ATOMIC EMISSION SPECTROSCOPY

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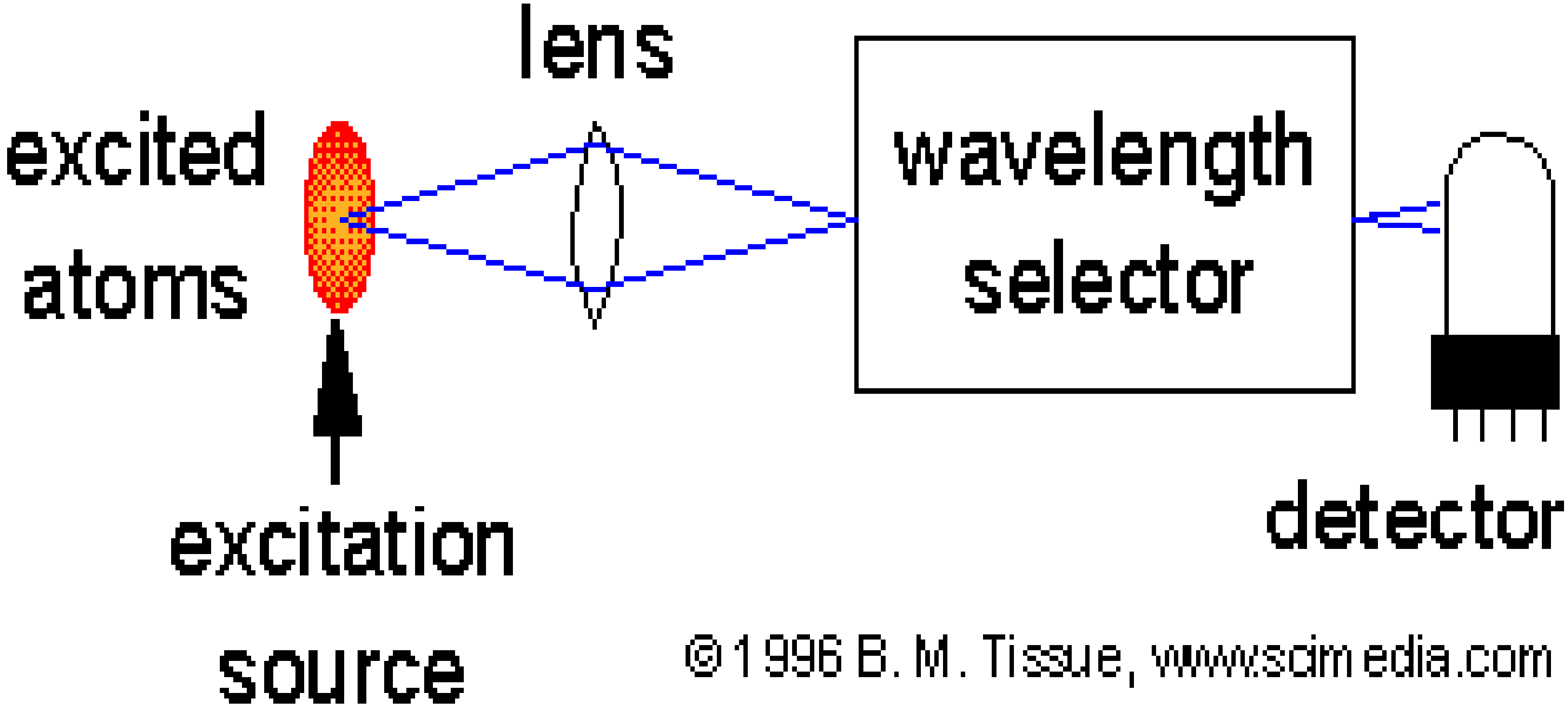
INTRODUCTION

- Emission spectroscopy is concerned with the characteristic radiation produced when atoms or molecules are introduced into thermal or electrical sources
- These sources excite the atoms to levels above the ground state
- When they return to lower energy states, the characteristic radiation is emitted in the form of discrete wavelengths of light, called *'spectral lines'*
- The wavelength of the spectral line is inversely proportional to energy difference between initial and final energy levels

An emission spectrograph



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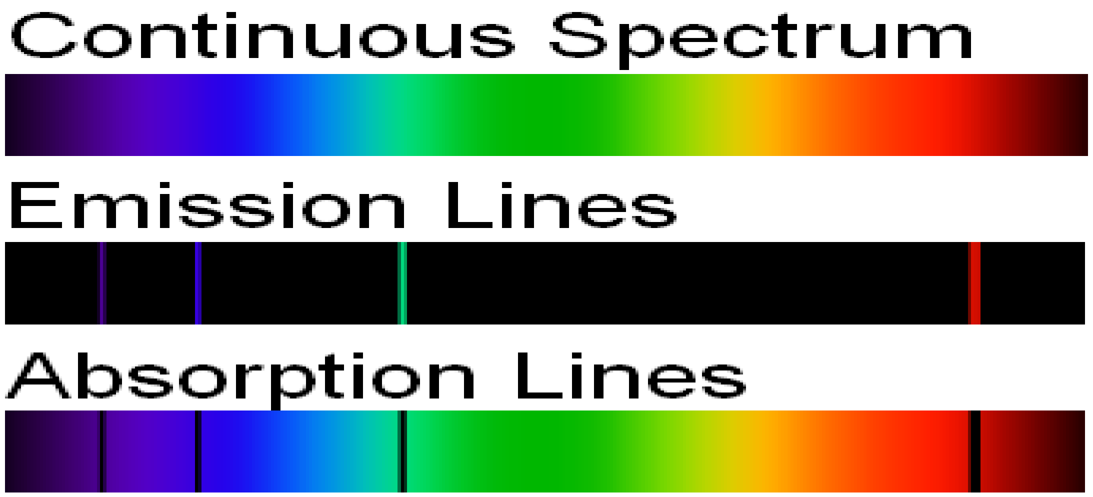
Types of Spectra

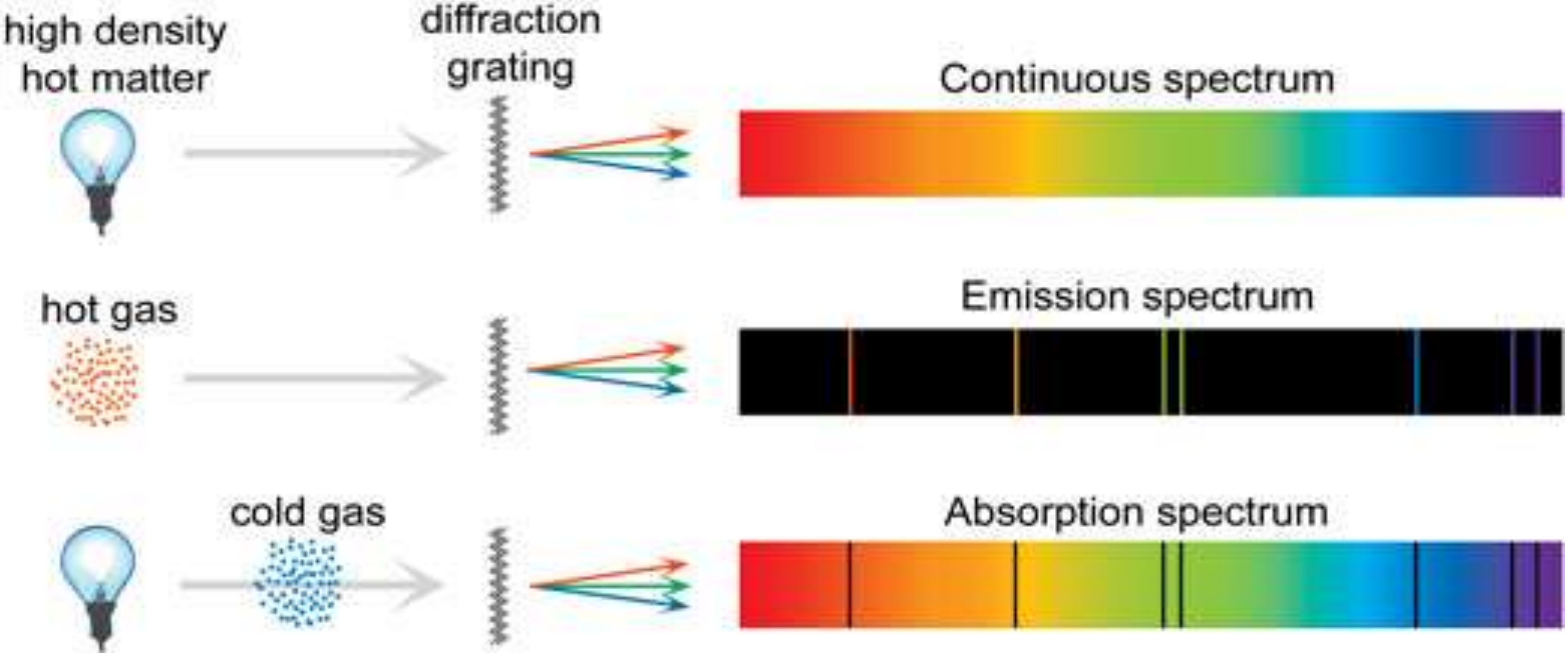


a) Emission spectra

b) Absorption spectra

a) Emission spectra: When a solid is heated to a high temperature or a discharge of electricity is passed through a gas, light is emitted.

On examining this light by a spectroscope, a spectrum has been found to be produced which is known as *‘emission spectra’*



high density
hot matter

diffraction
grating

Continuous spectrum

hot gas

Emission spectrum

cold gas

Absorption spectrum

b) Absorption spectra: When the light from the source emitting a continuous spectrum and then absorbed through a spectroscope, it will be observed that certain lines are missing in the spectrum which leaves dark lines or bands at their places

As the light of wavelength corresponding to black bands is absorbed by the substance through which the light is passed, the spectrum so obtained is known as *'absorption spectrum'.*

Types of Emission spectra

a) Continuous spectra:

- It is characterized by uninterrupted emission over a considerable wavelength region and by the absence of sharp lines or discrete bands.
- It is obtained whenever matter in the bulk is heated

Eg: Incandescent solids like Iron or Carbon

b) Band spectra:

- It consists of group of lines so close together
- We are not interested in band spectra. This can be avoided by providing sufficient energy to molecules so that they be broken up into individual atoms

c) Line spectra:

- A line spectrum consists of discrete irregularly lines
- This type of spectrum is obtained when the light emitting substance is in atomic state

Excitation-Energy Requirements

- For any element to emit a single spectral line, energy equivalent to the ‘*excitation potential;* of the element must be absorbed
- The complete spectrum is only possible when the energy equivalent to the *‘ionization potential’* must be absorbed
- By using an enough energetic source, all the elements in the periodic table could be excited to produce emission spectra
- But most of the spectral lines fall in the vaccum-UV region which cannot be studied easily
- So it is mainly limited to metals and metalloids not for non-metals

INSTRUMENTATION

The sample is excited by thermal or electric method and thus becomes the source of radiation

↓

Then the radiation is passed through a monochromator to select the desired wavelength

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Then passed into the detector which measures the radiation for qualitative analysis

The Instrumentation of Emission spectroscopy will contain the following components

1) Excitation source
2) Electrodes
3) Sample holders
4) Monochromators
5) Slits
6) Detectors

1) Excitation source

It must accomplish the following process:

- ✓ The sample must be vapourised
- ✓ It must be dissociated into atoms
- ✓ The electrons in the atoms must be excited to higher energy levels above the ground state
- ✓ It should provide sufficient line intensity so as to detect these lines within detection limit
- ✓ It should provide reproducible excitation conditions from sample to sample

The various sources of excitation are:

a) Flames:

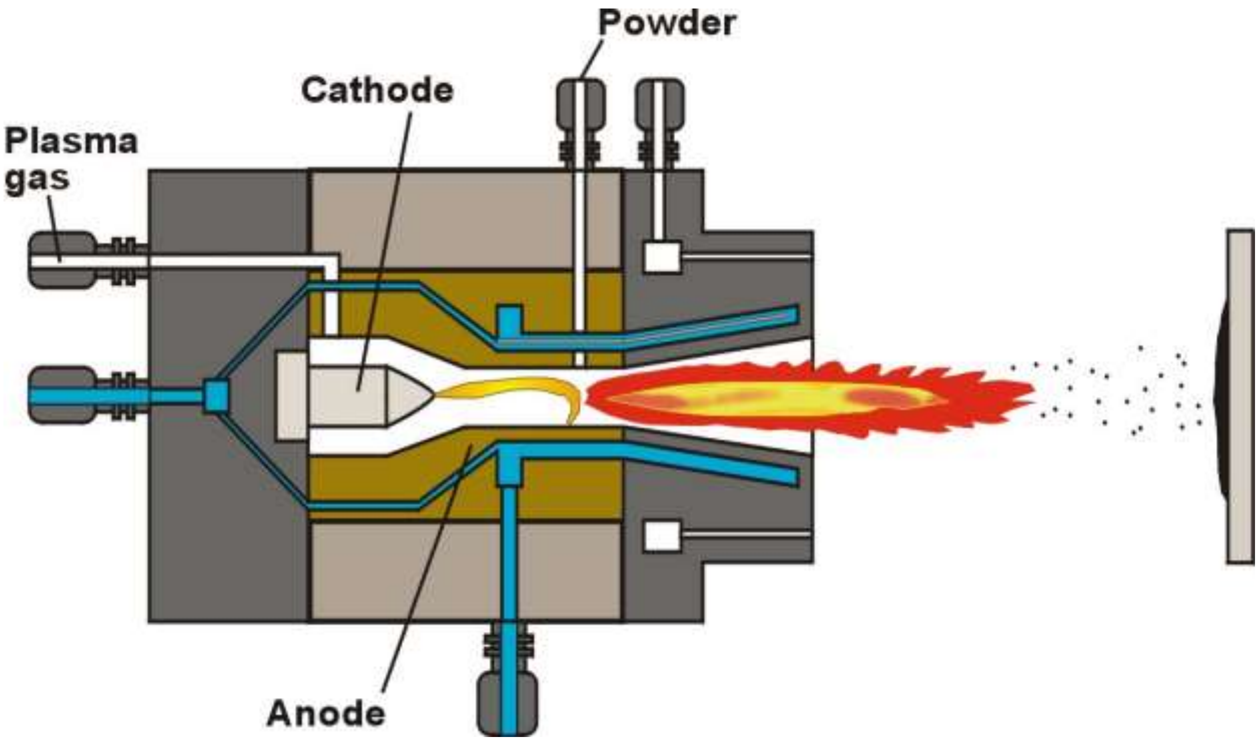
It is used for those molecules which do not require very high temperatures for excitation & dissociation into atoms

The temp of the flame is determined by following factors:

- Type of fuel & oxidant
- Fuel to oxidant ratio
- Type of burner
- Region in the flame that is focused into the entrance slit of the spectral isolation unit

b) Direct current arc:

- The DC source is usually a regulated power supply that furnishes 110 to 220V at 3 to 30A.
- The current is made to flow across the arc gap in series with a variable resistor R and an inductance coil L



- The sample in the form of a solid or liquid is kept on the lower electrode in the arc gap
- Once the current starts flowing, the temp in the gap rises rapidly & then the electrodes are separated byabout 20mm to 1cm

- Immediately, the electric arc will be established across the gap
- By this arc, emission species are neutral atoms rather than ions

“The excitation energy provided by this arc is not electrical but mainly thermal and is thus sufficient for exciting all the elements”

c) Alternating current arc:

- A high voltage of 2000-5000V is maintained by a transformer
- This voltage helps the arc to jump the gap
- Current is alternating at a frequency of 60Hz
- As the arc picks out the new surface area after each cycle, the whole surface of the sample is arched & excited
- The stop and start nature of this source is that the gap temperature is much less than with the direct current arc, with a lower sensitivity

d) Alternating current spark:

- Most spark sources employ a pair of spark gaps arranged in series
- The spark is produced by connecting a high voltage transformer across two electrodes
- The current may be increased by connecting a condenser in parallel with spark gap
- The sample is dissociated into atoms and ions, then volatilizes in a spark

2) Electrodes:

a) Self electrode: When the material under investigation is a good conductor and can withstand high temp, the material as such is used for the electrodes called self-electrode

b) Graphite electrode: When the material under investigation is not a good conductor and cannot withstand high temp, it is placed in a small cavity of the lower graphite electrode whereas the upper electrode is also made up of graphite which is brought to a point in a pencil sharpener

3) Sample Holders:

- The function of the sample holder is to introduce the sample into the electrical discharge

a. Solid Sample Holder:

- Many samples are handled by being first reduced to a powder and then loaded into a carbon sample holder.
- After it is loaded, the sample holder is placed in a position as one of the electrodes used in the discharge
- During discharge, from top surface of electrode the sample is vapourised into the plasmaof the discharge and spectrographic emission takes place

b. Liquid Sample Holders:

1. Porous cup container:

- It permits the liquid sample to percolate through it at a steady rate into the electrical discharge
- The sample slowly runs into the discharge, which can be sustained until the base of the holder is burned away

2. Rotating disk electrode:

- It rotates through the sample, which wets the surface of the disk
- It carries the sample into the discharge at steady rate, emitting the radiation from the excited sample in the discharge

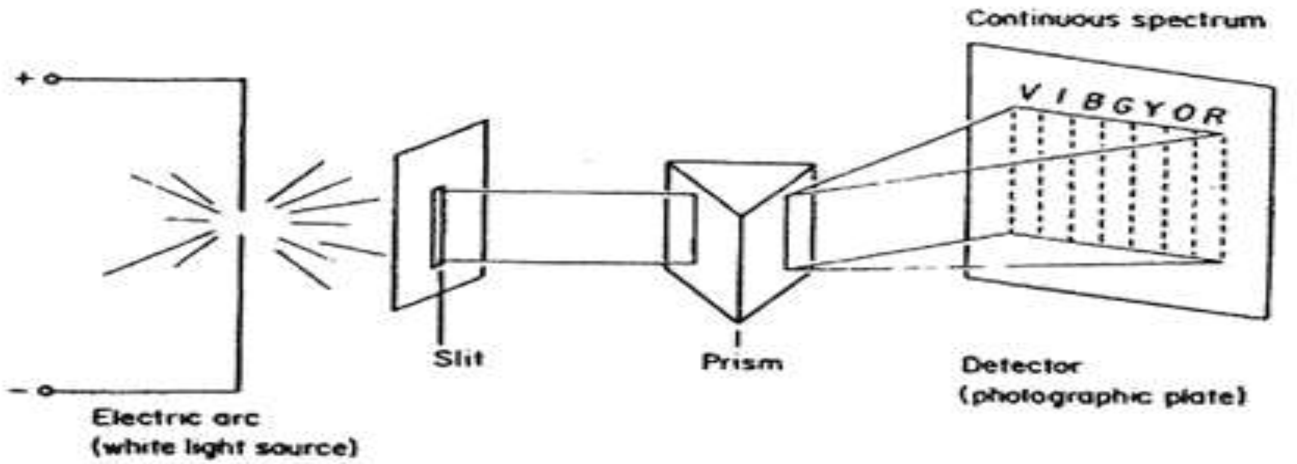
4) Monochromators:

- The function of the monochromator is to separate the various lines of a sample’s emission spectra
- Both ‘*prism’* and ‘*grating’* monochromators are used

Prism monochromator:

- ➢ When one light of one wavelength is passed through the quartz prism, it emerges from the prism as two lines
- ➢ This causes the loss of half of the light’s intensity
- ➢ This can be overcome by using two half prisms

- The first half splits the light into two beams whereas the second half recombines them to a single beam (cornu type prism)



Disadvantage of prism:

- The dispersion of a prism is not constant over a wide wavelength range

Grating monochromator:

- It consists of a large no of parallel, wqually spaced lines ruled upon a glass surface or metal coating on a glass
- The spectrum produced by a grating is dispersed nearly linear with respect to wavelengths
- It replaced the prism as the dispersing element
- By employing gratings the identification of lines become very simple

Disadvantage:

- Higher-order wavelengths overlap but this can be overcome by using filters or by using detectors which are not sensitive to the higher orders

5) Slits:

- All spectrographs are fitted with entrance and exit slits
- **‘Entrance slits’** keep out stray light and permit only the light from the sample to enter the optical path
- **‘Exit slits’** placed after the monochromator stop all but the desired wavelength range from reaching the detector
- A narrow slit is necessary to obain resolution of two lines at similar wavelengths
- If the slit is too wide, both lines pass through & reach the detector without being resolved
- If the slit is too narrow, there is loss in the intensity of radiation

6) Detectors:

- Two types of detectors are widely used

  a) Photo-multipliers

  b) Photographic plates

Photographic detection:

- The intensity of spectral lines is registered on a photographic emulsion
- A beam of light is passed through a clear portion of the film and then the intensity is measured of the transmitted beam by a phototube fitted in the densitometer

- Again a beam of light is passed through the blackened portion of the film and the intensity is measured
- Now the logarithm of the ratio of the intensity of light passing through the clear film and through the blackened film is computed
- Then it is plotted against the log of the exposure

Photomultiplier detection:

- Direct-reading emission spectrographs involve photomultiplier tubes for detection instead of a photographic plate
- A direct-reading instrument is a grating with an opaque barrier pierced by 12 or more slits
- Behind each slit is mounted a photomultiplier tube and the output of each tube is recorded automatically

Advantages of using photographic plates over photo-multipliers

- A large no of spectral lines can be recorded simultaneously
- The photographic plate provides a permanent record if the spectrum
- The emission intensity can be integrated by a photographic emulsion over a period of time
- Photographic emulsions are preferred because of their high sensitivity through out UV and Visible regions
- The cost of an emission spectrograph having photographic detector is much less than that having photo-multiplier detector

Advantages of emission spectroscopy

- Excellent method of elemental trace analysis as the parts per million level, *i.e,* a low a conc level as 0.0001%
- Used for all metals & metalloids
- Usually no chemical separations or concentration steps are required
- A small sample is sufficient for analysis
- The method can be used for routine quality control work
- It is an ideal method for geological samples, metals & alloys, plants, forensic exhibits, soils and environmental and biological samples

Disadvantages of emission spectroscopy

- The cost of emission spectrometer is very high
- The sample gets destroyed in the process of analysis
- This method cannot be used for concentrated solutions, it is difficult to gethigh precision if the constituent desired is present in a conc much above 30%
- The method is limited to the analysis of elements

Applications:

- It is used for elemental qualitative and quantitative analysis

1.Qualitative Analysis:

Comparision of Spectra and Lines – Obtained by comparision of the sample spectrum with the spectrum produced by pure known standard samples

Last lines, RU lines – As the conc of metallic compound made successively more and more dilute, the number & intensities of the lines in the resulting spectra will vary

- Upon dilution the weaker lines disappear and the stronger lines become less intense
- Ultimately only the strongest lines remain
- These last lines to remain upto successive dilutions are referred to as **raies ultima** or **RU** lines

2.Quantitative Analysis:

Comparision sample method:

The spectra of the unknown sample and various standards are photographed alternately on the same plate under the same set of conditions

After developing the plate, one can calculate the conc of the desired constituent by comparing the blackening of the lines of this constituent with the samelines on the standards

Internal standard method:

- The internal standard is added in known amount
- When the sample having internal standard is exited in the electrical discharge, the sample as well as internal standard emit spectral lines
- These are photographed on photographic plate

Measurements are:

- ✓ Intensity of the sample emission line is measured
- ✓ Intensity of the internal standard emission line is measured

We know the conc of IS and the ratio of the two lines

From these data, we can calculate the conc of the element which is being determined

3) Specific applications:

- Ceramics for both traces and major constituents
- Metals, for trace metal constituents as well as oxygen and nitrogen
- Aluminium, for traces of cobalt
- Graphite, for traces fo cobalt, nickel, molybdenum & vanadium
- Spent nuclear fuels, for rare earths
- Blood, for trace amounts of Ca, Cu & Zn
- Pancreas tissue, for Zn
- High purity acids and other analytical reagents, for a variety of trace metal impurities

thankyou