

MODULE-4

SPECTROMETRIC TECHNIQUES

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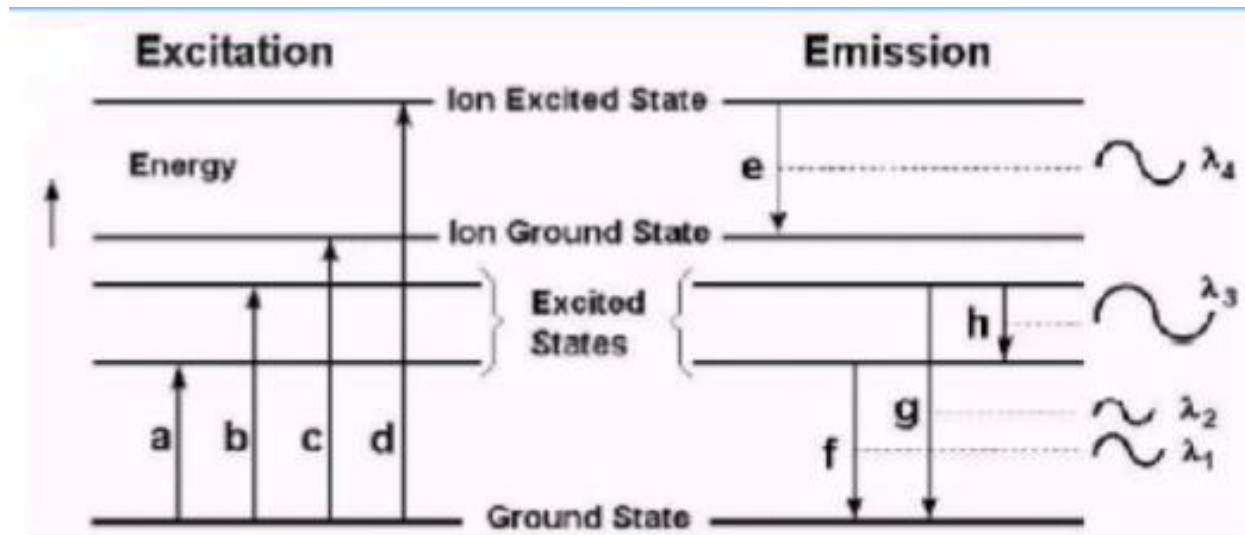
Introduction- atomic spectroscopy

- The science of atomic spectroscopy involves three techniques for analytical use: atomic emission, atomic absorption and atomic fluorescence.
- The process of excitation and decay to the ground state of an atom is involved in all three fields of atomic spectroscopy.
- Either the energy absorbed in the excitation process or the energy emitted in the decay process is measured and used for analytical purposes.
- Atomic Emission Spectroscopy
- Atomic Absorption Spectroscopy

Atomic Emission Spectroscopy

- In atomic emission, a sample is subjected to a high energy, thermal environment in order to produce excited state atoms, capable of emitting light.
- The energy source can be an electrical arc, a flame or more recently, a plasma.
- The emission spectrum of an element exposed to such an energy source consists of a collection of allowable emission wavelengths, commonly called emissions lines, because of the discrete nature of the emitted wavelengths.
- This emission spectrum can be used as unique characteristic for qualitative identification of the element.
- Atomic emission using electrical arcs has been widely used in qualitative analysis.

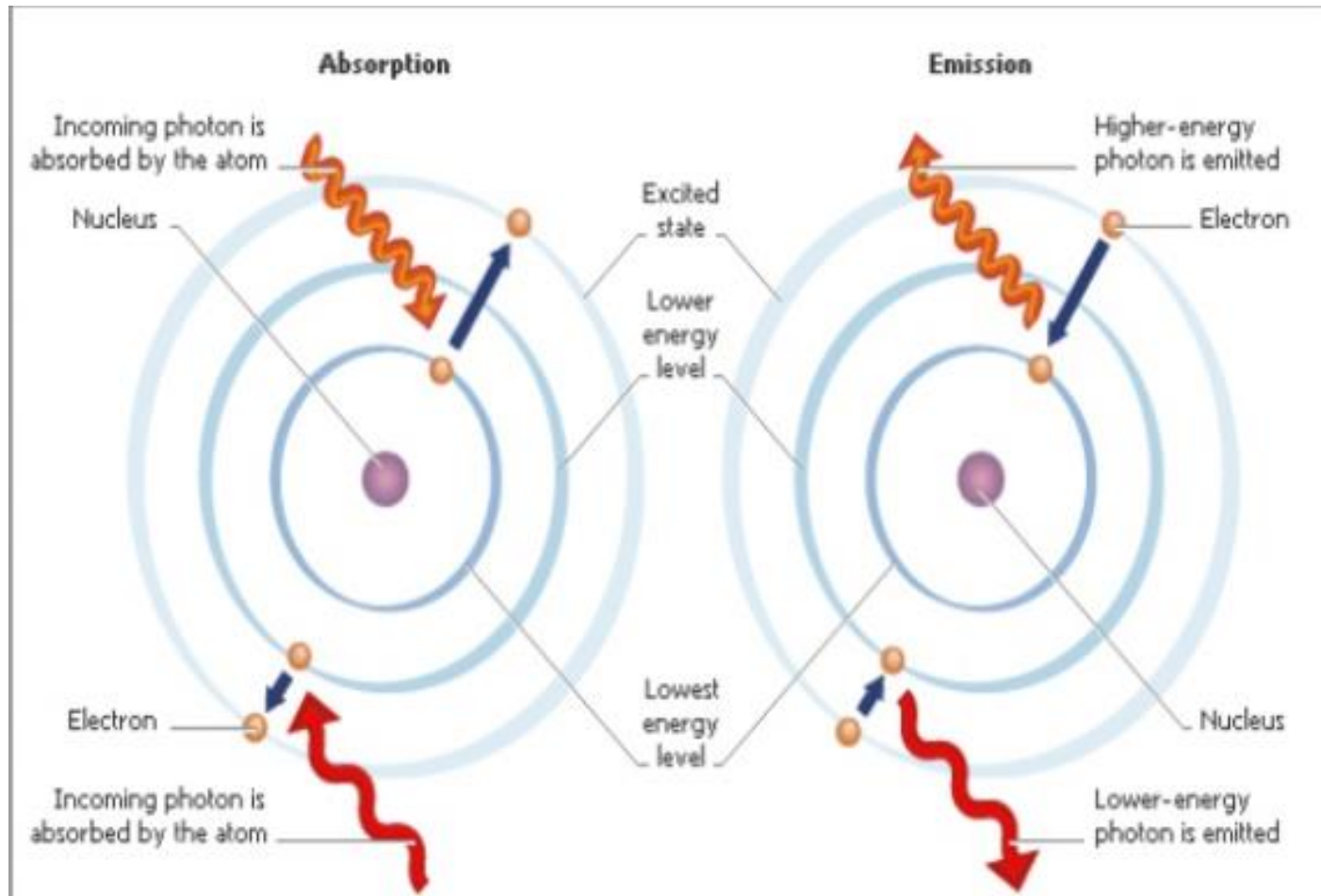
Energy level states



Atomic absorption spectroscopy

- Atomic absorption spectroscopy consists in measuring the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms.
- As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made.
- The use of special light source and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

Absorption versus emission



Atomic Fluorescence Spectroscopy

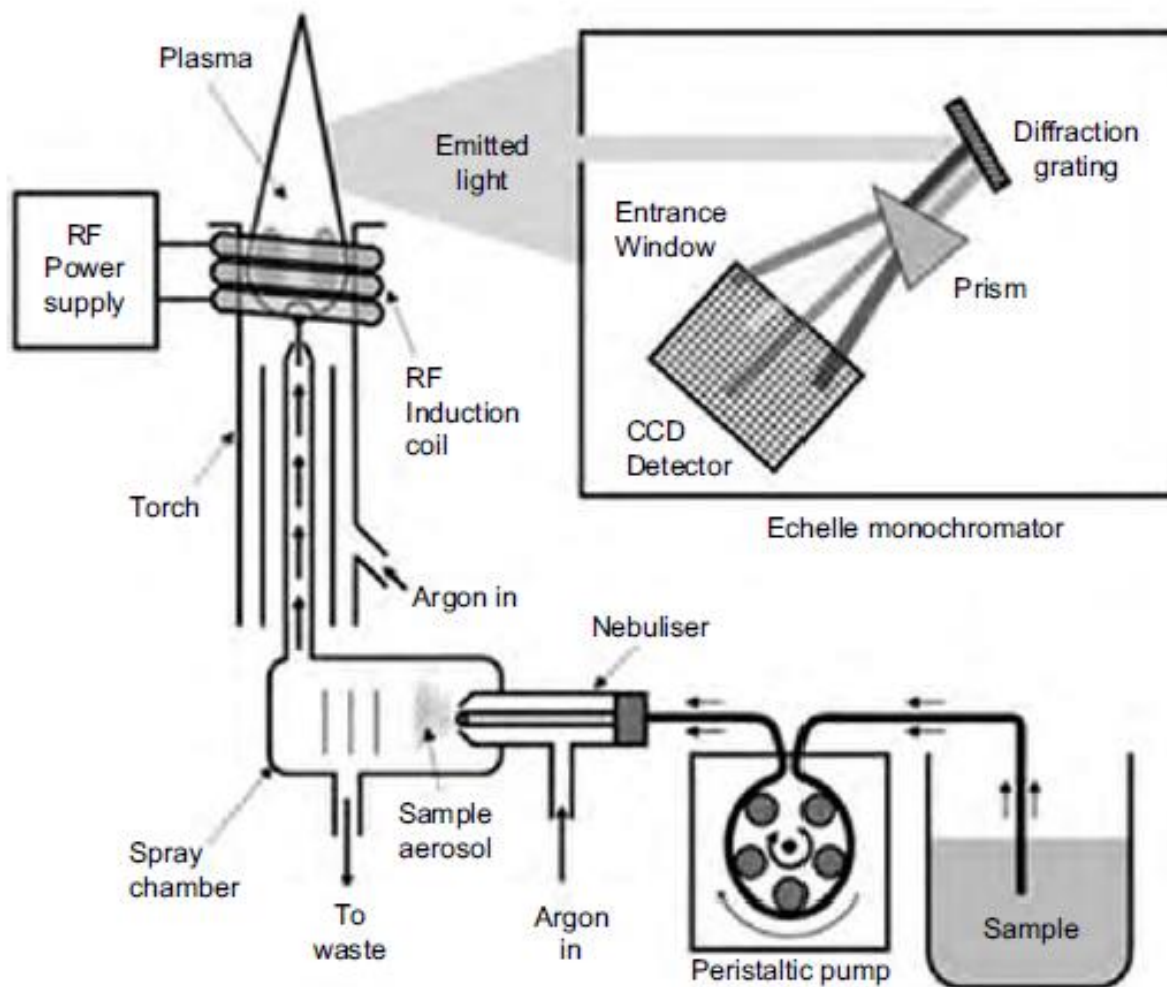
- Atomic fluorescence spectroscopy technique incorporates aspects of both atomic absorption and atomic emission.
- Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light into the atomic vapour.
- Instead of looking at the amount of light absorbed in the process, the emission resulting from the decay of the atoms excited by the source light is measured.
- The intensity of this 'fluorescence' increases with increasing atom concentration, providing the basis for quantitative determination.

Atomic Emission Spectrophotometer

- Atomic emission requires a means for converting a solid, liquid or solution analyte into a free gaseous atom.
- The same source of thermal energy usually serves as the excitation source.
- The most common methods are flames and plasmas, both of which are useful for liquid or solution samples.
- Solid samples may be analysed by dissolving in a solvent and using a flame or plasma atomiser.
- Atomisation and excitation in flame atomic emission is accomplished using the same nebulisation and spray chamber assembly used in atomic absorption.
- The burner head consists of single or multiple slots, or a Meker-style burner.

- In the inductively coupled plasma-atomic emission spectrophotometer (ICP-AES), the sample is exposed to the extremely high temperature of an argon plasma (up to 10,000 K) that breaks the sample into atoms, ionises these atoms and electronically excites the resulting ions.
- When the excited electrons in these ions fall back to lower energy levels, they emit light.
- The wavelengths of light emitted by a particular element serve as a 'fingerprint' for that element.
- Therefore by measuring the **wavelengths of light emitted** by the sample, we can **identify the elements** in the sample; and by measuring the **amount of light emitted** by a particular element in the sample, we can **determine the concentration of that element**.

Block diagram of ICP-AES instrument



Working Principle

- The sample solution is pumped by a peristaltic pump into the nebuliser where it is broken into an aerosol of fine droplets by a fast stream of argon gas.
- From the nebuliser it passes through the spray chamber (which eliminates the larger droplets) and on to the quartz plasma torch.
- The plasma ionises and excites the atoms of the sample.
- Emitted light from the ions in the plasma then passes through the entrance window to the monochromator where it is separated into its various wavelengths (colours).
- The monochromator is a high-resolution 'Echelle' design that makes use of both a diffraction grating and a prism to generate a two-dimensional pattern of individual wavelengths of light.
- This light hits the charge-coupled device (CCD) detector, similar to what you find in a digital camera, where thousands of individual picture elements (pixels) capture the light and turn it into a digital signal that we can measure.

Types of Excitations-atomic emission spectroscopy

- Atomic emission spectroscopy (AES) is a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample.
- The wavelength of the atomic spectral line in the emission spectrum gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element.
- The sample may be excited by various methods.

Flame

- A sample of a material (analyte) is brought into the flame as a gas, sprayed solution, or directly inserted into the flame by use of a small loop of wire, usually platinum.
- The heat from the flame evaporates the solvent and breaks intramolecular bonds to create free atoms.
- The thermal energy also excites the atoms into excited states that subsequently emit light when they return to the ground state.
- Each element emits light at a characteristic wavelength, which is dispersed by a grating or prism and detected in the spectrometer.
- A frequent application of the emission measurement with the flame is the regulation of alkali metals for pharmaceutical analytics.

Flame excitation



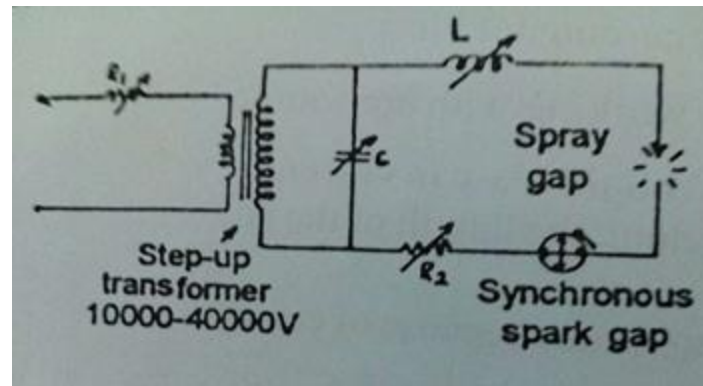
Plasma excitation

- In order to produce strong atomic emission from all chemical elements, it is necessary to have temperatures in the range 7000K–14000K which are generated from an inert-gas plasma.
- Plasma is a hot gas which is electrically conductive because of the major concentrations of essentially free electrons and highly charged cations present.
- Plasma is very effective medium for volatilisation, atomisation and ionisation.
- The plasmas used in atomic emission are formed by ionising a flowing stream of argon gas, producing argon ions and electrons.

- A plasma's high temperature results from resistive heating as the electrons and argon ions move through the gas.
- Because plasmas operate at much higher temperatures than flames, they provide better atomisation and a higher population of excited states.

Spark

- It consists of the primary circuit a voltage of 110-220V is maintained. The high voltage is obtained from a setup transformer which converts the line power to 10000-40000V which then charges the capacitor. When energy stored in the capacitor, synchronous trigger the spark between the electrodes.



Arc Discharge

- An **electric arc**, or **arc discharge**, is an electrical breakdown of a gas that produces a prolonged electrical discharge.
- The current through a normally nonconductive medium such as **air** produces a **plasma**; the **plasma** may produce **visible light**.
- An arc discharge is characterized by a lower voltage than a glow discharge and relies on thermionic emission of electrons from the electrodes supporting the arc.



Arc Discharge

DC ARC	AC ARC
<ul style="list-style-type: none">• Used for quantative analysis.	<ul style="list-style-type: none">• Also used for quantative analysis.
<ul style="list-style-type: none">• Source: regulate supply is 110 to 220 V(temp 4000 to 8000K).	<ul style="list-style-type: none">• In this alteration at a frequency of 60 HZ (2000 to 5000V) that maintain by transformer.
<ul style="list-style-type: none">• When the sample (solid and liquid) is kept on the lower electrode in the arc gap then start the current flow in the gap & electrical arced is established which is responsible for excitation.	<ul style="list-style-type: none">• Once arc is picks out in the gap, current flow start which arced the sample and create excitation.
<ul style="list-style-type: none">• Graphite electrodes is used and Less sensitive.	<ul style="list-style-type: none">• More sensitive.

Thermal

- Atoms with low ionization potentials can be ionized by contact with the heated surface of a metal, generally a filament, having a high work function (the energy required to remove an electron from its surface) in a process called thermal, or surface, ionization.
- This can be a highly efficient method and has the experimental advantage of producing ions with a small energy spread characteristic of the filament temperature, typically a few tenths of an electron volt, as compared with beam energies of thousands of electron volts.
- The filaments, generally made of platinum, rhenium, tungsten, or tantalum, are heated by current.

- Surface ionization requires a nearby source of atoms, often another filament operating at lower temperatures.
- Samples can also be loaded directly on the filament, a widely used and successful technique.

Types of excitation summary

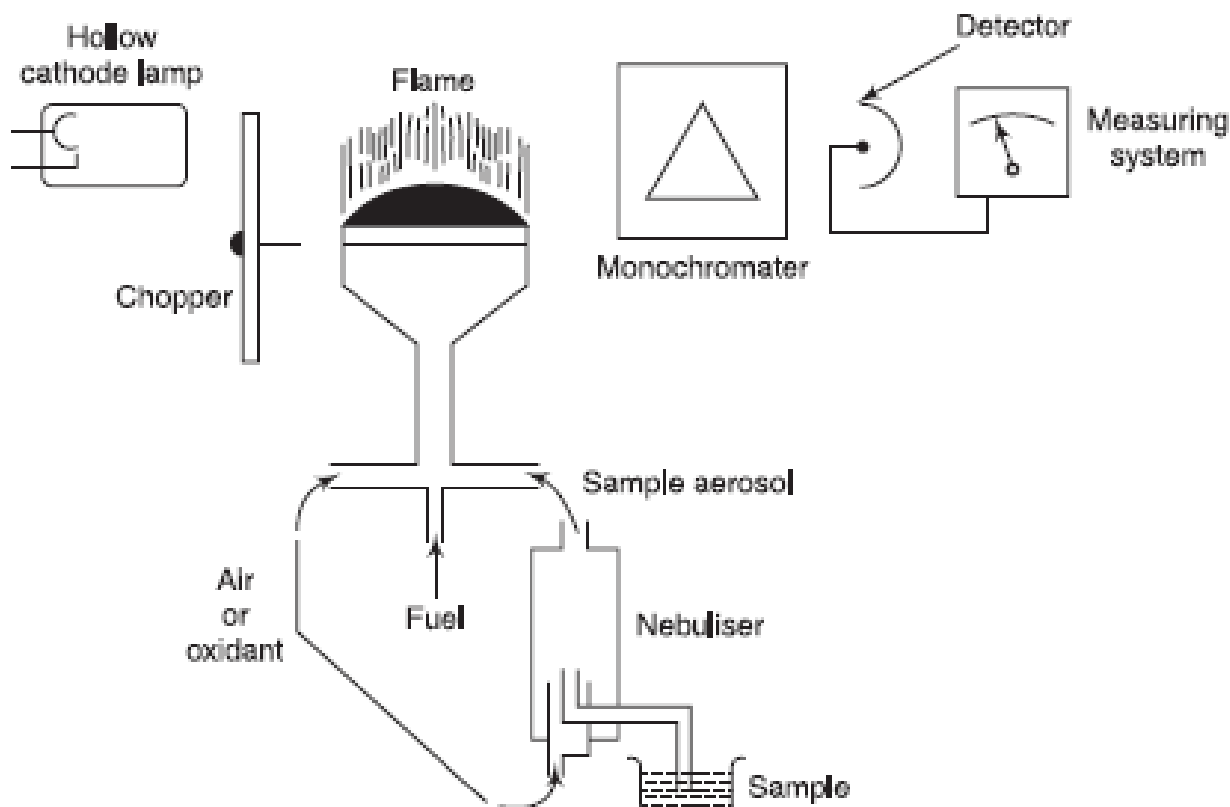
<u>Type</u>	<u>Method of Atomization</u>
Arc	sample heated in an electric arc (4000-5000°C)
Spark	sample excited in a high voltage spark
Flame	sample solution aspirated into a flame (1700 – 3200 °C)
Argon plasma	sample heated in an argon plasma (4000-6000°C)

Atomic Absorption Spectroscopy

- Atomic absorption spectroscopy is an analytical technique based on the absorption of radiant energy by atoms.
- When a beam of light is made to pass through the flame, a portion of it will be absorbed by dispersed atoms, in the same manner that a beam of light passing through a solution will be absorbed by the dispersed molecules of a solute.
- It is possible to find a series of absorption bands corresponding to the energy levels of the atoms sprayed into the flame.
- The wavelength of the bands is characteristic of the atoms of the element concerned and the absorbance of the band is proportional to the concentration of the atoms in the flame.

- A source is chosen for the element to be tested, which emits the characteristic line spectrum of that element.
- The sample, normally in liquid solution for fine suspension, is sprayed into a flame.
- The flame vaporises the sample and puts the atoms in a condition where they can absorb energy.
- The atoms must be chemically uncombined and in their minimum energy or ground state.
- A monochromator selects a characteristic sample line and illuminates adjacent lines.
- A photodetector measures the light passing through the flame, both before and after introduction of the sample into the flame.
- The amount of light absorbed by the atoms in the flame is proportional to the concentration of the element in the sample solution.
- The unknown concentration of the element in the sample may be determined by comparing the absorbance reading on a metre with a calibrated chart showing the relationship of absorbance versus concentration made from data of known concentrations of the element.

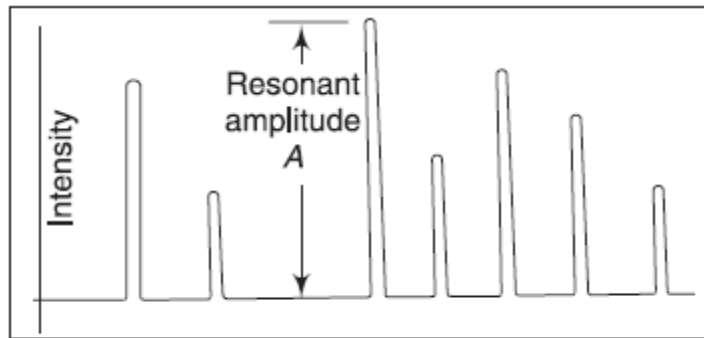
Block Diagram of an atomic absorption spectrophotometer



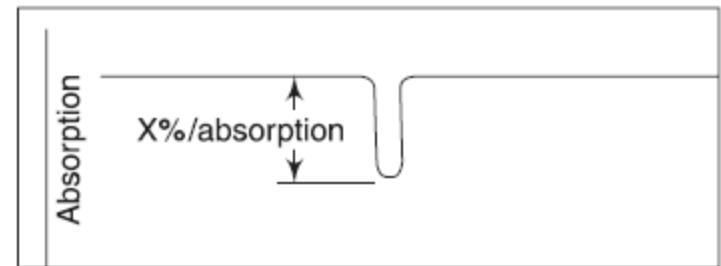
Working principle

- The light source normally used is a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL).
- A hollow cathode lamp is inserted into the AAS machine which emits a distinctive spectrum for that particular metal element.
- This spectrum passes through an air-acetylene flame into which a solution of the metal being tested for is sprayed using a nebuliser to obtain a fine mist.
- The metal ions being tested absorb some of the wavelengths passing through the flame.
- The light beam then passes through a monochromator which acts as a filter to separate light of the chosen wavelength from other light.
- In the past, photomultiplier tubes have been used as the detector. However, in most modern instruments, solid-state detectors are now used.

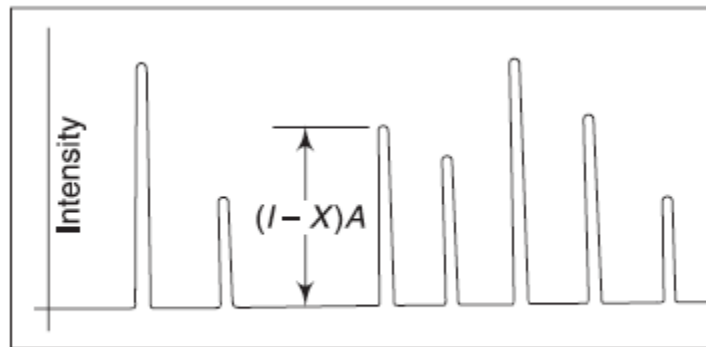
- The atom source used must produce free analyte atoms from the sample.
- The source of energy for free-atom production is heat, most commonly in the form of an air/acetylene or nitrous oxide/ acetylene flame.
- The sample is introduced as an aerosol into the flame by the sample introduction system consisting of a nebuliser and spray chamber.
- The burner head is aligned so that the light beam passes through the flame, where the light is absorbed.
- The major limitation of Flame AA is that the burner-nebuliser system is a relatively inefficient sampling device.
- Only a small fraction of the sample reaches the flame, and the atomised sample passes quickly through the light path.
- An improved sampling device would atomise the entire sample and retain the atomised sample in the light path for an extended period of time, enhancing the sensitivity of the technique.
- Which leads us to the next option – electrothermal vaporisation using a graphite furnace.



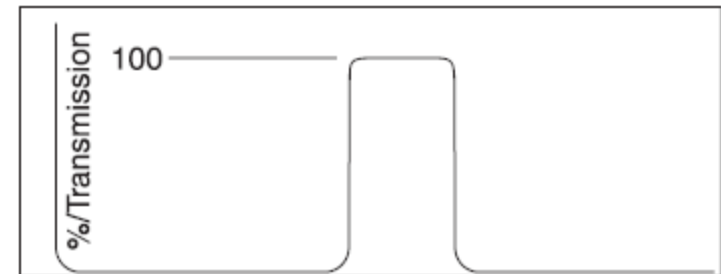
(a)



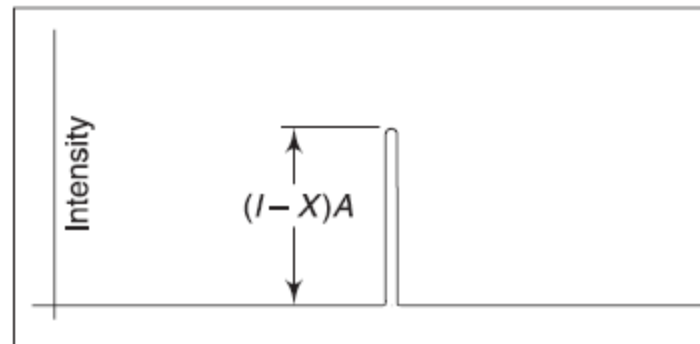
(b) Sample absorbs energy at resonance line



(c) Resultant spectrum after absorption by sample



(d) Monochromator isolates resonance wavelength and rejects all others



(e) Photodetector sees only the resonance line diminished by sample absorption

Figure: Principle of AAS

Self study: Comparison of AES and AAS

Flame photometer

Principle of Flame Photometry

- When radiation falls on a material, or the material is supplied with extra energy in some form, some part of the energy is taken up by the material and results in altering the state of the atoms or molecules of which it is composed.
- The atoms or molecules of the material are promoted to higher energy states.
- However, the higher energy states are rather unstable.
- The particles at the higher energy levels tend to lose the extra energy and return to the original level or ground state, either by undergoing a chemical reaction or by dissipating the energy as heat, or by emitting the energy as radiation.

- If it loses all or part of the energy as radiation, it will emit photons of an energy corresponding to difference between two energy levels.
- Since the levels are clearly defined for a given atom, the radiation will be emitted at clearly defined frequencies only.
- The frequencies are shown up as bright lines if the emitted light is dispersed as a spectrum.
- By measuring the wavelength of the emission, one can find out what atoms are present.
- Also, by measuring the intensity of the emission, one could compute the concentration of the element.

- In short, the principle of flame photometry is based on the fact that if an atom is excited in a flame to a high energy level, it will emit light as it returns to its former energy level.
- By measuring the amount of light emitted, we can measure the number of atoms excited by the flame.

Element Emission	Wavelength (nm)	Flame Colour
Barium (Ba)	554	Lime Green
Calcium (Ca)	622	Orange
Lithium (Li)	670	Red (Carmine)
Potassium (K)	766	Violet
Sodium (Na)	589	Yellow

Table: Emission wavelength of various metals

Basic Flame Photometer

- A solution of the sample to be analysed is prepared.
- A special sprayer operated by compressed air or oxygen is used to introduce this solution in the form of a fine spray (aerosol) into the flame of a burner operating on some fuel gas, like acetylene or hydrogen.
- Conversion of sample solution into an aerosol by atomiser does not bring about any chemical change in the sample.
- However, the heat of the flame which vaporises sample constituents, molecules and ions of the sample species are decomposed and reduced to give atoms.
- The heat of the flame causes excitation of some atoms into higher electronic states.
- Excited atoms revert to the ground state by emission of high energy of characteristic wavelength.

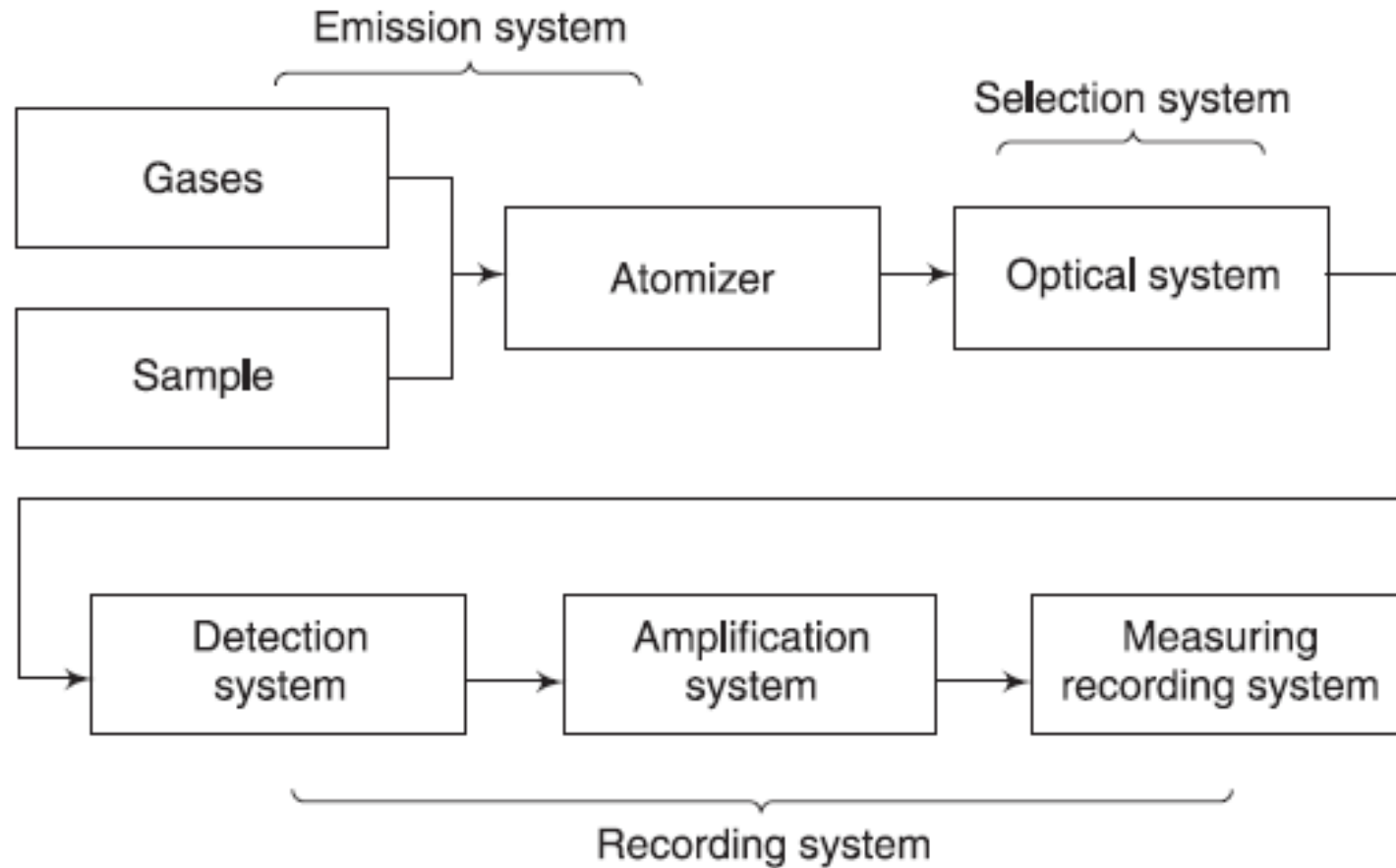
- The radiation of the element produced in the flame is separated from the emission of other elements by means of light filters or a monochromator.
- The intensity of the isolated radiation is measured from the current it produces when it falls on a photocell.
- The measurement of current is done with the help of a galvanometer, whose readings are proportional to the concentration of the element.
- After carefully calibrating the galvanometer with solutions of known composition and concentration, it is possible to correlate the intensity of a given spectral line of the unknown sample, with the amount of the same element present in a standard solution.

Constructional Details of Flame Photometers

A flame photometer has three essential parts

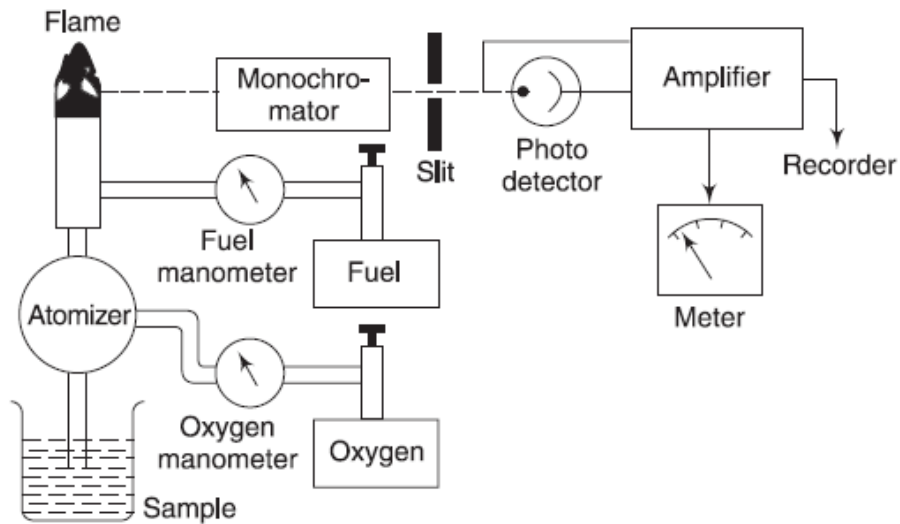
- **Emission System:** It consists of the following:
 - (i) Fuel gases and their regulation: comprising the fuel reservoir, compressors, pressure regulators and pressure gauges.
 - (ii) Atomiser: consisting of the sprayer and the atomisation chamber, where the aerosol is produced and fed into the flame.
 - (iii) Burner: receives the mixture of the combustion gases.
 - (iv) Flame: the true source of emission.

Essential parts of a flame photometer



- **Optical System:** It consists of the optical system for wavelength selection (filters or monochromators), lenses, diaphragms, slits, etc.
- **Recording System:** It includes detectors like photocells, phototubes, photomultipliers, etc., and the electronic means of amplification, measuring and recording.

Block diagram of a flame photometer



Emission System

- ***Fuel gases and their regulation:***
- ***Pressure Regulators:*** A 25-lb gauge for the oxygen or air supply and a 10-lb gauge for the fuel are generally used.
- ***Flowmetres:*** A flow metre may be inserted in the line from the gas reservoir to the atomiser in order to detect any clogging of the orifice. The flow rates usually vary from 2 to 10 Cu. ft/h.
- ***Fuel Supply:*** The fuel gas normally used in flame photometry is the acetylene gas. Consumption of acetylene ranges from 1 to 5 s Cu. ft/h. The other fuels used in flame photometry are propane, butane and hydrogen.
- ***Oxygen Supply:*** Oxygen from cylinders should be supplied to the burner through a regulator capable of delivering approximately 12 Cu. ft/h. at a pressure of 12–15 lb per sq. inch.
- ***Air Supply:*** The air supply can be supplied from a cylinder of compressed air or from an air compressor through a tank held at about 10 lb/sq. inch.

Atomiser

- One of the most exacting problems in the flame photometer design is the manner in which the sample is fed to the flame at a uniform rate.
- The usual method is to prepare solutions of known concentrations and to spray these into the flame, using some form of aerosol production.
- Use of an aerosol permits the distribution of the same throughout the body of the flame, rather than its introduction at a single point.
- In flame photometry, the name atomiser is given to a system which is used to form aerosol by breaking a mass of liquid into small drops.
- This little device is responsible for introducing the liquid sample into the flame at a stable and reproducible rate. The atomiser must not be attacked by corrosive solutions.

- Two types of atomisers which are in common use are:
 - (i) Those which introduce the spray into a condensing chamber and into the flame by the air of the combustible gas air mixture. Large droplets are removed in the condensing chamber.
 - (ii) Those in which the sample is introduced directly into the flame (i.e. the atomiser and the burner are an integral unit).

Burner

- The burner brings the fuel, oxidant and sample aerosol together, so that they may react safely and produce a good flame. Burners used in flame photometry must fulfil the following conditions:
 - (i) Supply fuel and oxygen at constant pressure to enable the shape, size and temperature of the flame will remain constant.
 - (ii) Assist in a perfect distribution of the mixture of gases and the aerosol, which carries the atomised solution under analysis.
 - (iii) Have a tip of suitable shape to produce a symmetrical flame and ensure a homogeneous flow and distribution of the gases, avoiding a strike back in the burner from accidental fluctuations in the feed system.
 - (iv) Prevent condensation of the aerosol in the stem of the burner, which would reduce the effective quantity of the sample brought into the flame.

- The most commonly used burner for low temperature flames is Meker type.
- Here, the fuel-gas issues from a small orifice and passes through a venture throat, where considerable air is entrained.
- The mixture of gas and the entrained air passes up the burner tube and burns at the top of the burner, where the combustion is assisted by the surrounding air.

Flame

- The flame is the most important part of the flame photometer, since it forms the source in which the light radiations characteristic of the elements under analysis are produced. The flame performs the following functions:
 - (i) It converts the constituents of the sample to be analysed from the liquid or solid state into gaseous state.
 - (ii) Decomposes these constituents into atoms or simpler molecules.
 - (iii) Excites the resulting atomic or molecular species to emit light radiations.
- In order to produce accurate results, the flame must be very stable

Optical System

- The complex light emission produced in the flame by a solution containing one or more elements, makes it necessary to select the radiations of different wavelengths for each of the elements present in the solution.
- This is done by the optical system, which collects the light from the stable part of the flame, provides it to monochromatic and then focuses it on to the surface of the photodetector.
- A concave mirror is often placed behind the flame, with its centre of curvature in the flame. In this way, the intensity of the emitted light is nearly doubled.

- **Filters:** Atoms in the vapour state give line Spectra and not band spectra because no covalent bonds and hence no vibrational sub-levels to cause broadening. Therefore, wavelength selection may be done by optical filters or monochromators. Less expensive instruments make use of filters, which may be absorption type or interference type.
- **Monochromators:** Monochromators are incorporated in the instruments, which are expected to provide better isolation of spectral energy. By using narrow slit widths and sensitive detecting circuits, quite narrow bands of radiant energy can be isolated. In flame photometry **prism monochromators** have been most widely accepted. They may be of glass or quartz. Dispersal of light may also be obtained by means of **diffraction in a grating**. A grating is produced by ruling grooves at extremely close intervals, of the order of 15,000 grooves per inch, on a highly polished surface. The dispersion is linear, which permits a constant bandwidth to be used throughout the spectrum. The wavelength scale in this case is linear.

- **Other optical components:** Reflectors and condensing lenses can be placed in the optical path to concentrate the light.
- **A concave metal mirror** with its focus in the flame itself is placed immediately behind the flame. Condensing lenses are used to render parallel beams of light before it falls on the interference filters.
- **Iris diaphragm, uniform metal grids.**
- The **slit** is of special importance in apparatus fitted with monochromators.

Recording System

- The final step in recording the light radiations produced in the source of emission consists in transforming the electrical signal produced by the selected radiation in the photosensitive element into a reading which is related to the concentration of the solution under analysis.
- Amplifiers for phototube circuits
- Amplifiers for use with photomultiplier tubes

- <https://youtu.be/1F6CxVF5I9g>

Mass spectrometer

Contents

- Mass spectrometer-Introduction
- Principle of operation
- Types of Mass spectrometers
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 - Time of Flight Mass spectrometer
 - Radio frequency Mass spectrometer
 - Quadrupole Mass spectrometer
- Components of a mass spectrometer

Mass spectrometer-Introduction

- In a mass spectrometer, the sample to be analysed is first bombarded with an electron beam to produce ionic fragments of the original molecule.
- These ions are then sorted out by accelerating them through electric and magnetic fields, according to their mass-to-charge (m/e) ratio.
- A record of the numbers of different kinds of ions is called the mass spectrum.

- The procedure for analysing a substance by mass spectrometry starts by converting the substance into a gaseous state by chemical means.
- The gas is introduced into the highly evacuated spectrometer tube, where it is ionised by means of an electron beam.
- The positive ions thus formed are deflected and focused by means of suitable magnetic and electric fields.
- For a given accelerating voltage, only positive ions of a specific mass pass through a slit and reach the collecting plate.
- The ion currents thus produced are measured by using a sensitive electrometer tube.
- By varying the accelerating voltage, ions from other mass species may be collected, and the ion currents measured in such cases would be proportional to the amount of the given mass species present.

Principle of operation

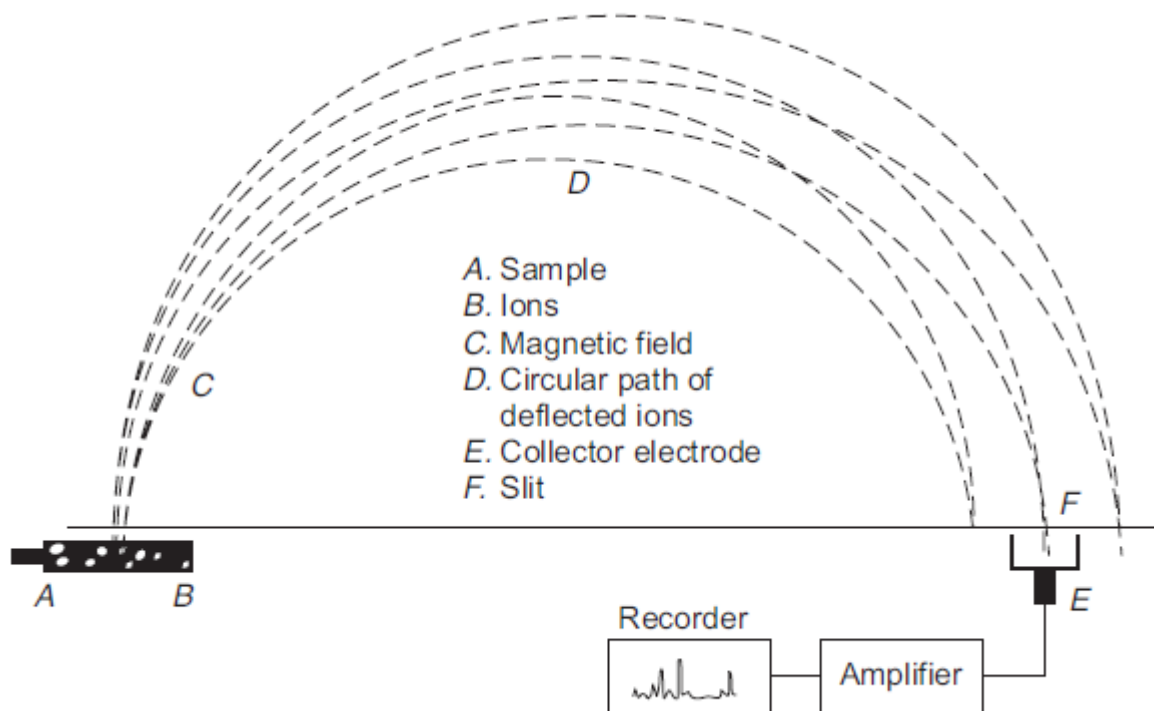


Figure: Principle of operation of a mass spectrometer

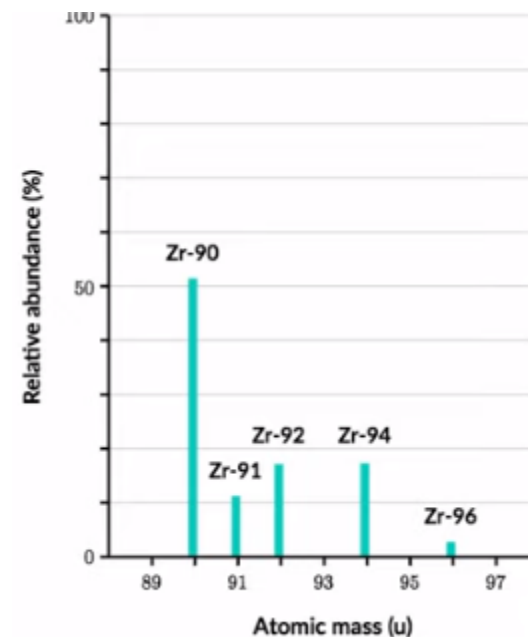


Figure: Mass spectrogram

- The molecules in the gas sample (A) to be analysed are bombarded with electrons to produce ions (B).
- These ions are accelerated in a high vacuum into a magnetic field (C), which deflects them into circular paths (D).
- Since the deflection for light ions is greater than that for heavy ions, the ion stream separates into beams of different molecular weight.
- A suitably placed slit (F) allows a beam of a selected molecular weight to pass through to a collection electrode (E).
- As the accelerating voltage on the ion source is gradually reduced, ion beams of successively greater mass pass through the slit.
- When these ions fall on the collector electrodes, they produce minute electric currents, which after suitable amplification, may be measured.
- Their amplitude will indicate the number of ions in each beam.

- The proportion of molecules of different masses in the gas sample may be found and a complete analysis of the gas sample may be made; provided all the constituent gases have a different molecular weight.
- Mass spectrometers are used for all kinds of chemical analyses, ranging from environmental analysis (e.g. detection of poisons such as dioxin) to the analysis of petroleum products, trace metals and biological materials (including the products of genetic engineering).

Types of Mass spectrometers

- The principle difference between the various types of spectrometers lies in the means for separating the ions according to their m/e ratio.
- The important types are listed below:
 - Magnetic deflection Mass spectrometer
 - Time of Flight Mass spectrometer
 - Radio frequency Mass spectrometer
 - Quadrupole Mass spectrometer

Magnetic deflection Mass spectrometer

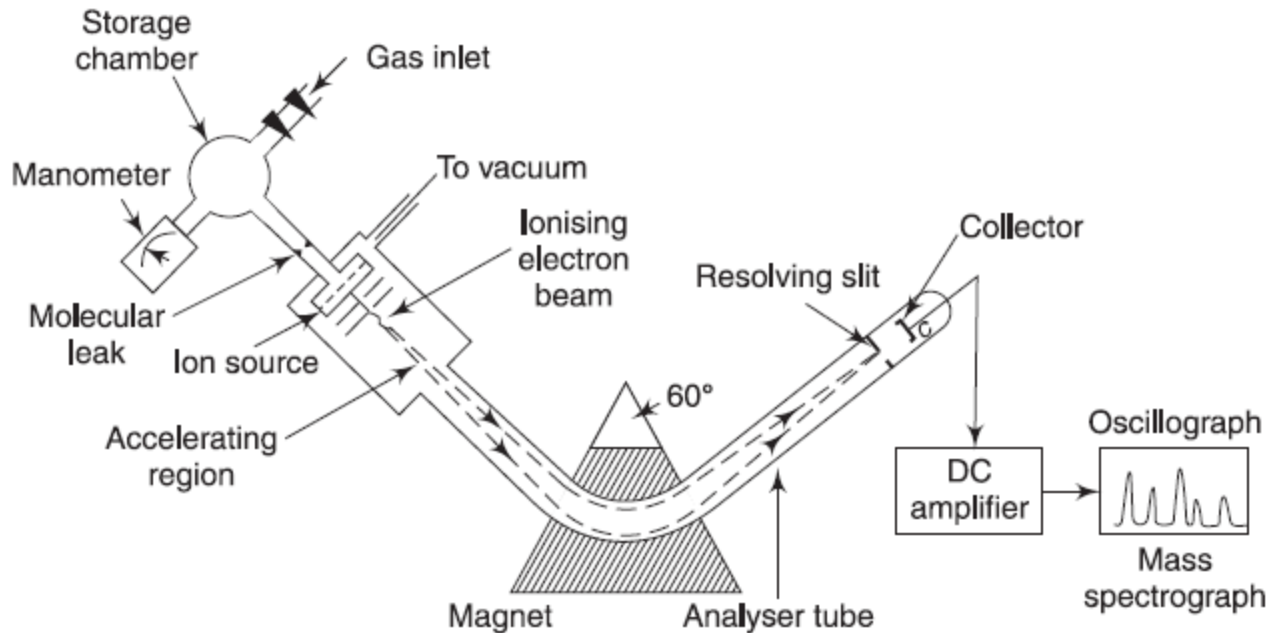
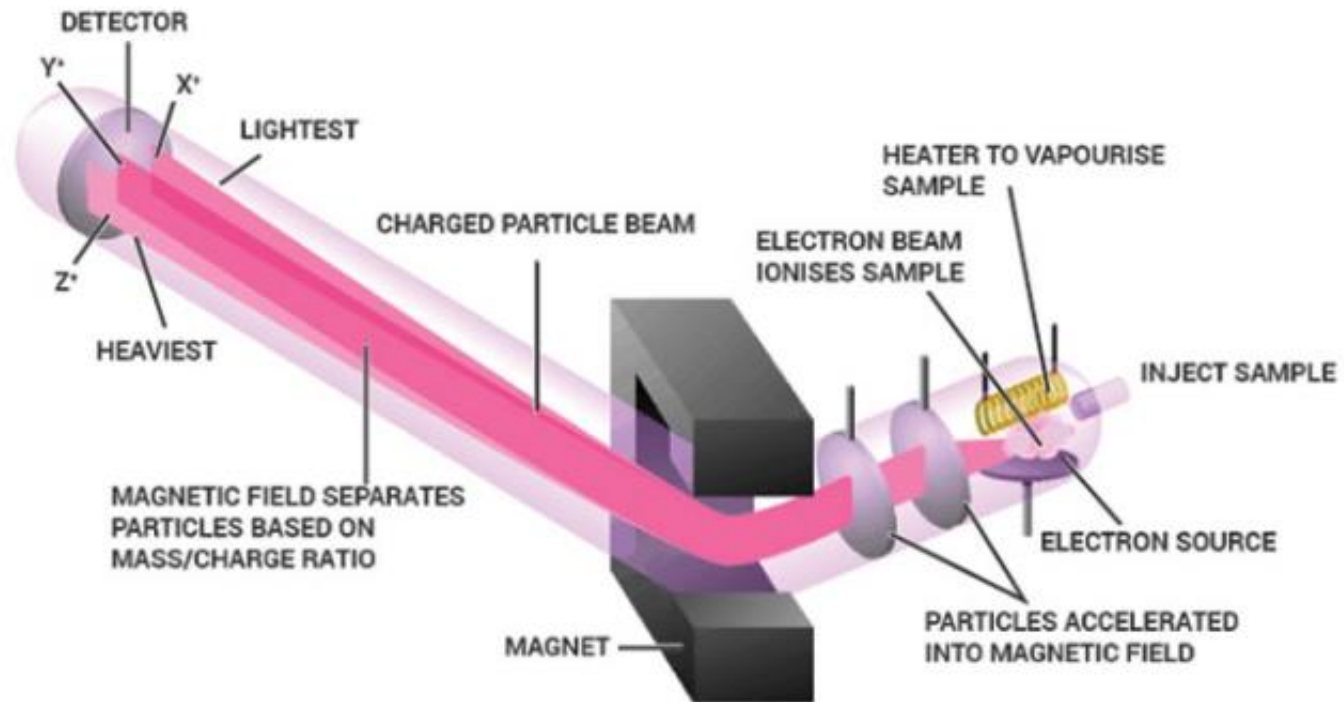


Figure: Schematic diagram of a Nier 60° sector mass spectrometer

Magnetic deflection Mass spectrometer

The essential parts of a typical magnetic deflection mass spectrometer tube due to Nier.



<https://www.youtube.com/watch?v=RuwbeA22rew>

- The heated tungsten filament produces an electron beam, which passes between plates A and B.
- A difference in electrical potential between A and B pulls ions out of the beam, so that they pass through the slit in B into the region between B and C.
- The potential difference between B and C is adjustable from 0 up to several thousand volts.
- The ion beam then enters the space between two trapezoid shaped magnet poles, where it is deflected through an angle of 60, 90, 120 or 180.
- When ions of mass m and charge e pass through an accelerating electric field, they would attain a velocity V which can be expressed in terms of the accelerating voltage V as follows:

$$\frac{1}{2} mv^2 = eV \quad (1)$$

where $\frac{1}{2} mv^2$ is the kinetic energy of the ion as it leaves the electric field.

- From Eq. (1), v can be written as follows:

$$v = [2 \text{ eV/m}]^{1/2} \quad (2)$$

- If the ions next enter a magnetic field of constant intensity h , which is applied at right angles to their direction of motion, the ions would be diverted into circular orbits.
- From physics, it is known that when acceleration is applied perpendicular to the direction of ion motion, the objects velocity remains constant, but the object travels in a circular path.
- Therefore, the magnetic sector follows an arc.
- The radius and angle of the arc vary with different in optical designs.
- Equating the centripetal and the centrifugal forces results in the following formula:

$$mv^2/r = hev \quad (3)$$

- The radius of curvature of the trajectory is given as follows:

$$r = \frac{mv}{eh} \quad (4)$$

Substituting for v from Eq. (2), we get

$$\begin{aligned} r &= \left[\frac{2eV}{m} \right]^{1/2} \times \frac{m}{eh} \\ &= \left[\frac{2eV}{m} \times \frac{m^2}{e^2 h^2} \right]^{1/2} \\ &= \left[\frac{2V}{h^2} \times \frac{m}{e} \right]^{1/2} \end{aligned} \quad (5)$$

- This equation shows that the radius of the orbit is a function of the m/e ratio of the particles.
- In practice, all the quantities of Eq. (5) are kept constant with the exception of m and V .
- By varying the accelerating voltage V , it is possible to cause an ion of any mass to follow the path which may coincide with the arc of the analyser tube in the magnetic field.
- Ions of different m/e ratio strike the tube at some point and would get grounded.
- Under specified conditions, the ions which will be collected would follow the expression:

$$m/e = h^2 r^2 / 2V \quad (6)$$

- The relationship (6) shows that for obtaining a mass spectrum, the accelerating voltage or the magnetic field strength can be varied.
- Usually, it is the magnetic field which is kept constant and the voltage is adjusted to bring focus specific m/e .
- For a particular instrument, the angle of deflection (radius) is fixed for a given analyser tube (180° , 90° , 60°).
- Therefore, Eq. (6) can be written as
$$mV = \text{constant}$$

Components of a mass spectrometer

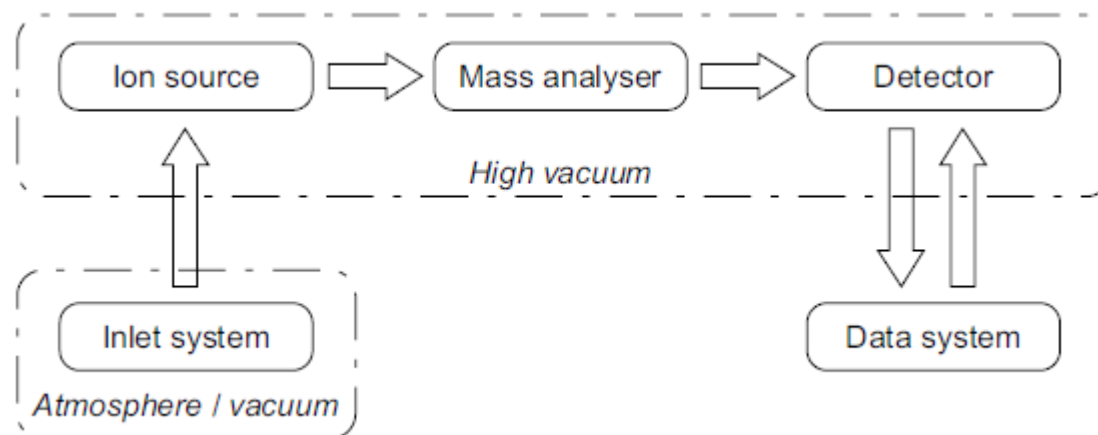


Figure: Diagram of the major components common to all typical modern mass spectrometers

- The inlet sample system
- The ion source
- The mass analyser
- The amplifier and the detector
- The data system and display system
- Vacuum system.

The Inlet Sample System

- ***Gaseous Samples:*** Introduction of gases involves merely transfer of the sample from a gas bulb into the metering volume. The arrangement is a small glass of known volume attached to a mercury manometer. The pressure range is generally from 30 to 50 mm of Hg.
- ***Liquid Samples:*** Liquid samples may be introduced by hypodermic needle and injected through a silicon rubber dam, or by a break-off device which consists in touching a micro-pipette to a sintered glass disc under mercury. The low pressure in the reservoir draws in the liquid and vaporises it instantly.
- ***Solid Samples:*** Solid samples can be vaporised to gaseous ions by instantaneous discharges with a power up to 100 kW by using a rf (1 MHz) spark. Under these conditions, all constituents of the sample are converted to gaseous form at an equal rate without regard to their vapour pressure, thereby eliminating the possibility of preferential vaporisation.

Ion Sources

- The ionisation chamber is maintained at a low pressure (10^{-4} to 10^{-7} mm Hg) and at a temperature of 200°C.
- The electron gun is located perpendicular to the incoming gas stream.
- Electrons are emitted from a filament normally of carbonised tungsten, but for special purposes, tantalum or oxide coated filaments may be used.
- They are drawn off by a pair of positively charged slits, through which they pass into the body of the chamber.
- The potential present in the slits control the electron emission and the energy of the electrons.
- An electric field applied between these slits accelerates the electrons, which on subsequent collisions with molecules of the passing gas stream produce ionisation and fragmentation.

- To obtain a mass spectrum, the electric field is kept between 50 and 70 V.
- The electron beam is usually collimated by a magnetic field, which is confined to the ionisation region.
- Inductively Coupled Plasma (ICP) as ion source
- Glow discharge ion source
- Plasma discharge
- Electron impact
- Electrospray ionisation
- Fast-atom bombardment
- Field ionisation
- Laser Ionisation
- Matrix-assisted laser desorption ionisation
- Thermal ionisation

Electrostatic accelerating system

- Positive ions, which are separated from electrons by a weak electric field, are accelerated in a strong electrostatic field between the first and second accelerating slit.
- Voltages of the order of 400–4,000 V accelerate the ions to their final velocities of up to 1,50,000 miles/s. and they acquire a kinetic energy of a few thousand electron volts.
- Such a relatively high kinetic energy is imparted to the ions to produce an almost mono-energetic beam, when it finally emerges out of the final accelerating slit, which is approximately 0.076 mm in width.
- The electrostatic voltages are highly stabilised to an accuracy of better than 0.01%.

Ion detectors and recording of mass spectrograph

- Faraday Cup
- Channeltron
- Electron multiplier tube
- Micro-channel plate

Vacuum System

- To prevent undue scattering by collision of ions with residual gas molecules, the mass spectrometer requires a good vacuum system.
- Generally, separate mercury or oil diffusion pumps are employed in the source and analysing regions of the spectrometers.
- The two important parameters of a vacuum pump are its lowest attainable pressure and its pumping speed.

Self study topic: Difference between all the types of mass spectrometers

NMR spectrometer

Introduction

- Nuclear magnetic resonance (NMR) spectroscopy is a non-destructive technique for mapping molecular structures and learning how molecules function and relate to each other.
- It is recognised as one of the most powerful techniques for chemical analysis.
- NMR spectrometer provides an accurate and non-destructive method of determining structure in liquids and soluble chemical compounds.
- The study of absorption of radio frequency (rf) radiation by nuclei in a magnetic field is called nuclear magnetic resonance.
- The absorption lines in the rf region of the electromagnetic spectrum indicate the chemical nature of the nucleus and the spatial positions of neighbouring nuclei.

- NMR spectroscopy can be used for quantitative measurements, but it is most useful for determining the structure of molecules along with IR spectroscopy and mass spectrometry.
- <https://www.youtube.com/watch?v=RZLew6Ff-JE>
- <https://www.youtube.com/watch?v=ywR6aLpfjI0>

Principle of NMR

- *Nuclear Spin:* Elementary particles such as electrons or a nucleus are known to behave as if they rotate about an axis and thus have the property of spin.
- The angular momentum associated with the spin of the particle would be an integral or a half-integral multiple of $h/2\pi$, where h is Planck's constant.
- The maximum spin component for a particular particle is its spin quantum number I .
- Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes.

- *Nuclear Energy Levels:* Since a nucleus possesses a charge, its spin gives rise to a magnetic field that is analogous to the field produced when an electric current is passed through a coil of wire.
- The resulting magnetic dipole or nuclear magnetic moment m is oriented along the axis of spin and has a value that is characteristic for each kind of particle.
- When spinning nucleus is placed in a strong uniform magnetic field (H) the field exerts a torque upon the nuclear magnet.
- This would make the nucleus to assume a definite orientation with respect to the external field.
- The torque is a vector with its direction at right angles to the plane of m and H .
- This results in a rotation of the nuclear axis around the direction of the external field.
- This is called precessional motion.

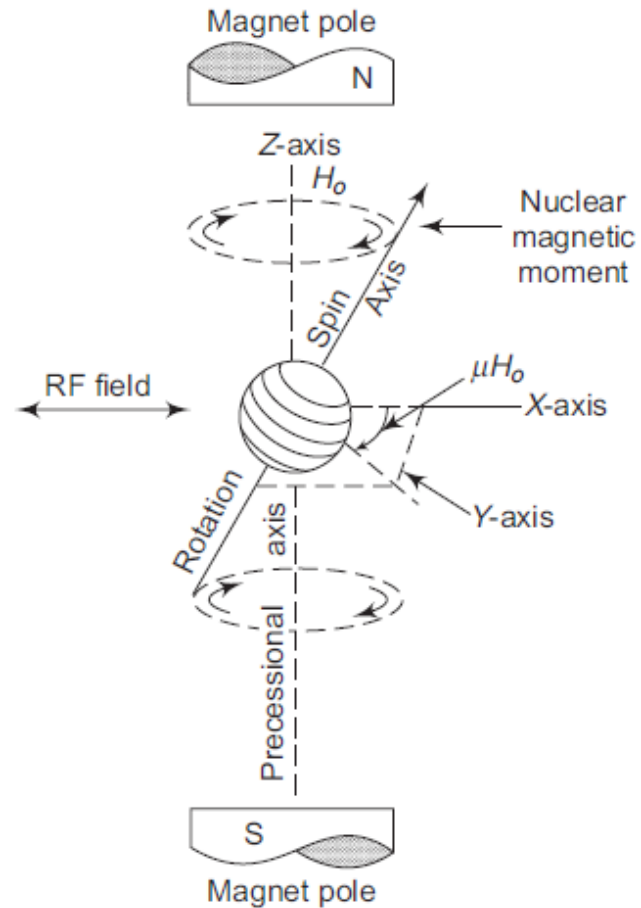


Figure: Spinning nucleus in a magnetic field

- *Resonance Conditions:* When an alternating rf field, superimposed over the stationary magnetic field, rotates at exactly the frequency of an energy level, the nuclei will be provided enough energy to undergo a transition from a lower energy level to a higher-energy level. In general, the energy difference between states is given by

$$\Delta E = \mu \beta H_0/I$$

where H_0 is the strength of the external magnetic field in gauss, β is a constant called the nuclear magnetron. 5.049×10^{-24} ergs – gauss⁻¹, μ is the magnetic moment of the particle expressed in units of nuclear magnetrons.

- The frequency ν of the radiation that will effect transitions between energy levels can be determined from the Planck's equation as given below:

$$\Delta E = h\nu = \mu \beta H_0/I$$

- *NMR Absorption Spectra:* For understanding NMR absorption spectra, the behaviour of a charged particle in a magnetic field needs to be understood. NMR absorption spectra can be obtained either by changing the frequency of the rf oscillator or by changing the spacing of the energy levels by varying the magnetic field.

- ***Relaxation Process:*** When a nuclei in the higher-energy state return to the lower state, emission of radiation takes place.
- At radio frequencies, re-emission is negligible.
- Therefore, nonradiative relaxation processes will give more useful information.
- The following are the two major relaxation processes:
 - Spin-lattice (longitudinal) relaxation
 - Spin-spin (transverse) relaxation

- *Spin lattice relaxation:* Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the lattice.
- Nuclei in lattice are in vibrational and rotational motion, which creates a complex magnetic field.
- The magnetic field caused by motion of nuclei within the lattice is called the lattice field. This lattice field has many components.
- Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest.
- These components of the lattice field can interact with nuclei in the higher-energy state, and cause them to lose energy thereby returning to the lower state.
- The energy that a nucleus loses increases the amount of vibration and rotation within the lattice resulting in a tiny rise in the temperature of the sample.

- *Spin-spin relaxation:* Spin-spin relaxation describes the interaction between neighbouring nuclei with identical precessional frequencies but differing magnetic quantum states.
- In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state.
- There is no net change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease.
- This can result in line-broadening.

- *The Chemical Shift:* It is the phenomenon that occurs in which a specification, that is, a carbon or hydrogen atom, in a given molecule resonates at a slightly different frequency based on its local chemical environment.
- In other words, the difference between the field necessary for resonance in the sample and in some arbitrarily chosen reference compound is called the chemical shift.
- The chemical shift is expressed as follows:

$$\delta = \frac{H_{\text{sample}} - H_{\text{TMSi}}}{H_1} \times 10^6$$

- where H_{sample} and H_{TMSi} are the positions of the absorption peaks for the sample and reference material respectively in Hz and H_1 is the rf of the signal used. The chemical shift ' δ units' is expressed in parts per million.

Types of NMR spectrometers

- There are two NMR spectrometer designs.
- Continuous-wave (CW) and
- Pulsed or Fourier transform (FT-NMR).

Continuous-Wave NMR Spectroscopy

- A CW-NMR spectrometer consists of a control console, magnet, and two orthogonal coils of wire that serve as antennas for rf radiation.
- One coil is attached to an rf generator and serves as a transmitter.
- The other coil is the rf pick-up coil and is attached to the detection electronics.
- Since the two coils are orthogonal, the pick-up coil cannot directly receive any radiation from the generator coil.
- When a nucleus absorbs rf radiation, it can become reoriented due to its normal movement in solution and re-emit the rf radiation in a direction that can be received by the pick-up coil.

- This orthogonal coil arrangement greatly increases the sensitivity of NMR spectroscopy.
- Spectra are obtained by scanning the magnet and recording the pick-up coil signal on paper at the control console.
- CW NMR spectrometers have largely been replaced with pulsed FT-NMR instruments.
- But due to the lower maintenance and operating cost of CW instruments, they are still commonly used for routine ^1H NMR spectroscopy at 60 MHz.
- Low resolution CW instruments require only water-cooled electromagnets instead of the liquid-He-cooled super-conducting magnets found in higher-field FT-NMR spectrometers.

Fourier Transform NMR Spectroscopy

- FT NMR spectrometers use a pulse of rf radiation causes nuclei in a magnetic field to flip into the higher-energy alignment.
- All of the nuclei will re-emit rf radiation at their respective resonance frequencies, creating an interference pattern in the resulting rf emission versus time, known as a free induction decay (FID).
- The frequencies are extracted from the FID by a Fourier transform of the time-based data.
- An FT-NMR spectrometer consists of a control console, magnet, and a coil of wire that serves as the antenna for transmitting and receiving the rf radiation.
- Only one coil is necessary because signal reception does not begin until after the end of the excitation pulse.

- Because the FID results from the emission due to nuclei in all environments; each pulse contains an interference pattern from which the complete spectrum can be obtained.
- Because of this multiplex advantage, repetitive signals can be summed and averaged to greatly improve the signal-to-noise ratio of the resulting FID.

Self study: Differentiate continuous and fourier transform NMR spectrometer.

Constructional details of NMR spectrometer

- It is a complex system integrating several technologies into an analytically powerful, information rich system.
- The Key parts of the system are:
 - A magnet, which produces magnetic field in the range 10,000–25,000 gauss
 - Radio frequency transmitting system
 - The signal amplifier and detector
 - A display device, which may be a recorder or an oscilloscope
 - A non-magnetic sample holder, which holds the sample
 - Computer workstation which stores and processes the NMR data using complex software to generate spectrum for the same

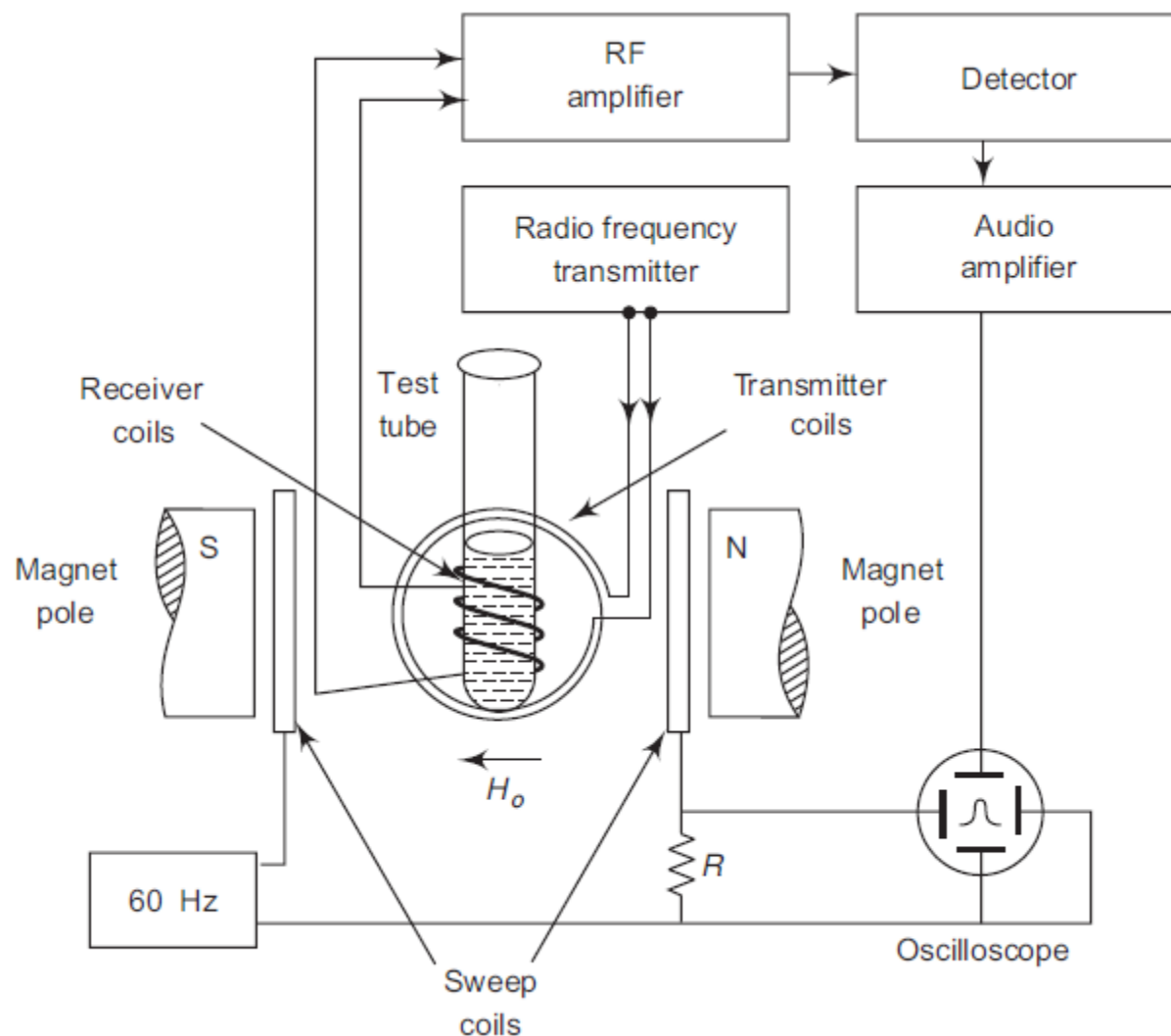


Figure: Block diagram of a nuclear magnetic resonance spectrometer

Courtesy: A Handbook of Analytical Instruments by R.S.Khandpur, 3rd Edition

- **Magnetic Field:** The magnet used in these instruments may be permanent magnet or electromagnet.
- Alternately, the magnetic field may be produced from super-conducting solenoids.
- In electromagnets, stability of the magnetic field is achieved by continuously compensating for small rapid fluctuations in magnetic field with coils wound around the pole faces and by controlling the temperature of the magnet to minimise thermal fluctuations.
- The magnet is placed in a thermostated oven and is surrounded by heavy thermal insulation.
- In case of electromagnets, the pole pieces are about 12 inches in diameter and are spaced about 1.75 in apart.
- In addition to the main coil, a super-conducting magnet contains additional super-conducting coils, shim coils, which produce specific magnetic field gradients that can be used to improve the basic homogeneity of the main coil.

- A typical super-conducting solenoid is 26 cm long, with a 3 cm bore and outside diameter 8.36 cm.
- It is wound with Nb-Zr 25% wire and produces a field of 5T ($1 \text{ T} = 10,000 \text{ gauss}$) with a current of about 20 Å.
- Permanent magnets can yield maximum magnetic fields, approximately 14,000 gauss, whereas electromagnets can produce fields up to about 24,000 gauss.
- Super-conducting solenoids have been used to give approximately 70,000 gauss.

- **The Radio-Frequency Transmitter:** The rf transmitter is a 60 MHz crystal controlled oscillator.
- The rf signal is fed into a pair of coils mounted at right angles to the path of the field.
- The coil that transmits the rf field is made in two halves, to allow insertion of the sample holder.
- The two halves are placed in the magnetic gap. For high-resolution work, the transmitted frequency must be highly constant to about 1 part in 10^8 .
- The oscillator is of low power, generally of less than 1 W. The basic oscillator is usually crystal controlled, at a fundamental frequency of 15 MHz.
- It is followed by a buffer doubler, the frequency being doubled by tuning the variable inductance to the second (30 MHz).
- It is further connected to another buffer doubler, with the connector inductance, tuned to 60 MHz.
- A buffer amplifier is provided to avoid circuit loading on the tuned doubler. Precision resistors are used in the transmitter for their low noise characteristics.

- **The Signal Amplifier and Detector:** The rf signal produced by the resonating nuclei is detected by means of a coil that surrounds the sample holder.
- This coil consists of a few turns of wire and is placed at right angles to the source coil and the stationary field to minimise pick up from these fields.
- The coupling between transmitting and receiving coils cannot be completely eliminated and some leakage is always known to be present.
- The problem of this coupling is solved to some extent by using devices called paddles, which act as inductors mutually coupled to both receiver and transmitter.
- The signal results from the absorption of energy from the receiver coil, when nuclear transitions are induced and the voltage across the receiver coil drops.
- This voltage change is quite small and must be amplified in an rf amplifier before it can be displayed.

- **The Display System:** The detected signal is applied to the vertical plates of an oscilloscope to produce the NMR spectrum.
- The total amplification required is usually of the order of 10^5 . The spectrum can also be recorded on a chart recorder.
- NMR spectrometers have built-in electronic integrators for measuring the relative areas under the peaks.
- The integrated spectrum is a step function, with the height of each step being directly proportional to the area under the peak corresponding to the step.

- **Data Display and Record:** Modern NMR machines are computer controlled. General purpose digital computers are used for data acquisition and data display.
- Functions such as pulse timing, delay and acquisition timing, digitisation rate, filter bandwidth, transmitter and decoupler offsets, receiver gain, noise bandwidth, plotter and pulse sequence can be placed under computer control.
- This leaves only a few essential manual adjustments, such as establishing the NMR lock for field-frequency ratio stabilisation and trimming up the field homogeneity controls.
- In modern NMR spectrometers, the computer workstation and complex software directs the NMR experiment from start to finish.
- NMR signals are subjected to complex digital signal processing algorithm, including the Fourier Transform, to convert the NMR information into a form that is easily interpreted by the end user.
- The signals are displayed as a series of peaks or spectrum, on the workstations monitor.
- The data are usually stored on a disc and the processed data are plotted on a paper or displayed on a graphics display terminal.

- **The Sample Holder:** The sample holder for NMR studies consists of a glass tube, generally of 0.5 cm outer diameter.
- Micro-tubes for smaller sample volumes are also available. The sample is invariably in the liquid form.
- In case studies are to be made on solid or gaseous samples, the solids may be studied above their melting point, and gaseous samples below their liquification point.
- Samples can be less than 1/1,000 cubic inch of the gas, liquid or solid.
- The sample holder is placed in a sample probe, which also contains the sweep source and detector coils.
- This ensures reproducible positioning of the sample with respect to these components.
- The sample probe is also provided with an air-driven turbine for rotating the sample tube along its longitudinal axis at several hundred rpm.
- This rotation averages out the effects of inhomogeneities in the field and provides better resolution.