4. Atomic Spectrometry

4.1. Atomic absorption spectrometry

Introduction

- is a technique used to determine the concentration of a metallic element in a sample
- Spectroscopic studies of atoms can only be performed in a gaseous medium and free atoms has to be generated from the sample
- The absorption of electromagnetic radiation by atoms is measured and the analyte concentration is determined

Principle of AAS

- The sample, usually a solution, is introduced into a flame, Solvent is first vaporized, leaving particles of solid sample which is then vaporized into gaseous state
- Gaseous molecule dissociate to give free atoms which can be excited to a higher energy level
- Free atoms absorb ultraviolet or visible light and make transitions to high electronic energy levels

Instrumentation

An atomic absorption spectrophotometer consists of

1. Light source

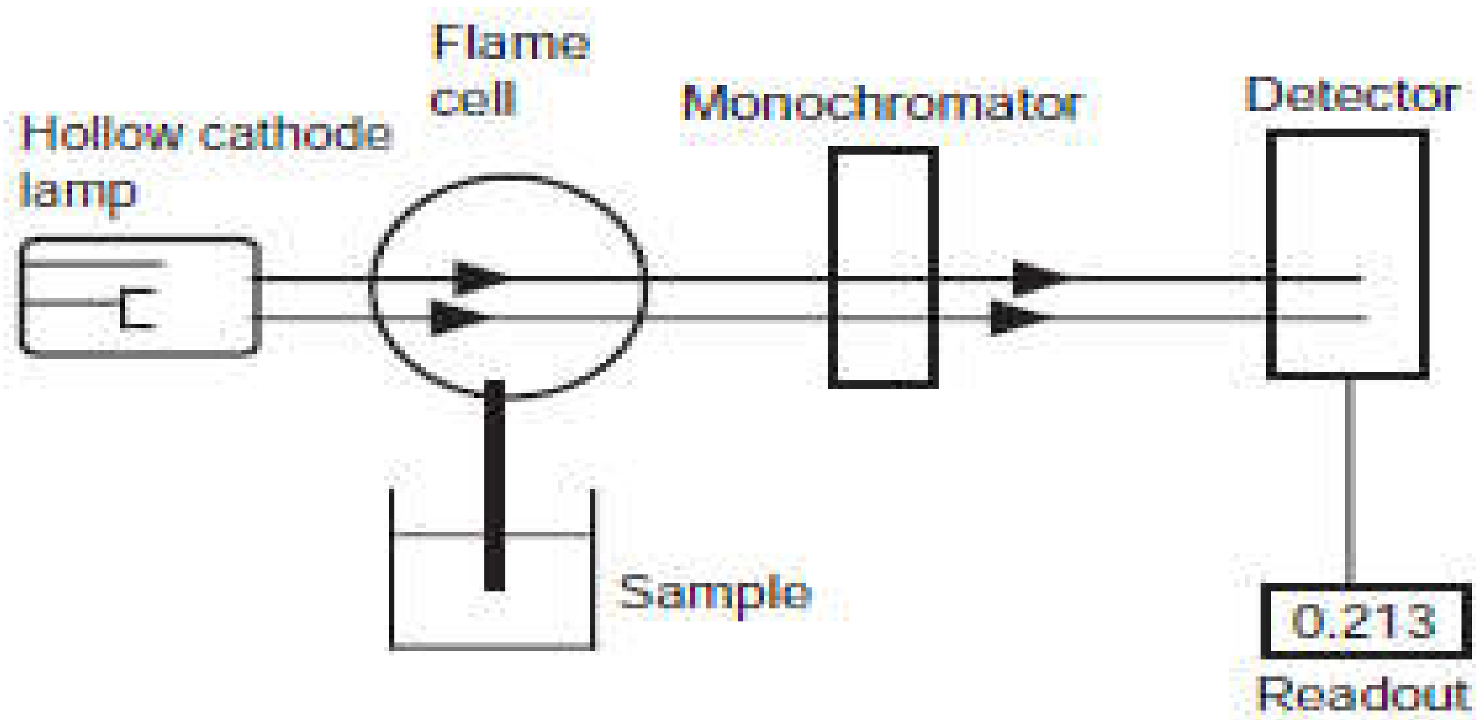
- Hollow cathode lamp are the most common radiation source
- The radiation source emits radiation of a wavelength that is specific for the element being analyzed
- The beam of light from the hollow-cathode lamp is directed through the flame
- the cathode is coated with the metal which is to be analyzed
  - E.g. for the analysis of zinc (Zn), a Zn-coated cathode is used and free Zn atoms in the flame can easily absorb the emitted radiation line at a wavelength of 214 nm
- Each element has its own unique lamp used for that analysis
- A disadvantage of the hollow-cathode lamp is that only one element can be analyzed at a time

2. Flame

- The flame is usually air/acetylene, providing a temperature of 2500°C
- Nitrous oxide/acetylene may be used to produce temperatures up to 3000°C
- Atomization
  - is a process in which the sample is volatilized and decomposed to produce free atoms
  - is the most important step in all atomic spectroscopic procedures
  - It is done by exposing the analyte to high temperatures in a flame
- The samples, usually solutions, are drawn into the flame where the sample evaporates and is broken into free atoms
- The flame replaces the cuvette in conventional spectrometry and the path length of the flame is typically 10 cm

3. Monochromator

- Used to select the specific wavelength of light which is absorbed by the sample, and to exclude other wavelengths
- Directs the radiation to the detector
- The selection of the specific light allows the determination of the selected element in the presence of others
- The hollow-cathode lamp emits all radiation lines for a particular element and also the flame itself emits radiation at a number of wavelength lines
- Hence, a monochromator is necessary to select the wavelength of radiation directed to the detector



Schematic diagram of an AAS

4. Detector

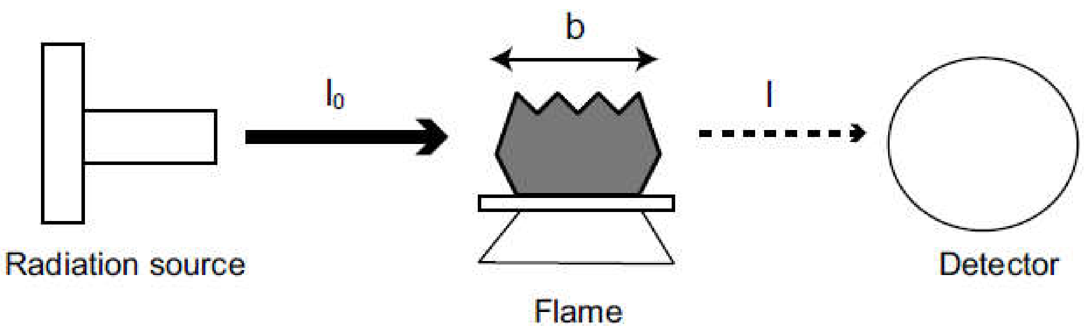
- The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube

- convert the light signal into an electrical signal proportional to the light intensity

- The intensity of radiation directed to the flame (I_0), is reduced in the flame because free atoms absorb radiation

- The intensity of transmitted radiation (I) is measured with a detector and the signals are converted to absorbance unit [A=log(I0 /I)] shown on the instrumental display

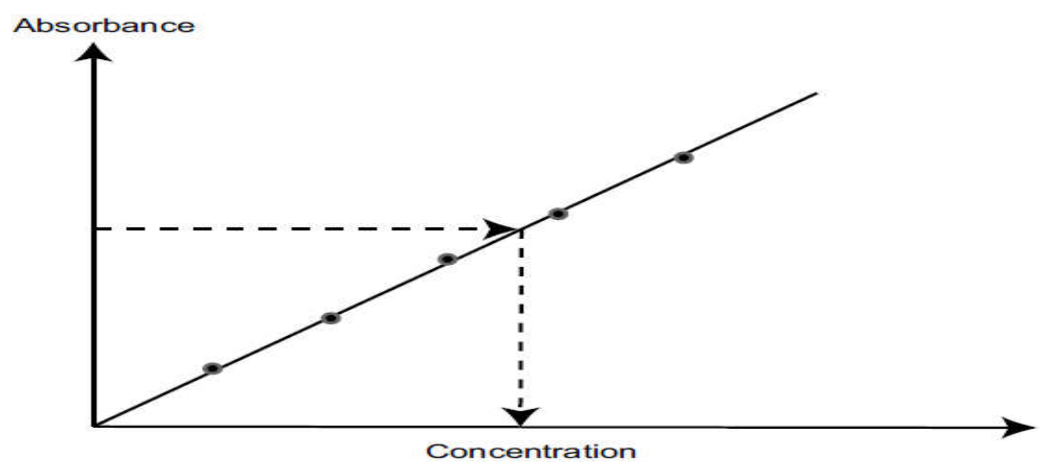
- Based on Beer's law, the measured absorbance is converted to concentrations



$$A = \log(I_0/I) = a \times b \times c$$

Calibration Curve

- used to determine the unknown concentration of an element in a solution
- The instrument is calibrated using several solutions of known concentrations
- The absorbance of each known solution is measured and then a calibration curve of concentration vs absorbance is plotted
- the absorbance of the element in the sample solution is measured and the concentration of the element in the sample is determined from the curve



Pharmaceutical applications of AAS

- used in a number of limit tests for metallic impurities in d/t pharmaceutical preparations
  - magnesium and strontium in calcium acetate, palladium in carbenicillin sodium, and lead in bismuth subgallate
- It is also used to assay metals in a number of other preparations
  - zinc in zinc insulin suspension
  - copper and iron in ascorbic acid
  - zinc in acetylcysteine
  - silver in cisplatinum
  - and calcium, magnesium, mercury and zinc in water used for diluting haemodialysis solutions

4.2. Atomic emission spectrophotometry (AES)

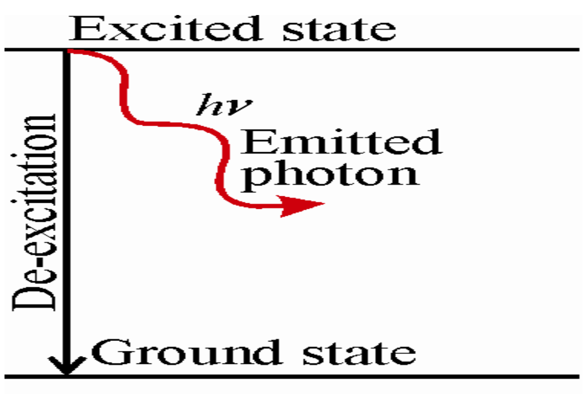
Introduction

- Atomic emission spectrometry (AES) is a method that uses the emission of light to determine elements in a sample
- AES can determine the identity of an element, but the main application area is the quantitative determination of elements
  - The wavelength of colour tells what the element is (qualitative)
  - The color's intensity tells us how much of the element present (quantitative)
- Various metals emit a characteristic colour of light when heated

ELEMENT	EMISSION WAVELENGTH(nm)	FLAME COLOUR
Sodium(Na)	589	yellow
Potassium(K)	766	violet
Barium(Ba)	554	Lime green
Calcium(Ca)	662	orange
Lithium(Li)	670	Red

Principle of AES

- The sample is atomized and free atoms are transferred to the excited state
- The excited atoms are unstable and return to the ground state by emission of electromagnetic radiation
- Each element emits radiation at a characteristic wavelength and the intensity of the emitted radiation is proportional to the amount of element in the sample
- The measurement of emitted photons forms the basis of flame photometry



Introduction…………………

- AES can be used to determine elements that are easy to excite, such as lithium, sodium and potassium
- AES plays an important role in the control of sodium, potassium and lithium in a number of raw materials and formulations
- Most other elements need a higher temperature than that created in a flame to be transferred to the excited state

Instrumentation

- Instruments for AES are similar in design to AAS, except that in the AES, the flame acts as a radiation source
- The hollow cathode lamp is therefore unnecessary for AES
- An atomic emission spectrophotometer is composed of:

(i) Flame

- The flame is similar to the flame in AAS
- The sample containing the metal is volatilized in a natural gas/compressed air flame at 2000 C
- A higher temperature (2500C) may be obtained using air/acetylene

Instrumentation……………….

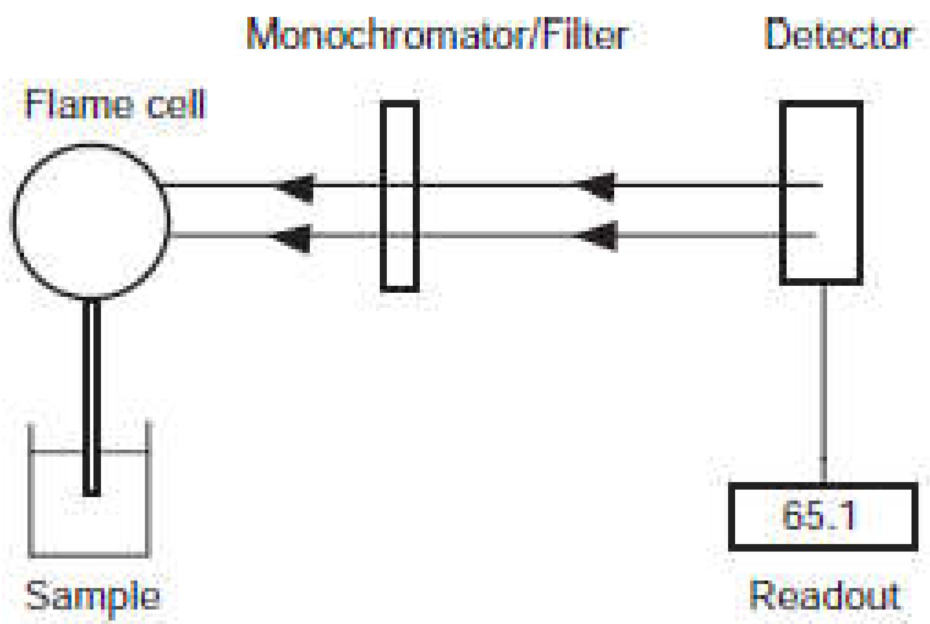
- an atomizer (flame) to generate and excite atoms
- Because the temperature of a flame is low (<3000 K), flames are not powerful enough to cause emission for many elements, and Consequently few elements can be determined

(ii) Monochromator

- The radiation emitted by the excited atoms is passed through a monochromator and a narrow band of emitted radiation is selected
- To avoid interferences from irrelevant elements, the use of a monochromator for wavelength selection is essential

(iii). Detector

- The intensity of the selected radiation is then measured using a photosensitive cell
- A calibration curve is necessary to establish the relationship between the intensity of the signal and the concentration of element



Exercise

- Potassium in KCl IV infusion is determined by atomic emission spectrometry and the assay was carried out as follow.
- A narrow-range calibration curve was constructed within the expected concentration of the diluted KCl IV infusion and the linear regression equation for a calibration curve was Y= 0.2976x + 0.005, where x is in mg/100 ml
- 5 ml of the KCl IV infusion sample was diluted to 100 ml with water and the following reading was obtained: 0.95
- Calculate the percentage of w/v of potassium in the infusion.

Pharmaceutical application of AES

1. To analyze different metallic preparations
   - Lithium carbonate tablets
   - Antacid and multivitamin tablets
2. K, Na and Ba in calcium acetate used to prepare dialysis solutions
3. Ca in vaccines (e.g. diphtheria and tetanus)
4. Assay for KCl, NaCl in glucose i.v. infusion

Summary

Atomic absorption spectrophotometry (AAS)

Principles

- Atoms of a metal are volatilized in a flame and their absorption of a narrow band of radiation produced by a hollow cathode lamp, coated with the particular metal being determined, is measured

Applications in pharmaceutical analysis

- Determination of metal residues remaining from the manufacturing process in drugs

Strengths

- More sensitive than AES
- A highly specific method of analysis useful in some aspects of quality control

Limitations

- Only applicable to metallic elements
- Each element requires a different hollow cathode lamp for its determination

Atomic emission spectrophotometry (AES)

Principles

- Atoms are thermally excited so that they emit light and the radiation emitted is measured

Applications in pharmaceutical analysis

- Quantification of alkali metals in: alkali metal salts, infusion and dialysis solutions
- Determination of metallic impurities in some of the other inorganic salts used in preparing these solutions

Strengths

- Flame photometry provides a robust, cheap and selective method based on relatively
- simple instrumentation for quantitative analysis of some metals.

Limitations

- Only applicable to the determination of alkali and some alkaline earth metals