

**SHREE H. N. SHUKLA INSTITUTE OF PHARMACEUTICAL
EDUCATION AND RESEARCH**



B.PHARM

(SEMESTER –VII)

SUBJECT NAME: INSTRUMENTAL METHOD OF ANALYSIS

SUBJECT CODE: BP701TP

CHAPTER 2 : FLAME PHOTOMETRY

- **Introduction**
- **Principle**
- **Instrumentation**
 1. Sharp line radiation source
 2. Nebulizer and Burner
 3. Monochromator
 4. Photomultiplier
 5. Recording system
- **Flameless vaporization techniques**
 1. Electrothermal atomizers
 2. Cold vapour systems
 3. Hydride generation systems

Interferences in atomic absorption spectroscopy

1. Special
 2. Chemical
 - Advantages
 - Disadvantages
- Applications

INTRODUCTION

Atomic absorption spectrometry (AAS) detects elements in either liquid or solid samples through the application of characteristic wavelengths of electromagnetic radiation from a light source. Individual elements will absorb wavelengths differently, and these absorbances are measured against standards. In effect, AAS takes advantage of the different radiation wavelengths that are absorbed by different atoms.

In AAS, analytes are first atomized so that their characteristic wavelengths are emitted and recorded. Then, during excitation, electrons move up one energy level in their respective atoms (figure 1) when those atoms absorb a specific energy.

As electrons return to their original energy state, they emit energy in the form of light (figure 2). This light has a wavelength that is characteristic of the element. Depending on the light wavelength and its intensity, specific elements can be detected and their concentrations measured.

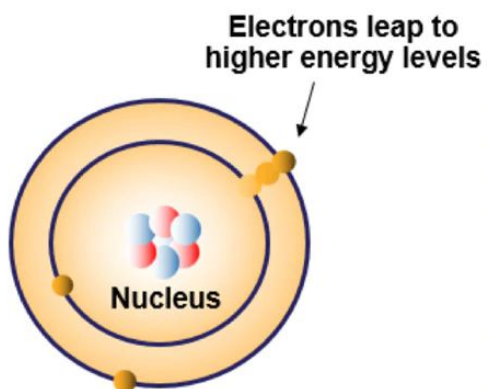


Figure 1. Excitation of an atom

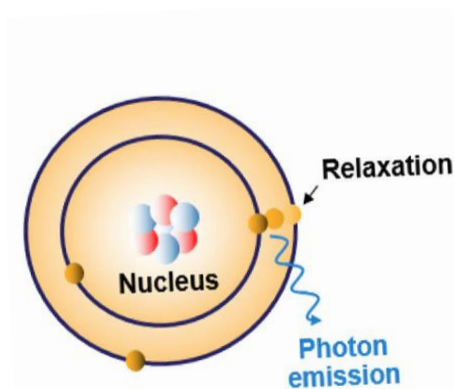


Figure 2. Relaxation and photon emission of an atom.

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	Mb	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															

Elements detectable by atomic absorption are highlighted in pink in this periodic table

● Principle

The extent to which radiation of a particular frequency is absorbed by an atomic vapour is related to the length of the path transversed and to the concentration of absorbing atoms in the vapour. This is analogous to the Beer – Lambert's law relating to samples in solution. Thus, for a collimated monochromatic beam of radiation of incident I_0 passing through an atomic vapour of thickness l , $I = I_0 e^{-kvl}$

Where I is the intensity of the transmitted radiation

kv is absorption coefficient

The value of kv is determined by the concentration of atoms which can absorb at frequency ν is given by the expression :

$$\int kv \, d\nu = \frac{e^2 N \nu^2 f}{4\pi m c^3}$$

Where m & e are the mass and charge of the electron

N is the number of atoms per cm^3 capable of absorbing radiation of frequency ν (ie., ground state atoms)

f is the oscillator strength (defined as the number of electrons per atom capable of being excited by the incident radiation)

Hence, for transitions from the ground state, integrated absorption is proportional to $N\nu$,

which approximates to the concentration (c) of the element in the sample

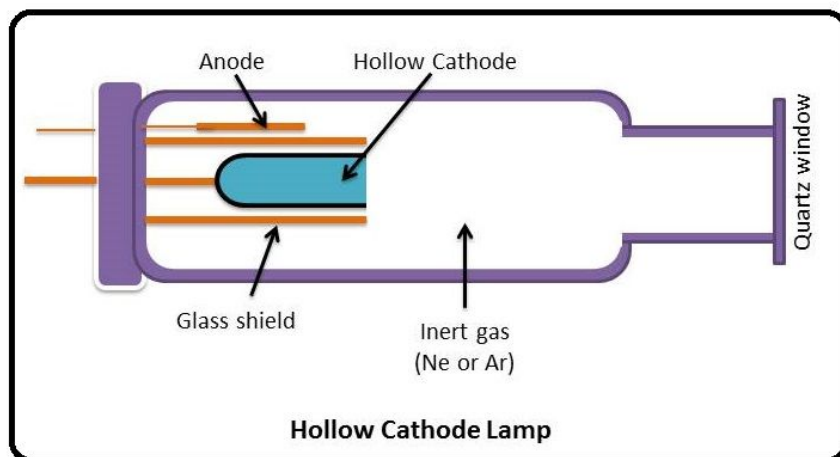
INSTRUMENTATION

- ❖ Sharp-line radiation source (usually a hollow-cathode lamp)
- ❖ A solution nebulizer and burner (an electrically heated furnace)
- ❖ Monochromator
- ❖ Photomultiplier and
- ❖ Recording system

SHARP-LINE SOURCES

The absorption line width for the ground state atoms may be from 0.001-0.01nm. So the light sourced must emit radiation of a line width less than that of the absorption line width of the element being determined. This is achieved by vapour discharge lamps for certain easily excited elements, e.g. sodium and potassium.

HOLLOW CATHODE LAMP



Namrata Heda

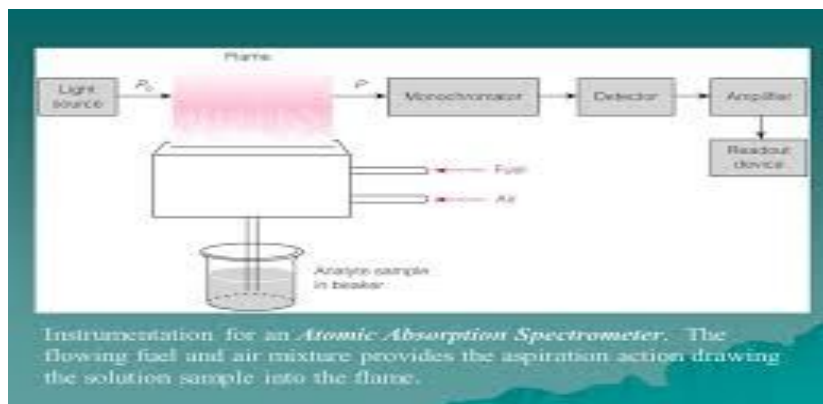
When a current flows between the anode and cathode in these lamps, metal atoms are sputtered from the cathode cup, and collisions occur with the filler gas. A number of metal atoms become excited and give off their characteristic radiation.

SAMPLE VAPORIZATION BY FLAME

The production of an homogeneous atomic vapour from a sample is achieved by aspirating a solution into a flame or evaporating small volumes in an electrically heated tube furnace or from the surface of a carbon rod.

In all cases, the thermal energy supplied must (a) Evaporate the solvent and (b) Dissociate the remaining solids into their constituent atoms without causing appreciable ionization.

INSTRUMENTATION OF ATOMIC ABSORPTION SPECTROSCOPY



QUESTIONS	ANSWER
In Atomic Absorption Spectroscopy, which is generally used as a radiation source?	Hollow cathode lamp
In Atomic Absorption Spectroscopy, with what material is the cathode in Hollow cathode lamp constructed?	Element to be investigated. The anode is made of tungsten.
How can the intensity of radiation be increased in Hollow cathode lamp?	Addition of non-conductive protective shield of mica
Which of the following is the function of the Flame or Emission system in Atomic Absorption Spectroscopy?	To reduce the sample into atomic state
Atomic absorption spectroscopy is also called Absorption Flame Photometry.	True
Who is the function of the atomiser in	To break large mass of liquid into

the emission system of Atomic Absorption Spectroscopy?	small drops To break large mass of liquid into small drops
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BURNER WITH FUEL AND OXIDANT (NEBULIZER)

The burner consists of a metal block containing a row of circular holes or one or more slots about 10 cm long. The most generally useful flame is air-acetylene, The cooler air-propane and the Hotter nitrous oxide-acetylene flames are also used. (It is particularly useful for samples containing refractory elements (e.g. aluminium.)

NEBULIZER

Some well known fuels with **oxidants** are

Air Propane 2200 K

Oxygen – Hydrogen 2450 K

Oxygen – Acetylene 2800 K

Nitrous oxide – Acetylene 3230 K

POTENTIAL ADVANTAGES OF FLAMELESS VAPORIZATION:

- (1) The elimination of anomalous results arising from interactions between the sample and components of the flame.
- (2) Increased sensitivity arising from a longer residence time within the beam of radiation from the lamp.
- (3) Residence times in flames are low because of strong vertical thermal currents.
- (4) Increased sensitivity because of a higher proportion of the analyte being converted to free atoms. (The conversion may be as low as 0.1% for flame atomization.)
- (5) The ability to handle very small samples such as clinical specimens. (A nebulizer, spray chamber, burner arrangement consumes several cm³ of sample per minute, most of which runs to waste).

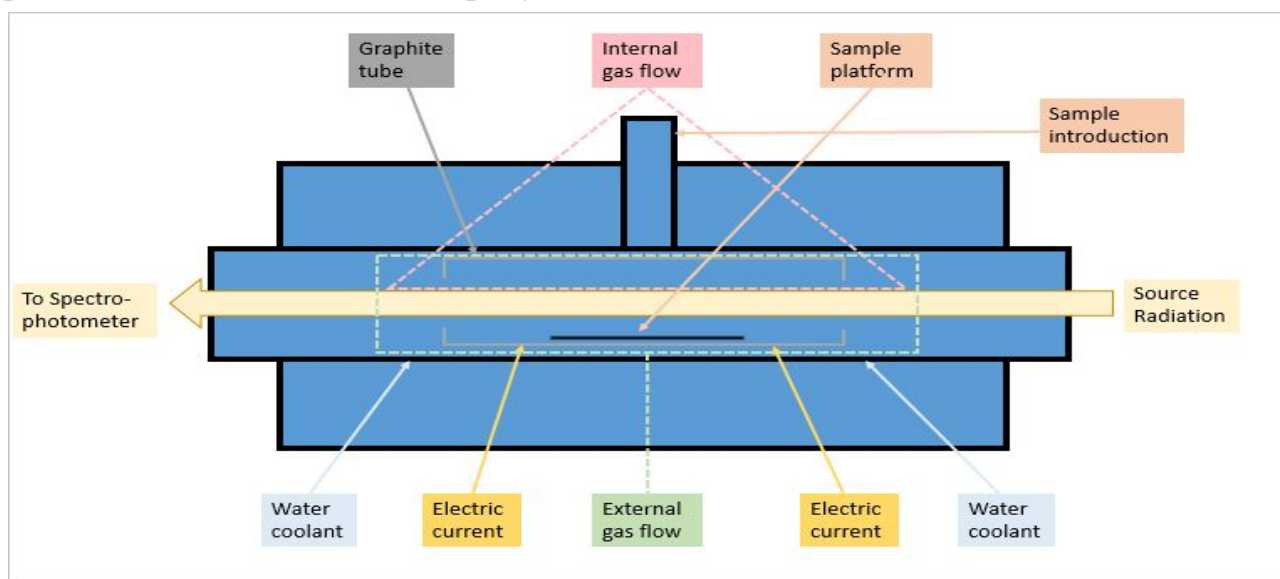
FLAMELESS VAPORIZATION TECHNIQUES

1. **Electrothermal Atomizers**
2. **Cold vapour systems**
3. **Hydride generation systems**

1. ElectroThermal Atomizers

The most widely used Electrothermal atomizers system is a graphite tube (3-5cm long 0.5-1cm diameter) which is heated electrically in a furnace containing an inert gas, e.g. argon.

The sample is inserted through a hole in the centre of the tube, which is then positioned in the light path in place of flame burner and heated according to a predetermined program as follows:



Electro thermal Atomisers: Graphite Tube

Stage 1: Drying at about 100°C to remove water

Stage 2: Ashing (300-500°C) to remove organic constituents

Stage 3: Atomisation (2000-2900°C) to liberate the elements as gaseous atoms

Stage 4: Removal of remaining inorganic matter at the maximum operating temperature about (3000°C)

Advantages Of Electro-thermal Atomisation:

- Only a small sample weight or sample volume is required, typically 10-20 µg or µl.
- The atomisation efficiency and the sensitivity is greater than that given by flame atomisation by up to 10,000 times.
- Chemical pretreatment of samples is not usually required.
- Useful for the assay of trace levels of metals & of small quantity, e.g. blood.

Disadvantage:

- Reduction of precision

2. Cold Vapour Systems

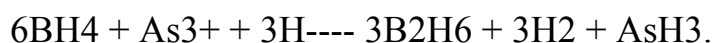
Mercury is a unique metal in that it has a significant vapour pressure at room temperature. Furthermore, the vapour is monatomic and unreactive. Thus it may be entrained in a gas stream and measured by the atomic absorption of this cold vapour.

A typical analytical method first involves the use of an oxidizing mixture such as sulphuric acid and potassium permanganate to destroy organic matter.

The mercuric sulphate thus produced is then reduced with stannous chloride to produce mercury vapour, which is swept through a narrow quartz cell about 15 cm long with a diameter of about 0.75 cm.

3. Hydride Generation Systems

A number of elements such as arsenic, tellurium and selenium may be reduced by a suitable reagent, e.g. sodium borohydride in acidic solution, to their hydrides as follows..

**Monochromator**

Some elements have a single emission line (principal line). But several elements have more than one emission line (secondary line). Hence it is necessary to isolate the required absorption line from a radiation source by a grating monochromator.



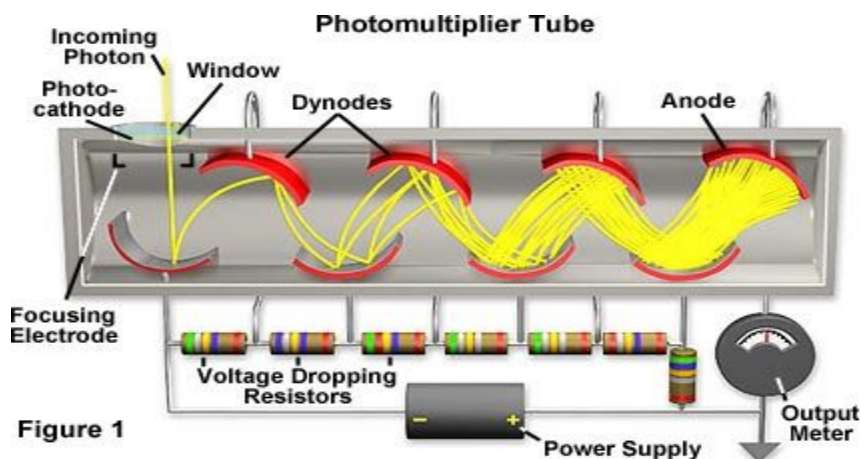
VACUUM MONOCHROMATOR

DETECTOR AND READOUT DEVICE:

The intensity of radiation absorbed by elements in the UV or visible region (190-900nm) can be detected using a photometric detector like a photomultiplier tube.

Photomultiplier Tubes

A photomultiplier tube, useful for light detection of very weak signals, is a photoemissive device in which the absorption of a photon results in the emission of an electron. These detectors work by amplifying the electrons generated by a photocathode exposed to a photon flux.



Photomultipliers acquire light through a glass or quartz window that covers a photosensitive surface, called a photocathode, which then releases electrons that are multiplied by electrodes known as metal channel dynodes. At the end of the

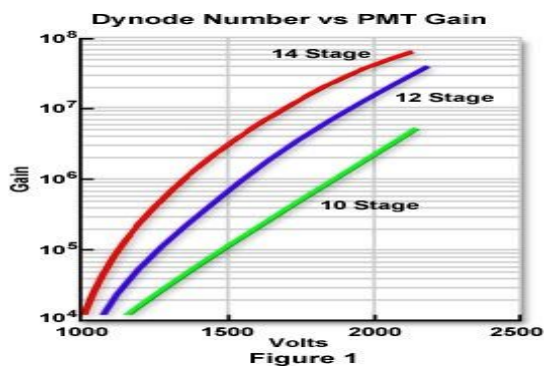
dynode chain is an anode or collection electrode. Over a very large range, the current flowing from the anode to ground is directly proportional to the photoelectron flux generated by the photocathode.

The spectral response, quantum efficiency, sensitivity, and dark current of a photomultiplier tube are determined by the composition of the photocathode. The best photocathodes capable of responding to visible light are less than 30 percent quantum efficient, meaning that 70 percent of the photons impacting on the photocathode do not produce a photoelectron and are therefore not detected. Photocathode thickness is an important variable that must be monitored to ensure the proper response from absorbed photons. If the photocathode is too thick, more photons will be absorbed but fewer electrons will be emitted from the back surface, but if it is too thin, too many photons will pass through without being absorbed. The photomultiplier used in this tutorial is a side-on design, which uses an opaque and relatively thick photocathode. Photoelectrons are ejected from the front face of the photocathode and angled toward the first dynode.

Electrons emitted by the photocathode are accelerated toward the dynode chain, which may contain up to 14 elements. Focusing electrodes are usually present to ensure that photoelectrons emitted near the edges of the photocathode will be likely to land on the first dynode. Upon impacting the first dynode, a photoelectron will invoke the release of additional electron that are accelerated toward the next dynode, and so on. The surface composition and geometry of the dynodes determines their ability to serve as electron multipliers. Because gain varies with the voltage across the dynodes and the total number of dynodes, electron gains of 10 million (Figure 1) are possible if 12-14 dynode stages are employed.

Photomultipliers produce a signal even in the absence of light due to dark current arising from thermal emissions of electrons from the photocathode, leakage current between dynodes, as well as stray high-energy radiation. Electronic noise also contributes to the dark current and is often included in the dark-current value.

The readout device is capable of displaying the absorption spectrum as well as the absorbance at a specified wavelength.



INTERFERENCES IN ATOMIC ABSORPTION SPECTROSCOPY

Interferences in atomic absorption measurements can arise from spectral chemical and physical sources

SPECIAL INTERFACE resulting from the overlap of absorption lines is rare because of the simplicity and the sharpness of the lines. However, broadband by molecular species can lead to significant background interface. Correction for this may be made by matrix matching of samples and standards, or by use of a standard addition method.

CHEMICAL INTERFERENCE

Include stable compound formation and ionization, both of which decrease the population of free atoms in the sample vapour and thereby lower the measured absorbance. Ex: Reactions between alkaline earth metals and oxyanions such as aluminum, vanadium, boron etc

ADVANTAGES OF AAS

Solutions, slurries and solid samples can be analysed.

Much more efficient atomization Greater sensitivity Smaller quantities of sample (typically 5 – 50 μL) Provides a reducing environment for easily oxidized.

DISADVANTAGES

Expensive

Low precision

Low sample throughput

Requires high level of operator skill

Sample must be in solution or at least volatile

Individual source lamps required for each element

APPLICATIONS OF AAS

Atomic absorption spectroscopy is one of the most widely used techniques for the determination of metals at trace levels in solution. Its popularity as compared with that of flame emission is due to its relative freedom from interferences by inter – element effects and its relative insensitivity to variations in flame temperature. Only for the routine determination of alkali and alkaline earth metals, is flame photometry usually preferred.

Over sixty elements can be determined in almost any matrix by atomic absorption.

Ex: 1. Heavy metals in body fluids

2. Polluted waters

3. Food stuffs

4. Soft drinks and beer

5. Analysis of metallurgical and geochemical samples

6. Determination of many metals in soils, crude oils, petroleum products and plastics etc

7. PURIFICATION OF WATER PETROLEUM PRODUCTS FOOD STUFF

Detection limits generally lie in the range 100- 0.1 ppb but these can be improved by chemical pre – concentration procedures involving solvent extraction or ion exchange. Peak – Peak noise curve. Currently a balance seems to have reached in the use of various techniques for the determination of metals at trace levels. In its modern form AAS remains important and competitive where small ranges of elements need to be determined in samples.