

ANALYTICAL CHEMISTRY RESEARCH: FLAME PHOTOMETRY

A. S. Vimala*, Ruban Raj U., Rosini R. and Rohit A. S.

Department of Pharmaceutical Chemistry, SSM College of Pharmacy, Jambai, Erode.

The Tamilnadu Dr MGR Medical University, Chennai.

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*Corresponding Author: A. S. Vimala

Department of Pharmaceutical Chemistry, SSM College of Pharmacy, Jambai, Erode.

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ABSTRACT

Flame photometry, or flame emission spectroscopy, is a technique used to analyze metal elements by measuring the intensity of light emitted when a metal is introduced into a flame. The wavelength of the emitted light identifies the element, while the intensity indicates its concentration. It is most effective for elements in the first two columns of the periodic table, such as sodium, potassium, and calcium, and is useful in fields like medicine, agriculture, and plant science. Flame photometry works by vaporizing a liquid sample, exciting atoms in the flame, and measuring the emitted light. The emitted photons correspond to specific energy transitions within the atom, with their wavelength determined by the energy difference between levels. However, this method has limitations, including its inability to analyze metals that require higher energy levels for excitation, such as noble metals and inert gases. Additionally, it cannot provide information on the molecular form of the metal in the sample and is limited to liquid samples. Instrumentation involves components like burners, which control flame temperature, and the type of fuel and oxidant used. While flame photometry offers simplicity, sensitivity, and reliability, it is less suitable for complex analyses requiring high energy, like those of transition metals.

KEYWORDS: Flame photometry, Metal analysis, Emission spectroscopy, Excitation, Wavelength, Concentration.

INTRODUCTION

- Flame photometry is based on the measurement of intensity of the light emitted when a metal is introduced into a flame.
- The wavelength of colour tells us what the element is, and the colour's intensity tells us how much of the element is present.
- Flame photometry is also named as flame emission spectroscopy because of the use of a flame to provide the energy of excitation to atoms introduced into the flame.

- Flame photometry, coupled with simple read out devices provides high sensitivity and high reliability for the determination of elements in the first two columns of the periodic table.
- Among the elements are sodium, potassium, lithium, calcium, magnesium, strontium and barium.
- The measurement of these elements is very useful in medicine, agriculture and plant science.
- Flame photometry is also successful in determining certain transition elements such as copper, iron and manganese.
- By making a wavelength scan of the emission spectrum, it is also possible to do qualitative analysis by employing flame photometer, but the application is severely limited.
- In addition to the determination metals, it can be applied to non metal analysis by utilizing the infrared region of the spectrum.
- Flame photometry as a simple, rapid method for the routine determination of elements that can be easily excited.

LIMITATIONS OF FLAME PHOTOMETRY

- The concentration of the metals may be measured by flame photometry, but frequently that technique is not the method of choice because of the relatively low energy available from a flame and therefore the relatively low intensity of the radiation from the metal atoms, particularly those that required large amounts of energy to become excited.
- Although flame photometry is a means of determining the total metal concentration of a sample, it tells little or nothing about the molecular form of that metal in the original sample.
- It has not been used for the direct detection and determination of the noble metals, halides, or inert gases.
- All of these elements require more energy than the flame provides in order to become excited.
- Although flame photometry is a means of determining the total metal content present in a sample, it does not provide information about the molecular form of the metal present in the original sample.
- Flame photometry cannot be used for the direct detection as well as for the determination of the inert gases.
- Only liquid samples may be used. In some cases, lengthy steps are necessary to prepare liquid heads, samples.
- Flame photometry cannot be used for the direct determination of all metal atoms; there is a limitation on the number of elements that can be analysed by this method.

GENERAL PRINCIPLE OF FLAME PHOTOMETRY

When a liquid sample containing a metallic salt solution is introduced into a flame the process involved in flame photometry is a simplified version of events:

- The solvent is vaporised, leaving particles of the solid salt.
- The salt is vaporised or converted into the gaseous state.
- A part or all of the gaseous molecules are progressively dissociated to give free neutral atoms or radicals.
- These neutral atoms are excited by the thermal energy of the flame. The excited atoms, which are unstable, quickly emit photons and return to lower energy, state, eventually reaching the unexcited state.
- The measurement of the emitted photons, i.e., radiation, forms the basis of flame photometry.

If E_2 and E_1 represent the energy of the higher and lower energy levels concerned, the radiation emitted during the jump may be defined by equation.

$$E_2 - E_1 = h\nu$$

Where h is the Planck's constant, and ν the frequency of emitted light which is defined as follows:

$$\nu = c/\lambda$$

On combining equations, we get

$$E_2 - E_1 = hc / \lambda$$

$$[\text{or}] \lambda = hc / E_2 - E_1$$

From equation can calculate the wavelength of the emitted radiation which is characteristic of the atoms of the wavelength of the emitted radiation which is characteristic of the atoms of the particular element from which it was emitted.

- The following is a concise description of the sequence of events that normally occurs in flame photometry.
- The fraction of free atoms that are thermally excited is governed by a Boltzmann distribution which is as follows:

$$N^* / N_0 = A e^{-\Delta E/kt}$$

Where,

- N^* is the number of excited atoms,
- N_0 the numbers of atoms remaining in the ground state,
- A constant for a particular element,
- ΔE the difference in energies of the two levels,
- k the Boltzmann's constant, and
- T the temperature of flame.

The temperature of fuel is controlled by the type of fuel and oxidant used. Some flame temperatures are given in Table.

Fuel	Oxidant	Flame temperature (c°)
Propane	Air	1900
Propane	Oxygen	2800
H ₂ O	Air	2100
H ₂ O	Oxygen	2800
Acetylene	Air	2200
Acetylene	Oxygen	3000

- The energy available in the flame for exciting atoms is dependent on the flame temperature as defined by the Boltzmann distribution.
- Flames have only limited amounts of energy available when compared to excitation sources such as emission spectrographs or plasma emission torches (ICP).
- For this reason, flames are most useful only for elements that require low amounts of energy to become excited.
- This means that the method is most useful for the determination of the alkali metals and alkaline earth metals.
- They are not the method of choice for transition metals and most of the other metals in the periodic table.
- These metals generally require significantly more energy in order to become excited.
- They are most often done by emission spectrographs or plasma emission where much higher energy is available. However, it must also be stated that when we try to analysis group I and group II elements in these high-energy sources, we run the risk not only of exciting them but of ionizing them.

- Although the Boltzmann distribution would lead us to believe that the emission intensity would be greatly increased in plasma emission for the group I and group II elements, in practice it is found not to be so because the atoms are ionized and this results in a loss of atoms and the generation of ions.
- Ionization causes a complete change of energy levels and therefore the entire emission spectrum, with a reduction in the intensity of the atomic spectra.

Instrumentation

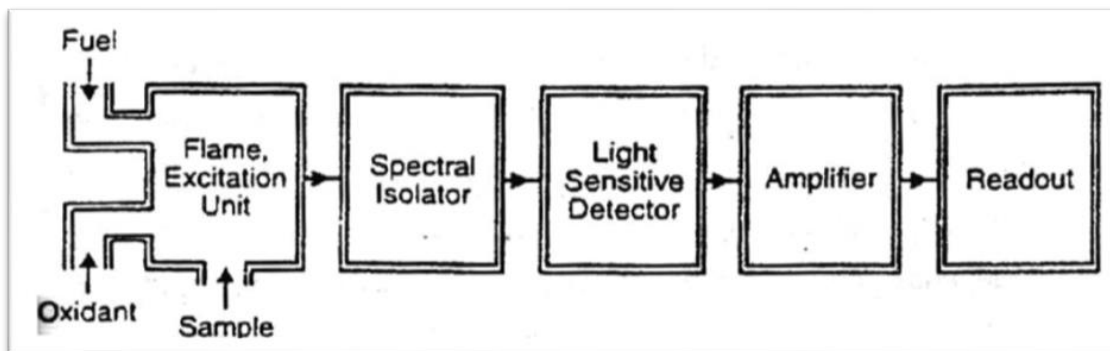


Figure 1: Basics of flame photometer.

The various components of the instrument are described as follows:

Burner: The flame used in the flame photometer must possess the following functions:

- The flame should possess the ability to evaporate the liquid droplets from the sample solution resulting in the formation of solid residue.
- The flame should decompose the compounds in the solid residue formed in step (i) resulting the formation of atoms. (ii) The flame must have the capability to excite the atoms formed in step (iii) and cause them radiant energy. For analytical purposes, it becomes essential that emission intensity should be over reasonable periods of time (1-2 min).
- The temperature of the flame, which is primarily responsible for the occurrence of the above mention processes is controlled by several factors which are summarised as follows:
 - Type of fuel and oxidant and fuel-to-oxidant ratio
 - Type of solvent for preparing the sample solution
 - Amount of solvent which is entering into the flame
 - Type of burner employed in flame photometer
 - The particular region in flame which is to be focussed into the entrance slit of the spectral isolation unit

Types of Burners

- Mecker burner
- Total consumption burner
- Premix burner
- Lundengarph's burner
- Shielded burner
- Nitrous oxide – Acetylene burner

Mecker Burner

- This was the primitive type of burner used in flame photometry and was used earlier.
- It generally works with aid of natural gas and oxygen as fuel and oxidant.
- The temperature so produced in the flame was relatively low resulting in low excitation energy.
- Now a days it is not used but it was best suited for alkali metal.



Figure 2: Mecker Burner.

Total Consumption Burner

- Due to the high pressure of fuel and oxidant the sample solution is aspirated through capillary.
- As soon as liquid sample drawn into the base of flame oxygen aspirates sample solution leaving solid residue.
- Atomization and excitation then occurs.
- Hydrogen and oxygen are generally employed as fuel and oxidant.

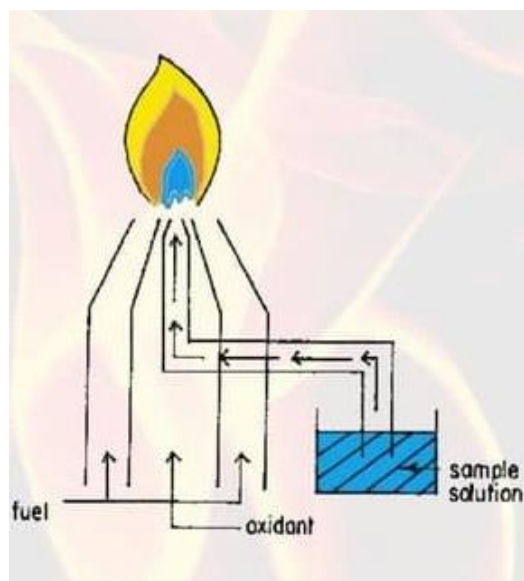


Figure 3: Total consumption burner.

Premix of laminar flow burner

- In this burner the sample fuel oxidant are thoroughly mixed before aspirated and reaching to flame.
- Gases move in non turbulent fashion i.e. laminar flow.
- Only small portion (about 5%) of the sample in the form of small droplet reaches the flame and is easily decompose.

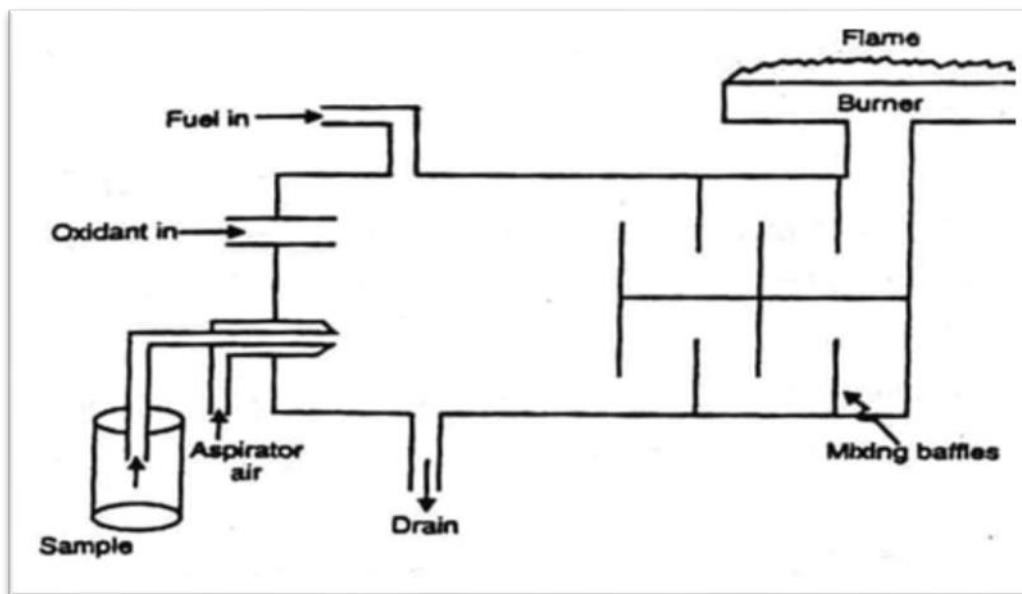


Figure 4: Premix of laminar flow burner.

Lundengarph's Burner

- The sample must be in liquid form.
- A small sample liquid droplet vaporized and move to base of flame in the form of cloud.
- Large droplet condensed at side and then drained off.

Shielded Burner

- In this flame was shielded from the ambient atmosphere by a stream of inert gas.
- Shielding is done to get better analytical sensitivity.
- Following results are obtained with shielded burner.

Nitrous Oxide – Actylenee Flame

- These flames were superior to other flames for effectively producing free atoms.
- E.g.- metals with very reflective oxides such as aluminium and titanium.

The Drawbacks of it is:

- The high temperature reduces its usefulness for the determination of alkali metals as they are easily ionized.
- Intense background emission, which makes the measurement of metal emission very difficult.

Sequence of events in a flame

- The water or other solvent is evaporated leaving minute particles of dry salt.
- The dry salt is vapourised or converted into gaseous state.
- A part or all of the gaseous molecules are progressively dissociated to give free neutral atoms or radicals.
- A part of the neutral may be thermally excited or even ionized.
- A portion of the neutral atoms or radical in the flame may combine to form new gaseous compound.

Mirrors

- The radiation from the flame is emitted in all directions in space.
- Much of the radiation is lost, and loss of signal results.
- In order to maximize the amount of radiation used in the analysis, a mirror is located behind the burner to reflect the radiation back to the entrance slit of the monochromator.
- This mirror is concave and covers as wide a solid angle from the flame as possible.
- To per the best results, the hottest and steadiest part of the flame is reflected onto the entrance slit of the monochromator. This helps reduce flame flicker from upper parts or the flame where light intensity is reduced and noise is increased.
- The reflecting surface of the mirror is front-faced. If the reflecting surface were on the rear as in went the normal household mirror, the radiation from the flame would have to go through the support material such as glass or quartz twice before it is reflected to the entrance slit.
- Since the support material absorbs some radiation, there would be a considerable loss of signal, particularly at the shorter wavelengths front surface mirrors are most efficient, but they are not physically protected.
- They are very easily scratched and subject to chemical attack.

SLIT

- With the best equipment, entrance and exit slits are used before and after the dispersion elements.
- The entrance slit cuts out most of the radiation from the surroundings and allows only the radiation from the flame and the mirrored reflection of the flame to enter the optical system.
- The exit slit is placed after the monochromator and allows only a selected wavelength range to pass through to the detector.
- For many purposes it is essential that this wavelength range be narrow that is of the order of few Nanometers.
- This is necessary if emission lines from other components in the flame have wavelength similar to those of the emission lines of the elements being determined.
- The slit must prevent such and interfering lines from reaching the detector.

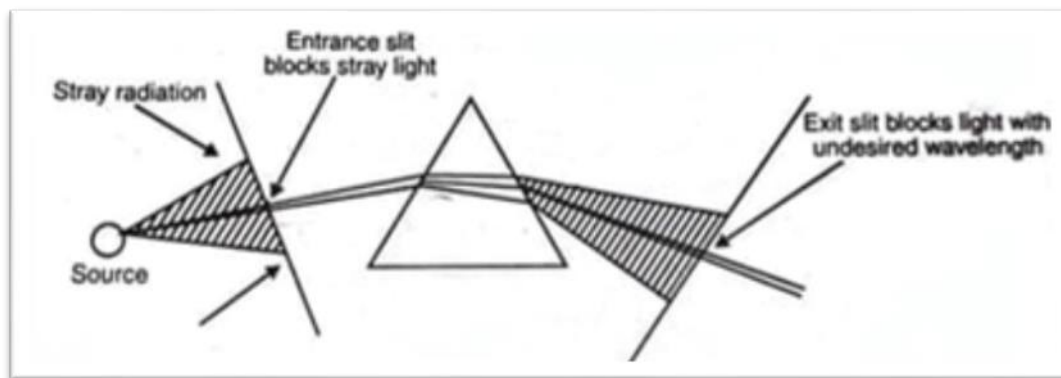


Figure 5: Mechanism of flame photometr.

Monochromators

- In simple flame photometer, the monochromator is the prism but in expensive models the grating monochromators are used.
- Quartz is the materials most commonly used for making prisms even though its dispersive power is less than that of glass.
- The reasons for this is that quartz is transparent over the region.
- The grating monochromator employs a grating which is essentially a series of parallel straight lines into a plane surface.

Filters

- In some elements, the emission spectrum contains a few lines.
- In such cases wide wavelength ranges will be allowed to enter the detector without causing any serious error.
- In such a situation an optical filter may be used in place of the slit and monochromator system. The filter is made from a material which is transparent over a narrow spectral range. When a filter is kept between the radiation of the desired wavelength from the flame will be entering the detector and measured. The remaining undesired wavelength will be absorbed by the filter and not measured.
- The flame photometers which use filter monochromators are very convenient for simple repetitive analysis.
- However, such instruments can be used for a small number of elements. The reason for ha is that a large number of filters are employed.
- The radiation coming from the optical system is allowed to fall on the detector where radiation of the appr measures the intensity of radiation falling on it.
- The detector should be sensitive to radiation all wavelengths that may be examined.
- In good flame photometers, the photomultiplier detectors are employed which produce an electrical signal from the radiation falling on them.

Instruments

First type

- The burner used in flame photometer is a total consumption type but a premix burner can also be used.
- A collimating mirror is used behind the flame to increase the emission intensity but this mirror is often emitted when premix burner having a long flame path are used.

- This is sometimes necessary to remove the backing mirror in multiple beam instruments where a sufficient room is not available to include such mirrors.
- The sample solution is sucked by an atomiser operated by one of the flame producing gases.
- Then the sample solution is aspirated into the flame in the form of a spray.
- Spectral emission comes from excited atom formed during the process of combustion in a flame.
- The emitted radiation is collected by a collimating concave mirror from the flame and is then permitted to pass through a prism and slit.
- The radiation of the approximately selected wavelength strikes a photo detector and the magnitude of the electrical signal developed is out on a meter.
- In order to adjust the temperature of a flame; the flow rates and ratio of fuel to oxidant are adjusted by introducing pressure regulators and flow meter in the gas lines.

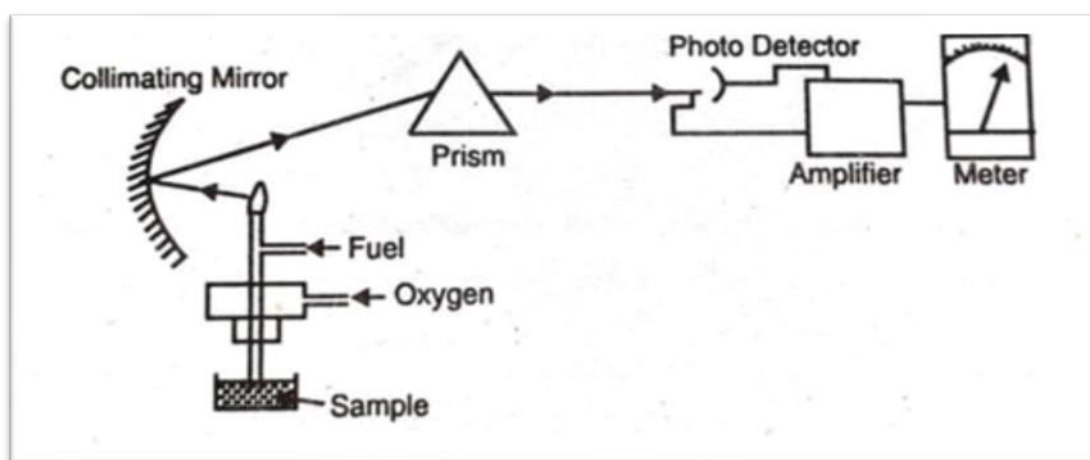


Figure 6: Schematic diagram of a modified flame spectrophotometer type 1.

Second type

- Another type of flame photometer is internal standard flame photometer.
- Lithium is used as an internal standard and an equal concentration is added to the standard and sample solutions.
- The sample solution containing internal standard (lithium) is sucked by an atomiser operated by one of the flame producing gases and as to be the spray is fed into the flame.
- The emitted radiation is collected by a mirror through a filter.
- The emitted radiation from the mirror is divided into two parts.
- One part arises due to the internal standard (lithium) By into areas the second part arises due to the presence of element to be measured.
- Both these parts are med by separate amplifiers and are then fed to the common detecting system which records the intensity of the element (to be determined) to that of internal (lithium).
- Thus, this flame photometer gives a direct and simultaneous reading of the ratio of intensities.
- The use of this flame photometer removes the effects of momentary fluctuations in flame characteristics caused by fluctuations in fuel or oxidant pressures.
- Therefore, internal standard flame photometer is better than the first type as discussed above.

- In internal standard flame photometer, the errors due to differences in viscosity and surface tension are minimised considerably. However, the effect of radiation may or may not be reduced, depending on the similarity of the effects on the two elements.

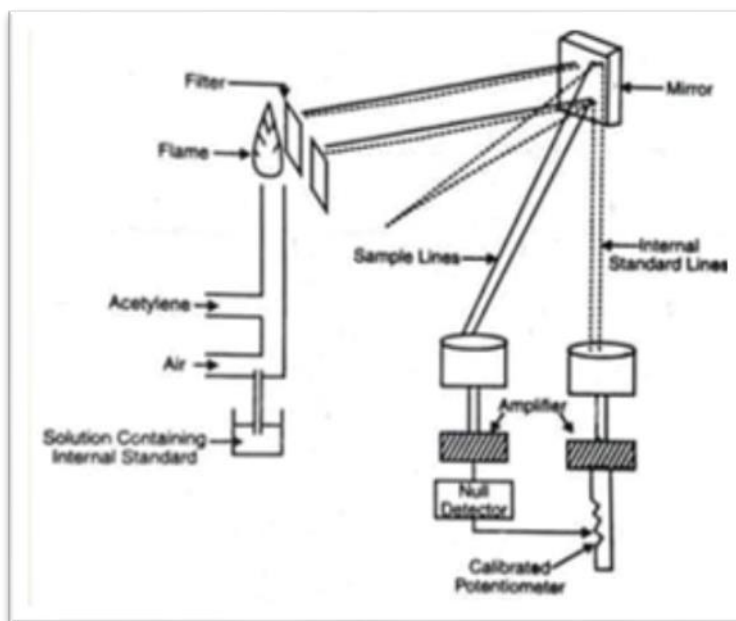


Figure 7: Schematic diagram of a modified flame spectrophotometer type 2.

Interference in flame photometry

- The radiation intensity may not accurately represents the sample concentration because of presence of other materials in the sample.
- These materials result in an interference in the analytical procedure.
- It is only through adequate control of this interference that flame photometry would provide analytical results.
- Following are the more commonly interference process in the flame photometry.

Spectral Interference

- Occurs when the emission lines of two elements cannot be resolved or arises from the background of flame itself.
- They are either too close or overlap or occur due to high concentration of salt in the sample.

IONIC Interference

- High temperature flame may cause ionisation of some of the metal atoms.
- E.g: sodium
- The Na^+ ion possesses an emission spectrum of its own with frequencies which are different from those of atomic spectrum of the Na atom.

Chemical Interference

- The chemical interferences arise out of the reaction between different interferents and the analyte.

Includes**Cation Anion interference**

- The presence of certain anions such as oxalate, phosphate, sulfate, in a solution may effect the intensity of radiation emitted by an radiation.
- E. g. calcium + phosphate ion forms a stable substance as $Ca_3(PO_4)_2$ which does not decompose easily resulting in the production of lesser atoms.

Cation-cation interference

- These interference are neither spectral nor ionic in nature.

E.g. Aluminium interference with calcium and magnesium.

Factors that include the intensity

A number of factors will influence the intensity of light emission from a given solution. some of these are as follow:

Viscosity

- The addition of a substance which increases the viscosity of the solution (e.g: sucrose) decreases the intensity of light emission.
- This decreases result in due to a reduction in the efficiency of atomization.

Presence of Acid

- When an acid is present in the sample solution this decreases the light intensity.
- The decreases arises due to the disturbance of the initial dissociation equilibrium.

Presence of other Metal

- If other metals are present these also alter the intensity of emitted radiation.
- In order to remove this defect special filter are used which will absorb radiation due to the elements which is to be estimated in the sample solution.

Application**Qualitative application**

- Used for the determination of alkali and the alkaline earth metals in samples which are easily prepared as aqueous solution.
- Example – sodium produces yellow flame.
- Non radiating elements such as carbon, hydrogen and halides cannot be detected.

Quantitative Analysis

- The concentration of various alkali and alkaline earth metal is important in determining the suitability of the soil for cultivation.
- Used for determination of the concentration of sodium and potassium ions in body fluids since their controls the action of muscles including the heart.
- Analysis of water from various sources is carried out to determine its suitability for drinking, washing, agriculture and industrial proposes.
- Used for determination of lead in petrol.

- Analysis of soft drinks fruit juices and alcoholic beverages can also be analysed by using flame photometry.
- The calibration curve is prepared by measuring the intensity of emission for a series of solution of different concentration prepared by using a standard solution.
- Plotting a graph between emission intensity and concentration of the ionic species of elements of interest.
- The concentration of the elements in the unknown sample can then be found out from the standard plot as is done in visible spectrophotometry.

Table: Detection limits and flame spectra of the elements.

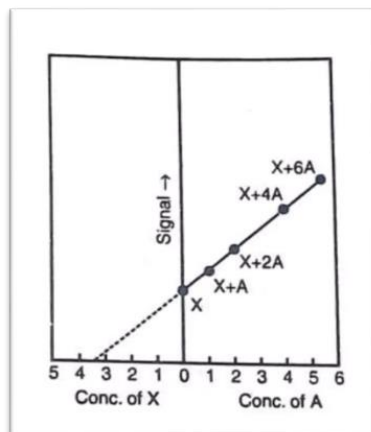
ELEMENTS		Detection Limit ppm	Elements		Detection limit ppm
Aluminium	3962	0.5	Copper	3247	0.6
	4840	0.5		3720	2.5
Antimony	2528	1.0	Iron	3860	2.7
Arsenic	2350	2.2	lead	4058	14
Barium	4555	3	Lithium	6708	0.067
	5536	1			
Bismuth	2231	6.4	Magnesium	2852	1.0
				3830	1.6
	4227	0.07	Mercury	2536	2.5
Calcium	5540	0.16	Nickel	3524	1.6
	6620	0.6	Palladium	3635	0.1

Experimental procedure for quantitative analysis

- Whenever quantitative analysis is to be carried out the first job is to introduce the sample solution into the flame and then the intensity of radiation is measured at the pertinent wavelength.
- From radiation intensity one can determine the concentration of metal present in the sample by employing one of the following methods:
- Standard addition method
- Internal standard method
- Let us discuss these method one by one.

Standard Operating Procedure

- In this method known amount of a standard solution is added to identical aliquots of the sample and the absorbance is measured.
- The first reading is the absorbance of sample alone and the second reading is absorbance of sample containing analyte plus a known amount of analyte.
- Similarly in flame photometric determinations increasing amounts of a standard solution of the salt of the elements to be determined are added to series of solution of the sample.
- The intensity of emission for all these solutions is then measured.
- A curve of intensity versus concentration of the added elements is obtained and extrapolated to zero value of intensity to give concentration of the elements in the sample.



Advantages

- The method is useful for determining very low concentration of the elements present in the sample.
- This method compensates for any unexpected interfering material present in the sample solution.
- This method can be used to estimate such elements which are rarely analysed.

Precaution

- Whenever standard addition method is to be employed a correction should be made for background emission from the flame.
- This can be done by injecting the solvent into the flame and then its signal intensity called background emission is measured.
- When calculations are to be made the intensity of background emission must be subtracted from the emission due to sample.

Internal Standard Method

- In this method a constant amount of another metal which is not present in the sample is added to both the unknown sample and series of standard solution of the elements is determined.
- This is called internal standard.
- For example, lithium is added in the determination of sodium metal.
- Since both the elements and the internal standard are in the same solution the emission readings at and the elements to be enclosed are simultaneously determined.
- The intensity ratio for the two elements is then plotted against concentration of the standard solution.
- From the observed ratio for the sample the concentration of the elements in it can be determined.

CONCLUSION

- The Flame photometry coupled simple read out device provides high sensitivity and high reliability for the determination of element in the first two columns of the periodic table.
- Among these elements are sodium, potassium, lithium calcium, magnesium, strontium and barium the measurement of these elements is very useful in medicine agriculture and plant science.
- Flame photometry is also successful in determination certain transition element, such as copper, iron and manganese.

- In internal standard flame photometer, the errors due to differences in viscosity and surface tension are minimized considerably.
- Flame photometry is only use to detect element of groups I and II of the periodic table.
- This is one of the most useful applications of flame photometry.
- This is used for the rapid quantitative determination of the elements in groups I and II of the Periodic table.
- If high optical resolution equipment is used, other metallic element besides that of I and II group can also be determined.
- Internal Standard Method is used with a simple flame photometer. The effects of momentary fluctuations in flame characteristics will not be eliminated.
- However, these fluctuations can be overcome by using a direct-reading instrument which gives a direct and simultaneous reading of the ratio of two intensity.
- Every element cannot be chosen as the internal standard method. However, it should fulfil the following characteristics
- Its amount should be very small in the original sample
- It should give an emission line which reacts to interferences as the line of the element (to be determined) does.

REFERENCES

1. B. L. Glendening, D. B. Parrish, and W. G. Schrenk. Spectrographic Determination of Rubidium in Plant and Animal Tissues. *Analytical Chemistry*, 1955; 27(10): 1554-1556.
2. A. O. Rathje. Flame Photometric Determination of Silver in Cadmium and Zinc Sulfide Phosphors. *Analytical Chemistry*, 1955; 27(10): 1583-1585.
3. W. G. Schrenk and B. L. Gendening. Performance of Interference Filters in Simple Flame Photometer. *Analytical Chemistry*, 1955; 27(6): 1031-1033.
4. O. W. Adams and W. C. McCrone. Crystallographic Data, Triphenylacetic Acid.
5. S. K. Love and L. L. Thatcher. Water Analysis. *Analytical Chemistry*.
6. C. W. Pifer and E. G. Wollish. Potentiometric Titration of Salts of Organic Bases in Acetic Acid. *Analytical Chemistry*, 1952; 24(2): 300-306.
7. P. W. West. Inorganic Microchemistry. *Analytical Chemistry*, 1952; 24(1): 76-85.
8. G. D. Patterson and M. G. Mellon. Automatic Operations in Analytical Chemistry, *Analytical Chemistry*, 1952; 24(1): 131-143.
9. A. H. Hale and J. W. Stillman. Development of Efficient Analytical Record System, *Analytical Chemistry*, 1952; 24(1): 143-149.
10. KENNETH W. GARDINER. Flame Photometry, 1956; 219-280.
11. William J.L. Sutton, Emory F. Almy. Separation of Sodium, Potassium, Magnesium, and Calcium in Milk Ash by Ion-Exchange Chromatography. *Journal of Dairy Science*, 1953; 36(11): 1248-1254.
12. Barney V. Pisha, David Speier. A rapid method for the determination of sodium in biological fluids. *Archives of Biochemistry and Biophysics*, 1952; 37(2): 258-265.
13. Irwin Stone, Philip P. Gray, Morris Kenigsberg. Flame Photometry-Sodium, Potassium, and Calcium in Brewing
14. Materials. Proceedings. Annual meeting - American Society of Brewing Chemists, 1951; 9(1): 8-20.