
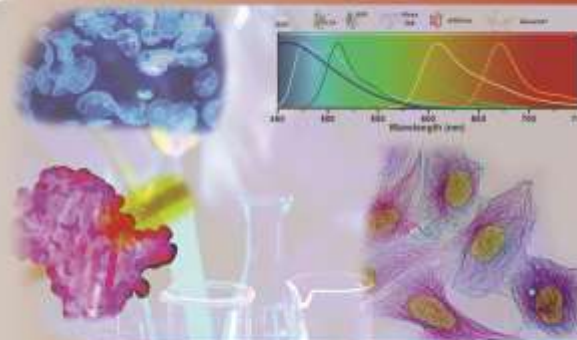


**Subject: Analytical Chemistry / Instrumentation**

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**Paper No. : 06 Atomic Spectroscopy**

**Module :03 Instrumentation Atomic Absorption spectrometry**



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**Analytical Chemistry  
/ Instrumentation**

**Atomic Spectroscopy**

**Instrumentation Atomic Absorption spectrometry (AAS)**

## Description of Module

<b>Subject Name</b>	Analytical Chemistry / Instrumentation
<b>Paper Name</b>	Atomic Spectroscopy
<b>Module Name/Title</b>	Instrumentation Atomic Absorption spectrometry (AAS)
<b>Module Id</b>	03
<b>Pre-requisites</b>	
<b>Objectives</b>	Parts of the atomic absorption spectrometer Various types of light sources, Detectors How to select the wavelength and what is its importance. Difference between gratings and monochromators
<b>Keywords</b>	Atomic Absorption spectrometry (AAS),Hollow cathode lamp, Echelette Gratings, Interference Wedges, Interference Filters, Wavelength Selectors, Oxidants used in Flame Atomizer

## 1. Introduction:

Atomic absorption spectroscopy efficaciously facilitates the estimation of particular elements in the presence of many other elements. Most of the atomic absorption instruments are capable of measuring both atomic absorption and atomic emission. For the operator it is important to understand the processes that occur in each technique. The basic components of any type or brand of atomic absorption include the following:

- 1 Light Source
- 2 Burner/Nebulizer
- 3 Sample Atomizers
- 4 Wavelength Selectors
- 5 Detector
- 6 Readout devices

## 2. Light Sources

Since atoms absorb light at very specific wavelengths, it is necessary to use a narrow-line source which emits the narrow-line spectra of the element of interest. Narrow-line sources provide high intensity and make atomic absorption a specific analytical technique. The main sources used for atomic absorption are the *hollow cathode lamp* (HCL) and the *electrodeless discharge lamp* (EDL).

### 2.1. Hollow cathode lamp

'Hollow cathode lamp' is the common source of light in Atomic Absorption spectroscopy (*Fig. 1*). It consists of cathode which is a hollowed-out cylinder made of the element to be determined and a tungsten anode. At a pressure between  $1 \text{ Nm}^{-2}$  and  $5 \text{ Nm}^{-2}$  the glass tube is filled with an inert gas – neon or argon in which cathode and anode are sealed. For appropriate transmittance of the emitted radiation the glass cylinder has a quartz or UV glass window.

The best lamp intensity is achieved by the optimum gas fill while the spectral interferences from either neon or argon are also considered. The potential difference of about 300–400 V between the anode and the cathode are applied for the ionisation of some gas atoms which bombard the cathode and eject metal atoms from it in a process called sputtering. Some sputtered atoms are in excited states and release radiation of characteristic atom as they fall back to the ground level – eg  $Pb^* \rightarrow Pb + h$  (Fig. 2).



Fig 1:Hollow cathode lamp

Adopted from *The Royal Society of Chemistry*

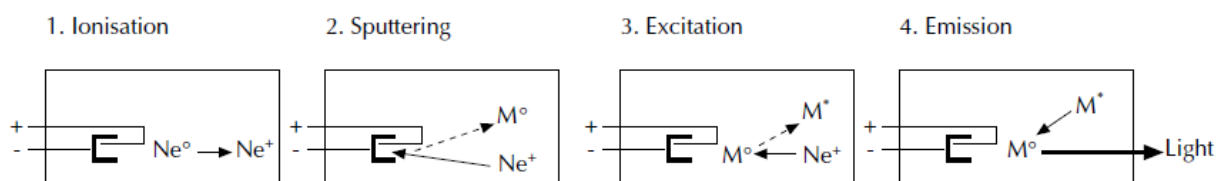


Fig 2: Adopted from *The Royal Society of Chemistry*

The radiation is concentrated into a beam with the shape of the cathode which then passes through a quartz window and the shape of the lamp allows the redeposition of the sputtered atoms on the cathode. A typical atomic absorption instrument holds several lamps each for a different element. There are two types of HCP

### 2.1.1. Single-Element Lamps:

In this type of lamp the hollow cathode is generally made from a very pure metal resulting in a very pure emission spectrum. The cathode of a hollow cathode lamp is generally constructed from a very pure metal resulting in a very pure emission spectrum.

### 2.1.2. Multielement Lamp:

The hollow cathode is generally constructed from a mixture or alloy of several metals. The resulting "multielement" lamp can be used as a source for all the metals contained in the cathode.

## 2.2. Electrodeless Discharge Lamps(EDLs)

The hollow cathode lamp is a completely satisfactory source for most of the elements in atomic absorption. However in certain cases it has some limitations, primarily in case of the more volatile elements, where low intensity and short lamp life are a problem. In such cases electrodeless discharge lamps are a better alternative with brighter and more stable source.(Fig 3)

An EDL is constructed of a quartz bulb filled with an inert gas containing the element or a salt of the element for which the lamp is to be used. The antenna is coiled around a ceramic cylinder in which bulb is placed for RF generation. The inert gas present inside the bulb gets ionized when an RF field is applied and the vaporized atoms inside the bulb gets excited with the coupled energy which causes emission of characteristic light. The main advantage of EDL's is better precision and lower detection limits

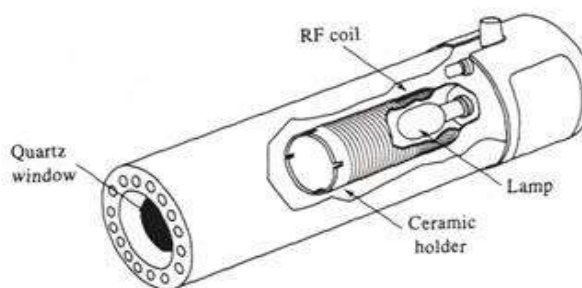


Fig: 3 Electrodeless Discharge Lamps

Adopted from internet

In comparison to hollow cathode lamp the useful life of an EDL is considerably longer for the same element.

## 3. NEBULIZERS:

The general term nebulizer refers to an apparatus that converts liquids into a fine mist. Nebulization is a process in which the sample is converted into a fine mist of finely divided

droplets by using jet of compressed gas. The flow of the gas carries the sample into the atomization region.

**Types of nebulizers:** Most common types of nebulizers used are Pneumatic nebulizers (most common) and ultrasonic nebulizer

### 3.1. Pneumatic nebulizers.

Pneumatic nebulizers are further divided into three types:

1.1.1. **Concentric tube.** This is the most common type of pneumatic nebulizer used. In this type of pneumatic nebulizers, the liquid sample is drawn up by the pressure drop generated as the nebulizer gas passes through the orifice. This is also called “free running” or “self aspiration” Due to high velocity the sample breaks down into a mist and is carried to the atomization region.

Advantage- – Generally, the ion signal produced is much more stable. However this type of nebulizers have some limitations. They are as it cannot handle the sample with high total dissolved salts (TDS - 0.25% m/v solids); i.e. 250 mg sample dissolved in 100 g of solution.

1.1.2. **Cross-flow** In this case, the flow of jet stream is at right angles to the capillary tip. Sometimes the sample is pumped through the capillary.

1.1.3. **Fritted disk:** the gas jet is flowed through the fritted disk in which the sample is pumped. With this the aerosols obtained are finer than the others.

### 3.2. Ultrasonic Nebulizer

The sample is fed to the surface of a vibrating piezoelectric transducer operated at a frequency of between 0.2 and 10 MHz. The mist obtained is more homogeneous and denser than

pneumatic nebulizers. The production of aerosols is also very efficient and independent of gas flow rate unlike pneumatic nebulizers.

The efficiency and detection limits of ultrasonic nebulizer are better than the pneumatic nebulizers. However long wash-out times and lots of glassware required, bad memory effects and cost are some of the limitations for its use.

#### 4. Sample Atomizer

In atomic absorption spectroscopy it is a requirement to convert the sample to gaseous state, which absorb radiation. The sample is mostly introduced as a solution and the solution is taken to the nebulizer through a small tube. In nebulizer the gaseous sample is broken up into a fine mist which is then carried to the atomizer, such as a flame, by a carrier gas. Upon reaching the flame the intense heat of flame breaks up the sample into its individual atoms. This complete process is called atomization.

There are two main types of atomizers:

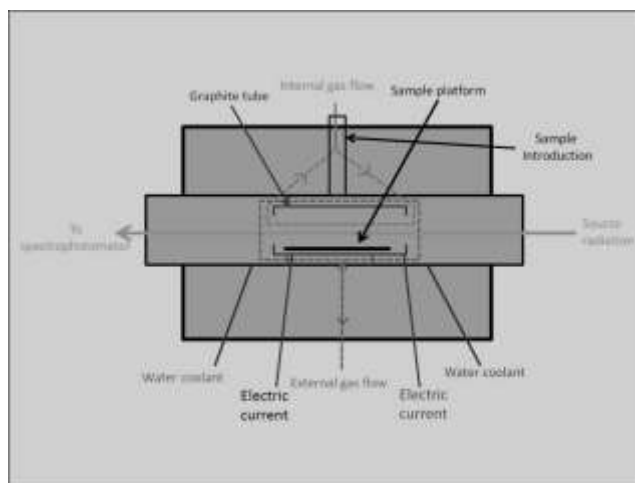
4.1. **Discrete atomizers:** The most common example of discrete atomizer is electrothermal atomizer. In this type of atomizers the sample is introduced in a discontinuous manner with a syringe or auto sampler.

##### 4.1.1. Electrothermal Atomization

A hollow graphite tube with a platform is shown in **fig 4.25**  $\mu\text{l}$  of sample is placed onto the platform through the sample hole with an automated micropipette and sample changer. By passing electric current the tube is heated in a pre-programmed series of steps.

The conditions may vary with the sample but typically to evaporate the solvent it might be 30–40 seconds at 150 °C, to drive off any volatile organic material 30 seconds at 600 °C and to vaporize and atomize elements with a very fast heating rate (*ca* 1500 °C s<sup>-1</sup>) to 2000–2500 °C for 5–10 seconds. The tube is further heated to *ca* 2700 °C to clean it for next sample.

During this heating cycle the graphite tube is prevented from burning by flushing it with argon gas during this heating cycle. The sample is atomized almost 100% in electrothermal atomization. This makes the technique much more sensitive than flame AAS



**Fig: 4.** Electrothermal atomizers (EA). Adopted from blogs/Maryville.com

Electrothermal atomizers (EA) have high sensitivity and have been used for quantitative determinations based on signal peak area and height. It has advantage of using smaller sample size. The spectral interferences in EA are low because of the high temperature of the graphite furnace.

However, EA has limited analytical range and slow measurement time which limits its use. Additionally, the graphite tube needs replacing with time when the analyte and matrix diffuse into it, increasing the maintenance and cost associated with electrothermal atomization.

4.2. **Continuous.** The most common example of Continuous atomizer is Flame atomizer. In this type of atomizers the sample is introduced in a continuous manner.

## 5. Flame atomizer.

The process of atomization takes place in a flame after nebulization of the sample. Once the sample reaches the flame the process of atomization involves three more steps desolvation, volatilization, and dissociation.

- Desolvation is a process in which the solvent is evaporated to produce molecular aerosol.
- Volatilization is in which gaseous molecules are produced from the aerosol and
- Dissociation is in which atomic gas is formed by the dissociation of molecules. In this process of ionization of atomic gases some cations and electrons are also formed.



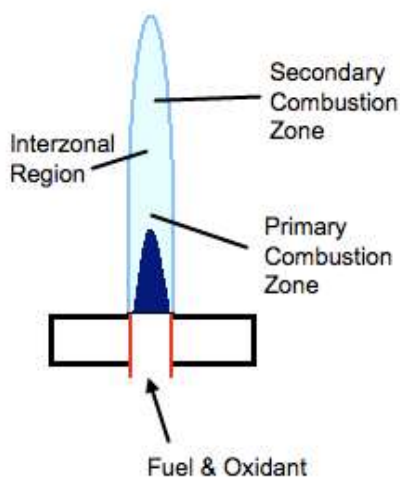
## 6. Fuels and Oxidants used in Flame Atomizer.

To produce flames of interest most common fuels and oxidants used in AAS are listed in the table 1. To achieve specific temperature range a mixture of different oxidants and fuels can be used.

**Table 1.**List of common fuels and oxidants used to produce flames

Oxidant	Fuel	Temperature °C	Max Burning velocity (cm/s)
Oxygen	Natural Gas	2700-2800	370-390
Oxygen	Hydrogen	2550-2700	900-1400
Oxygen	Acetylene	3050-3150	1100-2480
Air	Natural Gas	1700-1900	39-43
Air	Hydrogen	2000-2400	300-440
Air	Acetylene	2100-2400	158-266
Nitrous Oxide	Acetylene	2600-2800	285

## 7. Flame Structure



Fuel (usually acetylene) and air are added mixed with a nebulizer mist. This mixture is then introduced into the flame.

**Fig.5:** Structure of Flame Adopted from blogs/Maryville.com

The different regions of flame have different temperature and in fuel to oxidant ratio. **The three important regions of flame are primary combustion zone, interzonal region and secondary combustion zone (Fig 5).** The mostly widely part of the flame used for spectroscopic analysis is interzonal region, the second region, because it is the hottest region of the flame and is prevalent in free atoms. The flame usually rises about 5 cm above the burner tip with max temperature point at 2.5 cm. The portion of the flame used for AAS is specific as to what element is being analyzed. For different elements the maximum absorbance is achieved at different distances (cm) above the burner due to the formation of oxides.

### Performance

For all the liquid- sample introductions Flame atomic atomization is the most reproducible, however it has many limitations.

- Sensitivity of flame atomization is lower than electrothermal atomization
- The absorbance of samples are reduced due to formation of oxides
- . Fluctuations of flame affect the absorbance of samples.

By using variety of means the sample is converted to the vapor of atoms that is to be analyzed by the AAS. In addition to the methods previously discussed other techniques that can be very useful for AAS, are hydride atomization, glow-discharge atomization, and cold-vapor atomization.

### 8. Wavelength Selectors

To limit the radiations absorbed by a sample wavelength selectors are used to restrict the radiations to a certain wavelength or a narrow band. This helps in improving the sensitivity of an AAS while as the high transmission improves the detectability.

Number of wavelength selectors are available. However it wont be possible to discuss all of them in this chapter we will limit our discussion to filters and monochromators only.

## 8.1.Filters

Filters transmits selectable *narrow band* of *wavelengths* of light or other *radiation*. Four categories of filters are known: absorption filters, cut-off filters, interference filters, and interference wedges.

### 8.1.1. Absorption Filters:

*Absorption Filters* absorb most of the polychromatic radiation and allow transmission of only a specific band of wavelengths. They only transmits about 10-20% of the incident radiation. Since they can be made from colored glasses or plastics they are economical and simple. An absorption filter transmits only about 10-20% of the incident radiation (Fig 6).

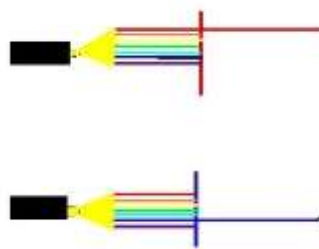


Fig: 6.Absorption filters

Adopted from

<http://chemicalparadigms.wikispaces.com>

8.1.2. **Cut-off Filters:** These type of filters transmit most of the radiation (nearly 100%). It transmits wavelengths of specific band which rapidly decreases to zero over the remainder of the spectrum (Fig 7). These types of filters are not usually used as wavelength selectors but to reduce the bandwidth of the absorption filter they are used in combination with them. The wavelengths transmitted will be the common one between the two filters which will result in narrower bandwidth than absorption filters alone (Fig 8).

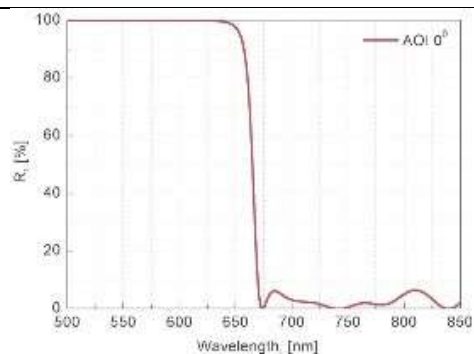


Fig: 7. Spectrum of a specific cut-off filter

Source <http://www.optida.lt/product/cut-off-filter-coatings>

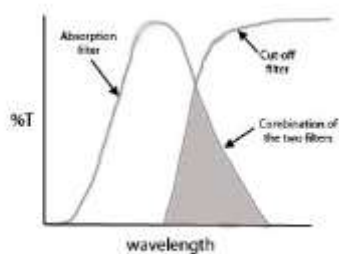


Fig: An absorption filter and a cut-off filter used in combination will only transmit their common wavelengths. Adopted from

<http://www.optida.lt/product/cut-off-filter-coatings>

### 8.1.3. Interference Filters

The interference filters also called Fabry-Perot filters are dependent upon the concept of wave interference. Interference filters work on the principle of transmittance of some wavelengths of radiation while reflect others.

The *interference filter* are made of a film of dielectric material which is transparent sandwiched between two semi-transparent metal films and protected by glass plates (Fig 9). The dielectric material thickness and metallic films should be selected carefully as the dielectric material and the reflectivity of the metallic films controls the transmittance of wavelengths. The radiation transmitted through interference filters therefore, has a very narrow bandwidth.

### 8.1.4. Interference Wedges

A wide range of wavelengths can be transmitted by wedge dielectric of different thicknesses without changing the interference filters in an instrument (Fig 10). The wavelengths with a bandwidth of about 20 nm can be isolated by choosing correct position of the wedge.

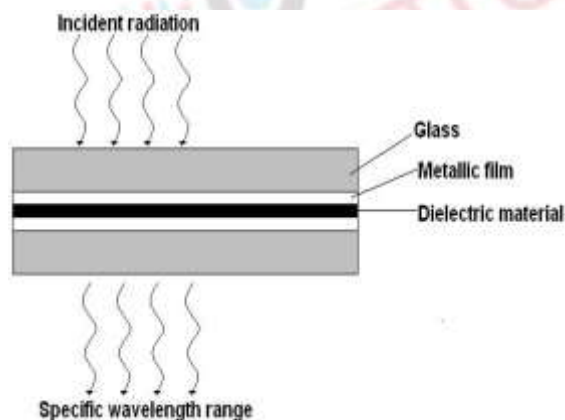


Fig: 9. Interference filters

Adopted from [http://chemwiki.ucdavis.edu/Analytical\\_Chemistry](http://chemwiki.ucdavis.edu/Analytical_Chemistry)

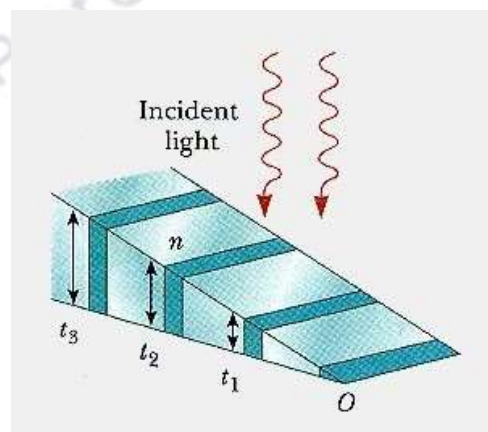


Fig: 10. Interference Wedge

Adopted from <http://nothingnerdy.wikispaces.com>

## 8.2. Monochromators :

The two basic types of monochromators are Grating Monochromators and Prism Monochromators

### 8.2.1. Grating Monochromators

Grating monochromators are placed within compartments of some AAS instruments which are capable of producing narrow bands of radiation

There are five components in most grating monochromators viz. an entrance slit, a collimating lens or mirror, a reflection grating, a focusing element, and an exit slit (Fig 11).

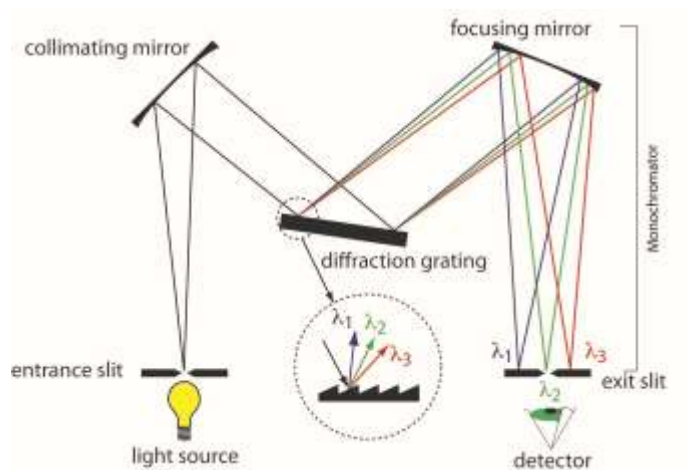


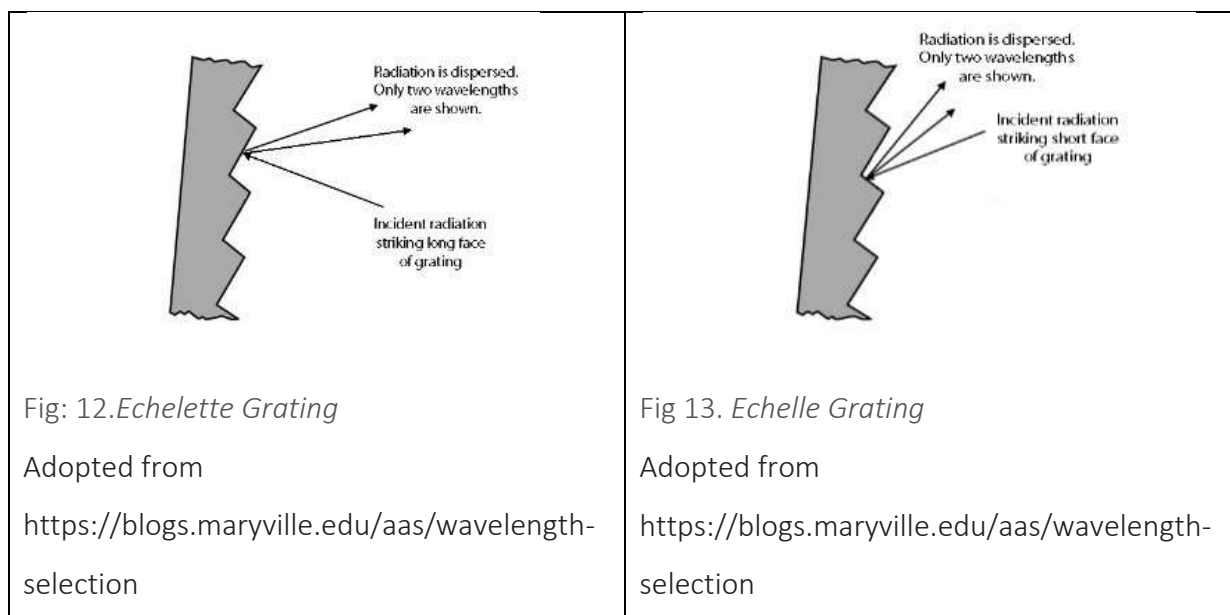
Fig: 11. Grating Monochromator .

Adopted from <http://chemwiki.ucdavis.edu>

In spectroscopic instruments the reflection gratings usually used are of two types echelette and echelle gratings

#### 8.2.1.1. Echelette Gratings:

The most common type of gratings used in spectroscopic instruments is echelette gratings which may contain 300-2000 grooves/mm. The most common echelette gratings used in AAS has on an average, density of 1200-1400 grooves/mm. These gratings use the long face of the groove for the linear dispersion of radiation (Fig 12).



### 8.2.1.2. Echelle Gratings

For the dispersion of radiation short face of the grooves is used in Echelle gratings. They contain less number of grooves per millimeter approximately 80-300 grooves/mm but these are known for their very high dispersion (Fig 13).

### 8.2.2. Prism Monochromators

Prisms create angular dispersion by refracting the light at the surface of two interfaces and can be used to disperse all the three types of radiations viz ultraviolet, visible, and infrared radiation (Fig 14).

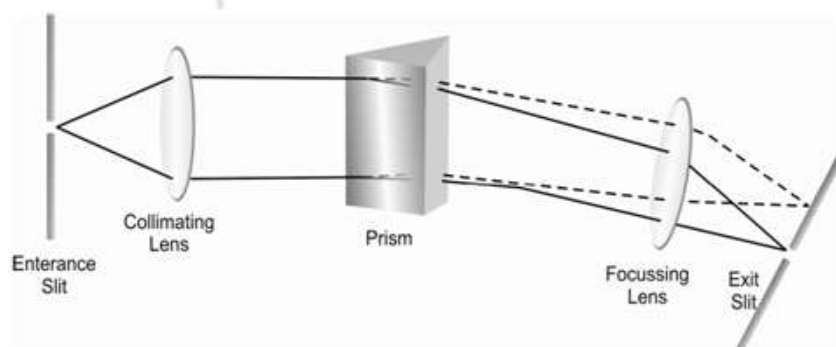


Fig:14. Prism Monochromators

Adopted from <http://www.expertsmind.com>

Despite low dispersion a prism has an advantage of having wide spectrums. However it has limitation for focusing a desired wavelength through the exit slit as the method used by prisms is non-linear dispersion.

The wavelength and dispersion are inversely proportional, where increased dispersion is caused

by shorter wavelengths. The figure below depicts the nonlinear dispersion of a prism.

## 9. Detectors

Detectors are of several kinds iePhotodiode, PN Junction, Photodiode Array and Photomultiplier Tube

### 9.1.Photodiode

A photodiode is a kind of light detector that converts light into voltage or current, which is generated from the absorption of photons. Photodiodes consist of a reverse-biased pn junction which converts the light falling on the junction, to a proportional current.

### 9.2.PN Junction

The pn junction consists of two types of semi-conductor material, p-type and n-type. Both types contain silicon crystal which is commonly used in semiconductor.

In a silicon crystal, each silicon atom is bonded to its neighboring atom by four electrons, forming covalent bonds.

The p-type material is differentiated from the n-type material by alteration in the silicon crystal by a process called doping. During this process, the impurities are added to the intrinsic semiconductor silicon crystal. In case of p-type material, boron atoms are added as a doping agent which have only three valence electrons. This results in the formations of "electron holes" in the silicon lattice of the p-type material. In case of n-type material phosphorus atoms are doped which have five valence electrons, an extra valence electron which results in the formation of an extra electron free from the covalent bonds in the silicon lattice. The free mobile electrons of the n-type material diffuse in the electron holes of the p-type material, making the atom positively charged with newly filled holes. The mobile electron holes also diffuse to the electrons of the n-type material, making the atom negatively charged.



This formation of negatively and positively charged ions creates a region absent of mobile charge carriers known as the depletion region. Further diffusion of charge carriers is prevented by the potential difference, when it reaches at its peak in the depletion region. This results in the reduction of conductance nearly to zero in this region. When the radiation is applied across the diode in this region, it swept through the device to produce a current that is proportional to the radiant power.

Photodiodes can easily be used in portable and battery powered instruments as they require very low voltage. They are less sensitive than photomultiplier tubes, and have a spectral range from about 190nm to 1100nm.

### 9.3. Photodiode Array

Photodiode Array (PDA) consists of individual photosensitive elements called photodiodes. It has a linear array of discrete photodiodes placed on a large integrated circuit (IC) of a silicon chip than a single photodiode. PDAs are one-dimensional transducers in which the photosensitive elements are arranged linearly on the transducer face

### 9.4. Photomultiplier Tube

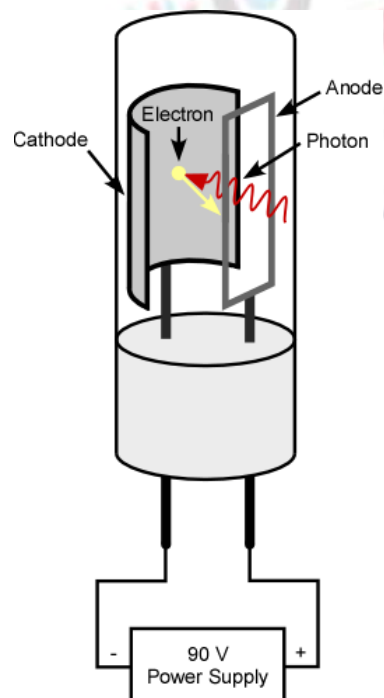


Fig: 15. Traditional Phototube (Adopted from internet)

Among all the present photosensitive devices used, photomultiplier tube (PMT) is a versatile device. It has extremely high sensitivity and is used for the measurement of low radiant

power. The schematic of a PMT is similar to that of a traditional phototube. The traditional phototube consists of two electrodes, a cathode and an anode. When the voltage is applied to the electrodes, the electrons are generated at the cathode and move towards the anode. This flow of electrons generates photocurrent in the anode which is measured. The diagram of a traditional phototube is shown in the fig 15.

PMT contains series of electrodes called dynodes, each dynode is given slightly more positive potential than that of the neighboring nearer to the photocathode. The anode is kept more positive than any electrode. When the photon impinges the cathode, the electrons are accelerated towards the dynodes because of the increasing positive charge. The electrons gather at the anode where they are collected in the form of a current. This current is then converted to a voltage and measured. However, these tubes are limited to measure low power radiation because if the source of radiation is intense it can cause irreversible damage to the photoelectric surface. PMTs are stored in a light-tight compartment to avoid damage by harsh radiation. However the major sensitivity limitation's associated with the PMTs is the noise resulted from the thermal dark currents. These dark currents usually result from thermal emission which can be reduced by cooling the transducer to  $\sim -30$  degrees Celsius. A coolant can be circulated around the PMT to achieve this. With the proper set-up and care, PMTs can be used to detect individual photons at the cathode.

### 10. Readout Devices

The system requires a type of display that can process the information that the instrument is sending to enable to read the signal,. This is achieved through an electronic component that displays the information in a format the researcher can use effectively. The analog based data collected by the instrument needs to be converted into a digital format for the display, which is accomplished by a transducer. The transducer sends the digital energy to the processor, which allows for the processing of discrete times, frequencies, and domains of the signal. This signal is put into a sequence of numbers or symbols that can be displayed on a readout.

Several types of readout devices are used in modern instruments. These devices include Digital Meters, Recorders, Cathode-Ray Tubes, LCD panels, and Computer Displays.

### 11. Summary:

The topic discusses about instrumentation of atomic absorption spectroscopy. How should be source of light selected. It discusses about the method of selection of wavelength. Use of prism monochromators and grating is also discussed. The working of photomultiplier tube is also elaborated.

