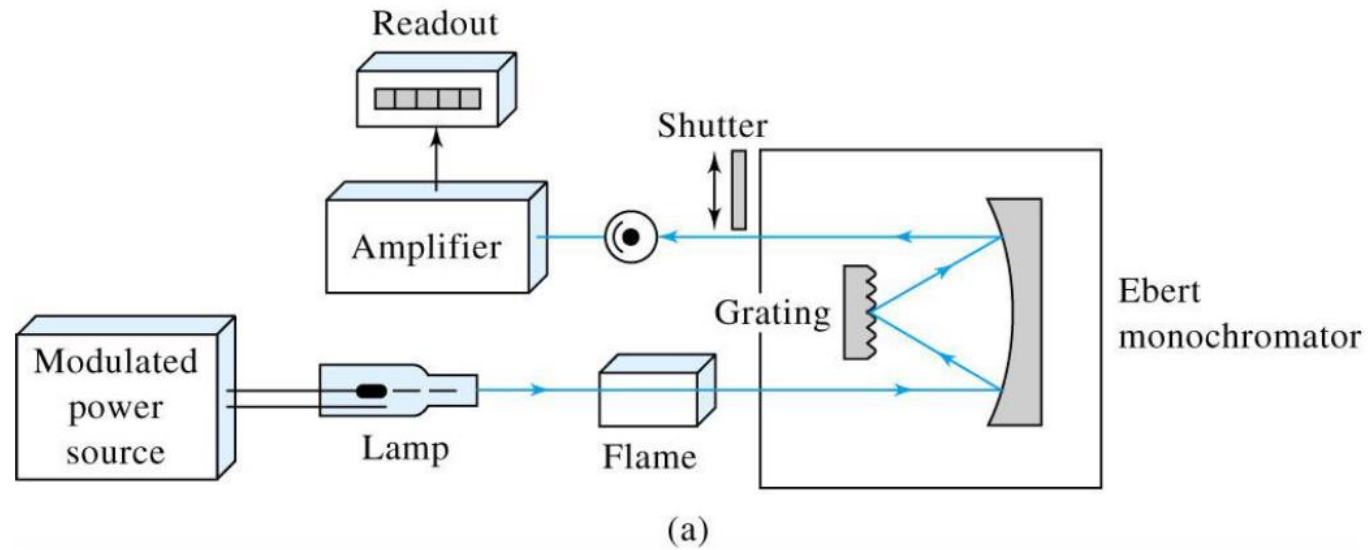
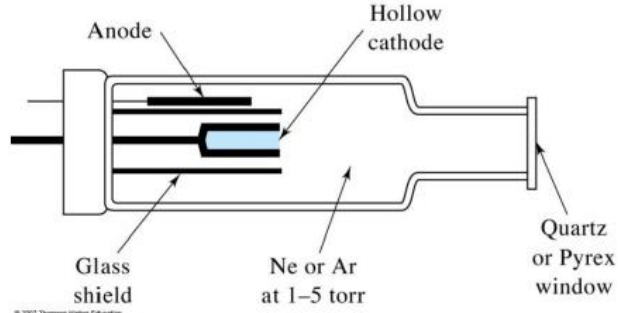
$S_2$  = absorbance of standard solution

$C$  = Concentration of lead in  $\mu\text{g/mL}$  in standard solution in

# Atomic Absorption Spectroscopy



# Atomic Absorption Spectroscopy



# Atomic Absorption Spectroscopy

