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A Novel Review on Atomic Absorption Spectroscopy and Atomic Emission Spectroscopy

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ABSTRACT :

Atomic absorption spectroscopy (AAS) is a spectro analytical procedure for the quantitative analysis of chemical elements. AAS is based on the absorption of light by free metallic ions that have been atomized from a sample. In analytical chemistry, the technique is used for determining the concentration of a particular element in a sample to be analysed. Atomic emission spectroscopy (AES) is a chemical analysis method that employs the intensity of light produced at a certain wavelength from a flame, plasma, arc or spark to quantify the quantity of an element in a sample. In this review, it consists of introduction, principle, instrumentation and applications of Atomic Absorption Spectroscopy (AAS) and Atomic emission spectroscopy (AES) and differences between them.

INTRODUCTION

Atomic absorption spectroscopy :

AAS is a spectroanalytical procedure for the quantitative measurement of chemical elements, based on the absorption of light by the free metallic ions that have been atomized from a sample. In analytical chemistry, this technique is used for determining concentration of a particular element (analyte) in a sample to be analysed.

Atomic emission spectroscopy :

AES is a chemical analysis method that employs the intensity of light produced at a certain wavelength from a flame, plasma ,arc, or spark.The wavelength of the emitted light determines the element and the intensity of the light produced is proportional to the number of atoms of that element.

HISTORY OF AAS :

In 17th century , sir Isaac Newton discovered that when white light is passed through a glass prism, it breaks into constituent spectral colours from which he proposed corpuscular theory of light .The English chemist, Wollastan observed dark lines in the solar spectrum that became known as Fraunhofer lines. Brewster ,In 1832 discovered that atomic vapours in the atmosphere absorbs radiation from the Sun resulting in the detection of these lines.Bunsen and Kirchoff demonstrated that chemical element had a characteristic colour or spectrum when heated they were able to reproduce the black lines observed in the solar spectrum in the laboratory allowing the identification of absorbing atoms in the corona through emission spectrum.

HISTORY OF AES :

Based on the theory proposed by Newton , different ideas were developed overtime by scientists (William Herschel,JW ritter, Joseph Fraunhofer, and William bunsen).In 1859, Gustav Kirchoff discovered that each element has its own Unique spectrum by which we can determine its chemical composition. Kirchhoff law states that the emitted power and absorbed power is same for all bodies at the same temperature at a given wavelength. Although the quantitative application based on atomic emission from electric sparks was developed by sir Norman lockyer, a British scientist and astronomer credited with discovering helium in the 1870's,it was Henrik Lundegardan who pioneered this technique.

PRINCIPLE :

ATOMIC ABSORPTION SPECTROSCOPY :

The technique makes use of the Atomic absorption spectrum of a known analyte content to establish the relation between the measure absorbance and analyte concentration and relies on the beer-Lambert law. The procedure is as follows :

The sample is typically dissolved in a suitable solvent like acid or water to create liquid solution this ensures analytes are present as free atoms ready for absorption.

The prepared solution is nebulized into a fine mist and introduced into a high temperature flame like acetylene or nitrous oxide acetylene mix.The intense heat in the flame excite the electrons in the analyte atoms into higher energy levels.Simultaneously,a hallow cathode lamp emits a specific wavelength of light which passes through an atomized sample,some photons are absorbed by excited analyte atoms causing them to return to their ground state.This absorption decreases the intensity of the light at a specific wavelength.The light intensity before and after passing through the sample is measured by a detector. Difference in intensity of light is directly proportional to the concentration of the analyte in the sample follows the beer-Lambert law :

A = €cl **,where

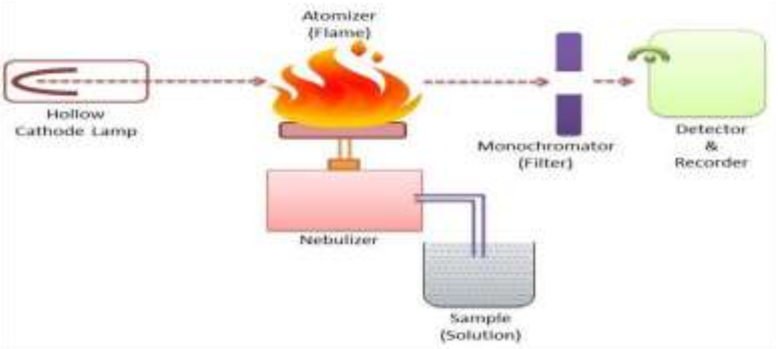
‘A’ is the absorbance measured.

‘€’ is the molar absorptivity (constant specific to the element and wavelength).

‘C’ is the concentration of the analyte.

‘I’ is the path length of the light through the sample.

To determine the actual concentration of the analytes the instrument is calibrated using standard solutions containing known concentrations of the element by comparing the measured absorbance the sample to the calibration curve the concentration of the analyte in original sample can be calculated.



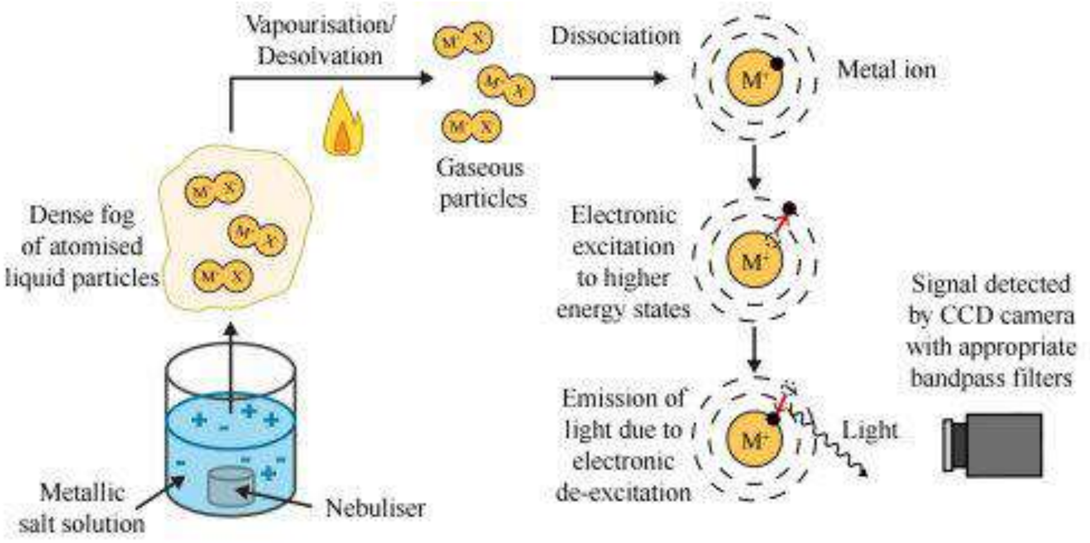
ATOMIC EMISSION SPECTROSCOPY :

AES technique is based on the principle that conversion of solid or liquid sample to free gaseous atoms and excitation of electrons from lower energy levels to higher energy levels by absorption of a specific wavelength when heated at high temperatures.When the excited species leave the high temperature region they return to the ground state by emission of radiation in the form of discrete wavelength packets.These emissions pass through a monochromator or filter and the wavelength of photons emitted is recorded. The procedure is as follows :

Sample which is to be analysed is dissolved in a suitable solvent to form a liquid sample solution.

The prepared solution is nebulized into dense fog of atomised particles and vaporization of these particles to gaseous particles (Aerosol form) is done and subjected to excitation source. The same source of thermal energy is used for atomization as well as excitation.

Energy is applied to a substance in the form of heat or light which excites electrons in the substance to a higher energy level The excited state is unstable, so the electrons decay back to a lower energy level, releasing energy in the form of a Photon .Each element and its light at a specific wavelength, which can be used to identify the element.Spectrometer detects the light emitted by the substance which is dispersed by a prism or grating.



INSTRUMENTATION :

1.EXCITATION SOURCE :

Atomic absorption spectroscopy :

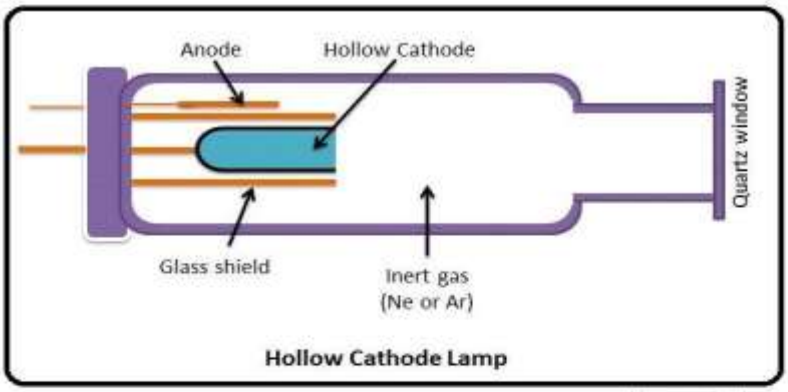
A Hallow cathode lamp (HCL) is a light source used in Atomic absorption spectroscopy (AAS) to generate narrow emission lines for specific elements. This type of lamp consists of :

- Tungsten anode
- Cylindrical cathode

These two are sealed in a glass tube filled with inert argon or neon gas. The cathode is constructed by using desired metal. Voltage is applied across the anode and cathode. The argan gas is ionised to Ar+ at the anode.The Ar+ ions are drawn towards the cathode, and the metal ions on the cathode are excited. The excited metal ions then emit photons with wavelengths that match the element being analysed. The efficiency of the hollow cathode lamp depends on its

- Geometry and
- The operating voltage

High voltages, and thus high currents, lead to greater intensities. A separate hallow cathode lamp is required for each element to be measured.



ATOMIC EMISSION SPECTROSCOPY :

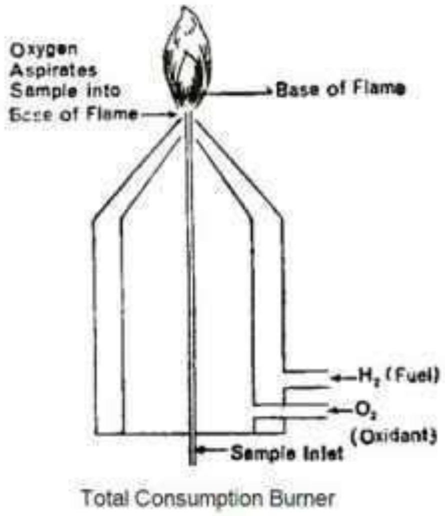
Burners are used to produce analytical flame, which atomises and excites the sample. They are as follows:

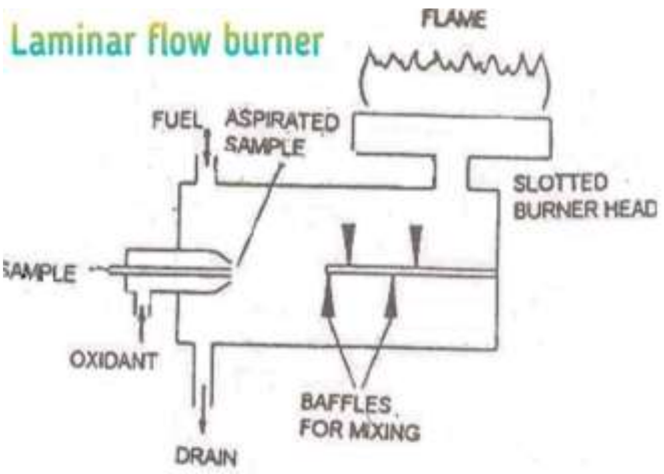
- *Total consumption burner :* hydrogen and oxygen acts as fuel and oxidant respectively. Total amount of sample that enters capillary tube will enter the flame regardless of droplet size.

- *Premix (or) laminar flow burner :* it is widely used due to uniformity in flame intensity. The flame produced in this burner is non-turbulent, noiseless and stable.

Other burners used in AES are :

- Meckner burner
- Lundergardh burner
- Shielded burner
- Nitrous oxide-acetylene burner.



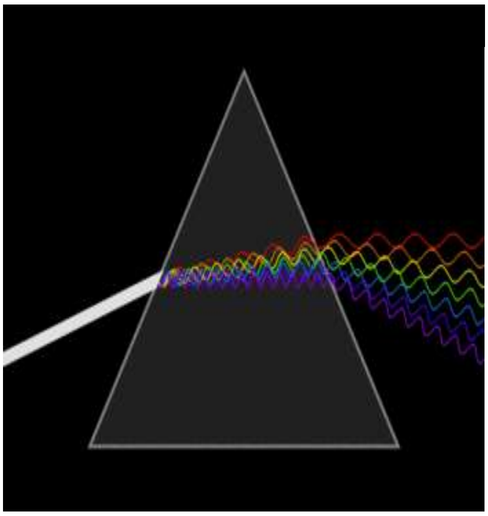


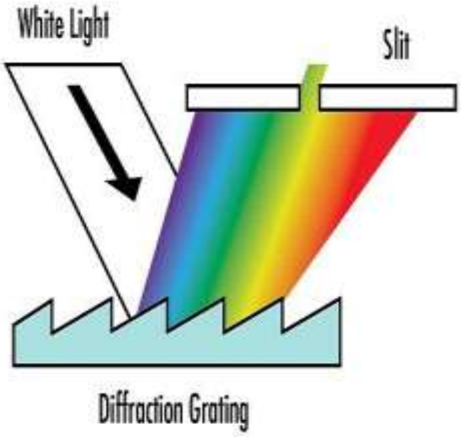
2.MONOCHROMATORS :

AAS and AES :

Monochromator selects a specific wavelength of radiation from a sample and removes any other radiation. Prisms and diffraction gratings are both types of monochromators.

- *PRISMS :* Prisms can disperse ultraviolet, visible, an infrared radiation. They have a wide spectrum, but they have limited ability to focus a specific wavelength through an exit slit.
- *DIFFRACTION GRATINGS :* diffraction gratings are more accurate and have better resolution than prisms. The disperse light into its component wavelengths by reflecting it off an angled grating surface.

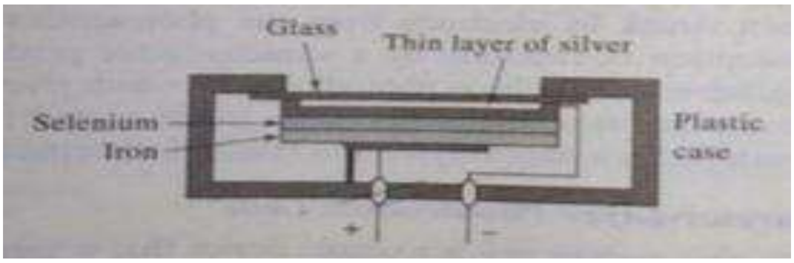




3.DETECTORS :

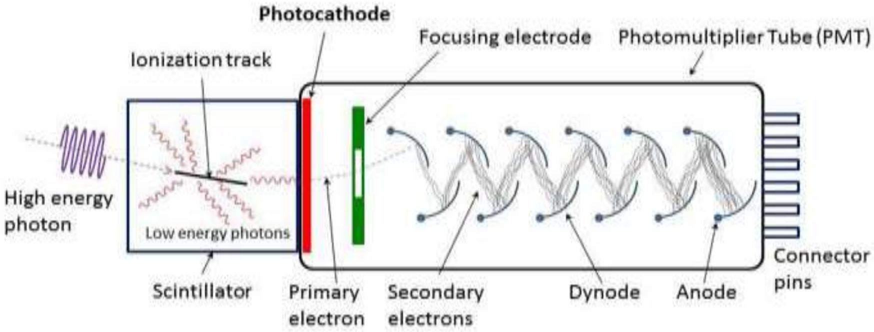
ATOMIC ABSORPTION SPECTROSCOPY :

- *Photovoltaic cell :* It is also known as barrier layer. It is employed in in expensive instruments for example: Filter Fluorimeter. It consists of a copper plate coated with a thin layer of cuprous oxide (Cu2o). A semi transparent film of silver is laid on this plate to provide good contact. When external light falls on the oxide layer, the electrons emitted from the oxide layer move into the copper plate. Then oxide layer becomes positive and copper plate becomes negative. Hence and electromagnetic force (emf) develops between the oxide layer and copper plate and behaves like a voltaic cell. So it is called photovoltaic cell. A galvanometer is connected externally between silver film and copper plate and the deflection in the galvanometer shows the current flow through it. The amount of current is found to be proportional to the intensity of incident light.



ATOMIC EMISSION SPECTROSCOPY :

- *Photo multiplier tubes* : It consists of a photo cathode and series of anodes (dynodes). Each dynode is maintained at 75 to 100 volts higher than preceeding.At each stage, electron emission is multiplied by a factor of 4 to 5 due to secondary emission of electrons and hence overall factor of 10^6 is achieved. They are very sensitive and can detect light in a wide range of wavelengths.



DIFFERENCES BETWEEN AAS AND AES :

AAS	AES
1.The amount of light absorbed by ground state atoms is measured.	1.The amount of light emitted by excited atoms is measured.
2.It is less sensitive than AES in visible region and can detect elements at parts per million [ppm] levels.(but more sensitive at wavelength below 300 nm).	2.It is more sensitive and can detect elements at parts per billion [ppb] and parts per trillion [ppt] levels.
3.Only one element can be estimated at a time [Single elemental analysis].	3.Multiple elements can be estimated in a single run [Multielemental analysis].
4.It cannot be used for the direct analysis of solid samples.	4.It can be used for the direct analysis of solid samples.
5.Hollow cathode lamp is used as light source.	5.Burners are used as light source.
6.The most commonly used atomisation and excitation source in AAS are flame and graphite furnace.	6.The most commonly used atomisation and excitation sources in AES are flame,plasma,laser,arc,sparc or glow discharge etc.

7.The wavelength of light absorbed by an atom is specific to the type of atom and energy level of its electrons , whereas intensity of light absorbed is proportional to concentration of element in sample.	7.Wavelength of specral line detects the identity of element [Qualitative analysis],whereas intensity of emitted light determines no.of atoms of element [Quantitative analysis].
8.Beer-lambert’s law is applicable over a wide range of concentration.	8.Beer-lambert’s law is not applicable.
9.Limited number of elements are are estimated . Ex : Cd,Ni,Co,Fe,Mn,Cu,Ag etc	9.Nearly 70 elements are estimated. Ex : Silicon,Vanadium,Chromium, molybdenum,lead etc
10.It is sensitive to complex matrix interferences, especially in complex samples. Careful sample preparation and matrix matching may be required to overcome interferences.	10.It is highly tolerant of complex sample matrices including solids,liquids and gases. It can handle samples with high concentrations of dissolved solids or matrix interferences.
11.AAS produces an absorption spectrum characterised by dark bands in a spectrum of light frequencies.	11.AES produces an emission spectrum known as line spectrum [Coloured spectrum].
12. Curve between absorption intensity vs concentration of analyte is much linear.	12.Curve between emission intensity vs concentration is not linear.
13.Due to low temperature of flame, all the atoms of an elements are not excited.	13. High temperature of plasma leads to effective and uniform excitation of all atoms in a sample.
14.The analytical signal is generated by a lamp.	14. The signal is generated by the relaxation of excited atoms in a plasma.
15.Most commonly used detectors are photomultiplier tube and photovoltaic cell.	15.Most commonly used detectors are photomultiplier tube and charge coupled devices.
16.AAS is typically used for analyzing higher concentration of elements.	16.AES can detect very low concentrations of elements [as low as 1ppm].
17.Absorption intensity and signal response is independent of temperature.	17.Excitation process and signal response is influenced by flame temperature.
18.AAS depends on no.of ground state atoms.	18.AES depends on no.of excited atoms.
19. Drugs analysed by AAS are as follows: ● NSAIDs – Naproxen, ibuprofen etc ● Antihypertensives : Ramipril,enalapril,fosinopril etc ● Multiminerals and multivitamin tablets and capsules containing Mg,Ca,Fe,Zn,Cu etc	19.Drugs analysed by AES are as follows: ● Anti cancer drugs – Cisplatin, methotrexate ● Anti histamines: Pizotifen,Ketotifen,cetrizine,loratadine,fexofenadine ● Antibiotics -Sulfonamides .
20.Useful for the determination of Calcium in serum, cadmium in urine,Zinc in plant leaves, mercury in air,water and soil ,lead in petrol and tin in fruit juices.	20.Useful for the determination of Calcium, copper,zinc in blood;analysing Vanadium, arsenic,lead,tin and manganese and their alloys in oils and sodium in serum etc.
21.It is generally less expensive.	21.ICP AES is more expensive and complex than AAS.

CONCLUSION :

It can be concluded from the entire review that Atomic absorption spectroscopy (AAS) is used in the pharmaceutical industry to analyze the composition of drugs and their packaging. It can be used to identify impurities (AAS can identify and quantify trace metal impurities in raw materials, manufacturing processes, and packaging),assess drug stability (AAS can monitor metal content during storage to assess stability and predict shelf life) and ensure compliance with quality standards. Atomic emission spectroscopy (AES) is used in the pharmaceutical industry to analyze the presence of trace elements in drugs, including metal catalysts.This helps ensure the safety and efficacy of the drug. AES can detect trace elements in illicit drug powder samples, such as heroin. AES can analyze samples for the presence of metals, such as heavy metals in patient's urine or blood.Hence both AAS and AES are used as analytical tools for pharmaceutical purpose based on absorption and emission of light .

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