CHAPTER 4

ATOMIC ABSORPTION SPECTROMETRY

Expected Outcomes

Able to explain the principles of AAS
Able to state the function of each components of AAS instrumentation
Able to discuss the sources of interferences of AAS and and how their effects can be minimized.
Able to state the applications of AAS

4.1 Principles of AAS

- Atomic absorption spectroscopy involves the study of the absorption of radiant energy by neutral atoms in the gaseous state.
- These atoms are in the ground state and the amount of radiation absorbed is proportional to the concentration of atomic vapour in the flame – Beer’s Law

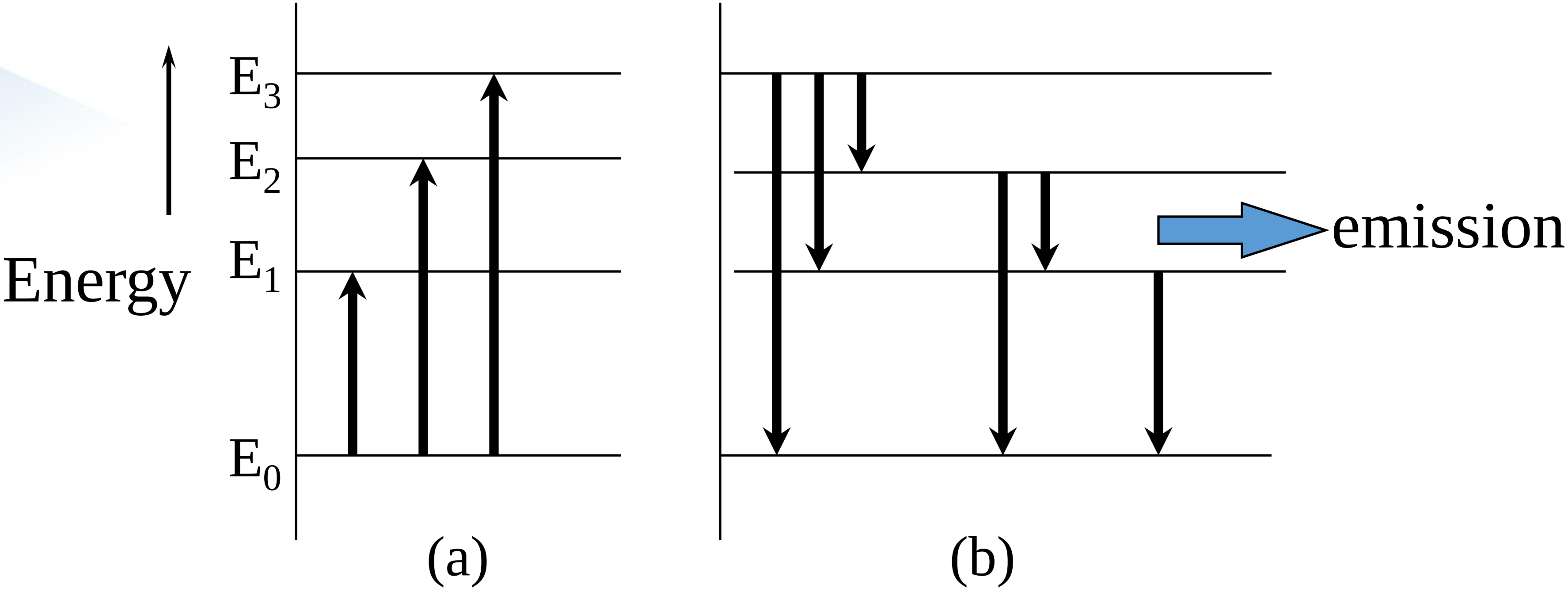
Atomisation

- Atomisation – process of converting an analyte in solid, liquid, or solution form to a free gaseous atom.
- Main difference between molecular and atomic absorption is the need to convert the analyte into a free atom.
- Two methods of atomisation:
  - Flame atomisation
  - Electrothermal atomisation

Atomic Absorption

- When atoms absorb radiation, only electronic transition takes place.
- Electronic transition – the transition of an electron between two orbitals or energy levels.
- Line spectrum can be observed.

Atomic Absorption and Emission



(a) absorption of energy from flame, furnace or plasma.

(b) emission of energy

Comparison of Instrumentation of Atomic Emission and Absorption Spectroscopy

Emission

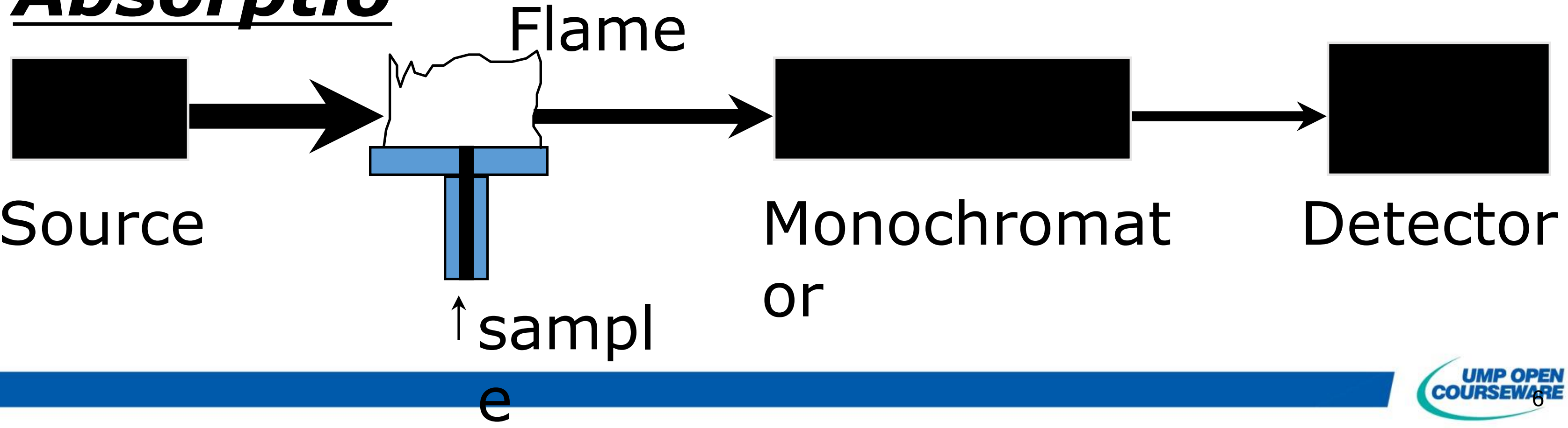
Flame

Monochromator

Detector

↑sample

Absorptio



Flame

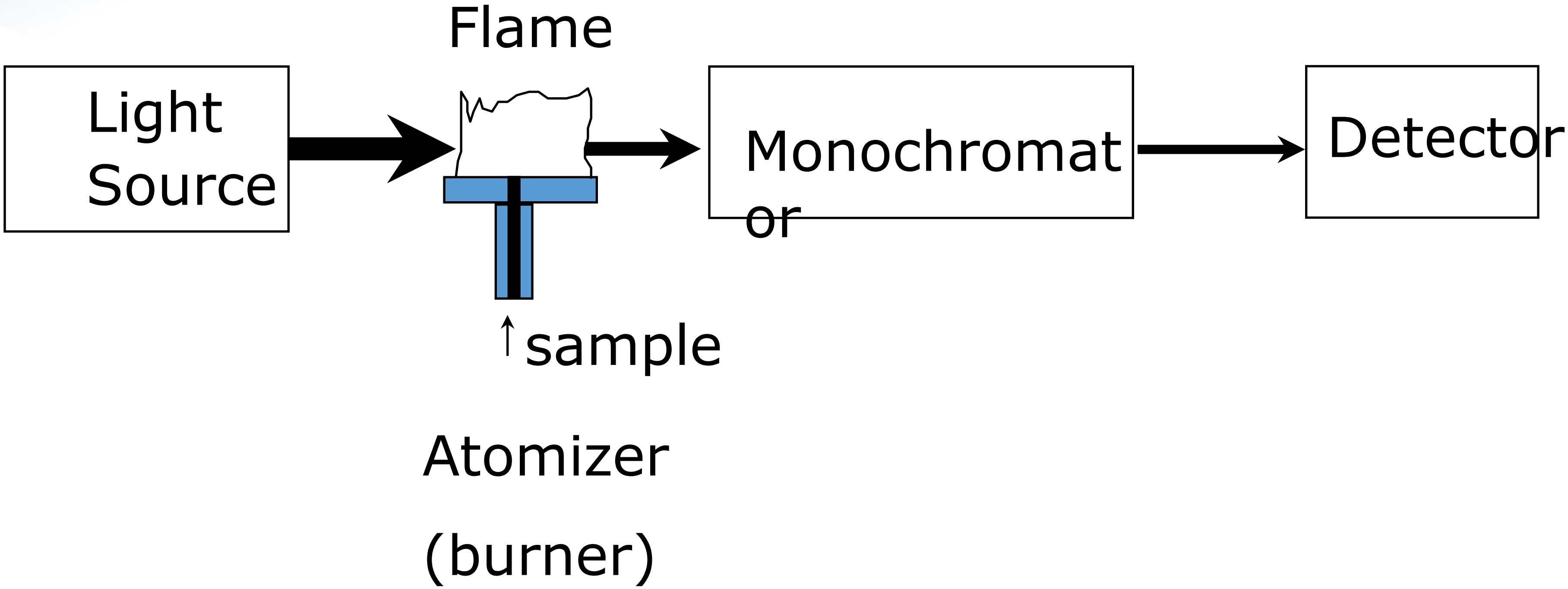
Source

Monochromator

Detector

↑sample

4.2 Instrumentation of Atomic Absorption Spectroscopy



Flame

Light Source

Monochromator

Detector

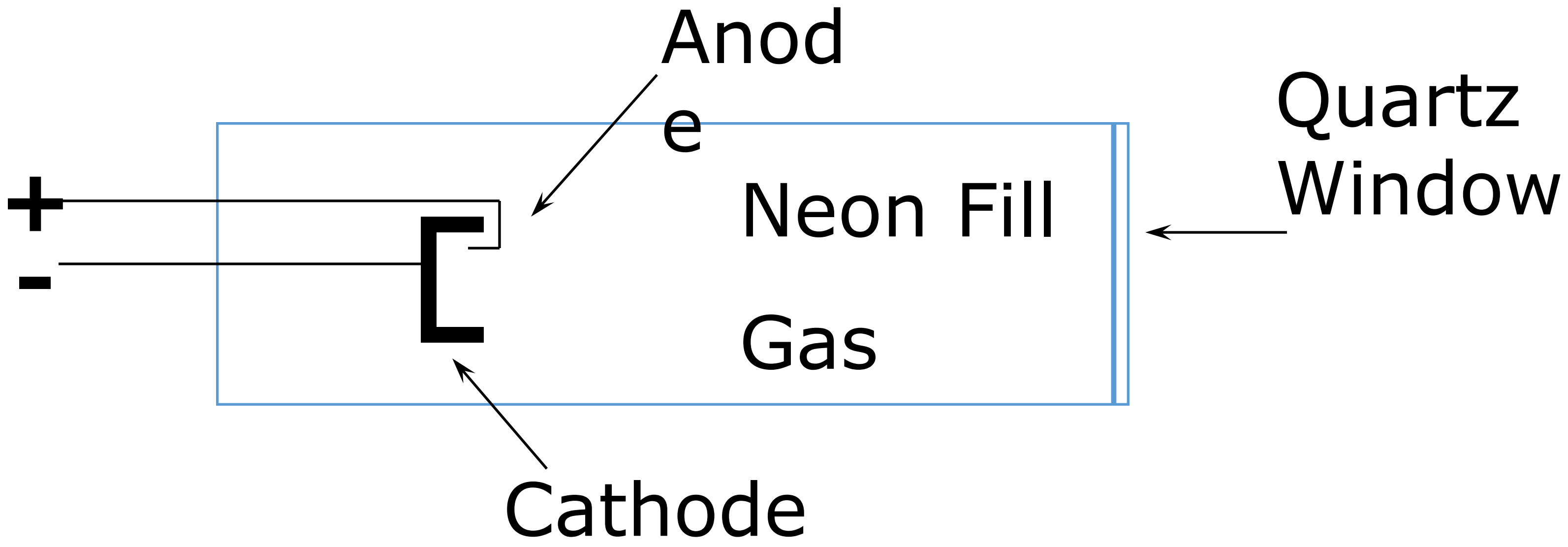
sample

Atomizer

(burner)

Instrumentation

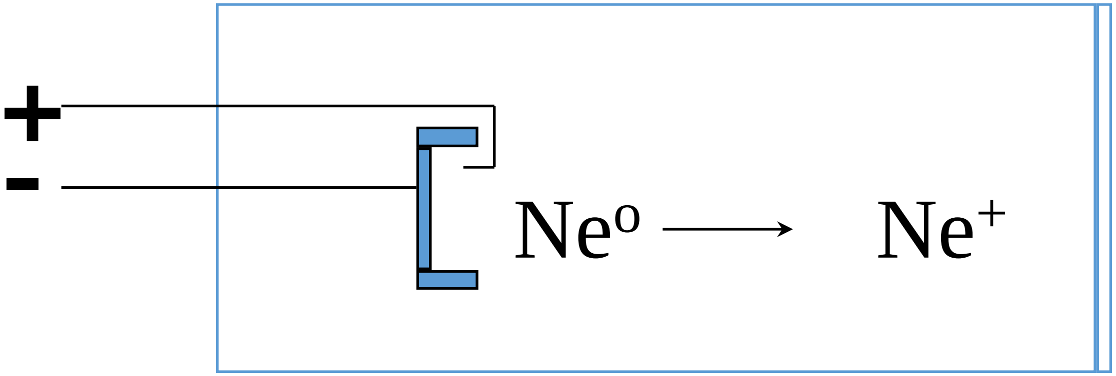
a) **Light source**: Hollow Cathode Lamp



Hollow Cathode Lamp

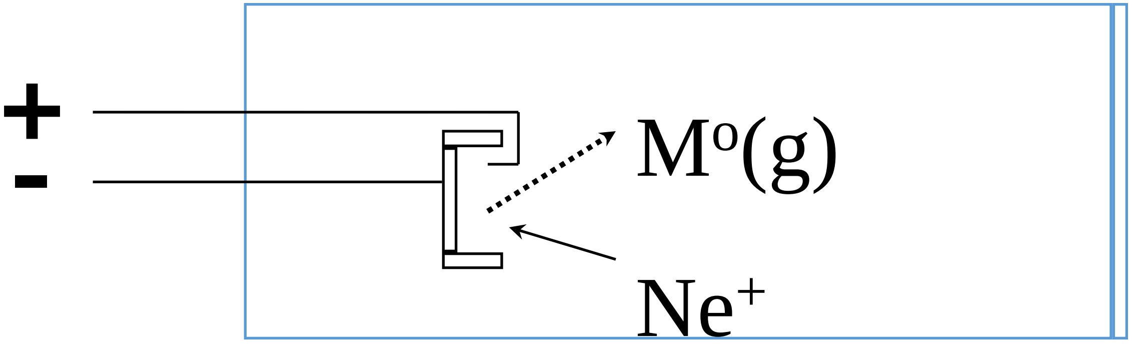
Process

1. Ionization



$Ne^o \longrightarrow Ne^+$

2. Sputtering

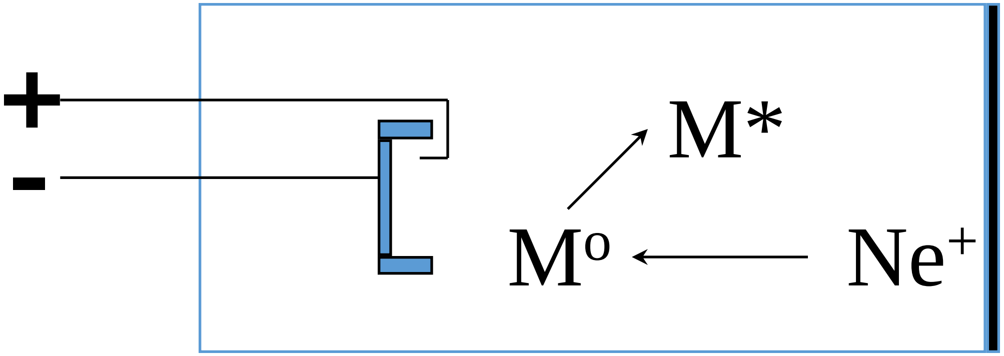


$M^o(g)$

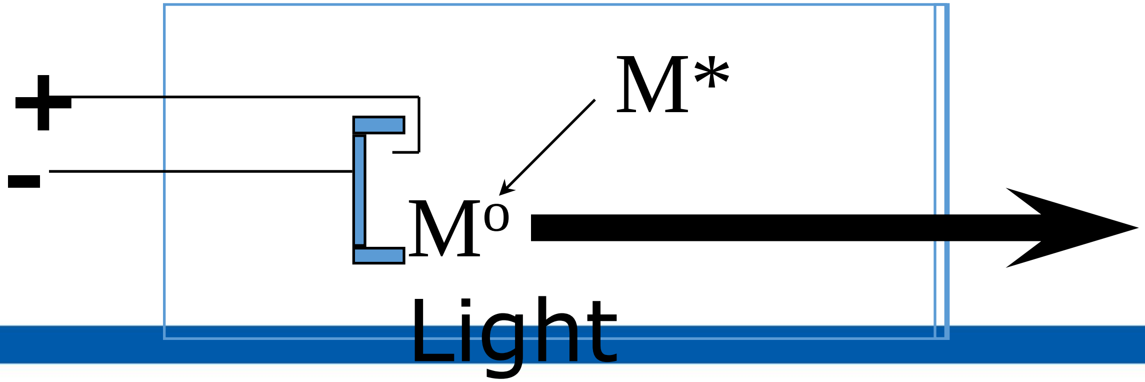
Ne^+

Hollow Cathode Lamp

3. Excitation



4. Emission

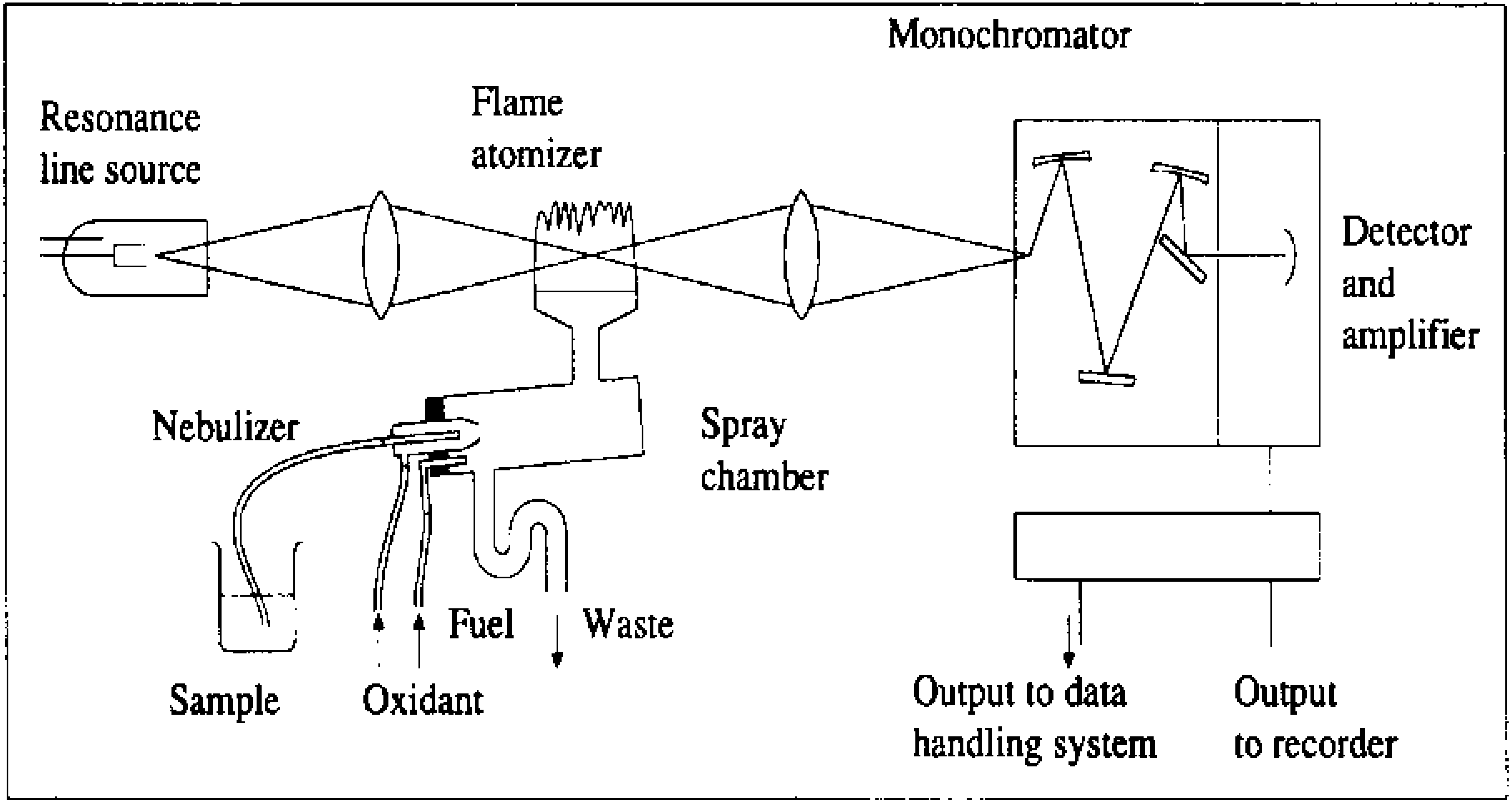


Instrumentation

b) Atomizer

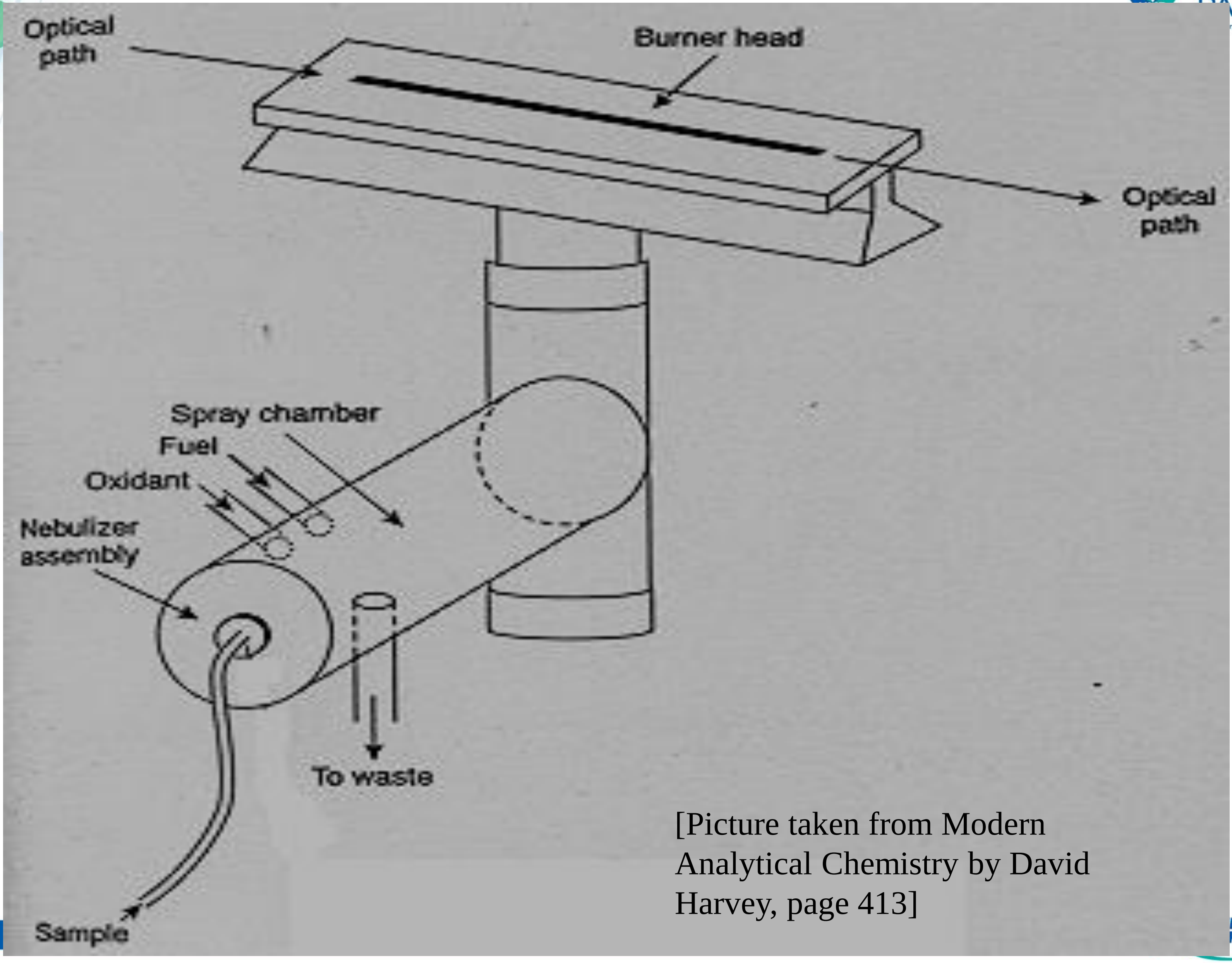
- Convert sample into atomic vapour.
- A flame atomizer consists of:
  - Nebulizer
  - Mixing (spray) chamber
  - Burner

Instrumentation



(extracted from Lajunen L.H.J., 1992, Spectrochemical Analysis by Atomic Absorption and Emission, pg 31)

Instrumentation



[Picture taken from Modern Analytical Chemistry by David Harvey, page 413]

Atomization

- The liquid sample is sucked through a capillary tube by a high-pressure stream of gas flowing around the tip of the tube.
- The sample is converted into a fine mist (small droplets of solution) through the **nebulizer**.
- The sample is aspirated into a spray chamber. The impact of the sample with the glass impact bead produces an aerosol mist.

Atomization

- The aerosol mist mixes with combustion gases in the spray chamber → Burner
- At burner, combustion of fuel and oxidant
- The heat at the burner vaporizes the aerosol particles → gaseous molecules, ions and free atoms
- The analyte atoms absorb the radiation from the light source.(absorbance α conc)

Flame Atomization

Use air-acetylene flame with a temperature of about 2300 ° C or the nitrous oxide ($N2O$)-acetylene flame with a temperature of about 2700 ° C

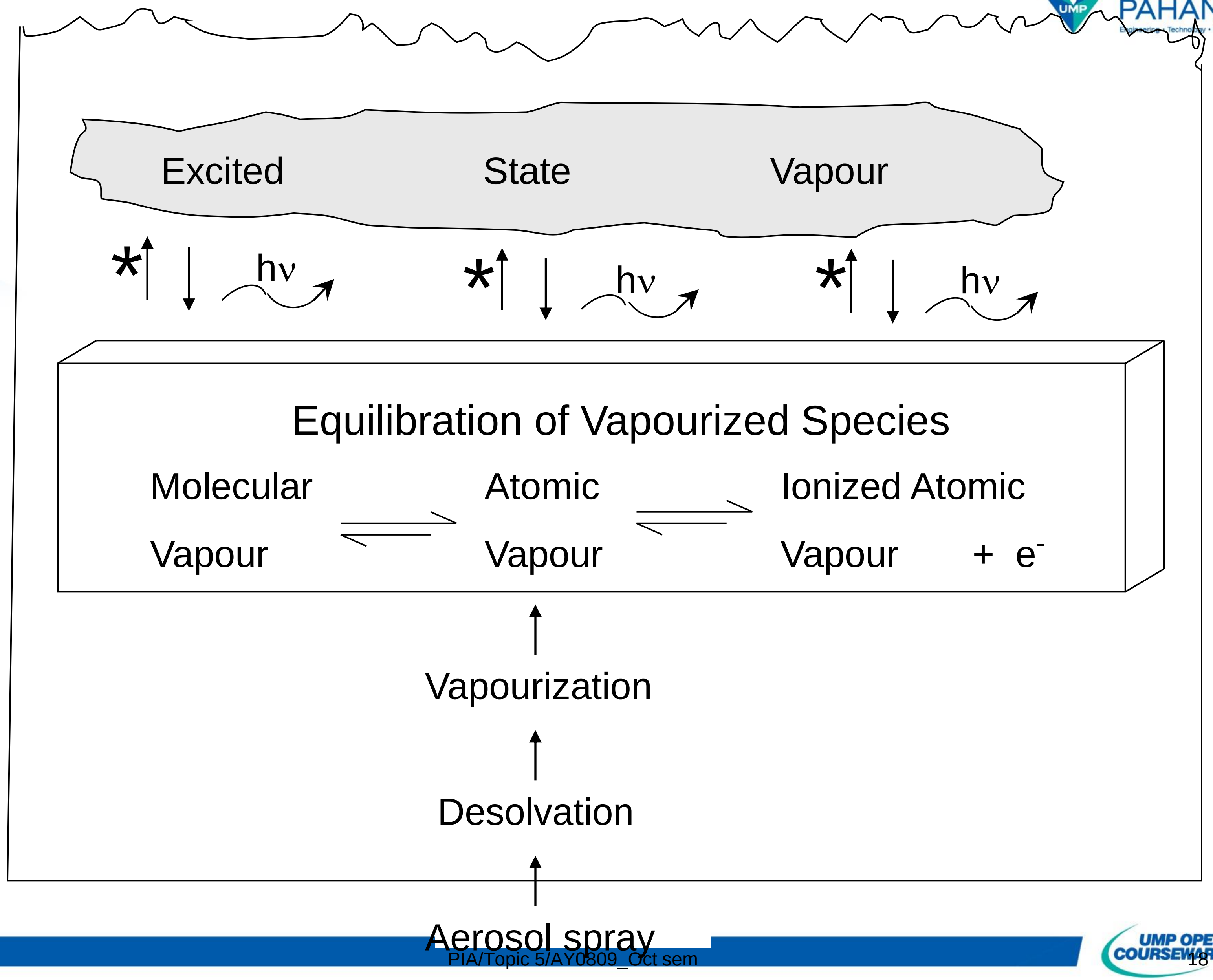
- Desolvation (drying) – the solvent is evaporated and the dry sample nano-particles remain;
- Vaporization (transfer to the gaseous phase) – the solid particles are converted into gaseous molecules;
- Atomization – the molecules are dissociated into free atoms;
- Ionization – depending on the ionization potential of the analyte atoms and the energy available in a particular flame, atoms might be in part converted to gaseous ions.

Electrothermal Atomization

Use graphite tube

- Drying – the solvent is evaporated
- Pyrolysis – the majority of the matrix constituents is removed
- Atomization – the analyte element is released to the gaseous phase
- Cleaning – eventual residues in the graphite tube are removed at high temperature

Atomization



Excited State Vapour

Equilibration of Vapourized Species

Molecular Vapour $\rightleftharpoons$ Atomic Vapour $\rightleftharpoons$ Ionized Atomic Vapour + e^-

Vapourization

Desolvation

Aerosol spray

Nebulizer Selection

- ❑ Stainless Steel
  - ➢ Less than 5% acid
- ❑ Pt / Rh
  - ➢ Conc. acids
  - ➢ Not aqua regia or HF
- ❑ Corrosion resistant plastic
  - ➢ Conc. acids
  - ➢ Aqua regia and HF
  - ➢ High total dissolved solid

Burner Head Selection

- **10-cm** head: for general purpose and lean (hot) Air-C_2H_2 flame
- **5-cm** head: N_2O-C_2H_2 flame

Criteria for Burner Head Selection

- Allow to pass through highly dissolved solids without blockage.
- Made of stainless steel or titanium to avoid corrosion.
- Construction of burner depends on the oxidant/fuel gas mixture to prevent the flame from flashback.
- 5-cm head is used for N_2O-acetylene gas.

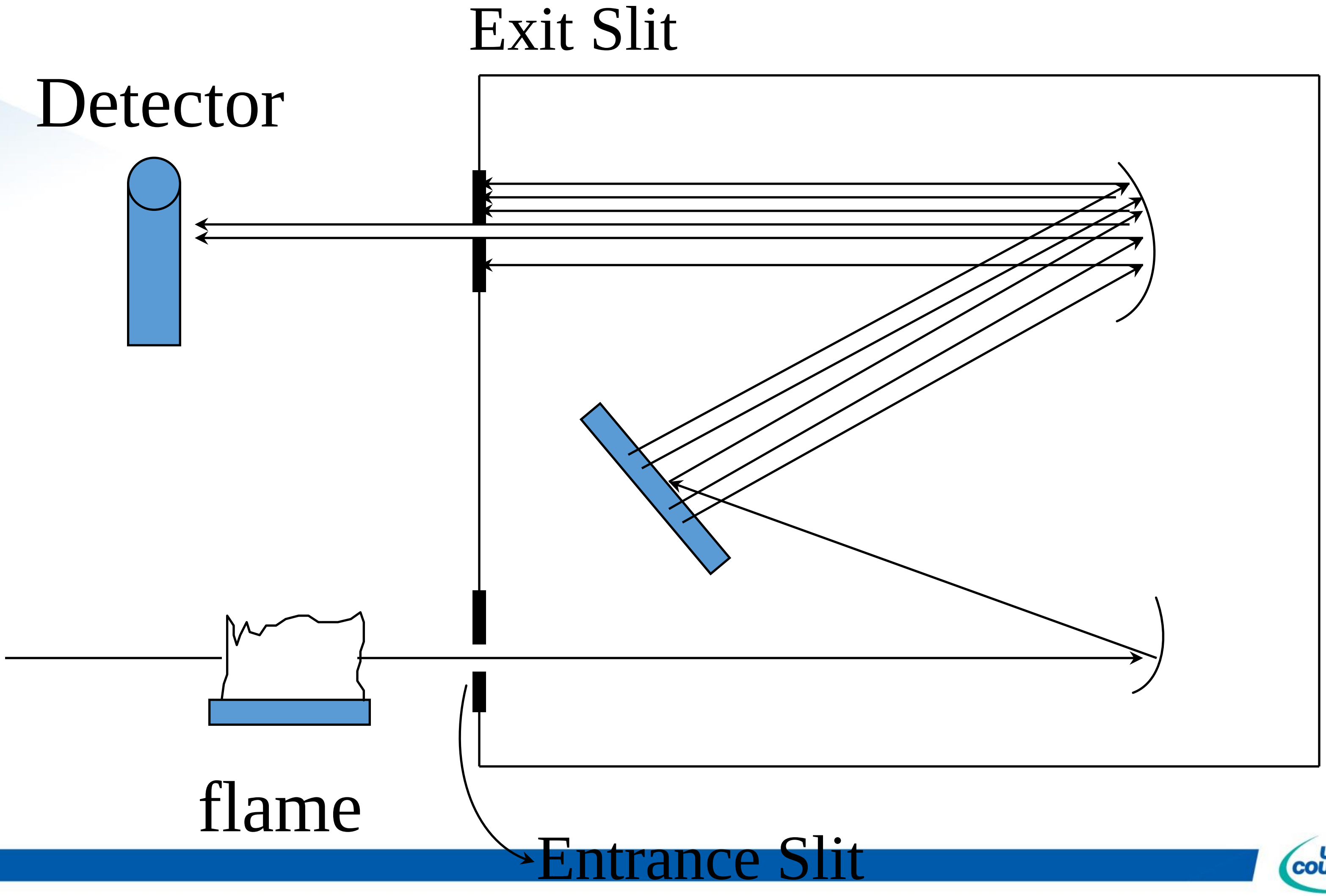
Commonly used Fuels and Oxidants

Fuel	***Oxidant***	***Temperature range***
Natural gas	air	1700 – 1900
Hydrogen	air	2000 – 2100
acetylene	air	2100 – 2400
acetylene	Nitrous oxide	2600 – 2800
acetylene	oxygen	3050 - 3150

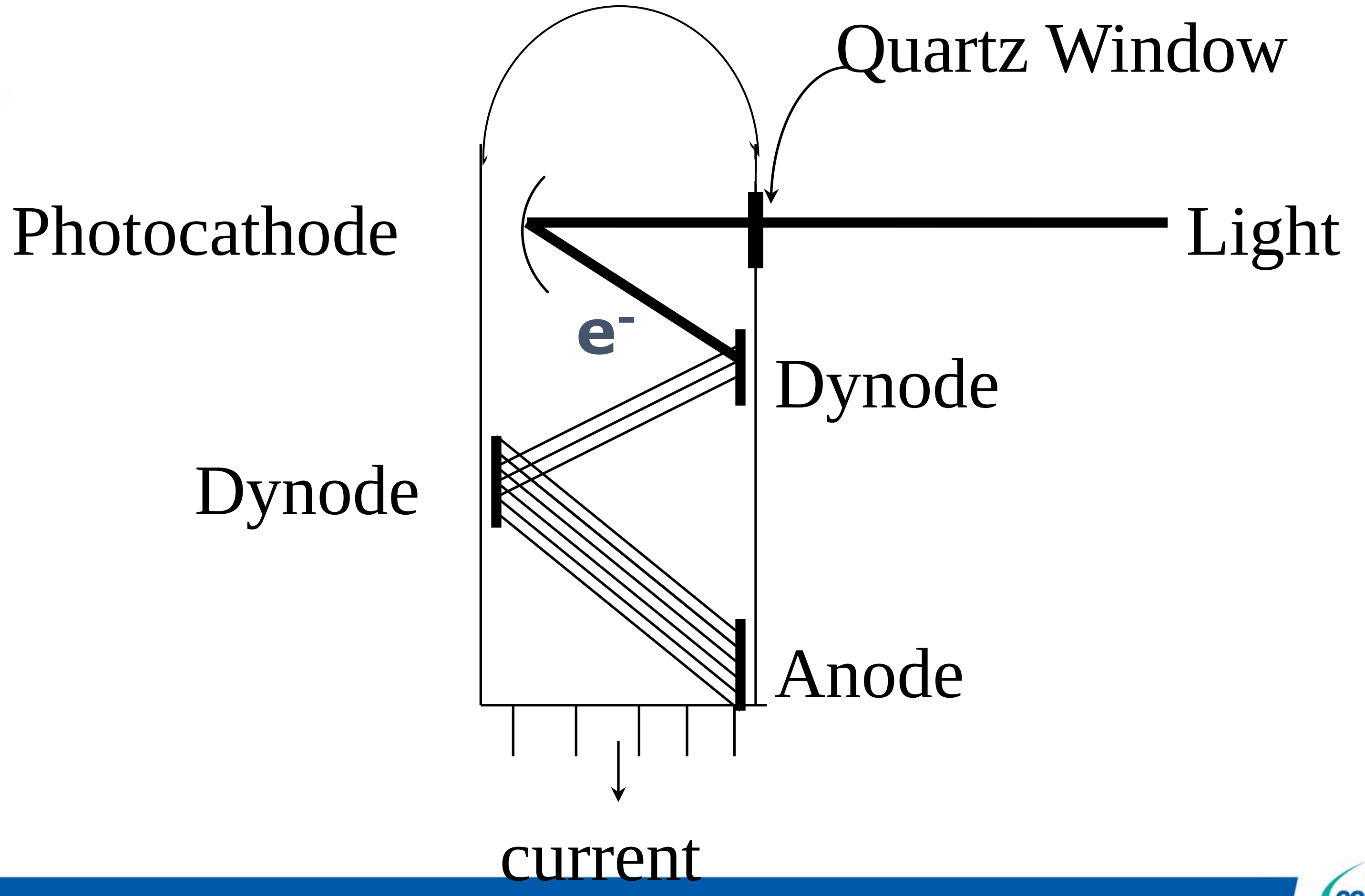
Commonly used Fuels and Oxidants

- Air-acetylene flame –
  - Absorbs at <200 nm
  - Possible chemical interferences
- Nitrous oxide-acetylene (high temp)
  - May cause ionisation interference
  - Useful for elements that tend to form heat-stable (refractory) oxides in air-acetylene flame.
  - Able to overcome chemical interferences in air-acetylene flame.

c) Monochromator



d) Light Detector -- Photomultiplier Tube



4.3 Applications of AAS

❑ **Qualitative analysis**

- AAS is used for confirmation of presence of suspected elements.

❑ **Quantitative Analysis**

- Standard curve method (External Standard Method)
- Standard addition method

5.2 Applications of AAS

Characteristic Concentration

- The concentration of an element (mg/L) required to produce a signal of 1% absorption
- 1% absorption = 0.0044 absorbance

5.2 Applications of AAS

Characteristic Concentration

- In the linear working range, characteristic conc. can be determined by reading the absorbance produced by a known concentration.

$$Characteristic\ conc. = \frac{0.0044 \text{ x } conc.\ of\ \ std}{Abs\ of\ \ std}$$

5.2 Applications of AAS

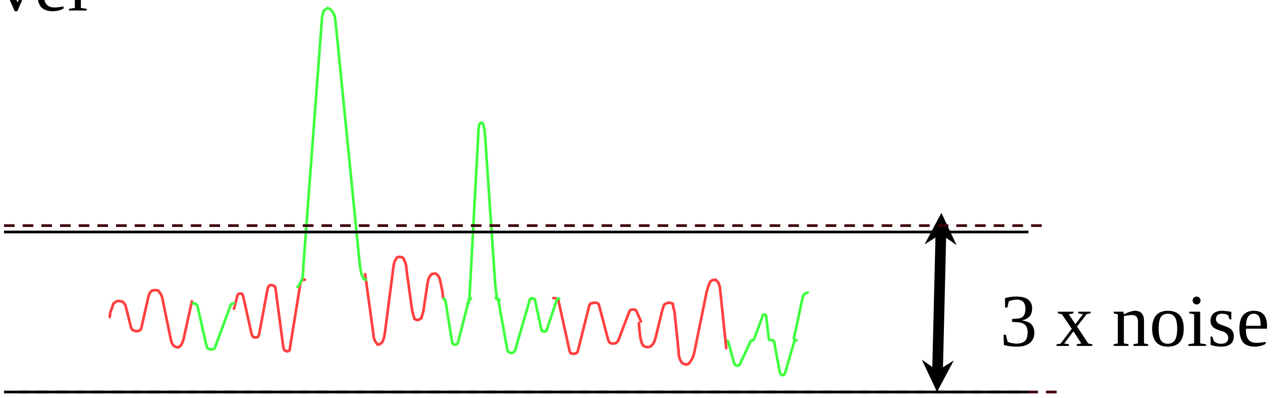
Example:

Is the AAS in the best working condition if a 6 ppm Fe standard gives 0.12 in absorbance. (The characteristic conc. of Fe at the specified wavelength is 0.11 ppm)

5.2 Applications of AAS

Detection limit (d.l.)

- The detection limit is the smallest amount of an element which can be detected with a reasonable certainty.
- A valid signal produced by an element > 3 x noise level



5.3 Applications of AAS

Factors affecting optimisation

- Size of the droplets formed in the nebulizer
  - smaller size, better evaporation rate, better atomisation.
- Choice of fuels and oxidants
- Choice of solvent

5.2 Applications of AAS

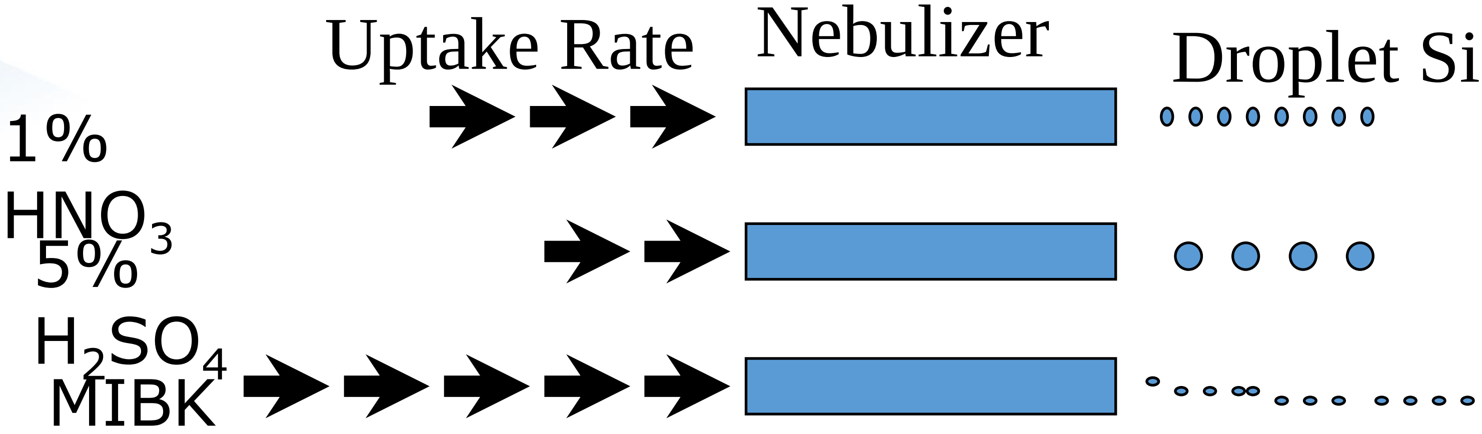
Sample preparation

- To obtain the sample in the form of solution.
- Solid: dissolution in appropriate solvent
- Insoluble solids: digestion with strong acids
- To concentrate samples: liquid-liquid extraction using organic solvent

5.4 Interferences of AAS

- Matrix interference
- Chemical interference
- Ionisation interference
- Spectral interference
- Background absorption

Matrix Interferences



Uptake Rate

Nebulizer

Droplet Size

1% HNO_3

5% H_2SO_4

MIBK

Viscosity and surface tension affect

- Uptake rate
- Droplet size
- Sensitivity

Chemical Interferences

- Occur when the sample contains a thermally stable compound => does not atomised.
- Number of atoms in the flame capable of absorbing light is reduced => ↓ absorbance
- E.g. phosphate reacts with calcium ions to form calcium pyrophosphate ($Ca_2P_2O_7$) in the flame. Solution: add high conc of lanthanum or use nitrous oxide-acetylene flame

Overcoming Chemical Interferences

- ❒ Removal of interfering anions by separation technique.
- ❒ Use a hotter flame.
- ❒ Addition of Releasing Agents (like La, Sr salt).
- ❒ Addition of Protective Agents (like EDTA, 8-hydroxyquinoline..).

Ionisation Interferences

- Occur when the flame temperature has enough energy to cause the removal of an electron from the atoms → ions
- => result in less ground state atoms for radiation absorption => ↓ absorbance

Ionisation Interferences

- Solution:
  - Add excess of an easily ionisable element(e.g. K, Na, Rb, Cs) to the blank, standards and sample to suppress ionisation of analyte.
  - Use a cooler flame, but chemical interferences may result.

Spectral Interferences

- Occur when an absorbing wavelength of an element (not analyte) present in the sample falls within the bandwidth of the absorption line of the analyte → Higher than actual absorbance.
- When multi-element lamps are used, the slit width normally used with single-element lamps may allow an absorbing wavelength of another element to pass through. This can be overcome by using a smaller slit or selecting another wavelength.

Background Absorption

- ❑ 2 causes --
  - Light scattering between particles in the flame.
  - Absorption of light by undissociated molecular forms of matrix materials in the flame.
- ❑ → Higher than actual absorbance
- ❑ How to compensate?
  - Install a continuum source (H_2 or D_2 arc lamp) in the optical system to measure background absorption.