Chapter - 6

Flame Emission and Atomic Absorption Spectrometry :

Theory, Nebulization, flames and flame temperatures, interferences, flame spectrometric techniques.

Unit - III

SYLLABUS

FLAME EMISSION AND ATOMIC ABSORPTION SPECTROMETRY

3.1 INTRODUCTION

The absorption and emission of radiant energy by atoms provide powerful analytical tools for both quantitative and qualitative analysis of substances. Flame emission and atomic absorption spectroscopy is a method of elemental analysis. These methods are particularly useful for determining trace metals in liquids and is almost independent of the molecular form of metal in the sample. These methods are very sensitive and can detect different metals in concentrations as low as and frequently lower than 1 ppm. The limitations of these methods are :

1. They have limited ability to distinguish among oxidation states and cnemical environment of the analyte elements.
2. They are insensitive to non-metallic elements.

In flame emission spectroscopy, the concentration of the analyte present in sample is proportional to the intensity of emitted radiation. In atomic absorption spectroscopy, the concentration of analyte is measured by absorbance relating to the signal by Beer-Lambert's Law.

3.2 THEORY

In these methods, the analytes in the solution are convened into atoms in vapour phase freed from their chemical surroundings by means of combustion flames. These free atoms are then transformed into excited electronic states by either absorption of additional thermal energy from flame or absorption of radiant energy from an external source of radiation.

In flame emission spectroscopy, the energy from the flame supplies energy necessary to move the electrons of the freed atoms from ground state to excited states. These excited atoms while returning to ground states emit radiation and the intensity of radiation is the basis for analytical determination.

In atomic absorption spectroscopy (AAS), the flame that contain free atoms act as sample cell. The free atoms absorb radiations which are focussed on the cell from an external source. The incident radiation absorbed by the free atoms in moving from ground state to excited states is the basis for analytical determination.

In these methods, the sample solution is introduced as an aerosol into the flame, where the analyte ions are converted into free atoms. The free atoms are then detected or determined quantitatively.

3.3 INSTRUMENTATION

The various steps involved in analysis of components by flame spectrometric methods are :

(i) Delivering the analyte to the flame.

(ii) Inducing the spectral transitions necessary for the determination of the analyte.

(iii) Isolating the spectral lines required for analysis.

(iv) Detecting the increase or decrease in intensity of radiation at the isolated lines.

(v) Recording the intensity data.

Pretreatment of Sample :

The analyte is to be dissolved in a solution in order to undergo nebulization and is suitable to the flame. The analyte must be free from substances which interfere with absorption or emission measurements and they must be removed or masked if present in the analyte. The reagents employed to dissolve samples must not contain interfering substances.

Delivery of Samples :

The device that is used to deliver the sample into the flame plays an important role in determining the accuracy of analysis. The most popular method is nebulization of liqud sample to provide a steady flow of aerosol into a flame. The delivering device for liquid samples consists of three components.

(i) A nebulizer to break up the liquid into small droplets.

(ii) An aerosol modifier to remove large droplets from the stream and allow only droplets smaller than a certain size to pass, and

(iii) The flame or atomizer to convert the analyte into free atoms.

Nebulization :

Pneumatic nebulization technique is used in most atomic spectroscopy determinations. The sample solution is introduced through an orfice into a high velocity gas jet, usually the oxidant The sample stream may be introduced into the gas stream in either a parallel or perpendicular manner. The sample solution is drawn through the sample capillary by the difference in pressure generated by the high-velocity gas stream passing over the sample orfice. The sample stream begins to oscillate producing filaments, which collapse to form droplets in the aerosol modifier or spray chamber.

In the aerosol modifier, the large droplets are removed from the sample stream by mixer paddles or broken into small droplets by impact beads on wall surfaces. The final aerosol formed in form of fine mist is combined with oxidizer / fuel mixture and carried into the burner.

Atomization :

The atomization step converts the analyte in aerosol into free atoms in ground state for analysis. Very small sample volumes or solid samples can be handled by flameless electrothermal methods.

Flame Atomizers :

When the aerosol droplets enter the flame, the solvent is evaporated, leaving small particles of dry solid.

The solid is next converted to vapour. Finally a portion of the molecules are dissociated to give neutral free atoms. These atoms absorb radiation in atomic absorption spectroscopy and emit radiation in flame emission spectroscopy. The efficiency with which the flame produces neutral analyte atoms is important in all the flame techniques. The flame is most generally used atomizer than electrothermal methods. A satisfactory flame source must provide the temeperature and fuel / oxidant ratio required for a given analysis.

Burners :

Burner plays an important role in flame photometry as it helps in producing flame. Various types of burners which utilize different combinations of fuel and oxidant are as follows :

Types of Burners :

The various burners used are : Mecker burner, total consumption burner, premix burner (or Laminar flow burner), Lundergraph burner.

(a) **Mecker Burner :** This burner utilizes natural gas (fuel) along with oxygen (oxidant). It is employed for the determination of alkali metals only because of two reasons;

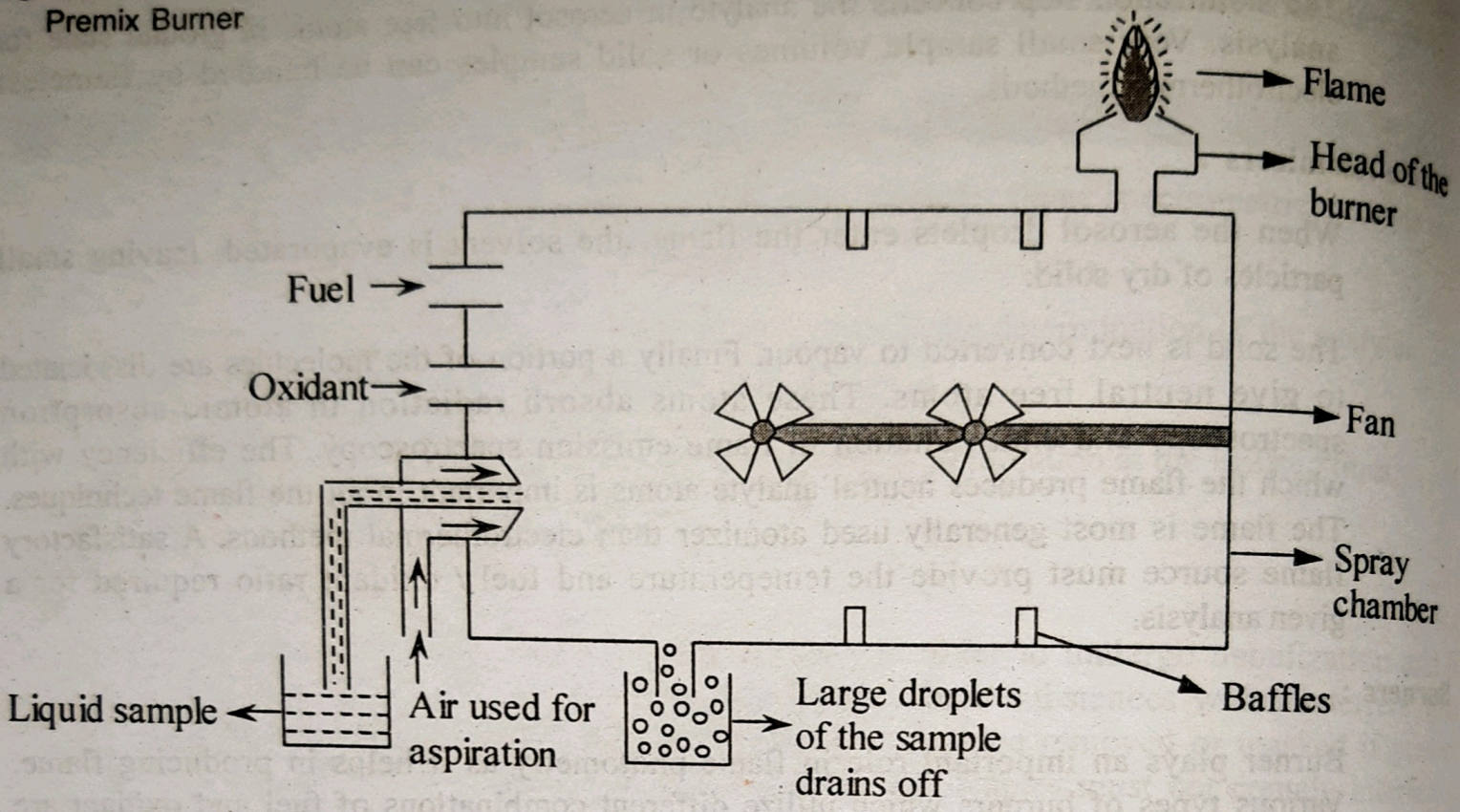
(i) It produces very low temperature.

(ii) It has low excitaton energies.

The flame produced by this burner consist of two different regions i.e., oxidising and reducing respectively. These regions effect the excitation process and produce different concentrations of excited atoms. Due to the above reasons, this burner is not used currently.

(b) **Total Consumption Burner :** This burner uses hydrogen (fuel) along with oxygen (oxidant) in order to produce hot flame. In this type of burner, liquid sample, fuel and oxidant are introduced into the burner through different inlets. Fuel and oxidant are burnt together to produce flame at the top whereas liquid sample is drawn from the bottom. This liquid sample when reaches the base of the flame, oxygen (oxidant) aspirates the lquid sample into fine droplets. The residue left is further reduced into atoms followed by their excitation.

Figure :
Premix Burner



Advantages :

(i) The total amount of sample entering the inlet completely aspirates, irrespective of the droplet size.

(ii) There is no chance of occurrence of hazards.

(iii) Simple in design.

Disadvantages :

(i) Burner produces lot of noise.

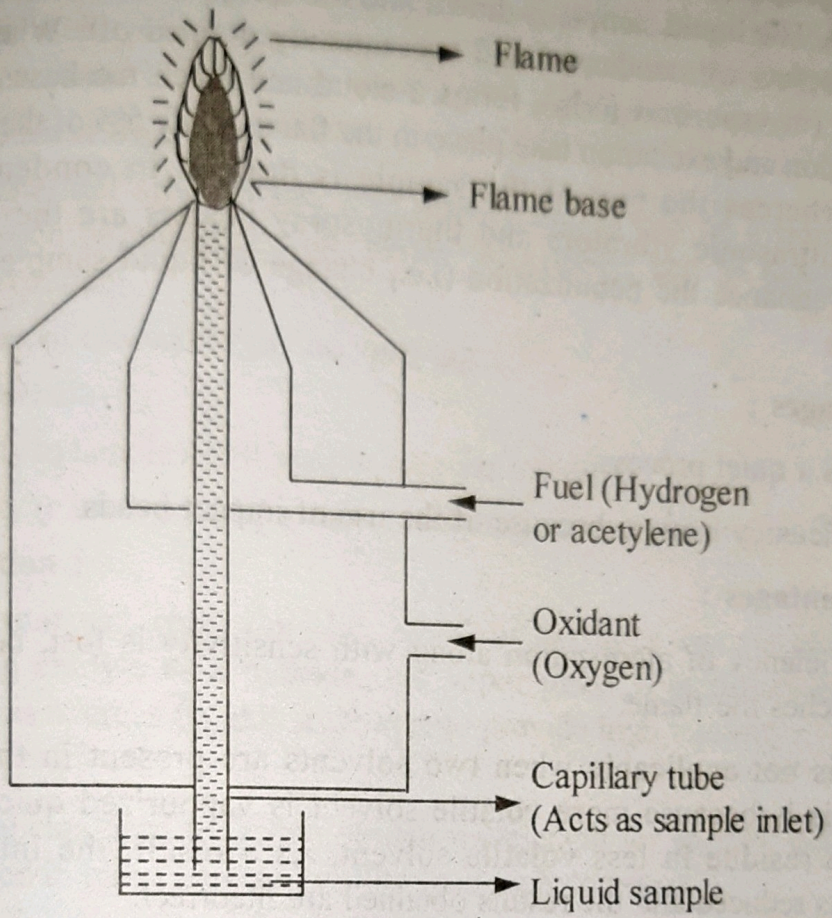
(ii) Flame is turbulent.

Due to the above disadvantages, use of this burner is reduced and has been replaced by other burners.

(c) Premix Burner or Laminar Flow Burner : Premix burner is also called laminar flow burner because the gases moves in laminar (parallel) or non-turbulent fashion. In this type of burner, the liquid sample is aspirated with air and then thoroughly mixed with fuel and oxidant.

Then, the mixture reach the opening of the burner and enters into the flame. Only about 5% of the sample in the form of the fine droplets reach the flame whereas large droplets i.e., 95% of the sample drains out from the side of the spray chamber (burner). This small portion of sample is easily decomposed in the flame and helps in effective atomization of the sample.

Figure : Total Consumption Burner



Advantages :

(i) Flame produced is stable

(ii) It is a quiet process i.e., the burner does not produce noise.

(iii) Non-turbulent flame is produced.

(iv) Effective atomization of the sample takes place.

(v) Clogging of the sample solution does not occur.

Disadvantages :

(i) Mixture of solvents having different volatilities when used in preparing the sample creates problem. The more volatile solvent vaporizes quickly, leaving behind the residue in less volatile solvent. As a result, less number of atoms reach the flame.

(ii) Intensity of emission is also reduced due to the presence of two solvents in the sample solution. This intrun gives incorrect results.

(iii) Explosion may occur in the mixing chamber of burner.

(iv) Sensitivity is lost because lot of sample is wasted.

(d) Lundergraph Burner : The sample used in this type of burner should be in the form of liquid. The liquid sample is drawn into the spray chamber of the burner where the large droplets are condensed and subsequently drained off. Whereas, small sample droplets (in vaporized form), forms a cloud and reach the base of the flame. Then atomization and excitation take place in the flame. Only 5% of the sample reaches the flame whereas the rest of the sample is drained in condensed form. Impact beads, ultrasonic vibrators and thermospray heaters are the devices which are used to enhance the nebulization (i.e., change of liquid sample into fine droplets) process.

Advantages :

(i) It is a quiet process.

(ii) Efficiency is more because of the use of impact beads.

Disadvantages :

(i) Efficiency of atomization along with sensitivity is lost, because, less sample reaches the flame.

(ii) It is not applicable when two solvents are present in the sample solution. This is because more volatile solvent is vapourized quickly leaving behind the residue in less volatile solvent. As a result, the intensity of emission gets reduced and the results obtained are incorrect.

Temperature of the Flame :

Flame temperature plays a very critical role in flame photometry. The temperature of the flame depends on the type of fuel and oxidant used. It should be within a range of 1000 – 3000^0 C. Various combination of fuels and oxidants used in flame photometry are listed below :

Table : Fuel & Oxidant Mixtures

Mixture of Fuel and Oxidant	Temperature (^{0}C)
Hydrogen + Oxygen	2800
Hydrogen + Air	2100
Acetylene (C_2H_2) + Oxygen	3000
Acetylene (C_2H_2) + Air	2200
Propane (C_3H_8) + Oxygen	2800
Propane (C_3H_8) + Air	1900
Butane (C_4H_{10}) + Oxygen	2900
Butane (C_4H_{10}) + Air	1000
Cyanogen gas (C_2N_2) + Oxygen	4580

Note : By using the combination of cyanogen (fuel) and oxygen (oxidant), highest temperature of the flame i.e., 4580^0 C can be obtained. The most preferred fuels are acetylene and hydrogen.

The spectrum of the flame should not interiere with the emission or absorption lines of the analytes. The temperature of the flame determining its utility in flame emission or atomic absorption spectroscopy. The concentration of unexcited atoms and excited atoms in a flame is determined by the fuel / oxidant ratio.

Electrothermal Atomization :

In electrothermal atomization, free analyte atoms can be produced by an electrically heated carbon atomizer. A wide variety of samples can be handled directly with little or no pretreatment.

The features of electrothermal analysis are :

1. High sensitivity
2. Ability to handle small sample volumes of liquids.
3. Ability to analyze solid samples without pretreatment.

Chemical Vaporization :

Elements that can form volatile, covalent hydrides can be efficiently atomized by transferring analyte as a hydride into vapor phase. Electrodeless discharge lamps are often used as sources for this technique to provide high intensity.

Spectrometers :

The components used to isolate desired wavelength for specific determination are similar to those used in ultraviolet and visible spectrophotometers.

Detectors :

The detectors help in measuring the intensity of radiation falling on them from the source. The detector should be sensitive to all the radiations (of different wavelength) falling on it. Photomultiplier detector is generally used in flame photometry as it produces electrical signals when the radiations fall on them.

3.4 INTERFERENCES

The sample solution contains other materials along with the element to be analysed. The presence of this extraneous material in the sample solution results in interferences. These interferences causes inaccuracy in measuring the intensity of desired radiation. Proper care should be taken to avoid intereferences, so that good analytical results can be obtained.

Various types of intereferences occuring in flame photometry are as follows :

1. Spectral interferences.
2. Chemical interferences.
   (a) Anion interferences.
   (b) Cation interferences.
3. Interference due to ionization.
4. Background absorption interferences.
5. Interference due to oxide formation.

1. **Spectral Interferences :** The various spectral interferences and their corrective measures are as follows :

   (a) The spectra obtained from the two components have different wavelengths, but partial overlapping of these spectra (from two components) may occur. This overlapping of spectra results in interference. The detector cannot distinguish between the sources of radiation (element to be analysed and extraneous material) and records the total signal which is incorrect. High temperature of the flame results in spectral interference because more number of spectral lines are produced.

   Examples :

   (i) Iron emits the radiation (spectrum) at 3247.28 A^0 which is overlapped by radiation emitted by copper at 3247.54 A^0.

   (ii) Iron emits the radiation at 2852.13 A^0 which is overlapped by radiation emitted by magnesium at 2852.12 A^0.

   Correction : This spectral interference can be avoided by removing the interfering element by extraction method or by using calibration curve. This calibration curve is obtained by using standard solution which have interfering element in the same quantity as that of the element to be analysed.

   (b) Spectra of two or more elements having wavelengths differing only by few A^0 also results in interference. The spectra of these elements do not overlap each other. Interference occurs due to the filters used in flame photometer. These filters allows spectral lines separated by 50 – 100 A^0 to pass through them. When these spectral lines fall on detector, it gives incorrect result.

   Correction : This type of spectral interference can be avoided by increasing the resolution power of spectral isolation system i.e., filter or by using monochromators.

   (c) Spectral interferences also arises due to the presence of high concentration of salts (alkali and alkaline metals) in the sample solution. These salts emits radiations which results in continuous background. This continuous background interferes with the desired spectral lines and results in interference. Organic solvents like methylisobutyl ketone also gives rise to continuous background. These solvents alters the viscosity and surface tension of the solution. This alteration influences the rate at which the sample is fed into the flame. As a result, intensity of emitted radiation of desired element is influenced.

   Correction : By the use of scanning techniques, this type of interference can be avoided.

2. **Chemical Interferences :** These type of interferences occur due to reaction between the atoms to be analysed and other materials present in the solution. They are of two types :

(a) Anion Interferences : The intensity of radiations emitted by the atom under analysis are decreased due to the presence of certain anions like aluminate, oxalate, phosphate, sulphate etc., in the solution.

Examples :

(i) calcium react with phosphate ions forming a stable molecule. As a result, there is a decrease in the intensity of radiation emitted by calcium. This is because, calcium phosphate cannot decompose easily to liberate free calcium ions. This will result in a critical analytical error.

(ii) Barium chloride decomposes easily to liberate free chloride ions, when compared to barium sulphate in the same concentration. As a result, barium sulphate emits low intensity of radiation, when compared to barium chloride. This is mainly due to the difference in anions of the two compounds.

(b) Cation Interference : The presence of certain cations in the sample solution results in interference. As a result, there is a decrease in the intensity of radiation emitted by the element to be determined.

Examples :

(i) The signal intensity of aluminium (element to be determined) reduces due to the presence of calcium and magnesium in the sample solution.

(ii) Sodium interferes with potassium.

3. **Interference due to Ionization :** Atoms undergo ionization at high temperature. The ion formed is capable of producing its individual emission spectrum with frequencies different from those of the atomic spectrum of the same element. As a result, the radiant power of atomic emission is reduced.

Example : Sodium metal undergoes ionization and forms sodium ions.

$$Na \rightleftharpoons Na^+ + e^-$$

Correction : The ionization of sodium can be prevented by adding more quantity of potassium salt to the sample as well as standard solutions. Potassium itself undergoes ionization, thereby preventing the ionization of sodium and enhancing its emission.

4. **Background Absorption Interferences :** These type of interferences occur due to nature of the flame, sample matrix, scattering and absorption of radiations by similar alkali salts mainly halides present in the sample solution.

Flame background occurs due to scattering of radiation in monochromators. This can be avoided by using base line technique. By using radiation buffers, the interaction between metals can be avoided, as these interactions, either increases or reduces the luminescence. But, the main drawback is addition of buffer causes loss in sensitivity.

Correction : This type of intereference can be avoided by using grating monochromators.

5. **Intereference due to Oxide Formation :** This type of intereference is most seen in the alkaline earth metals. These metals form stable oxides, if oxygen present in the flame. The formation of oxides lead to reduction in intensity emission since most of the free metals are removed from the flame due to formation of oxides.

Correction : By using very high temperature flames, oxides can be dissociated into free metal atoms which undergo the process of excitation. Another way of overcoming this intereference is by using oxygen free atmosphere, where free metal atoms does not form oxides and produce excited atoms.

3.5 FLAME SPECTROMETRIC TECHNIQUES

Flame Emission Spectroscopy :

In this technique, the sample solution is nebulized and introduced into the flame where the solvent is removed, vaporized and atomized rapidly. Atoms and molecules are raised to excited states by thermal collissions with the constituents of the flame gases. When they return to lower or ground state, the excited atoms and molecules emit radiation characteristic of the sample components. The emitted radiation is detected and measured by means of spectrophotometric arrangement as in UV-Visible spectrophotometer. The wavelengths emitted usually fall in UV-Visible region and can be detected by photomultiplier tube.

Atomic Absorption Spectroscopy : In this technique, the analysis of a sample is divided into two major processes -

1. The production of free atoms from sample, and
2. The absorption of radiation by atoms from an external source.

The analyte is converted into free atoms in the flame. The free atoms absorb radiation from an external source and rise to the excited state from ground state.

The atomic absorption spectrum of an element consists of series of resonance lines which are originated with the ground electronic state and terminated in various excited states. The transition between the ground state and the first excited state is known as first resonance line and it is the line which is having strong absorptivity. The absorptivity of a element decreases as the energy difference between the ground state and excited state increases.

To obtain results with high sensitivity, the first resonance line of the analyte is used in analysis.

Atomic Fluorescence Spectrometry : The principle of atomic fluorescence spectroscopy is same as molecular fluorescence. When free atoms of analyte absorb radiation from an external source rise to excited state and return to ground state by fluorescence the analyte can be detected. It has greatest sensitivity for elements that have high excitation energies.

3.6 APPLICATIONS

These methods are mainly used to detect the trace metals present in the samples.

Applications of Flame Emission Spectroscopy :

1. **Qualitative Determination :** Flame photometry helps in detecting the elements from group IA and IIA, mainly barium, calcium, lithium, magnesium, potassium, sodium and strontium.

2. **Quantitative Determination :** This is one of the most useful applications of flame photometry. Apart from determining elements from group IA and IIA, it also determines other elements, such as aluminium, antimony, arsenic, bismuth, iron, lead, palladium, nickel etc.

The main procedure used for carrying out quantitative determination is the sample solution is first aspirated into the flame. Then intensity of the emitted radiation is measured which determines the concentration of the sample.

The different methods by which quantitative determination can be carried out, are as follows:

(a) Method of direct comparison.

(b) Method of calibration curve.

(c) Method of standard addition.

(d) Method of internal standard.

(a) Method of Direct Comparison : In this method, the flame intensity due to sample solution is compared to that of the standard solution. The concentration of the ion in the sample solution can be determined by the formula give below.

$$\text{Concentration of ion to be analysed in the sample} = \frac{\%\text{ of flame intensity from sample}}{\%\text{ of flame intensity from standard}} \times \text{Concentration of ion in standard solution}$$

Advantages :

(i) This method requires less time for analysis.

(ii) There is no need of preparing more number of standard solutions.

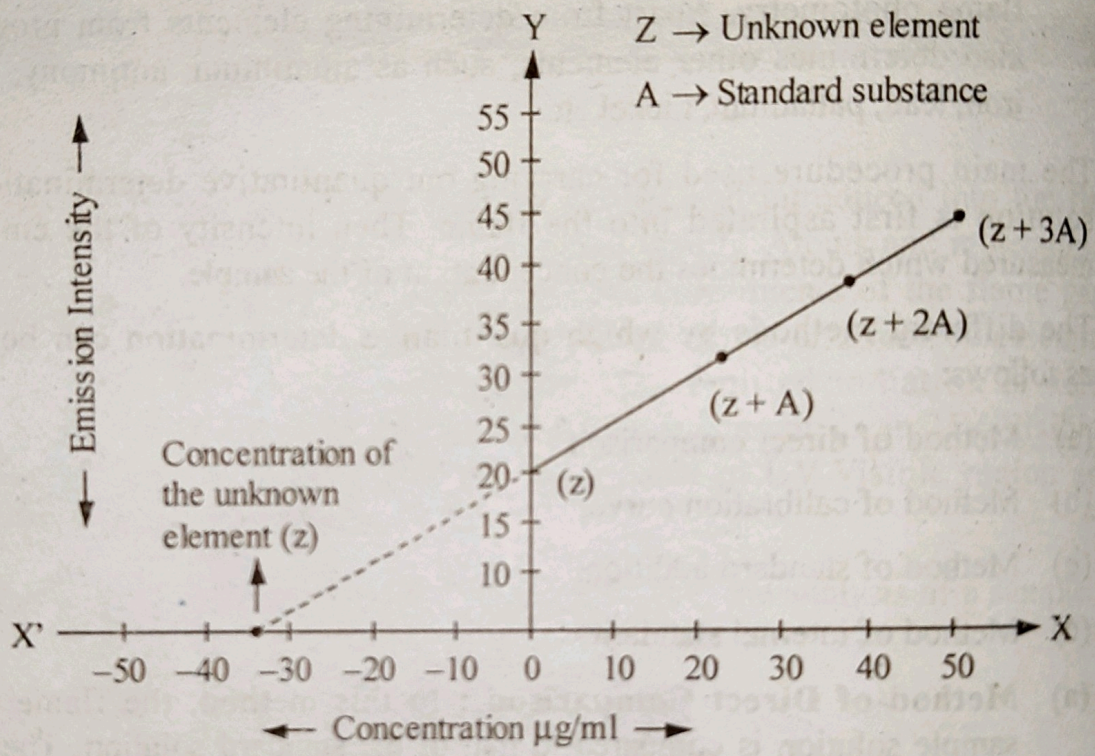
Disadvantage : Any deviation from the linear region of the concentrations of standard and sample solution may lead to errors.

(b) Method of Calibration Curve : Standard solutions which contain the element whose concentration is to be determined are prepared in series (i.e., 10, 15, 20, 25 µg/ml etc). Then a calibration curve is obtained by plotting a graph between concentration and flame intensity. With the help of this curve, unknown concentration of the sample solution can be determined.

(c) Method of Standard Addition : In this method, the intensities of sample and standard solutions are determined. This is done by preparing a sample solution containing an unknown element (z). This solution is then aspirated into the flame and its emission intensity is determined.

The various solutions containing unknown element (z) along with increasing amounts of standard substance (A) are prepared. These solutions are aspirated into the flame and their emission intensitites are determined.

A graph is plotted between the emission intensity and concentration.



(z + A), (z + 2A) and (z + 3A) are the increasing amounts of standard substance and unknown element z in a solution.

From the above graph, the concentration of the sample solution containing unknown element (z) can be determined. This can be obtained through intersection of the curve on the negative axis of the concentration.

Advantages :

(a) Sample solutions containing even minute concentrations of the elements can be easily determined by this method.

(b) Elements which are difficult to analyse can be easily determined.

(c) Interferences due to other elements present in the sample solution are minimised.

Note : While carrying out the analysis of the unknown element by this method the background emission should be corrected. Background emission is the emission intensity obtained when the solvenet used in preparing sample solutions is aspirated into the flame. This background emission is then subtracted from the emission obtained from the sample.

Correction = Emission from the Sample – Background Emission.

(d) **Method of Internal Standard :** In this type of method, a series of standard solutions and sample solutions (of unknown concentraions) are prepared. First, the standard solution containing lithium as internal standard element of known quantity are prepared. These standard solutions are aspirated into the flame and their intensities are measured.

Then, the sample solutions of unknown concentrations are aspirated into the flame and their intensities are measured. Ratio of intensities of sample and standard solutions is calculated. Calibration curve is obtained by plotting a graph between ratio of the two intensities of y-axis and concentration on x-axis. From this curve, the concentrations of the samples can be determined by their signal intensity.

Internal standard element (i.e., lithium or any other element) used in this method should possess the following properties :

(i) It should be present in negligible amount in the orignal solution.

(ii) The emission line obtained by internal standard element should react to interferences in the same way as that of emission line obtained from unknown element.

Analysis of Multielement :

Flame photometry also helps in simultaneous multielement analysis. This analysis can be done by two methods, namely :

(a) Mitchell et. al, method

(b) Busch et.al., method

(a) Mitchell et.al., Method : In this method, vidicon detection system was used along with 0.25m monochromator. This detector helps in the detection of wavelength ranging from 20 - 1680 A^0. Around ten elements can be determined at a time by this method.

(b) Busch et. al., Method : In this method, vidicon detector with silicon diode is used along with 0.5m monochromator. Each time eight elements can be determined. This method can be employed for the detection of elements like aluminium, potassium, molybdenum, iron, titanium, manganese and calcium present in the sample solution.

Other Applications :

(a) (i) Flame photometry method helps in determining Na, K, Al, Ca, Co and Fe in biological fluids, tissues and in analysis of soil.

(ii) Flame photometry is also used in the determination of elements like Na, K, Al, Ca, Co and Fe in glass, cement, petroleum products, agronomic materials and water used for natural as well as industrial purposes.

(b) It is used in detecting non-metals i.e., halides. This is done by measuring the radiations emitted by these non-metals in IR region of the flame.

(c) Flame photometry helps in determining traces of sodium present in aluminium and its alloys and in calcium.

(d) It also helps in determining boron in organic compounds.

Applications of Atomic Absorption Spectroscopy :

The following are some of the applications of Atomic absorption spectroscopy.

1. Estimation of trace elements in body fluids.
2. Estimation of elements like copper, nickel and zinc in food products.
3. Estimation of zinc in insulin injection.
4. Estimation of mercury in thiomersal solutions.
5. Estimation of elements in soil samples, water supply, effluents, ceramics, etc.