Atomic Absorption Spectrophotometry

“Theory and Technique”

Introduction

- Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. It is so sensitive that it can measure down to parts per billion of a gram (µg/L) in a sample.
- <u>Basic advantages for the technique:</u>
  - Quantification of about 80 elements
  - Detection limits may reach parts per billion
  - Minimum sample size at least µL

Uses and applications of the technique through analysis of:

- Biological samples: Blood, urine, tissue, hair, nails ..etc.
- Environmental samples: Air, water, soil, plants, parts of animals.. etc.
- Industrial samples: Metal industries, Foods, Pharmaceuticals .. etc.

General limitations of the technique:

- No information on chemical form of metal
- Time-consuming sample preparation
- Destructive
- No multi-element analysis per run.

Theory of Atomic Absorption

- The normal and most stable orbital configuration of an atom is known as the "ground state." If energy is applied to an atom, It will be absorbed and an outer electron will be promoted to a less stable configuration known as the "excited state." Since this state is unstable, the atom will immediately return to the "ground state," releasing light energy.

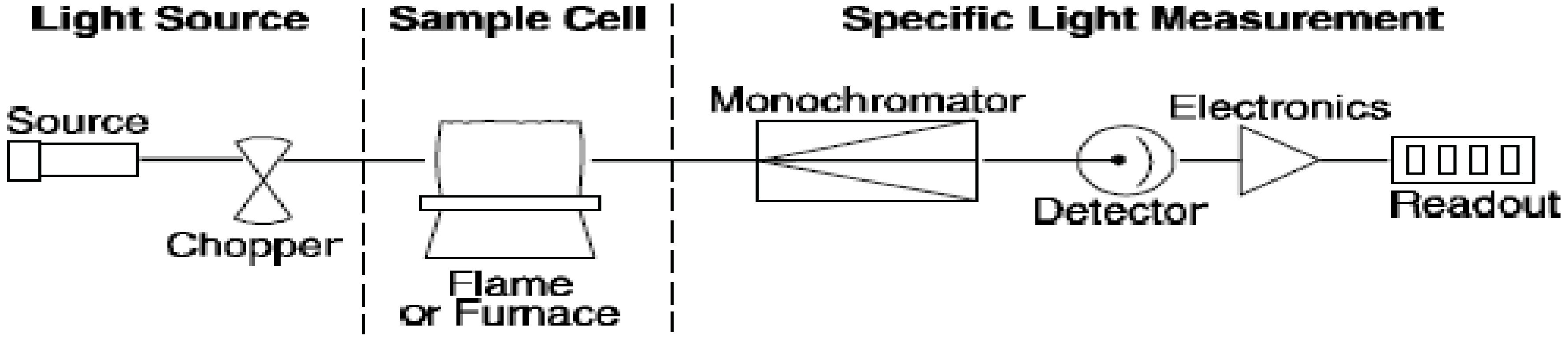
Theory of Atomic Absorption

As the number of atoms in the light path increases, the amount of light absorbed also increases. By measuring the amount of light absorbed, a quantitative determination of analyte can be made. The use of special light sources and careful selection of wavelengths allow the specific determination of individual elements.

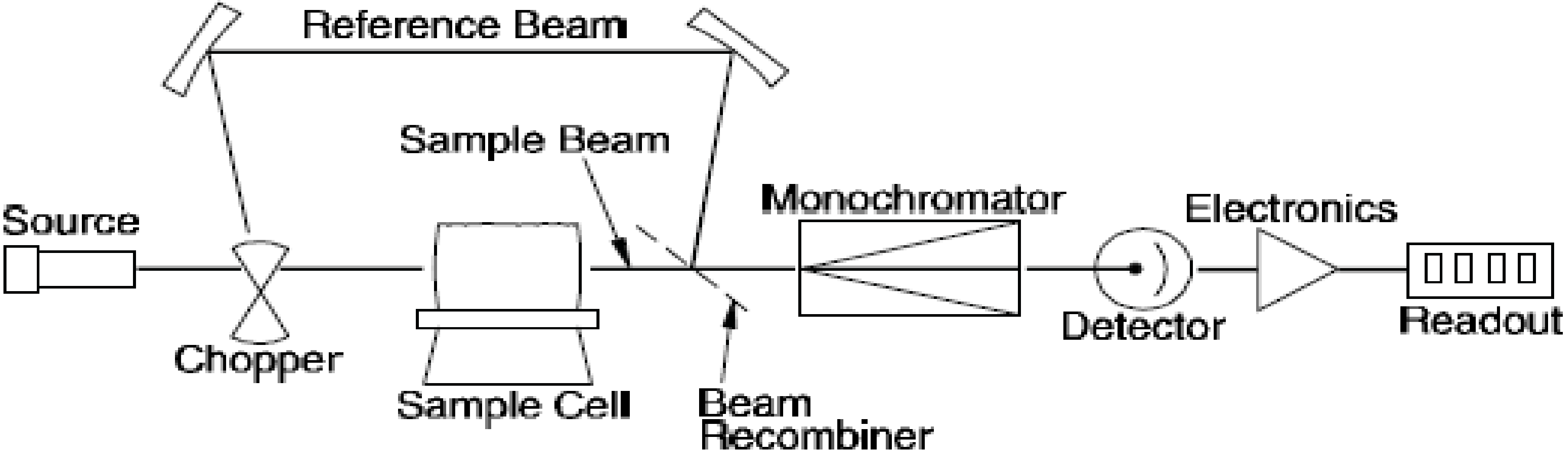
Theory of Atomic Absorption

A calibration curve is constructed by running several samples of known element concentration under the same conditions as the unknown. This enables the calculation of the analyte concentration in the unknown sample.

Main components of the Atomic Absorption Spectrophotometer



Single beam Atomic Absorption Spectrometer



Double beam Atomic Absorption Spectrometer

Main components of the AAS

1) Source of radiation: a) Hollow Cathode Lamp
   b) Electrodeless Discharge Lamp

2) Cell or burner:
   a) Flame
   b) Graphite Furnace (Electrothermal or Flameless)
   c) Hydride Vapor Generator
   d) Cold Vapor

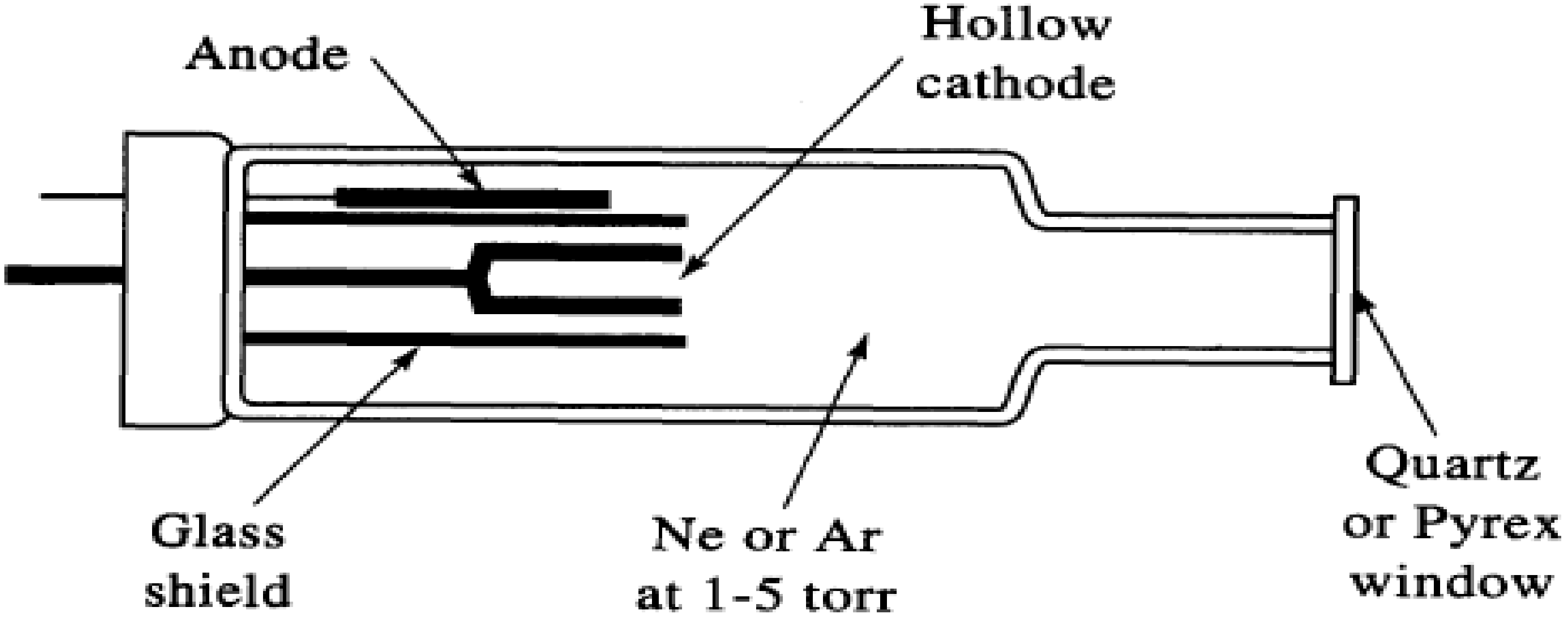
3) Monochromator

4) Detector (Photomultiplier Tube)

5) Readout system (Computer and Printer)

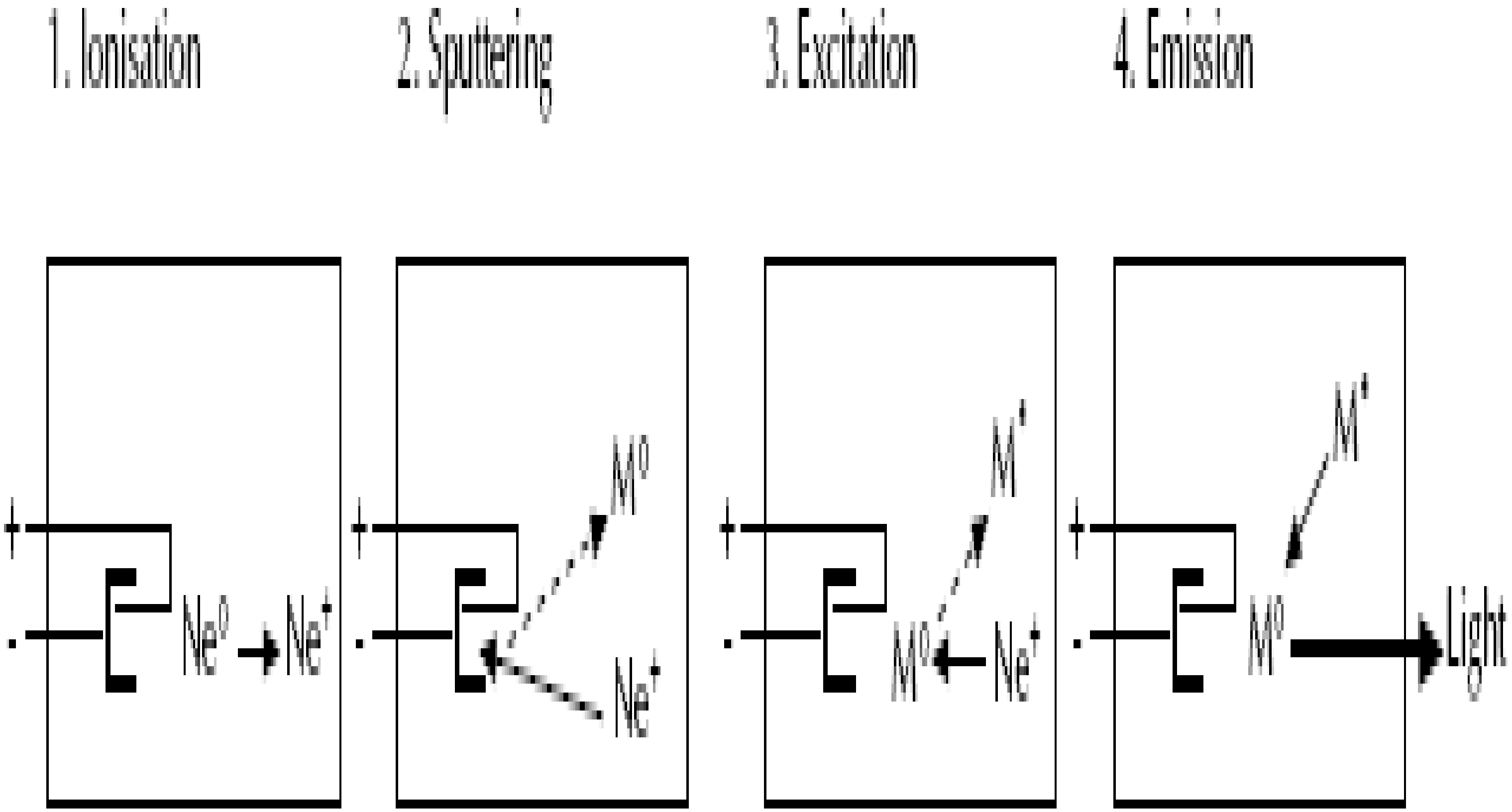
Main components of the AAS

1)Source of radiation: a) Hollow Cathode Lamp



Main components of the AAS

1)Source of radiation: a) Hollow Cathode Lamp



Main components of the AAS

2) Cell or burner

a- Flame

b- Graphite Furnace (Electrothermal or Flameless)

c- Hydride Vapor Generator Technique

d- Cold Vapor Technique

Main components of the AAS

2- Cell or burner a- Flame Cell

Basic steps involved in atomization of aqueous solution sample:

- $MX\ (aq) \rightarrow MX\ (s) \rightarrow MX\ (g) \rightarrow M^0\ (g) + X^0\ (g)$

1. **Nebulization**: Sample solution, get into fine droplets by spraying through thin nozzle or passing over vibrating crystal.

1. **Desolvation:** Conversion of analyte to solid crystals.

2. **Vaporization:** Conversion of solid to molecular vapor.

3. **Atomization:** Dissociation of molecular vapor into atomic vapor.

4. **Excitation**: With light, heat, etc. for spectra measurement.

Main components of the AAS

Cell or burner

a- Flame Cell

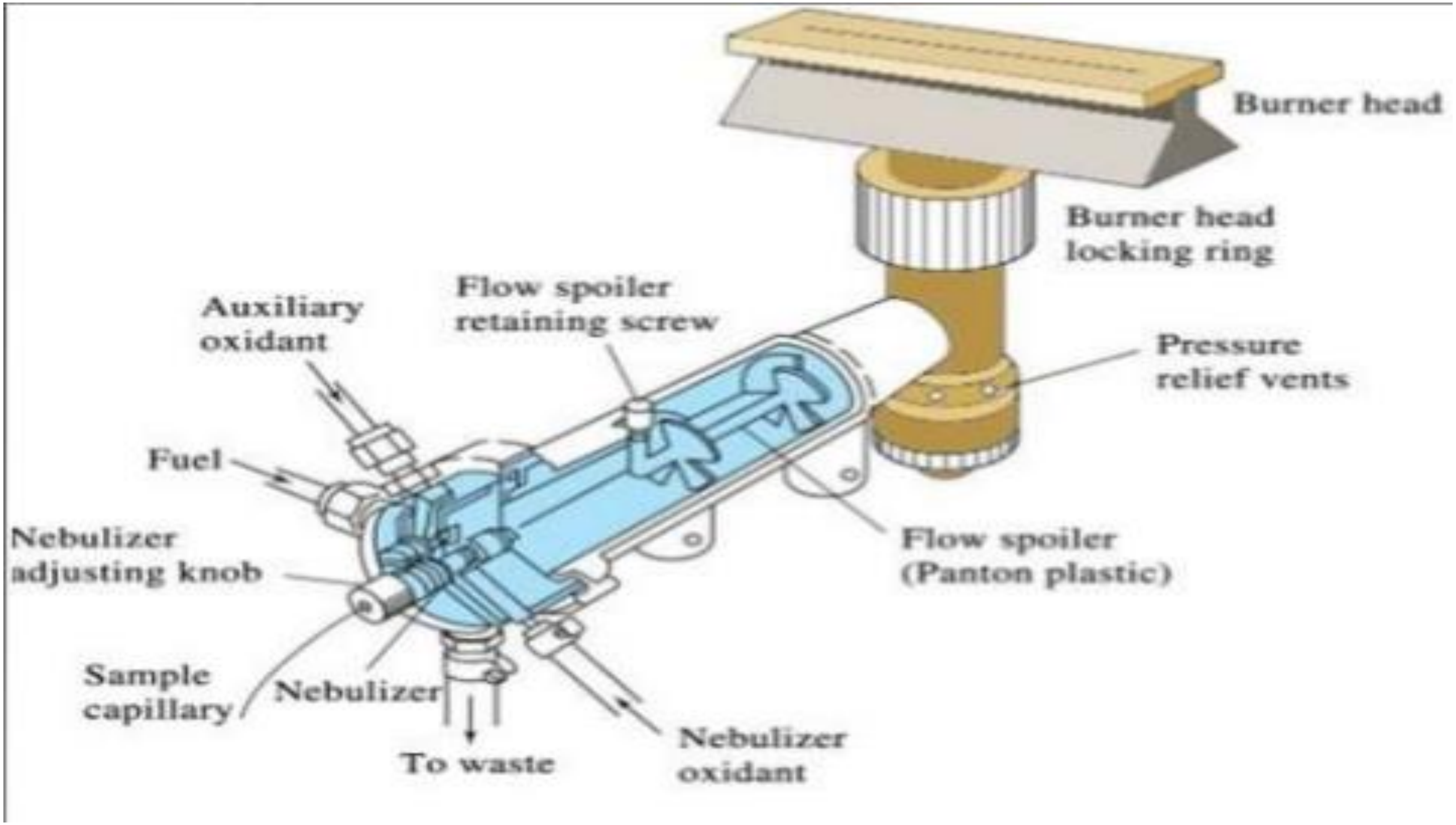


Figure illustrating the basic components of the flame cell

Main components of the AAS

2- Cell or burner a- Flame Cell

- The sample is atomized by the flame according to the gas mixture used.
- The sample is nebulized and aspirated to the flame through the nebulizer and aspirator which forms a uniform aerosol of the sample.
- Temperature differs according to the gas mixture used, and according to the element to be analyzed.

Main components of the AAS

2- Cell or burner a- Flame Cell

The following table determines the gas mixtures with the temperatures obtained:

Gases mixture	Average Temperature (°C)
Natural Gas/Air	1700-1900
Hydrogen/Air	2000-2100
Acetylene/Air	2100-2400
Hydrogen/Oxygen	2550-2700
Acetylene/Nitrous Oxide	2600-2800
Acetylene/Oxygen	3050-3150
Cyanogen/oxygen	4800

Main components of the AAS

2- Cell or burner

b- Graphite Furnace Cell (Electrothermal-Flameless)

- It depends on electrothermal energy to generate high temperatures to convert a sample to an atomic vapor.

- Using a graphite tube in parallel with the radiation generated from the source, a specific volume of the sample (in the volume of microliters, added by an automatic syringe) is heated in this tube till it is converted to an atomic vapor, where the concentration can be measured.

Main components of the AAS

2-Cell or burner

b- Graphite Furnace Cell (Electrothermal-Flameless)

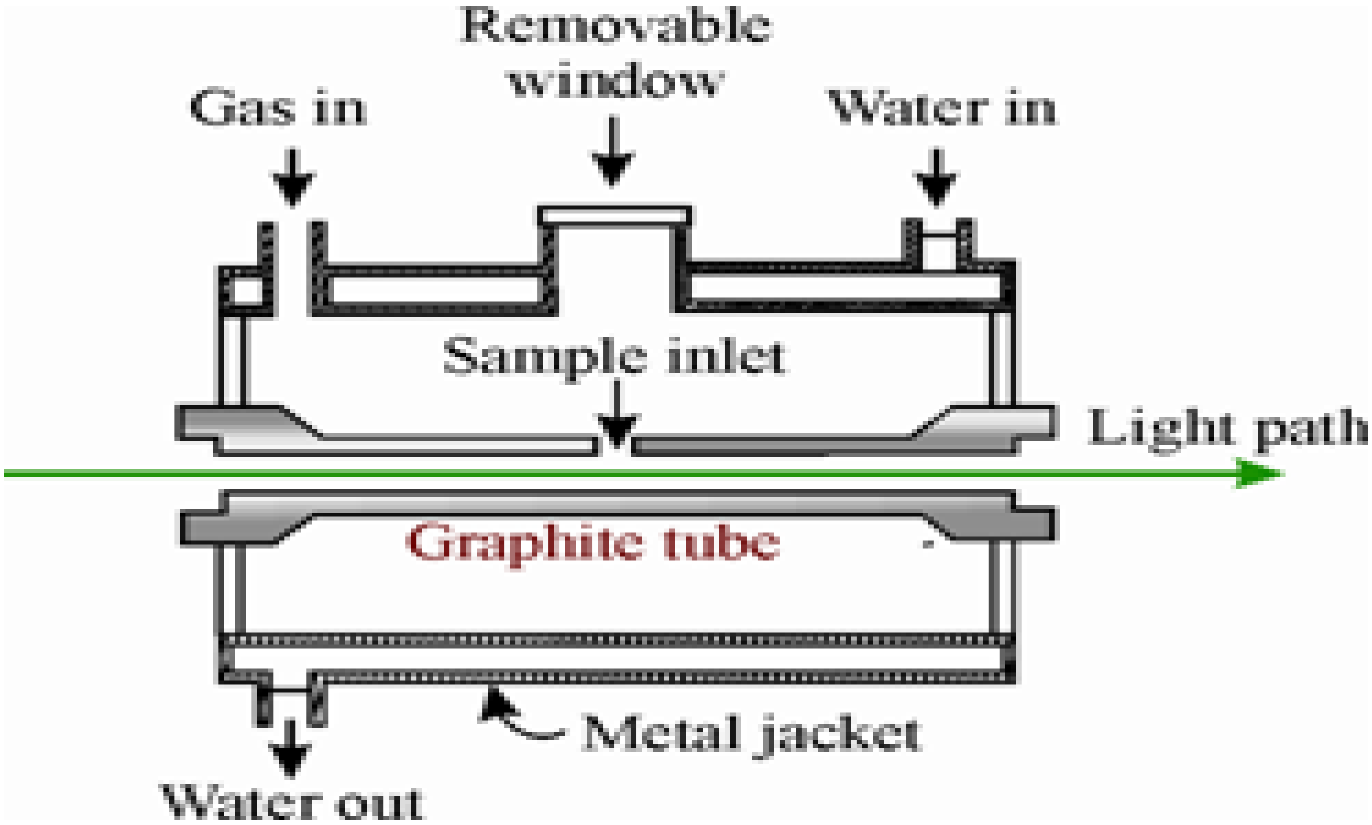


Figure illustrating the basic components of the graphite furnace cell

Main components of the AAS

Cell or burner

b- Graphite Furnace Cell(Electrothermal-Flameless)

Sample is heated in the graphite tube through the following stages:

1) **Drying** : (100 to 200°C) for several seconds.

2) **Decomposition** :(500 to 1400°C) to decompose organic compounds

   (Argon gas circulating to flush the smoke and prevent the graphite tube from oxidation at high temp.)

3) **Atomization** of sample (3000°C)

4) **Pyrolysis** for the “cleaning” of the inner of the graphite tube.

Flame and Electrothermal cells, brief comparison

Point of difference	**Flame cell**	**Electrothermal cell**
Absorbance period	Continuous	Pulsed/ Transient
Sample consumption	1-5% of the sample	100% of the sample
Volume of sample used	Milli Liters	Micro Liters
Detection limits (In some elements)	Part Per Million (Part Per Billion)	Part Per Billion (Part Per Trillion)
Absorbance time	Short (ms)	Long (s)
Source of atomization	Fuel gases	Electrothermal energy

Main components of the AAS

2-Cell or burner

c- Hydride Vapor Generator Technique

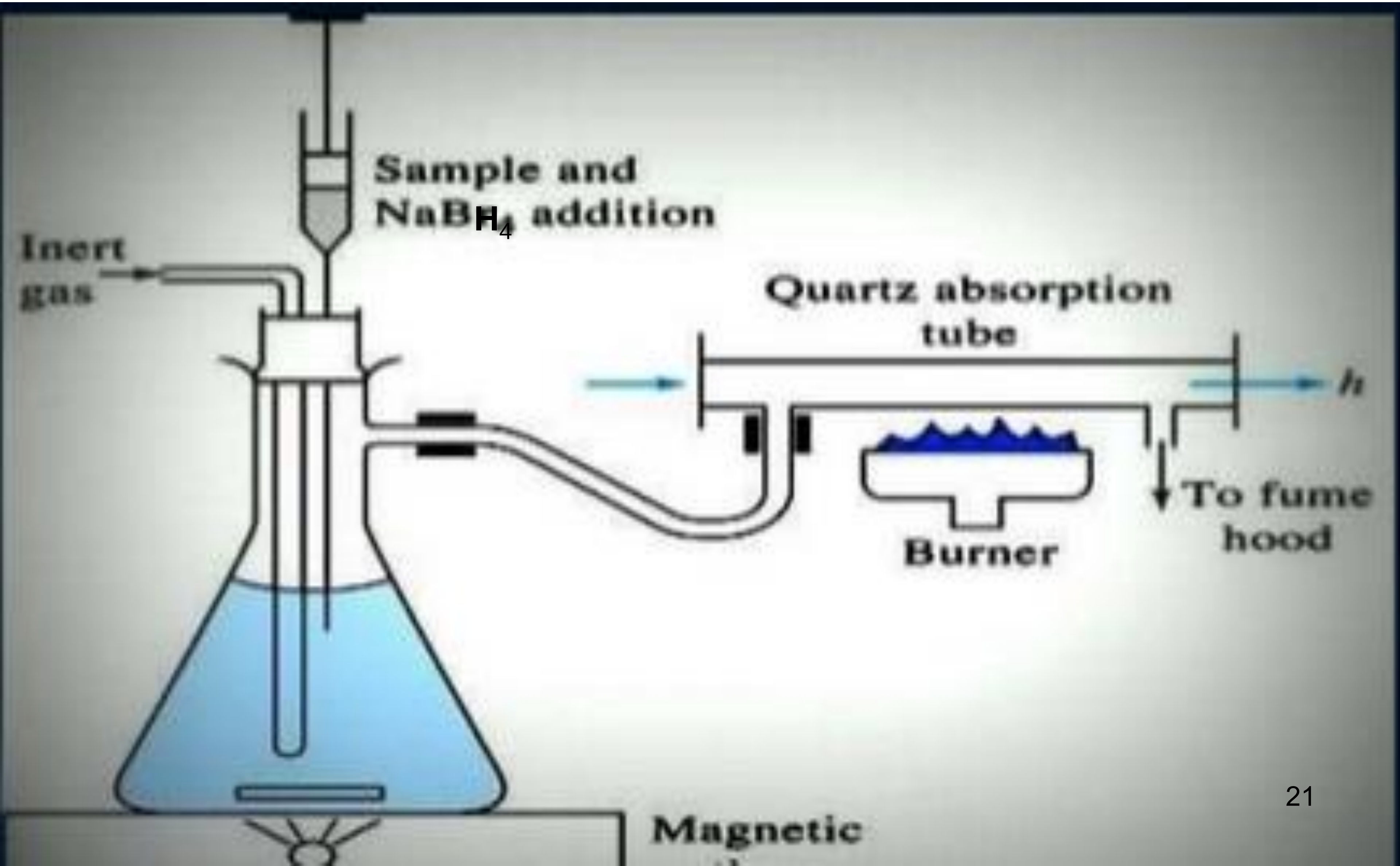
Some elements (such as As, Bi, Sb, Se, Hg and Sn) are difficult to reduce in a flame when they are in higher oxidation states.

For these atoms, the sample is reacted with a reducing agent prior to analysis (Sodium borohydride or tin chloride in acidic media) in a separate vessel.

The volatile hydride formed is carried by a make up gas into a quartz cell placed in the flame.

Main components of the AAS

2-Cell or burner c- Hydride Vapor Generator Technique



Main components of the AAS

2-Cell or burner

c- Hydride Vapor Generator Technique

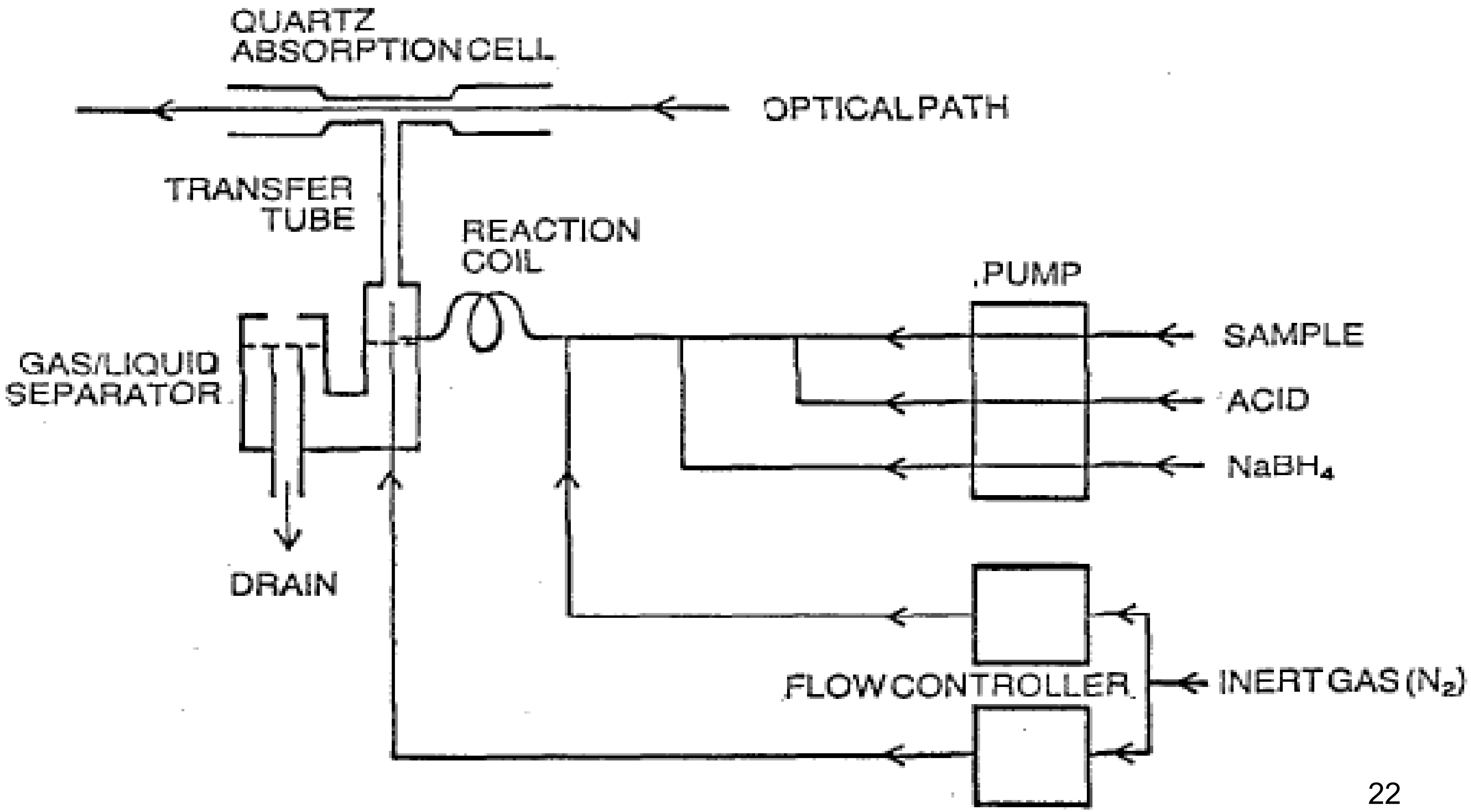


Figure illustrating Hydride Vapor Generator Technique

Main components of the AAS

2-Cell or burner d- Cold Vapor Technique(analysis of Hg)

- Mercury ions in solution can be reduced by $SnCl_2$ to metallic mercury which is swept out of the solution by an inert gas to a long-path quartz absorption cell for AAS measurement.

Main components of the AAS

3- Monochromator

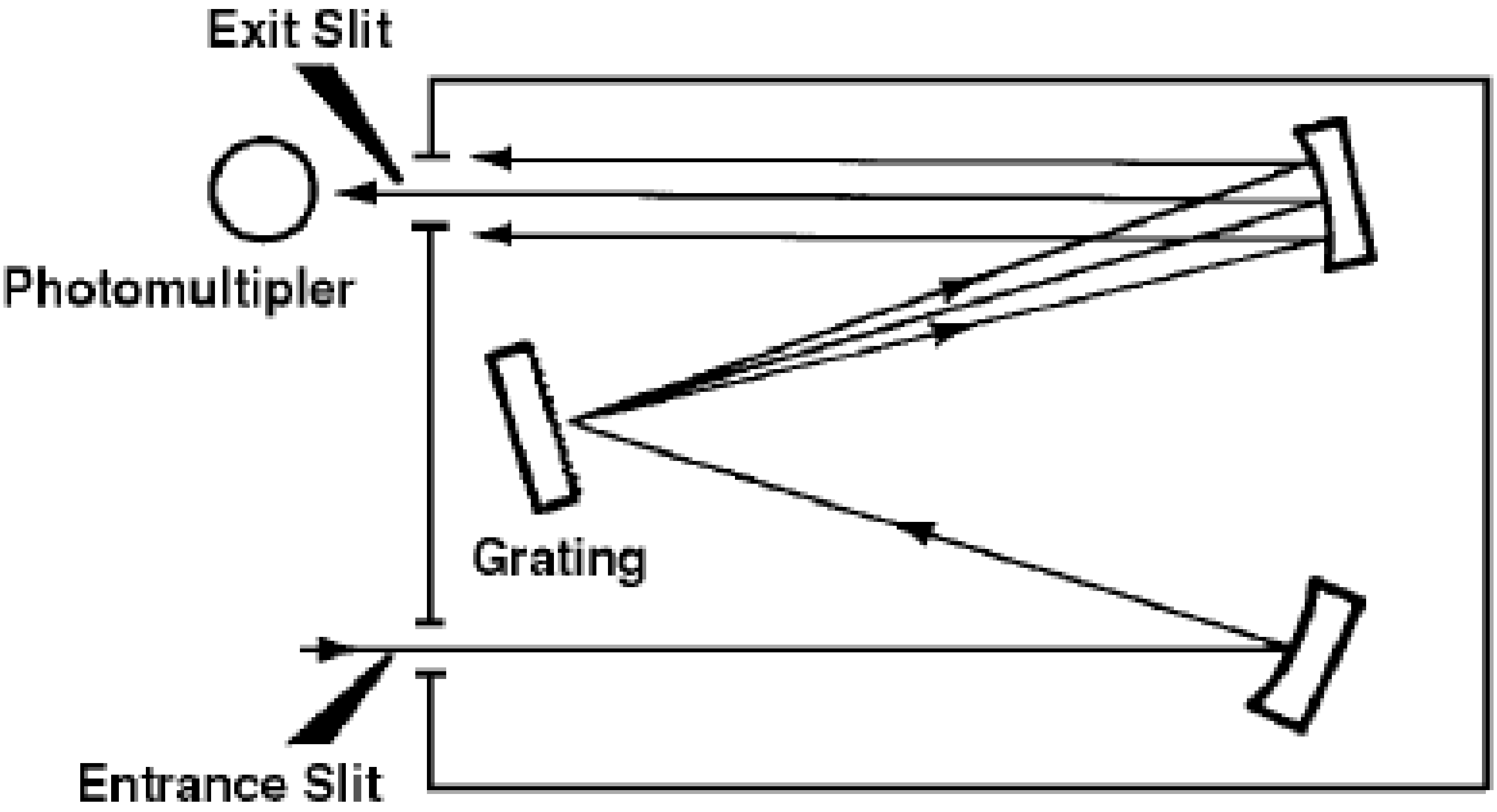
The function of a monochromator:

- **Isolate analytical lines' photons passing through the flame.**
- **Remove scattered light of other wavelengths from the flame so,**

  only a narrow spectral line impinges on the Photomultiplier Tube.

Main components of the AAS

3- Monochromator



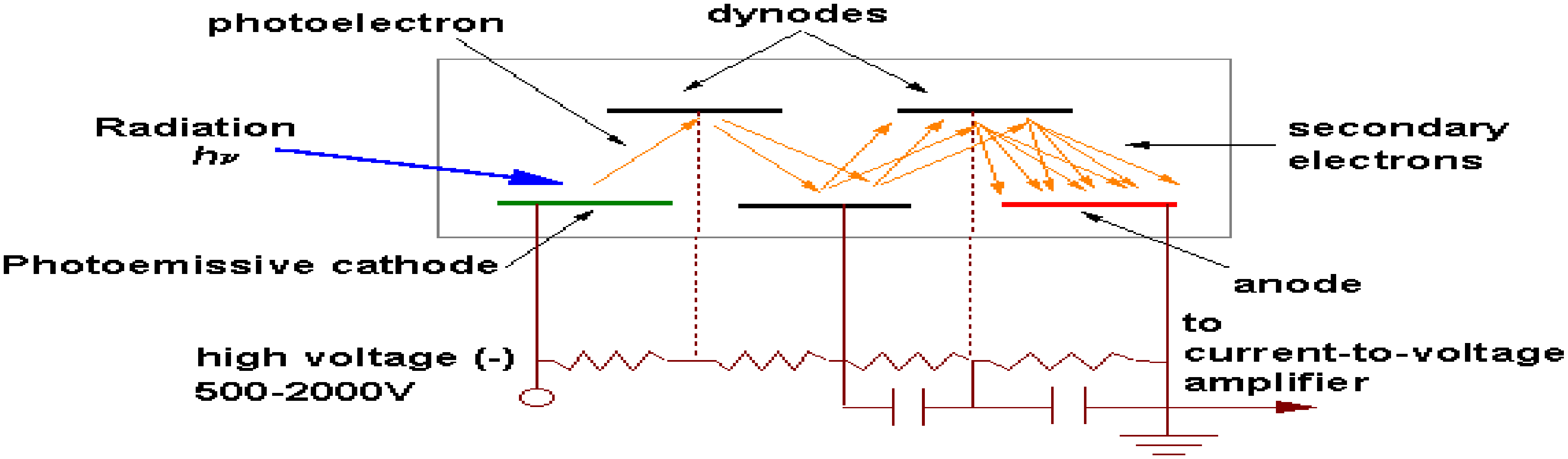
Main components of the AAS

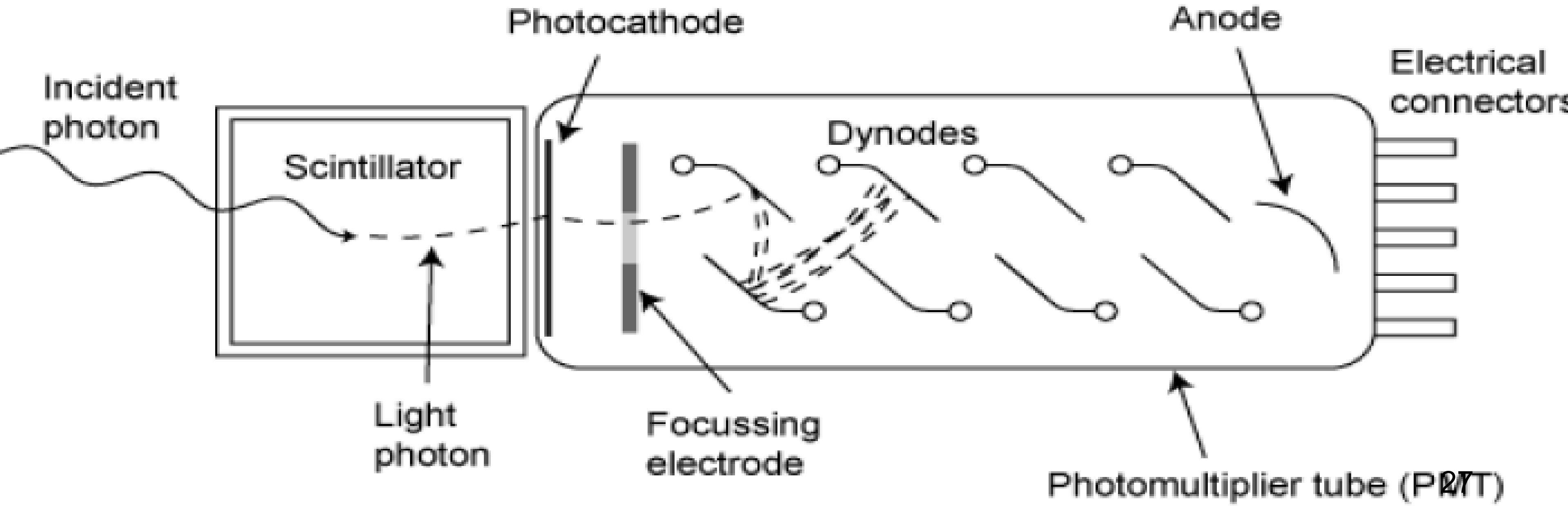
4- Detector (Photomultiplier tube)

- It consists of a series of electrodes (dynodes), each at a more positive potential (50 to 90 V) than the one before it.
- When a primary electron is emitted from the photoemissive cathode by a photon, it is accelerated toward the next electrode, where it releases many more secondary electrons.
- These, in turn, are accelerated to the next electrode where each secondary electrode releases more electrons, and so on, up to 10 stages of amplification. The electrons are finally collected by the anode. The final output of the photomultiplier tube may, in turn, be electronically amplified.

Main components of the AAS

4- Detector (Photomultiplier tube)





Main components of the AAS

5-Readout (Computer and printer)

Types of Interferences in AAS

- **Spectral interference.**
- **Ionic interference (especially for alkaline rare earths)**
- **Chemical interference (salts- minerals- organic and refractory compounds)**
- **Physical interference (viscosity- Surface tension- Electrical Conductivity)**
- **Matrix interference**

Overcoming interferences effects

- Overcoming interferences by adding accessories to the instrument:
  - Deuterium lamp
  - Zeeman effect
  - Smith Hieftje effect
- Using standard addition method for making calibration curves
- Using N_2O/C_2H_2 for analysis of refractory elements like Al & V
- Solvent extraction (especially for marine samples)
- Using suitable graphite tube and suitable sample volume to be injected in the graphite tube.
- Using matrix modifiers

- *"To know that we know what we know, and to know that we do not know what we do not know, that is true knowledge."* Copernicus Polish astronomer (1473-1543)

- *"What is written without effort is in general read without pleasure."* Samuel Johnson (1709-1784)

References

- Beaty RD and Kerber JD (2nd edition, 1993) *"Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry"* Norwalk, CT: The Perkin-Elmer Corporation 96 pp.
- Douglas A. Skoog and James J. Leary (4th edition, 1992) *"Principles of Instrumental Analysis"* Saunders College Publishing (Chapter 10)
- Francis Rouessac and Annick Rouessac (English Edition, 2000) *"Chemical Analysis Modern Instrumentation Methods and Techniques"* John Wiley & Sons, Ltd (Chapter 14 & 11)
- Gary D. Christian (5th edition, 1994) *"Analytical chemistry"* John Wiley & Sons, Inc (Chapter 15)
- S.J. Haswell (Analytical Spectroscopy Library-Volume 5, 1991) "Atomic Absorption Spectrometry: Theory, Design and Applications" ELSEVIER (Chapter 4)
- *SHIMADZU Cookbook*
- Thompson KC and Reynolds RJ (2nd edition, 1978) *"Atomic Absorption, Fluorescence and Flame Emission Spectroscopy- A Practical Approach"* Charles Griffin & Company LTD (Chapter 4)
- http://www.chemsoc.org/pdf/LearnNet/rsc/AA_txt.pdf